Title

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Authors

Pohlit, Helmut M.
Erwin, Wallace.
Lin, Tz-Hong.
et al.

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Helmut M. Pohlit, Wallace Erwin, Tz-Hong Lin, and Richard M. Lemmon

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Hot-atom Chemistry of Carbon-14 Ions in Solid Benzene at Kinetic Energies between 5 and 100 eV[1]

by Helmut M. Pohlit, Wallace Erwin, Tz-Hong Lin, and Richard M. Lemmon

Laboratory of Chemical Biodynamics, Lawrence Radiation Laboratory, University of California, Berkeley, California 94720

The yields of seven major hydrocarbon products from the interaction of energetic carbon-14 ions with solid benzene (-196°) were determined for carbon ion energies between 5 and 100 eV. As one goes toward the lower kinetic energy, the yields of benzene, biphenyl, and diphenylmethane appear to remain essentially constant, that of phenylcycloheptatriene appears to increase, and those of toluene, cycloheptatriene, and phenylacetylene definitely decrease by a factor of 5 to 10. These results are additional support for previously postulated mechanisms, and lead to the conclusions that

1) hydrogen and carbon pick-up reactions proceed up to rather high kinetic energies (50-100 eV), and

2) insertions into carbon-hydrogen or carbon-carbon bonds with preservation of the adduct is limited to energies below 5 eV.

Introduction

In two previous papers we reported the identities, the yields between 100 eV and 15 KeV, and the partial degradations of the eight major products of energetic ^{14}C ions and atoms (from an ion accelerator) in solid benzene: benzene (B), toluene (T), cycloheptatriene (CHT)

phenylacetylene ($\phi C{\equiv}CH$), "U-2" (subsequently identified as benzaldehyde),[2] biphenyl (ϕ_2), diphenylmethane (ϕ_2CH_2), and phenylcycloheptatriene (ϕCHT).[3,4] As a result of recent improvements in the ion accelerator used in this work,[5] we have extended our studies to the 100-5 eV kinetic energy range. This paper reports the yields of the hydrocarbon products at these lower energies.

Experimental

The procedures for irradiations and yield determinations were identical to those described previously.[3] "Yield" is defined as the percent of the activity in an aliquot portion (of the target) that appears in the glpc peak of the product. The total activity in the target after an irradiation is roughly equal (80-100%) to the time-integral of the $^{14}C^+$-beam intensity.

The toluene degradations were performed via oxidation to benzoic acid followed by the hydrazoic acid (Schmidt) reaction to aniline and CO_2; the latter two compounds were purified by gas-liquid chromatography, and the activity determined in a liquid scintillation counter. Details of these procedures are given in the Ph.D. thesis of T. H. Lin.[6]

A recent report describes the electronic and mechanical details of the ion accelerator, and includes a discussion of the chemical identity (as well as the charge state) of the irradiating carbon species.[5]

Results

The yields of the products, as a function of the kinetic energy of the irradiating carbon, are shown in Figures 1-4. The energy measurements are accurate to within $\pm$2 eV. Because of the possibility of imperfect charge neutralization at the target, the actual energies of

our nominally 5 eV irradiations are more likely to be lower, rather than higher, than that figure. The yield data exhibit appreciable scattering; this is due to the trapping techniques for yield determinations,[3] and apparently is also due to imperfectly controlled irradiation conditions, such as the beam's density. Each point represents the average of 2-5 yield determinations from one irradiation.

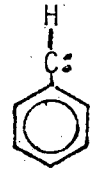
The activity distribution in the toluene product, as a function of the kinetic energy of the irradiating carbon, is shown in Table I. For comparison with our present results in the 5-100 eV range, we have included some earlier results obtained at higher energies.

Discussion

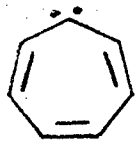
We interpret the strong decrease in the yields of toluene and cycloheptatriene from 100-5 eV as being caused by a decreasing chance for the irradiating carbon atoms to pick up hydrogens, presumably in sequence, to form the assumed precursor CH_2. The same applies for the assumed precursor to phenylacetylene, C_2H_x. These precursors probably react with a ground-state benzene molecule, via insertion and/or substitution, without subsequent disintegration. Guideline classical-mechanical calculations (the subject of a forthcoming paper) suggest that the latter reactions (insertion and substitution) can occur only at kinetic energies below 5 eV; at higher energies the collision complex would have scant chance to survive. In contrast, hydrogen pick-up reactions can proceed at rather high energies (possibly up to 50-100 eV; that is, the internal energy of the pick-up product (CH, etc.) may be only a very small fraction of the product's kinetic energy. There is good support in the literature for a hydrogen stripping

mechanism in the formation of CH and CH_2 from C and CH respectively.[7,8] The sharp decrease in our yields of phenylacetylene at carbon beam energies below 100 eV also indicates a C-stripping mechanism in the formation of C_2H_x.

Adduct formation is expected to require a substantial conversion of kinetic into internal energy, causing decomposition of the adduct unless its internal energy is only a little above bond energies ($\tilde{<}$ 5 eV) so that subsequent collisions quickly stabilize the product. The apparently unchanged yield of ϕ_2CH_2 and increased yield of ϕCHT are, therefore, interpreted here as being due to this energy limitation for the formation of the assumed precursors, benzylidene (I) and cyclo-heptatrienylidene (II)[4]



I



II

which subsequently react with another benzene molecule to form ϕ_2CH_2 and ϕCHT. The approximately constant yields of benzene and biphenyl point to intermediates in their formation of molecular weight similar to I or II. We are ignoring the "billiard-ball" hypothesis (which is, statistically, extremely unlikely) for the formation of our reentry product, benzene. We belive that the intermediate to benzene-^{14}C is a short-lived C_7H_6 adduct, and, considering the small energy range (between activation energy and less than approx. 5 eV) within which the intermediate's formation occurs, it is not unreasonable to assume that the precursors to biphenyl and benzene, and to the above two carbenes I and II, are but different manifestations of the same short-lived intermediate. Unfortunately, energy inaccuracies do not allow

us at present to probe into this most interesting energy range below 5 eV.

We do, however, have degradation data (Table I) from toluene formed in 5-eV experiments, and this data indicates a possible route, other than through a CH_2 intermediate, for toluene formation at or below that energy. (The degradation data for cycloheptatriene in this energy region, presented in the accompanying manuscript, is compatible with the CH_2 mechanism.) For the toluene, there is an essentially constant distribution of activity until the 5 eV region is reached; at this energy there is a great increase in ring activity (Table I). This is in contrast to toluene-^{14}C formed from photolytic $^{14}CH_2$ (with a maximum K.E. of 1.7 eV[4]); in this case the activity is entirely in the methyl group. One interpretation of these data is that a bare carbon atom, rather than CH_2, first interacts with benzene (in the below-5 eV region) in the mechanism leading to toluene. That such a process should suddently appear only in the below-5 eV energy region is a matter for further investiation--it may be that a particular spin state of carbon is present only in the nominally 5 eV irradiations. A discussion of this possibility is given in the thesis of T. H. Lin.[6]

Table I

Toluene-^{14}C Activity Distributions (%)

	K.E. of irradiation carbon, eV					
Position	5,000[a]	4,000	500[a]	100[a]	31	5
Me	85	84	82	80	83	29
ring	13	14	16	15	12	66

[a]Previously reported in ref. (4).

We have previously discussed the likelihood that the carbon ions of our beams are rapidly neutralized after the ions enter the target.[3] However, at lower energies, not only elastic collisions but possibly also reactive collisions may compete successfully with neutralization, and it might be argued that the decrease of yields of T, CHT, and $\phi C{\equiv}CH$ is just a representation of this competition.

References

(1) The work reported here was supported by the U. S. Atomic Energy Commission and by a grant to one of us (HMP) from the Bundesministerium für Wissenschaftliche Forschung and the Deutscher Akademischer Austauschdienst of West Germany.

(2) The increasing yield with decreasing energy of this product indicates, as does the appearance of oxygen, an origin foreign to the expected hot atom chemistry. Its appearance will be the subject of a forthcoming paper.

(3) H. M. Pohlit, T. H. Lin, W. R. Erwin, and R. M. Lemmon, J. Am. Chem. Soc., 91, 5421 (1969).

(4) H. M. Pohlit, T. H. Lin, and R. M. Lemmon, ibid., 91, 5425 (1969).

(5) H. M. Pohlit, et al., Rev. Sci. Inst., 41, 1012 (1970).

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(7) A. Henglein and G. A. Muccini, Z. Naturforsch., B, 18, 753 (1963).

(8) A. Henglein and G. A. Muccini, ibid., 17a, 452 (1962).

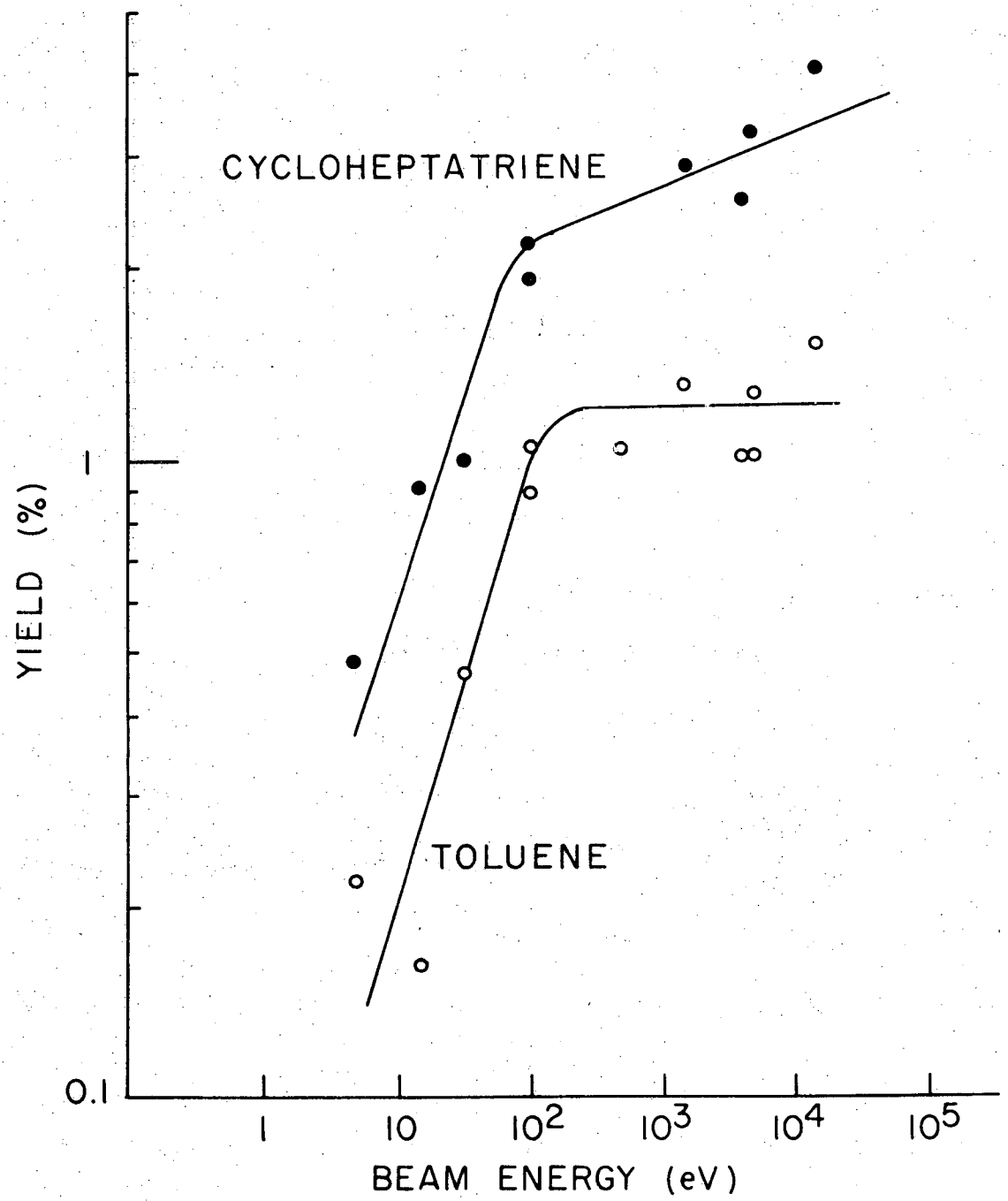

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Figure 1. Yields of cycloheptatriene (●) and toluene (○) versus $^{14}C^-$ ion energy.

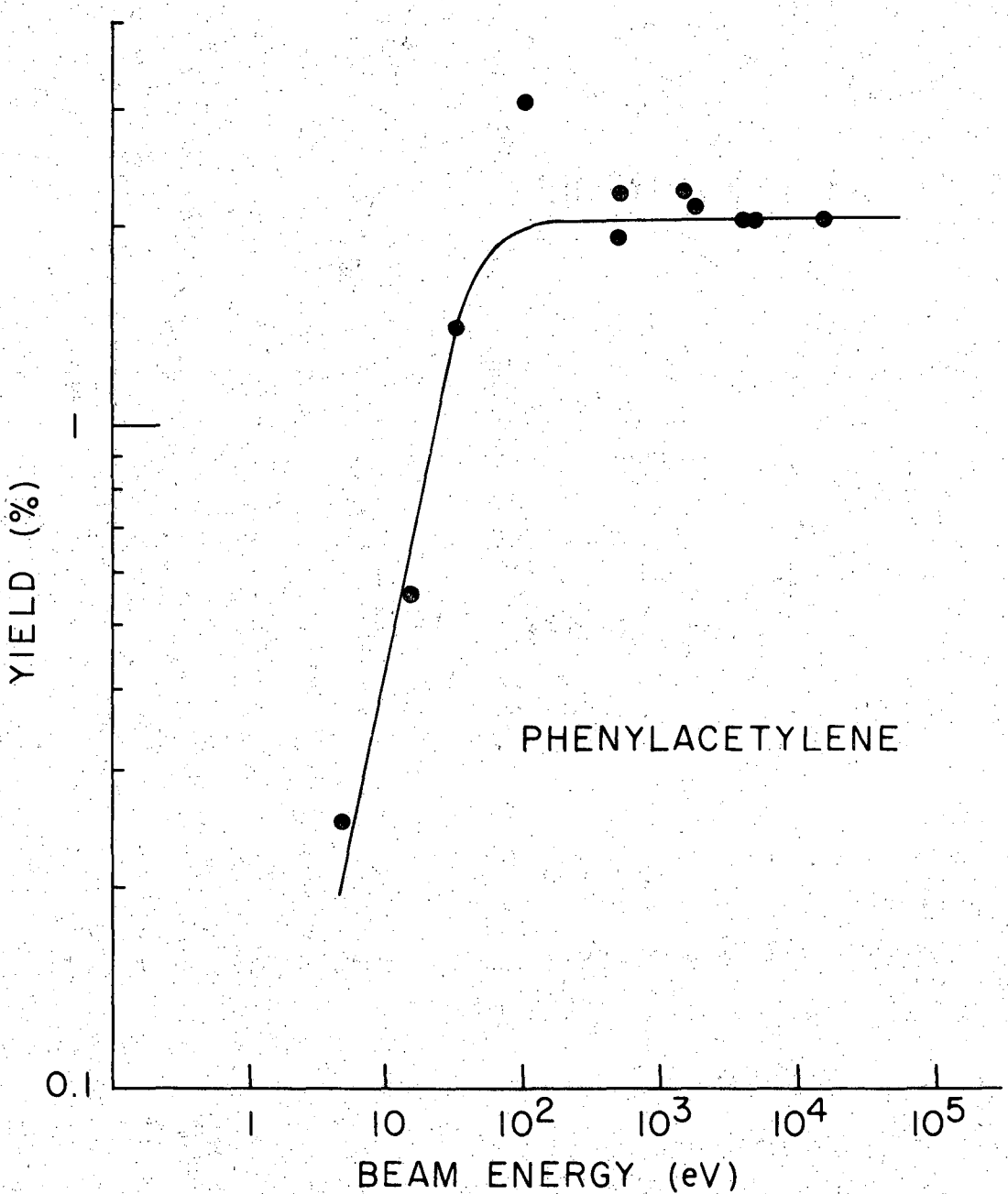

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Figure 2. Yields of phenylacetylene versus $^{14}C^+$ ion energy.

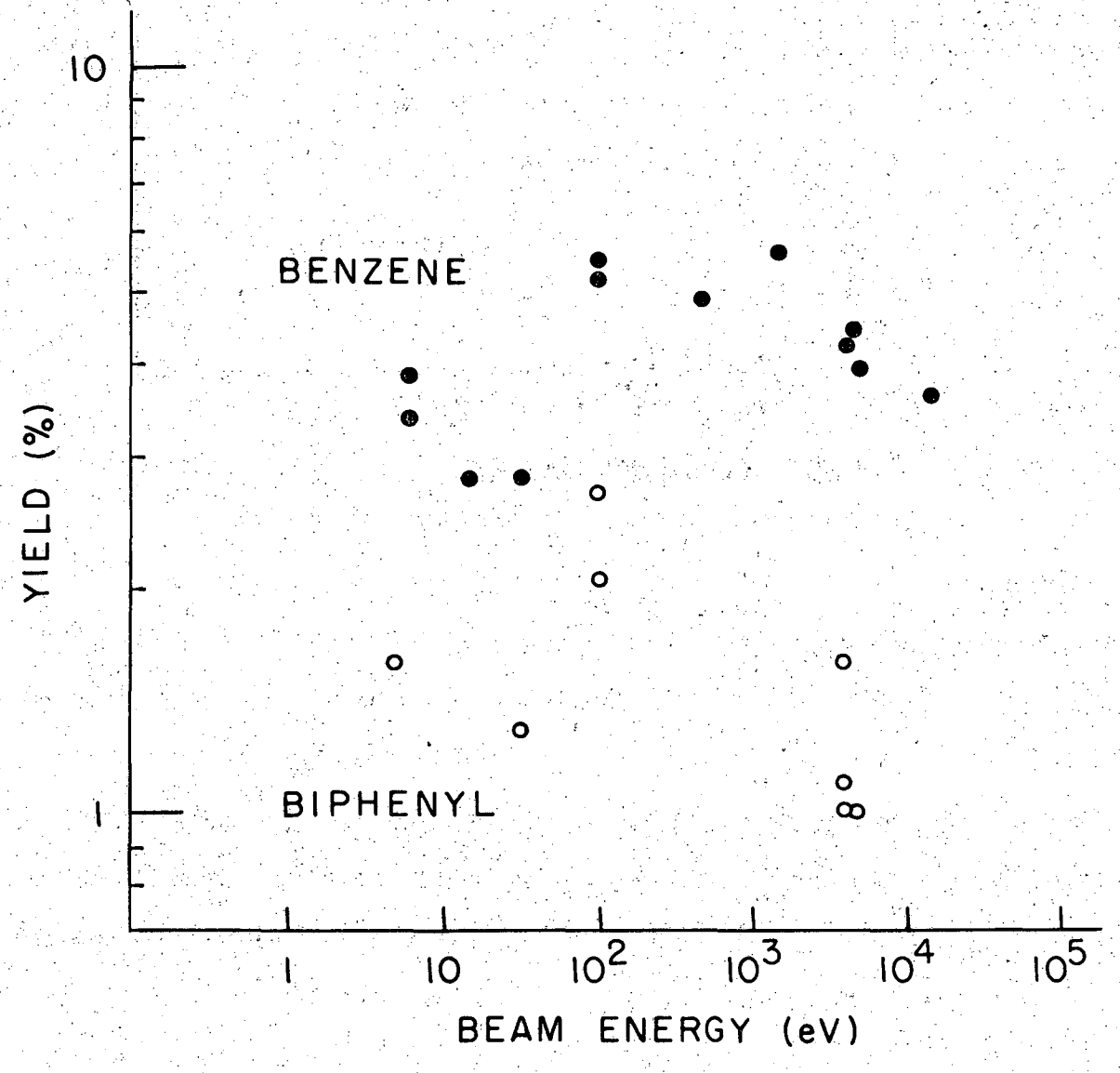

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Figure 3. Yields of benzene (●) and biphenyl (○) versus $^{14}C^+$ ion energy.

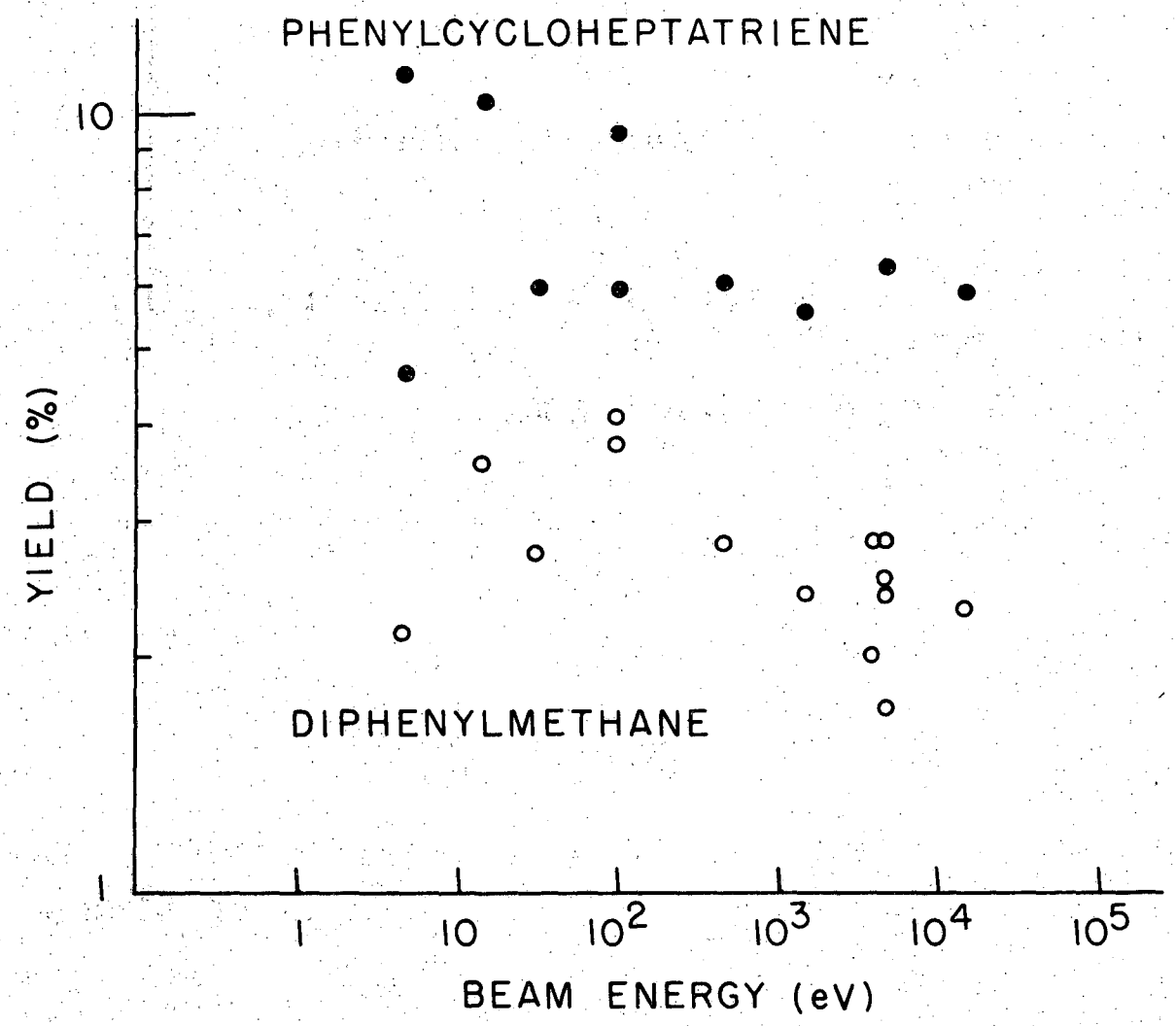

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Figure 4. Yields of phenylcycloheptatriene (●) and diphenylmethane (○) versus $^{14}C^+$ ion energy.

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LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720