

Lawrence Berkeley National Laboratory

Recent Work

Title

THE HOT-ATOM CHEMISTRY OF LOW ENERGY CARBON IONS IN BENZENE

Permalink

<https://escholarship.org/uc/item/3fr6j871>

Author

Pohlit, Helmut Martin.

Publication Date

1969-06-01

cy. Z

RECEIVED
LAWRENCE
RADIATION LABORATORY

JUL 23 1969

LIBRARY AND
DOCUMENTS SECTION

THE HOT-ATOM CHEMISTRY OF LOW ENERGY
CARBON IONS IN BENZENE

Helmut Martin Pohlitz
(Ph. D. Thesis)

June 1969

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

cy. Z

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

ABSTRACT

A 10-KV ion accelerator is described with which $^{14}\text{C}^+$ -beams of 1-2 μA intensity and variable energies between 3 eV and 15,000 eV (at ca. 3 eV energy spread) are obtained. The chemistry of these fast $^{14}\text{C}^+$ -ions with various chemical substances in which they are absorbed can be investigated.

At energies above ca. 100 eV the hot-atom chemistry of nucleogenic carbon isotopes can be simulated with this equipment. Below 100 eV, the dependence of the product-yields on the kinetic energy can give valuable information about the mechanisms and kinetics underlying the product formation. Methods, and their limitations, employable in this new area of chemical experimentation are discussed.

The formation of products from fast ^{14}C -ions and atoms in solid benzene (-196°) were investigated. The yields of the seven major products (benzene, toluene, cycloheptatriene, phenylacetylene, biphenyl, diphenylmethane, and phenylcycloheptatriene) were determined as a function of the beam energy. The yields of toluene, cycloheptatriene, and phenylacetylene strongly decrease as the beam energy decreases below 100 eV, while those of all other compounds remain constant. The energy-independent yields indicate that the corresponding products are formed from carbon atoms with less than 3 eV energy. At least 15% of the initially fast carbon ions end up in this form. The energy-dependent, i.e. decreasing yields of toluene and cycloheptatriene, are interpreted as being due to the decreased

chance of hydrogen pick-up to form the precursors CH_2 , as the beam energy decreases below 100 eV. A similar conclusion is drawn for the assumed precursor C_2H_x for phenylacetylene. This indicates that pick-up of hydrogen or carbon extends up to 50 eV or more. At least 6% of the (high energy) carbon ions react in the form of CH_2 and 3% in the form of C_2H_x .

One additional major product (benzaldehyde-"U-2") contains oxygen, posing a problem which occurs uniquely in this particular accelerator technique, namely possible contamination of the chemical system during the "irradiation". "U-2"'s abnormal yield dependence on various experimental parameters (e.g. the yield increases three-fold as the beam energy is lowered from 15,000 eV to 100 eV) is discussed in this context.

A partial degradation of cycloheptatriene shows a large extent of isomerization, indicating that the reacting CH_2 carries high internal and/or kinetic energy into the product.

A method is suggested which permits the investigation of reactivity integrals in terms of the ratio of ^{12}C -products to ^{14}C -products, the fast ^{12}C -atoms being a consequence of the energy loss of the fast ^{14}C -ions. This method may become a useful adjunct to moderator experiments in hot-atom chemistry.

ACKNOWLEDGMENTS

During the six years which I stayed at this laboratory and during a part of which this thesis was prepared, I have come to work and interact with a large number of people both in this laboratory and outside of it, both temporary and permanent associates of the Lawrence Radiation Laboratory and the University of California. I cannot attempt to express my appreciation to each one even though, knowingly or not, his help or advice may have been crucial for my advancement. However, as I am also about to conclude my rather extended visit to this country, I would like to mention those who have been most influential in making this period profitable.

I owe to Dr. Calvin the privilege of pursuing this project at his laboratory with ample and generous support. To Dr. Lemmon I am grateful for unceasing encouragement and patience during the long and rather unproductive periods of instrumental development of the accelerator. He has confidently supported me in many unclear and difficult situations and advised me in academic and personal as well as scientific problems.

Tz-Hong Lin has been a good companion in many common experiments. Had it not been for his knowledge, skill and endurance, many of our achievements would not have been possible.

Last, but certainly not least, I want to thank all those who have directly and frequently cooperated with me on my many

projects: Wallace Erwin, our glass blower Bill Hart, carpenter Dick O'Brien, our electronics staff Bob Creedy and John Despotakis, Pete Dowling and Del Coleman of Donner Laboratory, and Reed Johnson of the Student Machine Shop. It was their fine and imaginative work which supplied elegant and effective solutions to numerous complex instrumental requirements.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	-i-
ACKNOWLEDGMENTS	-iii-
TABLE OF CONTENTS	-v-
<u>I. INTRODUCTION</u>	1
1. The Scope	1
2. Equivalence of the Hot-atom and Accelerator Chemistry of Carbon Isotopes	4
a) Atomic Parameters	4
b) Radiation Damage	5
3. Relation to other Beam Experiments	8
<u>II. THE ACCELERATOR</u>	11
1. Introduction	11
2. Ion Source	15
a) Filament	16
b) Wall-Voltage	24
c) Anode	26
d) Gas Supply and Efficiency	27
e) General Performance	32
3. State of the Carbon Ions	36
4. The Kinetic Energy and State of the Carbon-atom Beam	40

TABLE OF CONTENTS (continued)

	<u>Page</u>
5. Mean Energy and Energy Spread of the C^+ -Ion Beam	44
6. Ion-Optics	56
a) Extraction and Electrostatic Focus Lenses	56
b) The Decelerator	61
c) Alignment	65
d) Magnet	65
7. Vacuum	68
8. Target	70
a) Geometry and Accessories	70
b) Benzene Deposition	71
c) Charge Build-up in the Target	72
9. The "U-2" Problem	75
10. Dummy Irradiations	80

III. HOT-ATOM PHYSICS AND CHEMISTRY

1. Interaction of the Ion Beam with the Solid Benzene	83
a) Surface Penetration	84
b) Energy Loss and Range	85
c) Macro-Structure of the Solid Benzene	93
d) Charge and Electronic State of ^{14}C in the Solid Benzene	96
1) Experimental background	96
2) Theoretical background	100

TABLE OF CONTENTS (continued)

	<u>Page</u>
2. Hot-Atom Chemistry of Carbon	105
a) Experimental Background	105
b) Interpretations	106
c) Theoretical Background	108
3. Accelerator Chemical Experiments	114
a) General Irradiation Procedure	114
b) Recovery of the Sample	115
c) Identification of Products	116
d) Hydrogenation of the Irradiation Mixture	121
e) Routine Yield Determination	121
f) Miscellaneous Irradiations (^{14}C -atom beam, $^{14}\text{CO}^+$ -beam, etc.)	132
4. Interpretation of the Yield-Energy Data	134
a) Toluene and Cycloheptatriene	137
b) Phenylacetylene	141
c) Benzene, Biphenyl, Diphenylmethane, and Phenylcycloheptatriene	146
<u>IV. DEGRADATION OF CYCLOHEPTATRIENE</u>	147
1. Introduction	147
2. Degradation Attempts	149
a) Via Diels-Alder Adduct	149
b) Via Oxidations	159
c) Via Reductions	160

TABLE OF CONTENTS (continued)

	<u>Page</u>
3. Partial Degradations of ^{14}C -Cycloheptatriene from 5 KeV-Irradiations	162
4. Interpretation	165
 <u>V. APPENDICES</u>	
A. Sources for Fast Carbon Particles	169
B. Derivation of Collision Functions and Yield- Energy Curves	170
C. Classical Mechanics of Bimolecular Collisions (Pick-up and Insertion Reactions)	202
D. Some Enthalpy of Reaction Values	210
E. The S/K Method	214
 <u>REFERENCES</u>	 223

I. INTRODUCTION

1. The Scope

Interest in hot-atom chemistry (the chemistry of fast atoms, molecules, etc.) is of both a practical and a theoretical nature. The isolation of artificial isotopes from nuclear transformations is facilitated by opening chemical pathways to them which are inaccessible to other products, or, in particular, which are not accessible to their natural isotopes.¹ Through hot-atom chemical experiments, improved or new methods might be developed for this practical purpose. However, high energy species enable one also to extend reaction kinetics and mechanistics well beyond reaction energy thresholds up to the upper energy limit of any chemical reaction. The importance for the study of the general theory of molecular dynamics is obvious.^{2,3}

Nuclear transformations are also a means of producing atomic species which are otherwise available only through elaborate equipment. Single carbon atoms, for instance, can be brought to react with chemical systems only by introducing them through thermal atomic^{4,5} or fast ionic beams, or through nucleogenesis (see Appendix A). However, since the initial energy of nucleogenic carbon atoms is both invariable and well above chemical energies, the kinetics can be investigated only in terms of the state of the target material (i.e. through temperature, density, and phase dependence), in terms of alterations of the primary collision density by

the addition of moderators to the reaction mixture, and by a third method outlined in Appendix E. The yield, y , of a compound is related to the collision density, K , through an integral⁶

$$y = \int_{E_a}^{E_{\max}} r(E) \cdot K(E, E_B, S) dE ,$$

where $r(E)$ is the ratio of reaction cross section to kinetic cross section at the energy E , E_a is the threshold energy ("activation energy" of the chemical reaction), $E_{\max}$ is such that $r(E) = 0$ for $E > E_{\max}$, and E_B is the maximum energy (= beam energy) that a fast particle can attain. That the collision function also depends on the constitution of the system is expressed by the variable S . Because of this integral relationship between K and y , changes in y will become apparent only through large changes of K . The dependence of y on E_B is appreciable only if E_B is in the order of magnitude of $E_{\max}$. The different initial energies in the nucleogenesis of carbon isotopes, however, is always much larger than $E_{\max}$, and the dependence of y on E_B can be studied only with equipment which produces carbon ions or atoms with energies variable in the chemical range--such as the accelerator described in this thesis. Accelerator hot-atom chemistry is therefore, in general, a valid extension of classical (nucleogenic) hot-atom chemistry, and may also be a valuable tool in general reaction kinetics.

In principle, if K is known, the kinetically interesting and important function $r(E)$ can be calculated from the experimentally determined function $y(E_B)$. However, K is not known for most systems,

and only certain gross features of $r(E)$ have been determined.⁷ However, the yield functions $y(E_B)$ also give valuable information about intermediates and precursors,⁸ as this thesis reports.

Unlike molecular beam experiments, where absolute cross sections pertaining to specific elementary reactions can be determined, hot-atom chemical experiments yield, at best, "cross sections" in terms of another cross section (elastic scattering) for a complete reaction, i.e. including also the stabilization of the product. $r(E)$ is therefore also system dependent. In addition, both functions, i.e. K and r , are averages over all quantum and configurational states of the colliding systems. All details of atomic movements are completely blurred. However, it is exactly for this reason that this new field of organic chemical experimentation can serve as a link between thermal organic chemistry and crossed-beam experiments.

It is not surprising, therefore, that the interpretation of hot-atom results uses the language and approaches of either field. Here, as certainly in many other areas of the experimental sciences, experimental difficulties (occasionally very great), not to speak of the difficulties of combining the results (finally obtained but possibly adulterated by experimental compromises) with theory, frustrate progress towards the final goal. In approaching such a relatively new experimental field it is probably most profitable to first explore its extent and limitations rather than to pursue one particular objective in (perhaps unjustifiable) depth. This thesis is the result of such extensive research.

2. Equivalence of the Hot-atom and Accelerator Chemistry of Carbon Isotopes

a) Atomic Parameters

Disregarding for a moment the radiation damage that any high energy interaction inflicts upon the system under study, the main differences between ion- (or atom-) beam and nucleogenic hot-atom chemistry are: 1) external versus internal generation, 2) different initial energy, and 3) different initial electronic states.

1) If the kinetic energy of the external ion is sufficiently high that it penetrates the surface layers of our solid benzene target sufficiently deeply so that the "chemical" interactions are with "bulk" benzene rather than "surface" benzene, there must be equivalence concerning point 1). The penetration even at 200 eV kinetic energy is sufficiently good (i.e. more than five molecular diameters, see Chapter III, 1) so that above this limit equivalence obtains.

2) The interactions of fast heavy particles with matter are discussed in many comprehensive reviews.^{9,10} At velocities above the Bohr-limit, energy loss proceeds via ionization and excitation. Below the Bohr-limit, elastic collisions with whole atoms become the prime energy loss mechanism (see Chapter III, 1). Since the chemical energy range lies at least two orders of magnitude below the Bohr-limit, the question concerning point 2) can be reformulated: To what extent does the collision function $K(E, E_B, S)$ depend on E_B ? It can probably be derived from general theory of entropy that the larger the number of statistical events involved in the evolution of a state, E from E_B , the smaller is the correlation with the first event, which is not

statistical (the first collision has to occur at the energy level of entry). Therefore, the larger E_B the lesser is $K(E, E_B, S)$ a function of E_B . Placzek¹¹ has calculated the collision function K for different values of E_B assuming only hard-sphere elastic scattering. The result is that the asymptotic solution, i.e. the function K for $E \ll E_B$, is independent of E_B , and it is a good approximation to the actual solution, if $E \leq 0.3 E_B$. Thus, as long as the initial energy is 2-3 times the upper energy limit for chemical reactions, i.e. certainly above 200 eV, equivalence obtains again.

3) The electronic state of a fast particle after slowing down to chemical energies is the subject of a later chapter (III, 1). It is concluded there that charge state equilibration is a very rapid process and that, if the ion beam energy is, again, higher by a factor of about 5 than the maximum chemical energy, the fate of carbon particles from the different sources is identical. The problem concerning the relative abundance of the metastable states of carbon are also common to all generation procedures, i.e. at energies above 200 eV, this accelerator and nucleogenic hot-atom chemistry are totally equivalent.

b) Radiation Damage

Nucleogenesis of ^{11}C or ^{14}C is always accompanied by ionizing radiation which may or may not interfere in the chemical reactions to be studied. However, since ^{11}C is so short-lived (20 min), only a small number of radioactive isotopes need be introduced for detection of the products.¹² Radiation levels below 0.01 eV per molecule are considered negligible.

In accelerated ion experiments such as ours there is only negligible Bremsstrahlung production, even if all of the ions are assumed to be decelerated to low energies before they are neutralized. The total energy incorporated into the sample via bond ruptures and momentum transfer is therefore equal to the energy of the ion multiplied with the number of ions incorporated during the irradiation. At 10 KeV energy, 1 μ A intensity, and ca. 100 μ l/hr benzene deposition (i.e. benzene:carbon, $10^4:1$), the average "radiation dose" is approximately 1 eV/molecule, a rather large figure. In criticisms of this accelerator ^{14}C -hot atom chemistry, this "radiation damage" seems to have been attributed to the ^{14}C -isotope, which is incorrect, as the following paragraph points out. The reason for this error is that most of the nucleogenic hot-atom chemistry with ^{14}C has been abandoned in favor of ^{11}C because of the large "radiation effects" on the chemical system which had to be tolerated in order to obtain detectable amounts of ^{14}C -labeled products. However, this radiation damage is a consequence of the generation procedure and not of the isotope. Therefore, accelerator ^{14}C -hot atom chemistry is in general at no fundamental disadvantage over ^{11}C -nucleogenic hot-atom chemistry.

As pointed out in detail in Chapter III, 1 and Appendix E, the initial energy of any fast particle is transferred to a target by quasi-elastic collisions mainly with other carbon atoms setting up an avalanche of secondary carbon atoms. In a solid or liquid target, such an avalanche comprises a certain volume out of which the target molecules do not drift. Possible interference between the primary particle and secondary particles in this volume cannot be avoided.

But the overlap of the avalanche-areas of different fast particles can be avoided. If this is guaranteed (although it may not be really necessary) the $^{14}\text{C}^+$ -beam chemistry should be, if anything, superior to the much higher energy, ^{11}C -nucleogenic hot-atom chemistry.

To obtain a rough idea of the "avalanche-volume" we consider a 10 KV carbon ion which has a penetration depth of ca. 0.75×10^{-4} cm and may be scattered into a cone with a generating angle of 39° (Chapter III, 1). The volume of such a cone comprises ca. 10^9 benzene molecules. At 10 KeV the ideal ratio between benzene molecules to ^{14}C -ions should be, therefore, 10^9 or larger (from which we are far off). The "avalanche-volume", however, varies approximately as the second to third power of the energy, i.e. at higher energies (^{11}C) this ratio should be even much larger, while e.g. at 100 eV energy the ratio need to be only between 10^3 and 10^5 , so that at and below 100 eV, with the ratio of 10^4 , our hot-atom chemistry of carbon in benzene should be free of any interference from the overlapping of "avalanches". That the above derived ratios are perhaps unnecessarily high can be seen from this (compare Appendix E): The number of secondary atoms created by a 10 KV ^{14}C -ion is approximately $10^3 - 10^4$. Most of these secondary atoms will collide with only a few benzene molecules because of their low energy. Therefore, the ratio between benzene molecules and secondary atoms will be 10^4 or more, so that the chance for double hits within this avalanche is extremely low.

3. Relation to Other Beam Experiments

In the experiments of this thesis as well as most other hot-atom chemistry, the number of collisions which have to be considered in the product formation is practically infinite. The collision probability K is determined by the cross section for elastic scattering, q_{es} , and, treated usually as perturbation, by the total reaction cross section, q_{tr} , all of which are functions of the energy. In order to measure them, single collision scattering experiments (crossed-beam, thin gas target) have to be performed. Differential cross sections and energy analysis of the product beams usually permit the detailed analysis of the collision dynamics due to the well-developed theory of scattering.³

If such experiments cannot be performed and many collisions have to be tolerated, one can attempt to compute the collision function by making assumptions about the differential cross sections, both reasonable from a theoretical point of view and in agreement with comparable experimental data.¹³ Many very specific features of these cross sections will be averaged over in this computation, making the collision function probably not very dependent on them. It is apparently because of this that collision functions obtained from probably grossly incorrect assumptions have been relatively useful in the analysis of hot-atom data.¹² With K known, the Dodson-Miller⁶ expression for the yield, y , of a compound,

$$y_{(E_B)} = \int_{E_a}^{\min(E_B, E_{11})} r(\epsilon) \cdot K(\epsilon) d\epsilon ,$$

can be used to compute

$$r \equiv \frac{q}{q_{rt} + q_{es}} = \frac{q}{q_{total}} ,$$

where E_B = beam energy
 E_a, E_{ll} = energy limits below and above which $q = 0$
 q = total cross section for the reaction leading
to the product under consideration
 ϵ = integration variable, energy
 E = energy .

In general, $K(E)$ turns out to be a function of the beam energy E_B .

a) If $K(E)$ is not a function of E_B , $r(E)$ can be determined by a graphical differentiation of $Y(E_B)$:

$$\frac{dY}{dE} = r(E) \cdot K(E) , \quad \text{and}$$

$$r(E) = \frac{1}{K(E)} \cdot \frac{dY}{dE} .$$

b) If the dependence of K on E_B can be expressed in the form

$$K(E, E_B) = K_1(E) \cdot K_2(E_B) ,$$

$r(E)$ is obtained again rather easily:

$$r(E) = \frac{1}{K(E, E)} \cdot \frac{dY}{dE} - Y(E) \cdot \frac{d \ln K_2}{dE} .$$

c) Outside these cases, $r(E)$ has to be computed on a trial and error basis. The computation of the reaction cross section can be calculated from the definition of r :

$$q(E) = r(E) \cdot q_{\text{total}}(E) ,$$

if $q_{\text{total}}(E)$ is known sufficiently accurately.

Thus, in conjunction with other measurements ($q_{\text{es}}, q_{\text{tr}}$) many-collision beam experiments can yield total reaction cross sections. This method could be employed profitably if, for certain reasons, single collision experiments cannot yield the desired data.

II. THE ACCELERATOR

1. Introduction

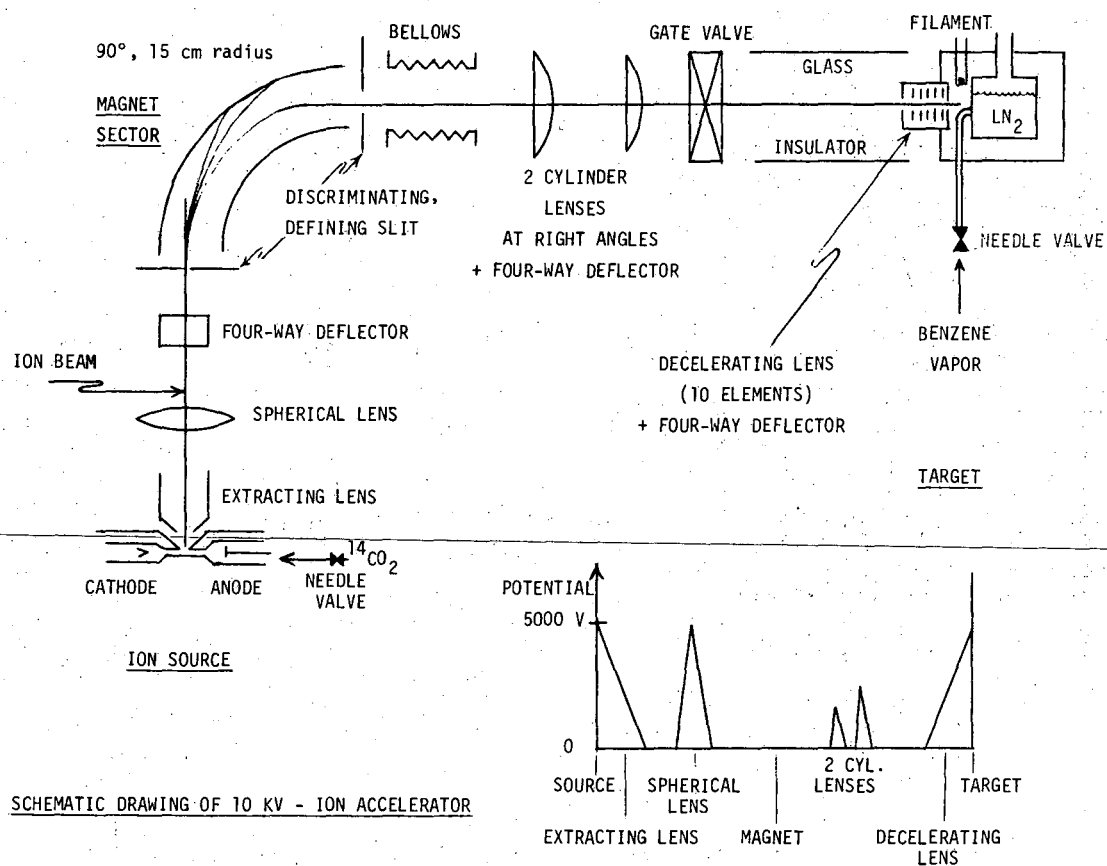
At the outset of this work the accelerator had been in operation already with its main components (see Figures 1a and 1b): ion source, accelerating electrode and first focusing lens, magnet, and target end. Several irradiations of benzene with $^{14}\text{C}^+$ -ions had been performed.¹⁴ Since a good part of this thesis deals with the technical and physical problems of operating this accelerator and with necessary changes, it is in place to mention here briefly the original objectives and considerations that the designers had followed (1959):

a) The Objective¹⁵

A beam of $^{14}\text{C}^+$ -ions of kinetic energy between <1 and 5000 eV with an intensity of approximately 1 μA was the objective. Such a beam would produce approximately 2×10^4 dpm activity per hour in a product of 1% yield (with respect to the total incorporated activity). This is not only sufficient for detection of this product but also allows for further possible low yield processing, such as chemical degradations.

b) Implementation

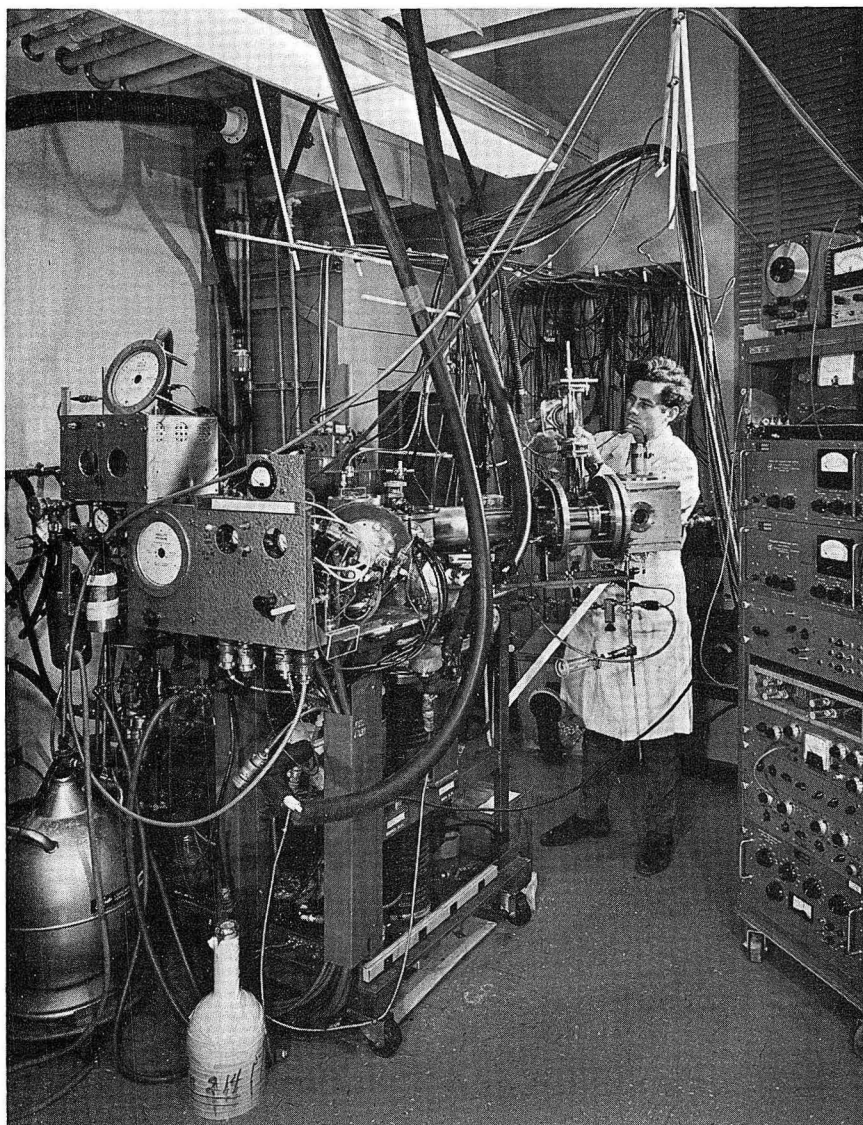
Among the many types of available ion sources, some of which were able to deliver several mA beams, the capillary-arc type¹⁶ was chosen because it was at that time considered the only one which would produce a sufficiently intense beam together with a sufficiently small (<1 eV) energy spread. (A small energy spread is necessary in



XBL 691-4085

Figure 1a. Schematic drawing of the 10 KeV-Ion Accelerator.

Distances: Arc source-magnet front face, 30 cm; magnet rear face-target, 70 cm.



CBB 691-642

Fig. 1b. Total view of the 10 KV-ion accelerator.

order to make low energy experiments, i.e. at less than 10 eV energy meaningful.) Separation of the $^{14}\text{C}^+$ -ions from other ions was to be made in a magnetic sector field which required that the kinetic energy was >1000 eV. The capillary arc chamber was known to produce maximum intensity beams at extraction voltages around 5000 V, which fitted nicely to the separation requirement. The energy of the ion beam at the target was to be controlled by appropriate deceleration immediately before impinging upon the target. This was to be achieved by raising the electrically isolated target and target box whose entrance aperture was covered by a fine wire grid (ϕ 2 mil, 10 mil spacing) to the appropriate decelerating potential.

However, the realization of the mentioned objectives was beset by many problems:¹⁴ The striking and maintenance of the arc was difficult, the length of irradiation too limited due to short filament lifetime, and the beam intensity at the target, particularly at low energy, was too small. It was recognized that, in order to perform reproducible experiments in hot-atom chemistry, the functioning of the tool, the accelerator, had to be much improved.

In the meantime, ample technical knowledge has evolved concerning particular features of ion sources, ion beams, and ion optics, so that, if this accelerator were to be built again today, it would be designed quite differently. The prime interest was, however, on its application in hot-atom chemistry, and improvements and changes were dictated by the requirements of hot-atom chemical experimentation rather than by the application and advancement of accelerator know-how for its own sake. This report is therefore incomplete as an analysis

of the accelerator and, for the same reason, the apparatus may appear--to today's knowledge--awkward, if not clumsy. Figure 1a shows a schematic diagram of the accelerator.

2. The Ion Source

The ion-source is of the metal-capillary type. It and its glass version have been described in a few early reports.¹⁶⁻²⁰ In most cases this type has been used for the production of high energy proton beams with 1-10% efficiency.^{21,22} Besides this relatively low efficiency (for protons) the main drawback was the difficulty and unreliability of operation. Seemingly, it was used for the production of carbon beams only on a trial basis.¹⁷

C⁺-ion beams for ¹⁴C hot-atom chemistry, i.e. with about 1 μ A intensity, have been employed by Aliprandi et al.²³ and Maddock.²⁴ The first group used a magnetically confined hot-filament discharge as ion source, the latter's ion source is not known. C⁺-ion beams of much smaller intensity for various applications have been obtained from a variety of sources.²⁵

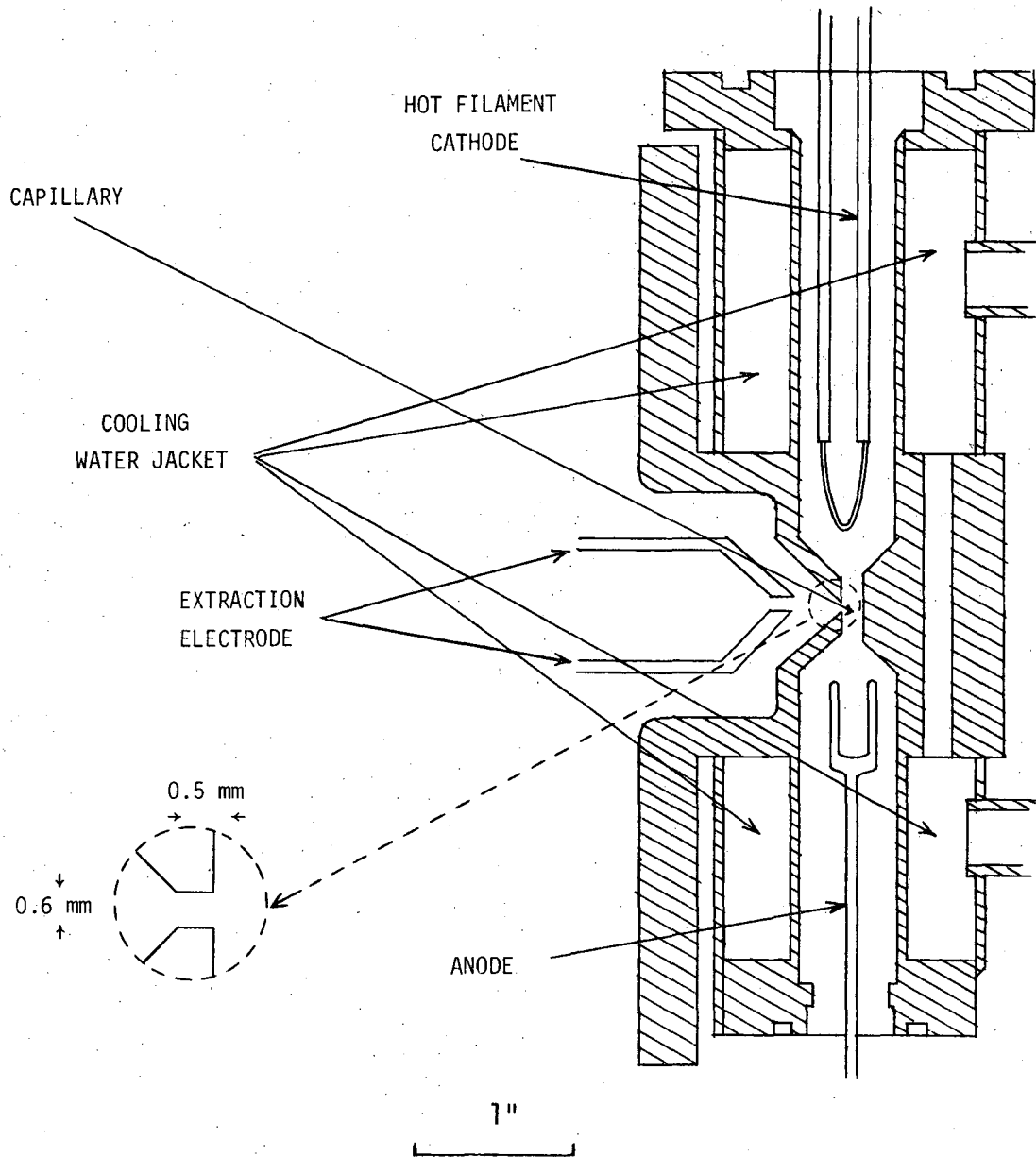
Most of the observations with capillary arcs described by others¹⁹ have been made here again. It seems that in view of its low efficiency, its relatively large energy spread (see Chapter II, 5), and

its difficult operation it might soon be replaced by a more modern ion source.

A schematic of the arc chamber is shown in Figure 2a. A hot filament supplies the electrons which, after acceleration by the field between filament and chamber wall, ionize the atmosphere. Due to the impact of the positive ions which are accelerated into the cathode, more electrons and positive ions are generated and a regular discharge develops. When the potential of the anode and wall are raised sufficiently high and when the pressure is increased to about 50μ , the plasma is drawn through the capillary towards the anode. (This latter operation is in the following referred to as "striking" of the arc in the narrower sense.) The arc is now in its normal operating condition, the pressure can be lowered again to $10\text{-}50 \mu$, depending on the gas used. The metal wall acts like a giant probe and mainly serves to increase the current density and consequently the ion density of the constricted plasma, *i.e.* in front of the extraction orifice on the side of the capillary.

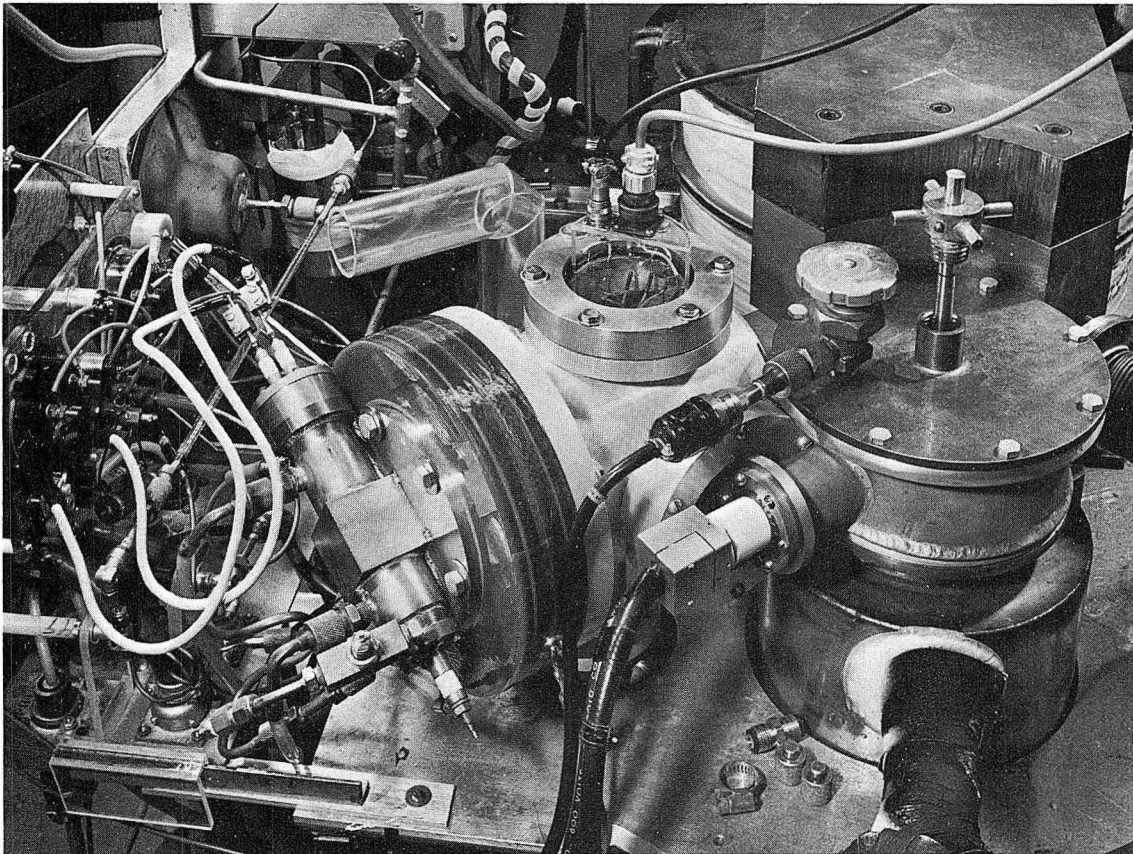
a) Filament

1) Power supply. It was recognized that the formerly ac-heated filament (usually a $1/16"$ x $5/1000"$ Rhe-strip, spot-soldered on stainless steel rods) did not provide a continuous source for electrons. Due to sufficient heat-conduction in the surrounding atmosphere, the temperature of the filament fluctuated with the frequency of power input, 120 Hz, around an average value. The temperature was, therefore, during certain phases of the oscillations, low enough to stop or at least substantially decrease thermionic emission.



XBL 695-4231

Figure 2a. Arc chamber, schematically.



CBB 691-644

Figure 2b. Arc source (lower left); magnet yoke (upper right).

Since this type (low pressure) arc is maintained primarily by an external supply of electrons from an externally heated filament, the discharge changed its characteristics with the changing filament temperature. Proof for this situation was obtained when a complex energy modulation (30-40 V p.t.p. at 120 Hz) of the beam was observed at the discriminator slit (see Figure 1) passed the magnetic field (see Chapter II, 5): Apparently, the plasma (bulk) potential from which ions are extracted varied in a complex manner according to the intensity pulsations of thermionic emission. After provision of dc-heating of the filament, most of this modulation had disappeared, the remaining modulation being due to the ripple on other power supply outputs. The adjustable dc-power supply delivers maximal 750 W, with 25 amp maximum current. However, most filaments require only 10-15 amps (decreasing with age) at 5-8 V. The thermionic emission is then approximately 500 mA. The maximum current ripple is 0.1 amps p.t.p. at 10 amps load.

2) Lifetime. At the same time with the change to dc-current heating, the lifetime of the filament, around three hours before, decreased to sometimes only 15 min, depending on the number of times of "striking" the arc. This and the large arc current peaks observable during "striking" of the arc immediately led to the solution of the lifetime problem: Most electrical discharges exhibit, at least over a certain range of arc parameters, a negative voltage-current characteristic, i.e. are electrically unstable. By switching in series with the arc impedance a sufficiently large real impedance, the overall load to the arc power supply has a positive characteristic

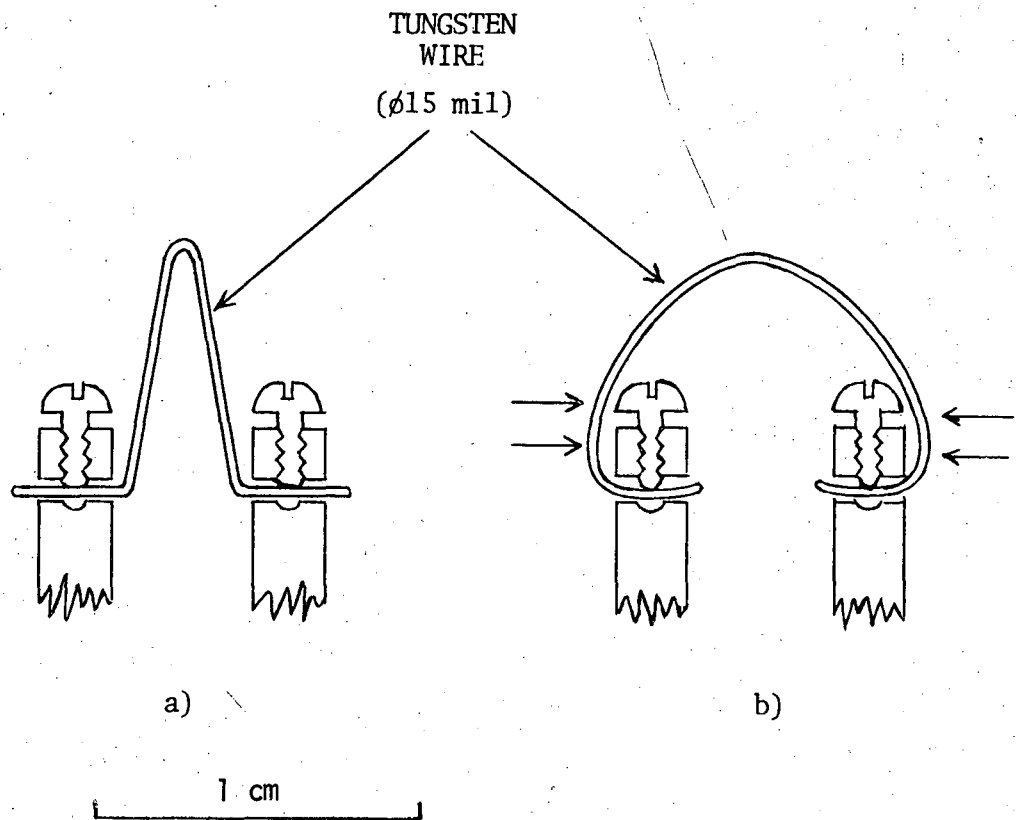
and the system is stable. However, when the arc current is limited by the limited emission of electrons from the hot filament, no such external stabilization, or very little only, is needed. An arc with an ac-heated filament may be current-limited on the average over the ac-cycle and may therefore not require extensive external stabilization. A 300 Ω series resistor had, therefore, been found adequate, previously. However, during the ac-phases of high emissivity the arc was temporarily unstable and high current spikes were apparently able to develop. Such currents are known to cause local heating of the cathode to such an extent that evaporation of the filament material may result. After changing to dc-heating, however, the electron emission was constant, and the previous current limiting phase of the electron emission was missing. While the arc was relatively stable once it was "struck", it exhibited a violent phase during "striking": The arc current jumped for a moment up to more than 3 A and the filament current meter registered a change by several amps. After a few repetitions of this striking procedure, the filament was burned out because of vaporization of the filament material. The same process, only with less intensity, yet periodically with 120 cycles and aided by some 10 μ F filter capacitors (which acted here as a short-lived, high current source), is believed to have been the prime cause for the short filament lifetime of 3 hrs or less, previously found with ac-heating.

After increasing the external resistor to 1000 Ω , the current spikes were sufficiently small and the lifetime jumped to around 25 hours and seemed to be independent of the frequency of striking the

arc. The lifetime seems to be limited now by ordinary sublimation of filament material aided possibly by chemical ("getting") interactions with the atmosphere or plasma.²⁶ However, the limitation is not serious since after approximately 25 hrs operating time the whole arc chamber has to be disassembled and thoroughly cleaned, at which time filament replacement is quite opportune. Similar life spans of filaments under comparable conditions have been observed by others, too.²⁷

3) Material. It was recognized at the same time that the filament material had no apparent effect on the lifetime, contrary to earlier reports.¹⁴ The claim that Rhe also has the advantage of not forming a carbide,²⁸ the main cause for the brittleness of tungsten and presumed cause for emissivity fluctuations after brief usage, is incorrect. This was shown by the inability to dissolve all of a used Rhe filament in concentrated HCl. A shell of, most likely, a Rhe-carbide persisted. It is true, however, that a used Rhe-filament is far less brittle, and therefore less likely to break under mechanical stress than tungsten. However, the ease of availability and mounting of tungsten wire, a stock material, dictated the use of tungsten as filament material. Another possible advantage is that the rate of evaporation of tungsten is about 150 times lower than that of phenium at equal thermionic emission.²⁸ Barring any chemical effects, this should make a tungsten filament more long-lived. Tantalum and thoriated tungsten wire have been tried also. However, no large difference from tungsten was apparent.

4) Geometry and position. Yet another phenomenon turned out to be of importance: Breakage of filament, whether rhenium or tungsten, always occurred at a place least expected--near the holding rods (see arrows in Figure 3, b). Inspection of the filament after some intermediate operating time showed a definitely decreased thickness in the same areas. Most likely, these were also, and not the tip, the area of most intense electron emission at that phase of filament life. (Comparison with Figure 2a shows that the initial arc, between filament and wall, would be localized at quite a distance from the entrance to the capillary--thus increasing the difficulties of "striking" the arc through it (see Chapter II, 2e). In order to alleviate these difficulties the emission was usually increased by increasing the filament current, thus accelerating the consumption of filament material. It was, however, the problem of striking the arc at late stages of the filament life and not the desire to lengthen the lifetime that led to the investigation of this phenomenon. Usually, the filament was mounted as shown in Figure 3, b. Protection of the area, indicated by arrows, by ceramic tubes did not improve the situation very much. Finally, since it was felt that the consumption of the filament material at these points had something to do with the closeness of the arc chamber wall, the filament was mounted as shown in Figure 3, a. The overall filament length was also smaller now. The effect was ease of striking of the arc at all filament ages and eventual burn-out at the tip. The higher consumption of filament material near the arc chamber walls, however, is essentially not understood. There is no indication that



XBL 695-4229

Figure 3. Hot-filament cathodes.

the shape of the filament, or whether it is round wire or strip, has any effect upon the arc operation.

Lamar et al.¹⁹ had found that the distance of the cathode (and anode) must not be too large for smooth arc operation. To investigate this effect and in the hope that the early "striking" and maintenance difficulties could be alleviated, the filament was mounted on an actuator with a travel of ca. 1.5 cm along the capillary axis. The result was that at a distance of 1-2 mm between filament and the capillary entrance the arc "struck" very easily. However, the energy spread in the ion beam (see Chapter II, 5) was increased at the same time (which was undesirable). Only at distances greater than 2 cm did the striking become markedly more difficult. The filament-capillary distance was therefore held between 0.5 and 1.5 cm.

The filament can easily be removed and replaced by a new one so that the accelerator is back in operation after not more than 30 minutes (if not too good a vacuum in the accelerator is required).

b) Wall-voltage Power Supply

Previously, the voltage of the arc chamber wall with respect to the cathode was supplied from the anode through a 40 K Ω resistor.¹⁴ By increasing the output of the anode power supply, both anode and wall potential were raised until the arc struck, causing a larger current across the external series resistor and lowering both potentials simultaneously.

For several reasons it was found advantageous to be able to adjust the wall voltage independently:

1) Previously, in order to obtain sufficiently high wall voltages (which is necessary for "striking"), the voltage drop across the $40\text{ K } \Omega$ resistor had to be small, that is, the cathode to wall current, and thus the thermionic emission, had to be small. This, however, was adverse for the maintenance of the arc immediately after striking.

2) Higher arc stability and resistance to breakage, caused by occasional discharges (see Chapter II, 2e), was observed at higher wall voltages than those obtainable with the above set-up.

3) The energy of the ions depended somewhat on the wall voltage (see Chapter II, 5), and it was expected that a more stable wall voltage would also stabilize the energy.

4) Both beam intensity and energy spread seem to depend on the wall voltage. An adjustable wall voltage was expected to allow for optimization of both. Similar effects had been observed by Lamar et al.¹⁹ with H_2 as feeding gas.

A power supply was therefore built which delivers up to 120 V at 1.5 A dc, unregulated, with a ripple of 0.25 V p.t.p. at 400 mA. Before striking the arc the filament current is adjusted so that at about 90 V wall voltage and approximately $20\text{ }\mu$ pressure the current to the wall is approximately 400 mA. As soon as the anode voltage is raised above 100 V the arc strikes through the capillary. The wall voltage can now be adjusted between 0 and a value ca. 40 V below anode voltage. The arc extinguishes if the wall voltage is made negative with respect to the filament. If one attempts to raise it

above a certain limit the anode voltage begins to rise also, staying ca. 40 V above that of the wall; the arc current, i.e. the current across the anode, drops.

The effect of varying the wall voltage upon the beam output are very complex.¹⁹ The main effect is the decrease of the energy spread with increased wall potential and the higher arc stability. The effect upon the intensity is small if the anode voltage is high.

With wall voltages up to 120 V available, the "striking" is very easy even at low gas pressures. Thus the overall consumption of gas ($^{14}\text{CO}_2$!) is greatly reduced.

c) Anode

Since the voltage ripple on the anode power supply output under operating conditions was several volts, an LC-filter was switched in series with the arc load. This decreased the ripple to ca. 0.15 V p.t.p. at ca. 100 V and 400 mA between cathode and anode. Thus, the potential of any point in the arc discharge with respect to the cathode was time independent within 0.2 V p.t.p., unless high frequency oscillations appeared (see below, II, 2e).

The influence of the anode/capillary distance was investigated also by mounting the anode on an actuator with the same travel and direction as that of the cathode. Only if the anode was closer than 1-2 mm to the capillary was there an adverse effect upon the stability of the arc, i.e. the minimum operating pressure was larger (see Chapter II, 2d).

The shape did not seem of any influence. It was only to increase its area that it was given the cup shape (see Figure 2a),

because it was noticed that the anode accumulated an insulating deposit which made the operation of the arc very difficult. We hoped that an increased area would lengthen the time between the necessary cleanings. However, the speed of accumulation seems to be dependent on so many factors that it is not possible to tell whether the hoped for effect has materialized.

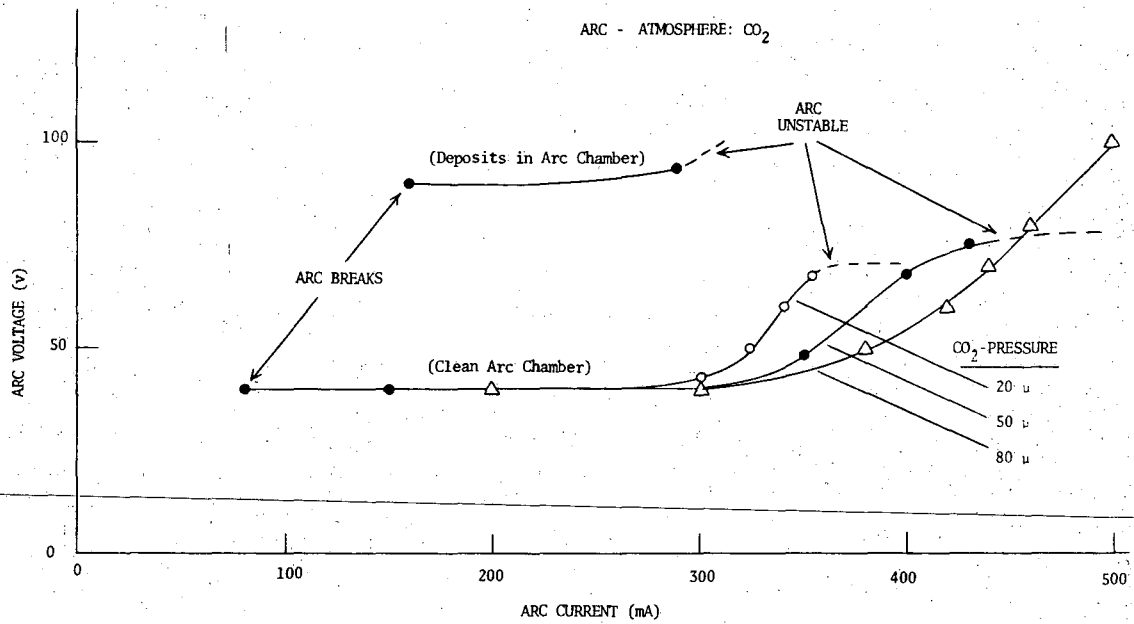
The accumulation of deposits, probably particularly on the anode (see Chapter II, 5) has a profound effect upon the energy spread and the true mean energy of the emitted ions. The spread increases strongly, and the mean energy can decrease by as much as 10 eV.

Figure 4 depicts the current-voltage characteristics for this capillary arc (somewhat schematically).

d) Gas Supply and Efficiency

Gases are supplied from reservoirs at 10 to 50 mm Hg pressures at ground potential. They are insulated from the arc chamber (at high voltage) by ca. 20 cm long, 7 mm O.D. glass tubes. The pressure in this glass tube has to be either sufficiently small or sufficiently high to prevent glow discharges from striking across it,²⁹ e.g. CO₂ has to be kept above 5 mm Hg, Ar above 50 mm Hg. A needle valve at the entrance to the arc chamber regulates the gas flow from each reservoir.

In order to monitor the gas pressure inside the arc chamber, a thermocouple gauge (Hastings "T", 1-1000 μ), was te-ed into the gas supply line near the entrance to the arc chamber. The power supply for this thermocouple gauge, of course, is insulated to 10 KV.



XBL 695-4226

Figure 4. Arc operating characteristics for different states of the arc chamber surface and for different arc atmosphere pressures.

A check showed that the arc chamber pressure at the location of the filament was equal to the pressure measured in the gas input line within the error limits of the instruments.

With two separate gas reservoirs, the actual feeding gas can be mixed, if this is desired, just prior to entering the arc chamber. This may be necessary for "difficult" gases, where support gases, as Ar, have been found to facilitate the operation.

It was also found that admixtures of He to CO_2 in ratios up to 5:1 did not make the operation of the arc much more difficult, i.e. the minimum pressure in this mixture was not much higher than that for pure CO_2 (see Table I), while the C^+ -beam intensity remained unaffected. That is, the efficiency increased by approximately a factor of five since the CO_2 flow rate and partial pressure were decreased. This He-effect has been found also by others in H_2 and in different ion sources.³⁰

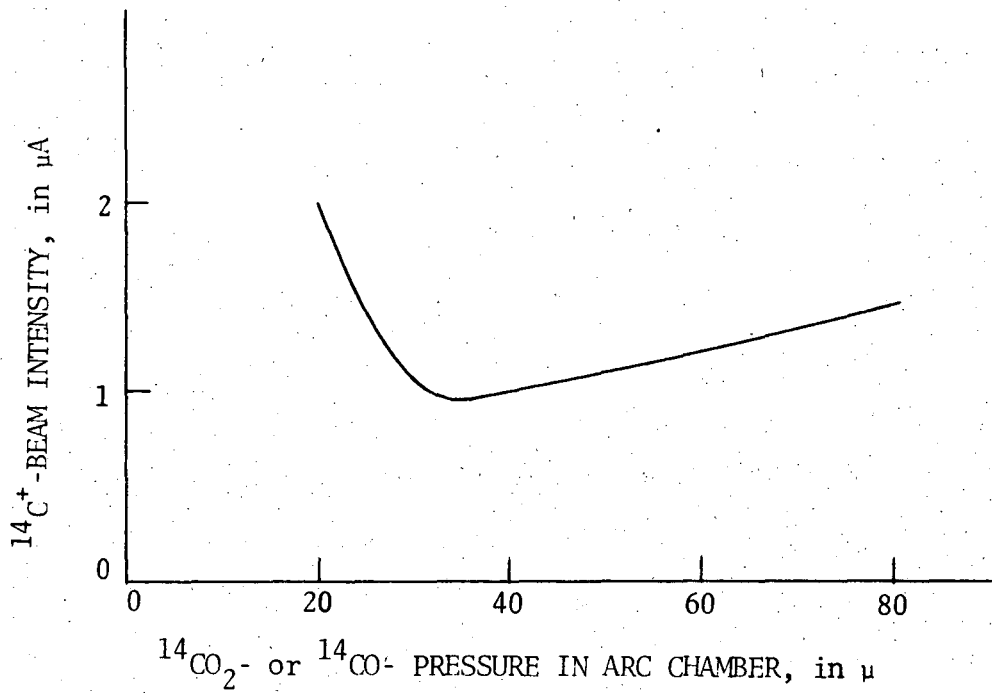
For pure gases the beam intensities depend on the pressure as indicated for C^+ from CO_2 or CO in Figure 5. At the minimum operating pressure, luckily, both the beam intensity and efficiency are maximum. The ion output also increases with increasing anode voltage, i.e. in the positive characteristic region (compare with Figure 4). The arc is therefore always operated at minimum pressure and maximum arc voltage, although this is a rather unstable condition. The maximum C^+ -ion beam at the target is ca. 2 μA . The yield is, therefore, with 1×10^{-8} moles/sec CO_2 feed at 20 μ : 0.2%. With admixtures of He, this yield can be increased to 0.5 - 0.8%. This may seem like a very poor efficiency; however, to our knowledge it is the highest ever reported.

TABLE I
Typical Arc Conditions¹⁾

Gas	AV	AC	WV	WC	P	P _{break}	P _{strike}	Major Ion Beams ²⁾ (μA)	Remarks
He	60	360	0	0	300	110	300	He ⁺ :10	
Ne ³⁾	60	350	0	0	50	17	45	Ne ⁺ :10	The WC increases to 700 shortly before striking
Ar	50	360	0	50	8	5	15	Ar ⁺ :20	
Xe	30	360	0	20	5	1	5	(>20) ⁴⁾	
H ₂ /Ar(1:1)	50	360	0	0	20	15	20	H ⁺ :0.5; H ₂ ⁺ :1; H ₃ ⁺ :0.3	
N ₂	50	300	0	0	45	17	50	N ⁺ :2; N ₂ ⁺ :15	
O ₂ ⁵⁾	65	300	0	0	60	50	100	O ⁺ :1; O ₂ ⁺ :15	
Cl ₂ ⁶⁾	600	300	100	300	60	40	60		
CO ₂	50	350	0	0	25	20	40	C ⁺ :1-2; O ⁺ :1; CO ⁺ :15; CO ₂ ⁺ :5	
CO	70	360	0	0	15	15	30	C ⁺ :1-2; O ⁺ :1; CO ⁺ :15	
CH ₄	80	300	100	200	170	150	170	H ⁺ :1; H ₂ ⁺ :3; H ₃ ⁺ :1; C ⁺ :0.1; CH ⁺ :0.5; CH ₂ ⁺ :1; CH ₃ ⁺ :2; CH ₄ ⁺ :5	
HC≡CH	50	350	0	0	30	15	40	CH ⁺ :0.3; M ₂₄₋₂₆ :10	These conditions for 1:1 Ar/CH ₂ Cl ₂ ; pure CH ₂ Cl ₂ : P _{strike} : 100 μ; however, no stable arc resulted.
CH ₂ Cl ₂	50	350	0	0	30	15	20		

AV = Arc voltage (V)
AC = Arc current (mA)
WV = Wall voltage (V)
WC = Wall current (mA)
P = Pressure (μ) at which intensity of ion beams is determined.

- 1) These are operating conditions. Conditions before striking of arc: WV, 100V; WC, 500; P, P_{strike}; AV, 300-700V; AC, 0.
- 2) Estimated from e/m scans behind the discriminator slit (Figure 1a) 0.3 mm wide, at arc conditions as indicated.
- 3) "Spark chamber gas", contains 10% He.
- 4) At 4000V acceleration, maximum mass to pass through discriminator slit, at 3500 gauss: ca. 50.
- 5) From Pacific Oxygen, 99.6% O₂ (2000 ppm Ar).
- 6) From Matheson Co., 99.5% Cl₂.



XBL 695-4228

Figure 5. $^{14}\text{C}^+$ -beam intensity at the target versus arc atmosphere pressure, schematically.

Another advantage of the two-gas reservoir system is that the transient higher pressure usually needed during "striking" can be supplied by the "easy" (see Table I) and inexpensive Ar. Thus the $^{14}\text{CO}_2$ pressure is always kept at the minimum operation pressure, and Ar is admitted for a short time only for striking. This, too, decreases the consumption of $^{14}\text{CO}_2$ considerably if frequent re-striking should be necessary.

The gas consumption is monitored by 0 - 50 mm Hg pressure gauges (Wallace and Tiernan) connected with the reservoirs whose volume had been determined (0.63 - 1). The relation between gas flow, dn/dt , in moles/sec, and pressure decrease, dp/dt , in mm Hg/sec, is therefore

$$\frac{dn}{dt} = 3.4 \times 10^{-5} \frac{dp}{dt}.$$

The relation between gas flow and arc chamber pressure is, of course, dependent on the nature of the gas. Also, the flow through the orifice (0.6 mm) changes from molecular to viscous as the arc chamber pressure increases to and beyond ca. 100 μ . At 20 μ the flow rate for $^{14}\text{CO}_2$ is ca. 1×10^{-8} moles/sec and approximately pressure proportional up to ca. 200 μ . Other gases (Table I) exhibit similar (within a factor of two, equal to that of CO_2) flow vs. pressure curves.

e) General Performance of the Ion Source

1) Different arc chamber charges. It was hoped that this ion source would also produce, with sufficient efficiency, other

ionic species from other arc chamber charges, in particular $^{14}\text{CH}_x^+$ ion beams from $^{14}\text{CH}_4$, with $x = 1, \dots, 4$ for low energy interaction studies.¹²³ This source was, therefore, tested for different charges, and Table I gives a summary of this brief survey.

It is surprising to find that H_2 , CH_4 , and other hydrocarbons are relatively "poor" arc gases, since this ion source had been originally designed for the production of H^+ .^{15,19} However, we believe that relatively minor changes, for instance in the geometry of the arc chamber, might make it a more efficient source for these ions. This belief is encouraged by a lack of reproducibility of conditions for these gases, a similar situation as existed originally for CO_2 ,¹⁴ which established itself as a good arc gas after extensive investigation of the respective arc behavior. The ion beam intensities were measured at the discriminator slit (Figure 1a) by scanning the magnetic field, and by recording the voltage drop across a 100 K Ω resistor from an intercepting plate on a 5 mV - 100 V Moseley recorder. Corrections for secondary electrons were not made.

2) Radio-frequency oscillations. Radio-frequency oscillations are common in ionic plasmas.³¹ Such oscillations can be generated in this source with all gases and for a variety of arc conditions. A clear-cut relation between these and the oscillations could not be observed. The oscillations were undamped, or damped and pulsating at irregular intervals. The rf-frequency, however, was always rather constant at 0.6 MHz. Amplitudes ranged up to 5 V p.t.p. As described in Chapter II, 5, these rf-oscillations may or may not have an appreciable effect upon the mean ion energy and the

energy spread. This, again, depends on arc conditions in a very complex way. In any event, it is necessary, in low-energy irradiations, to continuously monitor the rf-level of the source, since during any irradiation conditions may develop (e.g. because of the slowly changing thermionic emissivity of the arc filament) towards excitation of oscillations. The rf-level is monitored by coupling an oscilloscope through a 1 nF, 10 KV capacitor directly to the arc chamber body. Apparently, a large inductance of the rather long connecting high voltage cable prevents the shunting of this signal through the output capacitance (0.1 uF) of the acceleration voltage power supply. In the absence of rf-oscillations, only a ca. 0.3 V p.t.p. "hash" (noise) is generated by the arc.

3) Difficulties in striking and maintaining the arc discharge.

a) Deposits: It was found that after ca. 30 hrs operation time in CO₂, particularly the narrow capillary, but also the anode, had to be freed from insulating deposits. This is achieved by the use of fine mechanical abrasives. All deposits cause great difficulties and may even prevent the striking of the arc. A clean arc chamber allows current adjustment over a wide range (see Figure 4) without arc breakage. With deposits present, this range is greatly decreased and the arc voltage always appears higher than usual at the same current. Sometimes the anode voltage rises slowly on its own from 70 to 120 V before the arc breaks. With deposits, the arc can usually not be run at the minimum pressure.

With some gases, such as hydrocarbons, the build-up of deposits seems quicker than with gases like CO₂, CO, N₂, O₂, etc.

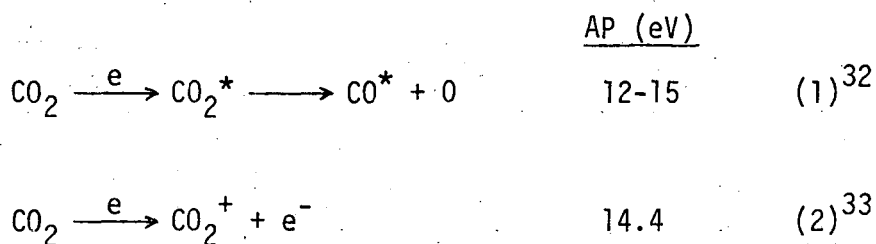
b) Discharges: In this state, i.e. with deposits in the chamber, the arc is also very sensitive to external influences; for example, occasional minor discharges in the beam region (due to surface charge build-up). Such a discharge almost invariably caused the breakage of the arc and produced another discharge between the arc chamber body near the extraction hole and the extraction electrode (see Figure 1a). This secondary discharge caused the build-up of deposits on both surfaces, which in turn gave rise to secondary electron emission and further discharges. Thus, finally, the arc could be maintained only at rather high pressures.¹⁴ The accumulation of surface charges in the extraction region is prevented, or at least substantially decreased, by periodical cleaning (with liquid metal polish) of all surfaces and/or by coating them with carbon colloid "Aquadag".

With all the previously mentioned stabilizing factors, clean arc chamber, and clean beam electrodes, the arc can be maintained for several hours at low pressure without interruption. This is not only expedient for $^{14}\text{CO}_2$ economy, but it is the precondition for meaningful low energy irradiations which, too, last several hours and which require that the true mean ion energy which is a sensitive function of the plasma conditions remains constant within approximately 1 eV over at least the same period.

3. The State of the Carbon Ions

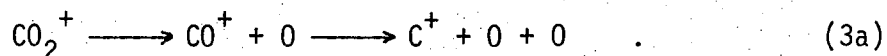
Although no explicit information is available on the state of the fast carbon particle after it has been collision-slowed into the chemical energy range in the target material, it is of general interest to know the state that a carbon ion attains under the present conditions of formation before it enters the target. In particular, if the carbon ion is generated with a certain kinetic energy this will be of importance to the energy spread. The problem is complicated because of the possibility of chemical reactions (resulting, e.g. from bimolecular collisions) in the arc source. The mean free path at 20 μ pressure, approximately 0.5 cm, is comparable to the arc dimensions, and one has to expect many collisions before an ion diffuses into the extraction channel and leaves the arc. On the other hand, these chemical reactions may be the reason for the relatively high yield in the formation of carbon ions from CO_2 or CO . There are many routes by which C^+ -ions are formed from CO_2 in an ionic plasma as ours. For some of the elementary reactions which are involved in these routes, detailed physico-chemical data are available. These permit one to tentatively piece together the chemistry as well as to deduce the possible electronic state of the carbon ion.

Primary reactions:





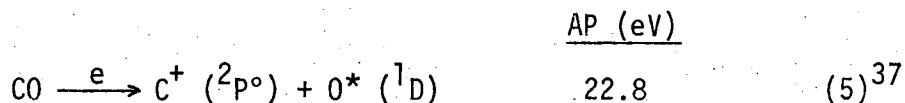
Reaction (3) is probably the prime source for C^+ from CO_2 . Inoue et al.³⁴ believe that this reaction involves the sequence of spontaneous decays



They found that C^+ has an initial kinetic energy of 0.9 eV.

McConkey et al.³⁶ have crossed a CO_2 beam with an electron beam with energies between 20 - 1000 eV and have been unable to detect any radiative states of C, O_2 , and CO. While this experiment does not rule out the existence of metastable states of these fragments, it makes them unlikely. The carbon ion is, therefore, most likely in its ground state (^2P).

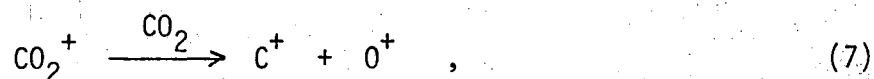
The large cross section ($2 \times 10^{-16} \text{ cm}^2$) of reaction (1) and its low AP make this reaction another possible source for carbon ions via the following sequence:



Hagstrum determined the energy distribution of C^+ from CO and found for (5) and (6) a mean energy of zero, with an energy spread of ca.

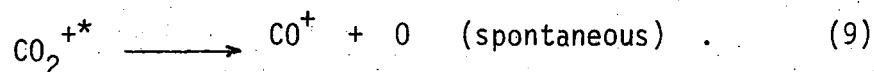
2 eV, somewhat tailing towards higher energies.³⁷ This reaction certainly is the main source of C^+ from CO.

On the other hand, Dixon observed that most of the emission from a discharge in CO_2 was due to CO_2^+ .³⁸ This, together with Kuprianov et al.'s interpretation of collision disintegration broadened odd-mass peaks from CO_2 as being due to³⁹



make this possibly another major source of C^+ from CO_2 since any CO_2^+ certainly undergoes many collisions with CO_2 molecules before leaving the source. Unfortunately, no energy measurements have been made at these C^+ -beams.

Another route may be the decomposition of CO_2^{++} from (4). Several authors⁴⁰⁻⁴³ conclude that CO_2^{++} decomposes by the following sequence



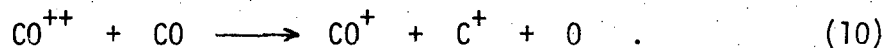
If C^+ is formed from this sequence it should obtain a high energy since CO^+ does (5 eV).⁴⁰ Field and Franklin⁴¹ observed indeed a high energy tailing in the C^+ peak believed to be made from CO_2^{++} .

The observation that the most intense ion beam extracted from CO_2 in this ion source (see Chapter II, 2) is CO^+ seems to make (3a) and possibly (8) and (9) dominant reactions in this plasma. However,

it is questionable if the cathode fall, probably the only discharge region where electrons can gain very high (>30 eV) energies, is large enough to provide 42 eV electrons for the appearance of CO_2^{++} .

From the presented data, it is reasonable to conclude that reactions (3a) and (2), followed by (7), are most likely the main sources for C^+ from CO_2 . Most of the C^+ ions are in the ground state (^2P) and their initial energy spread may be ca. $\pm 1\text{eV}$.

Reactions (5) and (6) are undoubtedly the major sources for C^+ from CO. Another contribution is likely to come from⁴³



It is noteworthy in this context that the arc conditions and C^+ -production efficiency are almost exactly identical for CO_2 and CO as source charge. The conclusions concerning state and energy of the carbon ion from CO are the same as for C^+ from CO_2 .

4. The Kinetic Energy and State of the Carbon-atom Beam

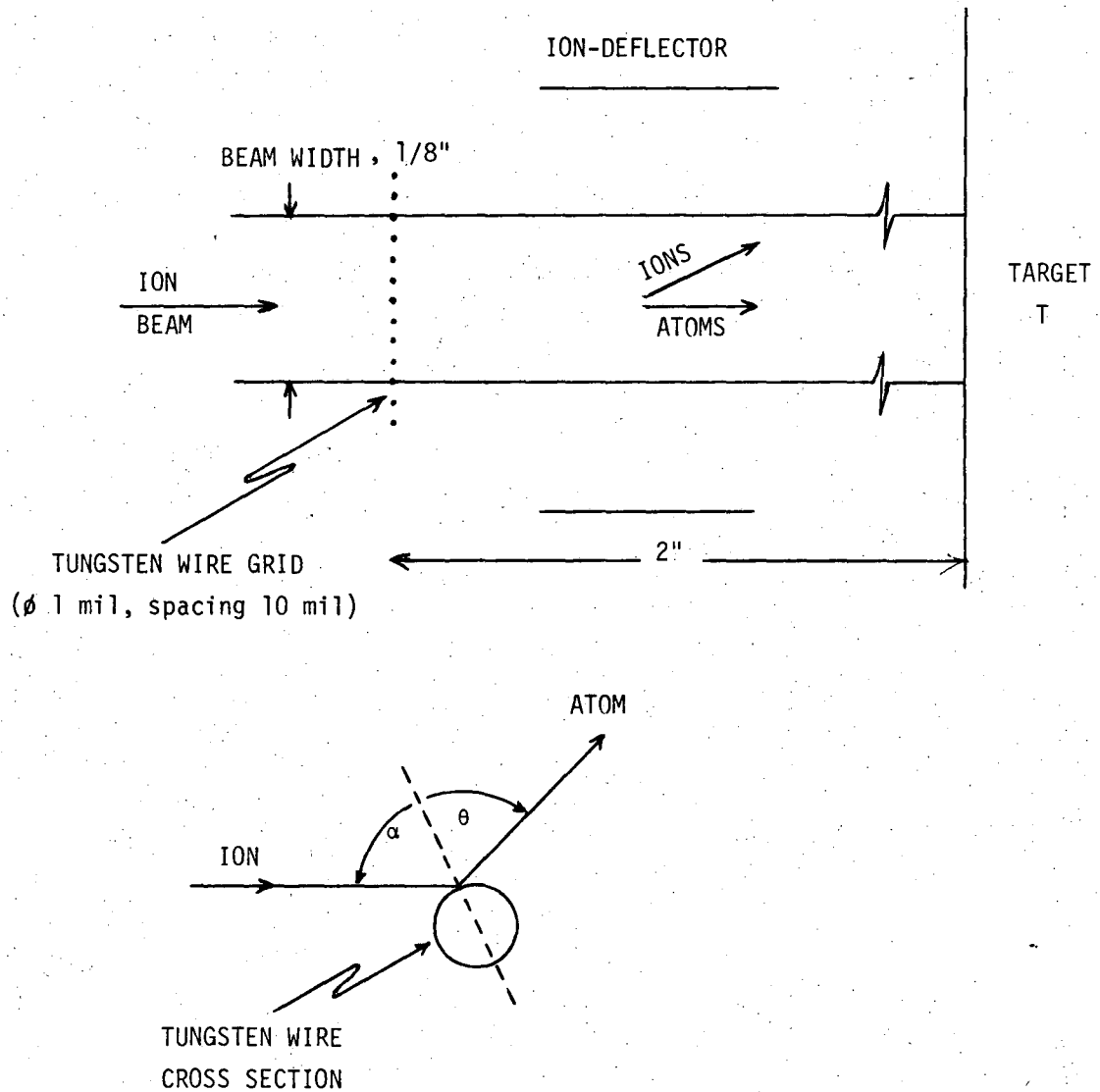
In a few irradiations the ion beam was neutralized by charge exchange at a W-wire grid (ϕ 1 mil, 10 mil spacing). Connecting to the previous chapter the state and energy of this atomic carbon beam is discussed.

The phenomena of ion impact on metal surfaces have been reviewed by M. Kaminsky in 1963.⁴⁴ No comparable data have, in the meantime, become available which deal with the specific question of the energy and state of an atom beam produced in the above manner. The processes leading to the production of these atoms are a function of: the kind, state, and energy of the ion; the angle of incidence, α , and departure, θ , with respect to the surface normal; and the kind and state of the metal surface. It is well known that metal surfaces accomodate layers of residual gases from the vacuum atmosphere, and also accomodate incident beam particles.

a) Kinetic Energy

Figure 6 shows an approximately scaled schematic of the neutral beam experiment. It shows that, in general, for the neutral beam particles, collected at target, T, the angles of incidence on the metal surface are large, i.e. between 90° and approximately 45° . The same is true for the angle of departure. However, as will be argued, the predominant contribution probably arises from grazing angle collisions, i.e. $\alpha \approx \theta \approx 90^\circ$.

The problem is dissected best along the two categories of "reflection" and "scattering". Neutralization may occur in both models, and the actual atom beam generation on the metal surface may involve



XBL 695-4250

Figure 6. Neutralization of the $^{14}\text{C}^+$ -ion beam by grazing collision with a metal surface.

a chain of interactions, in particular, scattering of the neutral particle at another metal atom. It is fairly well established that the scattering properties can be described as occurring between the incident ion and an isolated metal atom if the incident ion energy is large compared to the metal atom binding energy ($\approx 10-20$ eV). If neutralization occurs via this "scattering model" it is connected with a small angle of deflection and practically no kinetic energy loss. This is generally observed in scattering of ions in low pressure gas targets. The possibility of subsequent collisions with other metal atoms should be small for "grazing" collisions ($\alpha \approx 90^\circ$) and should increase as this angle decreases. However, the probability for scattering into an angle permitting the atom to reach the target should decrease when α decreases. Furthermore, the probability that the ion or atom gets "stuck" on the surface increases as the collision departs from "grazing". Therefore, in this model, neutralization should proceed predominantly with "grazing" angle of collision.

Neutralization can occur under "reflection condition", i.e. when $\alpha \approx \theta$, only if the projection of surface irregularities (height d) in the direction of incidence is smaller than the wavelength, and if the contact time is small compared to vibrational periods (10^{-13} sec). The latter is fulfilled considering the time of approximately 10^{-15} sec for the ion to traverse a lattice atom separation. The first condition requires an angle of incidence within 10^{-6} rad of 90° . (This is calculated from $d \cdot \cos \theta < \lambda$, with $d \approx 10^{-5}$ cm; $\lambda = 10^{-11}$ cm, the deBroglie wavelength of C at ca. 1 KeV kinetic energy).

Energy changes under these conditions seem to be due only to electronic transitions. Important are the differences between the recombination energy of the ion and the work function of the metal surface, about 5 eV; in addition, Auger-effects can produce secondary electrons with kinetic energies up to maximal 15-20 eV.⁴⁴ The total rate of production of these secondary electrons is 10-15%, with a mean energy of ca. 8 eV. Thus, one can say, whatever the mechanism of neutralization, the loss of kinetic energy is small compared to the beam energy (0.5 to 5 KeV), and the beam divergence is small.

b) The State of the Carbon Atoms

Even less is known to deal with this problem. To judge from recombination processes, one has to expect the occurrence of the three (known) metastable states of C (3P , 1D , 4S). Their abundance cannot be ascertained. Other excited states, if produced, should have decayed because of the long flight time of ca. 10^{-7} sec between the grid and the benzene target.

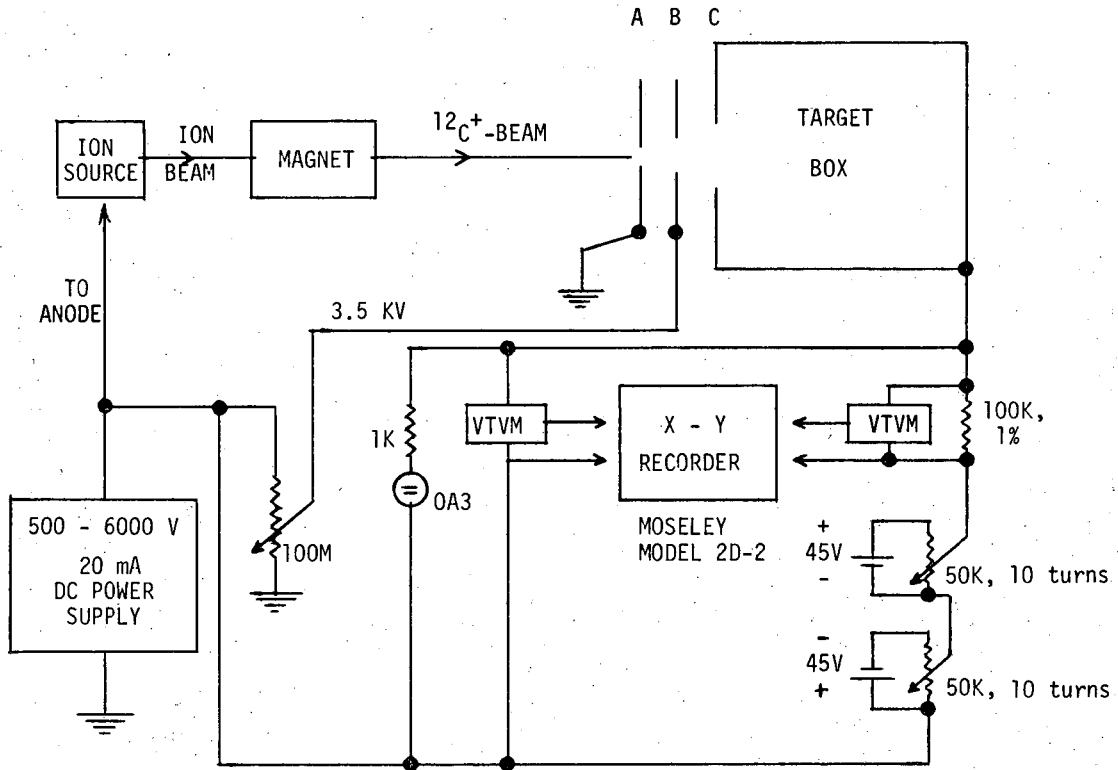
5. Mean Energy and Energy Spread of the C^+ -Ion Beam

The kinetic energy of an ion hitting the target at potential D is determined by i) the accelerating field, ii) the initial kinetic energy of an ion leaving the plasma, iii) the plasma bulk potential from which the ions are extracted, with time-dependent and local (time-independent) variations, and iv) the potential of the target. The experimental procedure to determine the kinetic energy and energy spread is depicted in Figure 7. All experiments were performed on $^{12}C^+$ -beams generated under identical conditions as $^{14}C^+$.

If the energy of each ion were exactly equal to the acceleration voltage, the current to the cage C (as monitored by the y-VTVM) should drop sharply to zero as soon as the potential of the cage relative to the source potential, a quantity which could be varied between -45 and +45 volts, passes from minus to plus (see Figure 8). The differentiation of a real curve, however (see Figure 8) had a certain width ("energy spread") and a peak ("minimum energy") at a voltage different from 0. The orifice B was necessary to obtain well-defined fall-off curves. B acts both as a focussing device for the ion beam and a sink for the secondary electrons produced mainly by positive ions returned from cage C and accelerated into plate A. Without B the current at y was indeed "negative" at certain cage potentials (see Figure 9).

a) Energy Spread and Resolution

The required resolution, i.e. less than 1 in 4000 eV, for such an energy spectrometer, is extreme even by today's standards.



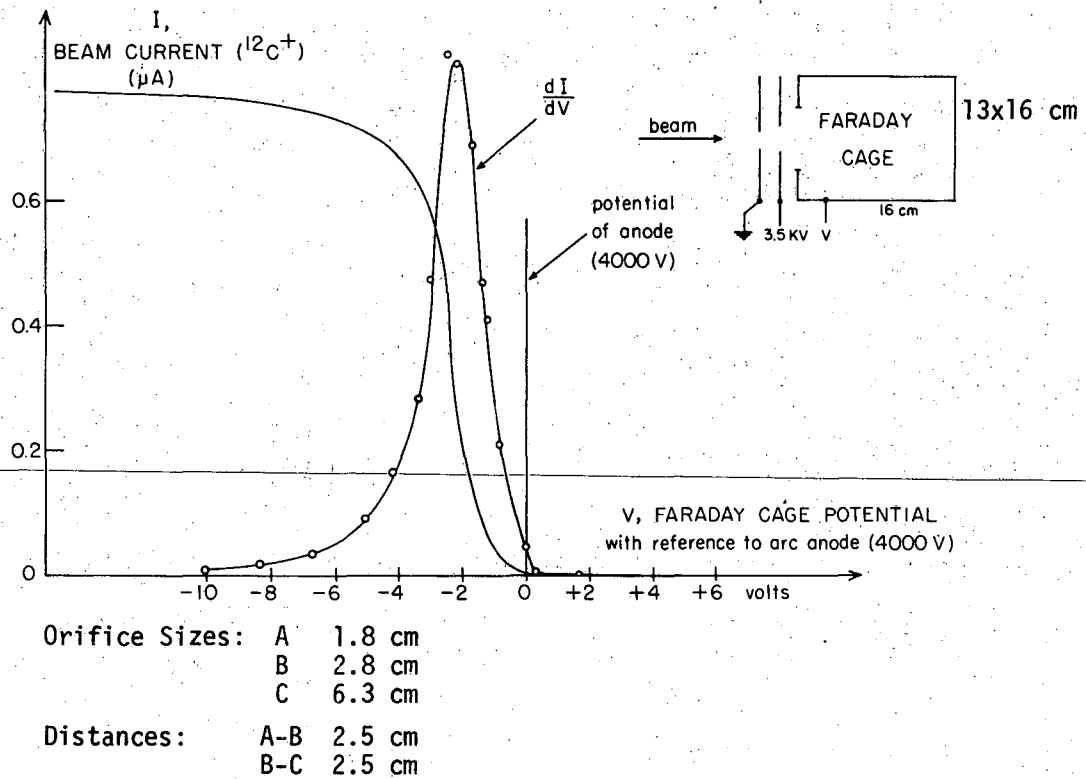
XBL 695-4252

Figure 7. Ion beam energy spectrometer (see Figure 8 for sizes of A, B, C).

VTVM: Keithley Model 220

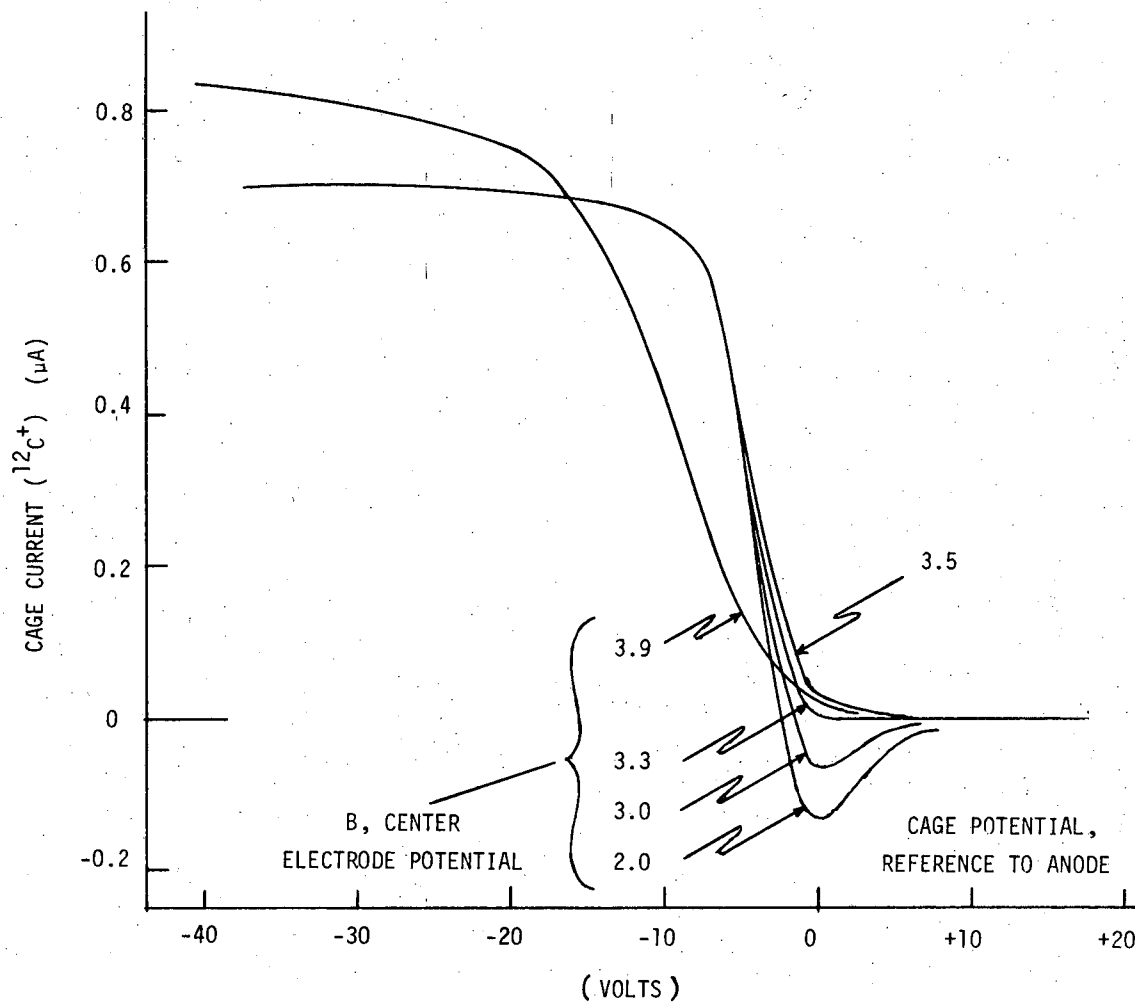
AC-power for VTVM, etc. through 10 KV isolation transformer

OA3: This tube protects the metering equipment from over-voltages (100 V) which are caused by discharges between the target box and the grounded plate A. These discharges are triggered by secondary electrons formed at plate A and/or B when ions of the divergent low-energy beam escape from cage C and are accelerated backwards into plate B or A.



XBL 695-4253

Figure 8. Fall-off curve, mean energy, and energy distribution of 4000 eV $^{12}C^+$ -ion beam.



XBL 695-4249

Figure 9. Apparent fall-off curves for a 4000 eV $^{12}\text{C}^+$ -ion beam for various B-plate potentials (compare Figure 8).

It cannot be predicted for a particular set-up. In order to optimize it, this energy spectrometer was constructed according to measurements and calculations by J. A. Simpson.⁴⁵ The resolution was checked by varying the acceleration voltage between 2000 and 6000 volts. If poor resolution contributed, the apparent energy spread should increase linearly. However, no large changes were observed. Yet, in view of the many factors (degree of beam divergence, beam parallax, potential of plate B (see Figure 9), secondary electron currents) which have been observed to effect the shape of the fall-off curve one cannot speak of a rigorous check of resolution. Nevertheless, it is believed that the measured energy spread represents rather well the true initial energy variation in the beam. This energy spread is possibly caused by (time-independent) variations of the bulk plasma potential over the area from which the ions originate, and, more likely (see Chapter II, 3), by the initial kinetic energy of the C^+ -ions. Time-independent potential fluctuations have been eliminated as described in Chapter II, 2, or can be avoided (rf-oscillations) by monitoring the arc chamber wall potential (see Chapter II, 2). A contribution to the energy spread from thermal motions is believed to be negligible (compared to 2 eV) since the ion-temperature in the plasma, as opposed to the electron temperature, is rather low (1000°K or less), contributing variations of at most 0.1 eV.

The energy spread of ca. 2 eV compares well with that of 2-5 eV quoted by M. v. Ardenne⁴⁶ without reference to an experimental procedure, and that expected from Chapter II, 3. It is much larger

than has been usually assumed.^{14,15} It is slightly dependent on arc conditions. However, as in the case of the rf-oscillations, no clear-cut dependence of just one parameter could be established. The energy spread, however, increased sharply (sometimes to 10-12 eV) when the arc was not operating "normally" (see Chapter II, 2e), i.e. when extensive deposits had formed on anode and arc chamber walls.

The relatively large energy spread rules this ion source out for work below 3 eV energy (see Chapter II, 5b). If, indeed, one should attempt greater energy accuracy with this accelerator, a large number of problems would arise simultaneously on a much higher level of experimental difficulty (compare with Chapter II, 5c, below).

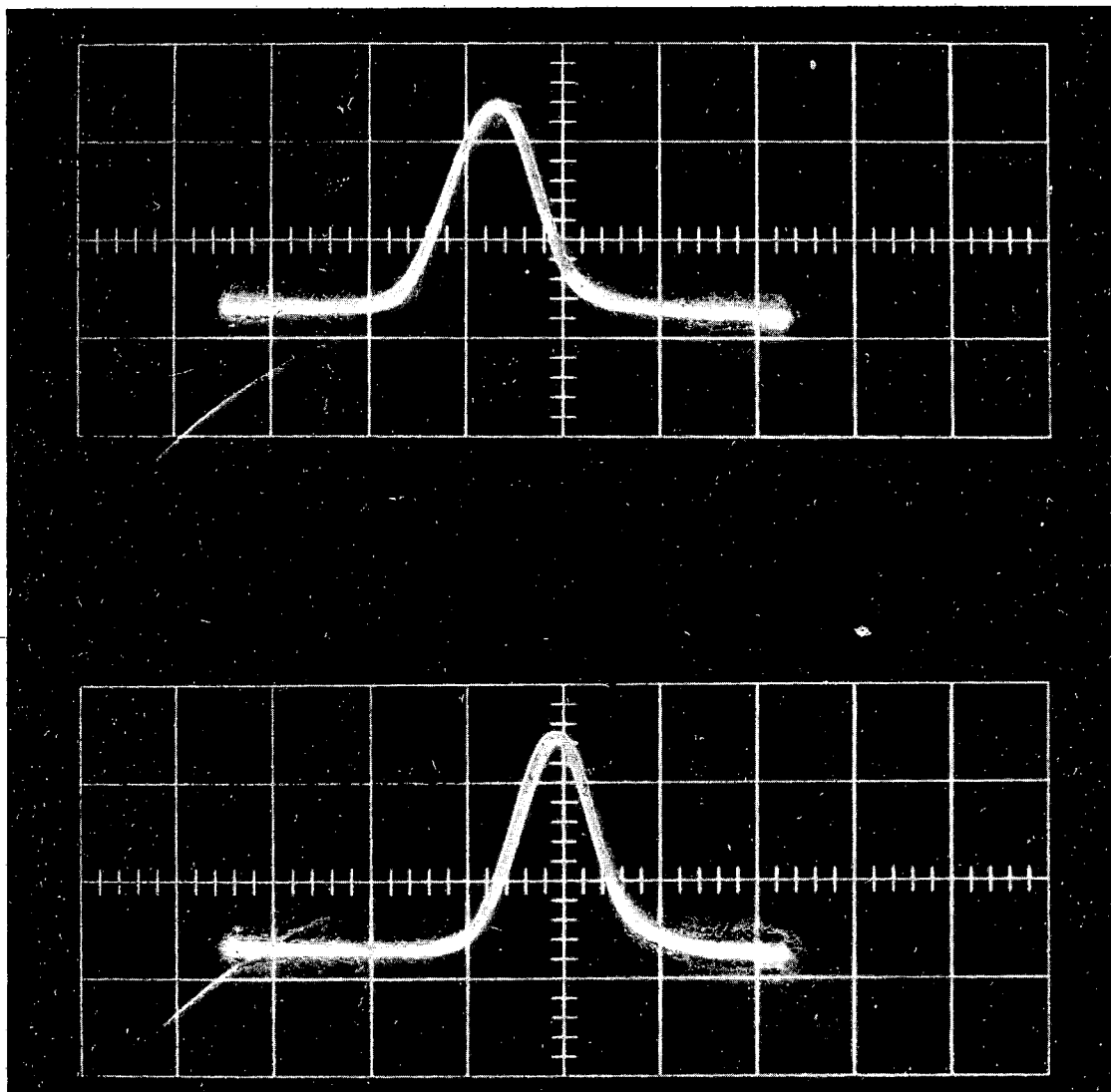
b) Medium Energy of the Beam

Originally, the accelerating field was defined by the potential of the arc chamber wall (equal to the output of the high voltage power supply) with respect to the apparatus ground (tank).¹⁴ It turned out, however, that under these conditions the medium energy (compare Figure 8) was shifted to ca. +45 V and varied over a range of ±10 eV dependent on arc conditions. This finding, coupled with the impossibility to standardize and reproduce arc conditions, and thus medium beam energies, led to attempts to stabilize the energy. However, it was discovered later that if the ion energy was defined with respect to the arc anode (rather than wall) the "shift" was only small and variations were within the apparent energy spread.

For this reason, the arc anode was connected to the high-voltage power supply, leaving the potential between arc chamber and extraction electrode dependent on arc conditions. The results of Figure 8 were obtained under these conditions. Like the energy spread, the medium energy varied appreciably, i.e. up to ± 10 eV, only when deposits in the arc chamber prevented a "normal" operation. Otherwise variations were in the order of 1-2 eV.

The interpretation of this result is that the potential of that part of the plasma from which ions are drawn, presumably directly in front of the extraction hole, is 1 to 2 volts below the anode potential, a difference varying only slightly over a large range of arc conditions. It seems hardly at all influenced by the filament and wall potential, which is rather surprising in view of the extraction mechanism (compare Figure 2a).

That the plasma potential determines the energy shift was also demonstrated when the $^{12}\text{C}^+$ -beam was energy modulated by 100 Hz ac (inductively coupled into the acceleration voltage via a 1:1, 10 KV isolation transformer) and the beam intensity at the discriminator slit (2 mil) displayed on an oscilloscope (intensity vertically, modulation horizontally). The resulting symmetrical curve (see Figure 10) with an equivalent width of ca. 8 eV is not an energy distribution, but the scan of the image of the ion source at this location. However, before changing to dc heated filaments in the ion source, and before decreasing the ripple of most of the power supplies for the arc, a wide (≈ 60 eV) and complicated curve was observed - even without "external" modulation. This curve was,



XBB 695-3027

Figure 10. Scan of the ion source image at the discriminator slit (width $0.01 \text{ cm} \approx 6 \text{ eV}$) transmitted by a $5000 \text{ eV } ^{12}\text{C}^+$ -ion beam. Abscissa: $1 \text{ cm} = 12 \text{ V}$. Modulation frequency: ca. 30 Hz . Time between the two pictures: 30 sec . The shift of the maximum indicates an energy shift by ca. 8 eV within 30 sec due to changing arc conditions when ion energy is referenced to the arc chamber wall.

for the most part, indeed, a display of energy oscillations (ca. 120 Hz) caused by similar potential oscillations in the extraction region of the plasma.

c) Stabilization of the Mean Energy

Before realizing (and contenting ourselves with) the improved energy stabilization by referencing all beam potentials to the arc anode (see the preceding chapter), attempts were made to stabilize the mean beam (kinetic) energy. One method which suggests itself immediately is to use the magnetic field as an energy discriminator (as well as a mass discriminator) according to the formula:

$$\frac{\Delta E}{E} = 2 \cdot \frac{\Delta R}{R},$$

if mass and magnetic field strength are constant, and if

E = energy, and

R = radius of curvature of the 90° magnetic sector field (= 15 cm).

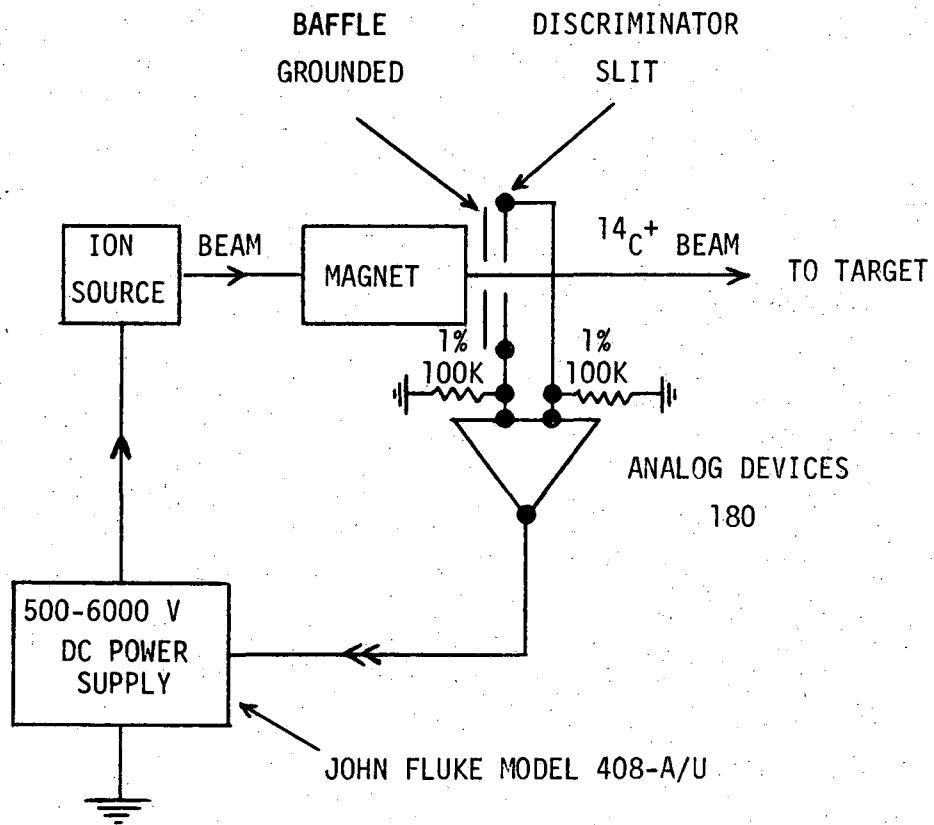
At a desired resolution of $\Delta E = 1$ eV (in $E = 5000$ eV) the discriminator slit would have to be less than 1.5×10^{-2} mm wide (≈ 0.6 mil). Including the imaging properties of the extracting and accelerating field, the two imaging devices, focus lens, and magnetic field, produce an image of the extraction hole (0.6 mm ϕ) at the discriminator slit with an approximate width of 0.4 mm (compare Figure 10).

The source or defining slit width would have to be decreased to less than 0.04 mm, decreasing simultaneously the $^{14}\text{C}^+$ -beam intensity beyond feasibility (besides the technical difficulties in drilling 1 mil ϕ holes).

A method was therefore investigated which should yield the desired energy stability at full intensity (see Figure 11): Focus lens and magnet produce an image of the ion source in the plane of the discriminator slit. The discriminator slit intercepts only a small part (5% or less) on either side of the beam. The difference between the currents to each slit side, as measured by the voltage drops across the 0.1 M Ω resistors, accurately and sensitively indicates the position and thus the energy of the whole beam with respect to the discriminator slit. Sufficiently amplified, it drives the acceleration voltage power supply output in such a way that initial energy fluctuations occurring in the arc source are sufficiently compensated.

Assuming a beam intensity profile at the discriminator slit of triangular shape, with its base equal to the image width, a loop gain of ca. 200,000 was calculated to be necessary to reduce fluctuations of ca. 25 V (the apparent energy fluctuations) to 0.1 eV. The operational amplifier was a Analog Devices 180. The high voltage power supply afforded a gain of 20.

It is obvious that in this system the energy of the ion beam is defined by the trajectory of the ions, including beam intensity profile, and the magnetic field. Its stability was monitored by a proton magnetic resonance probe, whose resonance frequency was



XBL 695-4251

Figure 11. Schematic for stabilization of mean ion energy.

measured occasionally (stability better than 1 in 10^5). The stability of the magnetic field was better than 1 in 3000 gauss per hour, or, in terms of energy, ca. 3 eV in 5000 eV per hour. With some care this figure can be decreased to less than 1 eV. The energy of the ions at the target, after deceleration, however, is determined by the difference between the beam energy and the target potential. The beam energy is given by the proton resonance frequency (in a mechanically stable system), and the target potential is delivered by a Fluke 408 A/U, 500-6000 V dc power supply with a stability of better than 0.4 in 5000 V. The total energy error should amount to ca. 2 eV, and could be decreased if necessary.

~~When tested, the energy regulation was stable for fluctuations~~
over a range of 40-50 V with a rest deviation of less than 0.2 V.
However, the geometric stability of the trajectory was so poor that
the energy regulator introduced larger energy fluctuations than
were originally present. Variations of the focus voltage, for instance, or repulsion due to temporary build-up of electric charges somewhere near the beam, could cause trajectory instabilities. Most of these possibilities had been reduced or eliminated. The main cause, however, for trajectory fluctuations were apparently shifting positions of the first image (near the extraction hole) of the ion source. This image depends strongly on the shape of the plasma sheath near the extraction hole. Because of the short focal length of this lens, any small change is very much amplified by the subsequent long-focal-length lenses (first focus lens and the magnetic field). For instance, moving the hot-filament cathode of

the arc by 0.5 mm along the arc axis (a change which was found later to have no discernible effect upon the ion energy), was translated by the energy regulator into an energy shift of ca. 10 eV. Other arc parameters (pressure, current, arc voltage, wall voltage) caused similarly drastic effects. This system was therefore abandoned.

In the first described arrangement, the ion energy is defined with an accuracy of ± 1 eV at ca. 2 eV energy spread. This seemed satisfactory for first, exploratory experiments in low-energy, hot atom chemistry of carbon.

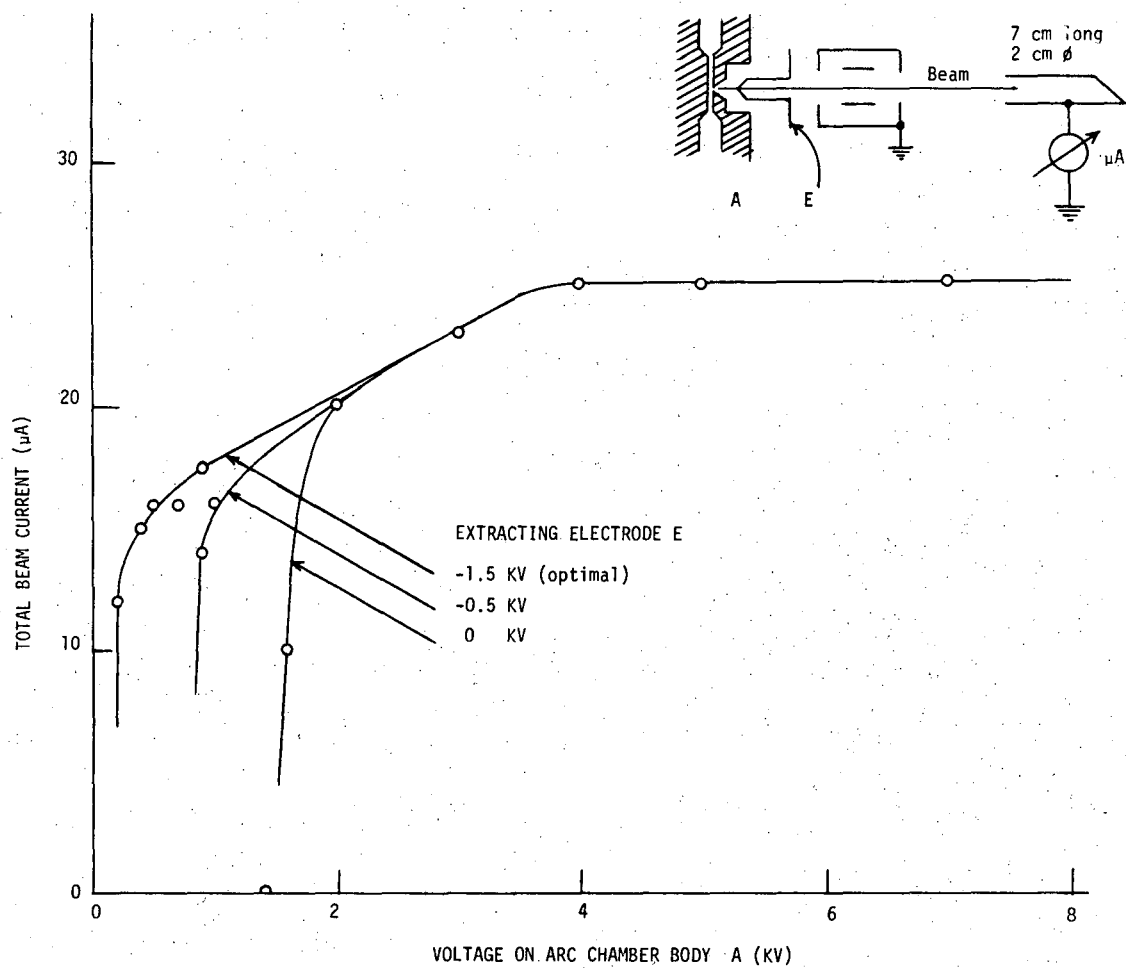
6. The Ion-Optics

The objective of the accelerator, to deliver a beam of $^{14}\text{C}^+$ -ions at the target (of ca. 1 cm diameter, ca. 2.50 m from the source) whose flux density and energy can be varied, is achieved by an appropriate system of ion-optical devices, deflectors, and the magnetic sector field (see Figure 1a). The plane of all ion trajectories is horizontal. There are six imaging devices incorporated into the accelerator: extracting and accelerating field, first focus lens, 90° -magnetic sector field, first and second cylinder lenses, and deceleration lens system.

a) Extraction and Electrostatic Focus Lenses

1) Extraction. Because of the small penetration of fields through fine holes in metal surfaces, a very small fraction of the accelerating field (between arc chamber and extraction electrode) appears as an extracting field at the plasma boundary in the extraction hole. The geometry of this boundary determines the initial beam properties.⁴⁷ At optimum acceleration voltages (4-5 KV), a concave plasma sheath produces an initially converging ion beam with a focal point somewhere between the pin hole and the extraction electrode.

The dependence of the total ion beam emerging from the extraction electrode on the acceleration voltage is depicted in Figure 12. Various shapes for the extraction electrode did not product marked differences; neither was the gap between arc chamber wall and extraction electrode critical. A gap of ca. 2 mm, however, proved not too small for high voltage breakdown and gave good long-time



XBL 695-4248

Figure 12. Total usable ion beam versus ion energy. Parameter: extraction voltage.

performance, particularly with respect to build-up of material on its arc-side surface (see Chapter II, 2e).

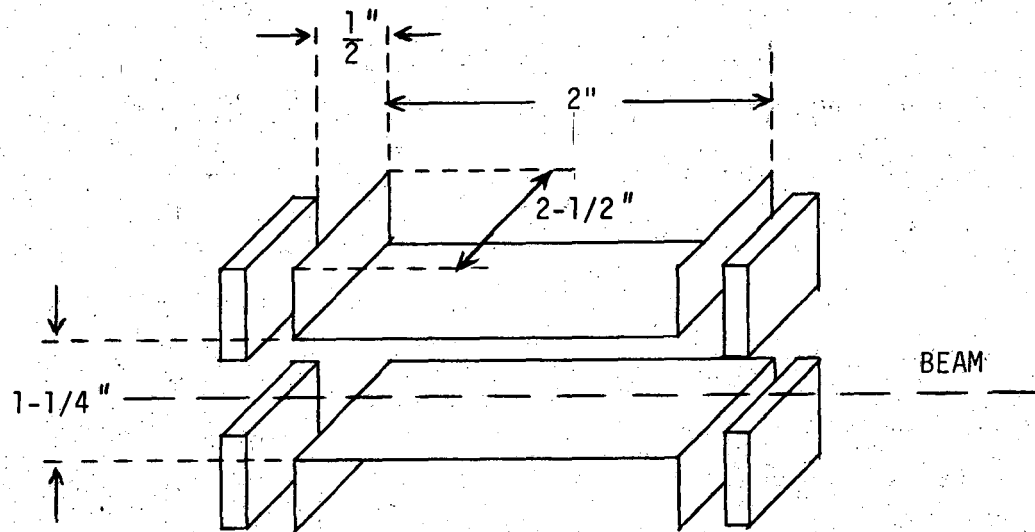
In connection with the experimentation towards deceleration of the ion beam, from initially 4-5 KeV energy to less than 10 eV, the feasibility of decreasing the initial energy was investigated. However, substantial loss in intensity occurred at extraction voltages (and energies) below 2 KV. This situation was improved by biasing the extraction electrode (see Figure 12) negatively, thus maintaining the extracting field at an optimum, with deceleration of the beam between extracting electrode and first focus lens to an energy about equal to the potential of the arc chamber. Beams of as low as 500 eV energy were obtained with relatively good intensity (see Figure 12). However, the optical properties of a low energy beam generated in such a way were very poor and it turned out to be more feasible to decelerate a high energy beam (with good optical properties) by a large ratio than a poor quality, low energy beam by a proportionately smaller ratio. With a more appropriate lens system, low energy beams with acceptable optical properties should be available from this source.⁴⁸

2) First focus lens. The first focus lens (two concentric cylinders of 1/16" Dural, inner cylinder $\phi = 3.5$, length = 4 cm; outer, $\phi = 7.5$, length = 10 cm) permits focusing over a range from ca. 10 cm to infinity by varying the potential of the inner cylinder between ca. +0.8 and +0.95 of the acceleration voltage. The outer cylinder is grounded. A separate 2-10 KV dc power supply with 0.2 V

p.t.p. ripple at 5 KV, 100 M Ω load, and better than 2×10^{-4} stability (ca. 5 mA maximum current), supplies the necessary voltage. All surfaces of the lens are coated with "Aquadag".

3) The electrostatic cylinder lenses. The first focus lens and the magnet are able to "image" the source (laterally and vertically with different magnification) only at one particular position. For reasons of greater optical flexibility, and because of the need for a beam of almost circular profile at the entrance to the decelerating lens system (see Chapter II, 6b), an electrostatic "cylinder" lens was built (Figure 13) which permitted imaging at right angles to that of the magnetic field. This system of three lenses suffices, theoretically, to produce an almost circular image of the source hole anywhere down-stream of the last lens. In practice, however, a second "cylinder" lens, at right angles to the first, proved extremely helpful in obtaining a high transmission for the decelerator lens. The explanation for this is as follows: In order to obtain good transmission up to the decelerator, the first focus lens has to produce an image of the source at a place (probably near the position of the first cylinder lens) which is not optimal for maximum transmission through the decelerator. The second cylinder lens permits a greater flexibility for this optimization.

Both cylinder lenses are essentially identical (see Figure 13): The two parallel inner electrodes carry the (usually) positive high voltage; all outer electrodes are at ground potential. The two inner electrodes of each cylinder lens can be given symmetrical,



XBL 695-4255

Figure 13. Electrostatic cylinder lens. The four outer electrodes are at ground potential, the inner at ca. 25% of the acceleration potential.

bipolar biases, thus providing a convenient four-way deflection system.

Figure 14 shows the beam intensity profile of a 4000 eV $^{12}\text{C}^+$ -ion beam at the target. This profile was obtained by scanning the beam with a 2 mm wide, 5 cm long rod-target both "horizontally" and "vertically".

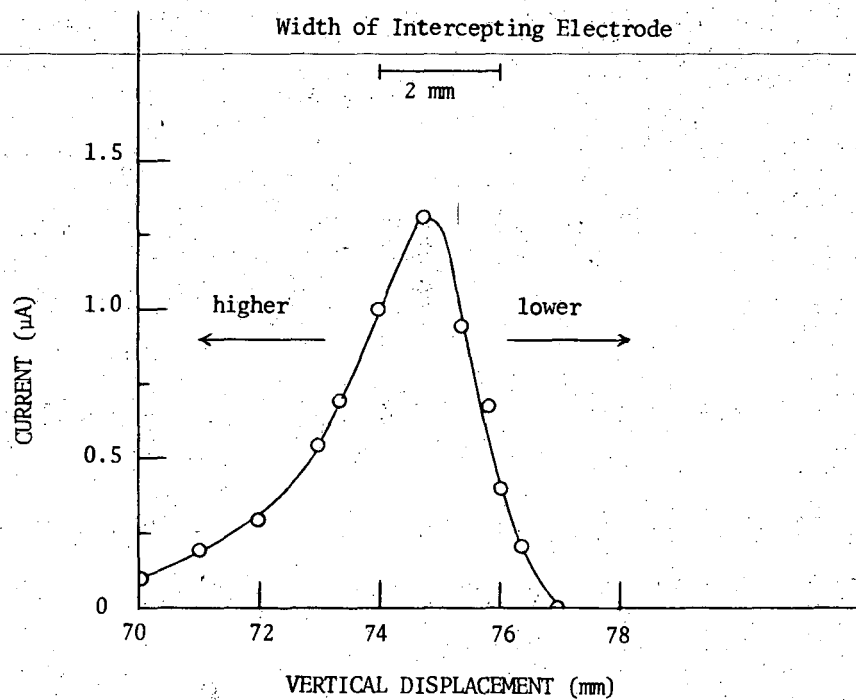
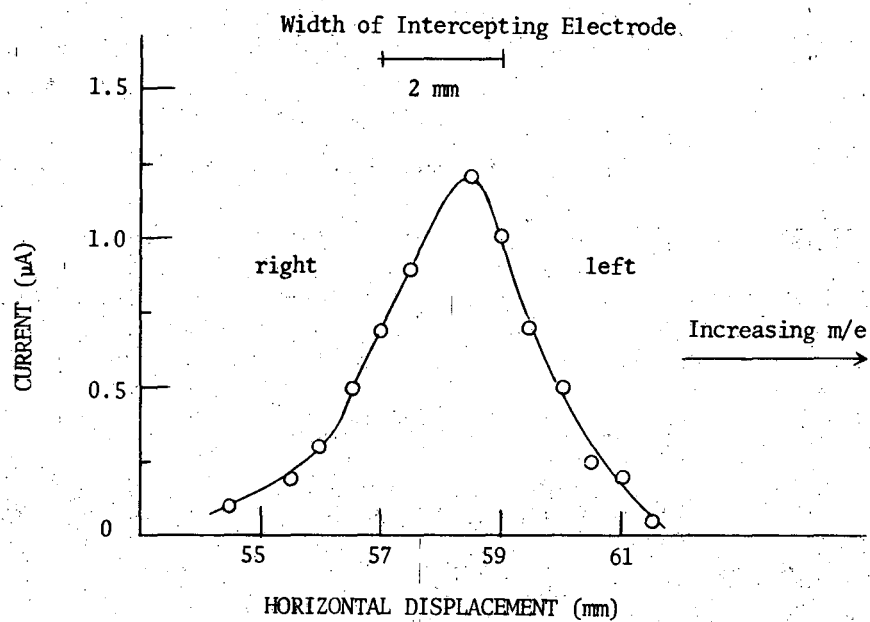
b) The Decelerator

Originally, it was planned to decelerate the ions in a (supposedly) homogeneous electric field between a grounded tank exit plate and the target box entrance plate (see Figure 1a) whose entrance orifice was covered with a wire grid (2 mil-tungsten wire, 10 mil parallel spacing).¹⁵ This arrangement was used for the first low energy experiments.¹⁴ However, in such an arrangement, the ion trajectories have to be ideally parallel, and perpendicular to the plane of the wire grid. For a deviation from perpendicularity of only 0.5° , the deflection after deceleration from 5000 eV to 50 eV will be 45° , increasing rapidly as the final energy is lowered further.

Similar arrangements have been used when intensity losses could be tolerated.^{49,50}

Ion-optically more feasible systems were suggested and investigated by Willmore,⁵¹ and Gustafson and Lindholm.⁵² Their contention was that deceleration to less than 0.03 of the initial energy was not practicable. Meanwhile, multi-element ion lenses have been used for deceleration for a variety of purposes. Menzinger,⁷ e.g. achieved

-62-



XBL 695-4225

Figure 14. Beam profile at target (4000 eV, $^{12}C^+$). Upper: horizontal scan; lower: vertical scan.

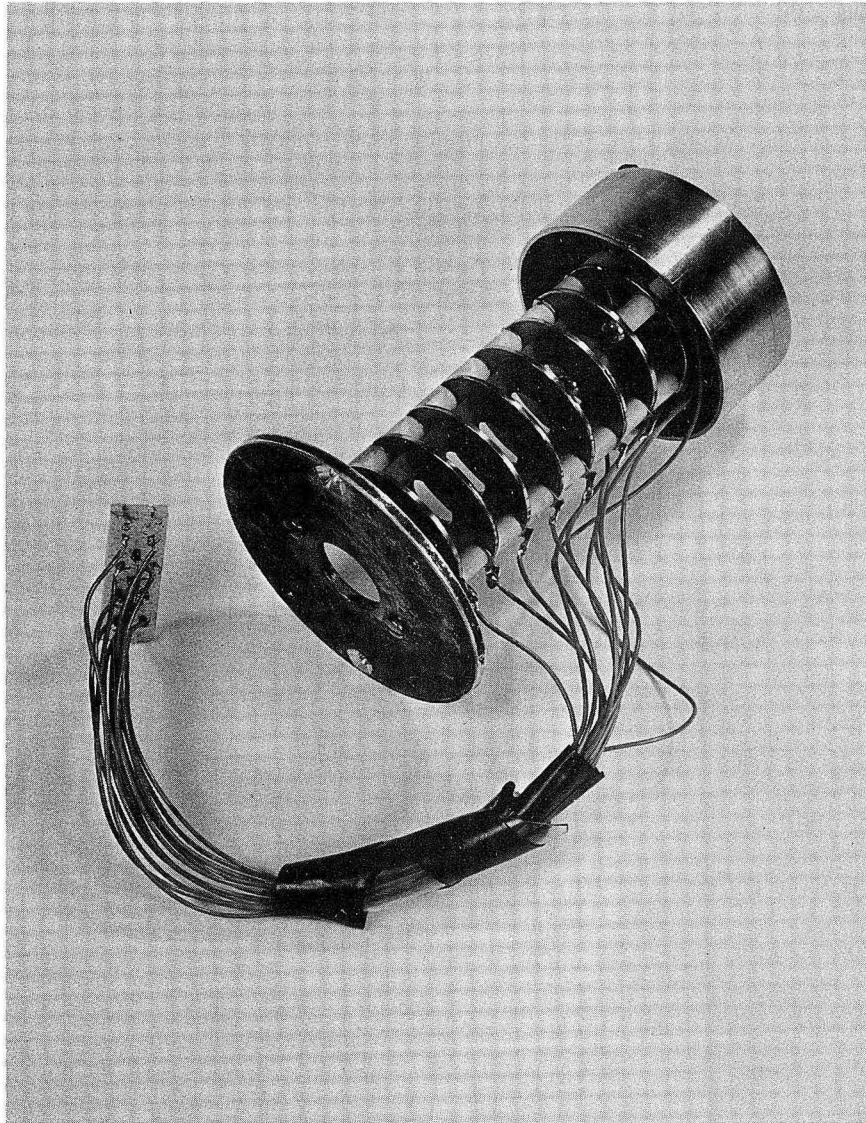
deceleration of T^+ and T_2^+ -ions for hot-atom chemical experiments, from 200 eV initial energy to ca. 2 eV (deceleration factor 0.01), with only 50% intensity loss over a target of ca. 1.5 cm diameter.

Common to all ion-optical decelerators is the first sharply (then slowly) increasing potential on a stack of orifices, sometimes of equal,⁷ sometimes of varying sizes and distances.⁵²

A three-element lens, i.e. grounded entrance plate, a second plate with variable positive potential, and a third plate at the entrance to the target box (the last being at the required final potential) proved to be effective for deceleration from 5000 eV to ca. 200 eV with little intensity loss over a 1 cm ϕ target.

For deceleration to as low as 3 eV, i.e. for a deceleration ratio of less than 0.001, a 10-element lens was built (see Figure 15). Its performance is indicated in Figure 16. The beam intensity was measured as current at the site of the actual benzene target, masked by a 1.5 cm ϕ orifice plate electrically connected with the target box.

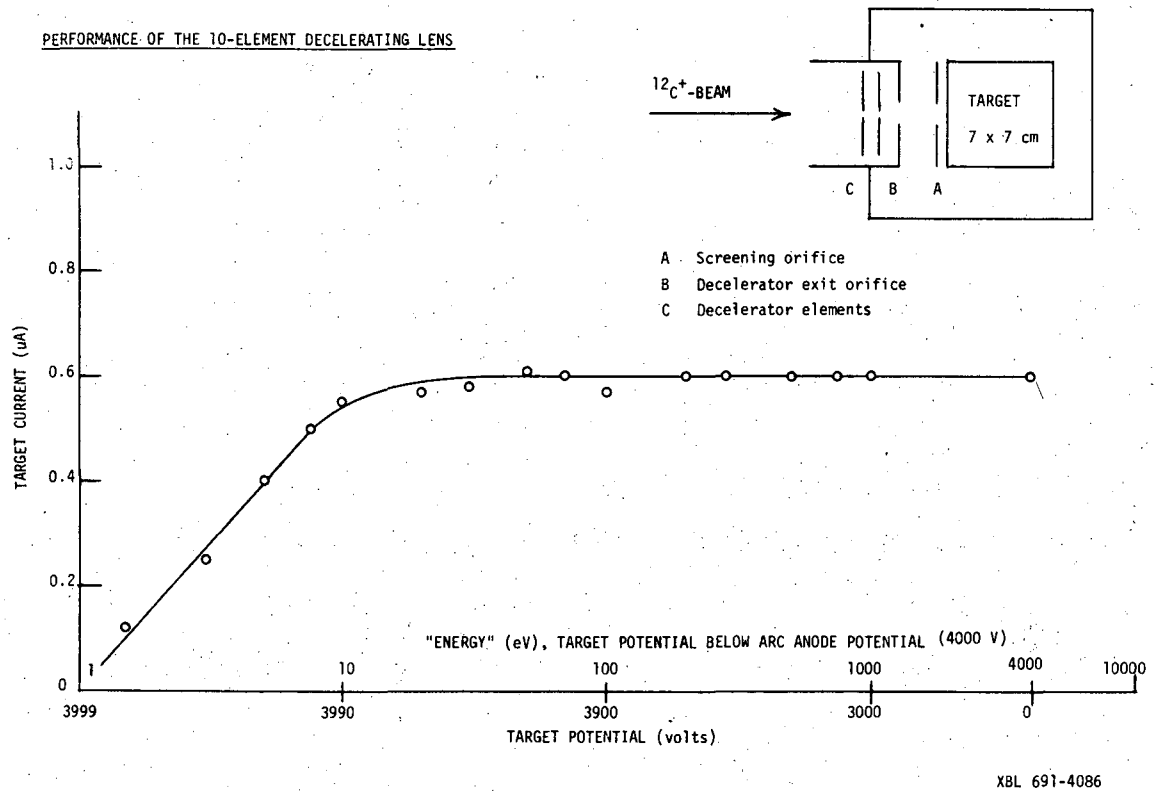
The potentials at the 10 decelerator plates were 3.2, 3.3, 3.4, 3.55, 3.65, 3.65, 3.4, 3.99 for deceleration from 4000 eV to below 10 eV. The transmission was not very critically dependent on these values. The target box and the target carry the same potential as the last orifice. Each of the two discs before the last are split diametrically into two halves, the two cuts being perpendicular to each other. Each pair can be biased by a symmetrical, bipolar dc voltage floating on the high-voltage (as above). This affords



XBB 691-641

Figure 15. 10-Element decelerator lens, entrance plate on left.

-64a-



another set of four-way deflectors for correction of the low-energy beam approximately 5 cm off the target.

c) Alignment

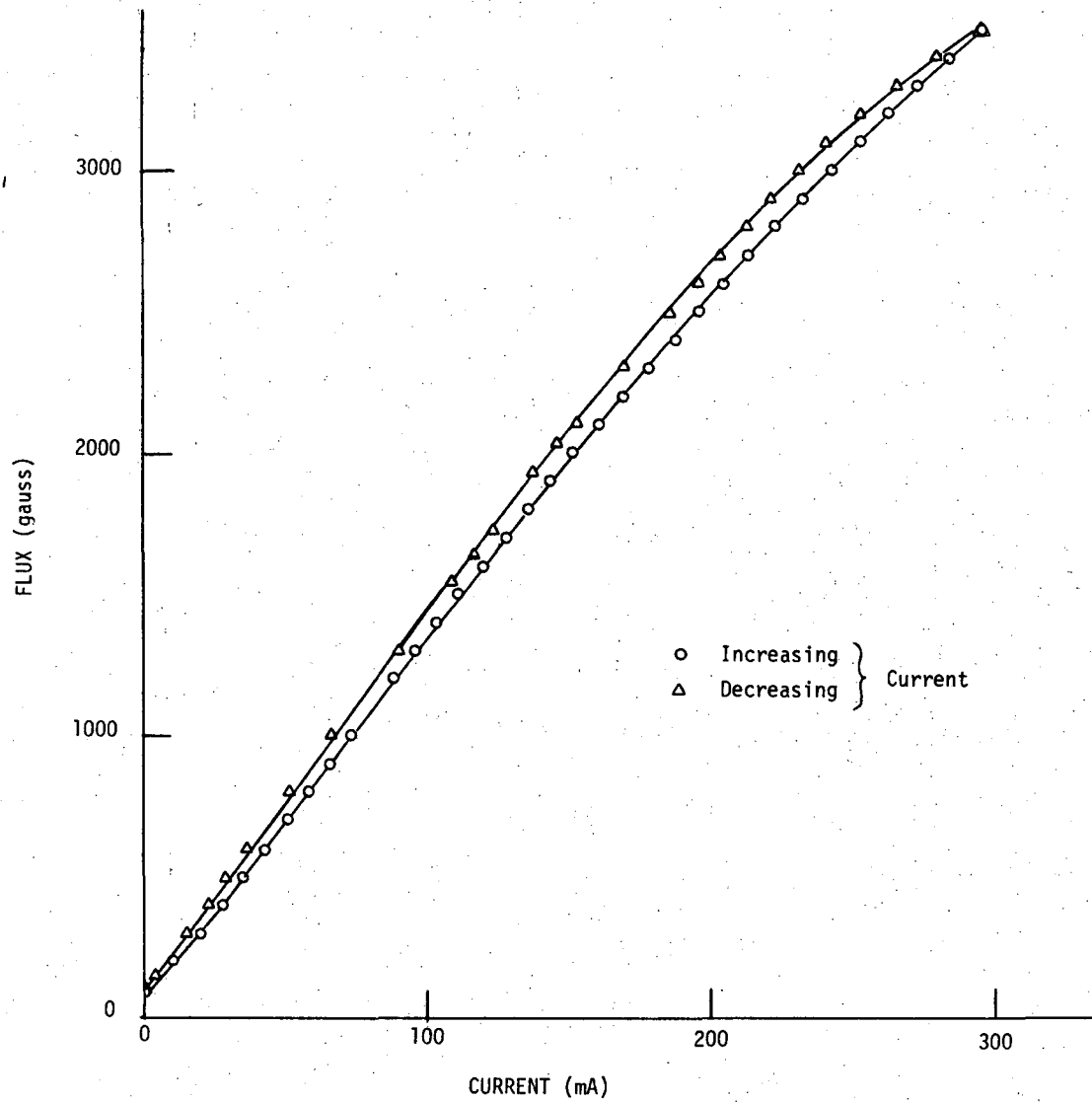
The most critical alignment requirement is that for the extraction electrode with respect to the extraction pinhole. The frequent disassembly of the ion source (for cleaning purposes) made it necessary to abbreviate the alignment procedures and to correct, with four-way deflectors, occasional deviations of the beam from the optical axis. These deflectors were necessary, in addition, since over the time of operation the beam tended to change position and direction, apparently due to charge build-up on deposits.

Besides the two four-way deflectors mentioned previously (inside the two cylinder lenses, and inside the decelerator) there is one immediately following the first focus lens. Again, the voltage across corresponding pairs of electrodes is bipolar and symmetrical with respect to ground, in order to avoid asymmetric focussing effects on the beam. The four-way deflector in the decelerator is also extremely advantageous for good ion transmission to the target. The reason is the same as for the extraction hole/extraction electrode system, namely the short focal length of the immersion ion lens at these locations. A slight displacement of the beam from the optical axis on the object side is magnified many times on the image scale.

d) The 90°-Magnet

The 90°-magnetic sector field acts as "cylinder lens (with a fixed focal length of 17 cm,¹⁵ a little more than the radius of

curvature due to fringe fields, the focal points being 2 cm off the respective pole faces), besides furnishing the dispersing element (ion separation according to momentum). Figure 17 shows the correlation between exciting current and magnetic flux (measured with a Hall-probe, "Bell 220", Incremental Gaussmeter). Because of the apparent hysteresis, the correct ion beam can be selected only roughly according to the exciting current. Fine-selection has to be made according to the sequence of predominant beams measured at the target or at a small Faraday cage which can be moved to intercept the beam before it enters the decelerator (see Figure 1a). The current is supplied by a 0-300 mA dc current power supply (Electronic Measurements, Model C633) with a current stability of 1 mA in 300 mA.



XBL 695-4247

Figure 17. Magnetic flux versus excitation current. Hysteresis for one-half cycle.

7. The Vacuum

a) Pumps

The vacuum is maintained by a MCF 300 diffusion pump in the source part of the accelerator, and a MCF 700 diffusion pump in the arc channel of the magnet. Both diffusion pumps are charged with silicon oil 704, and have a maximum pump speed of 1000 l at 10^{-5} mm Hg (500 l at 10^{-6} mm Hg). The forepressure is generated by two KC-5 rotary pumps operating on a manifold.

A separate KC-5 is used as roughing pump since the whole system had to be opened to 1 atm very frequently during the developmental work at the accelerator.

All pump exhausts are discharged through KOH traps (to trap $^{14}\text{CO}_2$) into the general ventilation system.

b) L-N₂-Traps

Each diffusion pump is baffled by a liquid nitrogen trap which is filled automatically approximately every hour. Both traps use approximately 80 l L-N₂ per day.

For reasons explained in "The U-2 problem" (Chapter II, 9), another doughnut shaped L-N₂ trap was inserted in front of the deceleration lens.

c) Gauges

One ionization vacuum gauge is located above the MCF 700 diffusion pump. It monitors the "main vacuum". Another similar gauge is located in the target box. It monitors the "target vacuum". Typical pressures are: main, 3×10^{-7} mm Hg; target, 4×10^{-6} mm Hg.

The mean free path at such a pressure is in the order of 100 m, affording a chance of better than 95% for an ion to reach the target without collision with a residual gas molecule.

d) Materials

All seals are made with Neoprene O-rings greased with silicon high vacuum grease. Parts of the accelerator tank are made of Dural, stainless steel, brass, and glass. Electrical feed-throughs are of glass. The insulating disc separating the arc chamber from the accelerator tank was originally made of bakelite. However, this material caused seepage of air at a rate of ca. 2×10^{-8} moles/sec. The vacuum improved by a factor of ten after replacing this flange by one made of layers of fiberglass which were glued together by epoxy, the whole flange having also been coated with epoxy, and then machined to specifications.

The apparent leak rate (including outgassing) for the whole accelerator is ca. 2×10^{-9} moles/sec (ca. 500 l/sec).

8. The Target

a) Geometry and Accessories

The target upon which the organic sample (benzene) is condensed during its bombardment with $^{14}\text{C}^+$ -ions is a regular cube of stainless steel, with 7 cm side length. The beam strikes one of the four vertical faces perpendicularly, approximately in the center of the square. The center well can be cooled with liquid refrigerants. It is electrically insulated from the target box, permitting the measurement of the beam current to the target. This current is measured by a battery powered VTVM (Keithley 200B) with an input impedance of 100 K, 1%. All monitoring and target accessories can be floated at up to 10 KV positive potential.

The target can be biased with respect to the target box by up to 300 V dc. This permits the determination of secondary electron contributions to the apparent beam current.

As described in more detail in "Charge Build-up" in this chapter, the beam current cannot be measured in the above manner if the ion energy is lower than 1 KeV. In this case, and as a general alternative method, the beam current is monitored by the electron current (emitted from the hot filament in front of the target) necessary to (electrically) neutralize the target. This electron current equals the positive ion beam exactly.

The beam current can be integrated over the irradiation time (3 hr) by an electric integrator which drives a 0-10 mV recorder with a full-scale switch. This switch resets the integrator within

ca. 0.5 sec. The full-scale rise time at $1 \mu\text{A}$ is approximately 20 sec. The electronic integrator is a vibrating reed electrometer as operational amplifier, with $1000 \text{ M } \Omega$ input impedance and $2 \mu\text{F}$ feedback capacitor.

The target is, at all instances of the irradiation, at the same potential (within 0.2 V) as the target box. The potential of this box with respect to the arc anode determines the energy of the ions (see Chapter II, 5). It can be measured and monitored with the same battery powered VTVM with an error of less than 5%.

More important than the potential of the metal target is the electric potential that a carbon ion sees when it hits the solid benzene. This potential may be quite different from that of the metal target due to the accumulation of space charges in the solid benzene (see Chapter III, 8c). This potential, however, could not be monitored.

b) Benzene Deposition

Benzene is supplied from a graduated glass tube of 2 ml volume at room temperature. Benzene vapor is admitted from the tube through a needle valve into a manifold which feeds the input nozzles and whose pressure is monitored by a thermocouple vacuum gauge.

There are four input nozzles of 2.5" length and $1/64$ " I.D. The orifices are at ca. 1 cm distance from the target surface, at equal distance (ca. 0.5 cm) from each other. They are directed towards one (center) point on the target, where maximum deposition

results. Under these conditions about 80% of the deposited benzene appears within a circle of ca. 1 cm diameter.

The flowrate of benzene, as determined from the meniscus changes in the graduated tube, is ca. 150 μ l per hour. About 70% of the benzene introduced into the target box is recovered after irradiation in the "solid-transfer" method, and 100% if gas-transferred into a suitable trap. Before starting any irradiation, ca. 100 μ l benzene were deposited to insure a normal growth of the solid and to avoid possible effects of the stainless steel surface on the hot-atom chemistry in benzene. Such an initial layer of benzene is approximately 10^{-2} cm thick, several orders of magnitude larger than the penetration depth of 10 KV C^{+} -ions.

Occasionally, particularly if the initial rate of deposition was larger than 200-300 μ l/hr, the solid benzene did not attach sufficiently well to the metal surface and began to flake off again. At high benzene vapor flowrates the solid tended to grow very unevenly, which also led to flaking-off. The irradiations had to be discontinued in these cases. It seems as if the rate of benzene deposition into such a small area cannot be increased by very much more than a factor of 2-3.

c) Charge Build-up in the Target

With a conductivity of less than 10^{-14} ohm $^{-1}$ $\cdot$ cm $^{-1}$, 154,155 benzene belongs to the class of electric "insulators". Continuous incorporation of the positive ^{14}C -ions will, therefore, build up a space charge which, if sufficiently large, will repel other approaching

ions, or will be neutralized when the field strength causes a breakdown of the insulator benzene (dielectric strength, 0.65×10^6 volts·cm⁻¹).¹⁵⁶ Electrons are emitted then from the metal surface of the target and freely move in the breakdown channel until most of the positive charges are neutralized.

If the benzene layer is sufficiently thin, this neutralization process is very efficient and does not lead to serious repulsion effects. However, as the ion energy is lowered and the target layer becomes thicker, it is more advantageous to admit electrons as above. A filament of a GE, No. 13 flash light bulb serves as source for electrons which are attracted to the benzene only, and as soon as positive charges build up there. The filament is supplied from a 6 V battery with a variable series resistor for fine adjustment of the emissivity. The filament emissivity is adjusted to somewhat above that required to neutralize the target, in order to prevent unnecessary, positive charge build-up there, when either the supply or the demand of electrons fluctuates. Clearly, an incomplete target neutralization will cause additional, non-uniform and varying deceleration of the ions and thus a blurring of the actual kinetic energy. On the other hand, a finite, albeit small, positive "error" charge at the target, and thus a small retarding field has to be present in order to effect the electron flow. How large this error is, is not known, since the electric potential of the benzene cannot be determined under these circumstances. In order to get an approximate idea of the possible error, the perveance, a , for the system filament-metal target (distance 1 cm) was determined

according to the formula $i = a \cdot V^{3/2}$ for space charge limited currents, i . V is the voltage between target and target box, the filament is on the same potential as the target box. A double-log plot of $\log(i)$ versus $\log(V)$ yielded the correct exponent, $3/2$, and for a , $0.5 \mu\text{A} \cdot (\text{volts})^{-3/2}$. From this one concludes that the target has to have a potential of ca. 7 volts to attract a $1 \mu\text{A}$ electron current, and ca. 4.5 volts for a $0.5 \mu\text{A}$ current. In other words, the error depends on the beam intensity. This demonstrates a certain drawback connected with ^{14}C which requires, for reasons of detection sensitivity, these relatively high beam currents. In the case of T^+ , with less than 10^{-8} A intensity,⁷ this method of neutralizing the non-conducting target introduces a much smaller error. In actuality, however, the error may be smaller also in our case since the distance between filament and benzene surface is less than 1 cm. Judging from the essential identity between the fall-off curve of the current at low energies (see Figure 16) for a bare (metal) target and for the benzene target neutralized with electrons, one concludes that the additional retardation can be at most 3-4 eV. Nevertheless, the finite perveance of this system is the source for the largest errors.

9. The U-2 Problem

One of the major products from $^{14}\text{C}^+$ -irradiations of benzene resisting identification longest (and labeled "U-2" during work towards identification) was finally identified as benzaldehyde. The following sources of the oxygen were considered: a) residual gas oxygen in contact with the benzene surface, or oxygen dissolved in benzene and co-deposited in the solid target; b) CO_2 from the ion source; c) other chemical forms of oxygen from the ion source; and d) contamination of the $^{14}\text{C}^+$ -beam by $^{14}\text{C}^{16}\text{O}^{++}$ ($m/e = 15$).

The following was established about "U-2" (all of the chemical details are described in Tz-Hong Lin's Ph.D. Thesis, Berkeley, 1969): i) its yield increased by a factor of 3-4 as the ion energy decreased from 15 KeV to less than 100 eV (see Figure 26); ii) the yield decreased by a factor of ca. 4 as the target temperature was increased from -195° (L- N_2) to -156° (freezing isopentane), and the yields of other products were unaffected by this temperature change; iii) the yield was unaffected when the residual gas pressure in the target was lowered from 10^{-4} to 4×10^{-6} mm Hg, i.e. when the rate of O_2 molecule incidence on the benzene target was decreased from 10^{-7} to 3×10^{-9} moles/sec/cm² (assuming 20% O_2 in the residual vacuum atmosphere); iv) thoroughly outgassing the benzene before introducing it into the target box--by transferring it in vacuum three times and trapping it at CO_2 /acetone temperature--did not affect the yield of "U-2".

a) O_2 -Incidence or Presence at the Benzene Target

Although the lowest rate of O_2 incidence of 3×10^{-9} moles/sec/cm² was still larger than the flux of $^{14}C^+$ -ions at the target (10^{-10} moles/sec/cm²), it is unlikely, from the foregoing, that atmospheric or dissolved O_2 is the source of oxygen in U-2 (benzaldehyde).

b) Deposition of $^{14}CO_2$ at the Target

When $^{14}CO_2$ was introduced into the accelerator at the rate under irradiation conditions (the arc was not "on") it was found that ca. 4.5% of it was deposited at the target. This is rather surprising since the CO_2 has to pass two liquid nitrogen traps and diffuse into the rather long and often constricted target arm. The amount of ^{14}C -activity reaching the target as $^{14}CO_2$ is about 40 times larger than that introduced by the $^{14}C^+$ -beam!

To eliminate this interference, $^{14}CO_2$ was converted to ^{14}CO before entering the arc chamber.⁵³ For this purpose a glass tube (20 x 1.5 cm I.D.) filled with Zn dust on asbestos wool was inserted between needle valve and arc chamber. This glass tube was heated externally (390-400°) by electric heating tape (ac) floating at the acceleration potential. The rate of deposition of $^{14}CO_2$ at the target was now 10^{-5} , i.e. decreased by about a factor of 4000. However, "U-2" and all other products appeared with unchanged yields. Therefore, the possible co-deposition of $^{14}CO_2$ in the target benzene could not account for "U-2".

c) Other Chemical Forms of Oxygen from the Ion Source

The large increase of the yield of U-2 as the ion energy decreased suggests that, at a lower rate of debris formation (at lower ion energies), more oxidant was available for the oxidation to benzaldehyde. The temperature dependence of the yield suggests that the oxidant is rather volatile. This idea is supported by the observation of a similar 4-fold yield decrease when a liquid nitrogen trap was inserted into the glass insulator just ahead of the entrance to the target box. The $^{14}\text{C}^+$ -beam passed through a tube traversing this trap. In this experiment the target was, however, at L-N₂ temperature again. Most of the volatile oxidant had apparently been trapped by the inserted L-N₂ trap.

If the oxidant was generated in the ion source, isolation of the source part of the accelerator from the rest should decrease its effect upon the target. The (unseparated) beam was therefore admitted into the magnet section through a 3 mm ϕ orifice decreasing a (presumed isotropic) flow of gaseous material from the ion source into the target section by a factor of 30. However, no change of the yield of U-2 occurred. One concludes that the oxidant is either not generated in the ion source or, if it is, it is carried into the central and target section of the accelerator via a beam. It should be noted in this context that, of the total ion beam of ca. 25 μA extracted from the source, there is 15-18 μA in the form of C^+ (1-2 μA), CO^+ (15 μA), and $^+\text{CO}_2$ (1-2 μA). The remainder could be oxides of the filament material.

Sources for oxidants outside the ion source could be silent or corona discharges at points under high-voltage carrying parts. According to R. J. Cvetanovic,⁵⁴ O-atoms could survive several collisions with the walls. Benzene could become a temporary acceptor for such an oxidant (O or O₃).^{55,56} It may transfer the oxygen to other hot-atom product molecules in an oxidation reaction, or it may be involved directly in the reaction with a hot-atom.

d) Contamination of the $^{14}\text{C}^+$ -Beam by $^{14}\text{C}^{16}\text{O}^{++}$

Because of the low resolution mode of the ion separator in which irradiations are usually performed and because of the procedure of identification and optimization of the $^{14}\text{C}^+$ -beam at the target (see Chapter II, 6d) it is possible, in theory, that $^{14}\text{C}^{16}\text{O}^{++}$ contributes to the beam at the target, and "U-2" may be an indication for this. However, the following experiments and observations exclude this possibility:

1) A more careful investigation of the ion beams obtained from $^{12}\text{CO}_2$ (under similar conditions as $^{14}\text{CO}_2$) shows an $m/e = 14$ ($^{12}\text{C}^{16}\text{O}^{++}$?) intensity of less than 10% of $m/e = 12$ ($^{12}\text{C}^+$).

2) Irradiations of benzene with $^{14}\text{CO}^+$ ($m/e = 30$) at energies between 5000 and 15 eV yield the same product and yield distribution as if the irradiations were done with $^{14}\text{C}^+$ of the same energy. This indicates that the fast CO^+ ion disintegrates in the target before the carbon-14 reacts chemically. $^{14}\text{C}^{16}\text{O}^{++}$ should have a similar fate. The yield of "U-2" was, indeed, unchanged-- which excludes CO^{++} as source for it.

The problem of the source of the oxygen in "U-2" remains basically unsolved. "U-2"'s existence, however, is a good demonstration of the relative "openness" of the actual chemical system, and it also demonstrates the complexities that such an instrument introduces. Probably the best way of eliminating this and any similar problem is to admit the beam to the target box through a small orifice only, and to pump the target section by a separate diffusion pump. This would secure best possible separation between the chemical system and the accelerator.

10. Dummy Irradiations

a) Check on Possible ^{14}C -Products Which Are Not Due to Fast ^{14}C Ions or Atoms

Somewhat suspicious because of the above observation, the following experiment was performed: The arc source was charged with 50% $^{12}\text{CO}_2$ and 50% ^{14}CO . However, only the $^{12}\text{C}^+$ -beam was used for an irradiation. All hot-atom and radiation chemical effects in the target are exactly identical to a ^{14}C -irradiation except that the beam intensity and "presence" of ^{14}C were, of course, lower by a factor of 2. After 1 hr, ca. 0.25 μC activity had been incorporated into the benzene. This is approximately 10% of "normal" activity incorporation. A GLC analysis of this irradiation sample showed two activity peaks, one in the "U-2" region, the other in the region of biphenyl. However, the yields were well below 1%. This experiment shows that some ^{14}C -activity may be introduced into the sample in ways other than through the beam. However, this can be considered of no consequence for the present study. The products (see Chapter III, 3, 4) observed in $^{14}\text{C}^+$ -irradiations are indeed products of the fast $^{14}\text{C}^+$ -beam ions.

b) Check on Incorporation of ^{14}C -Activity into the Sample via Accidentally Neutralized Ions

Neutralization of ions may occur in collisions with residual gas molecules or with metal surfaces. While this phenomenon does not interfere with the quantitative analysis of the sample if the irradiation is performed with an undecelerated beam, it may, and

increasingly so, when the beam is strongly decelerated. Particularly if neutralization occurs in the decelerator, i.e. relatively close to the target, the neutral atom may easily be able to hit the target. As the degree of deceleration increases the cross section of the beam may increase at certain places and some ions may collide with one of the decelerator elements and be neutralized. If these atoms have a much higher energy than the final desired ion energy, they will distort the yield-energy dependence at low beam energies. To determine the extent of neutralization, the ^{14}C -ion beam was decelerated to 5 eV; however, the ions were prevented from reaching the target by biasing it by 20 V (positive) with respect to the target box. During one hour the beam was admitted only occasionally (by removing the target bias and turning the electron emitter on (see Chapter II, 8c) in order to assure that the beam had not shifted position. When the sample was analyzed after one hour "irradiation", the total activity incorporation amounted to ca. 10% of the expected value. The GLC analysis showed a typically "low energy" yield distribution of the usual products (< 30 eV). This indicates that neutralization is sizable, although not serious, and that it produces primarily low energy atoms, which makes it even less serious an interference.

III. HOT-ATOM PHYSICS AND CHEMISTRY

In this chapter a survey is given of the factors which might be relevant in the interpretation of our chemical experimental data. Naturally, very little specific information is available for the system under investigation, i.e. fast carbon ions in solid benzene. Therefore, many quantitative conclusions which are drawn from comparison with other systems, or from general theories, are quite tentative. This is particularly serious in the low energy range (1-100 eV), for which the least theoretical and experimental data ~~have been published--however, which happens to be the most interest-~~ing range for the chemistry which this thesis deals with.

1. Interaction of the Ion Beam with the Solid Benzene

The following factors have to be considered: surface penetration; energy loss, range and scattering; charge and electronic state of the fast carbon, structure of the solid benzene; the constitution of the solid around the "track"; and chemical reactions.

In most studies of ion beam-solid state interactions, metals have been used as targets and noble gas ions as beam particles. However, the main differences between a metal and a solid such as benzene, i.e. the absence of a "free-electron gas" and the (generally) lower mass density in the latter, seem to be of minor importance except, perhaps, in the initial surface interaction. Also, if the kinetic energy of the beam particle exceeds the energy for displacement of a lattice atom (25 eV),⁵⁷ the chemical bonds between atoms (4-8 eV) are of negligible consequence and the molecular solid (benzene) can be considered to consist of a mixture of free atoms (carbon and hydrogen).

For some aspects, such as scattering and range, etc., even the presence of hydrogen atoms is of only minor effect because of their small mass compared to the ^{14}C beam particle. At least, as far as processes are concerned which involve energies larger than chemical (≈ 100 eV), the differences between different beam particles in their interactions with the target atoms seem to be accountable by differences in mass, nuclear charge, and velocity. The scarcity of specific data on C-ion beams is, therefore, not serious since generalizable models permit their deduction. The only model which

does consider the specific electron orbitals of a specific atom, that by Hartree, exhibits, indeed, only a slight dependence of the interaction potential on the kind of orbitals.

a) Surface Penetration

The effects connected with the penetration of the solid surface are best discussed in terms of various sputtering theories. Three models have been suggested: the "hot-spot",^{58,59} the "hot-spike",^{57,60,61} and the "collision" model.⁶² A critical review of these theories was given by Kaminsky.⁴⁴ The first two models attempt to describe the effects of the ion impact on the solid as the motion of a two- (surface hot-spot), respectively, one-dimensional (linear hot-spike) statistical system within which an elevated temperature can be defined. Not considering the fundamental difficulties in establishing the validity of a Boltzmann statistics for these systems, the yield from such theories is small. Moreover, experimental results⁴⁴ do not seem to agree very well with them. A less round-about theory, the collision theory, pictures the interaction of the fast particle with the solid as a string of encounters with isolated atoms which recoil and are scattered, as secondary fast particles, at other target atoms--as long as their energy is larger than ca. 25 eV. At the surface, this may lead to emission (sputtering) of target atoms (the binding energy is as low as 5 eV), and possibly also reflection of the original beam particle. All experimental data available (ref. 44, p. 237) indicate a strong dependence of the reflection coefficient

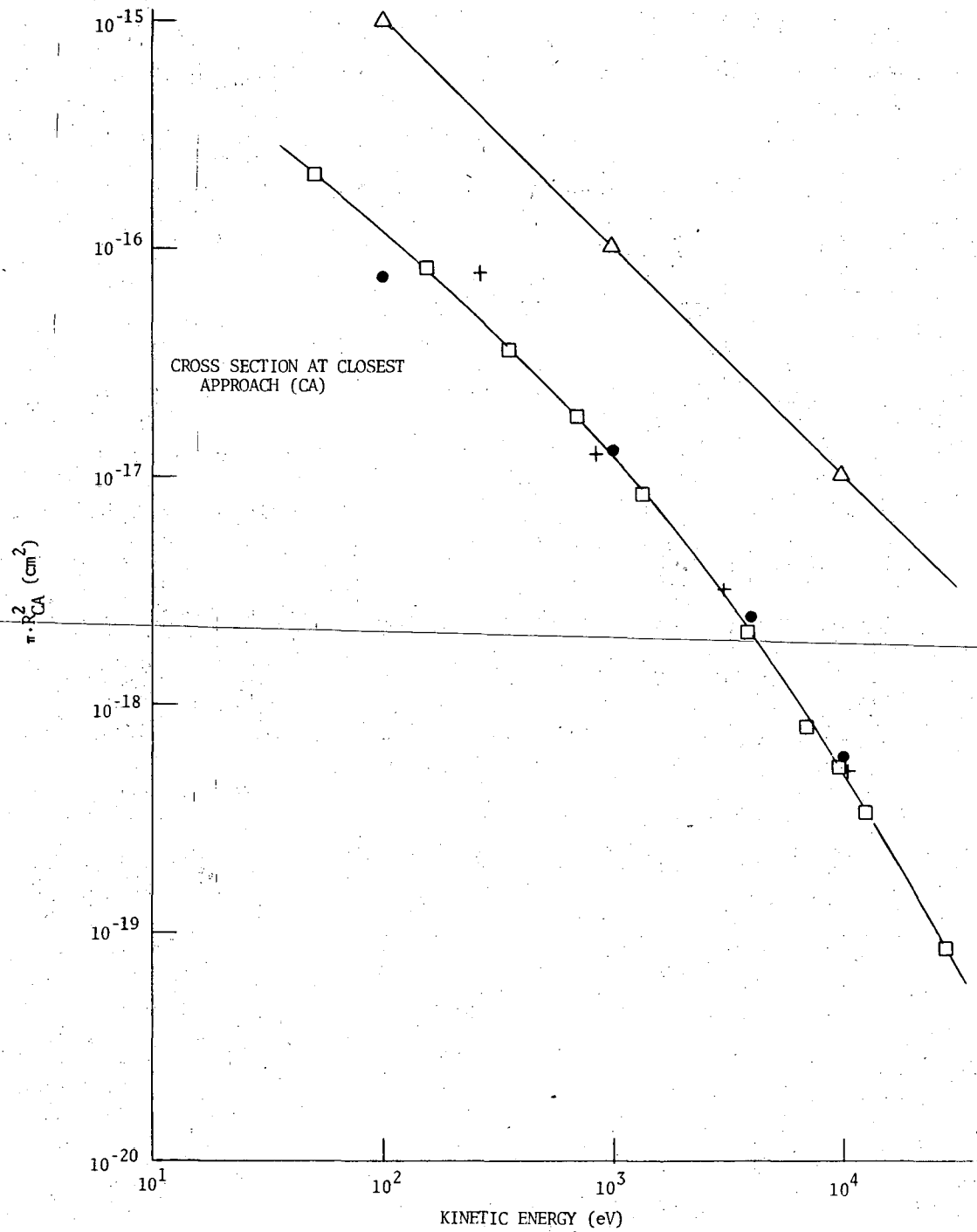
on the mass of the target atom. If, as it is the case here, the target atom mass is equal (^{12}C) or less (H) than the beam particle (^{14}C), the reflection coefficient for near normal incidence should be 5% or less. The remainder is scattered into the solid.

b) Energy Loss and Range

Energy loss and range of neutral atoms in solids has been reviewed by Nichols and van Lint⁶³ in 1966. As will be discussed below, among the first processes to occur upon penetration into the solid is neutralization of the ion. The subsequent energy losses can be derived, therefore, from the dynamics of neutral-neutral interactions. Since essentially all shell electrons of an atom contribute to the repulsive interatomic potential in a binary high-energy collision, the statistical atom models (Thomas-Fermi and Thomas-Fermi-Dirac), the self-consistent field model (Hartree-Fock), and other, empirical models are most profitably employed in obtaining the interaction energies in mathematical tractable forms.

In Figure 18, values $\pi \cdot R_{\text{CA}}^2$ are plotted versus the kinetic energy for the collision between two carbon atoms. Here, R_{CA} is the closest distance that these two carbon atoms can have in a head-on collision.

For the calculation, the following formulas were used (the Thomas-Fermi-Dirac potential was omitted because at lower energies, i.e., <100 eV, where it differs the most from the Thomas-Fermi potential, the question as to the charge and electronic state of the beam particle cannot be answered so clearly anymore anyway,



XBL 695-4230

Figure 18. Cross section of closest approach between two carbon atoms, calculated from various interaction models.

making the extension of calculations to below 100 eV rather dubious). This ambiguity did not warrant the somewhat more complicated calculations:

Thomas-Fermi-Firsov:⁶⁴ $U(R_{CA}) = \frac{Z_1 \cdot Z_2 e^2}{R_{CA}} \phi \left(\frac{R_{CA}}{a_F} \right)$
(Ref. 63, p. 11), where

$$Z_1 = Z_2 = 6, \text{ the nuclear charge}$$

$$e^2 = 27.2 \cdot a_0 \text{ eV} \cdot \text{cm}, \text{ the elementary charge squared}$$

$$a_0 = 0.529 \times 10^{-8} \text{ cm, Bohr-radius}$$

$$a_F = \frac{0.8853 \cdot a_0}{(Z_1^{1/2} + Z_2^{1/2})^{2/3}},$$

and ϕ = the Thomas-Fermi screening function.¹⁵⁷

Brinkman:⁶⁰ $U(R_{CA}) = \frac{Z_1 \cdot Z_2 e^2}{R_{CA}} \left(1 - \frac{R_{CA}}{2a_1} \right) \exp \left(-\frac{R_{CA}}{a_1} \right)$
(Ref. 63, p. 11), where

$$a_1 = \frac{a_0}{Z_1^{1/3}}.$$

Nielsen:⁶⁵ $U(R_{CA}) = Z_1 \cdot Z_2 e^2 a_B \cdot e \cdot \frac{1}{R_{CA}^2}$
(Ref. 63, p. 12), where

$$a_B = \frac{a_0}{(Z_1^{2/3} + Z_2^{2/3})^{1/2}}$$

Bohr:⁶⁶ $U(R_{CA}) = \frac{Z_1 \cdot Z_2 e^2}{R_{CA}} \exp \left(-\frac{R_{CA}}{a_B} \right)$
(Ref. 63, p. 10).

The good agreement between the different methods, except that by Nielsen, down to fairly low energies (see Figure 18) is noteworthy. Furthermore, if $\pi \cdot R_{CA}^2$ is taken as something like a scattering cross section, it becomes apparent that energy loss due to elastic scattering is more efficient at lower energies (ionization and excitation cross sections are in the order of 10^{-16} to 10^{-18} cm^2). This is important in the discussion of other processes, such as charge exchange, competing with elastic scattering (see below). The closest approach between two colliding carbon atoms, ca. $2 \times 10^{-9} \text{ cm}$ at 1 KeV kinetic energy, is only a fraction of the equilibrium carbon-carbon bond length in benzene ($1.395 \times 10^{-8} \text{ cm}$), justifying the concept of binary collisions between essentially free carbon atoms as the mode of energy dissipation.

In Figure 19, linear ranges are plotted using the data of Figure 18, and the following linear range expressions (the linear range is the total path length of a fast atom, irrespective of its shape, from the penetration of an idealized "surface" to the end of the track, which is reached when the kinetic energy of the fast atom has fallen below a minimum energy, E_f , necessary to "displace" a target atom. In the following calculations, this energy limit is assumed to be 10 eV. However, the range data are not very sensitive to this energy limit):

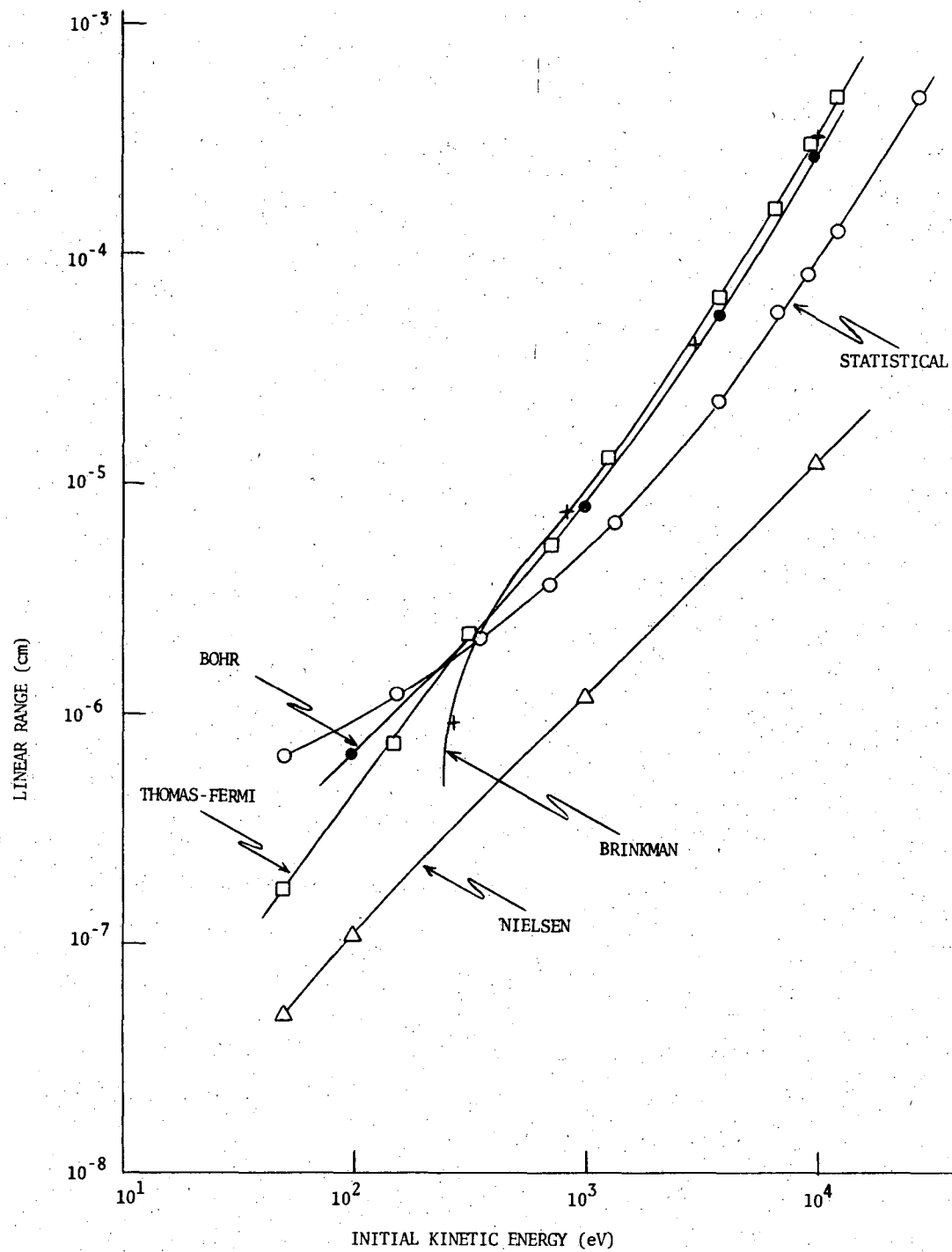
Thomas-Fermi:

Brinkman:

Bohr:

$$R_L = \frac{(\mu + 1)^2}{2 \cdot \mu N_S \pi R_{CA}^2} \log \frac{E_0}{E_f}$$

(Ref. 63, p. 22) ,



XBL 695-4224

Figure 19. Linear ranges for fast carbon atoms in a carbon target, calculated from various models.

where

$$\mu = \frac{M_2}{M_1}$$

M_2 mass of target atom (= 12)

M_1 mass of fast atom (= 14)

N_S number density of scattering atoms ($\approx 4 \times 10^{22} \frac{\text{carbon atoms}}{\text{cm}^3}$)

E_0 initial kinetic energy

E_f final kinetic energy (≈ 10 eV)

In the above formula the quantity determining most strongly the energy dependence of R_L is πR_{CA}^2 , not $\log E_0/E_f$.

$$\text{Nielsen:}^{65} \quad R_L = \frac{0.27 (1 + \mu)(E_0 - E_f)}{N_S \cdot Z_1 \cdot Z_2 e^2 a_B}$$

(Ref. 63, p. 23)

Here, $E_0 - E_f$ is the only energy dependent quantity.

The previous formulas were originally derived on the basis of hard-sphere collisions, i.e. isotropic scattering in the center of mass system, treating energy losses as a continuous process. With the same basis, however, treating these losses as discrete processes leads to a statistical analysis.

$$\text{Statistical:} \quad \langle R_L \rangle = \frac{\frac{3}{2} + \frac{R_{CA}}{a_B}}{N_S \cdot \pi R_{CA}^2}$$

(Ref. 63, p. 25).

In all previous range formulas the contributions to scattering and energy loss by hydrogen atoms were completely neglected. If one calculates the range of carbon atoms in a target consisting of only hydrogen atoms (with the same number density as above) one obtains values which are approximately 60-fold larger than those for carbon, except for the range according to Nielsen (and Brinkman at low energies) where the increase is approximately 3-fold. That is, the contribution from hydrogen to R_L is negligible except in the last case, where the previously calculated range decreases by about 26%.

It is usually found that ranges calculated with the Thomas-Fermi or Thomas-Fermi-Dirac potentials give fairly good agreement with experimental results (Ref. 63, p. 39). The range curve calculated for ^{14}C atoms in benzene (Figure 19) according to Thomas-Fermi is, therefore, regarded as the probably correct one.

The average distance between two neighboring benzene molecules in the solid is approximately 5.3×10^{-8} cm. The range extends therefore at 100, 1000 and 10,000 eV kinetic energy over 3-8, ca. 100, 10,000 benzene molecules, respectively.

The time between successive collisions, τ , is $\tau = 1/Qqv$, where v is the velocity and Q is the cross section at the velocity v . For a 1 KV carbon atom, $\tau = 2.5 \times 10^{-13}$ sec. This should be compared with the electron $1s$ -orbital period of hydrogen: 1.5×10^{-16} sec, and the order of magnitude of vibrational periods: 10^{-13} sec.

A measure for the lateral motion of a fast atom during its slow-down is the ratio between the linear and projected range, R_p . The

projected range is the length of the projection of the linear range in the direction of the initial motion of the atom. An approximate formula for R_L/R_p , when $\mu \leq 1$, was calculated by Lindhard and Scharff⁶⁷ for the $1/R^2$ potential (which did not give good results for R_L --(see Figure 19):

$$\frac{R_L}{R_p} \approx 1 + \frac{1}{3} \mu \quad (\text{Ref. 63, p. 23});$$

$$\text{with } \mu = \frac{12}{14}, \quad \frac{R_L}{R_p} = 1.29.$$

On the other hand, $R_p/R_L \approx \cos \alpha$, where α is the angle under which the stopping point appears with respect to the initial beam direction. $\alpha \approx 39^\circ$ for $R_L/R_p = 1.29$. This should be compared with Monte Carlo calculations of the rms scattering angle for a mass ratio of unity: $\sim 30^\circ$ (Ref. 63, p. 29). It indicates a remarkable correlation in the locations of the starting and stopping points.

Because of the statistical nature of the collision event, the calculated ranges are averages with a certain precision, the so-called "straggling". An approximate formula for it is:^{65,66}

$$\frac{(\langle (\Delta R_L)^2 \rangle)^{1/2}}{\langle R_L \rangle} = \frac{(\alpha \cdot \mu)^{1/2}}{1 + \mu}$$

(Ref. 63, p. 23).

For Bohr's potential:⁶³ $\alpha = 4/3$. For the $1/R^2$ potential,⁶⁷ $\alpha = 2/3$.

The relative "straggling" value is, therefore, between 0.57 and 0.40.

That is, the R_L 's form a rather broad distribution around the average R_L .

In some instances of specially oriented single crystals as target, larger than expected ranges have been observed.^{68,69} This phenomenon, usually referred to as "channeling" and "super-channeling", is most likely of no significance in this case because of the irregular growth of the benzene target (see the following chapter).

c) The Macro-structure of the Solid Benzene Target

In view of the widely observed difficulties in obtaining a single crystal, there is every reason to assume that the solid benzene target is just a conglomerate of small crystallites.

S. Zwerdling and R. Halford⁷⁰ grew a single crystal of benzene under similar conditions as ours: Benzene vapor, issuing through a 40 cm long 0.1 mm I.D. capillary from a liquid reservoir at 0°C, deposited at a small nickel rod at -60°C. The capillary exit was maintained at -35°C. The growth rate was approximately 2 μ l/hr. The small temperature difference (25°) between supply and condensation point is a necessary condition for controlled growth, as well as the slow admission of vapor, particularly during the nucleation period.⁷¹ In our experiments the temperature difference is 200° and the condensation rate 100 μ l/hr or more, far beyond conditions presumably necessary for single crystal growth. The density of molecules in the benzene vapor stream corresponds to a pressure of about 2×10^{-4} mm Hg, i.e. well above the equilibrium vapor pressure at -196°C (by extrapolation,³³ 10^{-15} to 10^{-20} mm Hg). These

conditions probably also favor the formation of small aggregates of benzene molecules in the gas phase believed to be the source for nuclei of condensation.⁷² Thus, nucleation probably abounds and prevents or interrupts regular growth. The crystal structure of benzene at -3°C has been determined by Cox et al.⁷³ and Koshin et al.⁷⁴

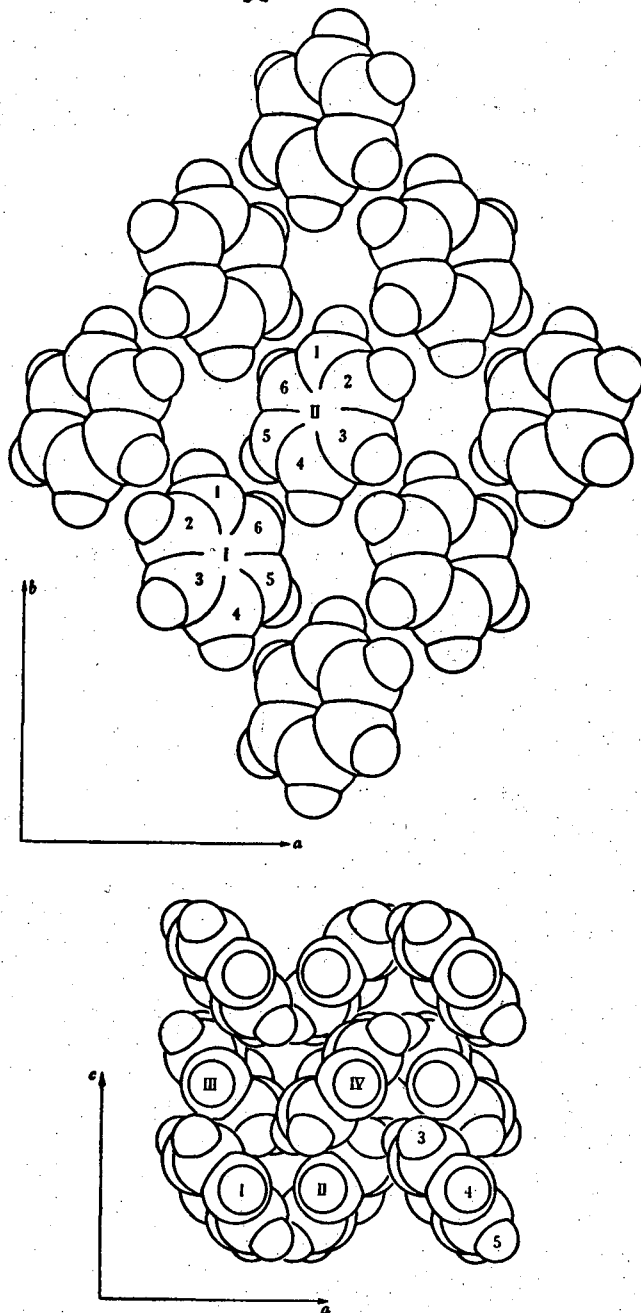
The unit cell size is (in Å):

<u>Temperature</u>	<u>a</u>	<u>b</u>	<u>c</u>
-3°	7.46	9.66	7.03
-20°	7.43	9.63	6.99
-170°	7.34	9.45	6.74
-195°	7.27	9.25	6.72

Figures 20a, b are a diagram of the crystal structure of benzene viewed along different unit cell axis (reproduced from Ref. 73).

It becomes apparent from this model how relatively loosely packed the benzene molecules are, even in the solid state.

The particular configuration between neighboring benzene molecules can be important only in bimolecular reactions between two such molecules. However, since in hot-atom chemistry one of the two reacting molecules would always be a product of a preceding reaction (e.g., addition or replacement of a carbon atom, see Chapter III, 4) one has to expect, in general, that the configuration of this product molecule is different from that of the reactant benzene molecule formerly at this place. Only in the low energy



XBL 695-4254

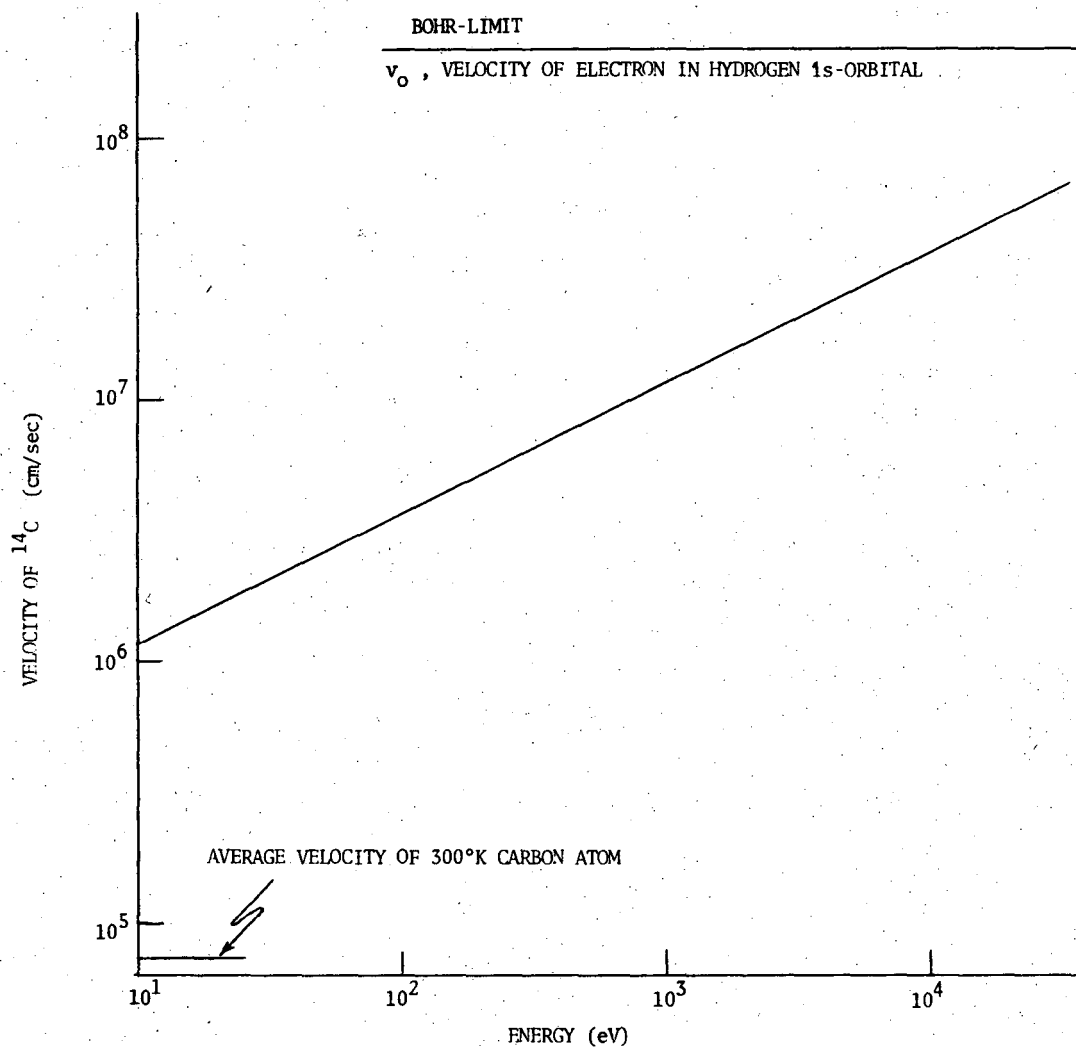
Figure 20. Molecular model of the benzene crystal unit cell (according to Cox et al.⁷³). I, II, III, and IV are the four crystallographically different benzene molecules.

limit can a correlation be expected. We do not, therefore, draw any conclusions from the crystal structure of the unperturbed crystal for the interpretation of hot-atom chemical results.

d) The Charge and Electronic State of the ^{14}C in the Solid Benzene

It was assumed in Chapter III, 1b ("Energy loss and range") that the carbon ion is neutralized immediately after penetrating the solid surface, and that the particular electronic state of the carbon atom is of no consequence as to its range, etc. However, the electronic state may be very important in the final chemical reactions (see below) and it is necessary, therefore, to consider this point explicitly. Unfortunately, again, very little specific theoretical or experimental work is available for comparison at present.

1) Experimental background. Charge state measurements on high energy (>50 KeV) carbon ions moving through low density absorbers were performed by several groups. There are fewer measurements in the intermediate range (20 - 10,000 eV) and very few at energies below 10 eV. Nikolaev et al.⁷⁵ determined the average charge of a beam of singly, doubly and triply charged ^{11}B , ^{13}C , ^{14}N , ^{16}O , and ^{20}Ne ions in the velocity range 3.5 to 11×10^8 cm/sec after passage through H_2 , air, Ar, and celluloid film. Since the velocities are between 1.5 and 5 times v_0 , the Bohr-velocity (see Figure 21), the equilibrium average charge is positive but decreases almost proportionally to the velocity. For example, the average

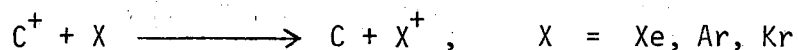


XBL 695-4227

Figure 21. Velocity versus energy diagram for carbon atoms between "thermal" energies and the Bohr limit.

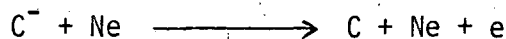
charge is approximately +0.5 for 6×10^8 cm/sec carbon particles (independent of the initial charge state and ca. +0.2 at 6×10^8 cm/sec velocity. Many other similar experiments^{76,77} show that as the average charge decreases, the width of the charge distribution also decreases, i.e. at lower energy the carbon particle is not only "on the average" neutral but also "more likely" neutral. This concurs well with results from actual charge changing cross section data (see below). These conclusions are confirmed by similar results on carbon beams with a different initial charge distribution.⁷⁸

J. B. Hasted et al.^{49,50,79} determined the cross section for the reaction



for C^+ energies between 25 and 40,000 eV. It increased from ca. 3×10^{-17} cm² to a maximum of approximately 3×10^{-15} cm² at energy values which depended on the gases. These and similar data on other ions and gases largely corroborate the resonance rule hypothesis (see below). An anomaly was found for Kr where the cross section varied only slowly in the region of the expected maximum.

Hasted also measured the detachment cross section according to:⁴⁹



between 100 and 3600 eV. The cross section increases monotonously from ca. 10^{-16} to 5×10^{-16} cm².

Fogel et al.^{80,81} investigated the two-electron capture of C^+ in gas molecules between 10 and 55 KeV, according to



where $X = \text{He, Ne, H}_2, \text{N}_2, \text{O}_2, \text{Ar, Kr, and Xe}$. They found the cross section to increase in the above order from 10^{-19} cm^2 to $6 \times 10^{-17} \text{ cm}^2$ at 55 KeV. All cross sections drop by a factor of approximately 10 when the energy decreases to 10 KeV. These results are also considered in agreement with the resonance rule hypothesis.⁸²

Phipps et al.⁸³ determined the number of ion pairs when C^+ ions of energies between 25 and 50 KeV are stopped in Ar. They find 657 pairs at 25 KeV (55 eV/pairs) and 1099 pairs at 50 KeV (45 eV/pair). It is surprising that so many ion pairs are formed, although the ion velocity is well below v_0 . However, the following consideration points out a significant aspect: Since ion-pair formation is due to excitation, etc., by the fast-passage of a coulombic charge, one can assume that the energy per ion pair, W , should actually be a constant. The reported increase by 20% (from 45 to 55 eV/pair) as the energy decreases from 50 to 25 KeV indicates, under the above assumption, that the energy available for ion pair formation was only 42.5 KeV at 50 KeV and 17.5 KeV at 25 KeV, i.e. that below ca. 7.5 KeV no ion pairs are formed at all. The now constant value of ca. 38.5 eV/ion pair, however, has to be compared with 28 eV/pair measured in Ar for H^+ and He^{2+} in the high energy limit ($v \geq v_0$).⁸⁴ Perhaps (the average) W is indeed somewhat higher at lower energies than in the high energy average. W -values in hydrocarbon vapors (low molecular weights) are usually between 29 and 31 eV/pair.⁸⁵

As to the question of the relevance of charge exchange cross section data taken (mostly) from low-pressure gas-phase collision experiments to charge exchange in the solid benzene: P. M. Stier mentions in a review that pressure effects upon the cross sections have been suspected but not substantiated.⁸⁶ The qualitative similarity of cross section data is the strongest support for the possibility of applying gas phase data to solid benzene.

2) Theoretical background. In the interpretation of cross sections for inelastic collisions between atomic systems, with relative velocities below v_0 , probably the most frequently applied hypothesis is that of near resonance.^{87,88} It states that the transfer-of-excitation cross section between colliding systems is maximal if the net energy change, the resonance defect, is zero, and if the transition is "optically" allowed. In cases of unsymmetrical transfer, with a finite resonance defect, the cross section is a function of the relative velocity of the colliding systems. A relationship between the position of the maximum cross section on the velocity (or energy) scale is derived from the condition of adiabacy,

$$\frac{a|\Delta E|}{h\nu} \gg 1,$$

where E is the "resonance defect", h is Planck's constant, v is the relative velocity, and a is a length of the order of the atomic dimensions involved. Taking the above inequality as equation, Hasted et al.⁸⁹ found a mean value of $a = 7 \times 10^{-8}$ cm for many

charge transfer reactions of the type $A^{n+} + B \longrightarrow A^{(n-m)+} + B^{m+} + \Delta E$, while Fogel et al.⁹⁰ determined $a = 1.5 \text{ \AA}$ for $A^+ + \text{Kr} \longrightarrow A^- + \text{Kr}^{2+}$, where A are atoms with Z from 1-10. There are many more examples of the validity of the near-resonance hypothesis (Ref. 88, p. 278) but also apparent "failures", usually attributed to crossing of states during the formation of the collision complexes.^{50,89,91} Cross sections for these reactions seem to be in the order of 10^{-18} to 10^{-17} cm^2 .

Applying the adiabatic rule to the present system, the following state changes of the colliding systems are considered (Table II). The energy, E_m , of maximum cross sections are resonance defects, ΔE , for some reactions are listed in Table III.

From Table III, the predominant processes in the 5 KeV region should be ground state/ground state and ground state/¹S neutralization. Their cross sections should decrease towards lower energies, and neutralization into the ¹D state should dominate there. All transitions are optically allowed, and therefore their cross sections should be large (10^{-16} cm^2).

Direct neutralization of the metastable ⁴P ionic state should be infrequent at 5 KeV. Those into the ¹D and ¹S state are not even "allowed".

Conclusion: Taking into account the conclusion of Chapter II, 3, according to which the ¹⁴C⁺-ions generated in this ion source are most likely in their ground state (²P), one would derive from the application of the adiabatic hypothesis that: 1) The fast carbon ions are readily neutralized, and that the carbon atom can

Table II

Energy of Reaction Values for Some Elementary Processes

	<u>ΔE (eV)</u>	<u>Type</u>	<u>Ref.</u>
$C \longrightarrow C^+$	11.217	I.P.	33
$C_{(3p)} \longrightarrow C_{(1D)}$	1.3	from optical spectra	92
$C_{(3p)} \longrightarrow C_{(1S)}$	2.68		
$C_{(3p)} \longrightarrow C_{(5S)}$	-1.25		
$C_{(2p)}^+ \longrightarrow C_{(1S)}$	-8.58	R.E.	93
$\longrightarrow C_{(1D)}$	-10.00	"	"
$\longrightarrow C_{(3p)}$	-11.26	"	"
$C_{(4p)}^+ \longrightarrow C_{(5S)}$	-12.40	"	"
$\longrightarrow C_{(3p)}$	-16.58	"	"
$\longrightarrow C_{(1D)}$	-15.32	calc.	
$\longrightarrow C_{(1S)}$	-13.9	calc.	
$C_6H_6 \longrightarrow C_6H_6^+$	9.6	I.P.	33
$C_6H_6 \longrightarrow C_6H_6^*$	<4	vibrational excitation	

Table III

Maximum Cross Section Energies

	<u>ΔE (eV)</u>	<u>E_m (KeV)</u>
$C_{(2p)}^+ + C_6H_6 \longrightarrow C_{(3p)} + C_6H_5^+$	1.6	5.4
$\longrightarrow C_{(1D)} + C_6H_5^+$	0.4	0.16
$\longrightarrow C_{(1S)} + C_6H_5^+$	1.0	2.1
$C_{(4p)}^+ + C_6H_6 \longrightarrow C_{(3p)} + C_6H_6^+$	7.0	101
$\longrightarrow C_{(5S)} + C_6H_6^+$	2.8	16.5
$\longrightarrow C_{(1D)} + C_6H_6^+$	4.06	34.6
$\longrightarrow C_{(1S)} + C_6H_6^+$	2.7	15.4
$C_{(3p)} + C_6H_6 \longrightarrow C_{(4S)}^- + C_6H_6^+$	10	210

be considered the reactive species for most of the hot-atom chemistry investigated in this thesis. This conclusion is probably correct for initial energies larger than ca. 50 eV. At lower energies reaction and charge exchange cross sections are becoming increasingly comparable. 2) The dominant electronic state of the neutralized carbon should be 3P and 1S at energies above 2.1 KeV. At lower energies the first metastable state 1D should be most abundant. Whether deactivation of this state (and also that of the 1S state) to the ground state (3P) occurs with sufficient frequency so that most carbon atoms could be considered to be in their electronic ground state as they enter the chemical energy range cannot be predicted from the adiabatic theory.¹² In the absence of specific information one has to accept the possibility of a mixture of electronic states among the carbon atoms participating in chemical reactions. The relative abundance of states is also, most likely, a function of the initial kinetic energy of the carbon ion.

2. Hot-atom Chemistry of Carbon

a) Experimental

The hot-atom chemistry of carbon in benzene was investigated prior to this work by various groups: Libby⁹⁴ (1956), Wolf⁹⁵ (1956), Lemmon⁹⁶ (1956), and Vogt⁹⁷ (1963). During the completion of this study, Voigt⁹⁸ (1965) and Wolfgang⁹⁹ (1967) published data on the same subject.

Libby, and first also Wolf, generated fast ^{14}C by the ^{14}N (n,p) ^{14}C reaction. Nitrogen was present in the liquid benzene in the form of aniline, 2-methylpyrazine, or acetamide (at concentrations of about 10%). Later, Wolf¹⁰⁰ employed the ^{12}C (n,2n) ^{11}C reaction, Voigt and Wolfgang the ^{12}C (γ ,n) ^{11}C reaction to create fast radioactive carbon isotopes under conditions with smaller "radiation damage" to the chemical system than in the ^{14}N (n,p) ^{14}C reaction.¹² Lemmon used a mass spectrometer to produce a ^{14}C -ion beam of 10^{-9} to 10^{-10} amp intensity at 2 KeV. Here the benzene was in solid form at -155° . All other workers used benzene in liquid form.

All workers have found ^{14}C -benzene and toluene as products. Libby⁹⁴ also found di- and triphenylmethane. Lemmon^{14,101} found 1,3,5-cycloheptatriene, which was confirmed later by Wolfgang⁹⁹ and Voigt.¹⁰² Voigt⁹⁷ and Wolfgang⁹⁹ directed more attention to products with molecular weights smaller than benzene. The most abundant is acetylene (ca. 7%), followed by diacetylene with ca. (5%). Methane is found in yields of 0.2%.⁹⁷ Benzene, toluene, and cycloheptatriene were generally found with ca. 2, 1, and 4% yield.

Voigt also found phenylacetylene at 2% yield.¹⁰²

Wolfgang⁹⁹ investigated the yields in solid, liquid and gaseous benzene (70 mm Hg), the latter also in the presence of O_2 as scavenger (3.5 mm Hg), or Ne as moderator (benzene 40, neon 760 mm Hg).

b) Interpretations

Reviews of the experimental and theoretical work in hot-atom chemistry of carbon in various systems were given by Willard (1955),¹⁰³ Wolf (1964),¹⁰⁴ and Wolfgang (1965).¹²

The general reaction scheme can be concentrated like this:

1) Carbon forms CH_2 in hydrocarbons and reacts, in this form, in very much the same way as CH_2 from other sources. CH_2 was therefore assumed as precursor for toluene¹⁰⁰ and cycloheptatriene¹⁴ from benzene, and for various other analogous products in other systems.¹²

2) Carbon reacts initially by two insertion mechanisms: "C-H" and "C=C bond insertion". C-H insertion leads to the formation of a carbene which could undergo a bimolecular condensation with another substrate molecule. The observation of several C_5 -compounds from ethylene is a good indication for this.¹⁰⁵ Or, the carbene decomposes due to high internal energy (Wolfgang suggests that the spin state might be the determining factor¹²). Acetylene is believed to be the main product of this decomposition route.¹⁰⁶

C=C bond insertion is demonstrated by the observation of good yields of allene and methylacetylene from ethylene.¹⁰⁷ Allene was labeled in the center carbon by a ratio of ca. 2:1 over the end

carbons, while the methylacetylene showed a labeling pattern close to random.

For benzene, Wolfgang postulated " C_7H_6 adducts" of various conformations which were assumed to decompose to the low molecular weight products or form polymers in bimolecular (or chain) reactions. The increase of polymer, i.e. compounds with higher molecular weight than 100, from $80\% \pm 7$ to $93\% \pm 2$ when going from the pure vapor system to the neon-moderated (760 mm Hg Ne, 40 mm C_6H_6), was interpreted as an indication for this hypothesis.⁹⁹

The fact that scavengers (DPPH or O_2) do not seem to alter the hot-carbon chemistry in benzene is attributed to both the high reactivity of carbon and its primary adducts with benzene--all presumed to be "thermal" or near-thermal reactions. This interpretation, of course, is contrary to the usual hypothesis that scavengers are effective only for thermal, not "hot" radicals, i.e. an insensitivity of a product yield to the addition of scavengers is attributed to the "hot"-ness of the radicals involved. On the other hand, the variation of the yields in the moderated system, i.e. lowering of the acetylene and benzene yields, do not seem to be conducive to a definite interpretation.

The formation of ^{14}C -benzene, as in general the apparent replacement of ^{12}C by ^{14}C in the parental molecule, sometimes referred to as "retention", is essentially not understood in any of the investigated systems.

c) Theoretical

The only theory able to fully delineate hot-atom chemistry is, of course, quantum mechanics and quantum field theory. The absence of accurate solutions (or even tested approximations) to most chemical problems, however, make them almost totally useless, and semi-empirical theories have to be developed. The demands on any such "theory" are: It must reduce experimental data and allow generalizations on future experiments; and the terms through which reduction is achieved must be amenable to comparison with terms from other theories which deal with the same problem or, better yet, should be potentially directly calculable from quantum mechanics (see Chapter I, 3).

Probably suggested by the general propensity in hot-atom chemical systems to form the parental molecule, early quantitative theories were based on "cage models", i.e. the data were interpreted in terms of impact-induced dissociation of a molecule and recombination of the fragment radicals trapped in the cage, versus diffusion of reactive species away from the cage if their kinetic energy is sufficient to overcome the cage barrier.¹⁰⁸ The implied mechanisms seemed acceptable from the point of view of "mechanisms" developed in organic chemistry, and it was hoped that this approach would be applicable to other reactions and products as well, not just the above replacement reactions. The most fundamental quantity in this theory is the energy gap between the reaction threshold and the cage barrier. The larger this quantity the more successful

would this quantity determine certain gross features of hot-atom chemistry. Where this energy difference is small or even vanishes, as in gas phase reactions, the theory becomes inapplicable. The observation of many hot-atom products in all three phases and the self-imposed limitations (e.g., by assuming as basis certain mechanisms, such as "dissociation" and "recombination"), have made many researchers turn away from this approach. Even in the phase most amenable for application of it, the solid, experimental evidence for non-stochastic processes, as channeling and focussing,⁶³ make the assumption of a statistical quantity such as cage carrier, etc., a questionable basis.⁶

The "billiard ball" hypothesis,¹⁰⁹ suggested to account for replacement reactions, appeals for two reasons: First, it allows these reactions to occur at rather high energy (and it could, therefore, be a truly "hot"-reaction mechanism) if the collision is "head-on" (the initial kinetic energy is only limited by the finite kinetic energy after collision due to the isotopic mass difference [see Appendix C]); and, second, it is applicable to any isotope. However, it is partly the lack of analogy to orthodox organic-chemical mechanistics (for instance the implied absence of any chemical specificity), but mainly its conceptual incompatibility with established rate theories that this theory has found few friends. Cross and Wolfgang¹¹⁰ show, in particular, that an isotope effect of 3 would be expected for a billiard-ball mechanism in the reaction of tritium with (deuterated) methane, while the experimental value is very close to 1.

Conceptually quite different and more amenable to testing by experiment is the collision theory.^{6,11,111-114} The most fundamental term is the "collision", which is usually defined by the event of momentum change of the initial particle. "Reaction" is described to occur with a certain probability, $p(E)$ (a function of the relative energy, E) with respect to this collision. The "collision" probability, $n(E)$ (also a function of the energy) can be calculated from the kinetic theory under certain assumptions¹¹ and "yields" expressed in terms of $n(E)$ and $p(E)$:⁶

$$Y_v = \int_{E_1}^{E_0} p_v(E) n(E) dE$$

Here v refers to the v th product; E_0 and E_1 are the reaction threshold and upper limit, i.e. $p_v(E) > 0$ only if $E_0 \leq E \leq E_1$.

In the above equation, $n(E)$ must take into account the finite reactivity at energies higher than E . Wolfgang et al.^{112,113} found the following expression useful as a working assumption:

$$n(E) dE = \frac{1}{\alpha E} \left[1 - \sum_v \int_{E_1}^E f_v \cdot p_v(E) n(E) dE \right] dE,$$

where f_v is the relative probability of collision with component v ,

$$\alpha = -\ln \frac{E \text{ (after collision)}}{E \text{ (before collision)}}$$

This allowed them to express yield data in terms of "moderator" concentration $(1-f)$ (for the case of inert gas admixtures) and the

reactivity integral

$$I_v = \int_{E_0}^{E_1} \frac{p_v(E)}{E} dE : Y_v = \frac{f}{\alpha} I_v - \left(\frac{f}{\alpha}\right)^2 \cdot K_v ,$$

$$\text{where } K_v = \int_{E_0}^{E_1} \frac{p_v(E)}{E} \left[\int_E^{E_1} \frac{p_v(E)}{E} dE \right] dE .$$

I_v (and thus K_v) are obtained from the limiting value of $Y_v \cdot (\alpha/f)$ for infinite moderation. This application of the kinetic theory lends itself quite well to the analysis of nucleogenic hot-atom moderator experiments.¹¹³⁻¹¹⁵

Hsiung¹¹¹ and Gordus^{114,116} have investigated the effect of varying the assumptions that enter the derivation of the collision function $n(E)$. For instance, it is known that the assumption of isotropic (in the center of mass system) scattering between atomic particles is fairly good at large velocities (>1 KeV); however, at lower energies small angle scattering seems to be generally preferred. They conclude that, due to the absence of sufficiently accurate elastic scattering data in the chemically important range of 1-30 eV, an absolute evaluation of the reactivity integrals I_v is beset by large errors.

Their work points out very well the drawbacks connected with the calculation of the collision function from the Boltzmann transport equation:

$$n(E, E_{\max}, E_{\min}) = \int_{E_{\min}}^{E_{\max}} b(\epsilon) \cdot k(E, \epsilon) d\epsilon + \int_E^{E_{\max}} n(\epsilon) \cdot k(E, \epsilon) d\epsilon,$$

where $b(E)$ is the particle flux at energy E entering the absorber

$$\left[\int_{E_{\min}}^{E_{\max}} b(\epsilon) d\epsilon = 1 \right],$$

$E_{\min}$ and $E_{\max}$ are the energy limits for this initial particle flux; $k(E, \epsilon)$ is the probability that a particle has the energy E after a collision undergone at energy ϵ ($\geq E$); and ϵ is the integration variable on the energy axis. The removal of primary particles due to reaction is being taken care of usually by a perturbation calculation at the $n(E)$ determined from the above equation.

While this formulation allows the application of the well-known analytical calculus it is too restrictive in the forms that $k(E, \epsilon)$ can have in order to make the integral equation solvable. For isotropic scattering, it is simply $1/\epsilon$, and $n(\epsilon)$ can be evaluated. Not so, if the predominant small angle scattering is to be included. On the other hand, the appearance of the independent variable E as one of the integration limits makes it plausible that, if $E \ll E_{\min}$, the collision function will be independent of $E_{\max}$ and $E_{\min}$ and also rather insensitive to the fine structure of $k(E, \epsilon)$ at high energy. Therefore, if deviations from the asymptotic collision function, $n(E) = 1/\alpha E$, are found or expected at low energies, i.e. in the chemical range, it seems clumsy to have to evaluate integrals

covering a large energy range which may contribute only very little, while it is difficult to tell just how important it is. Furthermore, it seems equally clumsy to first calculate the collision function assuming certain reaction probabilities and then calculate the reactivity integral by making the same assumption again. R. N. Porter has, therefore, shown that the reactivity integral can be evaluated directly if the reaction probability $p(E)$ and the collision probability $k(E, \epsilon)$ are known,¹³ or, if reasonable assumptions about them can be made in the chemical energy range. This approach also seems more suitable for computation if $p(E)$ and $k(E, \epsilon)$ are available only in numerical, rather than analytical form.

Menzinger,⁷ who determined that the yields of tritiated products from fast T^+ -ions in cyclohexane are dependent on the kinetic energy of T^+ between 3 and 200 eV, applied Porter's method and obtained the reaction probability functions $p_v(E)$ for the different products. He also points out that with ordinarily obtainable accuracies this combined experimental and theoretical method does not admit the evaluation of $p(E)$ for values of E much larger than the threshold energy, E_{act} , because the yield values are always integrals over the whole energy range below the initial energy, and therefore rather insensitive to changes of $p(E)$ for $E \gg E_{act}$.

In the present investigations, the kinetic theory is applied to two different problems: the derivation, for a large energy range (1-100 eV) of the approximate collision function for one-, two- and three-step fast intermediates (Appendix B), and the approximate collision function for secondary (knock-out) ^{12}C atoms (Appendix E). In order to keep the rather complex calculations tractable, n was assumed to be $1/E$, and $k(E, \epsilon) = 1/\epsilon$.

3. Accelerator Chemical Experiments

During the course of work for this thesis, about 60 "irradiations" were performed involving ^{12}C , ^{14}C , ^{14}CO -ions and ^{14}C -atoms at energies between 3 eV and 15,000 eV. The target was benzene, except for one irradiation of toluene. The temperature of the target was -196°C with the exception of a few irradiations at -156° (freezing temperature of isopentane) for "U-2" experiments.

a) General Irradiation Procedure

Approximately 100 μl benzene were deposited on the target surface before the beam was turned on. This amount was sufficient to ascertain, by visual inspection, that the solid was growing (and would continue to grow) in an even way over the whole area to be exposed to the beam. Such a layer of benzene is also sufficiently thick so that all carbon ions are stopped within the solid.

The flowrate during the irradiation was 120-150 $\mu\text{l/hr}$, and the spacing of the nozzles such that about 80% of the deposited benzene was within a circle of about 1 cm diameter (see Chapter II, 8). The recovery of benzene was between 50 and 70% (with respect to the total amount of benzene introduced). Most irradiations lasted, depending on the purpose, between 1 and 3 hrs. When only yield data were to be taken, 1 hr was sufficient. Irradiations for subsequent degradations of the products lasted 3 hrs and in one case 16 hrs. (For technical details see Chapter II, 5, 8, 9 and 10).

b) Recovery of the Irradiation Sample

After the beam was turned off, another ca. 50 μ l were allowed to deposit. Then the target section was valved off from the rest of the accelerator vacuum chamber and brought to 1 atm by filling with dry N_2 . The target, still filled with the cooling fluid, was then removed from the target box directly into a glove box which was continuously flushed with dry nitrogen. The solid was then scraped off and transferred, in this form, into a LN_2 -cooled vial. In some cases a metal foil disc (ϕ ca. 1 cm, gold or copper, 25 μ thick) had been glued to the face of the cube target with silver paint, and the benzene had been deposited on it. The whole disc plus solid benzene could be easily pried off and transferred into the vial.

After completion of the sample removal (which takes between 5 and 10 min), the vial was closed and kept at dry-ice temperature until processing. Very volatile products such as acetylene are, of course, lost in this procedure. In order to recover these compounds a gas transfer and trapping method has to be employed. However, in this thesis the main interests were the non-volatile, build-up products.

The vial was made of a 1/4" "Covar" seal, the glass part drawn to a point, and the copper tube hard-soldered to a brass pipe fitting. As a lid we used an aluminum plate with a fine hole in the center to allow a syringe needle to pass through. This hole was covered (on the outside) by a larger rubber septum. A teflon O-ring established the seal between the brass fitting and the aluminum plate.

c) Identification of Products

Aliquots of the irradiation mixture were injected on gas-liquid chromatography columns ("Carbowax 20M", or "Apiezon L", 5% on chromosorb W, 10' x 1/4" I.D., 40 ml/min He, 70° for 12 min, 10°/min to 225°). Both columns separate hydrocarbons approximately according to their boiling points, making the guessing of the unknown products' structure easier.

The effluent of the column was mixed with methane at 40 ml/min flow and counted in a 20 or 85 ml cylindrical proportional counter tube (Nuclear Chicago). The counter tube and the connecting tubing between it and the column exit port were heated to 250° by electrical heating tape (in order to prevent condensation of the high-boiling compounds). The plateau of the counter, a function of temperature and flowrate, was determined in situ with a mild external γ -source. This plateau was usually around 1800-2000 V, the background 300 cpm. The electrical output of the proportional counter and the thermal conductivity detector of the gas chromatograph were recorded on a two-pen 0-10 mV recorder, and the two pens set so that for a test compound (toluene- ^{14}C) exact coincidence of the position of the two peaks was obtained. In the analysis of the irradiation mixture, the coincidence between an added carrier peak with one of the activity peaks was taken as indication for the identity of the unknown ^{14}C -product (see Figure 22). However, in order to substantiate the identity, the carrier plus activity were trapped in another run as they emerged from the chromatographic

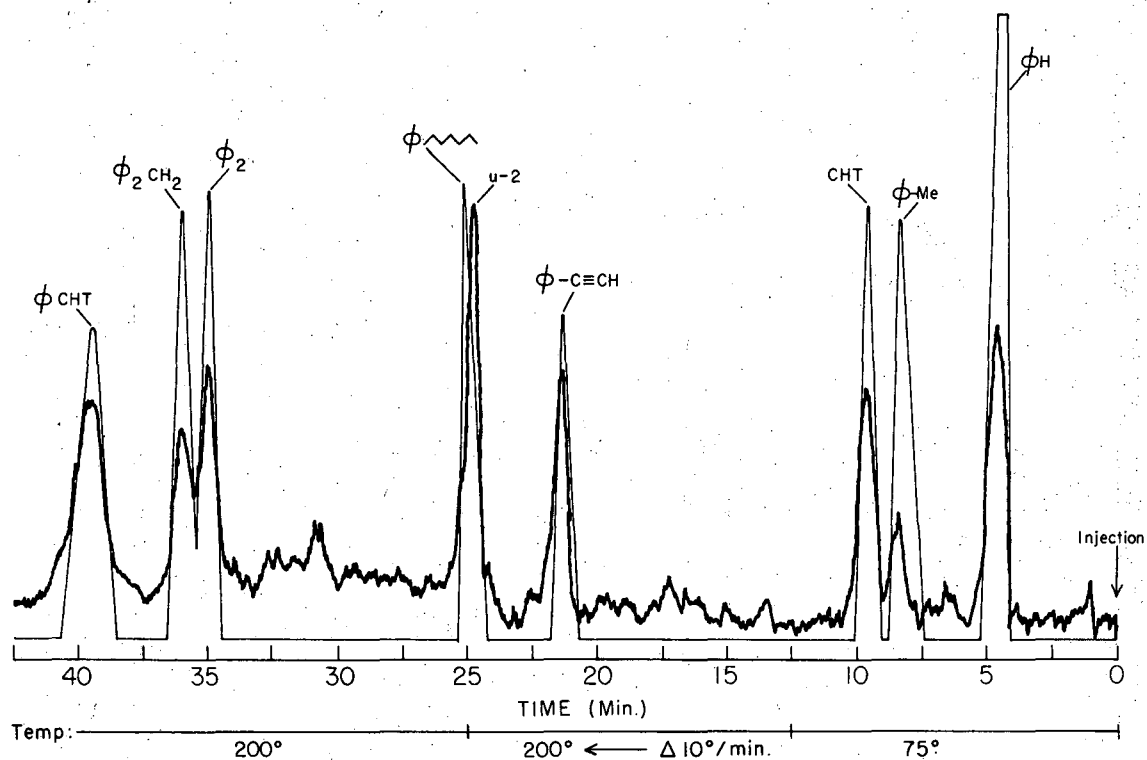


Figure 22. Typical glc-analysis of a $^{14}\text{C}^+$ -ion bombarded benzene sample (energy 5 KeV). Heavy, jagged line = proportional counter signal; light line = thermal conductivity cell signal from sample benzene and co-injected carriers. Phenylhexane serves as "marker" and co-precipitant for "U-2" (benzaldehyde).

column, and certain chemical reactions performed on them (see Table IV) which (preferably) produced a different carrier. Reinjection on the column of the product mixture and recording both the thermal conductivity and the activity of the effluent revealed whether the "activity" had undergone the same chemical reaction as the carrier, since, usually, the retention time of the products were different from the original compounds.

Actually, it is also necessary to establish that all of the activity trapped, or, better, recorded as activity peak, was the particular suspected compound. Some significant part of it being of a different structure and without a substantial amount of carrier could have been lost in the chemical reaction, trapping, etc. This check was done, e.g. with CHT, by measuring the apparent specific activity of the CHT peak and, later, that of its Diels-Alder-adduct (see Table V). The result was that the CHT peak contained at most 5% contamination. A particularly important compound in this respect was benzene. Because of the large amount (10-20 λ) the peak is rather broad and a number of other compounds could be buried under it. The product benzene was therefore trapped, its apparent specific activity determined and the same sample subjected to certain treatments as listed in Table VI. After each treatment the apparent specific activity was determined again. Within the experimental error limit (3%) no change could be observed. Unless the contaminant radioactive compound was as unreactive to Br_2 and Pt/H_2 as benzene, the "benzene" peak in Figure 22 consists of benzene only.

Table IV

Results of Specific Chemical Reactions on the Eight Major
Compounds Obtained from ^{14}C /Benzene Interactions

Compound	Reaction	Product
Benzene	Hydrog.	Unchanged
Toluene	KMnO_4 oxid.	Benzoic acid
	Hydrog.	Unchanged
CHT	Hydrog.	Cycloheptane
$\phi\text{C}\equiv\text{CH}$	Hydrog.	$\phi\text{CH}_2\text{CH}_3$
U-2	Hydrog.	Toluene ^{8,117}
		Methyl cyclohexane ^{8,117}
Biphenyl	CrO_3 -oxid.	Benzoic acid
	Hydrog.	Unchanged
$\phi_2\text{CH}_2$	SeO_2 -oxid.	$\phi_2\text{CO}$
	Hydrog.	Unchanged
ϕCHT	Hydrog.	ϕ cycloheptane

Table V

Radiopurity of Cycloheptatriene

<u>Sample</u>	<u>Expt. No.</u>	<u>Weight (mg)</u>	<u>Specific activity in (dpm/mole) x 10⁸</u>
Inject aliquots of n-pentane	1	1.763	1.61
solution of CHT- ¹⁴ C; trap	2	2.822	1.61
CHT	3	2.943	1.60
Diels-Alder adduct*	1	0.975	1.53
	2	2.035	1.53

*Dimethylacetylene dicarboxylate (prep. as in ref. 127).

Table VI

Radiopurity of Benzene

<u>Sample</u>	<u>Expt. No.</u>	<u>Weight (mg)</u>	<u>Specific activity in (dpm/mole) x 10⁻³</u>
Inject aliquots of n-pentane	1	4.627	1.95
solution, trap benzene- ¹⁴ C	2	4.120	2.01
	3	3.077	1.93
Hydrogenation		2.126	1.93
Bromination	1	4.304	1.93
	2*	1.430	1.96

*Here the trapped benzene was reinjected and re-trapped in order to eliminate some background mass contamination which appeared in the first run.

In this way the following products were identified: benzene, toluene, cycloheptatriene, phenylacetylene, biphenyl, diphenylmethane, and phenylcycloheptatriene.¹¹⁷ (It cannot be said which of the four isomers of phenylcycloheptatriene the actual product is, or if it is a mixture, since this compound isomerizes strongly under the high temperature conditions of the gas chromatography, presumably due to transannular hydrogen shifts.¹¹⁸)

d) Hydrogenation of the Irradiation Mixture

For two reasons it was found feasible to hydrogenate the reaction mixture before analysis: 1) Some (possibly highly strained) products might decompose on the hot injector (usually 250°) of the gas chromatograph or on the column and thus not be detected. Hydrogenation, however, might stabilize this compound. 2) There may be a large variety of compounds, such as various unsaturated n-alkylbenzenes, which are not separable on the column and which, therefore, make up the structure-poor rising background (see Figure 22). Hydrogenation, however, may lump many of them together to one and the same saturated product. This, indeed, was observed (Figure 23). n-Alkylbenzenes, with $n = 2, \dots, 7$, were identified, yields determined, and for the other compounds, mentioned in Figure 23, upper yield limits established (see T. H. Lin, Ph.D. Thesis, University of California, Berkeley, 1969).

e) Routine Yield Determination in the Unhydrogenated Sample

A simple method had to be established which would give, fairly reproducibly and quickly, yield data. The simplest would

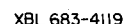
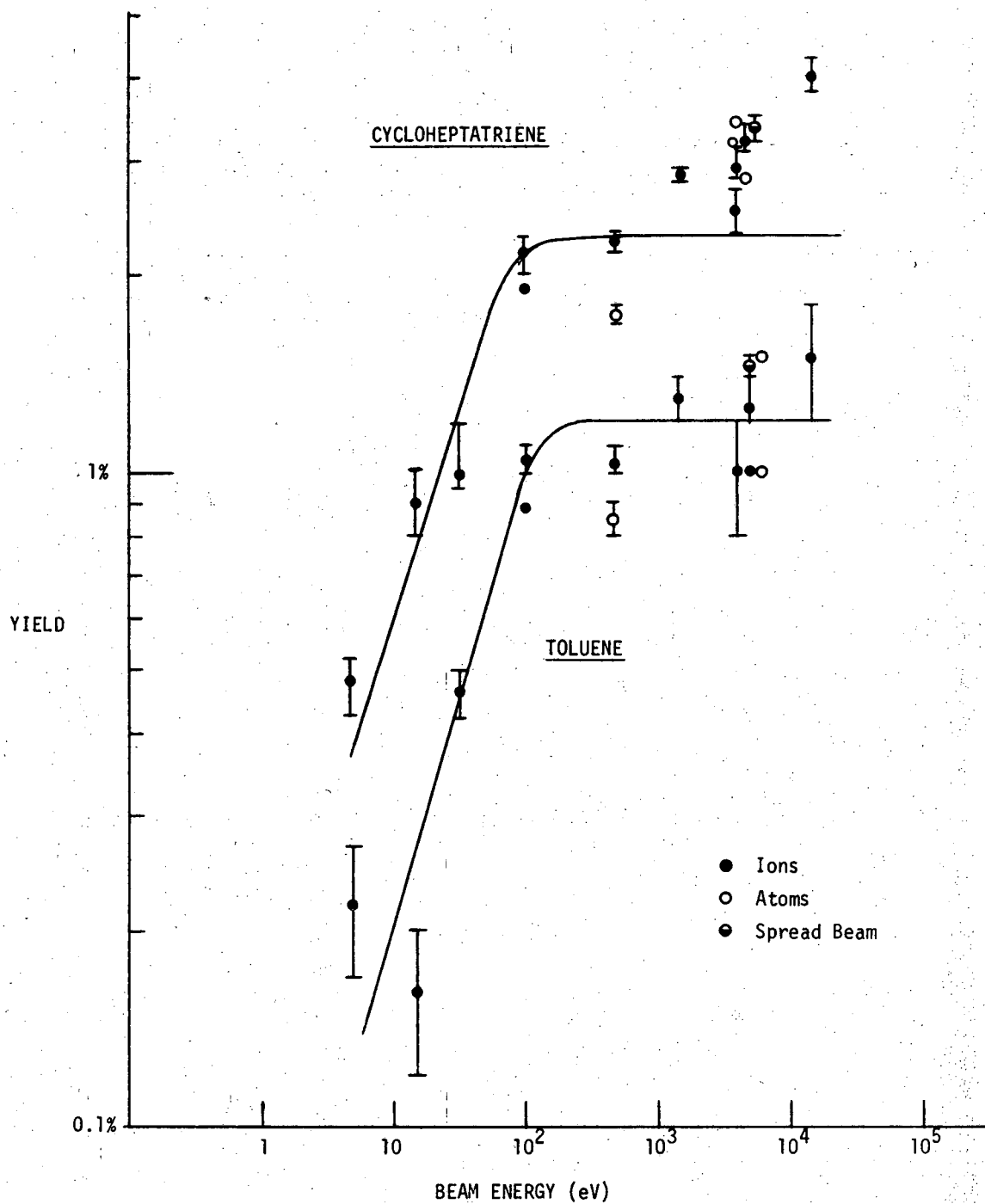


Figure 23. Typical glc-analysis of a hydrogenated, $^{14}\text{C}^+$ -ion bombarded benzene sample (energy 5 KeV). Heavy, jagged line = proportional counter signal; light line = thermal conductivity cell ~~signal from sample benzene and the hydrogenation products of~~ carriers added prior to hydrogenation. Dotted lines = approximate retention times of compounds which were sought, in separate analyses, for mechanistic reasons (Tz-Hong Lin, Ph.D. Thesis, University of California, Berkeley, 1969) but which were not co-injected with this sample.

have been to integrate the output of the proportional tube over the peak area and correct for residence time and efficiency. However, a few trial runs showed severe difficulties of reproducing data, and large changes in the efficiency. This is probably due to the high temperature at which the proportional counter tube has to be kept to prevent condensation. This high temperature has an adverse effect upon the "length" of the plateau, making the output rather sensitive to minor changes of the counting gas mixture.

The following method proved fast and relatively reliable (used for the yield data in Figures 24-28): After the benzene was melted the total volume was determined by drawing the liquid into a 500 μ l syringe and returning it again into the vial. An aliquot, usually 10 μ l, was then withdrawn and counted in "Toluene"-Scintillation solution (4.5 gr PPO, 0.1 g POPOP per liter toluene) in a scintillation counter. Using the aliquot factor the "total recovered activity" could be determined. This figure usually agreed within 10-15% with the "total incorporated activity" as determined by target current integration. The "yields", below, however, refer to "total recovered activity".

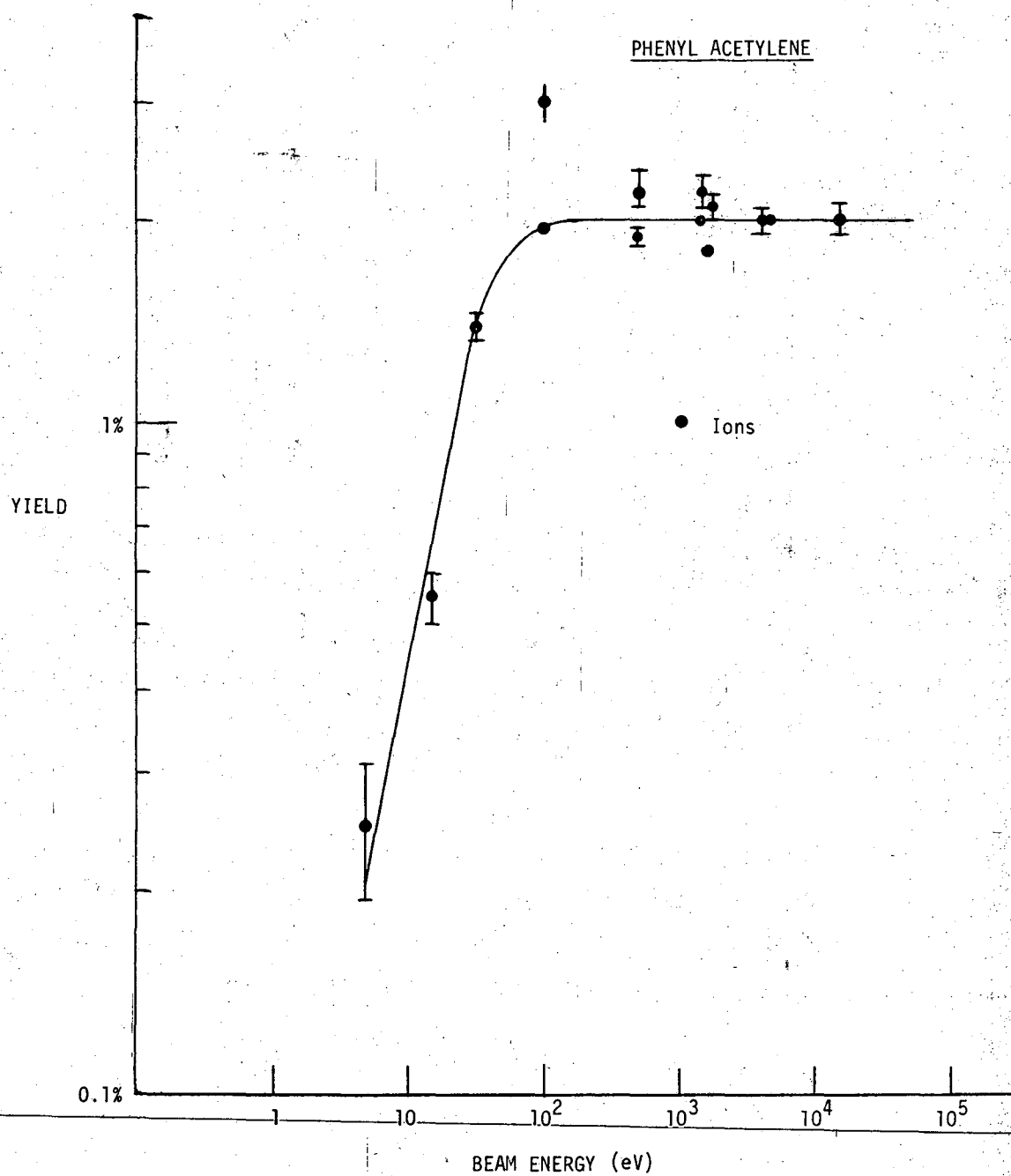
In most cases, 10-20 μ l aliquots were then mixed with a solution of the carriers (each 0.2 to 0.5 mg) and injected on the GLC column. A glass capillary was tightly connected to the exit port of the column (via a punctured rubber septum fitted into this port) and the effluent of the column bubbled into a standard (12 ml) scintillation counting vial filled with the scintillation solution. The vials were changed in accordance with the appearance of peaks from



XBL 691-4683

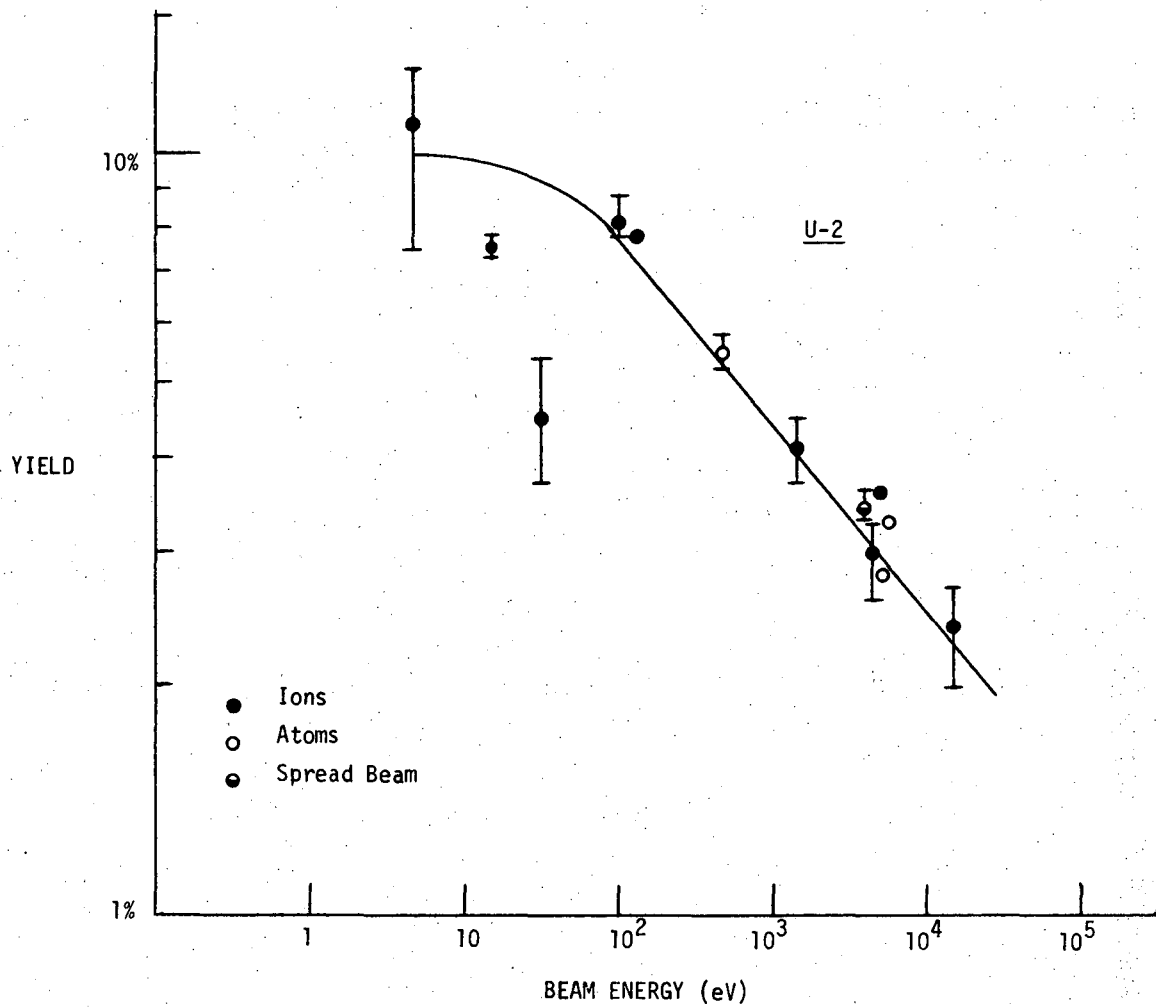
Figure 24. Yields of toluene and cycloheptatriene versus $^{14}\text{C}^+$ -ion beam energy.

-124-



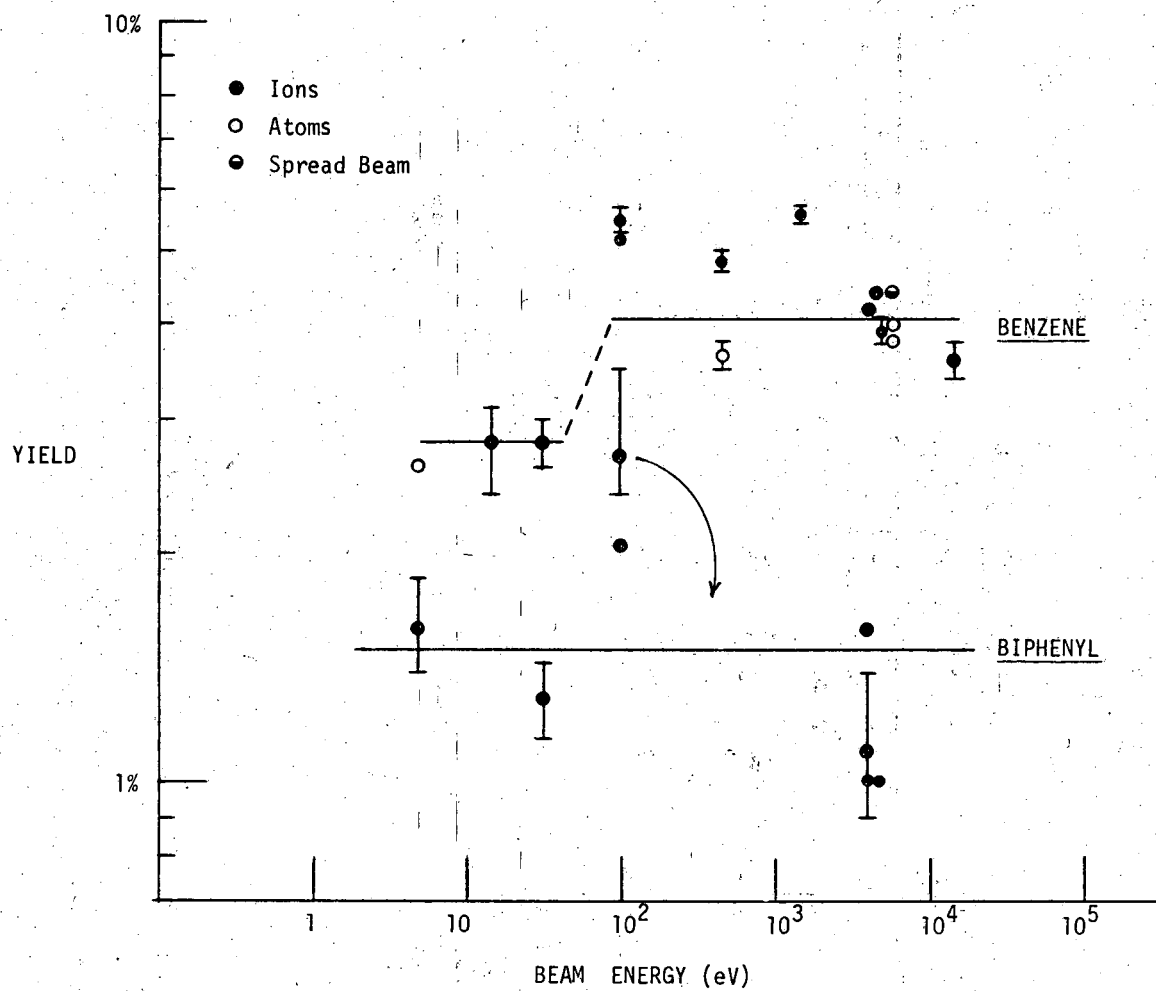
XBL 691-4080

Figure 25. Yield of phenylacetylene versus $^{14}\text{C}^+$ ion beam energy.



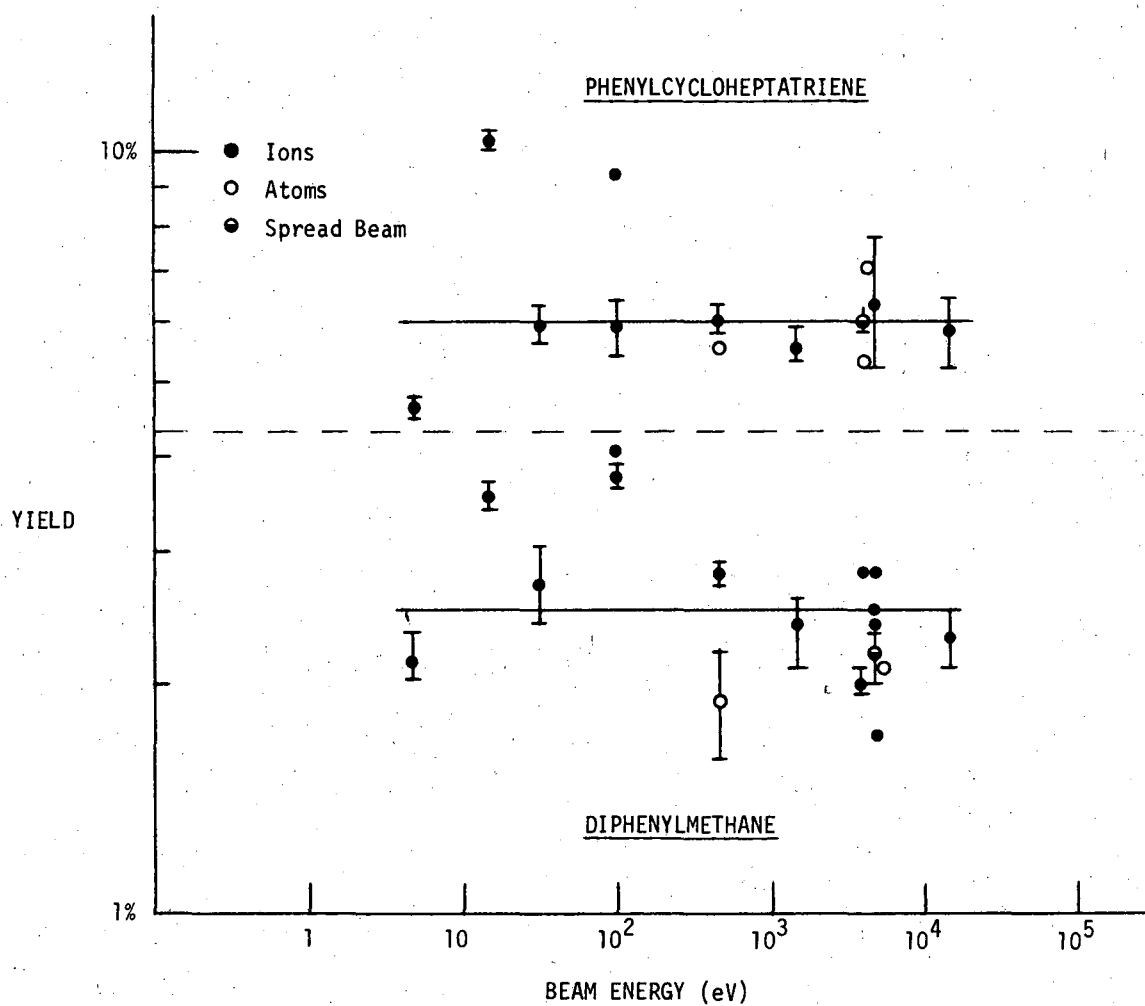
XBL 691-4082

Figure 26. Yield of "U-2" (benzaldehyde) versus $^{14}\text{C}^+$ -ion beam energy.



XBL 691-4081

Figure 27. Yields of benzene and biphenyl versus $^{14}\text{C}^+$ -ion beam energy.



XBL 691-4084

Figure 28. Yields of diphenylmethane and phenylcycloheptatriene versus $^{14}\text{C}^+$ -ion beam energy.

the thermal conductivity detection of the carriers. The glass capillary was changed and possible condensation flushed into the same counting vial after each trapping. Checks with a standard ^{14}C -toluene sample (column injection of $10\ \mu\text{l} = 1.23 \times 10^3\ \text{dpm}$) showed that the total activity trapped in the counting vial agreed within $\pm 5\%$ with that of a directly transferred $10\ \mu\text{l}$ amount. Figures 24-28 show the yield data for the main products.

By the above method it was also possible to get a gross analysis of the sample: not only the identified products were trapped but also whatever emerged between them, and what emerged, for 1 hr, after the last compound (phenylcycloheptatriene). Under the assumption that by then most of the volatile activity had been transported through the column and that the non-volatile products could not leave the beginning of the column, the usually-hollow "injector" tube (between the point of injection and the beginning of the actual GLC column) was filled, prior to injection, with column filling material. This tube was removed, by briefly disconnecting the column, when the last peak (phenylcycloheptatriene) had emerged. Its content was added to a counting vial and vigorously shaken with toluene-scintillator solution. This amount of activity is a good measure of the total amount of polymer formed in the hot-atom chemistry of the fast ^{14}C -ions and atoms. Table VII shows such an activity accounting. Table VIII compares the main groupings of activity for an original and a hydrogenated sample. The lower activity in the injector in the hydrogenated sample indicates a higher degree of stability after hydrogenation (as expected, above).

Table VII

¹⁴C Activity Distribution Observed in glpc Columns

<u>Area trapped from glpc</u>	<u>% of total activity injected</u>
Pre-benzene	0.4
Benzene	3.8
Benzene to toluene	0.8
Toluene	1.8
CHT	4.3
CHT to phenylacetylene	3.2
Phenylacetylene	2.2
Phenylacetylene to U-2	0.6
U-2	2.7
U-2 to biphenyl	8.0
Biphenyl	1.5
Diphenylmethane	2.5
Phenyl-CHT	6.4
Emerging from glpc during succeeding hr (at 250°)	7.0
Remaining in injector filling	<u>37.4</u>
Total:	82.6

Table VIII

Distribution of Radioactivity in
¹⁴C-Bombarded Benzene Target

<u>Activity Found</u>	<u>Percentage of Total Activity Injected on GLC</u>	
	<u>Non-hydrogenated</u>	<u>Hydrogenated</u>
In GLC injector	37	16
In identified compounds	25	30
Between identified compounds	13	23
Emerging during one hour following last identified compound	<u>7</u>	<u>14</u>
Total:	82	83

The above method yields good yield data if the products are separated and the "background" contamination is negligible. If these conditions are not fulfilled the apparent yields will be dependent on the general conditions of the chromatogram. The yield data of Figures 24-28 were accumulated over a long period of time during which not only the used column changed its performance, but also different columns were used (although all of these were CW 20M and in make-up nominally "identical" with one another) and occasionally different programs (upper temperature limits between 200° and 250°). Each entry represents one irradiation. A single dot indicates only one yield determination. Vertical bars indicate the range of "yields" when more than one chromatographic analysis was performed on one and the same irradiation sample (sometimes up to four or five). In general, the variations are large but not larger than between irradiations, so that the trapping method seems commensurate to the long-time reproducibility of the glc column conditions.

In order to avoid over-concentration of entries at 4-5 KV energy, some points are shifted horizontally. In view of the large "vertical" uncertainties, this seemed quite acceptable. The abscissa values (kinetic energy of the carbon ion) are uncorrected, i.e. they are the difference (in eV) between the potential of the arc anode and the liquid nitrogen cooled target. All corrections, however, would decrease the true ion energy: True beam energy (Chapter II, 5), -1 to -2 eV; finite perveance in neutralization of the benzene target (Chapter II, 8), -4 to -7 eV.

The gross analysis shows that in this method we are able to account for ca. 80-85% of the activity in the sample. The difference to 100% is due to experimental errors, volatile compounds (which are lost in this procedure and which may total 5-10%^{12,117}), and incomplete activity recovery (e.g. some activity may be permanently deposited in the column). The activity recovered immediately after irradiation is, within the experimental error of ca. 10%, equivalent to the irradiation-time integral over the beam current.

With only a minority, i.e. 25-30%, of the incorporated activity accounted for in identified compounds, it is impossible to delineate the chemical fate of fast carbon ions in benzene. One can, at best, attempt to set up, investigate, and perhaps substantiate particular mechanisms for these particular identified products.

As attention is being turned to the lower-yield products more sensitive methods for identification and yield determination are required (see T. H. Lin, Ph.D. Thesis, University of California, Berkeley, 1969). More accurate yield-energy data may be required by, or stimulate, more detailed theoretical work.

f) Miscellaneous Irradiations

1) ^{14}C -atom irradiations. $^{14}\text{C}^+$ -ion beams of 500, 1500, and 5000 eV energy were neutralized with approximately 30% yield as described in Chapter II, 4. The remaining ion beam was deflected electrostatically upon a second benzene target. The ion and atom

beam were well defined and the activity incorporated into each of the two targets was in close agreement with the intensity integration. Both samples were analyzed separately. The yield data are entered in Figures 24-28 as "atoms". There is no significant change in comparison with the "ion" yields, supporting the notion that, at least above 500 eV, the reacting species is independent of the initial charge state and is, most likely, atomic carbon.

2) Spread-beam irradiations. In "normal" (high energy) irradiations the ion beam was focused into a ca. 0.4 cm^2 area. In order to investigate whether a "radiation damage" in the sense of Chapter I, 2 exists, the beam flux density at the target was decreased by roughly a factor 10 by over- and underfocusing at the two cylinder lenses. Yield data are entered in Figures 24-28 as "Spread beam". Again, no significant change is observed. However, the spreading factor may not be large enough, and it is possible that the ratio of ions to benzene molecules may have actually been increased at the fringes of benzene deposition, thus canceling the effect of a decreased ratio at the center of deposition (compare Chapter I, 2).

3) $^{14}\text{C}^+$ and $^{12}\text{C}^+$ irradiations. These experiments were discussed in Chapter II, 9 in connection with the "U-2" problem. $^{14}\text{C}^+$ beams were available with ca. 15 μA intensity, $^{12}\text{C}^+$ -beams with the usual 1-2 μA intensity.

4) Irradiations at -156° . The experiments are also discussed in Chapter II, 9 ("U-2" problem).

5) Irradiation of toluene. The main purpose of irradiating toluene was to confirm mechanisms postulated for products from

irradiations of benzene (see below). The CH_2 -insertion products ethylbenzene, xylenes, and methyl cycloheptatrienes were identified in the irradiation of toluene; also styrene and phenylacetylene, as expected from carbon hot-atom chemistry in alkanes and alkenes.

4. Interpretation of the Yield-Energy Data

In this chapter an attempt is made to interpret the yield data of Figures 24-28. In Chapter III, 1d an account was given of the considerations pertaining to the question of the electronic state of the carbon atom or ion in the benzene target. It was concluded that, while at energies above 200 eV the prevailing species is atomic (^3P , ^1D , ^1S) there is an increasing possibility of carbon ions participating and determining the course of reactions at lower energies. In the same chapter it was also pointed out that collisions take place between essentially free atoms if the energy is 20 eV or more.

In Appendix C it is demonstrated that on the basis of classical mechanics of binary collisions even above this energy limit (20 eV), chemical bonds may be formed which are sufficiently long-lived to survive until stabilization occurs through subsequent collisions or

reactions. However, this seems to be limited to small molecules only. In contrast, complex formation with the large target molecule as a whole can succeed only at energies in the order of bond energies. The question as to the validity of the assumption of binary collisions (at very low energies) in such a dense target, and also the question concerning the actual freeness of the assumed fast intermediates CH_2 and C_2 , remain basically open and are valid criticisms.

We confine ourselves, therefore, to the high energy range, >10 eV, where these assumptions are fulfilled probably better than anywhere else. The calculations of the collision functions and yield-energy curves for pick-up products (see Appendix B) very basically hinge on these assumptions.

By what dynamics, or even just how probably a particular pick-up occurs, is very difficult to predict. That the energy of reaction is of importance is intuitively correct: A very exothermic reaction requires efficient energy dissipation away from the newly formed bond. The more positive μA (Appendix D) the smaller the chance for survival. Very large endothermic reactions, on the other hand, which are often excluded from thermal chemistry, may be more important in this hot-atom chemistry because of the large relative kinetic energy available to the colliding molecules. This is only true for large positive or negative values ΔH , because at lower ΔH the energy barrier of the reaction will determine the course of reaction.

At present, a lot of detailed information is coming from crossed-beam work on very specific atomic and ionic systems.³ While they exhibit occasionally some beautiful simplicity of interpretation, it is still very difficult to generalize from there to other chemical systems. McGowan et al.,¹¹⁹ e.g. find that in charge transfer reactions between Ar and N₂ at thermal energies, the endothermic reaction cross section is 20-fold smaller than the exothermic reaction in the same, however, electronically and vibrationally excited, system. It is unknown, however, under which conditions this finding can be generalized, so that possible reaction pathways could be excluded, for instance, on the basis of whether the enthalpy of reaction is positive or negative.

In face of the extreme complexity of our investigated system, we have to, in interpreting our results, make a few clearly defined assumptions (Appendix B) which are justified by a variety of reasons: Similarity with other systems, plausibility, simplicity, mathematical tractability, etc. If the conclusions, drawn from these assumptions, agree with the experimental results, it is taken as stimulus for more clarification rather than as a proof of the assumptions.

Next to the changes of the electronic make-up of the fast carbon ion, the simplest chemical reactions are the pick-up of other atoms, in particular hydrogen to form CH and in subsequent similar steps CH₂, CH₃, etc. Such reactions could well proceed via a "stripping" mechanism.³ Heavier atoms or even molecule fragments may also be "picked-up". However, the heavier the picked-up part becomes, the more questionable becomes the term stripping. Finally, the carbon

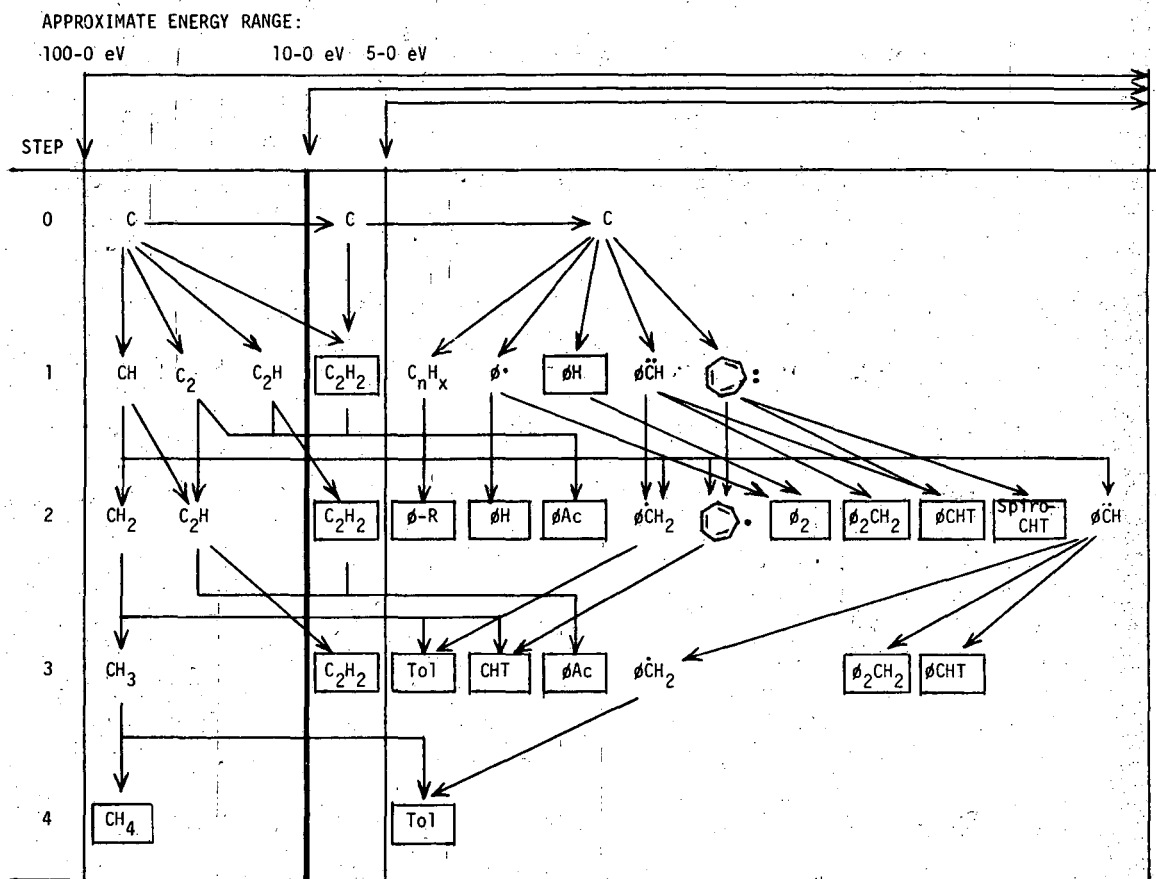
may form an "adduct" with a target molecule, and fragmentation may be incomplete or not occur at all.

Appendix C contains the mathematical details for the classical mechanical derivation that hydrogen atoms may be picked-up by a carbon atom at kinetic energies as high as 50 eV because the amount of internal energy appearing in the CH molecule after formation may be only a small fraction of the kinetic energy. As the mass of the picked-up part increases, this fraction also increases so that the upper energy limit at which such pick-up could occur decreases (C_2 formation). Finally, in the formation of adducts, almost all of the kinetic energy is converted into internal energy.

The sharply decreasing yields of toluene, cycloheptatriene, and phenylacetylene as the kinetic energy of the carbon ion decreases below 100 eV are, therefore, qualitatively interpreted as being due to a decreasing contribution from high-energy pick-up reactions to the final formation of these compounds. In contrast, the essentially constant yields of benzene, biphenyl, diphenylmethane, and phenylcycloheptatriene indicate that these products are formed in low-energy reactions, i.e. via initial formation of relatively stable "adducts", and subsequent rearrangement or further bimolecular reactions. A condensed representation of the possible reaction steps in different energy ranges is given in Figure 29.

a) Toluene and Cycloheptatriene

In agreement with previous postulates (see Chapter III, 2b), we assume that toluene and cycloheptatriene are formed from CH_2 in



SCHEME OF REACTIONS OF FAST CARBON ATOMS

XBL 691-4087

Figure 29. Scheme of reactions of energetic carbon atoms and final-product formation in benzene, for principal energy ranges. "Spiro-CHT" is the spiro[6,6]-1,3,5,8,10,12-tridecahexaene.

a bimolecular reaction with benzene. In Figure 29 are outlined also routes with CH or CH₃ as precursors. These, too, may exhibit qualitatively the observed yield-energy dependence. Quantitatively, however, the dependence should be different, i.e. the decrease should be the steeper the more pick-up steps are involved in the formation of the precursors. This is demonstrated in Appendix B, where under very simplifying assumptions for the collision density K and the reaction probability r in the Dodson-Miller formula for the yield of any product (reaction probability r),

$$y = \int_{E_0}^{\min(E_B, E_1)} r(E) K(E) dE$$

the collision density functions for C, CH, CH₂ and CH₃, and the yield versus energy curves for the final products, cycloheptatriene and toluene, were calculated. A qualitatively correct curve shape was obtained. However, our results are too inaccurate as yet, as that a quantitative analysis could be performed. Assuming for the H pick-up probability an energy dependence of the form

$$r(E) \propto \frac{1}{E^n}$$

one finds that n has to be very small in order to obtain a value for E_{1/2} (the energy at which the yield is 0.5 of the high-energy yield; see Figure 33) as high as observed for toluene and cycloheptatriene. The interpretation of this result is that the pick-up probability is

very nearly energy independent, or, because of the definition of r (Chapter III, 2), that the pick-up reaction cross section varies approximately as $1/E^{1/2}$.

However, there are two points of great uncertainty: 1) At low kinetic energies it is not certain anymore that the carbon ion has been neutralized before it undergoes pick-up reactions. The yield drop could, therefore, just reflect the competition between charge exchange and pick-up reactions--if it is assumed that the carbon ion does not undergo the pick-up reaction. While there is no compelling reason for this or a similar assumption, this point must be borne in mind. 2) In the calculations of Appendix B it was assumed that the collision function K is independent of the initial energy E_B (except that $K = 0$, for $E > E_B$). This is almost certainly wrong. Platzek's¹¹ calculations of K , assuming hard-sphere isotropic scattering in binary collision between atoms of different masses, show that near E_B , K can be much smaller than the value extrapolated from the low energy, asymptotic branch of K . (In Appendix B only this asymptotic solution, which is independent of E_B , had been used.) If K shows a similar behavior in the system under study, some of the apparent yield decrease is due to a decrease of K over the range in which pick-up can occur. (Whether this changes the "half-point" value and thus n is not certain.) This decrease of K with decreasing E_B may, and most certainly does, become effective already where E_B is still well above the upper energy limit of the pick-up reactions. One can, therefore, not conclude that this limit coincides with the energy value at which the yield begins to decrease.

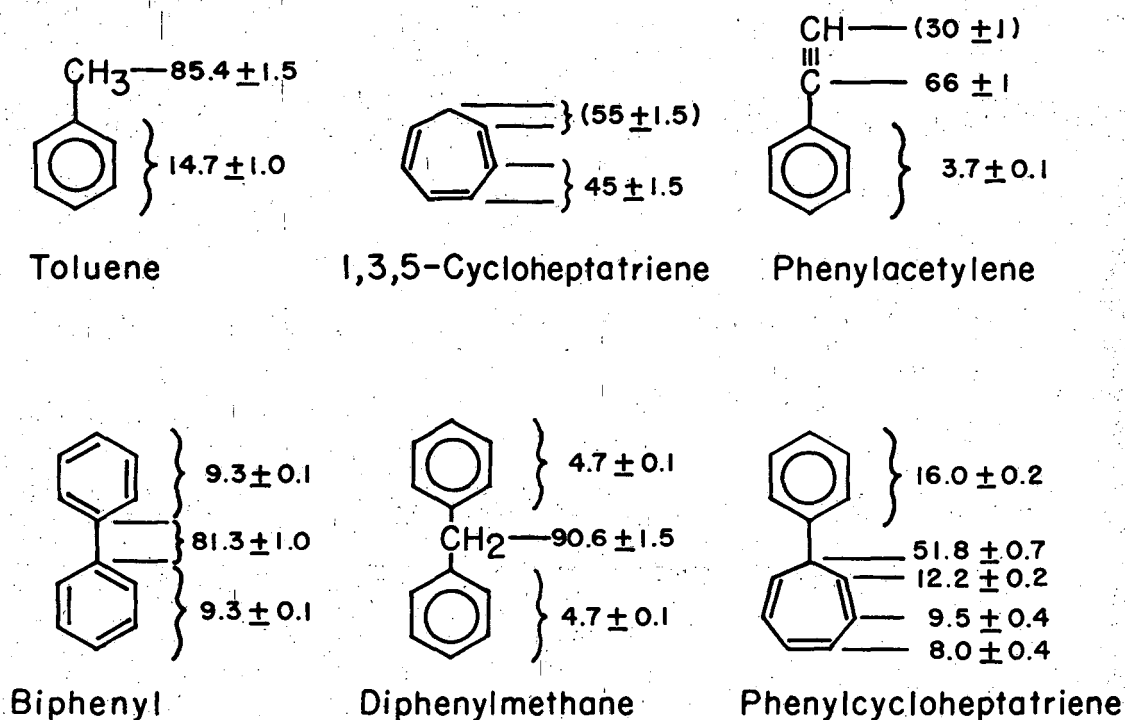
This discussion of the results points out the grave limitations that this experimental method is subjected to. As long as K is not known sufficiently accurately, even a qualitative evaluation of r seems out of the question. It permits only relative measurements and, if the accuracy in the yield versus energy measurement is improved, it may be possible to determine, e.g. whether the same manifold of precursors belongs to toluene and cycloheptatriene. As of now, the data indicate that if there were other precursors besides CH_2 , it would be CH_3 for T, rather than CH for CHT (Appendix B).

It is generally assumed that toluene arises from C-H bond insertion, cycloheptatriene from a C=C bond insertion reaction. Partial degradation results (see Figure 30) support this hypothesis well for toluene (86% labeling of the methyl carbon), not well for cycloheptatriene. However, it has been assumed,⁸ corroborated by many other pertinent observations (see Chapter IV, 4), that the deviations are due to intra-molecular isomerization immediately following the formation (see Figure 31). High energy in the initial collision complex may account for some isomerization to toluene.¹²⁰ A mechanism involving CH is quite analogous, except that the isomerization is interrupted by a hydrogen abstraction.

b) Phenylacetylene

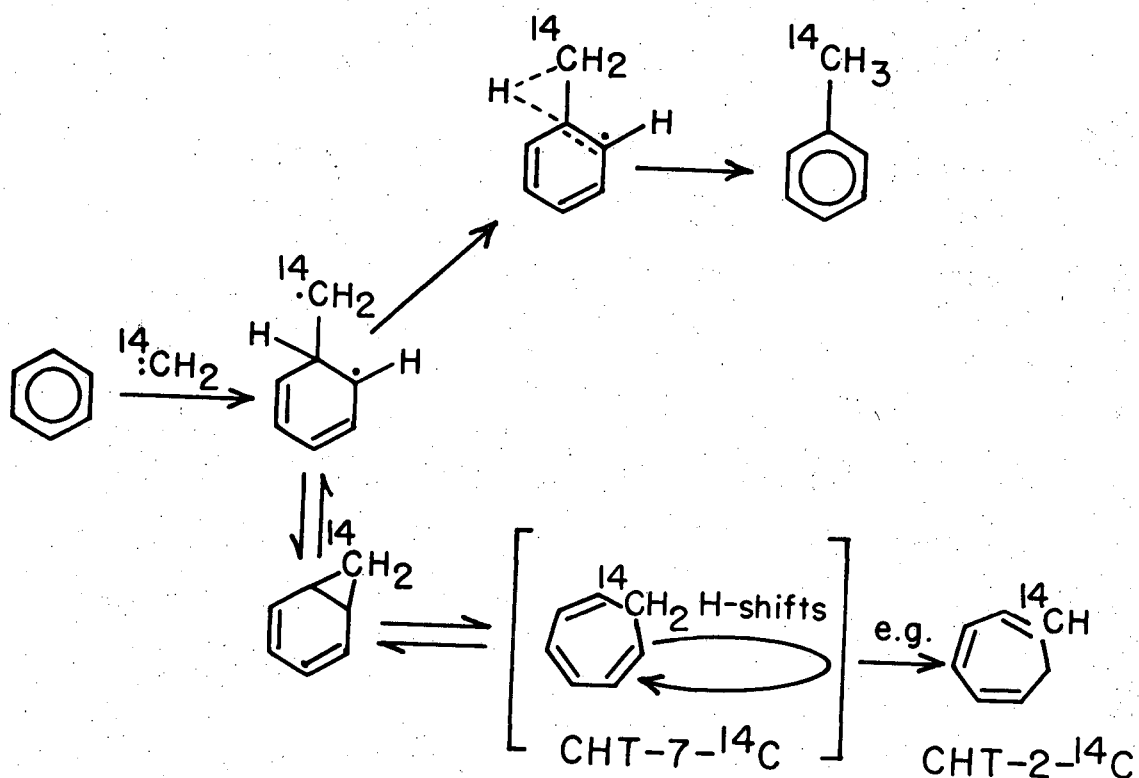
Similar difficulties in interpreting the yield versus energy curve arise for phenylacetylene. Again, it is fairly certain that a high-energy pick-up reaction contributes to the production of

DISTRIBUTION OF ACTIVITY IN MAJOR PRODUCTS FROM BENZENE + 5,000 eV. $^{14}\text{C}^+$ IONS



XBL 69I-4017

Figure 30. Results of partial degradations of the six major products from a 5 KeV $^{14}\text{C}^+$ -ion bombardment of solid benzene (according to Lin¹²⁸ and Pohlit et al.⁸).



XBL 691-4014

Figure 31. Proposed reaction scheme of CH_2 in benzene, isomerization of the intermediates, and final, partially isomerized products (toluene and cycloheptatriene).

phenylacetylene, but it is difficult to ascertain whether this reaction is due to a stripping mechanism, and just how large the upper energy limit for this reaction is. The precursor is very likely a C_2H_x , with $x = 0, 1$, or 2 . Appendix C, Figure 35, points out the similarities from a classical-mechanical point of view between H- and C-pick-up. The partial degradation of phenylacetylene supports this hypothesis, since 96% of the activity is found in the acetylene rest. The extensive scrambling of activity over the α - and β -carbon (ratio 2:1) is interpreted as an indication that some of the C_2H_x -precursors have been a free entity before undergoing the substitution reaction at benzene.

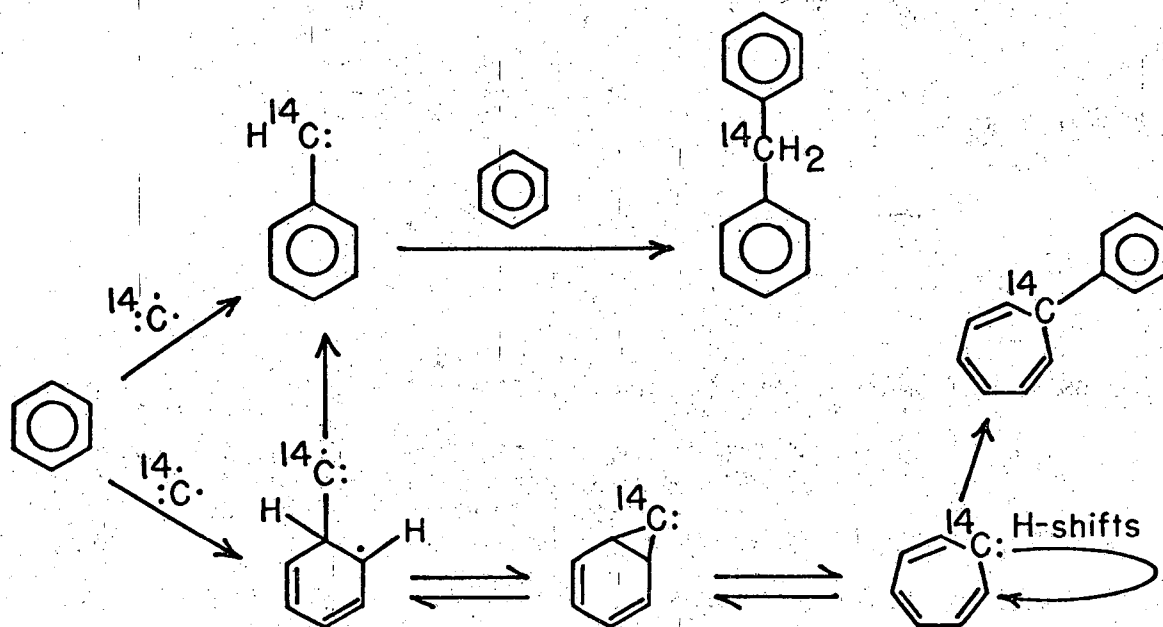
In Appendix B the yield versus energy curve is calculated for phenylacetylene by the same procedure as for toluene and cycloheptatriene. The same reservations, however, apply here also.

The above formation of C_2H_x -fragments may also be a mechanism leading to acetylene, which is usually the most abundant and most frequent product in carbon hot-atom chemistry in hydrocarbons.^{12,104} The yield of acetylene as a function of energy was not determined by us. Rose *et al.*⁹⁹ proposed a low energy mechanism for the formation of acetylene (C-H bond insertion by a carbon atom and subsequent breakage of the neighboring carbon-carbon bond, or, depending on the spin state, rearrangement to the unsaturated adduct). This mechanism was also based on results from double labeling experiments,^{106,121} which showed that in most cases both of the

hydrogens in acetylene originated from the same target molecule. Our high energy mechanism need not be in contradiction to this, since two hydrogens and the carbon may be stripped simultaneously (see Appendix D, $\Delta H = 35$ Kcal/mole for this process).

c) Benzene, Biphenyl, Diphenylmethane, and Phenylcycloheptatriene

From the independence of the yield of these products from the beam energy down to 3 eV, one concludes that in this case precursor and product formation take place below 3 eV. For diphenylmethane and phenylcycloheptatriene, the empirical formula ($C_{13}H_{12}$) suggests that a carbon atom forms an "adduct" with one benzene molecule, possibly with the conformation of carbenes (see Figure 32) which finally undergo another "insertion" reaction with a second benzene molecule. Partial degradation results (see Figure 30) make a benzyldiene the most likely precursor for diphenylmethane, while both benzyldiene and cycloheptatrienyldiene may contribute to the formation of phenylcycloheptatriene. It is interesting to note a similarly high degree of label isomerization in the cycloheptatriene part of phenylcycloheptatriene, as in cycloheptatriene itself (see Chapter IV, 3, 4). The deviations from the expected labeling pattern (100% in the α -carbon of diphenylmethane, 100% in the 7-carbon of phenylcycloheptatriene) are therefore, again assumed⁸ to be due to intramolecular isomerization (via hydrogen shifts) of the carbene cycloheptatrienyldiene.



XBL 69I-4015

Figure 32. Proposed reaction scheme of carbon atoms in benzene, isomerization of intermediates, and formation of the stable, partially isomerized end products.

No reasonable mechanism has been advanced as yet for the formation of benzene and biphenyl. From the present data one can conclude only that only low-energy reactions can account for their formation, putting an end to speculation about a possible high-energy "billiard-ball" type of replacement reaction (see Chapter III, 2). One has to expect that atomic carbon is at least as reactive as $\text{CH}_2\cdot$, which is known to react readily with benzene even after thermalization. With just enough energy, so that the initial adduct formation between carbon and benzene is reversible, but not too much energy, so that this adduct is sufficiently long-lived to undergo intramolecular rearrangement--this is most likely the mechanism leading to benzene. If in the adduct dissociation a ^{12}CH is ejected, the product is a ^{14}C -phenyl radical which might form biphenyl upon a second reaction step with benzene. This mechanism appeals mainly because it generalizes the reaction mechanism postulated for diphenylmethane and phenylcycloheptatriene (see Figure 32). The label distribution in biphenyl indicates the degree of isomerization before the presumed phenyl radical formation, and possibly also after it until it is trapped by another benzene molecule.

IV. DEGRADATION OF 1,3,5-CYCLOHEPTATRIENE-¹⁴C

1. Introduction

As part of the degradative investigations of the products, a partial degradation of 1,3,5-cycloheptatriene was carried out. A complete degradation was attempted; however, a practicable scheme could not be established.

Cycloheptatriene (CHT) was first prepared by R. Willstätter (1898).¹²² and first found as product of the hot-atom chemistry of ¹⁴C in benzene by Mullen and Lemmon in this laboratory, in 1960.^{14,123} The chemistry of CHT was reviewed last by F. Santavy¹²⁴ in 1953.

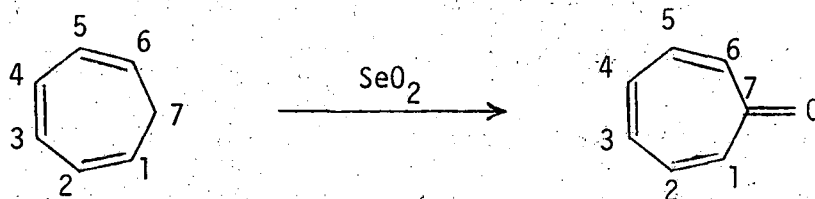
To our knowledge only one (partial) degradation of CHT has been performed previously.¹²⁵ A complete degradation, therefore, required the testing of a number of possible procedures. The following summarizes this.

The same reasons that make CHT an interesting object of studies of molecular dynamics make it also difficult to handle chemically: the general lability of conjugated trienes, the ease of formation of the symmetric tropylium ion, the ease of intramolecular hydrogen shifts, and the tendency to react in different tautomeric forms toward different reactants (particularly as norcaradiene).

To achieve the degradation of CHT requires, therefore, not only the establishment of the optimum conditions for a degradation procedure and its application to a radioactive sample, but also the elucidation of the mechanisms involved in the degradation

reactions. Relatively little is known of the basic chemistry of the unsubstituted CHT, and less of the mechanisms.

An example for this situation is its SeO_2 -oxidation product, tropone. As is well known, SeO_2 oxidizes the methylene vicinal to a double bond or phenyl ring.¹²⁶ One would, therefore, expect in the case of CHT that the correspondence between carbons in reactants and products are as indicated:



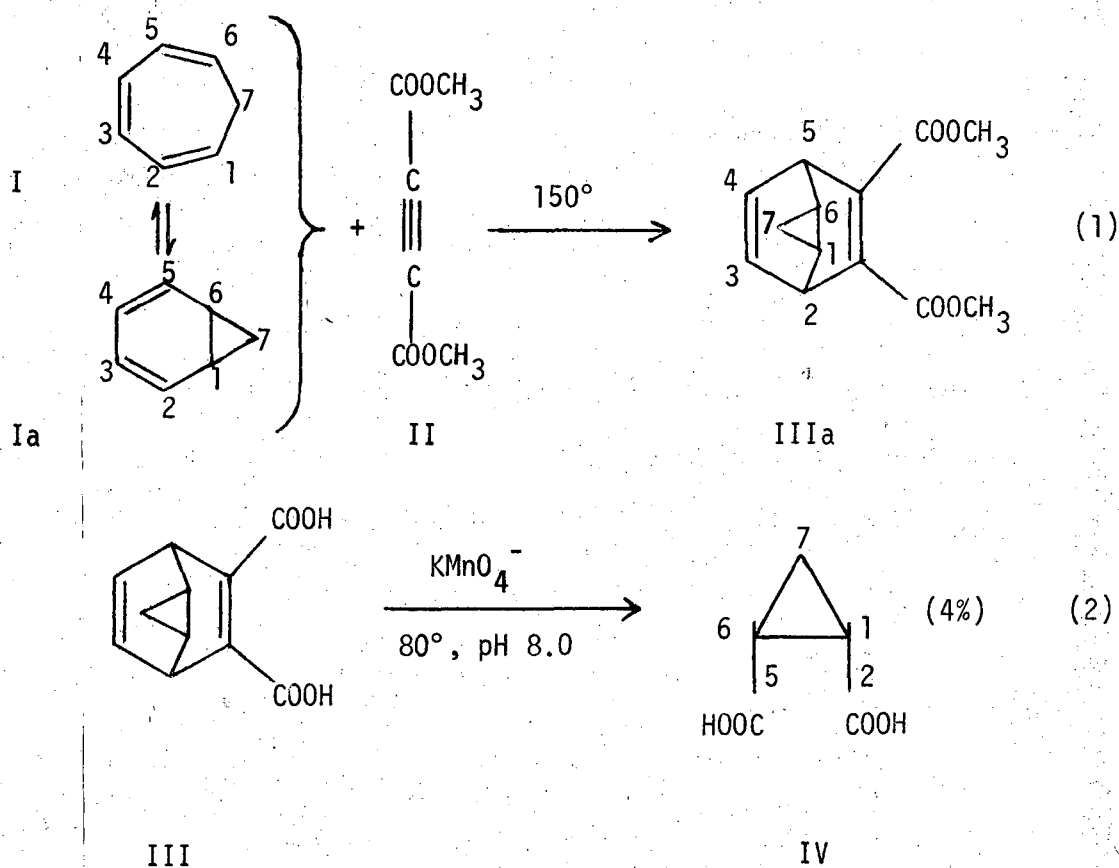
However (as described later), it turns out that all carbons are randomized prior to the formation of propone; thus, this possible degradation route had to be abandoned.

Besides mechanistic uniqueness, a degradation scheme must also keep some balance between the information which it eventually provides and the time and labor involved in its realization. Some procedures were eventually abandoned, or new proposals dismissed, because of this latter point.

2. Degradation Attempts

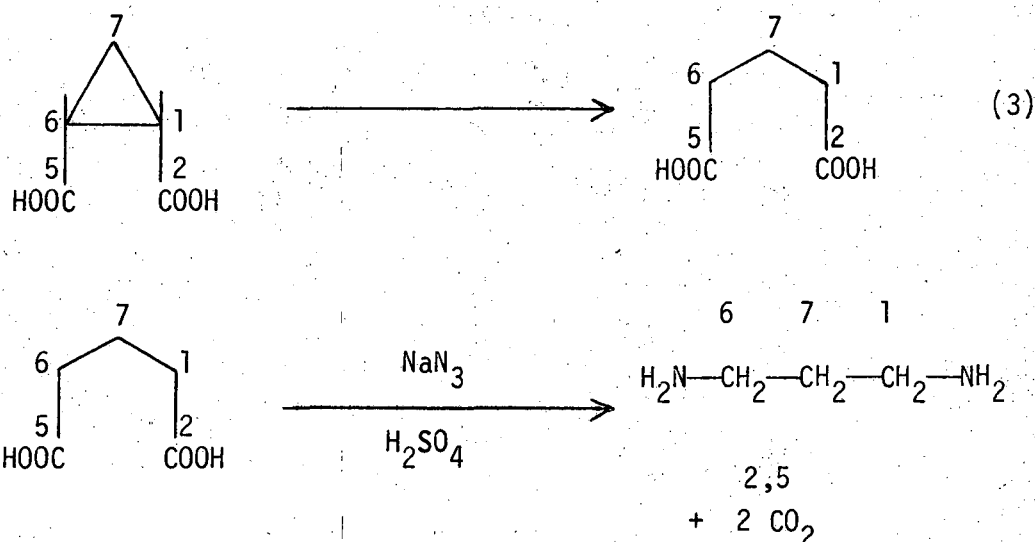
a) Degradation via the Diels-Alder Adduct with Dimethyl Acetylenedicarboxylate

The first and only previous attempt to degrade cycloheptatriene was made by Juppe and Wolf,¹²⁵ in 1961, who utilized the following scheme:¹²⁷

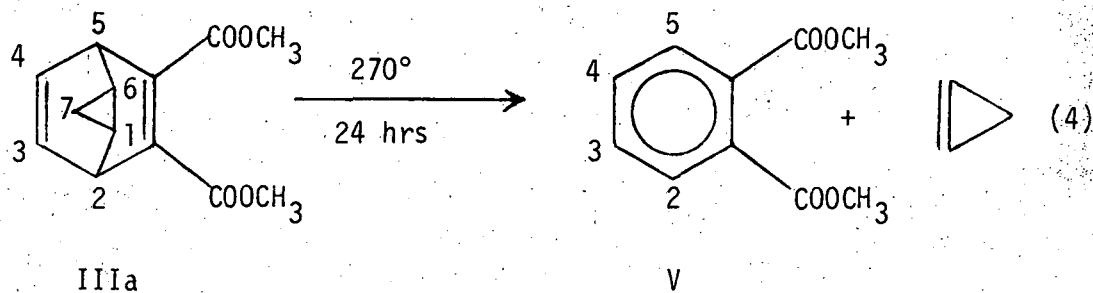


This partial degradation was sufficient for the solution of their problem, as they needed to decide only between randomized and specific labeling. Although Alder and Jacobs¹²⁷ report yields of 56% of IV by reaction (2), Juppe and Wolf (and we also)

obtained only 4%. This was felt to be prohibitively low for a continuation of the degradation, since the overall yield of IV is only 2%, and the chemistry of IV is not known very well. In addition, even a possible ring opening (3), followed by a Schmidt-degradation, would have led to the same problems of handling, counting, and further degrading of the propane diamine, as described elsewhere.¹²⁸



A much more convenient partial degradation was achieved by utilizing the thermal decomposition of IIIa to V:¹²⁷



Yields for V, including purification, were approximately 80%.

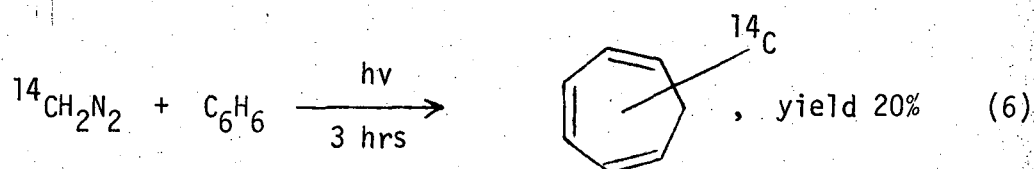
In order to test the validity of this degradation scheme, the following points had to be considered: i) isomerization of CHT (I) before it undergoes the Diels-Alder reaction (1),¹²⁹ ii) isomerization of CHT during (1) so that the correspondence of positions between I and IIIa is blurred, iii) IIIa is the only source for V, and iv) carbon skeleton correspondence between V and IIIa.

By choosing most favorable experimental conditions (e.g., up to 5-fold excess of II in (1), and no solvent, in order to decrease the residence time of CHT at the reaction temperature level, 150°), it was possible to establish that the above points are of no, or only minor, importance.

In order to show this, cycloheptatriene-7-¹⁴C was synthesized by a rather new method:^{130,131}



which was found to be far superior to the photolytic method:¹²²



both in yield as well as specificity. Doering et al.¹³² and Roth¹³³ observed that in the photolysis of CD_2N_2 in benzene the product CHT was extensively labeled in the 1 and 6 positions, apparently due to 1,2-hydrogen (deuterium) shifts. However, cycloheptatriene- d_2 according to (6) appeared specifically 7-labeled.¹³⁴

When glc purified cycloheptatriene- ^{14}C , prepared according to (5), was subjected to the degradation procedure (1) and (4), 2.5% of the molar specific activity of I and IIIa were found in V. This small label isomerization is believed to have occurred during synthesis (5), since a doubly purified sample of the same batch of cycloheptatriene revealed only 3% activity in V (see Table IX), rather than the 5%, expected if the isomerization had been caused by excessive heating or other processes in the gas chromatograph. That thermal isomerization during the Diels-Alder reaction also could not account for the 2.5% labeling was shown by subjecting cycloheptatriene- ^{14}C to the conditions of this reaction (150° , 6 hrs), without the presence of the dienophile II, before degrading it as above. (The possibility that the dienophile catalyzed the isomerization is not excluded, of course.) The labeling in V was now 3.9%. Assuming a first order decrease of I, because of the large excess of II, and ca. 94% completion, i.e. 4 half-lives for I, in 6 hrs, the average lifetime of a cycloheptatriene molecule in the reaction mixture (I) is

$$\tau = \frac{1}{6} \int_0^6 t e^{-kt} dt = \frac{1}{6k^2} [1 - e^{-6k}(6k+1)] ,$$

Table IX

Sample	Specific Activity x 10 ⁻⁸ mole/dpm ³⁾		
	CHT I	Adduct IIIa or IX	Phthalate V
A) Synthesis (catalytic)	11.6 ¹⁾	11.6	.294 .292
	=100%	=100%	=2.5%
B) ¹⁴ C-CHT(A) after 8 hrs at 150°	11.6	11.5	.457 .449
	=100%	=100%	=3.9%
C) Re-chromatography of 2 samples of ¹⁴ C-CHT recovered from a reaction mixture (tropone for- mation) in order to check on isomerization during this reaction	11.6 11.6	-- ²⁾ -- ²⁾	.331 .347
	=100%		=2.85% =2.99%
D) ¹⁴ C-CHT from irradiation #5, Inj. 220°, Col. 75°, Det. 250°	1.61 1.61 1.60	1.52 1.54	.732 .742
	=105%	=100%	=48.3% ⁴⁾
E) 7- ¹⁴ C-CHT, re-chromatographed: Col. 75°, Inj. 250°, Det. 250°	11.6	-- ²⁾	2.34 2.24
	=100%		=20%
F) Re-chromatography of a sample of 97.5% labeled 7- ¹⁴ C-CHT: Inj. 150°, Det. 150°, Col. 75°	11.6%	-- ²⁾	.290
	=100%		=2.5%

Table IX (continued)

Sample	Specific Activity x 10 ⁻⁸ mole/dpm ³⁾		
	CHT I	Adduct IIIa or IX	Phthalate V
G) ¹⁴ C-CHT from irradiation #16:	-- ²⁾	2.52	1.09
Inf. 150°, Det. 150°,		2.39	1.12
Col. 75°		2.39	
		2.52	
	-- ²⁾	=100%	=45.0%

1) Average of ca. 10 determinations

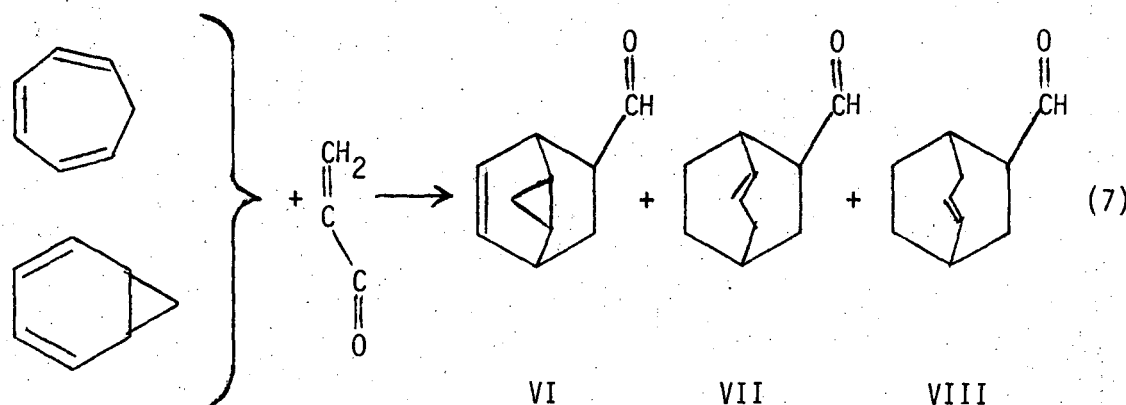
2) Not determined

3) The accuracy of the values listed in this table is placed through experience at $\pm 2\%$ or less.

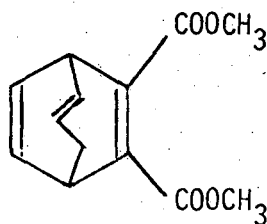
4) The difference of about 3% between this value and the corresponding from G) is, within the limits of experimental error, due to the same progress in isomerization of CHT, measured in units of k , t , as that of E).¹²⁹ The corrected value of D) and that of G) are therefore equal within the experimental error limits.

where $0.06 = e^{-k \cdot 6}$, i.e. $k = 0.462$, so that $\tau = 0.613$ hrs, i.e. approximately one tenth of the total reaction time. The increase of labeling in V should, therefore, be only ca. 0.15% (1/10 of 3.9 - 2.5%). Thus, the 2.5% label isomerization cannot have occurred during reaction (1).

1) Isomers of IIIa. Alder and Jacobs¹²⁷ believed that cycloheptatriene undergoes reaction (1) predominantly in its tautomeric norcaradiene form, Ia. There is no mention of any adduct isomers. However, a more careful glc analysis of a similar reaction mixture (7) by Milvitzkaya and Plate¹³⁵



yielded the adducts VII and VIII besides the expected VI. The same was found by us the reaction (1). Besides adduct IIIa there appeared an adduct, probably with the structure (IX):



IX

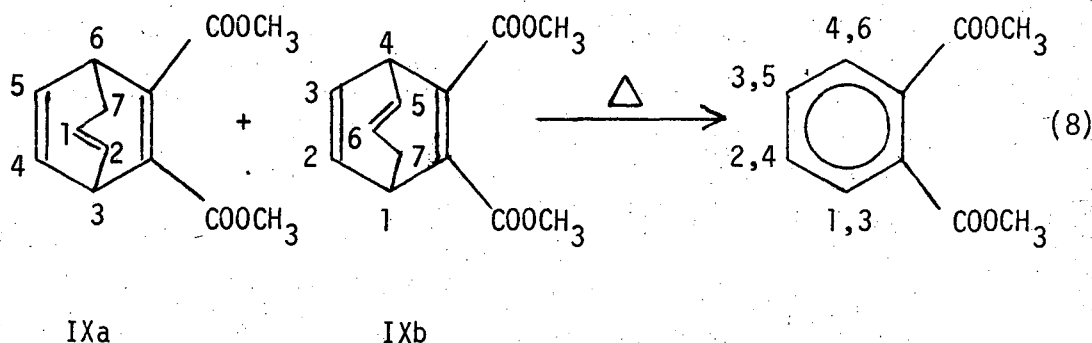
The yields were approximately 50% (IIIa) and 30% (IX). Attempts to separate the isomers by vacuum distillation failed. Thin layer chromatography (2.50 μ silica gel, petroleum ether:ethyl ether (3:1), development in I_2 vapor) was successful and opened the way for large scale separation by column chromatography. However, for small amounts, glc gave two well separated peaks. Identical micro-analyses and specific activities, when prepared from cycloheptatriene- ^{14}C , proved the isomery of the two peaks. (In fact, IX was later used to determine the specific activity of the adduct, while IIIa was used for further degradation.) The first emerging peak could easily be identified as IIIa due to its characteristic cyclopropyl absorption in nmr; this was absent in the second emerging peak.

The UV spectrum of each of the peaks exhibits a single band at 2450 Å with $\epsilon \approx 4 \times 10^3$ (mole/l) $^{-1} \cdot \text{cm}^{-1}$. Using Woodward's rules for unsaturated carboxylic acids, one calculates $217 + 2 \times 10$ (α, β -ring substituent) + 6 (carbomethoxy substituent) = 243 nm, in very good agreement with the experiment. The similarity of the two absorption spectra corroborates structure IX for the compound of the second peak.

IX seems to be thermally about as unstable as IIIa. However, it does not decompose to dimethylphthalate. This finding is in line with the general rule on the decomposition of 3,6-bridged-1,4-cyclohexadienes: Bridges consisting of an even number decompose as a reversed Diels-Alder addition; bridges with an odd

number decompose with difficulty and via different routes.¹³⁶ The cyclopropane bridge in IIIa is regarded as a substituted 2 carbon bridge.

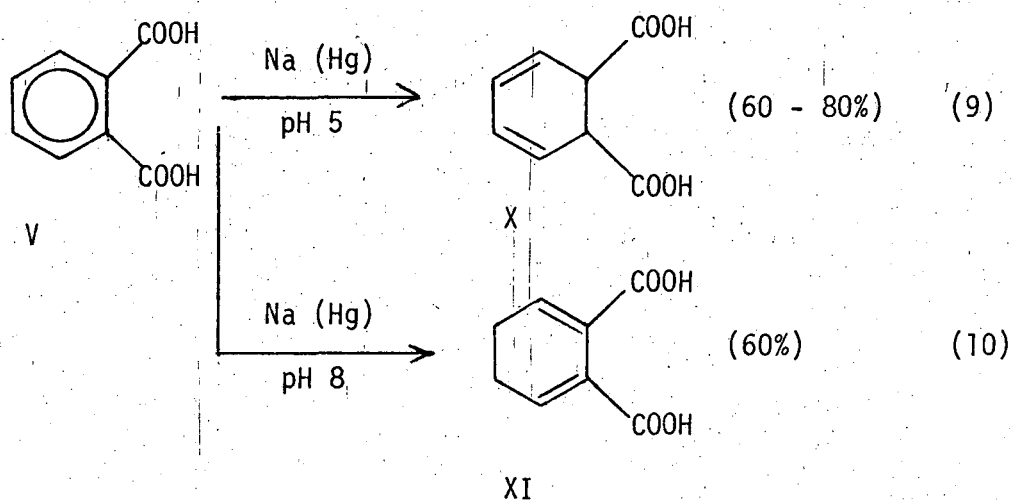
The second product of reaction (4), cyclopropene, is formed in only 1% yield.¹³⁷ This, together with the difficult chemistry of this compound, makes this product impractical for further degradation. It was hoped for some time that if adduct isomer IX also decomposes to dimethylphthalate, a further step in degradation could be achieved:



However, the mixing of non-equivalent positions, first due to the two optical isomers IXa and IXb, is continued in the resultant dimethylphthalate due to its symmetry. The gain in information would have been only small even if reaction (8) had worked.

Dimethylphthalate, according to (4), contains carbons 2 and 3, and their position equivalents 4 and 5, and it was hoped that the degradation could be extended to these positions of cycloheptatriene by degrading this phthalic acid.

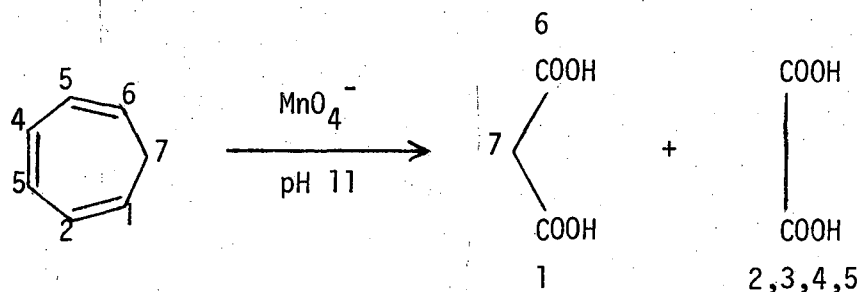
Phthalic acid was reduced according to Bayer:¹³⁸



Oxidation by $\text{MnO}_4^-/\text{IO}_4^-$ ¹³⁹ of X yielded about 60% oxalic acid while no succinic acid was obtained from XI. The overall yield in oxalic acid is approximately 8%. While, theoretically, oxalic acid from X would have yielded the activity of carbons 3 and 4, and thus by difference from V also that of 2 and 5, there were several factors militating against relying on this degradation scheme: i) the inherent ease of isomerization of X ¹³⁸ to isomers which could yield oxalic acid, stemming, however, from other carbons than 3 and 4; ii) the inability to measure the amount of isomeric impurities in X (column and gas-chromatography failed, e.g. to separate X and XI sufficiently well); iii) the possibility of isomerization during oxidation (see below) with the same effect as i); and iv) the many tedious procedures involved in obtaining the specific activity in this one position, coupled with the many sources of errors. This procedure was, therefore, abandoned in hope of a more direct degradation.

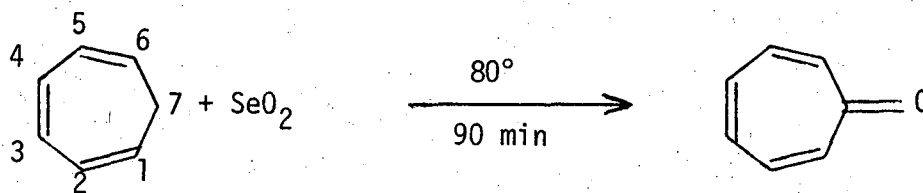
b) Oxidative Degradations of Cycloheptatriene

1) Permanganate oxidation. The oxidation products in alkaline permanganate should be malonic and oxalic acid according to:

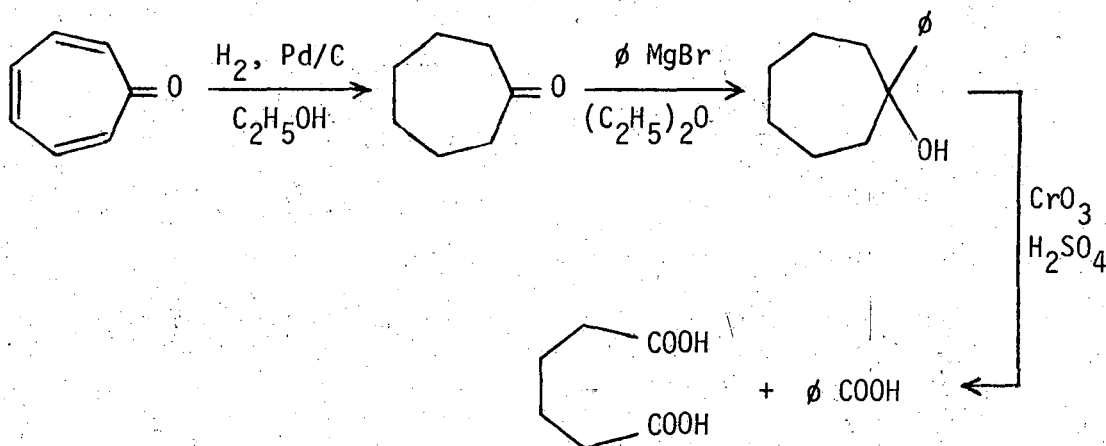


with the carbon correspondence as indicated. However, in this two-phase reaction, at most, 4% malonic acid and 18% oxalic acid were obtained. The yields varied considerably, and because of the likelihood of randomization via tropylium ion formation, this route was not further investigated.

2) SeO_2 oxidation. Tropone was obtained in ca. 40% yield by oxidizing CHT with SeO_2 in dioxane:



Degradation of tropone from 7- ^{14}C -cycloheptatriene according to the following scheme resulted in 6/7 label in the adipic acid, 1/7 in benzoic acid. The interpretation is that in the oxidation step or prior to it, randomization (probably via tropylium ion



formation) occurs. This degradation scheme was therefore not usable.

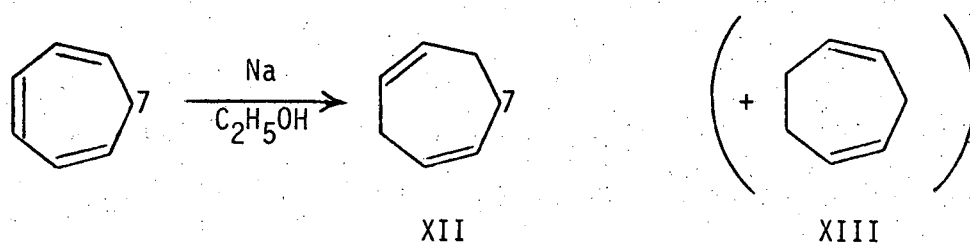
3) Ozonolysis. Ozonolysis was attempted at -80° ($\text{CO}_2/\text{acetone}$) in ethylacetate. The uptake of O_3 was uniform in time; and quantitative, and partial ozonolysis was therefore also attempted. However, in all cases, the yield in malonic acid or maleic acid after work-up with $\text{H}_2\text{O}_2^{140}$ was less than 5%. There always seemed to be a 3-5% yield in cyclopropane dicarboxylic acid, indicating that some of the cycloheptatriene reacted as norcaradiene.

c) Reductive Degradation of Cycloheptatriene

1) Partial hydrogenation. Partial hydrogenation of CHT was attempted in n-pentane over Pd/C. However, only very little 1,3-diene and no 1,4-diene was found. After 17 hrs the major product was cycloheptane. Apparently, catalytic hydrogenation proceeds, once started, rapidly to the cycloheptene--which is of no use for the degradation.

2) Reduction with Na. Reduction with metallic Na in C_2H_5OH (or 1:1 methanol/acetic acid) at -5° yielded ca. 30% cycloheptadiene-1,4 and 25% cycloheptene. No 1,3-diene was observed. It was very difficult to achieve completion of the reaction.

According to established mechanisms,¹⁴¹ the 1,4-diene is the asymmetric isomer XII with respect to the isotopic 7-position:



Even if this 1,4-diene is produced without admixtures from the symmetric 1,4-diene, XIII, a subsequent oxidative degradation of this diene "mixes" non-equivalent positions of the original ^{14}C -CHT. This makes this procedure very unappealing--not to speak of the definite possibility of isomerization during the oxidative degradation of XII.

Reduction of CHT with Na in liquid ammonia and excess ethanol produced only cycloheptene, which is almost certainly a mixture of isotope-isomers.¹⁴²

3. Partial Degradations of ^{14}C -Cycloheptatriene from 5 KeV Irradiations. Experimental Procedures and Results

The following are experimental procedures pertaining to the partial degradation of ^{14}C -CHT according to (1) and (4), and the checking procedures on the validity of this degradation.

1) Nitroso-methyl- ^{14}C -urea (NMU). 7.81 mg methylamine- $^{14}\text{C}\cdot\text{HCl}$ in 1.23 ml of 50% ethanol (0.50 millicuries) was added to a solution of 67 g $\text{CH}_3\text{NH}_2\cdot\text{HCl}$ and 200 g urea in 275 g H_2O . The mixture was refluxed for 3 hrs. After the solution was cooled we added 70 g NaNO_2 and cooled the solution to -7° . This solution was then added slowly, with stirring, to 400 g ice and 67 g H_2SO_4 . The resultant crystals were filtered with suction, and washed with a little water. After 2 days drying in vacuum over NaOH , 76 g of crystals were obtained. They contained 53% of the total activity. Specific activity (6.6 mg substance was dissolved in "Dioxane" scintillator solution): 10.78×10^8 dpm/mole.

2) Generation of $^{14}\text{CH}_2\text{N}_2$ and preparation of CHT-7- ^{14}C . 21 g NMU was added slowly to 50 ml 50% KOH below ca. 250 ml benzene. The solution of $^{14}\text{CH}_2\text{N}_2$ in benzene was then added very slowly to a boiling suspension of CuBr in 100 ml benzene. The CHT- ^{14}C was isolated using the Prepmaster glc (CW-20 M, 12', 3/4", 300 ml/min He). Yield: 3.8 ml, ca. 18% based on NMU.

3) General procedure for Diels-Alder reaction. CHT and dimethyl acetylenedicarboxylate were mixed, in a ratio of at least 1:3, and heated in a sealed tube at 150° for 6 hrs. The

adduct was isolated by trapping it from glc on 3', 1/4", SE-30 at 150° and 50 ml/min He flow.

4) Decomposition of IIIa to V. Enough of the Diels-Alder reaction mixture is injected on glc (as above) to trap 3-5 mg of the adduct, in a capillary, at room temperature. The capillary is sealed and heated at 270° for 24 hrs. The contents are dissolved in benzene and injected into the same glc column, and the formed IV (1-3 mg) trapped for weighing and counting.

5) General procedure in determining specific activities. The radioactive compounds are trapped as they emerge from glc, CHT in a glass capillary U-trap at -196°, IIIa and IX in a straight glass capillary at room temperature. In all cases, the length of the capillary is then reduced to close to the part containing the liquid. The capillary plus contents are weighed on the micro-balance and the contents flushed with counting solution directly into a counting vial. After it is cleaned and dried, the capillary is re-weighed, the difference taken as the weight of the sample. The weight of the capillary is in the order of 50-150 mg, samples in the order of 1-5 mg. This procedure was tested on various substances and it proved to be both accurate and very practical.¹⁵³

6) Degradation of CHT-¹⁴C from irradiation #5 (5 KeV). CHT-¹⁴C was isolated in 7 runs on glc (CW-20 M, 10', 1/4", 75°, 40 ml/min). Enough carrier CHT had been added to the irradiation sample so that each capillary trap contained ca. 2-3 mg CHT-¹⁴C. The contents of the traps were dissolved in ca. 1 ml n-pentane and

ca. 100 mg unlabeled, purified CHT was added. Aliquots of this solution were injected on the same glc column and the specific activity of the trapped CHT- ^{14}C was determined. The bulk of CHT- ^{14}C was purified on the Prepmaster glc (CW-20 M, 12', 3/4", 300 ml/min, 80°) and the trapped material added to ca. 500 μl dimethylacetylene dicarboxylate, followed by general procedures. The total activity in the sample was approximately 73 $\text{m}\mu\text{C}$.

7) Degradation of CHT- ^{14}C from irradiation #16 (5 KeV).

The same isolation procedure was employed (injector and detector being at 150°). However, the CHT- ^{14}C was not dissolved in n-pentane but directly added to 500 μl dimethylacetylene dicarboxylate; 100 mg unlabeled CHT were also added. The total activity was 118 $\text{m}\mu\text{C}$.

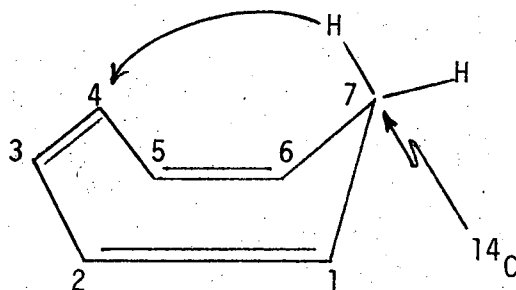
8) Micro-analysis of IIIa and IX.

	Calculated (%)	Found (%)	
	for $\text{C}_{13}\text{H}_{14}\text{O}_4$	IIIa	IX
C:	66.7	66.74	66.50
H:	5.98	5.77	6.22

4. Interpretation

A comparison with the other partial degradation data (Figure 32) shows that CHT exhibits probably the largest deviation from the labeling pattern that one would expect from the postulated mechanisms (Chapter III, 4a). The question arises as to what justifications there are to maintain the CH_2 -insertion mechanism in face of this discrepancy. However, there are several points which corroborate this hypothesis: i) CHT is known to be very prone to isomerize via intramolecular hydrogen shifts (whose effect in this case would be the isomerization of the ^{14}C -position in the molecule). ii) CHT- d_2 , produced from the photolysis of CD_2N_2 in benzene, shows a large departure from specificity (7,7- d_2 -CHT). iii) The similarity of the yield-vs-energy curve (Figure 24) with that of toluene, and its steep fall-off towards lower energy--which was interpreted to indicate the formation of the precursors CH and CH_2 .

TerBorg et al.¹²⁹ determined the energy (31.5 Kcal/mole) and entropy ($\log A = 10.9 - 11.5$) of activation for a transannular hydrogen shift (σ -tropic rearrangement of order [1,5]). This mode of isomerization would shift label predominantly into the part of the ring opposite to C-7, i.e. where we, indeed, found a large amount of activity:



Klump et al.¹⁴³ and Egger¹⁴⁴ (the latter for a methyl derivative) determined energy (51.1 Kcal/mole) and entropy ($\log A = 13.5$) of activation for the rearrangement to the corresponding benzene derivatives.

Berson et al.¹⁴⁵ found another thermal mode of skeleton rearrangement which seems to have an energy of activation between the two previous ones. It seems to involve the random opening and closing of the cyclopropane ring in norcaradiene (Ia).

Doering¹³² and Roth¹³³ observed that CHT-7-d underwent 1,2-hydrogen shifts under photolytic conditions. Srinivasan¹⁴⁶ observed toluene under the same conditions.

Doering¹³² observed that the (mild) photolysis of CD_2N_2 in benzene produced CHT with isomerized label (1,2-hydrogen shift). Lemmon et al.,¹⁴⁷ however, determined under the same conditions that $^{14}CH_2N_2$ produced (besides CHT) toluene- ^{14}C with more than 99.6% label in the methyl carbon. These two data parallel rather nicely our partial degradation results from CHT and toluene.

It is, of course, not possible to tell from our data exactly which mechanism applies in our system. Only when complete degradation has been achieved and when the label distribution has been determined also as a function of the beam energy, can more definite conclusions be drawn.

However, this much can be said now: Since the CH_2 molecule is likely to have a rather high kinetic energy, and since the benzene molecule is at a very low temperature (a situation similar to the photolysis of CH_2N_2 in benzene) the mode of isomerization will

be determined by the initial-bond formation mechanism. The initial collision complex will be far from thermal equilibrium of its degrees of freedom (an assumption which is much more correct for the above thermal isomerization mechanisms). Most of the internal energy is stored in the initial bond and will migrate into other degrees of freedom according to the dynamics of the initial collision complex--until (random) collisions with other target molecules not only remove kinetic and internal energy from this complex ("stabilization") but also introduce energy, via this secondary collision mechanism, into other degrees of freedom of the product molecule. Depending on the total incorporated initial energy and on the efficiency of energy diffusion, the number of collisions to sufficiently deactivate the complex may be large (larger than one, as usually assumed in thermal excitation). Therefore, at later stages of the deactivation collision sequence, modes of isomerization may be operative which are also observed in thermal systems. An indication for the rather high energy involved in the production of CHT can be seen in the appearance of a sizable ring labeling of toluene, 14%, compared with 0.4% in photolysis.¹⁴⁷ This isomerization is discussed in more detail in T. H. Lin's Ph.D. Thesis, University of California, Berkeley, 1969, and by Pohlitz et al.⁸

Other possible mechanisms are, for instance: Insertion of a CH molecule into the benzene ring, followed by a hydrogen abstraction by the CHT radical. This radical should, indeed, isomerize the

label very quickly. A CH precursor is compatible with the observed yield-energy curve, but it is not indicated by the analysis in Appendix B (see Chapter III, 4a).

Formation of CHT from a tropylium ion is--at least as the only mechanism--excluded because this mechanism should randomize the label completely, i.e. the label distribution should be 57.2%: 42.8%, rather than $45\% \pm 1 : 55\%$, as we found.

APPENDIX A

Sources for Fast Carbon Particles

The following table lists sources and atomic parameters for fast carbon particles:^{12,104}

Species	Source	Energy	Primary electronic state
Any isotope	Accelerator	≈ 1 eV to $\approx \text{MeV}$	C^+
^{14}C	$^{14}\text{N} (n,p) ^{14}\text{C}$	45 KeV	$^{14}\text{C}^-$
^{11}C	$^{14}\text{N} (p,\alpha) ^{11}\text{C}$	>1 MeV	$^{11}\text{C}^-$
	$^{12}\text{C} (\gamma,n) ^{11}\text{C}$	>500 KeV	^{11}C
	$^{12}\text{C} (n,2n) ^{11}\text{C}$	1.1 MeV	^{11}C
	^{12}C neutron stripping	≈ 100 MeV	^{11}C
	$^{12}\text{C} (p,pn) ^{11}\text{C}$	>1 MeV	^{11}C

APPENDIX B

Derivation of Collision Functions and Yield-Energy Curves

Table of Contents

	<u>Page</u>
Introduction	171
Glossary of Symbols	172
Assumptions	173
Derivation of Collision Functions	174
K_0	174
K_1	174
K_2	177
K_v	178
K_1 for first step products and inter- mediates (CH, C_2)	178
K_2 for CH_2	179
K_3 for CH_3	180
K_2 for C_2H	181
Derivation of Yield-Energy Curves	185
A) Toluene and Cycloheptatriene from CH_2	186
B) Toluene from CH_3	192
C) Phenylacetylene from C_2H_x	199
D) Other Products	199
Discussion of the Results	200

Introduction

This appendix contains the derivation of yield versus beam energy curves for products from hot-atom chemical reactions of carbon in benzene which are formed from presumably fast precursors. The precursors, in turn, may be themselves products of hot reactions involving possibly several steps (e.g. multiple pick-up of hydrogens by fast carbon atoms).

The general procedure for the calculations is as follows:

1) The collision function, $K_0(E)$, is derived for carbon atoms, assuming isotropic, elastic scattering at atoms of equal mass.

2) The probability per collision to form the first step product, $r_1(E)$, is assumed to be small compared to $K_0(E)$ so that the above collision function, K_0 , is essentially unperturbed. The probability per carbon atom of generating a first step product at energy E is, therefore, $r_1(E) \cdot K_0(E)$.

3) The collision function $K_1(E)$ for the first step product is calculated with $r_1(E) \cdot K_0(E)$ being the formation density at energy E .

4) Step 2) is repeated for $r_2(E)$ and $K_1(E)$, etc.

5) Final n -step product yield is obtained from

$$Y_n = \int_{E_{n0}}^{\min(E_B, E_{n1})} K_{n-1}(\epsilon) \cdot r_n(\epsilon) d\epsilon \quad \text{for } E_B \geq E_{n0},$$

and $Y_n = 0$ for $E_B < E_{n0}$.

Glossary of Symbols

E	Kinetic energy
E_B	Kinetic energy of the beam
E_{v0}, E_{v1}	($v = 1, 2, \dots$): lower and upper energy limit for the v th reaction step
$r_v(E)$	Reactivity probability per collision of a ($v-1$) step product to undergo the v th reaction step
$K_v(E)$	Collision probability at energy E for a v th step product particle
Y	Yield per original fast particle
ϵ, η	Integration variables
$k(E_2, E_1)$	Probability that a particle which has the energy E_1 before a collision has the energy E_2 afterwards.

Assumptions

The collision function K_0 is defined, according to the Kinetic Theory,¹¹ by

$$K_0(E) = k(E, E_B) + \int_E^{E_B} K_0(\epsilon) [k(\epsilon, E) - r(\epsilon)] d\epsilon \quad .$$

All other collision functions are calculated analogously.

Assume:

- 1) $k(E_2, E_1) = \frac{1}{E_1}$ (elastic, isotropic, equal-mass scattering)
- 2) $r(E) \ll \frac{1}{E}$
- 3) Loss of kinetic energy in a reactive collision ≈ 0 .

Derivation of Collision Functions

Derivation of K_0 :

In accordance with the above assumptions one obtains K_0 from

$$K_0(E) = \frac{1}{E_B} + \int_E^{E_B} K_0(\epsilon) \frac{1}{\epsilon} d\epsilon \quad (1)$$

Differentiation of (1) yields

$$\frac{dK_0}{dE} = -\frac{K_0}{E}, \quad (2)$$

which is solved by

$$K_0 = \frac{C_0}{E}, \quad (3)$$

with C_0 a constant which is determined by (1). Inserting (3) into (1) yields

$$C_0 = 1$$

Thus,

$$K_0 = \frac{1}{E}, \quad \text{for } E \leq E_B. \quad (4)$$

Derivation of K_1 :

If $E_B < E_{10}$, $K_1 = 0$.

For $E_B > E_{10}$ and $E \geq E_{10}$:

$$K_1' = \int_E^{\min(E_{11}, E_B)} \frac{1}{\epsilon} K_0(\epsilon) \cdot r_1(\epsilon) d\epsilon + \int_E^{\min(E_{11}, E_B)} \frac{1}{\epsilon} K_1' d\epsilon \quad (5)$$

Differentiation of (5) yields

$$\frac{dK_1'}{dE} = -\frac{1}{E} K_0(E) \cdot r(E) - \frac{K_1'}{E} \quad (6)$$

(6) is solved by

$$K_1' = \frac{C_1(E)}{E}, \quad E \geq E_{10}, \quad (7)$$

where $C_1(E) = - \int_0^E K_0(\varepsilon) \cdot r_1(\varepsilon) \cdot d\varepsilon + D_1$. (8)

The constant D_1 is obtained by satisfying (5) with (7) and (8):

$$\frac{- \int_0^E K_0(\varepsilon) \cdot r_1(\varepsilon) d\varepsilon + D_1}{E} = \int_E^{\min(E_{11}, E_B)} \left[\frac{1}{\varepsilon} \cdot K_0(\varepsilon) \cdot r_1(\varepsilon) d\varepsilon + \frac{- \int_0^\varepsilon K_0(\eta) r_1(\eta) d\eta + D_1}{\varepsilon^2} \right] d\varepsilon \quad (9)$$

It is readily realized that the square bracket on the right side of (9) is

the full differential of

$$- \frac{\int_0^\varepsilon K_0(\eta) \cdot r_1(\eta) d\eta + D_1}{\varepsilon}, \quad \text{so that}$$

the integration can be carried out immediately. One obtains

$$\frac{- \int_0^E K_0(\varepsilon) \cdot r_1(\varepsilon) d\varepsilon + D_1}{E} = \frac{- \int_0^E K_0(\eta) \cdot r_1(\eta) d\eta + D_1}{\varepsilon} \bigg|_{\varepsilon=E}^{\varepsilon=\min(E_{11}, E_B)} \quad (10)$$

From this one obtains D_1 :

$$D_1 = \int_{\epsilon=\min(E_{11}, E_B)}^{\epsilon=E} K_0(\eta) \cdot r_1(\eta) d\eta \quad (11)$$

Inserting (11) into (8) yields

$$C_1(E) = - \int_{\epsilon=E}^{\epsilon=\min(E_{11}, E_B)} K_0(\eta) r_1(\eta) d\eta + \int_{\epsilon=\min(E_{11}, E_B)}^{\epsilon=E} K_0(\eta) r_1(\eta) d\eta$$

$$C_1(E) = \int_E^{\min(E_{11}, E_B)} K_0(\epsilon) \cdot r_1(\epsilon) d\epsilon, \quad E \geq E_{10} \quad (12)$$

$$\text{Thus} \quad K_1'(E) = \frac{\int_E^{\min(E_{11}, E_B)} K_0(\epsilon) \cdot r_1(\epsilon) d\epsilon}{E} \quad (13)$$

for $E_{10} \leq E < E_B$.

Solution for K for $E \leq E_{10}$:

$$K_1''(E) = \int_{E_{10}}^{\min(E_{11}, E_B)} \frac{1}{\epsilon} K_0(\epsilon) \cdot r_1(\epsilon) d\epsilon + \int_E^{\min(E_{11}, E_B)} \frac{1}{\epsilon} \cdot K_1''(\epsilon) d\epsilon \quad (14)$$

Treating (14) as (5) leads to the solution

$$K_1''(E) = \frac{C_1}{E}, \quad (15)$$

where C_1 is now a constant which is determined, again, by inserting

(15) into (14). One obtains

$$\frac{C_1}{E} = \int_{E_{10}}^{\min(E_{11}, E_B)} K_0(\epsilon) \cdot r_1(\epsilon) d\epsilon + \int_E^{\min(E_{11}, E_B)} \frac{1}{\epsilon} \frac{C_1}{\epsilon} d\epsilon, \quad \text{and}, \quad (16)$$

after solving the second integral on the right

$$C_1 = \min(E_{11}, E_B) \cdot \int_{E_{10}}^{\min(E_{11}, E_B)} \frac{1}{\epsilon} K_0(\epsilon) \cdot r_1(\epsilon) d\epsilon. \quad (17)$$

Inserting (17) into (15):

$$\text{For } E \leq E_{10}: \quad K_1''(E) = \frac{\min(E_{11}, E_B) \cdot \int_{E_{10}}^{\min(E_{11}, E_B)} \frac{1}{\epsilon} \cdot K_0(\epsilon) r_1(\epsilon) d\epsilon}{E} \quad (18)$$

Derivation of $K_2(E)$:

If $E_B < E_{10}$: $K_2(E) = 0$

If $E_B > E_{10}$ and $E \geq E_{20}$:

$$K_2' = \int_E^{\min(E_{21}, E_{11}, E_B)} \frac{1}{\epsilon} K_1(\epsilon) \cdot r_2(\epsilon) d\epsilon + \int_E^{\min(E_{21}, E_{11}, E_B)} \frac{1}{\epsilon} K_2(\epsilon) d\epsilon \quad (19)$$

(19) has the same form as (5) and its solution is, corresponding with (13):

$$K_2'(E) = \frac{\int_E^{\min(E_{11}, E_{21}, E_B)} K_1(\epsilon) \cdot r_2(\epsilon) d\epsilon}{E} \quad (20)$$

Here, $K_1(\epsilon)$ stands for K_1' or K_1'' , depending on E.

If $E < E_{20}$:

$$K_2''(E) = \int_{E_{20}}^{\min(E_{21}, E_{11}, E_B)} \frac{1}{\epsilon} \cdot K_1(\epsilon) \cdot r_2(\epsilon) \, d\epsilon + \int_E^{\min(E_{11}, E_{21}, E_B)} \frac{1}{\epsilon} K_2''(\epsilon) \, d\epsilon \quad (21)$$

(21) has, again, the same form as (14) and its solution is, as (18),

$$K_2''(E) = \frac{\min(E_{11}, E_{21}, E_B) \cdot \int_{E_{20}}^{\min(E_{11}, E_{21}, E_B)} \frac{1}{\epsilon} \cdot K_1(\epsilon) \cdot r_2(\epsilon) \, d\epsilon}{E} \quad (22)$$

Derivation of $K_v(E)$, $v > 2$:

K_v can be derived from K_{v-1} in an analogous way as K_2 from K_1 .

Since there is only one product, toluene, besides methane, for which the knowledge of K_3 is necessary in order to determine the yield-energy curves and since in this case special simplifications can be made, K_3 is not evaluated in general.

Derivation of K_1 for any first step products and intermediates (CH or C_2):

Assuming $r_1(E) = \frac{r_1}{E^n}$, $n > 0$, and $r_1 = \text{const.}$,

inserting $K_0 = \frac{1}{E}$ into (13) and (18)

yields:
$$K_1'(E) = \frac{1}{E} \cdot \frac{r_1}{n} \left(\frac{1}{E^n} - \frac{1}{\min^n(E_{11}, E_B)} \right) \quad (23)$$

for $E_{10} < E \leq \min(E_{11}, E_B)$,

and
$$K_1''(E) = \frac{1}{E} \cdot \frac{r_1}{n+1} \left(\frac{\min(E_{11}, E_B)}{E_{10}^{n+1}} - \frac{1}{\min^n(E_{11}, E_B)} \right) \quad (24)$$

for $0 \leq E \leq E_{10}$.

Derivation of K_2 for CH_2 :

It is assumed that the lower and upper energy limits for the pick-up of hydrogen by CH are the same as those in the pick-up of the first hydrogen: $E_{10} = E_{20}$

$$E_{11} = E_{21}$$

$$r_1(E) = r_2(E) = \frac{r}{E^n}$$

From (20) one obtains for $E_{10} < E < E_{11}$:

$$K_2' = \frac{1}{E} r^2 \int_E^{\min(E_{11}, E_B)} \frac{1}{n} \cdot \frac{1}{\epsilon} \left(\frac{1}{\epsilon^n} - \frac{1}{\min^n(E_{11}, E_B)} \right) \cdot \frac{1}{\epsilon^n} d\epsilon \quad (25)$$

$$K_2' = \frac{1}{E} \cdot r^2 \cdot \frac{1}{2n^2} \left(\frac{1}{E^n} - \frac{1}{E_B^n} \right)^2, \quad (26)$$

if $E_B \leq E_{11}$.

From (22) one obtains K_2'' , for $E \leq E_{10}$:

$$\begin{aligned} K_{21}''(E) &= \frac{E_B}{E} \cdot r^2 \cdot \int_E^{E_B} \frac{1}{\epsilon} \cdot \frac{1}{\epsilon} \cdot \frac{1}{n} \cdot \left(\frac{1}{\epsilon^n} - \frac{1}{E_B^n} \right) \frac{1}{\epsilon^n} d\epsilon \\ &= \frac{E_B}{E} \frac{r^2}{n} \left(\frac{1}{2n+1} \left[\frac{1}{E_{10}^{2n+1}} - \frac{1}{E_B^{2n+1}} \right] - \frac{1}{E_B^n} \cdot \frac{1}{n+1} \left[\frac{1}{E_{10}^{n+1}} - \frac{1}{E_B^{n+1}} \right] \right) \end{aligned} \quad (27)$$

Derivation of K_3 for CH_3 :

It is assumed again that

$$E_{10} = E_{20} = E_{30} ,$$

$$E_{11} = E_{21} = E_{31}$$

$$r_1 = r_2 = r_3 = \frac{r}{E^n}$$

Analogous to (19), K_3 is defined by

$$K_3' = \int_E^{E_B} \frac{1}{\epsilon} \cdot K_2'(\epsilon) \cdot r(\epsilon) d\epsilon + \int_E^{E_B} K_3'(\epsilon) \frac{1}{\epsilon} d\epsilon , \quad (28)$$

with $E_{10} < E < E_B \leq E_{11}$.

(28) has the same form as (5), and its solution is

$$K_3' = \frac{\int_E^{E_B} K_2' \cdot r(\epsilon) d\epsilon}{E} \quad (29)$$

$$= \frac{r^3}{E} \frac{1}{2n^2} \int_E^{E_B} \frac{1}{\epsilon} \cdot \frac{1}{\epsilon^n} \left(\frac{1}{\epsilon} - \frac{1}{E_B^n} \right)^2 d\epsilon \quad (29)$$

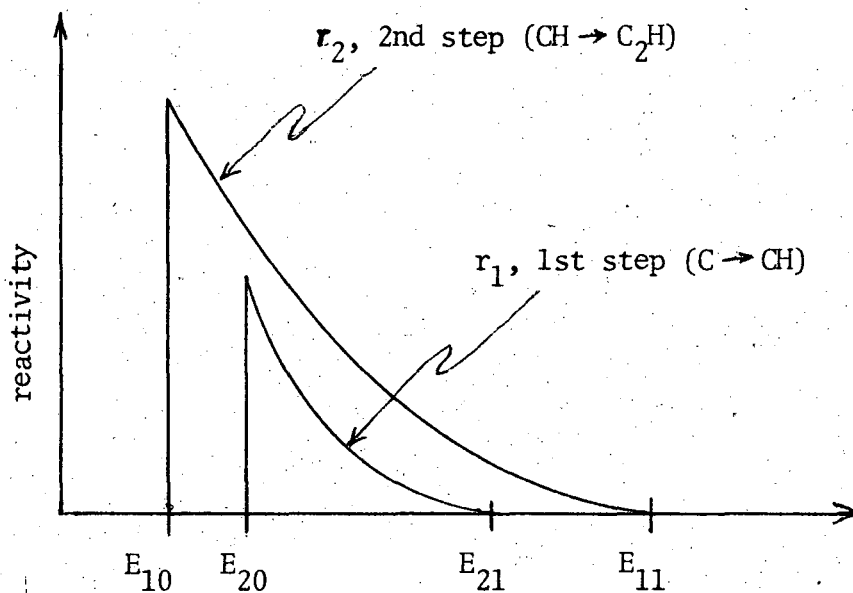
$$K_3' = \frac{r^3}{E} \cdot \frac{1}{6n^3} \left(\frac{1}{E^n} - \frac{1}{E_B^n} \right)^3 \quad (30)$$

Derivation of K_2 for C_2H :

a) $CH \rightarrow C_2H$

Assume: $E_{10} < E_{20}$, $E_{11} > E_{21}$,

$$r_2 = \frac{1}{E^n}$$



$$\text{From (19): } K_2' = \int_E^{\min(E_{21}, E_B)} K_1(\epsilon) \cdot \frac{1}{\epsilon} \cdot r_2(\epsilon) d\epsilon + \int_E^{\min(E_{21}, E_B)} K_2'(\epsilon) \cdot \frac{1}{\epsilon} d\epsilon, \quad (31)$$

$$\text{for } E_{20} \leq E < E_B.$$

The solution of (31) is (20); with $K_1 = K_1'$ from (23)

$$\begin{aligned} K_2' &= \frac{1}{E} \cdot \frac{r_1 r_2}{n} \int_E^{\min(E_{21}, E_B)} \frac{1}{\epsilon} \left(\frac{1}{\epsilon^n} - \frac{1}{\min^n(E_{11}, E_B)} \right) \cdot \frac{1}{\epsilon^m} d\epsilon \\ K_2' &= \frac{r_1 r_2}{n} \cdot \frac{1}{E} \cdot \left(\frac{1}{n+m} \left[\frac{1}{E^{n+m}} - \left(\frac{1}{\min(E_{21}, E_B)} \right)^{n+m} \right] \right. \\ &\quad \left. - \frac{1}{m} \left(\frac{1}{\min(E_{11}, E_B)} \right)^{n+m} \left[\frac{1}{E^m} - \left(\frac{1}{\min(E_{21}, E_B)} \right)^m \right] \right). \end{aligned} \quad (32)$$

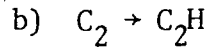
In this case, where E_{20} is presumably rather large, it may be important to compute K_2'' . According to (22) it is

$$K_2''(E) = \frac{\min(E_{21}, E_B)}{E} \cdot \int_{E_{20}}^{\min(E_{21}, E_B)} \frac{1}{\epsilon} \cdot K_1(\epsilon) \cdot r_2 d\epsilon. \quad (33)$$

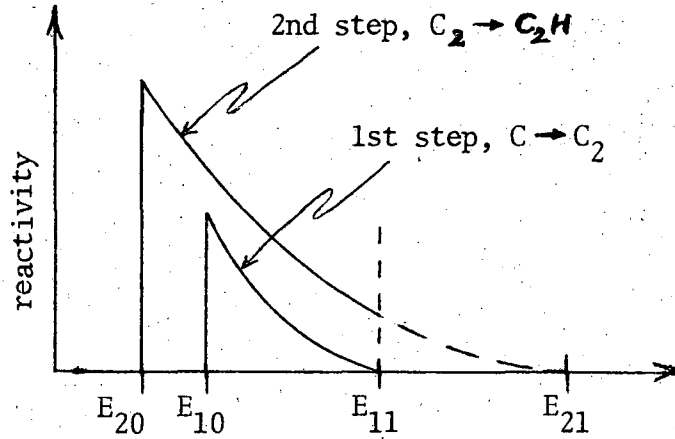
Inserting for K_1 K_1' , since $E_{10} < E_{20}$, and for r_2 , as above, $\frac{1}{E^m}$:

$$\begin{aligned} K_2''(E) &= \frac{\min(E_{21}, E_B)}{E} \cdot \frac{r_1 \cdot r_2}{n} \left(\frac{1}{n+m+1} \left[\frac{1}{E^{n+m+1}} - \left(\frac{1}{\min(E_{21}, E_B)} \right)^{n+m+1} \right] \right. \\ &\quad \left. - \frac{1}{m} \left(\frac{1}{\min(E_{11}, E_B)} \right)^n \cdot \left[\frac{1}{E^{m+1}} - \left(\frac{1}{\min(E_{21}, E_B)} \right)^{m+1} \right] \right), \end{aligned} \quad (34)$$

for $E \leq E_{20}$.



Assume: $E_{10} > E_{20}$, $E_{11} < E_{21}$, $r_2 = \frac{1}{E^n}$



For this case, (19) is:

$$K_2' = \int_E^{\min(E_{11}, E_B)} \frac{1}{\epsilon} K_1(\epsilon) \cdot r_2(\epsilon) d\epsilon + \int_E^{\min(E_{11}, E_B)} \frac{1}{\epsilon} K_2(\epsilon) d\epsilon \quad , \quad (35)$$

and (20) :

$$K_2' = \int_E^{\min(E_{11}, E_B)} K_1(\epsilon) \cdot r_2(\epsilon) d\epsilon \quad . \quad (36)$$

With r_2 as above, and $K_1 = K_1'$ from (13) with $r_1 = \frac{1}{E^m}$

$$K_1' = \frac{r_1}{E} \int_E^{\min(E_{11}, E_B)} \frac{1}{\epsilon} \cdot \frac{1}{\epsilon^m} d\epsilon = \frac{1}{E} \frac{r_1}{m} \left(\frac{1}{E^m} - \left(\frac{1}{\min(E_{11}, E_B)} \right)^m \right)$$

$$K_2' = \frac{r_1 r_2}{E \cdot m} \int_E^{\min(E_{11}, E_B)} \frac{1}{\epsilon} \left(\frac{1}{\epsilon^m} - \frac{1}{\min^m(E_{11}, E_B)} \right) \cdot \frac{1}{\epsilon^n} d\epsilon$$

$$= \frac{r_1 \cdot r_2}{E \cdot m} \left(\frac{1}{m+n} \left[\frac{1}{E^{n+m}} - \frac{1}{\min^{n+m}(E_{11}, E_B)} \right] - \frac{1}{\min^m(E_{11}, E_B)} \cdot \frac{1}{n} \cdot \left[\frac{1}{E^n} - \frac{1}{\min^n(E_{11}, E_B)} \right] \right), \quad (37)$$

for $E_{10} \leq E \leq \min(E_{11}, E_B)$.

For $E_{20} \leq E \leq E_{10}$

$$K_2' = \frac{1}{E} \left[\int_E^{E_{10}} K_1'' \cdot r_2(\epsilon) d\epsilon + \int_{E_{10}}^{\min(E_{11}, E_B)} K_1' \cdot r_2(\epsilon) d\epsilon \right]. \quad (38)$$

The second integral in (38) is K_2' as in (37), and the first integral,

with (18) and (24)

$$= \frac{r_1 r_2}{m+1} \int_E^{E_{10}} \frac{1}{\epsilon} \cdot \frac{1}{\epsilon^n} \cdot \min(E_{11}, E_B) \cdot \left(\frac{1}{E_{10}^{m+1}} - \frac{1}{\min^{m+1}(E_{11}, E_B)} \right) d\epsilon$$

$$= \frac{r_1 \cdot r_2}{n(m+1)} \cdot \min(E_{11}, E_B) \cdot \left(\frac{1}{E_{10}^{m+1}} - \frac{1}{\min^{m+1}(E_{11}, E_B)} \right) \cdot \left(\frac{1}{E^n} - \frac{1}{E_{10}^n} \right) \quad (39)$$

Therefore,

$$K_2' = \frac{r_1 \cdot r_2}{E} \left(\frac{\min(E_{11}, E_B)}{n(m+1)} \cdot \left[\frac{1}{E_{10}^{m+1}} - \frac{1}{\min^{m+1}(E_{11}, E_B)} \right] \left[\frac{1}{E^n} - \frac{1}{E_{10}^n} \right] \right.$$

$$+ \frac{1}{m(m+n)} \left[\frac{1}{E^{n+m}} - \frac{1}{\min^{n+m}(E_{11}, E_B)} \right]$$

$$\left. - \frac{1}{n \cdot m \cdot \min^m(E_{11}, E_B)} \left[\frac{1}{E^n} - \frac{1}{\min^n(E_{11}, E_B)} \right] \right). \quad (40)$$

Derivation of Yield-Energy Curves

The yield of a compound is, in accordance with the thus far applied concepts, in simplified form:

$$y(E_B) = \int_{E_0}^{\min(E_{11}, E_B)} K(E_B, \epsilon) \cdot r(\epsilon) d\epsilon, \quad (41)$$

where $K(\epsilon)$ and $r(\epsilon)$ as previously defined, and E_0 and E_1 the lower ("activation" energy) and upper energy limit for finite reactivity. E_B is the kinetic energy of the beam particles and $K(E)$ refers to the immediate precursor for the bi-molecular reaction product under consideration. Since K depends, in general, on E_B , y is also dependent on E_B even if $E_B > E_1$, i.e. even if the initial beam particle energy is larger than the upper energy limit for reaction. This is true also for the case of 1-step products since the collision function of the primary particles does depend on the initial energy if the latter is not sufficiently large. However, in the foregoing it was assumed that K_0 does not depend on E_B and any observable change in $K(E)$ (and therefore y , when $E_B > E_1$) indicates

precursor formation at higher energy than E_1 . It is the range of energy above ca. 10 eV, where such precursors can be formed, that these calculations apply to. This is also the energy range where justification exists for many of the above assumptions.

A) $\text{CH}_2 + \text{OH} \rightarrow \text{toluene, cycloheptatriene:}$

CH_2 is considered a 2-step product, T and CHT 3-step products.

Assume: $E_{30} = E_{10}$,

$E_{31} < E_{11}$, however, E_{31} may be different for T and CHT.

By definition:

$$y_{(E_B)} = \int_{E_{10}}^{\min(E_B, E_{31})} K_{2, \text{CH}_2}' \cdot r_3 \, d\epsilon$$

Inserting for K_2' (26) and r_3 (above):

$$\begin{aligned} y &= \frac{r^2 \cdot r_3}{2n^2} \int_{E_{10}}^{\min(E_B, E_{31})} \frac{1}{\epsilon} \left(\frac{1}{\epsilon^n} - \frac{1}{E_B^n} \right)^2 \cdot \frac{1}{\epsilon^m} \, d\epsilon \\ &= \frac{r^2 r_3}{2n^2} \left(\frac{1}{2n+m} \cdot \left[\frac{1}{E_{10}^{2n+m}} - \frac{1}{\min^{2n+m}} \right] + \frac{1}{m} \cdot \frac{1}{E_B^{2n}} \left[\frac{1}{E_{10}^m} - \frac{1}{\min^m} \right] \right. \\ &\quad \left. - \frac{2}{E_B^n (m+n)} \left[\frac{1}{E_{10}^{m+n}} - \frac{1}{\min^{m+n}} \right] \right), \end{aligned} \quad (42)$$

where $\min \equiv \min(E_B, E_{13})$.

The yield for $E_B \geq E_{11}$ is

$$Y_{\infty} = Y_{(E_B = E_{11})} , \quad (43)$$

and the relative yield R

$$R = \frac{Y}{Y_{\infty}} , \quad \text{for } E_B < E_{11} ; \quad (44)$$

$$R = 1 , \quad \text{for } E_B \geq E_{11} .$$

Analysis of the Yield-Energy Curve for T, CHF:

If the energy is measured in units of E_{10} , the term which determines the shape of the energy dependence is

$$\begin{aligned} x = & \frac{1}{2n+m} \cdot \left[1 - \left(\frac{1}{\min(x_B, x_{31})} \right)^{2n+m} \right] + \frac{1}{m} \frac{1}{x_B^{2n}} \left[1 - \left(\frac{1}{\min(x_B, x_{31})} \right)^m \right] \\ & - \frac{2}{x_B^n (m+n)} \left[1 - \left(\frac{1}{\min(x_B, x_{31})} \right)^{m+n} \right] , \end{aligned}$$

with $x_B = \frac{E_B}{E_{10}} ,$

$$x_{31} = \frac{E_{31}}{E_{10}} .$$

Position of Extrema:

A) If $x_{31} = 1 + \delta , \quad \delta \text{ small} , \text{ and}$

$$x_B > x_{31} :$$

$$x = \frac{1}{2n+m} \left[1 - \left(\frac{1}{1+\delta} \right)^{2n+m} \right] + \frac{1}{m} \frac{1}{x_B^{2n}} \left[1 - \left(\frac{1}{1+\delta} \right)^m \right] - \frac{2}{(m+n)x_B^n} \left[1 - \left(\frac{1}{1+\delta} \right)^{m+n} \right]$$

$$\frac{dx}{dx_B} = \frac{2n}{m} \cdot \left[1 - \left(\frac{1}{1+\delta} \right)^m \right] \cdot \frac{1}{x_B^{2n+1}} + \frac{2n}{m+n} \left[1 - \left(\frac{1}{1+\delta} \right)^{m+n} \right] \cdot \frac{1}{x_B^{n+1}}$$

$$\frac{dx}{dx_B} = 0 \quad \text{at } x_B \rightarrow \infty \quad \text{and} \quad x_B^n = \frac{m+n}{m} \left[1 - \frac{(1+\delta)^n - 1}{(1+\delta)^{m+n} - 1} \right]$$

For $\delta \rightarrow 0$, $x_B^n \rightarrow 1$; i.e. the yield energy curve is S-shaped and its flat parts are near E_{31} and at large E_B .

$$B) \quad x_{31} \approx x_{11}$$

$$x = \frac{1}{2n+m} \left[1 - \left(\frac{1}{x_B} \right)^{2n+m} \right] + \frac{1}{m} \frac{1}{x_B^{2n}} \left[1 - \left(\frac{1}{x_B} \right)^m \right] - \frac{2}{x_B^n (m+n)} \left[1 - \left(\frac{1}{x_B} \right)^{m+n} \right]$$

$$\begin{aligned} \frac{dx}{dx_B} &= \left(\frac{2n}{m} - \frac{2n}{m+n} \right) \cdot \left(\frac{1}{x_B} \right)^{2n+m+1} - \frac{2n}{m} \left(\frac{1}{x_B} \right)^{2n+1} \\ &+ \frac{2n}{m+n} \left(\frac{1}{x_B} \right)^{n+1} \end{aligned}$$

This differential quotient is zero at $x_B \rightarrow \infty$ and if

$$\frac{dx}{dx_B} \cdot x_B^{2n+m+1} = \left(\frac{2n}{m} - \frac{2n}{m+n} \right) - \left(\frac{2n}{m} - \frac{2n}{m+n} x_B^n \right) \cdot x_B^m = 0$$

This last equation can be solved for arbitrary $n, m > 0$ only if $x_B = 1$.

It can also easily be shown that the right side increases monotonously with x_B , if $x_B > 1$. Therefore, $x_B = 1$ is the only horizontal part in the S-curve, besides that at large E_B .

Position of Inflection Points:

A) If $x_{31} = 1 + \delta$, δ small, and $x_B > x_{31}$:

$$\frac{d^2x}{dx_B^2} = \frac{2n(2n+1)}{m} \left[1 - \left(\frac{1}{1+\delta} \right)^m \right] \frac{1}{x_B^{2n+2}} - \frac{2n(n+1)}{m+n} \left[1 - \left(\frac{1}{1+\delta} \right)^{m+n} \right] \cdot \frac{1}{x_B^{n+2}}.$$

This second differential quotient is zero for $x_B \rightarrow \infty$, and when

$$0 = \frac{d^2x}{dx_B^2} \cdot x_B^{2n+2} = \frac{2n(2n+1)}{m} \left[1 - \left(\frac{1}{1+\delta} \right)^m \right] - \frac{2n(n+1)}{m+n} \left[1 - \left(\frac{1}{1+\delta} \right)^{m+n} \right] x_B^n,$$

$$\text{i.e., at } x_B^n = \frac{(2n+1)(m+n)}{(n+1) \cdot m} \frac{\left[1 - \left(\frac{1}{1+\delta} \right)^m \right]}{\left[1 - \left(\frac{1}{1+\delta} \right)^{m+n} \right]}.$$

Comparing this with a similar one (above) for $\frac{dx}{dx_B}$ indicates that x_B is never significantly larger than 1.

B) A similar result is obtained when the restriction: δ small and

$E_B > E_{31}$, are dropped.

Analysis with the Assumptions: $m \gg 2n, x_B > x_{31}$.

$$x = \frac{1}{m} \left[1 - \left(\frac{1}{1+\delta} \right)^m \right] \left[1 + \frac{1}{x_B^{2n}} - \frac{2}{x_B^n} \right]$$

$$= \frac{1}{m} \left[1 - \left(\frac{1}{1+\delta} \right)^m \right] \left[1 - \frac{1}{x_B^n} \right]^2 .$$

Here $\frac{1}{m} \left[1 - \left(\frac{1}{1+\delta} \right)^m \right]$ can be considered a constant, and only $Z = \left[1 - \frac{1}{x_B^n} \right]^2$

need to be considered. Equation (44) is now:

$$R = \frac{\left(1 - \frac{1}{x_B^n} \right)^2}{\left(1 - \frac{1}{x_{11}^n} \right)^2} \quad \text{for } x_B \leq x_{31} . \quad (45)$$

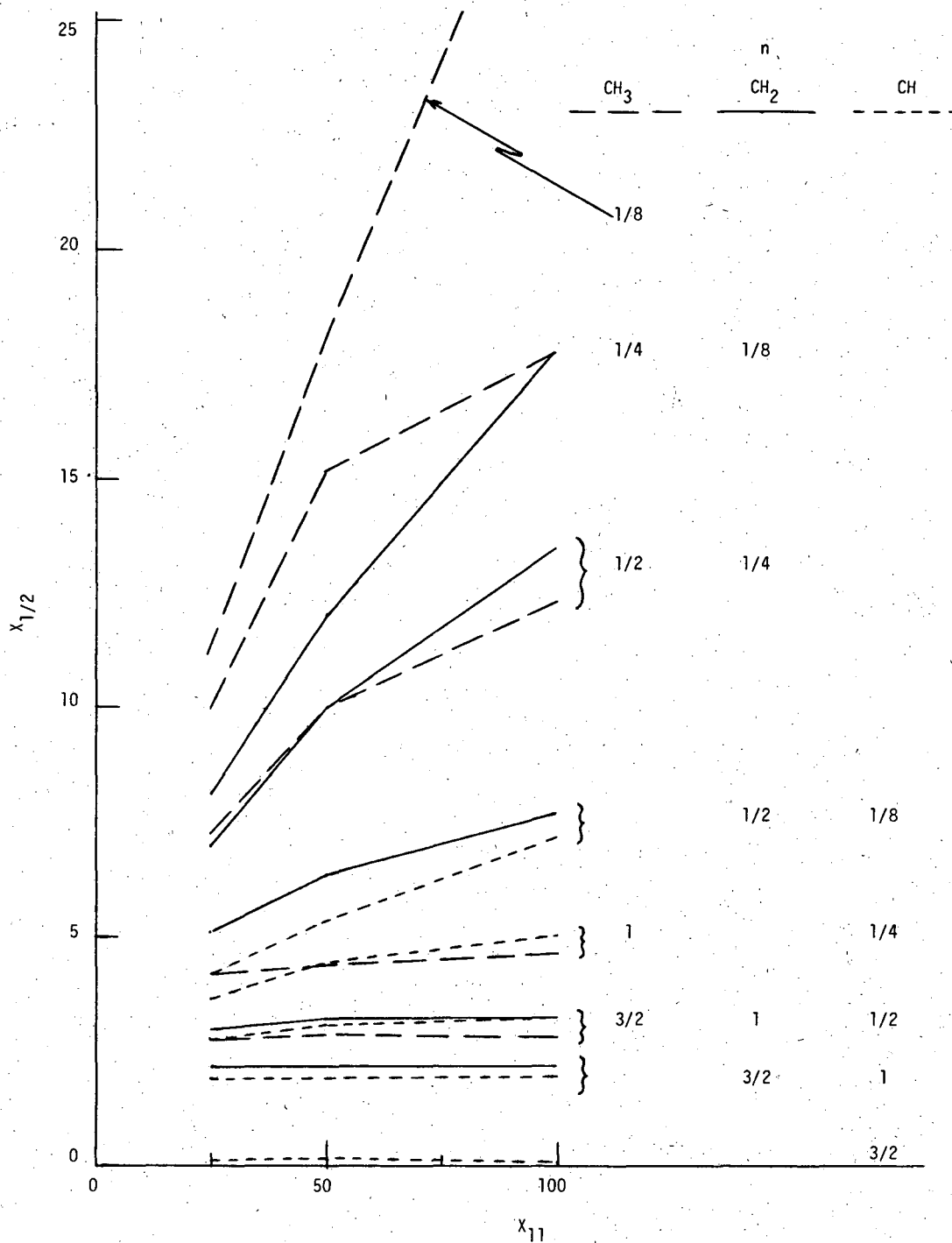
The "half-point" is attained at $x_B = x_{1/2}$, i.e. when

$$0.50 = \frac{\left(1 - \frac{1}{x_{1/2}^n} \right)^2}{\left(1 - \frac{1}{x_{11}^n} \right)^2} , \quad \text{or}$$

$$x_{1/2} = x_{11} \cdot \frac{1}{\sqrt[n]{0.294 \cdot x_{11}^n + 0.706}} . \quad (46)$$

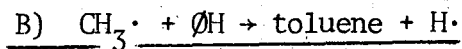
$x_{1/2}$ as a function of x_{11} , for various values of n , is plotted in

Figure 33 .



XBL 695-4245

Figure 33. Values ($x_{1/2}$) of the beam energy at which the yield of products from the precursors CH , CH_2 , and CH_3 is 1/2 of the high energy value-versus upper energy boundaries of reaction x_{11} (all energy values in units of the lower energy boundary E_{01}). The parameter n is the exponent in the reactivity curve $r = 1/E^n$.



$\text{CH}_3\cdot$ is considered a 3-step product.

Assume: $E_{40} = E_{10}$

$E_{41} < E_{11}$

$r_4(E) = \frac{r_4}{E^m}$

$y = \int_{E_{10}}^{\min(E_B, E_{41})} K_3 \cdot r_4 \, d\epsilon$

$y = \frac{r^3 \cdot r_4}{6n^3} \int_{E_{10}}^{\min(E_B, E_{41})} \frac{1}{\epsilon} \left(\frac{1}{\epsilon^n} - \frac{1}{E_B^n} \right)^3 \cdot \frac{1}{\epsilon^m} \, d\epsilon$

$= \frac{r^3 r_4}{6n^3} \left(\frac{1}{3n+m} \left[\frac{1}{E_{10}^{3n+m}} - \left(\frac{1}{\min(E_B, E_{41})} \right)^{3n+m} \right] \right.$

$\left. - \frac{3}{2n+m} \cdot \frac{1}{E_B^n} \left[\frac{1}{E_{10}^{2n+m}} - \left(\frac{1}{\min(E_B, E_{41})} \right)^{2n+m} \right] \right.$

$\left. + \frac{3}{n+m} \cdot \frac{1}{E_B^{2n}} \left[\frac{1}{E_B^{n+m}} - \left(\frac{1}{\min(E_B, E_{41})} \right)^{n+m} \right] \right.$

$\left. - \frac{1}{E_B^{3n}} \cdot \frac{1}{m} \left[\frac{1}{E_{10}^m} - \left(\frac{1}{\min(E_B, E_{41})} \right)^m \right] \right) .$

Analysis:

With the following abbreviations:

$$\frac{E_{10}}{E_{10}} = E_{40} \rightarrow 1$$

$$\frac{E_B}{E_{10}} = x_B$$

$$\frac{E_{11}}{E_{10}} = x_{11}$$

$$\frac{E_{41}}{E_{10}} = x_{41}$$

the term which determines the shape of the yield-energy curve is:

$$\begin{aligned} x = & \frac{1}{3n+m} \left[1 - \left(\frac{1}{\min(x_B, x_{41})} \right)^{3n+m} \right] \\ & - \frac{3}{2n+m} \cdot \frac{1}{x_B^n} \left[1 - \left(\frac{1}{\min(x_B, x_{41})} \right)^{2n+m} \right] \\ & + \frac{3}{n+m} \cdot \frac{1}{x_B^{2n}} \left[1 - \left(\frac{1}{\min(x_B, x_{41})} \right)^{n+m} \right] \\ & - \frac{1}{x_B^{3n}} \cdot \frac{1}{m} \left[1 - \left(\frac{1}{\min(x_B, x_{41})} \right)^m \right] . \end{aligned}$$

For $x_B > x_{41}$, and $x_{41} \approx x_{10}$:

$$\begin{aligned} \frac{dx}{dx_B} = & + \frac{3n}{2n+m} \cdot \frac{1}{x_B^{n+1}} \cdot \left[1 - \left(\frac{1}{x_{41}} \right)^{2n+m} \right] \\ & - \frac{6n}{n+m} \cdot \frac{1}{x_B^{2n+1}} \cdot \left[1 - \left(\frac{1}{x_{41}} \right)^{n+m} \right] \end{aligned}$$

$$+ \frac{3n}{m} \cdot \frac{1}{x_B^{3n+1}} \cdot \left[1 - \left(\frac{1}{x_{41}} \right)^m \right] .$$

$\frac{dx}{dx_B} = 0$ if $x_B \rightarrow \infty$, and when

$$\frac{dx}{dx_B} \cdot x_B^{3n-1} = \frac{3n}{2n+m} \cdot x_B^{2n} \left[1 - \left(\frac{1}{x_{41}} \right)^{2n+m} \right]$$

$$- \frac{6n}{n+m} \cdot x_B^n \cdot \left[1 - \left(\frac{1}{x_{41}} \right)^{n+m} \right]$$

$$+ \frac{3n}{m} \cdot \left[1 - \left(\frac{1}{x_{41}} \right)^m \right] = 0 .$$

This is a quadratic equation for x_B^n which has the two solutions:

$$x_B^n = \frac{\frac{2 \left[1 - \left(\frac{1}{x_{41}} \right)^{n+m} \right]}{n+m} \pm \sqrt{\frac{4 \left[1 - \left(\frac{1}{x_{41}} \right)^{n+m} \right]^2}{(n+m)^2} - \frac{4}{m(2n+m)} \left[1 - \left(\frac{1}{x_{41}} \right)^{2n+m} \right] \cdot \left[1 - \left(\frac{1}{x_{41}} \right)^m \right]}}{\frac{2}{2n+m} \cdot \left[1 - \left(\frac{1}{x_{41}} \right)^{2n+m} \right]} .$$

With the approximation

$$1 - \left(\frac{1}{x_{41}} \right)^k = 1 - (1 - k\delta) = k\delta ,$$

where δ is the assumed small quantity

$$\delta = x_{41} - 1 ,$$

the only physically relevant solution is

$$x_B^n = 1 .$$

Again, the yield energy curve is S-shaped with its horizontal at $x_B = 1$

and $x_B \rightarrow \infty$.

Analysis for $m \gg 3n$:

The term for consideration, now, is:

$$x = 1 - \frac{3}{x_B^n} + \frac{3}{x_B^{2n}} - \frac{1}{x_B^{3n}} = \left(1 - \frac{1}{x_B^n}\right)^3$$

$$R = \frac{\left(1 - \frac{1}{x_B^n}\right)^3}{\left(1 - \frac{1}{x_{11}^n}\right)^3} \quad (47)$$

The "half-point" is at $R = 0.50$, i.e., when

$$x_{1/2} = \frac{x_{11}}{\sqrt[n]{0.206 x_{11}^n + 0.794}} \quad (48)$$

Single Pick-up

For single pick-up precursor reactions the relative yield-energy curve is

$$R = \frac{1 - \frac{1}{x_B^n}}{1 - \frac{1}{x_{11}^n}}, \quad (49)$$

and the "half-point" value,

$$x_{1/2} = \frac{x_{11}}{\frac{n}{0.5 (1 + x_{11}^n)}} \quad (50)$$

In Figure 33 the "half-points" of R for single [(50), e.g. CH], double [(46), e.g. CH₂], and triple [(48), e.g. CH₃] pick-up reactions (as precursors to the final, stable products, CHT and T) are plotted versus the maximum energy, E₁₁, at which pick-up can occur (measured in units of the activation energy E₁₀). If one assumes that E₁₀ ≈ 1 - 2 eV, then x₁₁ ≈ 25 - 50, since E₁₁ could be as high as 50 eV (Appendix C). From the experimental yield versus energy curves (see Figures 24 and 25), the upper limits appear to be ca. 100 eV and the "half-points" at about 30 eV, i.e. x₁₁ ≈ 50 - 100 and x_{1/2} ≈ 15 - 30. Such large values for x_{1/2} are obtained for CH₃ as precursors only if n is equal or smaller than 1/8. n has to be smaller yet, if the precursor is assumed to be CH₂, and even smaller for CH. A small n, however, indicates that r is not very energy-dependent, or, that the pick-up reaction cross section varies with the energy as the cross

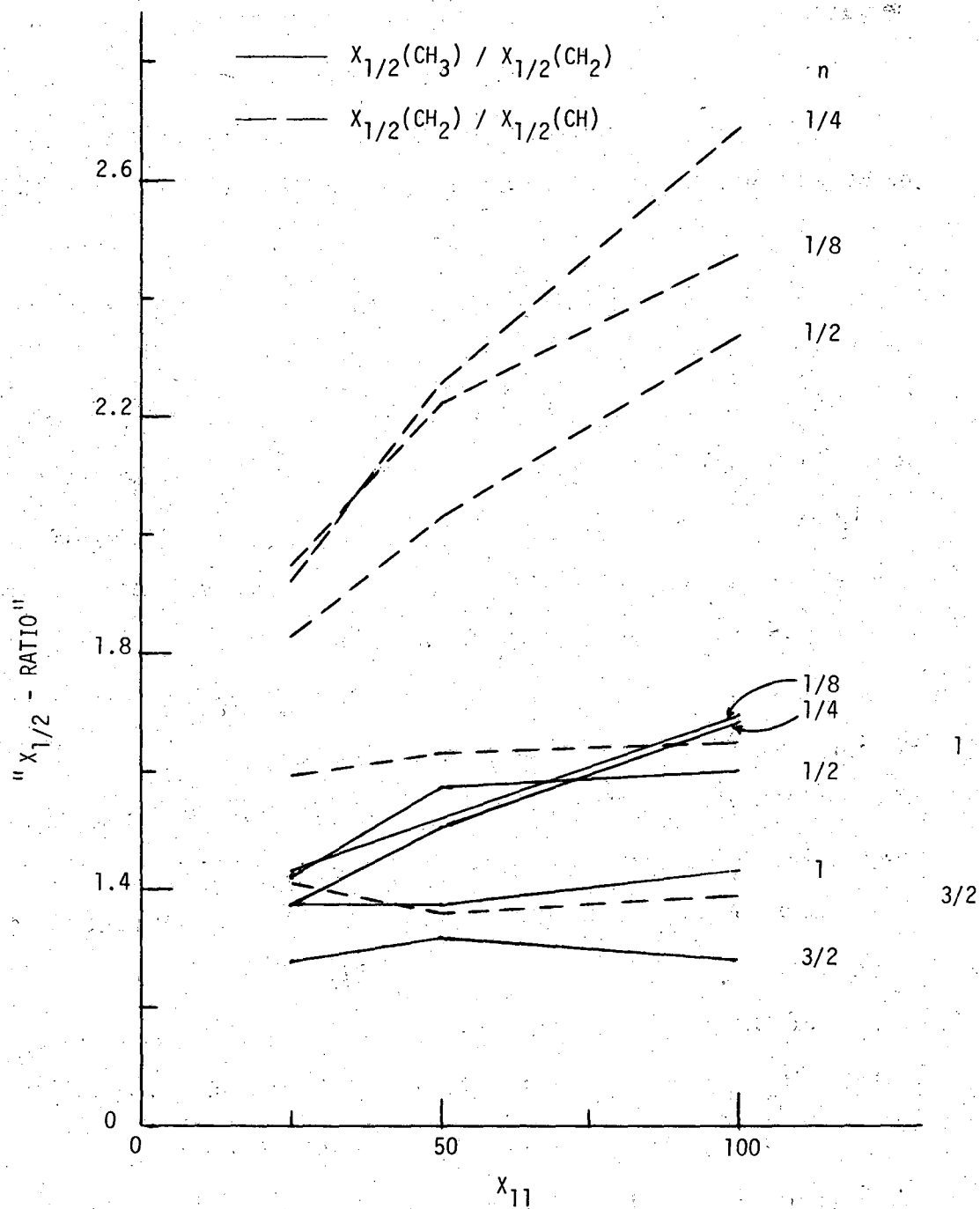
section for elastic scattering. From Figure 18 (Chapter III, 1), one gets a notion of how the elastic scattering cross section varies with energy. A cautious extrapolation of the curve into the range between 10 and 50 eV suggests that

$$\sigma_{\text{CA}} \propto \frac{1}{E^{1/2}}$$

The pick-up cross section will therefore have about the same energy dependence. This type dependence, however, is easy to accept (and widely ascertained): The cross section is inversely proportional to the velocity, or, proportional to the "duration of collision". This relation is found generally in resonance phenomena.

This is probably all that can be obtained quantitatively from the experimental and theoretical analysis.

Qualitatively, one would like to be able to determine, for instance, whether toluene and cycloheptatriene are products of the same precursors (a quantitative comparison of the experimental yield-energy curve and the R - curves is probably out of the question because of the many over-simplifications with regard to K_0 , etc.). In order to investigate the qualitative problem, the ratios of "half-point" values of the different pick-up sequences are plotted in Figure 34. From the preceding discussion, we know that n has to be very small. Unfortunately, the experimental value for the "half-point" ratio T/CHT is very inaccurate. It may be anywhere between 1 and 1.5. From Figure 34 the only small n-value curve which yields similar ratios, is that for $x_{1/2}(\text{CH}_3) / x_{1/2}(\text{CH}_2)$. This would



XBL 695-4246

Figure 34. Ratios of $x_{1/2}$ values for products from CH , CH_2 , and CH_3 (compare Figure 33) versus the upper energy boundary of reaction x_{11} .

indicate that some of T is formed from CH_3 rather than CH_2 . In any event, the deviation from the assumption that the precursors of toluene and cycloheptatriene are CH_2 tends to favor CH_3 as possible additional precursor for T, rather than CH for cycloheptatriene. However, these conclusions are extremely tentative, and have to await more accurate data-taking. The preceding was presented, indeed, to demonstrate the opportunities and limitations of this experimental and theoretical method rather than to advance definite results.

C) $\text{C}_2\text{H}_x + \phi\text{H} \rightarrow$ phenylacetylene

The preceding derivations of R-curves for single-step pick-up reactions etc., can be used again for the analysis of the experimental yield-energy curve for phenylacetylene. The curve seems to decrease more steeply than CHT or T, indicating that phenylacetylene might be the product of more-than-1-step precursors. However, a comparison between the yield-energy curves of CHT and T, and that of phenylacetylene is probably not admissible because of the almost certainly different dynamics involved in the formation of the respective precursors (see Appendix C).

D) Other Products

If the collision function does not change over a reactive range, when E_B is varied, i.e. if the yields of certain compounds, such as benzene, biphenyl, diphenylmethane, and phenylcycloheptatriene, are independent of E_B , for $E_B \geq E_0$, the only conclusion is that the

maximum energy for which the particular reaction proceeds is well below E_0 . This does not exclude the possibility of formation of "precursors" which may react in a bimolecular reaction again. However, such precursors must have extremely low kinetic energies ($<E_0$). For the above compounds, E_0 seems to be <3 eV.

This appendix cannot, of course, explain the increase in yield of "U-2" as the energy decreases (see Chapter II, 9). Kinetic theory always predicts decreasing or constant yields. Therefore, the yield behavior of "U-2" must be explained in connection with the problem of the origin of the oxygen.

Discussion of the Calculations and Results

The concepts of collision theory in general and the formulation of the product yield according to equation (41) are probably adequate for the hot-atom chemistry under investigation in this thesis. In contrast to classical experiments in collision theory, the energy range for binary and reactive collisions is much larger here (3-100 eV), and many factors which can be neglected there, or are only a small perturbation, become of primary importance here. One such factor is the collision function K . The method of varying only the maximum energy, (E_B), which reactants can attain, makes the interpretation of the experimental data very questionable because it is most certainly for energies close to E_B where K

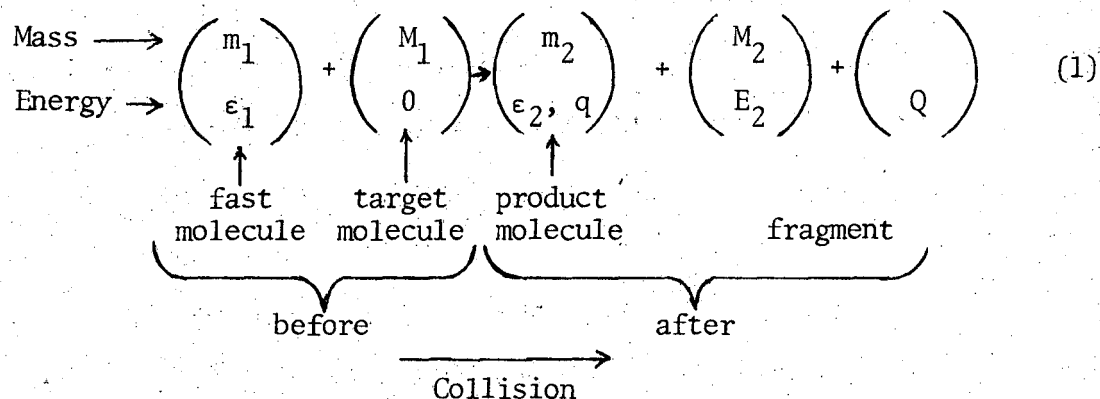
deviates very much from the asymptotic solution,¹¹ i.e. where the dependence of K on E_B is strongest. In other words, the experimental data are being interpreted in terms of quantities which are most unpredictable exactly there where they are most decisive. In order to keep the calculations tractable, we had to assume that K was not a function of E_B , except that $K = 0$ for $E > E_B$. From the above it is clear that the quantitative and qualitative analysis of experimental data depends crucially on the extent to which this assumption is correct, e.g. if $K(E)$ is much smaller than $1/E$ for $E \approx E_B$ a part of the observed yield decrease is due to a diminished K in the reactive energy range. It might be worthwhile to investigate which properties of the yield-energy curves are invariant when a certain hypothetical dependence on E_B is introduced into K . Perhaps a more realistic analysis of experimental data can then be undertaken.

APPENDIX C

Classical Mechanics of Bimolecular Collisions

(Pick-up and Insertion Reactions)

All bimolecular reactions considered in this text can be represented by the following scheme:



q internal energy of the (fast) product molecule

Q heat of reaction (see Appendix D), only ground state - ground state reactions considered

$$\text{Energy conservation: } \epsilon_1 = \epsilon_2 + E_2 + q + Q \quad (2)$$

$$\text{Momentum conservation: } \sqrt{2m_1\epsilon_1} = \sqrt{2M_2E_2} + \sqrt{2m_2\epsilon_2} \quad (3)$$

With this formulation we are considering only the two cases: "Both products are scattered forward," and "one product forward, the other backward." However, it can easily be shown that in these two cases the quantity $q + Q$ is maximum or minimum.

From the two conservation equations one obtains:

$$\frac{q + Q}{\epsilon_1} = 1 - \frac{\epsilon_2}{\epsilon_1} - \frac{m_1}{m_2} \left(1 + 2 \sqrt{\frac{m_2}{m_1} \cdot \frac{\epsilon_2}{\epsilon_1} + \frac{\epsilon_2}{\epsilon_1}} \right), \quad (4)$$

The following values pertain to the reactions to be considered:

Pick-up of H by ^{14}C :

$$m_2 = \frac{15}{14} m_1, \quad M_1 = \frac{78}{14} m_1, \quad M_2 = \frac{77}{78} M_1, \quad \frac{m_1}{M_2} = 0.180, \quad Q \approx 1 \text{ eV}$$

Pick-up of $^{12}\text{CH}_x$ by ^{14}C :

$$m_2 \approx 2m_1, \quad M_2 = \frac{5}{6} M_1, \quad \frac{m_1}{M_2} = 0.180, \quad Q \approx 4 \text{ eV}$$

Re-entry products (benzene):

$$m_1 = \frac{14}{80} m_2, \quad m_2 = \frac{80}{78} M_1, \quad M_2 = \frac{12}{14} \cdot m_1, \quad Q = 0$$

Insertion reactions: Since here the product molecule takes up all of the energy and momentum, the ratio between initial energy ϵ_1 and internal energy $q + Q$ is fixed:

Carbon into benzene:

$$\frac{q + Q}{\epsilon_1} = 1 - \frac{\epsilon_2}{\epsilon_1} = 1 - \frac{m_1}{m_2} = 0.848, \quad Q = -4 \text{ eV}$$

CH_2 into benzene:

$$\frac{q + Q}{\epsilon_1} = 0.83, \quad Q = -3 \text{ eV}$$

C₂ into benzene:

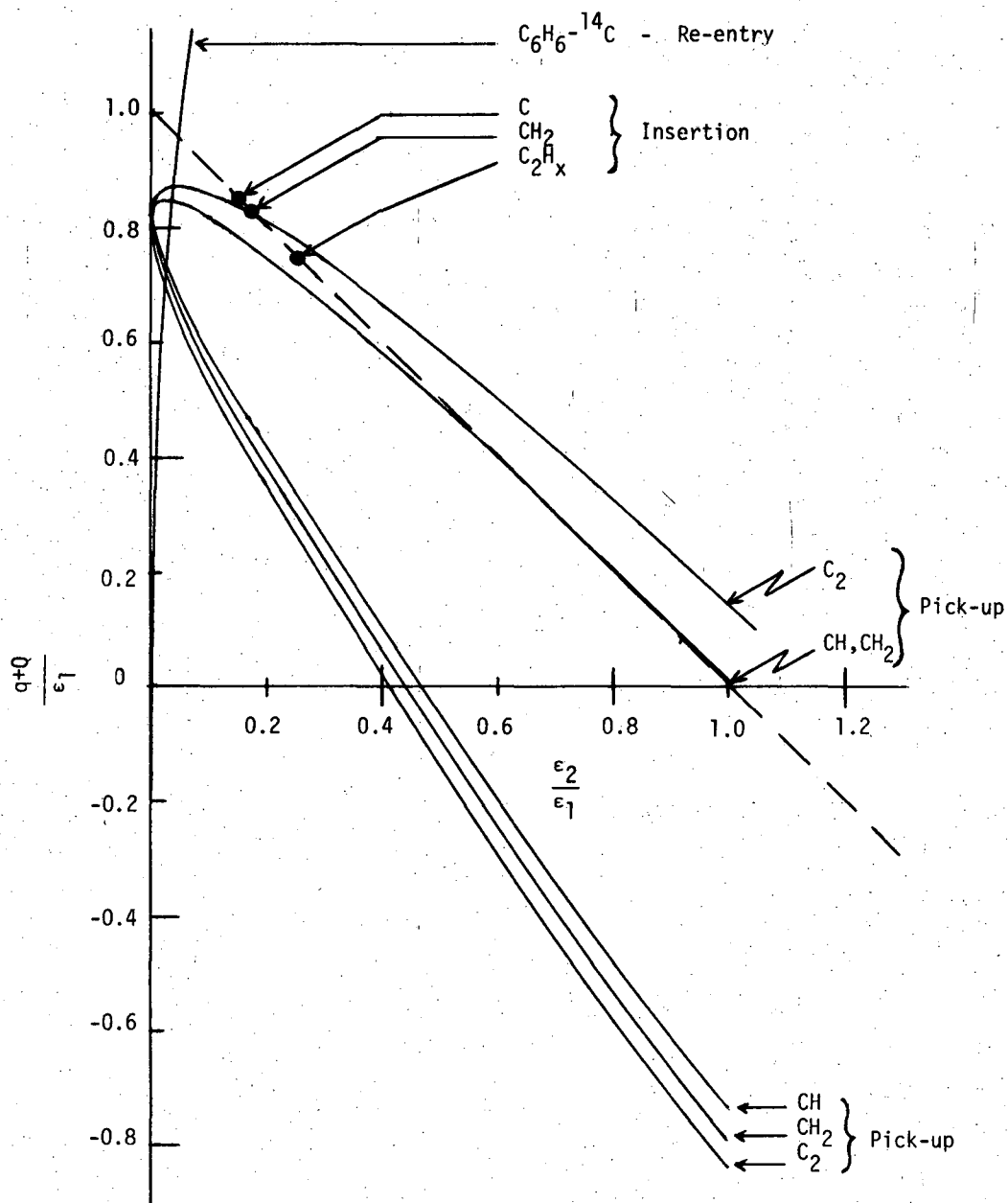
$$\frac{q + Q}{\epsilon_1} = 0.75, \quad Q = -4 \text{ eV}$$

Discussion

Pick-up reactions

In Figure 35 the relationship between $(q + Q)/\epsilon_1$ (the internal energy plus heat of reaction, relative to the kinetic energy of the fast particle) and ϵ_2/ϵ_1 (the kinetic energy of the fast product molecule with respect to the initial kinetic energy) is plotted for the different pick-up reactions.

The interpretation of these plots is as follows: Any point on this two-dimensional plot represents a bimolecular collision, the abscissa determines the kinetic energy of one of the products (e.g. CH), the corresponding ordinate determines the internal energy of the same product, the vertical distance to the diagonal determines the kinetic energy of the other product molecule (e.g. C₆H₅), all energies in terms of the kinetic energy of the reactant atom (e.g. C). If $Q = 0$, and if q is assumed always positive or zero, energy conservation requires all collision points to lie within the triangle (1, 0, 1). If $Q \neq 0$, the triangle shifts by an amount Q/ϵ_1 parallel to the ordinate. Now, momentum conservation requires also the collision points to lie within the closed curves of this



XBL 695-4244

Figure 35. Internal versus kinetic energy of products from various bimolecular pick-up reactions.

plot. The upper and lower boundary represent the two extreme cases described previously. Only quantum mechanical calculations can determine the probability with which a particular point within these boundaries is realized as a real collision..

The upper boundaries of the curves CH, CH₂ are, over a wide range, almost identical with the diagonal, i.e. the product molecule (C₆H₅·) from which the hydrogen molecule is stripped does not have any kinetic energy. This area describes the case of the "spectator stripping" mechanism,^{43,148} a dominant mechanism in many high energy reactions. One realizes that spectator stripping can occur over a considerable range in which the ordinate values are small, i.e. where the CH, or CH₂, molecule has little internal energy (i.e. is relatively stable) but its kinetic energy is large. If we set an upper limit for $(q + Q)/\epsilon_1$ (e.g. 0.05), then one realizes that the minimum kinetic energy of the product of the CH is still very high (>0.45). However, one cannot, of course, predict how frequently such a process occurs. Assuming for the pick-up of hydrogen ideal spectator stripping, i.e. where

$$\frac{q + Q}{\epsilon_1} + \frac{\epsilon_2}{\epsilon_1} = 1,$$

one finds from equation (4) that

$$\frac{\epsilon_2}{\epsilon_1} = \frac{m_1}{m_2} = \frac{14}{15}, \quad \text{and} \quad \frac{q + Q}{\epsilon_1} = \frac{1}{15}.$$

That is, if one assumes as upper limit for q ca. 3 eV, one finds $\epsilon_1 = 45$ eV and $\epsilon_2 = 42$ eV, i.e. the pick-up reaction may occur for a carbon atom with 45 eV and produce a CH molecule with 42 eV kinetic and 3 eV internal energy.

The similarity of the curve for C_2 (pick-up of carbon) with that of CH and CH_2 makes it plausible that a stripping mechanism contributes to the formation of C_2 - fragments as well (whether there are also hydrogens attached to this fragment is of no consequence in this approach except that it may determine Q (see Appendix D) and thus determine the exact position of the diagonal, i.e. the upper boundary of the area). In any event, all C_2 fragments may retain a considerable portion ($>0.4\%$) of the initial kinetic energy, i.e. be fast and "free".

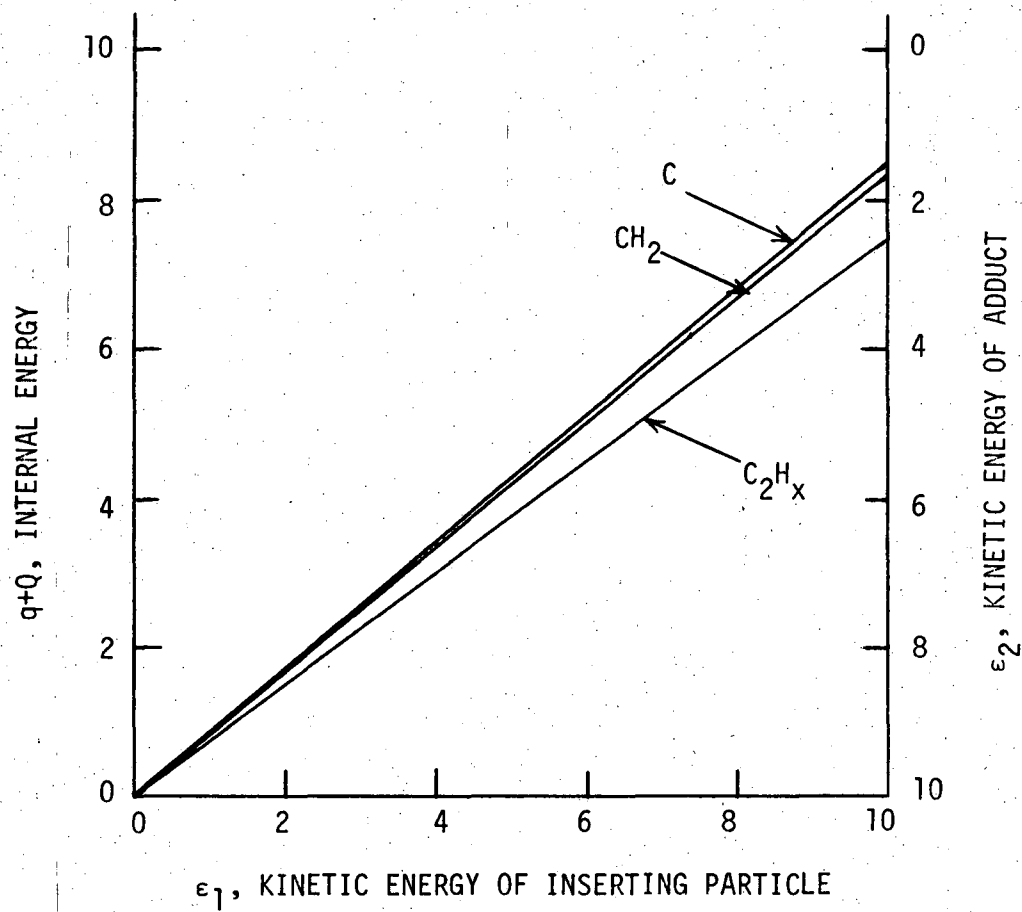
In order to demonstrate the difference to a reaction which must follow quite a different dynamic mechanism, we have also plotted a hypothetical "billiard-ball" type replacement of a ^{12}C by a ^{14}C atom. The curve " C_6H_6 - ^{14}C -reentry", running closely to the ordinate, corresponds to the above curves for pick-up reactions. For the product (^{14}C -benzene) to be able to survive successive collisions, its kinetic ϵ_2/ϵ_1 must be below a certain maximum. This limits the manifold of collision points to a rather small area near the zero point of this graph, the upper boundary being the steeply increasing "re-entry" curve.

Insertion Reactions

If there is only one product molecule formed in a collision ("complex"), the number of "degrees of freedom" (in this theoretical

approach) is decreased by one and the curve corresponding to CH-, etc., formation degenerates to a point. These must necessarily lie on the diagonal. (See points labeled "C-, CH₂-, C₂H_x- Insertion").

Figure 36 is perhaps a better representation for these cases. One realizes that the internal energy of the complex is always ca. 80% of the kinetic energy of the inserting particle. That is, the inserting particle must be sufficiently slow so that the complex has a chance to survive. Insertion reactions will, therefore, occur only at low energies (<4 eV).



XBL 695-4243

Figure 36. Internal versus kinetic energy in insertion reactions.

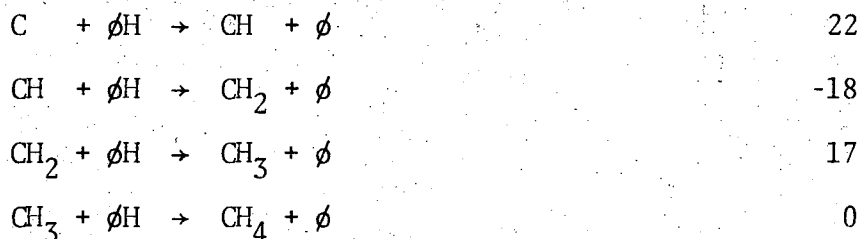
APPENDIX D

Enthalpy of Reaction Values for Several Reactions Considered in this Text:

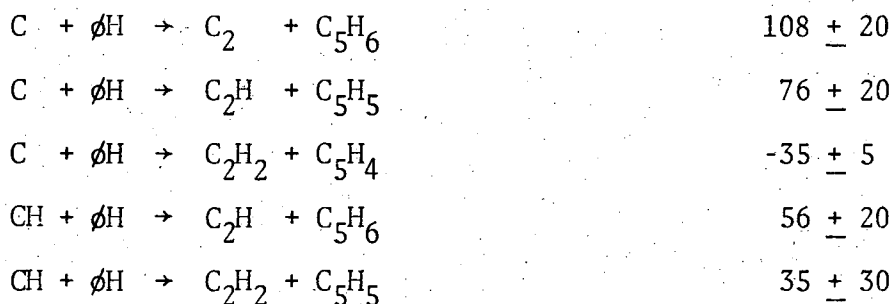
The first mentioned compound to the left of the arrow is always the carrier of the ^{14}C moiety and can in general be considered hot; the second, always benzene, is the "target" molecule. To the right of the arrow, only the first mentioned products are of interest; only these contain the ^{14}C atoms.

Reactions leading to CH_x

ΔH_o° (Kcal $\cdot$ mole $^{-1}$)

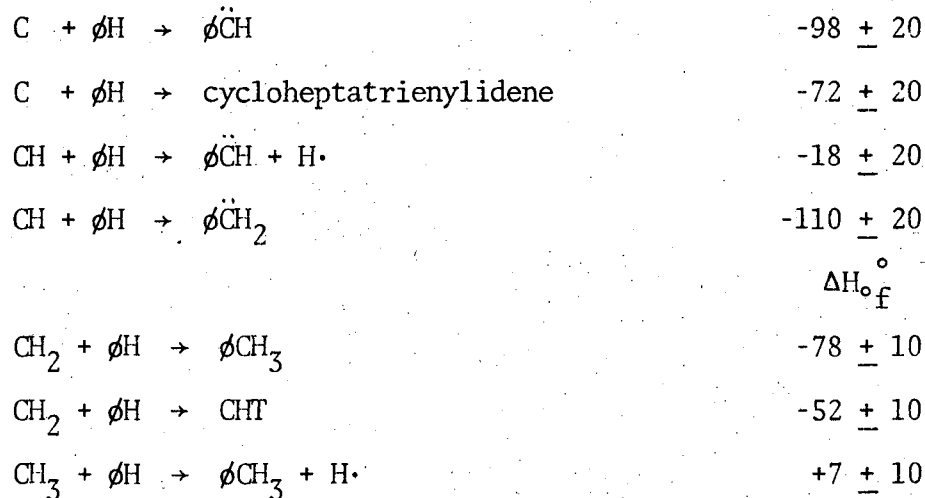


Reactions leading to C_2H_x

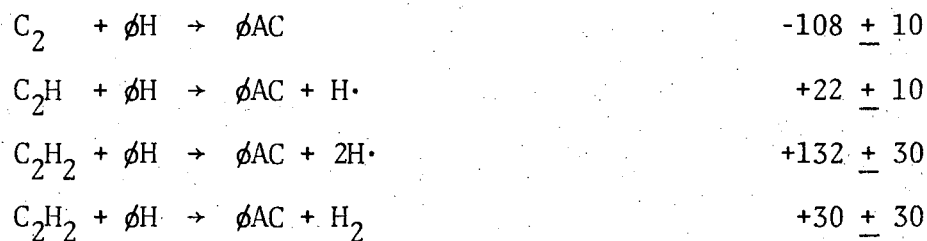


Reactions leading to C_7H_x

ΔH° (Kcal $\cdot$ mole $^{-1}$)



Reactions leading to C_8H_6 , phenylacetylene (ϕAC)

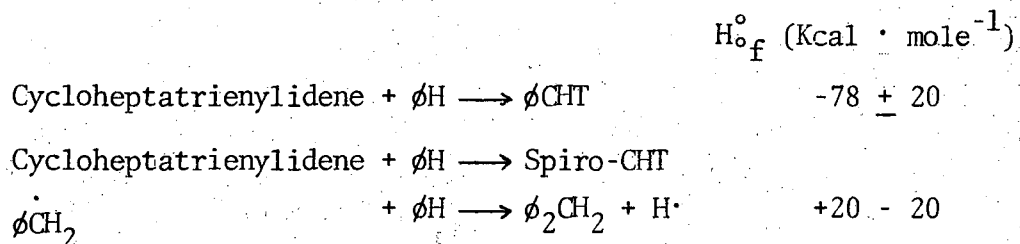


Reactions leading to ϕ_2



Reactions leading to $C_{13}H_{12}$





The above values were calculated via thermochemical cycles involving the following quantities (in Kcal $\cdot$ mole $^{-1}$):

			<u>References</u>
D (CH)	=	80	149
D (HC-H)	=	>120	149
D (H ₂ C-H)	=	<92	149
D (H ₃ C-H)	=	101	149
D (ϕ -H)	=	102	149
D (C ₂)	=	143	149
D (H ₂)	=	103.2	149,150
D (HC ₂ -H)	=	<121	149
D (CH ₃ - ϕ)	=	87 (?)	149

$\Delta H_{\text{of}}^{\circ}$ for toluene: 20, calculated from D (CH₃- ϕ) = 87.

D (ϕCH_2 -H)	=	77.5 (?)	149
D (ϕCH -H)	=	100 $\pm$ 20, estimated	
D (ϕ -C ₂ H)	=	80 $\pm$ 10, estimated	
D (C ₂ -H)	=	130, calculated	149,151
$\Delta H_{\text{of}}^{\circ}$ (benzene)	=	24	150
$\Delta H_{\text{of}}^{\circ}$ (C ₂ H)	=	117, calculated as <124	149-151
$\Delta H_{\text{of}}^{\circ}$ (C ₂ H ₂)	=	54.3	150
ΔH_{298}° (CHT)	=	43.5	152

$$\Delta H_{\text{f}}^{\circ} (\text{CHT}) = 46, \text{ calculated}^{(150,152)}$$

$$\Delta H_{\text{r}}^{\circ} (\text{CHT} \rightarrow \text{cycloheptatrienyldiene} + 2\text{H}) = 180 \pm 20, \text{ estimated}$$

$$\Delta H_{\text{r}}^{\circ} (\text{CH}_3 \rightarrow \text{CH} + 2\text{H}) = 180 \pm 20, \text{ estimated}$$

$$\Delta H_{\text{f}}^{\circ} (\text{CH}_4) = -16^{(150)}$$

$$\Delta H_{\text{f}}^{\circ} (\text{Cyclopentadiene}) = 25.2^{(151)}$$

$$\Delta H_{\text{f}}^{\circ} (\text{C}_5\text{H}_4) = 105 \pm 5, \text{ averaged from similar compounds}^{(151)}$$

$$\Delta H_{\text{f}}^{\circ} (\text{Cgas}) = 170^{(150)}$$

$$\Delta H_{\text{r}}^{\circ} (\text{n-C}_5\text{H}_6 \rightarrow \text{n-C}_5\text{H}_5) = 100 \pm 20, \text{ estimated}$$

$$\Delta H_{\text{r}}^{\circ} (\text{cy-C}_5\text{H}_6 \rightarrow \text{n-C}_5\text{H}_6) = 80 \pm 20, \text{ estimated}$$

APPENDIX E

The S/K-Method

In this appendix, a method is suggested which might be of use in the investigation of kinetic problems, some of which have been described in this thesis, i.e. those involving high-energy species and multiple collisions in the chemical energy range.

The general idea is as follows: Since at velocities below the Bohr-limit the prime energy loss from fast particles occurs through "elastic" collisions with whole atoms in the target, a large number of secondary atoms will be created if the energy of liberation of this atom is less than the kinetic energy of the fast particle. The secondary atoms, in turn, will be slowed by the same processes and create secondary atoms themselves, etc. In the case of fast ^{14}C -atoms in benzene, many of the daughter atoms are ^{12}C -atoms which may undergo the same reactions as the fast ^{14}C -atom, that is, besides the ^{14}C -labeled products there will also be produced the corresponding ^{12}C -products. To determine their yields, the secondary collision function, S (corresponding to K for the primary atom), has to be calculated. It turns out that S can be expressed in terms of K in the following way:

$$S(E) = f(E) \cdot K(E) , \quad \text{where} \quad f(E) > 1$$

is a strongly increasing function for decreasing E. The yield ratios of ^{12}C to ^{14}C products is, therefore

$$R \equiv \frac{{}^{12}\text{Y}}{{}^{14}\text{Y}} = \frac{\int_{E_a}^{E_{\max}} S(E) \cdot r(E) \cdot dE}{\int_{E_a}^{E_{\max}} K(E) \cdot r(E) \cdot dE} = 1 + \frac{\int_{E_a}^{E_{\max}} (f-1) \cdot K \cdot r \cdot dE}{\int_{E_a}^{E_{\max}} K \cdot r \cdot dE}$$

i.e. it is the smaller the larger $E_{\max}$ and E_a are. Thus, this ratio varies for different shapes and locations of r . By determining the "natural specific activity" (R^{-1}) of the products in the irradiation sample, one might thus be able to gain some more information with regard to the main features of the reactivity curves.

This method is entirely within the scope of kinetic theory as it has been applied to hot-atom chemistry,^{6,12,112-114} and it forms an adjunct to the moderator experiments. Its accuracy improves, of course, as more detailed kinetic data become available. However, it requires a high detection sensitivity for the ^{12}C -compounds, whereas the detection and mass determination of the ^{14}C -compounds do not pose any problem. This method fails for the target molecule as product (benzene), and whenever ^{12}C -products can be formed through other routes (e.g. biphenyl).

Required Detection Sensitivity

For 10 KeV primary ^{14}C -ions the ratio S/K at 10 eV is approximately $10^2 - 10^3$. With a 1% product yield and a $1\ \mu\text{A}$ $^{14}\text{C}^+$ -beam strength approximately 10^{16} molecules (ca. 10^{-5} g) of a particular ^{12}C -product are formed per hour. Separation of the products must be made on glc.

Methods for the Determination of the Yield Ratio R

1) Mass spectrometer: This is the most sensitive method (ca. 10^{-9} g). It also permits the ratio determination in conjunction with the glc separation in one measurement: Ratio of ^{14}C -parent ion to ^{12}C -parent ion intensity from the mass spectrometer output.

2) Glc/proportional counter: The total amount per ^{12}C -product is barely detectable with heat-conductivity detection, and absolute values may be rather inaccurate.

3) Perhaps the cheapest and most accurate method is the following: Products are trapped as they emerge from glc and dissolved in ca. 150 μl ethanol. A 5 cm glass capillary-cuvette (volume 150 μl) is filled with this solution and the concentration determined by UV. The activity concentration is determined for a known volume of the same solution in a liquid-scintillation counter.

Experiments

In order to test the feasibility of the suggested method, benzene was irradiated with a $^{12}\text{C}^+$ -ion beam and the whole sample

injected on glc (CW 20M, same conditions as previously discussed). Product peaks were observed and the trapping of the products was successful also. However, the UV spectra showed large background absorptions due to either column liquid-phase bleed-off or other effluent background, making the quantitative determination of the ^{12}C -content impossible. Further purification was difficult for some compounds because of detection problems.

Nevertheless, the GL-chromatogram showed that ^{12}C -toluene, ^{12}C -cycloheptatriene, and ^{12}C -phenylacetylene were formed in much lower yields than ^{12}C -diphenylmethane and ^{12}C -phenylcycloheptatriene, and lower, also, than would be expected from the corresponding ^{14}C -yield ratios. This indicates that the precursors for toluene, cycloheptatriene, and phenylacetylene are formed, on the average, at much higher energy than the other compounds or their precursors, in agreement with the conclusions of Chapter III, 4.

Calculation of the Secondary Collision Function

As in Chapter III, 2, the primary particle collision function is defined by

$$K(E) = k(E, E_B) + \int_E^{E_B} k(E, \epsilon) \cdot K(\epsilon) d\epsilon, \quad (1)$$

where

$k(E_2, E_1)$ probability that the colliding (primary)

particle of energy E_1 will have the energy E_2 after the collision

E_B beam energy

E energy

ϵ integration variable, energy.

If the beam particle is distinguishable from the target particles, the secondary collision function $S(E)$ is defined by

$$S(E) = k(E_B - E, E_B) + 2 \int_E^{E_B} S(\epsilon) \cdot k(E, \epsilon) d\epsilon + \int_E^{E_B} K(\epsilon) \cdot k(E - \epsilon, \epsilon) d\epsilon . \quad (2)$$

It is assumed again that

$$k(E_2, E_1) = \frac{1}{E_1} , \quad (3)$$

i.e. that the dynamics of the system can be described as if the collisions occur isotropically between free target molecules with masses equal to that of the beam particle.

Equation (2) becomes

$$S(E) = \frac{1}{E_B} + 2 \int_E^{E_B} \frac{1}{\epsilon} S(\epsilon) d\epsilon + \int_E^{E_B} K(\epsilon) \frac{1}{\epsilon} d\epsilon . \quad (4)$$

Differentiation of (4) with respect to E yields

$$\frac{dS}{dE} = -\frac{2}{E} S(E) - \frac{K}{E} \quad (5)$$

The solution of (1), with assumption (3), is

$$K = \begin{cases} \frac{1}{E} & \text{for } E \leq E_B \\ 0 & \text{for } E > E_B \end{cases} \quad (6)$$

The solution of (5), with K from (6), is

$$S(E) = -\frac{1}{E} + \frac{D}{E^2}, \quad (7)$$

where D is a constant which is determined by inserting (7) into (4):

$$D = 2 \cdot E_B, \quad \text{and}$$

$$S(E) = -\frac{1}{E} + \frac{2E_B}{E^2} \quad (= -K + S') \quad (8)$$

Since we are mostly interested in that part of S(E) where $\frac{E_B}{E} \gg 1$, the term $-\frac{1}{E}$ contributes negligibly much to S(E).

The ratio S/K is therefore

$$\frac{S}{K} = \frac{2E_B}{E}, \quad \text{and} \quad (9)$$

$$S(E) = f(E) \cdot K(E), \quad \text{where} \quad (10)$$

$$f(E) = \frac{2E_B}{E} > 1 \quad \text{and increases for decreasing energy } E. \quad (11)$$

In the above calculation it was assumed that the energy of liberating a secondary atom E_L is zero. The solution for S is therefore good only if E and E_B are large compared with E_L . If this is not the case the influence of E_L upon $S(E)$ can be determined through a correction at $k(E_2, E_1)$:

$$k(E_2, E_1) = \frac{1}{E_1} \cdot \frac{E_1 - E_L}{E_1} \quad (12)$$

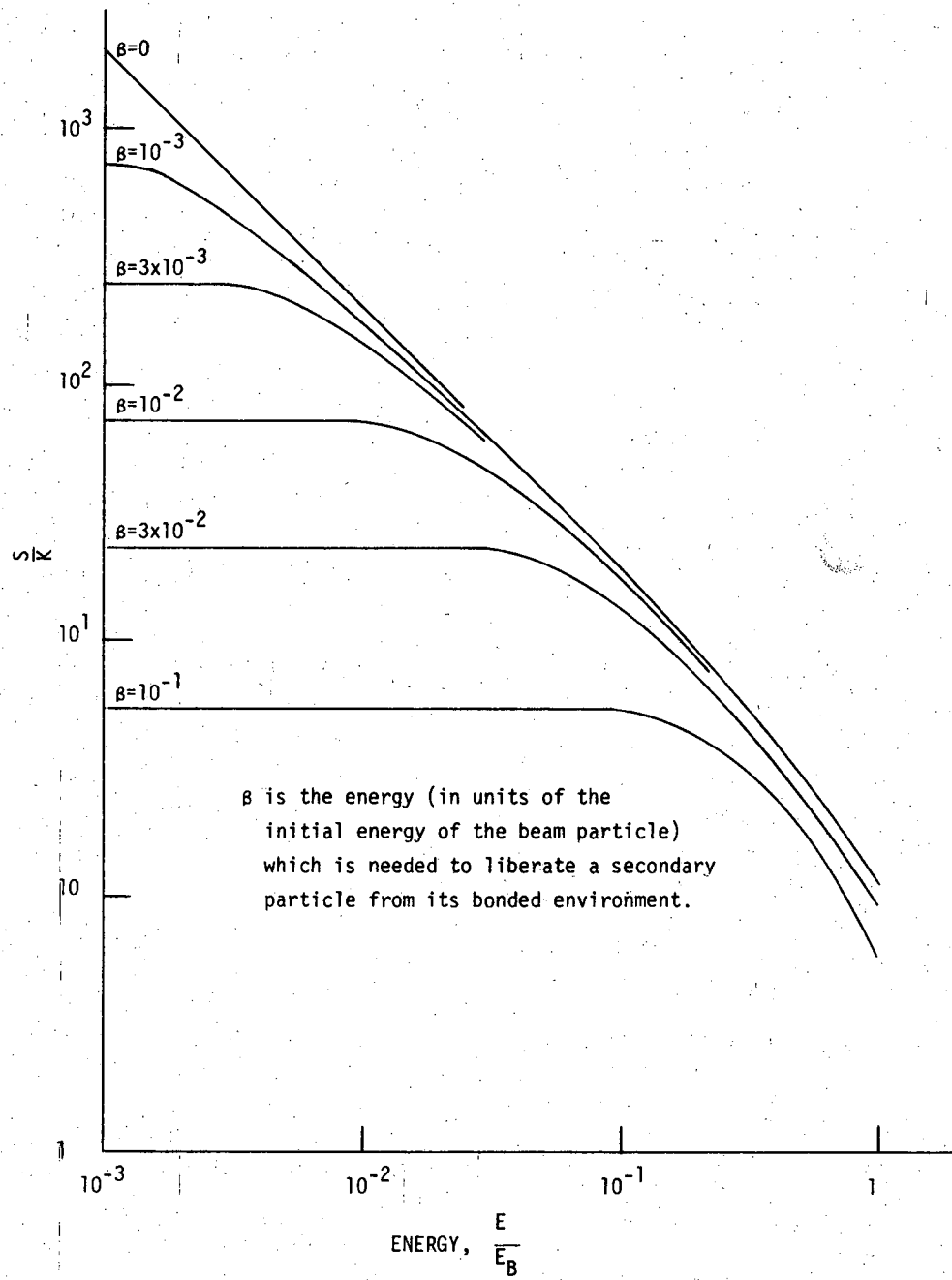
The integral equation for $S(E)$ is now

$$\begin{aligned} S(E) = & \frac{1}{E_B} \cdot \frac{E_B - E_L}{E_B} + \int_E^{E_B} \frac{1}{\epsilon} \cdot K(\epsilon) \cdot \frac{\epsilon - E_L}{\epsilon} d\epsilon \\ & + \int_E^{E_B} S(\epsilon) \cdot \frac{1}{\epsilon} d\epsilon + \int_E^{E_B} \frac{\epsilon - E_L}{\epsilon} \cdot \frac{1}{\epsilon} \cdot S(\epsilon) d\epsilon \quad (13) \end{aligned}$$

Solving (13) in the same manner as (4) yields

$$S(E) = -\frac{1}{E} + \frac{E_B}{E^2} \left(2 - \frac{E_L}{E_B}\right) \cdot e^{-\frac{E_L}{E_B}} \cdot e^{-\frac{E_L}{E}} \quad (14)$$

$-\frac{E_L}{E_B} \cdot \exp\left(-\frac{E_L}{E_B}\right)$ describes the deviation of $S(E)$ (according to [8]) if $E_L \approx E_B$. In most cases, however, this correction is negligible. $\exp\left(-\frac{E_L}{E}\right)$ describes the correction for $S(E)$ in the range where $E \geq E_L$. In Figure 37 are plotted the ratios S/K versus energy for different values $\frac{E_L}{E_B}$ ($\approx \beta$). " $\beta = 0$ " is $S(E)$ according to



XBL 695-4256

Figure 37. Ratios of secondary to primary particle collision density versus energy (in units of the beam energy E_B), for various values of β .

(8). All energies are expressed in terms of the initial energy E_B . (This transformation also transforms $S(E)$ and $K(E)$; however, the ratio S/K is invariant.)

The ratio S/K is constant if $E \leq E_L$. The relative change of S/K for $E \geq E_L$ is approximately independent of $\frac{E_L}{E_B}$. This indicates that not much information will be gained by determining the $^{12}\text{C}/^{14}\text{C}$ -yield ratios as a function of the initial energy -- except possibly an approximate value for E_L .

Secondary collision functions were also calculated for the case of unequal masses between beam and target particles. In this case, equation (4) has to be solved separately for separate energy intervals. This leads through a recursion procedure to an asymptotic solution for $S(E)$. However, the more realistic case of a target consisting of a mixture of atoms with different masses requires the solution of a system of integral equations for the secondary collision functions for the different atoms. The recursion method fails and analytic solutions can be obtained only with very simplifying assumptions. For moderator experiments the possibly numerical solution of this system of integral equations may be profitable.

REFERENCES

1. L. Szillard and T. Chalmers, Nature 134, 462 (1934).
2. R. Wolfgang, R. N. Zare and L. M. Branscomb, Science 162, 818 (1968).
3. B. H. Mahan, Acc. Chem. Research 1, 217 (1968).
4. P. S. Skell and R. R. Engel, J. Am. Chem. Soc. 88, 4883 (1966).
5. J. L. Sprung, S. Winstein and W. F. Libby, J. Am. Chem. Soc. 87, 1812 (1965).
6. J. M. Miller and R. W. Dodson, J. Chem. Phys. 18, 865 (1950).
7. M. A. Menzinger, Ph.D. Thesis, Yale University, 1968.
8. H. M. Pohlit, T. H. Lin and R. M. Lemmon, J. Am. Chem. Soc., In Press.
9. S. Wexler, "Primary Physical and Chemical Effects Associated with Emission of Radiation in Nuclear Processes," in Actions Chimiques et Biologiques des Radiations, Vol. 8, p. 105, ed. Haissinsky, Masson & Cie, Paris, 1965.
10. W. L. Fite, Excitation and Ionization Cross Sections, in Atomic and Molecular Processes, D. R. Bates, ed., Academic Press, p. 421, New York, 1962.
11. G. Placzek, Phys. Rev. 69, 423 (1946).
12. R. Wolfgang, Progress in Reaction Kinetics, 3, 97 (1965).
13. R. N. Porter, J. Chem. Phys. 45, 2284 (1966).
14. R. T. Mullen, Ph.D. Thesis, University of California, 1961, UCRL-9603.

15. F. R. Reynolds, UCRL-8618 (1959), p. 76.
16. M. A. Tuve, O. Dahl and L. R. Hofstad, Phys. Rev. 48, 241 (1935).
17. E. L. Yates, Roy. Soc. London Proc. A. 168, 148 (1938).
18. E. S. Lamar, W. W. Buechner and R. J. Van de Graaff, J. Appl. Phys. 12, 132 (1941).
19. E. S. Lamar, E. W. Samson and K. T. Compton, Phys. Rev. 48, 886 (1935).
20. E. S. Lamar, W. W. Buechner and K. T. Compton, Phys. Rev. 51, 936 (1939).
21. M. V. Ardenne, Tabellen Z. Angew. Physik, Bd. 1, VEB Deutscher Verlag der Wissenschaften, Berlin, 1962.
22. M. S. Livingston, M. G. Holloway and C. P. Baker, Rev. Sci. Instr. 10, 63 (1939).
23. B. Aliprandi, F. Cacace, L. Cieri, G. Giranni, R. Masironi and M. Zifferero, Ricerca Sci. 26, 3029 (1956).
24. A. G. Maddock, Private Communication.
25. J. B. Hasted, Charge Transfer and Collisional Detachment, Atomic and Molecular Processes, Academic Press, D. R. Bates, ed., p. 711, 1962.
26. S. Dushman, Vacuum Technique, John Wiley & Sons, London, 1949.
27. W. H. Zinn, Phys. Rev. 52, 655 (1937).
28. A. G. Sharkey, Jr., C. F. Robinson and R. A. Friedel, in Adv. in Mass Spectrometry, Pergamon Press, London, 1959, p. 193.
29. American Institute of Physics Handbook, 2nd Ed., McGraw-Hill, New York, 1963, p. 5-151.
30. W. R. Arnold, Rev. Sci. Instr. 23, 97 (1952).

31. "Handbuch der Physik," Vol. XXI, XXII, S. Flügge, ed., Springer, Berlin, 1956.
32. R. S. Freund and W. Klemperer, J. Chem. Phys. 47, 2897 (1967).
33. Handbook of Chem. & Phys., 42nd Ed., 1960, Chemical Rubber Publishing Company.
34. M. Inoue, T. Watanabe and A. Danno, Japan. J. Appl. Phys. 3, 761 (1964).
35. R. M. S. Hall, Nature 187, 683 (1960).
36. J. W. McConkey, D. J. Burns and J. M. Woolsey, J. Phys., B., Proc. Phys. Soc. Ser. 2, Vol. 1, 71 (1968).
37. H. D. Hagstrum, Rev. Mod. Phys. 23, 185 (1951).
38. R. N. Dixon, Proc. Roy. Soc. 275A, 431 (1963), and Disc. Farad. Soc. 35, 105 (1963).
39. S. E. Kuprianov, M. V. Tikhomirov, V. K. Potapov and P. Ja. Karpova, J.E.T.P. 3, 459 (1956).
40. C. Ottinger, Z. Naturf. 22a, 20 (1967).
41. F. H. Field and J. L. Franklin, "Electron Impact Phenomena", Acad. Press, N. Y., 1957.
42. R. Fuchs and R. Taubert, Z. Naturf. 20a, 823 (1965).
43. A. Henglein and G. A. Muccini, Z. Naturf. 18a, 753, 757 (1963).
44. M. Kaminsky, Atomic and Ionic Impact Phenomena on Metal Surfaces, Academic Press, Inc., New York, 1965.
45. J. A. Simpson, Rev. Sci. Instr. 32, 1283 (1961).
46. Reference 21, p. 651.
47. H. Thonemann, Progr. Nucl. Phys. 3, 177 (1963).

48. M. J. Kofoed, C. M. Braams and P. Zieske, *Rev. Sci. Instr.* 36, 1415 (1965).
49. J. B. Hasted, *Proc. Roy. Soc. London*, A 212, 235 (1952).
50. H. B. Gilbody and J. B. Hasted, *Proc. Roy. Soc. London*, A 238, 334 (1956).
51. A. P. J. Willmore, Ph.D. Thesis, University of London, London, 1955.
52. E. Gustafsson and E. Lindholm, quoted in *Atomic and Molecular Processes*, D. R. Bates, ed., Academic Press, Inc., 1962, p. 705; H. van Koch and E. Lindholm, *Arkiv för Fysik* 19, 123 (1960).
53. M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. S. Yankwich, "Isotopic Carbon", John Wiley & Sons, New York, 1949, p. 163.
54. R. J. Cvetanovic, Private Communication.
55. M. Ardon, "Oxygen", W. A. Benjamin, New York, 1965.
56. R. J. Cvetanovic, *J. Chem. Phys.* 25, 376 (1956); 41, 3703 (1964).
57. F. Seitz and J. S. Koehler, *Solid State Physics*, Vol. 2, Academic Press, Inc., New York, 1956, p. 305.
58. A. von Hippel, *Ann. Phys.* 80, 672 (1926); 81, 1043 (1926).
59. C. H. Townes, *Phys. Rev.* 65, 319 (1944).
60. J. A. Brinkman, *J. Appl. Phys.* 25, 961 (1954).
61. M. W. Thompson and R. S. Nelson, *Philos. Mag.* 7, 2015 (1962).
62. F. Keywell, *Phys. Rev.* 97, 1611 (1955).
63. D. K. Nichols and V. A. J. van Lint, in *Solid State Physics*, Academic Press, Inc., New York, Vol. 18, 1966, p. 1.

64. O. B. Firsov, Sov. Physics, **J.E.T.P.** (Engl. transl.) 6, 534 (1958).
65. K. O. Nielsen, Electromagnetically Enriched Isotopes and Mass Spectrometry, Academic Press, Inc., New York, 1956, p. 68.
66. N. Bohr, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 18, No. 8 (1948).
67. J. Lindhard and M. Scharff, Phys. Rev. 124, 128 (1961).
68. J. O. McCaldin, Nucl. Instr. Methods 38, 153 (1965).
69. Yu. V. Martynenko, Fiz. Tverdogo Tela. 9, 3646 (1967); Sov. Phys. Solid State 9, 2879 (1968).
70. S. Zwerdling and R. S. Halford, J. Chem. Phys. 23, 2215 (1955).
71. R. S. Bradley, in The Art and Science of Growing Crystals, J. J. Gilman, ed., John Wiley & Sons, Inc., New York, 1963, p. 55.
72. R. Becker, Disc. Faraday Society, No. 5, 55 (1949).
73. E. G. Cox, D. W. J. Crickshank and J. A. S. Smith, Proc. Roy. Soc. A247, 1 (1958).
74. V. M. Koshin and A. I. Kitaigorodski, Zhur. Fiz. Khim. 29, 2074 (1955).
75. S. Nikolaev, I. S. Dimitrico, L. N. Fateeva and Ia. A. Teplova, **J.E.T.P.** (Engl. transl.) 6, 1019 (1958).
76. J. Neufeld, ORNL-2365.
77. V. S. Nikolaev, I. S. Dimitriev, L. N. Fateeva and Ja. A. Teplova, Sov. Phys., **J.E.T.P.** 12, 627 (1961).

78. R. L. Wolke and V. J. Sodd, in Atomic Collision Processes, McDowell, ed., North-Holland Publ. Co., Amsterdam, 1964, p. 700.
79. J. B. Hasted, Proc. Roy. Soc. London A 205, 421 (1951).
80. Ja. Fogel, R. V. Mitin and A. G. Koval, J.E.T.P. (Engl. Transl.) 4, 359 (1957).
81. Ja. M. Fogel, R. V. Mitin and V. F. Kozlov, Sov. Phys., Tech. Phys. 3, 1410 (1958).
82. Ja. M. Fogel, R. V. Mitin, V. F. Kozlov and N. D. Romashko, Sov. Phys., J.E.T.P. 35, 390 (1959).
83. J. A. Phipps, J. W. Boring and R. A. Lowry, Phys. Rev. 135, A36 (1964).
84. G. J. Hine and G. L. Brownell, Radiation Dosimetry, Academic Press, New York, 1956.
85. W. P. Jesse and J. Sadauskis, Phys. Res. 97, 1668 (1955).
86. P. M. Stier, Natl. Acad. Sci., Natl. Res. Council Publ. No. 29, p. 65 (1960).
87. H. S. W. Massey, Rep. Prog. Phys. 12, 248 (1949).
88. N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions, 2nd Ed., Clarendon Press, Oxford, England, 1952.
89. J. B. Hasted and A. R. Lee (London Physical Society), Proceed. Phys. Soc. (London) 79, 702 (1962).
90. Ja. M. Fogel, R. V. Mitin, V. F. Kozlov and N. D. Romashko, Sov. Phys., J.E.T.P. 35, 390 (1959).
91. S. Dworetsky, R. Novick, W. W. Smith and N. Tolk, Phys. Rev. Lett. 18, 939 (1967).

92. Gmelin Handbuch, Kohlenstoff, 8. Auflage, Teil B, Liefg. 1, 1968, p. 122.
93. E. Lindholm, Z. Naturf. 9a, 535 (1954).
94. A. G. Schrodtt and W. F. Libby, J. Am. Chem. Soc. 78, 1267 (1956).
95. A. P. Wolf, B. Gordon and R. Anderson, J. Am. Chem. Soc. 78, 2657 (1956).
96. R. M. Lemmon, F. Mazzetti, F. L. Reynolds and M. Calvin, J. Am. Chem. Soc. 78, 6414 (1956).
97. E. Rack, C. Lang and A. F. Voigt, J. Chem. Phys. 38, 1211 (1963).
98. D. E. Clark and A. F. Voigt, J. Am. Chem. Soc. 87, 5558 (1965).
99. T. Rose, C. MacKay and R. Wolfgang, J. Am. Chem. Soc. 89, 1529 (1967).
100. B. Suryanarayana and A. P. Wolf, J. Phys. Chem. 62, 1369 (1958).
101. R. M. Lemmon, R. T. Mullen and F. L. Reynolds, UCRL-9397 (1960).
102. A. F. Voigt, Private Communication (1968).
103. J. E. Willard, ~~Ann.~~ Rev. Phys. Chem. 6, 141 (1955).
104. A. P. Wolf, Adv. Phys. Org. Chem. 2, 201 (1964).
105. J. Dubrin, C. MacKay and R. Wolfgang, J. Am. Chem. Soc. 86, 4747 (1964).
106. J. Dubrin, C. MacKay and R. Wolfgang, J. Chem. Phys. 41, 3267 (1964).

107. M. Marshall, C. MacKay and R. Wolfgang, J. Am. Chem. Soc. 86, 4741 (1964).
108. J. M. Miller, J. W. Gryder and R. W. Dodson, J. Chem. Phys. 18, 579 (1950).
109. W. F. Libby, J. Am. Chem. Soc. 69, 2523 (1947).
110. R. J. Cross, Jr. and R. Wolfgang, J. Chem. Phys. 35, 2002 (1961).
111. Chi-Hua Hsiung, Ph.D. Thesis; University of Michigan, 1962.
112. P. J. Estrup and R. Wolfgang, J. Am. Chem. Soc. 82, 2665 (1960).
113. R. Wolfgang, J. Chem. Phys. 39, 2983 (1963).
114. C. Hsiung and A. A. Gordus, J. Chem. Phys. 39, 2770 (1963).
115. A. Rosenberg and R. Wolfgang, J. Chem. Phys. 41, 2159 (1964).
116. C. Hsiung, K. C. Verosub and A. A. Gordus, J. Chem. Phys. 41, 1595 (1964).
117. H. M. Pohlitz, T. H. Lin, W. Erwin and R. M. Lemmon, J. Am. Chem. Soc. (In Press).
118. A. P. ter Borg and H. Kloosterziel, Rec. Trav. Chim. 82, 741 (1963).
119. J. W. McGowan, P. Marmet and L. Kerwin, in Atomic Collision Processes", M. R. C. McDowell, ed., John Wiley & Sons, New York, 1964, p. 854.
120. W. B. DeMore and S. W. Benson, Adv. in Photochemistry 2, 219 (1964).
121. J. Dubrin, C. MacKay and R. Wolfgang, J. Am. Chem. Soc. 86, 959 (1964).

122. R. Willstätter, Ber. 31, 1544 (1898).
123. R. M. Lemmon, R. T. Mullen and F. L. Reynolds, in Chemical Effects of Nuclear Transformations, Vol. II, Vienna, 1961, p. 27.
124. F. Šantavý, Chem. Listy. 47, 1534 (1953).
125. G. Juppe and A. P. Wolf, J. Am. Chem. Soc. 83, 337 (1961).
126. W. J. Hickinbottom, Reactions of Organic Compounds, 3rd Ed., John Wiley & Sons, Inc., New York, 1962, p. 57.
127. V. Alder and G. Jacobs, Chem. Ber. 86, 1528 (1953).
128. T. H. Lin, Ph.D. Thesis, University of California, Berkeley, 1969.
129. A. P. TerBorg, H. Kloosterziel and N. VanMeurs, Rec. Trav. Chim. 82, 717 (1963).
130. E. Müller and H. Fricke, Ann. 661, 38 (1963).
131. R. G. R. Bacon and H. A. O. Hill, Quarterly Reviews, 19, 95 (1965).
132. W. von E. Doering and P. P. Casper, J. Am. Chem. Soc. 85, 3043 (1963).
133. W. R. Roth, Angew. Chem. 75, 921 (1963).
134. W. von E. Doering and W. R. Roth, Tetrahedron, 19, 715 (1963).
135. E. M. Milvitzkaya and A. F. Plate, J. General Chem. (Russ.) 32,8, 2566 (1962).
136. H. L. Holmes, Organic Reactions, 4, 81 (1948).
137. K. Wiberg and W. E. Bartley, J. Am. Chem. Soc. 82, 6375 (1960).
138. A. V. Bayer, Ann. 269, 189 (1892).

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or*
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.*

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720