

Lawrence Berkeley National Laboratory

Recent Work

Title

GAS KINETICS

Permalink

<https://escholarship.org/uc/item/7sj19803>

Author

Mahan, Bruce H.

Publication Date

1965-12-01

University of California

**Ernest O. Lawrence
Radiation Laboratory**

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*

GAS KINETICS

Berkeley, California

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.

Submitted to Annual Review of
~~Physics~~ *Physical Chemistry*

UCRL-16612

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

GAS KINETICS

Bruce H. Mahan

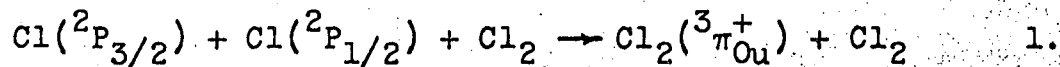
December, 1965

ELEMENTARY ATOM REACTIONS

Interest in this general area continued undiminished, and some of the problems that have persisted a number of years appear to have been solved satisfactorily. In some of the most recent work, emphasis is on the study of "new" atoms like sulfur and carbon, and on the investigation of the properties of atomic excited states.

Recombinations.-

The recombination of chlorine atoms from an electrical discharge has been studied by Bader and Ogryzlo (1,2) and by Hutton and Wright (3,4). The recombination proceeds by parallel nonradiative and radiative paths, with the latter involving the ($A^3\pi_{Ou}^+ \rightarrow {}^1\Sigma_g^+$) transition of the chlorine molecule. The intensity of the emission is proportional to the square of the chlorine atom concentration at all pressures investigated. According to Hutton and Wright (4), the light intensity is proportional to the molecular chlorine concentration at pressures lower than 2 mm, and independent of this quantity at pressures above 3 mm. The data of Bader and Ogryzlo (2) are not extensive enough to check this point. The existing data on the radiative recombination can be explained by



This mechanism is adequate, but not unique. Hutton and Wright find $k_1 = 0.94 \times 10^9$ liter²/mole²sec, and $k_2/k_3 = 2.7 \times 10^{-5}$ liter/mole. When the third body is argon, $k_1 = 2.35 \times 10^8$ liter²/mole² sec.

In their study of the nonradiative recombination, Hutton and Wright (4) found that the second order constant for the recombination reaction decreased as the chlorine atom concentration increased. This interesting feature is consistent with the atom-molecule complex mechanism:



$$\frac{-d(\text{Cl})}{dt} = \frac{2k_4k_6[\text{Cl}]^2[\text{Cl}_2]}{k_5 + k_6[\text{Cl}]}$$

In the limit of low chlorine atom concentration, k_4k_6/k_5 can be evaluated and is equal to 2.04×10^{10} liter²/mole²sec. This is in substantial agreement with the work of Bader and Ogryzlo (1) who found 2.7×10^{10} for the same quantity.

The radiative recombination of bromine atoms has been investigated by Gibbs and Ogryzlo (5), and behavior similar to that of the chlorine system found. The light intensity is proportional to the square of the bromine atom concentration, and to the first power of the bromine molecule concentration. The emission is a banded spectrum corresponding to the (${}^3\pi_{\text{Ou}}^+ \rightarrow {}^1\Sigma_g^+$) transition of the bromine molecule. No unique mechanism for population of the ${}^3\pi_{\text{Ou}}^+$ state has been assigned.

The dissociation of molecular chlorine in a shock tube in the temperature range from 1600 to 2600°K has been studied by Britton and coworkers (6). These authors correct for the light emission due to recombining chlorine atoms, and suggest that discrepancies among earlier investigations of this system are due to failure to make this correction. The value of the second order rate constant for dissociation is expressed as $\log k_D = 10.66 - 9930/T$ (liter/mole sec) where molecular chlorine is the collision partner. This corresponds to an activation energy of 45 ± 2 kcal, which can be compared to a dissociation energy of 58.02 kcal for the chlorine molecule. It is to be hoped that in the near future, a combination of shock tube work, flash photolysis, and discharge tube techniques can be used to obtain the dissociation-recombination rates in the chlorine system over a wide range of temperatures and atom concentrations.

The sources of the perplexing discrepancies among the various values for the rate constant of the reaction



have been located and largely eliminated. Kaufman and Kelso (7) and Mathias and Schiff (8) have obtained direct evidence for the catalytic decomposition of ozone and recombination of oxygen atoms by hydrogenous impurities in discharged oxygen. In addition, electrically discharged oxygen has been shown to contain electronically excited oxygen molecules (7,8,9,10) which are capable of dissociating ozone molecules. Thus in the past, apparent rate constants obtained for the recombination

of atoms in discharged oxygen have been seriously influenced by the catalytic effects of hydrogenous impurities and the inhibitory effect of ozone decomposition by excited oxygen species. The reactions involved are



where O_2^* is an electronically excited oxygen molecule. A possible scheme by which hydrogen impurities accelerate the recombination is



which together may be faster than (8).

Kaufman and Kelso (7) removed the hydrogen impurities and avoided electronically excited species by using the thermal decomposition of ozone as an oxygen atom source to measure the rate of reaction 7 directly. They obtained $k_7 = 2.72 \times 10^8$ liter²/mole²sec at 25°C. This is in fair agreement with the value of 1.33×10^8 liter²/mole²sec recently recalculated (11) from measurements of the reverse reaction that occurs in the decomposition of ozone. The discrepancy may lie in the uncertainty concerning the enthalpy of formation of ozone, although Basco (12) finds $k_7 = 1.1 \times 10^8$ liter²/mole²sec directly from flash photolysis experiments.

the 1D state. In the presence of propane, n-propanol and lesser amounts of isopropanol are formed, as well as hydrocarbon products that result from association reactions of radicals formed by hydrogen atom abstraction from propane. The yields of the alcohols increase relative to the hydrocarbon products as the pressure increases, as expected if the alcohols are formed by exothermic insertion reactions. The gases Xe, Kr, N_2 , and CO_2 noticeably deactivate 1D oxygen atoms to the 3P state, and their presence inhibits the insertion reactions. In general, the behavior observed in this system is similar to that found when $S(^1D)$ or $CH_2(^1A_1)$ react with parafins, except that the alcohols formed by insertion reactions are more difficult to stabilize due to their higher energy content.

Warneck (19) has shown that photolysis of CO_2 produces a somewhat stable product that is evidently CO_3 . This may be the result of addition of a 1D oxygen atom to CO_2 . This point of view is consistent with an earlier proposal of Katakis and Taube (20) who found evidence for CO_3 in the photolysis of CO_2-O_3 mixtures. However, recently the occurrence of 1D oxygen atoms in the photolysis of CO_2 has been questioned (21,22).

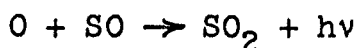
Doherty and Jonathan (23) have studied the concentration dependence of the intensity of light emitted by the O-NO reaction in the pressure range of 0.85-400 microns. The reaction remains overall second order down to the lowest pressures, and the authors interpret this in terms of a three-body mechanism in which the third body acts both as a catalyst for the association reaction and as a quencher and catalyst of a

dissociation process. Similar results were obtained earlier by Harteck and coworkers (24) who concluded that the O-NO reaction was an elementary bimolecular chemiluminescent process. It is difficult to reconcile the absolute intensity of the O-NO glow with a three-body process in which a substantial amount of excitation is quenched, but on the other hand it is hard to explain why the intensity of the glow depends on the nature (25) of the inert gas if the process is strictly bimolecular.

A similar difference of interpretation exists for the O-SO chemiluminescent reaction. Halstead and Thrush (26) found the intensity of the afterglow of an Ar-SO₂ discharge to be overall second order, first order with respect to oxygen atoms and SO molecules. Because the emission is banded, they feel that electronically excited SO₂ must be formed by a three-body process, and that the third body must also participate in quenching and dissociating excited SO₂. Harteck and coworkers (27) generated SO from the reaction



and studied the pressure dependence of



13.

They also find that the reaction 13 is overall second order in the range from 8 to 14 microns, and prefer the conclusion that 13 is an elementary bimolecular process.

Sharma et al (28) have found the chemiluminescent emissions from the reactions of oxygen atoms with CS₂, COS, and H₂S are identical with that obtained from $O + SO \rightarrow SO_2 + hv$, which

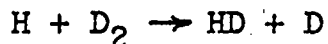
shows that in each of these reactions, SO must be produced as an intermediate.

Arrington et al. (29) have studied the chemiluminescence and chemionization that occurs in the oxygen atom-acetylene reaction. The CH chemiluminescence is produced by a complex set of reactions which involve two oxygen atoms and three acetylene molecules. No single satisfactory mechanism has been found.

The reactions of carbon atoms constitute a new and interesting area for kinetic investigations. So far no absolute rate data have been obtained, but carbon atoms generated from carbon vapor (30, 31, 32, 33) and by the $C^{12}(\gamma, n)C^{11}$ reaction (34, 35, 36) have been shown to undergo addition to olefinic double bonds to give cyclic hydrocarbons and linear rearrangement products. Differences in reactivity and stereospecificity have been observed and attributed to the presence of electronically excited as well as ground state carbon atoms. Before reliable rate constants for homogeneous reactions can be determined, an improved source of thermal carbon atoms must be found. Recent work by Stief and De Carlo (37) suggests vacuum ultraviolet photolysis of carbon suboxide produces carbon atoms.

Atom transfer reactions.-

The rate of the important reaction



14.

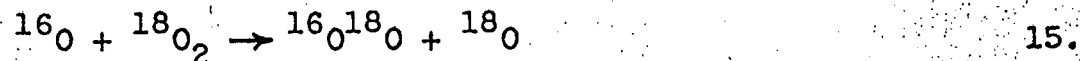
has been measured by Schulz and LeRoy (38) in the temperature range 368°-468°K. Using hydrogen atoms produced by thermal

dissociation of H_2 on tungsten, a calorimetric atom detector and product analysis by gas chromatography, they find $k_{14} = 4.37 \times 10^9 \exp[-7300/RT]$ liter/mole sec. Unfortunately the temperature range of this investigation lies far below those employed in earlier investigations of the thermal H_2 - D_2 reaction so that a meaningful comparison of the two sets of data is not possible. Further work over a greater temperature range and employing other atom detectors should be attempted.

In a second important paper (39) Schulz and LeRoy report an investigation of the reaction $H + p-H_2 = H + o-H_2$ in the temperature range 300-444°K. An Arrhenius plot was curved in the lower temperature region; which suggests some importance of quantum-mechanical tunneling. The temperature dependence of the rate constant can be fitted assuming a truncated parabolic barrier with an imaginary frequency of 12131 cm^{-1} , and a value of $9.7 \text{ kcal mole}^{-1}$ for the energy difference between the complex and reactants, measured from the zero point energy levels. The authors note that Eckhart-type barriers can lead to Arrhenius behavior even when tunneling is important. Consequently Arrhenius behavior does not necessarily indicate tunneling is unimportant. Insofar as transmission coefficients, anharmonicity, and vibration-rotation interaction are ignored in the usual rate theory, it is also fair to state that deviations from Arrhenius behavior do not necessarily indicate tunneling. The problem of the importance of tunneling can only be resolved by careful comparison of the experimental data with several formulations of rate theory using reliable potential energy surfaces.

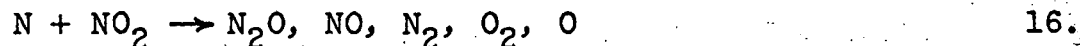
All three aspects of this problem deserve more intensive work.

The rate of the oxygen atom interchange reaction

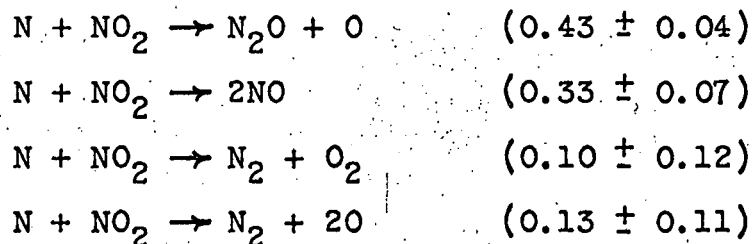


has been measured by Brennen and Niki (40) who find $k_{15} = (1.0 \pm 1) \times 10^9$ liter/mole sec, which is in satisfactory agreement with the value of 0.6×10^9 liter/mole sec found earlier by Herron and Klein (41).

Phillips and Schiff (42) investigated the reaction of nitrogen atoms with NO_2 in a flow system using a mass spectrometer and photometric techniques to determine the overall rate constant for nitrogen atom disappearance and the relative importance of four different reaction paths. For the reaction



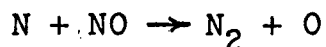
they obtain $k_{16} = 1.11 \times 10^{10}$ liter/mole sec, while the relative contributions of the primary reaction paths are



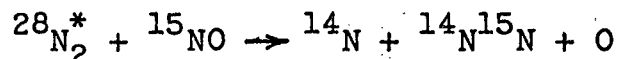
These results are rather different from those of Clyne and Thrush (43), who neglected the last reaction path in their analysis.

The discrepancy between the nitric oxide and ethylene titrations for the nitrogen atom concentration has been a long

standing problem. Nitrogen atom concentrations measured by the amount of nitric oxide consumed by the reaction



always exceed those determined by the HCN produced by the nitrogen atom-ethylene reaction. This year Fersht and Back (44) have presented evidence they feel supports the validity of the ethylene titration. They find that when nitrogen atoms are titrated by mixtures of ^{15}NO and C_2H_4 , the amount of HCN plus $^{15}\text{N}^{14}\text{N}$ produced is a constant as long as the $^{15}\text{NO}/\text{C}_2\text{H}_4$ ratio is less than approximately unity. At higher concentrations of ^{15}NO , the amount of $^{29}\text{N}_2$ plus HCN increases, which they interpret as indicative of a reaction of ^{15}NO with an excited nitrogen species, possibly



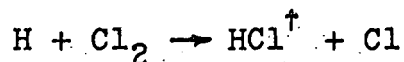
At low NO concentration this reaction may be unimportant since the excited nitrogen could be quenched by ethylene before reacting with nitric oxide.

A rather different conclusion was reached by Elias (45) who determined the nitrogen atom concentration in active nitrogen by measuring the pressure change due to the isothermal recombination of the atoms. The atom concentration determined this way agrees with the results of the nitric oxide titration, but not with the ethylene titration. Independent support for the validity of the nitric oxide titration has been found earlier by using electron paramagnetic resonance to determine atom concentrations

(46). The paramagnetic resonance work has recently been corroborated by further similar studies by Von Weissenhoff and Patapoff (47). They find that the nitric oxide titration agrees with the paramagnetic resonance results at low flow rates in the pressure range from 0.3-2.5 mm. At higher pressures and flow rates greater than 10 m/sec, the nitric oxide titration gives high results, which suggests excited species may dissociate nitric oxide under these circumstances.

Additional evidence in favor of the nitric oxide titration comes from recent mass spectrometric investigations of the nitrogen atom ethylene reaction (48). The products of this reaction can catalyze the recombination of nitrogen atoms, and this can explain the low values for the nitrogen atom concentration obtained by use of this titration. The weight of evidence seems to favor the reliability of the nitric oxide titration.

Polanyi et al (49) have carried out a careful reinvestigation of the reaction



where HCl^\dagger is a vibrationally excited molecule. A reliable set of relative rate constants for the production of the HCl in each of the first seven vibrational levels were obtained: $k_0 = 20$, $k_1 = 3$, $k_2 = 2$, $k_3 = 1$ (assumed), $k_4 = 0.3$, $k_5 = 0.04$, $k_6 = 0.004$. This corresponds to an absolute efficiency of 7% for the conversion of the energy of reaction into vibration. The rest of the energy must go into rotation of HCl and relative

translation of the products. This rather low efficiency of production of vibrationally excited products contrasts with observations (50) made on alkali atom--alkyl halide reactions, where as much as 90% of the energy goes into internal excitation of the products.

An investigation (51) of the reduction of carbon dioxide in a hydrogen-oxygen flame has led to a rate constant for the reaction



of $k_{16} = 8.4 \times 10^5$ liter/mole sec at 1072°K . The authors point out that two rather different Arrhenius expressions can be obtained for k_{17} from data already in the literature. A definitive absolute measurement of k_{17} over a range of temperatures is needed.

Gowenlock and Thomas (52) have measured the rates of reaction of sodium atoms with methylchlorosilanes by the diffusion flame technique. These reactions are all at least two orders of magnitude slower than the corresponding reactions with analogous carbon compounds, and the trend of increasing rate with increasing chlorination present in the carbon series is not found for the silicon compounds.

Investigation of atomic kinetics by electron paramagnetic resonance has been so far confined to hydrogen, oxygen, and nitrogen atom reactions. Westenberg (53) has provided intensity relations for the quantitative determination of concentrations of Cl, Br, I, and OH, which may stimulate work on the reactions of these species. Westenberg and deHass (54) have studied the

H-NO₂ reaction by ESR, determining both the concentrations of H and OH. They find $k = 1.2 \times 10^9$ liter/mole sec for $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$, which is in quite good agreement with the value reported by Kaufman and Del Greco (55).

Goy and Pritchard (56) have found $k = 10^{13.0} \exp(-35,000/RT)$ liter/mole second for $\text{I} + \text{CH}_4 \rightarrow \text{HI} + \text{CH}_3$, and Benson et al (57) found $k = 10^{8.5} \exp(-9,400/RT)$ for the addition of an iodine atom to cis-butene-2.

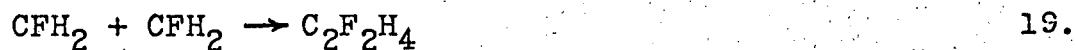
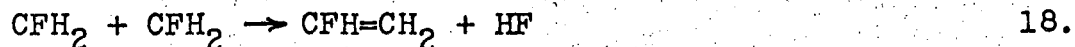
A number of rate constants for the disappearance of atoms have been obtained for systems in which the reaction mechanism is not fully characterized. These results are listed below without comment.

<u>Reaction system</u>	<u>Log k (liter/mole sec)</u>	<u>Reference</u>
O + CH ₄	9.84-7,300/(2.3 RT)	Cadle, Allen (58)
O + C ₂ F ₄	8.78	Saunders, Heicklen (59)
O + C ₂ H ₂	7.95	Sullivan, Warneck (60)
O + C ₂ H ₂	7.73	Arrington et al (61)
O + COS	~6.8	Rolfes, Reeves, Harteck (27)

ELEMENTARY RADICAL REACTIONS

Recombination.-

An interesting feature of the recombination of fluorinated methyl radicals has been found by G. O. Pritchard and coworkers (62,63,64) and by Whittle et al (65,66). The former group found that both the reactions



were important modes of recombination of CFH_2 radicals, with $k_{18}/k_{19} = 6$. Alcock and Whittle (65) then found that for the reactions



$k_{20}/k_{21} \cong 1$, independent of temperature. Considering this behavior, the finding of Pritchard and Bryant (63) that formation of HF is not important in the recombination of CF_2H radicals seems quite surprising, particularly since the reaction

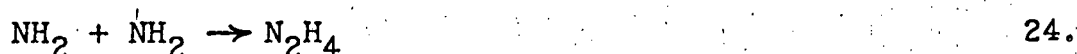
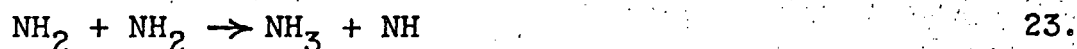


is known to occur (64). From a study of the pyrolysis of trifluoroacetaldehyde, Arthur and Bell (67) have deduced that the recombination rate of trifluoromethyl radicals is in the third order region at pressures up to 250 mm at a temperature of 500°C.

There have been rather few quantitative determinations of recombination rate constants. Basco and Norrish (68) studied the flash photolysis of $(\text{CN})_2$ and BrCN in the presence of nitric oxide by kinetic spectroscopy. In the presence of excess NO , a pseudo-first order rate constant for the reaction



was measured, but the effect of total pressure was not studied so it is not known whether the reaction is overall second or third order. Assuming the reaction is either second or third order gives $k_{22} = 2.2 \times 10^9$ liter/mole sec or $k_{22} = 1.2 \times 10^{11}$ liter²/mole²-sec, respectively. From another flash photolysis study, Salzman and Bair (69) deduced tentative values for the rate constants of



which are $k_{23} = 0.46 \times 10^9$ liter/mole sec and $k_{24} = 2.5 \times 10^9$ liter/mole sec.

Some more determinations of disproportionation-combination ratios for free radicals have been done. Gordon (70) finds for the reaction between the deuterio-methyl and cyclopentyl radicals $k_{\text{diss}}/k_{\text{comb}} \approx 0.3$, where disproportionation gives cyclopentene. This ratio is a bit higher than those found earlier for methyl-secondary radical interaction. The disproportionation-combination ratio for cyclohexadienyl radical with isopropyl radical is also large (71), particularly when the number of hydrogen atoms available for the disproportionation is considered. The authors conclude that in these reactions, products like benzene which have considerable delocalization energy may be favored. James and Troughton (72) have found evidence for disproportionation reactions of the allyl radical.

Addition reactions.-

Tedder and Walton (73) report Arrhenius parameters for the addition of trichloromethyl radicals to several olefins. The results are given in Table I. It is clear that differences in activation energy are principally responsible for the differences in reactivity at the various methylene groups. The absolute values of the Arrhenius A-factors are determined relative to the rate of recombination of trichloromethyl radicals, and seem rather small compared to A-factors for other radical additions to olefins. The recombination rate for trichloromethyl radicals also seems small, and would be worth redetermining.

James and coworkers (74,75) have determined Arrhenius parameters for the reactions of ethyl radicals with a series of vinyl monomers and acrylonitriles. The values are listed in Table I. The difference in reactivity is a consequence of the variation in activation energies, and the A factors show little variation, as would be expected.

Szwarc et al (76) have studied the effect of substituents at the reactive center on the rate of addition of CF_3 radicals to olefins. Methylation of a substrate lowers the activation energy for the addition, and for a given family of substituted olefin, there appears to be a linear relation between the activation energy for addition and the ionization potential.

The rates of addition of methyl, ethyl, propyl, and isopropyl radicals to nitric oxide and oxygen have been measured

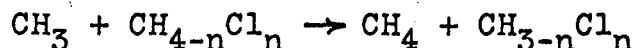
relative to the rate of the radical-iodine molecule reaction by Christie and Frost (77).

Kerr and Calvert (78) have determined that the activation energy for the addition of methyl radical to carbon monoxide is 3.8 kcal. This leads to -3.1 kcal for the enthalpy of formation of the CH_3CO radical.

Abstraction reactions.-

A number of rate constants for the abstraction of hydrogen atoms by methyl radicals have been measured (78,79,80,81,82, 83,84) and the Arrhenius parameters for these reactions are given in Table II. The A-factors lie in or near the expected range of 10^8 - 10^9 liter/mole sec, and the range of observed activation energies is not great.

The activation energies for the abstraction by deuteromethyl radicals of hydrogen atoms from CF_3H , CF_2H_2 , and CFH_3 have been found to be 10.2 ± 0.2 , 10.2 ± 0.2 , and 11.4 ± 0.2 kcal, respectively (85). This small variation in activation energy is surprising, considering that for the reactions

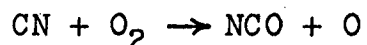


the activation energies are 9.4, 7.2, and 5.8 kcal for n equal to 1, 2, and 3, respectively.

Hydrogen atom abstraction from hydrocarbons and acetone by difluoroamino radicals has been studied by Trotman-Dickenson et al (86,87). The reported activation energies can be represented quite well by an Evans-Polanyi relation $E_a =$

1.00[D(C-H)-72.5] kcal. Similar relations for hydrogen abstractions by bromine atoms and methyl radicals are given.

Chlorine atom abstraction by methyl radicals from ethyl and neopentyl chloride and 1,2-dichloroethane, has been observed but no rate constants were determined (88). A series of relative rate constants for the abstraction of hydrogen atoms from methane, ethane and propane by cyanide radicals have been determined by H. O. Pritchard and coworkers (89). The difficulties of obtaining absolute rate constants for cyanide radicals generated photochemically or thermally is discussed in this paper. An attempt should be made to determine some absolute rate constants for this radical using paramagnetic resonance or optical absorption in a flow system. By using flash photolysis and kinetic spectroscopy, Basco (12) has found $k_{25} = 4.6 \times 10^9$ liter/mole sec for



25.

at room temperature.

Alcock and Whittle (65) have measured the Arrhenius parameters for the abstraction by trifluoromethyl radicals of hydrogen and halogen atoms from methane and methyl halides.

General radical chemistry.-

Bader and Generosa (90) have carried out a careful investigation of the pressure dependence of the products of the reaction of methylene with cis-butene-2. With fixed amounts of diazomethane and cis-butene-2 photolysed in the presence

of increasing amounts of He, Ar, Xe, N₂, and CF₄, they were able to observe an initial decrease in the fraction yield of trans-dimethylcyclopropane. This they attribute to increasing collisional deactivation of the cis-dimethylcyclopropane formed initially by the addition of singlet methylene to the olefinic bond. At higher inert gas pressures they found the fractional yield of trans-dimethylcyclopropane increased, which is clear evidence that triplet methylene is formed by collisional deactivation of the singlet species at the higher pressures. The surprising result is that triplet methylene appears to become important at pressures as low as 100 mm of CF₄ and 250 mm of N₂. This work appears to answer all criticism that the reactions of triplet methylene had not been observed. Also, by studying the pressure dependence of the pentenes formed in the reactions, the authors were able to reach conclusions as to their principal path of formation.

Frey (91) has discussed the chemistry of methylene and presented an argument that approximately 20-30 percent of the methylene radicals are produced directly in the triplet state in the photolysis of ketene and diazomethane.

The reactions of methylene with mono-, 1,1-di, and tri-fluoroethylene have been studied by Trotman-Dickenson and coworkers (92). Both insertion into C-H bonds and addition to the olefinic bond to form cyclopropanes were observed. The reaction products could be explained by a mechanism which involves only hydrogen atom migration upon isomerization, and no insertion into C-F bonds. It was also shown that the

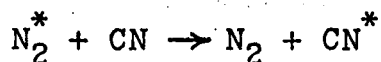
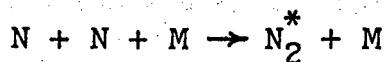
the susceptibility of the double bond to addition, and of the C-H bond to insertion, decreases as fluorine substitution increases. The yields of cyclopropanes were pressure dependent up to 2000 mm, but no trend in the isomerization rates among the various species could be discerned. Because of their simplicity and because the pressure dependent range of their isomerization rate falls in a convenient region, the fluorocyclopropanes could be used for further tests of unimolecular rate theory.

Other chemistry of methylene that has been investigated include the reaction with methyl chloride (93) where chlorine atom abstraction appears to occur, and the reactions with acetaldehyde and propionaldehyde (94). Heicklen, Cohen, and Saunders (95) have discussed the multiplicity of the related species difluorocarbene, and Simons (96) has presented an estimate of the enthalpy of formation of CF_2 .

Campbell and Thrush (97) have studied the behavior of CN radicals in active nitrogen and find kinetic evidence for the reactions



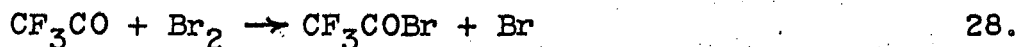
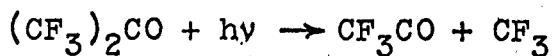
with $k_{26} = (5.6 \pm 1) \times 10^9$ liter²/mole²sec. The intensity of the light emitted by CN is proportional to the square of the nitrogen atom concentration, which they explain by the reactions



where the asterisks denote electronic excitation, and N_2^* may be the $A^3\Sigma^+$ state.

A new transient absorption attributed to the alkoxy radical has been observed by McGarvey and McGrath (98) after the flash photolysis of alkyl nitrites. The reaction of ethoxy-radicals with ethylene has been studied by Thynne (99) who finds diethyl ether and ethyl vinyl ether to be major products. These can be explained by a mechanism that involves addition of the ethoxy-radical to ethylene, followed by hydrogen abstractions by or from the resulting radical.

Tucker and Whittle (100) have found evidence for the formation of the trifluoroacetyl radical in the photolysis of hexafluoroacetone. Photolysing mixtures of bromine and hexafluoroacetone they find $CF_3Br/CO < 2$ at temperatures below $250^\circ C$, and CF_3COBr is found in approximately the amount expected. Their reaction mechanism is



with $k_{28}/k_{29} \approx 2 \times \exp[-6000/RT]$ liter/mole. Similar results are found upon photolysis of hexafluoroacetone-chlorine mixtures, but there is no evidence of CF_3COI when iodine is used. When

nitric oxide is present as a radical scavenger, only CF_3NO and CO in a 2/1 ratio are found, so either the reaction of CF_3CO with NO is slow, or yields CF_3NO .

UNIMOLECULAR REACTIONS

The experimental work on unimolecular reactions falls in three areas. In shock tube studies of the dissociation of relatively small molecules, the emphasis is on establishing a mechanism or electronic channel for dissociation and on studying the energy transfer process. In investigations of the pyrolytic decomposition or isomerization of large molecules in the high pressure regime, the interest is centered on determining the nature of the transition state and its relation to the high pressure frequency factor as well as discerning the effects of substituents on activation energies. For decompositions of intermediate sized molecules in the first- to second-order transition region, the interest lies in testing models for intramolecular energy transfer.

The unimolecular decomposition of SO_2 in a reflected shock wave has been reported by Wagner et al (101). Both SO_2 and SO were followed by optical absorption, and with only 0.3 percent of sulfur dioxide in argon in the temperature range from 4500-7500°K, the rate constant for the reaction



was found to be $k_{30} = 10^{11.4} \exp[-110,000/RT]$ liter/mole sec.

The bond dissociation energy of sulfur dioxide is 131 kcal/mole,

so the observed activation energy is reasonable if four Kassel oscillators are involved in activating the molecule. In a similar study of the unimolecular decomposition of CS_2 in the temperature range $1800^\circ\text{-}3700^\circ\text{K}$, Wagner et al (102) found $k_{31} = 10^{12.6} \exp[-80,300/RT]$ liter/mole sec for



Dissociation of CS_2 into CS and an excited ^1D sulfur atom requires 122 kcal/mole, while dissociation into a ground state atom requires only 96 kcal/mole. The observed activation energy is consistent with the latter path, if a small number of internal modes are involved in the activation process.

Brown and Darwent (103) have studied the rate of dissociation of tetrafluorohydrazine in the temperature range $344^\circ\text{-}410^\circ\text{K}$ and from 0.6 to 6.0 atm pressure. The reaction shows quasiunimolecular behavior, and the high pressure rate is approached but not reached at 6 atm. The second order region lies below 0.6 atm. At pressures of approximately 2 atm, the first order dissociation rate constant is $k = 10^{14.98} \exp(-19,400/RT) \text{ sec}^{-1}$, while the dissociation energy is 19.8 kcal/mole. Similar apparently high frequency factors have been found in the dissociation of the other small molecules N_2O_4 and C_2H_6 . Recently Tschuikow-Roux (104) has found $k = 4.3 \times 10^{17} \exp(-94,400/RT) \text{ sec}^{-1}$ for $\text{C}_2\text{F}_6 \rightarrow 2\text{CF}_3$ in the temperature range from 1300° to 1600°K .

Modica and Hornig (105) have followed the decomposition of NF_2 in an incident shock wave in the temperature range from

1400° to 2000°K. Earlier work by Diesen (106) had indicated that at least above 1900°K, the principal mode of decomposition is



for which Modica and Hornig find $k_{32} = 1.62 \times 10^{10} T^{1/2} \exp(-47,838/R)$ liter/mole sec. The N-F bond energy is 70 ± 12 kcal/mole, and consequently the observed activation energy seems quite low.

Davies (107) has reported measurements of the CO_2 dissociation rate in argon in the temperature range from 6000° to 11,000°K. Combination of these data with earlier results (108) in the temperature range from 2600° to 6000°K show that the apparent Arrhenius activation energy decreases as temperature increases, and has the value 68 kcal in the higher range. Although this is considerably less than the bond dissociation energy of 127 kcal/mole, the difference can be accounted for if approximately four degrees of freedom contribute to the activation process. Wagner et al (109) report an activation energy of 99 kcal in the temperature range 2800° to 4400°K, and summarize the results of other investigators. Earlier work on this reaction has also been discussed by Bauer (110). Other shock tube decompositions of small molecules have included ClCN (111), and CHF_3 (112).

As noted by Frey (113), there have now been five types of isomerism reaction discovered in studies of the pyrolysis of cyclopropanes. Besides the (a) well known isomerism of

cyclopropanes to olefins, and (b) the geometrical isomerism of dialkyl cyclopropanes, (c) vinylcyclopropane undergoes ring expansion to give cyclopentene, (d) ethylidene cyclopropane rearranges to 2-methylmethylenecyclopropane and (e) cis-1-methyl-2-vinylcyclopropane gives cis-hexa-1,4-diene by a 1-5 hydrogen atom shift with ring rupture. A second example of the type (e) reaction is reported (113) in which 1-isopropenyl-1-methylcyclopropane isomerizes to 1,2-dimethylcyclopentene by a homogeneous pressure independent process with a rate constant $k = 10^{14.16} \exp(-50,500/RT) \text{ sec}^{-1}$.

Ellis and Frey (114) have compared the thermal unimolecular isomerizations of cis- and trans-1-methyl-2-vinylcyclopropanes. Whereas the cis isomer gives only cis-hexa-1,4-diene by a hydrogen shift and ring rupture, the trans isomer gives both cis-hexa-1,4-diene and 3-methylcyclopentene in a 11.7/1 ratio. The isomerism of the trans-cyclopropane to the cis-hexadiene cannot proceed directly by 1,5 hydrogen migration, but must involve trans to cis isomerization by breaking the 1-2 bond in the cyclopropane. The activation energy of 48.6 kcal/mole, for the reaction is that of the trans to cis isomerization, which when compared to the activation energy for trans-cis isomerization of 1,2-dimethylcyclopropane suggests the lowering of the activation energy due to allylic resonance is approximately 11.9 kcal/mole.

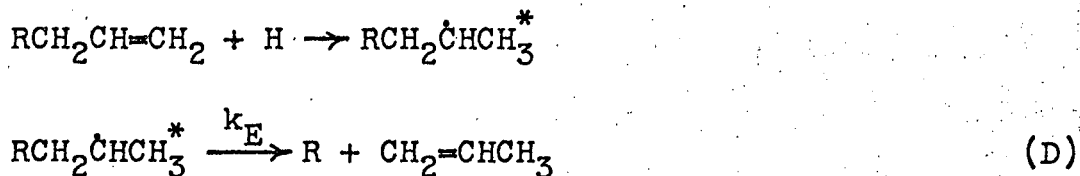
Srinivasan et al (115) and Frey and Stevens (116) investigated the isomerization of bicyclobutane to butadiene. The rate shows only slight pressure dependence in the range from

6-100 mm, and there is little evidence for heterogeneity. The activation energies determined by the two sets of workers agree fairly well (41.4 and 40.6 kcal) and are close to the value of 42 ± 1.4 found by Chesick (117) for the similar isomerization of 1,3-dimethylbicyclobutane. According to Carr and Walters (118), the related isomerization of cyclobutene to butadiene is a homogeneous, unimolecular process near its high pressure limit in the range from 48-1500 mm. At 1500 mm, they find $k = 10^{13.4} \exp(-32,900/RT) \text{ sec}^{-1}$. Frey and coworkers (119) investigated the thermal unimolecular isomerization of 1,3-dimethylcyclobutene to trans-2-methylpenta-1,3-diene, and of 1,4-dimethylcyclobutene to trans-3-methylpenta-1,3-diene in the high pressure limit. The activation energy for the former reaction is 33.0 kcal/mole, while that of the latter is 33.4 kcal/mole. Comparing activation energies for the various methyl substituted cyclobutenes, they suggest that a methyl group in the 1 or 2 positions raises the activation energy, while substitution in the 3 or 4 position lowers the activation energy. Frey and Marshall (120) studied the isomerization of 3-methylcyclobutene at low pressures in the presence of various gases. On a per collision basis, the deactivation efficiencies of the three pentane isomers are greater than that of 3-methylcyclobutane itself, which suggests that the common assumption of unit collisional deactivation probability for the parent compound is not necessarily correct. However, the conclusion rests on assumptions of the collision diameters for the various molecules

which may be misleading. Nevertheless, on a per molecule basis, n-pentane is slightly more efficient in removing energy than the parent compound, so the conclusion drawn may still be valid.

Other molecules whose isomerization or decomposition has been studied in the high pressure region include norbornylene (121), 1-chloropentane (122), cis-2-methylpenta-1,3-diene (123), 2,3-dimethylbutane (124), octafluorobutene-2 (125), trifluoromethyl- and trifluoroethylcyclopropane (126).

The rates of decomposition of chemically activated secondary alkyl radicals 2-butyl through 2-octyl have been measured by Pearson and Rabinovitch (127), and these data together with earlier work constitute measurements on the homologous series ethyl through 2-octyl. In the higher members of the series the important chemical reactions are represented by



where k_E is the rate constant for fragmentation of a radical with energy E and ω is the first order rate of radical stabilization by collision. The average decomposition rate for radicals is defined as $k_a = \omega(D/S)$ where D and S represent the decomposition and stabilization products respectively. The important feature of these chemically activated species that

the energy level density of the activated species affects the rate directly instead of cancelling out as it does in the high pressure limit of thermal unimolecular reactions. This can be seen if the high pressure limiting unimolecular rate constant is written

$$k_{\infty} = \int_{E_0}^{\infty} k_E K(E) dE$$

where $K(E)$ is the normalized Boltzmann distribution for the active degrees of freedom. Use of the Marcus-Rice expression for k_E and expansion of $K(E)$ gives

$$k_{\infty} = Z_a^+ / hZ_a \int_{E_0}^{\infty} \frac{\sum P(E^+) N(E) \exp(-E/kT) dE}{N(E) Z}$$

where Z_a is the partition function for adiabatic degrees of freedom of the complex (+) or molecule, Z is the partition function for active vibrations and rotations, the sum is over the degeneracy of the active energy states of the activated complex, and $N(E)$ is the density of energy levels for active modes at E . Whereas the structure dependent factor $N(E)$ cancels out in this case of thermal activation, it does not for chemically activated systems. In the latter case the Boltzmann distribution $K(E)$ is removed and replaced by $f(E)$, the normalized distribution of chemically activated molecules. The result is

$$k_a = Z_a^+ / hZ_a \int \frac{\sum P(E^+)}{N(E)} f(E) dE$$

and it is clear that increasing energy level density causes a decrease in decomposition rate. The experimental results of Pearson and Rabinovitch (127) show the effect on the rate of these quantum statistical weight changes due to the structural changes in the radicals, and support the idea that even in the most complex members of the series intramolecular energy randomization occurs and all vibrational and internal rotational degrees of freedom must be treated as active.

In a related work, Rabinovitch et al (128) measured the rates of decomposition of chemically activated 2-hexyl-d₁₂ and 2-octyl-d₁₆ radicals relative to their corresponding light radicals. A secondary isotope due to energy level density factors is involved, with the deuterated species decomposing slower than the light species due to the increase in energy level density upon deuteration. The measured isotope effects are in reasonable agreement with those calculated on the basis of the Marcus-Rice theory.

Additional support for the idea of energy randomization among all vibrational modes has been found by Halberstadt and Chesick (129) who studied the thermal isomerization of ethylcyclopropane over the pressure range 0.05 to 85 mm. From the rate of the decrease of the first order rate constant with decreasing pressure, it was concluded that the lifetime of an active methylcyclopropane molecule, which in turn is thirty times the lifetime of active cyclopropane.

Rabinovitch et al (130) have studied the fall off with pressure of the thermal unimolecular isomerization of deuterio methyl isocyanide in the range from 9.3 atm to 0.05 mm. At any pressure, the rate for CH_2DNC is less than that of CD_3NC and greater than that of CH_3NC , which is consistent with the increase of energy level density with increasing deuteration. The splitting of the degenerate vibrational modes upon mono-deuteration should, according to the Slater harmonic mode theory, considerably increase the effective number of modes participating, and no such increase is apparent experimentally.

Other molecular decompositions that have been studied include pyrolyses of some alkyl cyanides (131), ethyl iodide (132), ethane (133), and tetrafluoroethylene oxide (134).

THEORETICAL WORK

For some time there has been a discussion concerning the validity of dividing an equilibrium constant into a phenomenological rate constant for a dissociation reaction in order to obtain the rate constant for the reverse association reaction. In the case of thermal dissociation of diatomic molecules, it has been generally accepted that the observed rate constant for dissociation is smaller than the true equilibrium rate constant because of depletion of the higher vibrational states by reaction. When the reverse process of association is studied, the translational states of the atoms are not depleted significantly and consequently one might expect the equality $k_d(\text{obs})/k_a(\text{obs}) = K$

might not hold. It has been argued by Rice (135), however, that the relation

$$k_d(\text{obs})/k_a(\text{obs}) = k_d(\text{eq})/k_a(\text{eq}) = K$$

is valid, since redissociations of molecules formed by atom association lower the association rate by the same amount that vibrational state depletion lowers the dissociation rate. A similar conclusion has been reached recently by Snider (136) who showed that when the phenomenological rate equation

$$-\frac{d(A_2)}{dt} = \frac{1}{2} \frac{d(A)}{dt} = k_d[A_2][M] - k_a[A]^2[M]$$

holds, the ratio of the rate constants equals the equilibrium constant, even though nonequilibrium effects lower the individual magnitudes of the rate constants below their equilibrium values. Snider has also given some necessary conditions for the phenomenological rate equation to hold. A general discussion of the deductions drawn from the stochastic model on the relation between molecular transition probabilities and chemical rate constants has been presented by Widom (137). The conclusion drawn by these authors regarding the relation between the equilibrium constant and rate constants are in agreement with the existing experimental data (13,14).

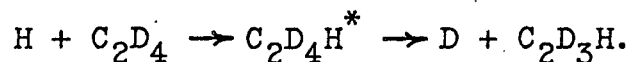
Keck and Carrier (138) have investigated the coupled vibrational excitation-dissociation-recombination processes of a dilute mixture of diatomic molecules in an inert gas. They show that a classical model involving a continuum of vibrational energies is more appropriate than a quantum model with stepwise

vibrational excitation. The master equation for the classical model can be reduced to an equivalent diffusion equation which can be solved for the population as a function of energy. Deviations from the equilibrium population appear and are most pronounced near the dissociation limit. The general agreement between calculated and observed recombination rates is fairly good, but the observed negative temperature dependence is not fully reproduced.

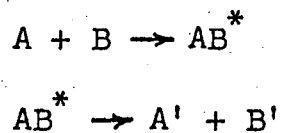
Woznick (139) has extended Keck's variational theory of atom recombinations to the case where the third body is strongly attracted to the combining atoms. A practical example of this situation is the oxygen atom recombination catalyzed by a third oxygen atom, for which the theory suggests that below 12,000°K, the oxygen atom should be a more efficient catalyst than a rare gas atom or an oxygen molecule, and at a few thousand degrees, it should be an order of magnitude more efficient.

Pechukas and Light (140) have published an amendment and extension of Light's (141) earlier phase space theory of chemical kinetics that is consistent with the detailed balance theorem. In this approach the reaction cross section is taken as the product of the cross section for forming a collision complex with specified energy and angular momentum times the probability that the complex will break up to give specified products. This latter probability is proportional to the phase space available to the products as restricted by energy and angular momentum considerations. There is contained in this

theory a strong coupling assumption between the modes of the complex which may prove to restrict application of the theory to low energy collisions or, more directly, to situations in which a long lived collision complex exists. Application of the theory has been made (142) to reactions between rare gas ions and isotopic hydrogen molecules, and HD^+ with the rare gas atoms, with very encouraging results. It is interesting to note that the predictions of the theory are in rather poor agreement with experiment in the case of the reaction of Ar^+ with H_2 . Recent investigations (143, 144, 145) of this reaction suggest that it is best described by a stripping mechanism rather than by a dynamical process involving a strongly coupled collision complex, even when the relative kinetic energy is of the order of 1 electron volt. A phase space theory would seem most appropriate for reactions that in effect proceed through a "chemically activated" intermediate, for example



Nikitin (146) has given a theory for reactions that proceed through a long-lived compound molecule state. The development follows the Breit-Wigner formalism originally applied to nuclear processes that proceed through a compound nucleus. For a process like



where A' and B' may be identical to, excited states of, or

different from the reactants, the final rate constant is the product of a capture rate constant for the compound molecule formation times a reciprocal lifetime for decay of the complex divided by a first order rate constant representing possible processes by which AB^* could be deactivated to a stable molecule. The lifetime for decay is evaluated both in terms of the Slater and Kassel models for the compound molecule. Nikitin carefully points out the difference between a compound molecule intermediate and the activated complex of transition state theory, a point which seems to be unclear to many.

Marcus (147) has considered the general formal problem of the separation of variables in the solution of the multidimensional Schrödinger equation. He shows in a second paper (148) how the major features of nonseparable potential energy surfaces can be matched in a limited region by a surface that allows separation in some orthogonal curvilinear coordinate system. In three subsequent papers (149, 150, 151) Marcus gives a generalization of the activated complex theory of reaction rates in classical and quantum forms, and in particular, removes the traditional assumption of a Cartesian reaction coordinate. As a result, methods are available to apply activated complex theory to systems that permit separation of variables only in curvilinear coordinates.

Nyeland and Bak (152) have treated the hydrogen atom exchange process $HX + X' \rightarrow HX' + X$ by a method originally developed to calculate the cross section for resonant electron exchanges like $K + K^+ \rightarrow K^+ + K$. The general idea of this

approach is that the degeneracy of the atom-ion system at infinite separation is split by the interaction of the two as they approach each other. The system then oscillates between the states K, K^+ and K^+, K with a frequency which is the splitting of the energy levels divided by Planck's constant. The phase of this oscillation when the collision is over determines whether there has been a particle transfer. The probability of the particle transfer is calculated as a function of impact parameter, and it is found that for impact parameters smaller than some critical value b_c , the probability of particle transfer oscillates rapidly between zero and one, as a function of impact parameter. The cross section for the transfer reaction is then taken as $1/2 \pi b_c^2$. When these ideas are applied directly to the hydrogen atom transfer problem, the not very surprising result is an expression which is the same as one would derive from simple collision theory taking the reaction probability to be one-half. The calculation of the critical impact parameter involves the energy level splitting of the two-state system as a function of distance, and this can only be crudely approximated for hydrogen atom transfers. It would also seem that effects of rotational states and of the momentum carried by the hydrogen atom would have to be considered before any quantitative use is made of this approach.

For some time there has been a discussion in the literature as to whether or not the use of rotational symmetry numbers correctly accounted for the degeneracy of reaction paths. Schlag and Haller (153) have applied group theoretic methods to the

problem of determining reaction path degeneracy, and have derived some simple rules for finding the degeneracy by direct count. Bishop and Laidler (154) discuss situations in which the symmetry number method fails, and also give a direct count method for finding the proper statistical factors.

Rather little work has been done this year on the theory of unimolecular reactions. Baetzold and Wilson (155) have discussed the effect of the nonrandom phase that can occur via the "strong collision" vibrational excitation mechanism, and shown how it can affect the pressure dependence of the rate of a quasiunimolecular reaction. Marcus (156) has extended his treatment of unimolecular dissociation and isomerization reactions to take account of centrifugal stretching effects and reaction path degeneracy.

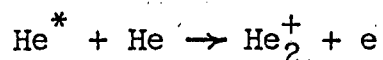
A potential energy surface for H_3 has been calculated by Conroy and Bruner (157) by a new method that leads to a shallow basin (1.3 kcal) for the symmetric configuration of the activated complex. The calculated activation energy for the $H + H_2$ reaction is 6.2 kcal. Edmiston and Krauss (158) performed configuration interaction calculations on H_2 and H_3 , and find an activation energy of 14.3 kcal, which they suggest might be lowered by 2 kcal from empirical considerations. Benson and Haugen (159) have applied a simple electrostatic model for the calculation of activation energies to a large number of four center reactions. In the cases where reliable experimental data exist, the agreement between experiment and empirical prediction is surprisingly good.

Other noteworthy theoretical papers include analyses of relaxation processes in multilevel systems by Carrington (160), and by Serauskas and Schlag (161), and investigation of the velocity distribution in chemically reacting gases by Kostin (162), and a treatment of a simple classical model for reactive collisions by Shin (163, 164).

IONIC REACTIONS

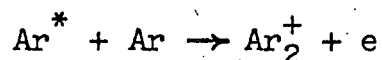
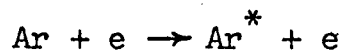
With the exception of high pressure mass spectrometry, kinetic phenomena involving gaseous ions have been until recently almost exclusively investigated by physicists. Several excellent reviews and monographs written from this point of view are available (165,166,167,168). The obvious importance of ionic reactions in chemically interesting situations as well as the unique opportunities these reactions offer for learning about fundamental processes has stimulated work in this area by chemists. The following is a summary of certain aspects of this recent activity. Ionic reaction mechanisms, much of high pressure mass spectrometry, and radiation chemistry have been avoided as these subjects are treated elsewhere in this volume.

Chemionization in simple systems has received some attention. The appearance potential of He_2^+ in a mass spectrometer is 23.1 eV, which is 1.5 eV smaller than the ionization potential of the helium atom. The He_2^+ is formed by a Hornbeck-Molnar process



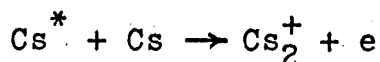
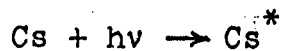
Franklin and Matsen (169) point out that since the lower limit for the bond energy of He_2^+ is 2.2 eV, one might expect an appearance potential as low as 22.4 eV, which is possible because the 3^3S , 3^1S , and 3^3P states of helium all lie above 22.7 eV and could act as He^* . The excitation cross section of the 3^1P state is 10 to 100 times those of the other states, however, and since the 3^1P state lies at 23.09 eV, it appears that molecule ion formation occurs almost exclusively through this state.

Becker and Lampe (170) have studied the process



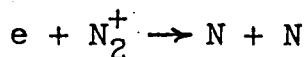
33

and find that three states (or groups of states) of argon whose excitation energies lie at 18, 30, and 65 eV are responsible for the formation of Ar_2^+ . They find k_{33} for the three excitation regions is 1.7×10^{-9} , 2.0×10^{-9} , and 1.3×10^{-9} cc/molecule sec for the 18, 30, and 65 eV excitations, respectively. Lee and Mahan (171) used photoexcitation to study the chemiionization in alkali metal vapors, and found two processes, as exemplified by

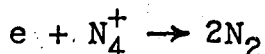


Molecular ion formation occurs when cesium, rubidium, and potassium are excited to their $(n+2)P$ states and higher, where n is the principal quantum number of the valence electron in the ground state. The positive-negative ion pair process has a threshold at slightly higher energies, and becomes increasingly important as the atomic ionization limit is approached.

Charge recombination processes that are the inverses of chemionization reactions have also been studied. Molecular ion-electron dissociative recombination has been studied for a number of years, but it is only relatively recently that definitive experimental results have been appearing. For a summary of work up to 1963, one should consult the review of Biondi (168). Recent work of greatest interest to chemists and those concerned with atmospheric processes includes the measurements of electron-ion recombination in nitrogen by Kasner and Biondi (172). These authors used combined microwave, mass spectrometric, and optical techniques to study the decay of electrons, ions, and excited atoms produced by microwave discharges in nitrogen-neon gas mixtures. At pressures of nitrogen less than 5×10^{-3} mm, N_2^+ is the principal ion, and the rate constant for

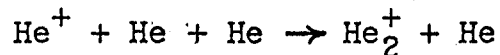


is 2.9×10^{-7} cc/molecule sec. At higher nitrogen pressures, N_4^+ becomes the dominant ion, and the important electron loss reaction is

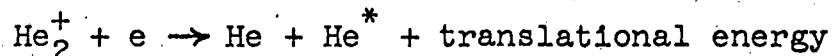


which has a rate constant of 2×10^{-6} cc/molecule sec. Another careful study of this type was made by Gunton and Shaw (173) who measured the rate of recombination of electrons with NO^+ produced by pulsed photoionization of nitric oxide-neon gas mixtures. At 298°K the rate constant for $e + \text{NO}^+ \rightarrow \text{N} + \text{O}$ is 4.6×10^{-7} cc/molecule sec, while at 196°K and 358°K the values 10×10^{-7} and 3.5×10^{-7} cc/molecule sec, respectively, were obtained.

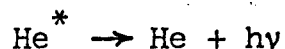
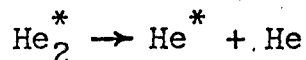
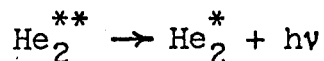
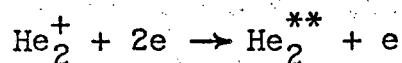
Ion-electron recombination in helium afterglows has been the subject of considerable work. Most recently, Rogers and Biondi (174) have shown the Doppler breadth of lines in the atomic helium spectrum increases with time after a discharge pulse. The explanation is that He_2^+ builds up after the pulse by the reaction



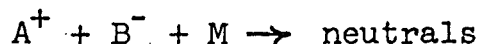
and then undergoes dissociative recombination with an electron to give a rapidly moving excited atom:



While dissociative recombination is prevalent at pressures of helium less than 2 mm Hg, at higher pressures a more complicated process known as collisional-radiative recombination becomes important, according to Robertson (175). Some of the processes involved are



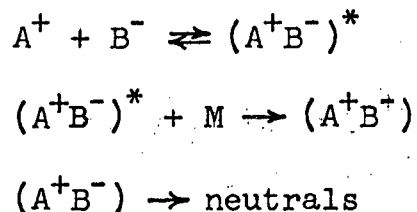
In electron attaching gases, electrons may be rapidly converted to negative ions, and charge neutralization occurs by the so-called ion recombination process. Mahan and Person (176) showed that this mutual neutralization occurs by parallel second and third order processes:



Strictly, ion recombination is a misnomer, or at least misleading, for the neutral products may be the separate A and B species in excited states, or fragments of them. The bimolecular neutralization reaction evidently proceeds through a potential energy curve crossing process in which the system is transferred from the ionic surface to one which leads to excited or dissociated neutrals. Carlton and Mahan (177) that the rate constants for the bimolecular neutralization process were close to 1.5×10^{-7} cc/ion sec for several ion pairs. One would not expect this rate constant to be particularly sensitive to molecular structure, especially if the neutrals are just the reactants in excited Rydberg states.

The three-body ion recombination process has been known since the time of J. J. Thomson, but with two exceptions, the

the older experimental data has been of highly questionable reliability. Recently, measurements of the rate of recombination of ions in a variety of inert gases have been made and interpreted (176,178). The three-body process occurs because ions which do not come close enough to undergo bimolecular charge transfer can be deactivated into bound elliptical orbits by a collision with a third body. If they are not redissociated, they may eventually undergo electron transfer and separate:



J. J. Thomson (179) proposed that if one of a pair of ions that had come closer to each other than some critical distance underwent collision with a neutral, the ion might lose enough kinetic energy to become bound. Thomson took this critical distance to be $R = e^2/(3/2 kT)$, or the distance at which the relative kinetic energy of the ions had increased by an amount equal to their average initial energy. The probability that either ion collided with a neutral while within this critical distance was calculated simply and a rate constant obtained. Subsequent elaborations of this theory, most notably by Natanson (180) and Brueckner (181), involved finding the value of the trapping radius more rigorously. Numerical calculations of Mahan and Person (178) indicated, however, that trapping that occurred beyond the critical radius made an important contribution to

the rate, and this has been confirmed recently by a numerical study by Feibelman (182). It appears also that collisions that redissociate weakly bound ion pairs are very important, and in effect, prevent the ion recombination rate from becoming infinite. Because ion recombination rates are relatively easy to measure, the ion-ion interaction potential is well known, and the mechanism of recombination is certain, their study should teach us about recombination processes in general.

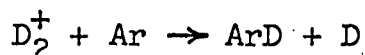
The three body association reaction between ions and neutrals has been studied recently. Beaty and Patterson (183, 184) found for



$k_{34} = 10.8 \times 10^{-32} \text{ cc}^2/\text{molecule}^2 \text{ second}$ and $k_{35} = 5.8 \times 10^{-32} \text{ cc}^2/\text{molecule}^2 \text{ second}$. Niles and Robertson (185) showed that the rate constant k_{34} is inversely proportional to temperature, and gave a simple derivation of the recombination rate that justifies this dependence. Since they neglect collisions that redissociate weakly bound molecules, the generality of their treatment is open to question. In a second paper (186) they calculate rate constants for ion neutral associations in other rare gases. Mahan (187) has pointed out that these associations may take place through a resonant charge exchange mechanism.

Bimolecular ion-molecule reactions have been studied extensively, but most notable are the results of the recently

applied technique of using tandem mass spectrometers. In this way the reactant ions may be mass and energy analysed, ambiguity concerning the reactants avoided, and the reaction cross section studied as a function of energy. Giese and Maier (188) studied the energy dependence of the cross sections for hydrogen atom and hydrogen ion transfer reactions, and showed the predictions of the Gloumousis and Stevenson theory were not followed even at relatively low energies (1-10 eV) in the center of mass system. They were also able to demonstrate the occurrence of both



and corresponding reactions for N_2 and D_2 . In addition, they showed that while

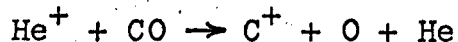


occurs, the reaction



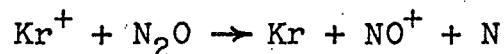
does not.

Subsequently, Giese and Maier (189) studied the reactions



as functions of ion kinetic energy. The latter two are endothermic and have onsets that are quite sharp, which occur at ion

energies that can be calculated from the energetics of the overall reaction. In a subsequent paper, Maier (190) reports investigations of the dissociative ionization of N_2 by Ne^+ and Ar^+ , and of N_2O by Kr^+ . The threshold energies for the nitrogen dissociation give the accepted value for the dissociation energy of nitrogen. For the Kr^+-N_2O reaction it was found that



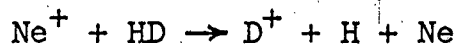
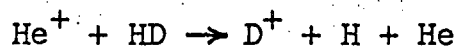
proceeds through an endothermic channel, even though the reaction is exothermic. Apparently the excess energy is tied up as vibrational energy of NO^+ or relative translational energy. Recently, Maier (191) has deduced values of bond energies for organic molecules from ion impact experiments.

Other recent investigations of ion-molecule reactions with tandem mass spectrometers have been made by Koski and coworkers (192,193) who studies the rare gas ion-methane reactions, and the $Ar-HD^+$ reaction. In the latter case, the isotope effect favors ArH^+ , and varies from 1.3 to 1.9 as the projectile energy increases from 2 to 25 eV.

Stebbing et al (194) report an investigation of the $N_2^+-D_2$ reaction in which they used a crossed beam technique and measured the angular distribution of N_2D^+ . Because of kinematic factors, the N_2D^+ is confined to a rather small cone which lies along the direction of the ion beam, so rather good resolution is required to obtain results sufficient to discriminate between various reaction models. The results seem to suggest that

products are scattered preferentially in the forward direction in the center of mass system, which might be consistent with a stripping model for the reaction.

Henglein et al (143,144,145,195) have determined the velocity spectra of ions formed in the reactions of Ar^+ , N_2^+ , and CO^+ with H_2 , HD, and D_2 . The velocity spectra and isotope effects favor a stripping model for the reactions in which the projectile in effect "collides" with only one atom of the diatomic molecule. Moran and Friedman (196) measured reaction cross sections and isotope effects in the AB-HD ion molecule reactions, where AB is N_2 , CO, O_2 and CO_2 . The $\text{ABH}^+/\text{ABD}^+$ ratio increased with increasing reactant ion velocity. The results were interpreted in terms of two factors: a unimolecular dissociation of the intermediate collision complex which is important at low collision energies, and a displacement effect that favors the configuration ABHD^+ over ABDH^+ , and which becomes more important at higher ion velocities. In another paper, Friedman and Moran (197) have noted that the cross sections for



are quite small, even though the reactions are exothermic. The reaction $\text{He}^+ + \text{H}_2 \rightarrow \text{HeH}^+ + \text{H}$ also has a very small cross section, and consequently one finds the apparently rare situation in which all channels for reaction are closed even though the possible reactions are exothermic.

Techniques for studying ion-molecule reactions under thermal field free conditions have been described and applied (198,199,200). The procedures, together with ion beam and conventional mass spectrometric techniques, should allow the study of ion reactions over wide ranges of energy.

MOLECULAR BEAMS

A number of reviews on this topic will soon appear, so here we mention only the most recent results on reactive scattering. Datz and Minturn (201) found the cross section for the reaction $\text{Cs} + \text{Br}_2 \rightarrow \text{CsBr} + \text{Br}$ was quite large, and that the angular distribution of product CsBr was consistent with a stripping mechanism. In this picture, the incoming Cs atom interacts strongly with only one of the Br atoms of the Br_2 molecule, and the momentum of the CsBr product is the sum of the initial momenta of the Cs and one of the Br atoms. This is to be contrasted with the rebound mechanism which operates in the $\text{K} + \text{CH}_3\text{I}$ reaction, where the product KI and CH_3 interact so that the KI is scattered back along the original direction of the incoming K atom. The rebound mechanism involves a closer approach of reactants than does the stripping process. Herschbach et al. (202) found the stripping model to be consistent with the reactions of Cs with Br_2 , ICl , IBr , and I_2 , and for the $\text{K} + \text{Br}_2$ reaction.

One of the difficulties in molecular beam investigations of the alkali metal-halogen or alkyl halide reactions is that the two-filament method of discriminating between unreacted

alkali atoms and product alkali halide is not sufficiently discriminating to allow measurements at angles close to the unscattered alkali atom beam. Herm et al (203) used inhomogeneous magnetic fields to deflect the alkali atom beam and showed that angular distributions calculated from previous two-filament measurements could be reproduced experimentally at small scattering angles.

Ackerman et al (204) studied the elastic and reactive scattering of K with HCl and HI, extending earlier work on the K-HBr interaction and reaction. Parameters for the exp-six potential were derived, and the probability for reaction as a function of the potential energy at the distance of closest approach of the reactants was deduced. Some indication was obtained that the probability of reaction increases when the potential energy is sufficient for KCl to be formed in excited vibrational states in the K + HCl reaction.

Grosser, Blythe, and Bernstein (205) studied the K + HBr reaction using velocity a selected K atom beam, and another velocity selector in front of their detector. In this way they obtained the velocity distribution of KBr as a function of scattering angle for different initial kinetic energies of reactant. The results indicated that the most probable internal excitation energy of KBr was 4.6 ± 0.7 kcal/mole out of a possible 5.1 kcal/mole. In a similar investigation of the K + Br₂ reaction, Grosser and Bernstein (206) found a broad internal energy distribution for KBr, covering a range of at least 30 kcal/mole from the maximum of 47 to 17 kcal/mole.

Investigations of the mechanics of reactive collision processes is a very important area of research which can tell us how sensitive such features of reactions as product angular distribution, energy partitioning, angular momentum distribution, and total cross sections are to the form of the potential energy surface. The most extensive investigation of this type so far has been by Karplus and Raff (207), who treated the $K + CH_3I$ reaction as a three atom, quasiclassical process. A comparison between two-dimensional and three dimensional trajectories was made, and it was found that although the total cross section and energy partitioning are similar for the two calculations, the form of the differential cross section and the angular momentum distribution are different. The calculated total cross section was much too large, and the calculated angular distribution of KI too intense in the forward direction of the K atom beam when a potential that emphasized long range attraction between the K atom and an I atom bonded to CH_3 was used. Attenuation of this K-I attraction brought the calculated results into qualitative agreement with experimental data. Although much computational effort is required even for three atom reactions, comparison between the results of these calculations of reactive scattering and experimental results from molecular beams will eventually provide criteria for the validity of various potential energy surfaces.

Table I
Arrhenius Factors for Radical Addition Reactions

Trichloromethyl Radicals			
<u>Addition to CH₂ of</u>	<u>log A</u> <u>(liter/mole sec)</u>	<u>E(kcal)</u>	<u>Reference</u>
CH ₂ CH ₂	5.6	3.2	73
CHFCH ₂	5.5	3.3	73
CF ₂ CH ₂	5.6	4.6	73
<u>Addition to CF₂ of</u>			
CH ₂ CF ₂	5.5	8.3	73
CF ₂ CF ₂	7.1	6.1	73
<u>Addition to CHF of</u>			
CH ₂ CHF	5.4	5.3	73
Ethyl Radicals*			
<u>Addition to vinyl group of</u>	<u>log A/A_r^{1/2}</u> <u>(liters/mole)^{1/2}</u>	<u>E - $\frac{1}{2}E_r$</u> <u>(kcal)</u>	
Acrylonitrile	2.6	3.4	74
Styrene	2.4	4.1	74
Vinyl n-butyl ether	2.2	6.1	74
Vinyl acetate	2.7	6.9	74
Methacrylonitrile	3.2	4.6	75
<u>cis-crotonitrile</u>	2.0	5.0	75
<u>trans-crotonitrile</u>	2.3	5.2	75
Octene-1	2.9	7.6	75
2-Methylpentene-1	2.9	7.3	75

* A_r and E_r refer to Arrhenius parameters for ethyl radical recombination.

Table II

Arrhenius Factors for H-atom Abstraction by Methyl Radicals

<u>Substrate</u>	<u>log A(liter/mole sec)</u>	<u>E(kcal)</u>	<u>Reference</u>
NH ₂ CHO	7.5	6.6	81
CH ₃ NHCHO	7.9	7.6	81
(CH ₃) ₂ NCHO	8.4	8.3	81
N ₂ D ₄	7.8	6.4	84
CH ₃ C-HO	8.5	6.8	78
H-CH ₂ N ₂ CH ₃	7.9	7.8	79
CH ₃ ONH-H	7.7	4.5	79
CH ₃ OND-D	7.5	5.9	79

LITERATURE CITED

1. Bader, L. W., and Ogryzlo, E. A., Nature, 201, 491 (1964).
2. Bader, L. W., and Ogryzlo, E. A., J. Chem. Phys., 41, 2926
(1964).
3. Hutton, E., Nature, 203, 835 (1964).
4. Hutton, E., and Wright, M., Trans. Faraday Soc., 61, 78
(1965).
5. Gibbs, D. B., and Ogryzlo, E. A., Can. J. Chem., 43, 1905
(1965).
6. van Thiel, M., Seery, D. J., and Britton, D., J. Phys.
Chem., 69, 834 (1965).
7. Kaufman, F., and Kelso, J. R., Disc. Faraday Soc., 37, 26
(1964).
8. Mathias, A., and Schiff, H. I., Disc. Faraday Soc., 37,
38 (1964).

9. Falick, A. M., Mahan, B. H., and Myers, R. J., J. Chem. Phys., 42, 1837 (1965).
10. Bader, L. W., and Ogryzlo, E. A., Disc. Faraday Soc., 37, 46 (1964).
11. Benson, S. W., and Axworthy, A. E., J. Chem. Phys., 42, 2614 (1965).
12. Basco, N., Proc. Roy. Soc., A283, 302 (1965).
13. Kieffer, J. H., and Lutz, R. W., J. Chem. Phys., 42, 1709 (1965).
14. Rink, J. P., Knight, H. T., and Duff, R. E., J. Chem. Phys., 34, 1942 (1961).
15. Knight, A. R., Strausz, O. P., Malm, S. M., and Gunning, H. E., J. Am. Chem. Soc., 86, 4243 (1964).

16. Wiebe, H. A., Knight, A. R., Strausz, O. P., and Gunning, H. E., J. Am. Chem. Soc., 87, 1443 (1965).
17. Gunning, H. E., Trans. Roy. Soc. Canada, 2, 293 (1964).
18. Yamazaki, H., and Cvetanovic, R. J., J. Chem. Phys., 41, 3703 (1964).
19. Warneck, P., J. Chem. Phys., 41, 3435 (1964).
20. Katakis, D., and Taube, H., J. Chem. Phys., 36, 416 (1962).
21. Warneck, P., J. Chem. Phys., 43, 1849 (1965).
22. Cvetanovic, R. J., J. Chem. Phys., 43, 1850 (1965).
23. Doherty, G., and Jonathan, N., Disc. Faraday Soc., 37, 73 (1964).
24. Reeves, R. R., Harteck, P., and Chace, W., J. Chem. Phys., 41, 764 (1965).

25. Clyne, M. A. A., and Thrush, B. A., Proc. Roy. Soc.,
A269, 404 (1962).
26. Halstead, C. J., and Thrush, B. A., Nature, 204, 992 (1964).
27. Rolfes, T. R., Reeves, R. R., and Harteck, P., J. Phys.
Chem., 69, 849 (1965).
28. Sharma, A., Padur, J. P., and Warneck, P., J. Chem. Phys.,
43, 2155 (1965).
29. Arrington, C. A., Brennen, W., Glass, C. P., Michael, J. V.,
and Niki, H., J. Chem. Phys., 43, 1489 (1965).
30. Skell, P. S., and Engel, R. R., J. Am. Chem. Soc., 87,
1135 (1965).
31. Skell, P. S., and Engel, R. R., J. Am. Chem. Soc., 87,
2493 (1965).

32. Skell, P. S., and Engel, R. R., J. Am. Chem. Soc., 87, 1135
(1965).
33. Sprung, J. L., Winstein, S., and Libby, W. F., J. Am. Chem.
Soc., 87, 1812 (1965).
34. Marshall, M., MacKay, C., and Wolfgang, R., J. Am. Chem.
Soc., 86, 4741 (1964).
35. Dubrin, J., MacKay, C., Pandow, M., and Wolfgang, R.,
J. Inorg. Nuclear Chem., 26, 2113 (1964).
36. Dubrin, J., MacKay, C., and Wolfgang, R., J. Chem. Phys.,
41, 3267 (1964).
37. Stief, L. J., and DeCarlo, V. J., J. Chem. Phys., 43,
2552 (1965).
38. Schulz, W. R., and LeRoy, D. J., Can. J. Chem., 42, 2480
(1964).

39. Schulz, W. R., and LeRoy, D. J., J. Chem. Phys., 42, 3869
(1965).
40. Brennen, W., and Niki, H., J. Chem. Phys., 42, 3725 (1965).
41. Herron, J. T., and Klein, F. S., J. Chem. Phys., 40, 2731
(1964).
42. Phillips, L. F., and Schiff, H. I., J. Chem. Phys., 42,
3171 (1965)
43. Clyne, M. A. A., and Thrush, B., Trans. Faraday Soc.,
57, 69 (1961).
44. Fersht, E., and Back, R. A., Can. J. Chem., 43, 1899 (1965).
45. Elias, L., J. Chem. Phys., 42, 4311 (1965).
46. Westenberg, A. A., and de Haas, N., J. Chem. Phys., 40,
3087 (1964).

47. Von Weyssenhoff, H., and Patapoff, M., J. Phys. Chem.,
69, 1759 (1965).
48. Herron, J. T., J. Phys. Chem., 69, 2736 (1965).
49. Airey, J., Getty, R., Polanyi, J., and Snelling, D.,
J. Chem. Phys., 41, 3255 (1964).
50. Herschbach, D. R., Disc. Faraday Soc., 33, 149 (1962).
51. Dixon-Lewis, G., Sutton, M. M., and Williams, A., Trans.
Faraday Soc., 61, 255 (1965).
52. Gowenlock, B. E., and Thomas, K. E., J. Chem. Soc., 5068
(1965).
53. Westenberg, A. A., J. Chem. Phys., 43, 1544 (1965).
54. Westenberg, A. A., and de Haas, N., J. Chem. Phys., 43,
1550 (1965).

55. Kaufman, F., and Del Greco, F. P., Symp. Combust. 9th,
Cornell University, Ithaca, N.Y., 1962, 659 (1963).
56. Goy, G. A., and Pritchard, H. O., J. Phys. Chem., 69, 3040
(1965).
57. Benson, S. W., Egger, K. W., and Golden, D. M., J. Am.
Chem. Soc., 87, 468 (1965).
58. Cadle, R. D., and Allen, E. R., J. Phys. Chem., 69, 1611
(1965).
59. Saunders, D., and Heicklen, J., J. Am. Chem. Soc., 87,
2088 (1965).
60. Sullivan, J. O., and Warneck, P., J. Phys. Chem., 69,
1749 (1965).
61. Arrington, C., Brennen, W., Glass, G., Michael, J., and
Niki, H., J. Chem. Phys., 43, 525 (1965).

62. Pritchard, G. O., Venugopalan, M., and Graham, T., J. Phys. Chem., 68, 1786 (1964).
63. Pritchard, G. O., and Bryant, J. T., J. Phys. Chem., 69, 1085 (1965).
64. Pritchard, G. O., Bryant, J. T., and Thommarson, R., J. Phys. Chem., 69, 2804 (1965).
65. Alcock, W. G., and Whittle, E., Trans. Faraday Soc., 61, 244 (1965).
66. Giles, R. D., and Whittle, E., Trans. Faraday Soc., 61, 1425 (1965).
67. Arthur, N., and Bell, T., Chem. Comm., 166 (1965).
68. Basco, N., and Norrish, R. G. W., Proc. Roy. Soc., A283, 291 (1965).

69. Salzman, J., and Bair, E. J., J. Chem. Phys., 41, 3654
(1964).
70. Gordon, A. S., Can. J. Chem., 43, 570 (1965).
71. James, D. G. L., and Suart, R. D., J. Am. Chem. Soc., 86,
5424 (1964).
72. James, D. G. L., and Troughton, C. E., Chem. Comm., 94
(1965).
73. Tedder, J. M., and Walton, J. C., Proc. Chem. Soc., 420
(1964).
74. James, D. G. L., and MacCallum, D., Can. J. Chem., 43,
633 (1965).
75. James, D. G. L., and MacCallum, D., Can. J. Chem., 43,
640 (1965).

76. Owen, G. E., Pearson, J. M., and Szwarc, M., Trans. Faraday Soc., 61, 1722 (1965).
77. Christie, M. I., and Frost, J. S., Trans. Faraday Soc., 61, 468 (1965).
78. Kerr, J. A., and Calvert, J. G., J. Phys. Chem., 69, 1022 (1965).
79. Thynne, J. C. J., Trans. Faraday Soc., 60, 2207 (1964).
80. Gray, P., Jones, A., and Thynne, J. C. J., Trans. Faraday Soc., 61, 474 (1965).
81. Cafferata, L., Kerr, J., and Trotman-Dickenson, A., J. Chem. Soc., 1386 (1965).
82. Mulcahy, M., and Williams, D. J., Austral. J. Chem., 18, 1329 (1964).

83. Mulcahy, M., Williams, D. J., and Wilmhurst, J. R.,
Austral. J. Chem., 17, 1329 (1964).
84. Gray, P., and Jones, A., Chem. Comm., 360 (1965).
85. Pritchard, G. O., Bryant, J. T., and Thommarson, R. L.,
J. Phys. Chem., 69, 664 (1965).
86. Grzechowiak, J., Kerr, J. A., and Trotman-Dickenson, A. F.,
Chem. Comm., 109 (1965).
87. Grzechowiak, J., Kerr, J. A., and Trotman-Dickenson, A. F.,
J. Chem. Soc., 5080 (1965).
88. King, K. D., and Swinbourne, E. S., Austral. J. Chem., 18,
121 (1965).
89. Goy, C. A., Shaw, D. H., and Pritchard, H. O., J. Phys. Chem.,
69, 1504 (1965).

90. Bader, R. F. W., and Generosa, J. J., Can. J. Chem., 43,
1631 (1965).
91. Frey, H. M., Chem. Comm., 260 (1965).
92. Casas, F., Kerr, J. A., and Trotman-Dickenson, A. F.,
J. Chem. Soc., 1141 (1965).
93. Setser, D. W., Littrell, R., and Hassler, J. C., J. Am.
Chem. Soc., 87, 2062 (1965).
94. Back, M. H., Can. J. Chem., 43, 106 (1965).
95. Heicklen, J., Cohen, N., and Saunders, D., J. Phys. Chem.,
69, 1774 (1965).
96. Simons, J. P., Nature, 205, 1308 (1965).
97. Campbell, I. M., and Thrush, B. A., Proc. Chem. Soc.,
410 (1964).

98. McGarvey, J. J., and McGrath, W. D., Trans. Faraday Soc.,
60, 2196 (1964).
99. Thynne, J. C. J., J. Chem. Soc., 5882 (1964).
100. Tucker, B. G., and Whittle, E., Trans. Faraday Soc., 61,
484 (1965).
101. Olschewski, H., Troe, J., and Wagner, H. G., Z. Phys. Chem.
(Frankfurt), 44, 173 (1965).
102. Olschewski, H., Troe, J., and Wagner, H. G., Z. Phys. Chem.
(Frankfurt), 45, 329 (1965).
-
103. Brown, L. M., and Darwent, B. deB., J. Chem. Phys., 42,
2158 (1965).
104. Tschuikow-Roux, E., J. Chem. Phys., 43, 2739 (1965).
105. Modica, A. P., and Hornig, D. F., J. Chem. Phys., 43, 2739
(1965).

106. Diesen, R. W., J. Chem. Phys., 41, 3256 (1964).
107. Davies, W. O., J. Chem. Phys., 43, 2809 (1965).
108. Davies, W. O., J. Chem. Phys., 41, 1848 (1964).
109. Michel, K. W., Olschewski, H. A., Richtering, H., and Wagner, H. G., Z. Phys. Chem. (Frankfurt), 44, 160 (1965).
110. Bauer, E. H., Ann. Rev. Phys. Chem., 16, 245 (1965).
111. Schofield, D., Tsang, W., and Bauer, S. H., J. Chem. Phys., 42, 2132 (1965).
112. Tschuikow-Roux, E., and Marte, J. E., J. Chem. Phys., 42, 2049 (1965).
113. Elliott, C. S., and Frey, H. M., J. Chem. Soc., 4289 (1965).
114. Ellis, R. J., and Frey, H. M., J. Chem. Soc., 5578 (1964).
115. Srinivasan, R., Levi, A., and Haller, I., J. Phys. Chem., 69, 1775 (1965).

116. Frey, H. M., and Stevens, I. D. R., Trans. Faraday Soc.,
61, 90 (1965).
117. Chesick, J., J. Phys. Chem., 68, 2033 (1964).
118. Carr, R. W., and Walters, W. D., J. Phys. Chem., 69, 1073
(1965).
119. Frey, H. M., Marshall, D. C., and Skinner, R. F., Trans.
Faraday Soc., 61, 861 (1965).
120. Frey, H. M., and Marshall, D. C., Trans. Faraday Soc.,
61, 1715 (1965).
121. Roquette, B. C., J. Phys. Chem., 69, 1351 (1965).
122. Grant, R. C. S., and Swinbourne, E. S., J. Chem. Soc.,
4423 (1965).
123. Frey, H. M., and Ellis, R. J., J. Chem. Soc., 4770 (1965).
124. Tsang, W., J. Chem. Phys., 43, 352 (1965).

125. Schlag, E. W., and Kaiser, E. W., J. Am. Chem. Soc.,

87, 1171 (1965).

126. Placzek, D. W., and Rabinovitch, B. S., J. Phys. Chem.,

69, 2141 (1965).

127. Pearson, M. J., and Rabinovitch, B. S., J. Chem. Phys.,

42, 1624 (1965).

128. Pearson, M. J., Rabinovitch, B. S., and Whitten, G. Z.,

J. Chem. Phys., 42, 2470 (1965).

129. Halberstadt, M. L., and Chesick, J. P., J. Phys. Chem.,

69, 429 (1965).

130. Rabinovitch, B. S., Gilderson, P. W., and Schneider, F. W.,

J. Am. Chem. Soc., 87, 158 (1965).

131. Hunt, M., Kerr, J. A., and Trotman-Dickenson, A. F.,

J. Chem. Soc., 5074 (1965).

132. Yang, J. H., and Conway, D. C., J. Chem. Phys., 43, 1296
(1965).
133. Dexter, R. W., and Trenwith, A. B., Proc. Chem. Soc.,
392 (1964).
134. Lenzi, M., and Mele, A., J. Chem. Phys., 43, 1974 (1965).
135. Rice, O. K., J. Phys. Chem., 65, 1972 (1961).
136. Snider, N. S., J. Chem. Phys., 42, 548 (1965).
137. Widom, B., Science, 148, 1555 (1965).
138. Keck, J., and Carrier, G., J. Chem. Phys., 43, 2284 (1965).
139. Woznick, B. J., J. Chem. Phys., 42, 1151 (1965).
140. Pechukas, P., and Light, J. C., J. Chem. Phys., 42, 3281
(1965).
141. Light, J. C., J. Chem. Phys., 40, 3221 (1964).
142. Light, J. C., and Lin, J., J. Chem. Phys., 43, 3209 (1965).

143. Henglein, A., Lacmann, K., and Jacobs, C., Ber. Bunsen Gesellschaft Phys. Chem., 69, 279 (1965).
144. Henglein, A., Lacmann, K., and Jacobs, C., Ber. Bunsen Gesellschaft Phys. Chem., 69, 286 (1965).
145. Lacmann, K., and Henglein, A., Ber. Bunsen Gesellschaft Phys. Chem., 69, 292 (1965).
146. Nikitin, E. E., Mol. Phys., 8, 473 (1964).
147. Marcus, R. A., J. Chem. Phys., 41, 603 (1964).
148. Marcus, R. A., J. Chem. Phys., 41, 610 (1964).
149. Marcus, R. A., J. Chem. Phys., 41, 2614 (1964).
150. Marcus, R. A., J. Chem. Phys., 41, 2624 (1964).
151. Marcus, R. A., J. Chem. Phys., 43, 1598 (1965).
152. Nyeland, C., and Bak, T. A., Trans. Faraday Soc., 61, 1293 (1965).

153. Schlag, E. W., and Haller, G. L., J. Chem. Phys., 42,
584 (1965).
154. Bishop, D. M., and Laidler, K. J., J. Chem. Phys., 42,
1688 (1965).
155. Baetzold, R. C., and Wilson, D. J., J. Phys. Chem., 68,
3141 (1964).
156. Marcus, R. A., J. Chem. Phys., 43, 2658 (1965).
157. Conroy, H., and Bruner, B. L., J. Chem. Phys., 42, 4047
(1965).
158. Edmiston, C., and Krauss, M., J. Chem. Phys., 42, 1119
(1965).
159. Benson, S. W., and Haugen, G. R., J. Am. Chem. Soc., 87,
4036 (1965).

160. Carrington, T., J. Chem. Phys., 43, 473 (1965).
161. Serauskas, R. V., and Schlag, E. W., J. Chem. Phys., 42,
3009 (1965).
162. Kostin, M. D., J. Chem. Phys., 43, 2679 (1965).
163. Shin, H., J. Phys. Chem., 68, 3410 (1964).
164. Shin, H., J. Phys. Chem., 69, 2411 (1965).
165. McDaniel, E. W., Collision Phenomena in Ionized Gases
(Wiley, New York, 1964).
166. Hasted, J. B., Physics of Atomic Collisions (Butterworths,
London, 1964).
167. Bates, D. R., Atomic and Molecular Processes (Academic
Press, New York, 1962).
168. Biondi, M. A., Adv. Electronics and Electron Physics, 10,
67 (1963).

169. Franklin, J. L., and Matsen, F. A., J. Chem. Phys., 41,
2948 (1964).
170. Becker, P. M., and Lampe, F. W., J. Chem. Phys., 42, 3857
(1965).
171. Lee, Y., and Mahan, B. H., J. Chem. Phys., 42, 2893 (1965).
172. Kasner, W. H., and Biondi, M. A., Phys. Rev., 137, A317
(1965).
173. Gunton, R. C., and Shaw, T. M., Phys. Rev., 140, A756
(1965).
174. Rogers, W. A., and Biondi, M. A., Phys. Rev., 134, A1215
(1964).
175. Robertson, W. W., J. Chem. Phys., 42, 2065 (1965).
176. Mahan, B. H., and Person, J. C., J. Chem. Phys., 40, 392
(1964).

177. Carlton, T. S., and Mahan, B. H., J. Chem. Phys., 40,
3683 (1964).
178. Mahan, B. H., and Person, J. C., J. Chem. Phys., 40, 2851
(1964).
179. Thomson, J. J., Phil. Mag., 47, 337 (1924).
180. Natanson, G. L., Soviet Phys.-Tech. Phys., 4, 1263 (1959).
181. Brueckner, K. A., J. Chem. Phys., 40, 439 (1964).
182. Feibelman, P. J., J. Chem. Phys., 42, 2462 (1965).
183. Beaty, E. C., and Patterson, P., Proc. Intern. Conf.
Ionization Phenomena in Gases, 6th Paris, 1963, 1, 311
(1965).
184. Beaty, E. C., and Patterson, P., Phys. Rev., 137, A347
(1965).

185. Niles, F. E., and Robertson, W. W., J. Chem. Phys., 42,
3277 (1965).
186. Niles, F. E., and Robertson, W. W., J. Chem. Phys., 43,
1077 (1965).
187. Mahan, B. H., J. Chem. Phys., 43, 3080 (1965).
188. Giese, C. F., and Maier, W. B., J. Chem. Phys., 39, 739
(1963).
189. Giese, C. F., and Maier, W. B., J. Chem. Phys., 39, 197
(1963).
190. Maier, W. B., J. Chem. Phys., 41, 2174 (1964).
191. Maier, W. B., J. Chem. Phys., 42, 1790 (1965).
192. Hertel, G. R., and Koski, W. S., J. Am. Chem. Soc., 87,
1686 (1965).

193. Berta, M. A., and Koski, W. S., J. Am. Chem. Soc., 86,
5098 (1964).
194. Turner, B., Fineman, M., and Stebbings, R., J. Chem. Phys.,
42, 4088 (1965).
195. Henglein, A., Lacmann, K., and Knoll, B., J. Chem. Phys.,
43, 1048 (1965).
196. Moran, T. F., and Friedman, L., J. Chem. Phys., 42, 2391
(1965).
197. Friedman, L., and Moran, F. T., J. Chem. Phys., 42, 2624
(1965).
198. Hand, C. W., and von Weyssenhoff, H., Can. J. Chem., 42,
2385 (1964).
199. Shannon, T. W., Meyer, F., and Harrison, A., Can. J. Chem.,
43, 159 (1965).

200. Ryan, K. R., and Futrell, J. H., J. Chem. Phys., 42,
824 (1965).
201. Datz, S. W., and Minturn, R. E., J. Chem. Phys., 41,
1153 (1965).
202. Wilson, K. R., Kwei, G. H., Norris, J. A., Herm, R. R.,
Birely, J. H., and Herschbach, D. R., J. Chem. Phys.,
41, 1154 (1965).
203. Herm, R. R., Gordon, R., and Herschbach, D. R., J. Chem.
Phys., 41, 1887 (1964).
204. Ackerman, M., Greene, E. F., Moursund, A. L., and Ross,
J., J. Chem. Phys., 41, 1183 (1964).
205. Grosser, A. E., Blythe, A. R., and Bernstein, R. B.,
J. Chem. Phys., 42, 1268 (1965).

206. Grosser, A. E., and Bernstein, R. B., J. Chem. Phys.,

43, 1140 (1965).

207. Karplus, M., and Raff, L. M., J. Chem. Phys., 41, 1267

(1964).

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.

