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Gas Phase Reaction of Diazomethane with Hydrogen Chloride, Bromide, and Iodide. An Example of Polar Transition States in the Gas Phase¹

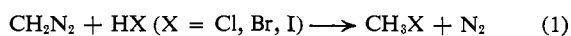
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Diazomethane reacts with HX ($X = Cl, Br, I$) in the gas phase to yield the corresponding methyl halide and nitrogen. The reaction, which is quantitative, stoichiometric, homogeneous, and extremely rapid, may involve a highly polar or "semi-ionic" transition state. Since the reaction is exothermic by approximately the heat of formation of diazomethane, the methyl halides may be generated in high-energy states. Observation of the subsequent unimolecular decomposition of the activated CH_3I indicates that much of the energy is distributed among the internal degrees of freedom of the methyl halide. Combining this information with the fact that CH_3Br did not undergo unimolecular decomposition leads to the reasonable limits of 64–77 kcal. mole⁻¹ for the ΔH_f^\ddagger of diazomethane. It was shown that O_2 does not react with these highly activated methyl halide molecules.

Introduction

Recently, polar or semi-ionic² transition states have been proposed as being important for some types of gas phase reactions. The heretofore unreported gas phase reaction of diazomethane with hydrogen halides appears to be an especially good example. Reaction 1, for a



variety of both inorganic and organic acids, is well known in ether and other solvents.^{3a} The mechanism

(1) This work was supported in part by the National Science Foundation; abstracted from the Ph.D. Thesis of J. C. Hassler, Kansas State University, 1965.

(2) (a) A. Maccoll and P. J. Thomas, *Nature*, **176**, 392 (1955); (b) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963); (c) S. W. Benson, *Advan. Photochem.*, **2**, 1, 219 (1964).

is apparently not fully understood; however, tentative proposals^{3b} involve polar transition states. It was impossible to measure the kinetics of reaction 1 in the gas phase with the present experimental arrangement because of the extremely rapid rate even at -78° . However, relative rates of formation of the hydrogen halides which were measured, as well as other pertinent information, strongly suggest that reaction 1 is a true homogeneous bimolecular reaction.

In addition to the novelty associated with the semi-ionic-type transition state, these reactions are of interest for at least two other reasons. In each of the three cases in (1), the heat of reaction is approximately equal to the heat of formation of diazomethane, and the resulting methyl halides may be chemically activated.⁴ Observation of the unimolecular decomposition of methyl iodide leads to the conclusion that much of the energy of the reaction resides in the internal degrees of freedom of the methyl halide. Also some closer limits are set on the possible values for the heat of formation of diazomethane; previous values⁵ range from 31–104 kcal. mole⁻¹.

Finally, there has been discussion⁶ as to whether or not O_2 will react with highly vibrationally excited hydrocarbon molecules at a bath temperature near 25° . The

(3) (a) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p. 69; (b) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 376.

(4) B. S. Rabinovitch and M. C. Flowers, *Quart. Rev. (London)*, **18**, 122 (1964). Reaction 1 corresponds to a type-IV chemical activation reaction.

(5) (a) J. A. Bell, *J. Chem. Phys.*, **41**, 2556 (1964); (b) G. S. Paulett and R. Ettinger, *ibid.*, **41**, 2557 (1964); **39**, 825, 3534 (1963).

(6) (a) D. W. Setser, D. W. Placzek, R. J. Cvetanović, and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 2179 (1962); (b) J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1302 (1964).

systems represented in eq. 1 do not possess as high a vibrational energy as might be desired; however, they do provide a case for testing the reaction of O₂ with highly activated molecules.

Experimental

Materials. Pure diazomethane was prepared from the precursor, bis(N-methyl-N-nitroso)terephthalamide,^{7a} and stored in di-*n*-butyl phthalate^{7b} at -198°. HCl, HBr, HI, and HCN were prepared by standard techniques. Matheson research grade CF₄ and *c*-C₄F₈ were used.

Apparatus and Procedure. All gas handling was performed with a conventional vacuum system. It was not necessary to exclude light from the reaction system since identical results were obtained with reactions run in sunlight and in the dark. The reaction is quite exothermic and it was necessary to include an inert gas (CF₄ or *c*-C₄F₈) in order to prevent explosion of diazomethane initiated by the localized heating. The reaction vessels were 5- to 500-cc. Pyrex spherical flasks. The inlet to the flask consisted of a capillary tube (1 mm. diameter) which extended to the center of the flask. A three-way stopcock connected the capillary inlet to the vacuum system and to a second small (1-5-ml.) Pyrex bulb. The experiments were done in the following way. The acid or mixture of acids, depending upon the particular experiment, with inert gas was transferred into the reaction flask and allowed to mix. Diazomethane and some inert gas were placed in the smaller bulb at a pressure exceeding that in the reaction vessels by a factor of two to four. Turning the stopcock allowed the diazomethane to flow into the center of the reaction vessel *via* the capillary inlet and reaction resulted. For the low temperature runs, the reaction vessel and capillary inlet, as well as the smaller bulb, were cooled in a Dry Ice-acetone bath. The length between the capillary inlet and the stopcock was made unusually long, about 20 cm., in an attempt to ensure that the incoming diazomethane was at -78°. The above described technique is not perfect; undoubtedly spurious mixing and pressure surges are present during the reaction. A true flow system would be more desirable but was beyond our present capabilities.

Analysis. In the determination of the rate constant ratio for reaction 1 with HCl, HBr, and HI, tetrafluoromethane was used as the inert gas. It was necessary to remove the CF₄ and excess HX before g.l.p.c. analysis could be done. CF₄ was conveniently removed by pumping on the condensed sample at liquid oxygen temperatures. The excess HX was removed by adding NH₃, and the excess NH₃ was in turn removed with Mg(ClO₄)₂. The mixture of methyl halides was then analyzed by g.l.p.c. with an Octoil S column. It may be worth noting that quantitative measurement and transfer of diazomethane is impossible owing to slow decomposition yielding polymer and N₂ on the surface of even seasoned Pyrex vessels.

The methyl halide unimolecular decomposition gives methyl radicals and halogen atoms. Two techniques were developed for determining the rate constants for these decomposition reactions.

One scheme involved measuring methane and nitrogen in the following way. The total quantity of methyl halide initially formed by reaction 1 was measured by analysis of the N₂ released to the reaction vessel. Since the abstraction reaction of methyl radicals with HX to give methane is fast and since HX was always present in excess, analysis for methane should give the quantity of CH₃X that dissociates. The difference between the nitrogen and methane is the stabilized CH₃X. In these particular runs the inert gas was perfluorocyclobutane. Analysis of products was performed by cooling the vessel and contents to -198°; the noncondensable N₂ and CH₄ were then quantitatively transferred directly into the gas chromatograph inlet with the aid of silica gel cooled to -198° and analyzed with a molecular sieve 5A column. The identity of N₂ and CH₄ as reaction products was confirmed by mass spectral analysis.

The second technique employed O₂ as a scavenger for methyl radicals. In these experiments oxygen was mixed with the inert gas, tetrafluoromethane. Excess diazomethane was added to a known quantity of HX which was measured in a mercury-free system. The measured quantity of CH₃X gave the stabilized portion of the reaction; the difference between this quantity and 100% yield was considered to be equal to the dissociated methyl halide. The deviation from 100% yield of CH₃X was then measured as a function of pressure. Further discussion and comparison of these two methods are given in the Results section.

Results

Diazomethane Reaction with HX. Some difficulties encountered in analyzing CH₃X in the presence of HX may be worth mentioning. The problem is the removal of the HX prior to g.l.p.c. analysis. Initially, excess HX was removed with solid NaOH. Entry 1 of Table I shows typical results obtained by this method; Table II shows the correct results and illustrates the magnitude of the error. Blank runs with prepared CH₃Cl-CH₃Br mixtures were not affected by the NaOH treatment, but the ratio changed when HX was added to the control mixture. Apparently, the H₂O formed in the reaction of HX with NaOH caused the CH₃X mixture to undergo basic hydrolysis, lowering the ratio of CH₃Br to CH₃Cl. The NH₃ method of removing HX, described in the Experimental section, was shown not to affect the product ratio and was used to obtaining the data of Tables I and II except where noted otherwise.

The reaction of diazomethane with the hydrogen halides is both rapid and exothermic. Experiments without inert gas resulted in mild diazomethane explosions which could be visibly detected by flashes of light in a darkened room. The use of a 1:1 diazomethane-CF₄ mixture but with no inert gas with the HX prevented these visible explosions; however, the results were erratic, as shown in entry 2 of Table I. It was necessary to use a 5:1 CF₄-HX ratio in order to increase the concentration of bath molecules relative to the reacted molecules, as well as some inert gas with the CH₂N₂, in order to obtain consistent results. Further increase of the ratio of CF₄ to HX did not affect the results.

The reactions of diazomethane with the hydrogen halides were too fast for the kinetics to be measured with the present equipment. Experiments 3, 4, and 5

(7) (a) Commercially available as EXR-101 from the Explosives Department, E. I. du Pont de Nemours and Co.; (b) H. M. Frey, *Proc. Roy. Soc. (London)*, A250, 409 (1959).

Table I.^a Reaction of HX with CH₂N₂

Expt.	Reactants	Products	Remarks
1 ^c A	(HCl-HBr = 1:1) + CH ₂ N ₂	CH ₃ Br/CH ₃ Cl ^b = 1.73	NaOH removal of HCl and HBr
B	(HCl-HBr = 1:1) + CH ₂ N ₂	CH ₃ Br/CH ₃ Cl ^b = 1.88	NaOH removal of HCl and HBr
2 ^c A	(HBr-HCl = 2:1) + CH ₂ N ₂	CH ₃ Br/CH ₃ Cl ^b = 22.4	$\left. \begin{array}{l} \text{NH}_3 \text{ removal of HCl and HBr} \\ \text{CF}_4\text{-CH}_2\text{N}_2 = 1:1; \text{ no inert gas with HCl-HBr mixture} \end{array} \right\}$
B	(HBr-HCl = 4:1) + CH ₂ N ₂	CH ₃ Br/CH ₃ Cl ^b = 18.2	
C	(HBr-HCl = 1:1) + CH ₂ N ₂	CH ₃ Br/CH ₃ Cl ^b = 7.9	
D	(HBr-HCl = 8:1) + CH ₂ N ₂	CH ₃ Br/CH ₃ Cl ^b = 6.7	
3 ^d A	(HCl-CF ₄ = 1:10) + CH ₂ N ₂	CH ₃ Cl, 101% yield	4:1 O ₂ -HCl
B	(HCl-CF ₄ = 1:10) + CH ₂ N ₂	CH ₃ Cl, 97% yield	1:1 O ₂ -HBr
4 ^d A	(HBr-CF ₄ = 1:10) + CH ₂ N ₂	CH ₃ Br, 101% yield	1:1 O ₂ -HBr
B	(HBr-CF ₄ = 1:10) + CH ₂ N ₂	CH ₃ Br, 100% yield	30:1 O ₂ -HBr ^e
C	(HBr-CF ₄ = 1:10) + CH ₂ N ₂	CH ₃ Br, 104% yield	No O ₂
5 ^d A	(HI-CF ₄ = 1:40) + CH ₂ N ₂	CH ₃ I, 88% yield	20:1 O ₂ -HI ^g
B	(HI-CF ₄ = 1:20) + CH ₂ N ₂	CH ₃ I, 74% yield	20:1 O ₂ -HI ^h
6 ^c	(HBr-CF ₄ = 1:10) + CH ₂ N ₂	CH ₃ Br, 90% yield	Yield calculated on estimated CH ₂ N ₂ added to vessel ^f
7 ^c	(4:1 HBr-HCl mixture with tenfold excess CF ₄) + CH ₂ N ₂	CH ₃ Br/CH ₃ Cl ^b = 7.5	Fiberglas added to reaction vessel to increase surface area

^a All experiments were done at 300°K. ^b The tabulated value is the experimentally measured ratio converted to the ratio that a 1:1 mixture of HCl-HBr would have yielded. ^c Experiments run with excess HX- or HX₁-HX₂ mixtures. ^d Experiments run with measured quantities of HX and excess CH₂N₂. CF₄ was also present in the CH₂N₂. ^e Low-pressure run (2 cm.) which shows that CH₃Br is not dissociating at this pressure. ^f CH₂N₂ always reacts to some extent on glass surfaces, and complete transfer of small samples is impossible. ^g Pressure, 400 cm. ^h Pressure, 240 cm.

Table II.^a Relative Rate Constants

Reactants HX ₂ -HX ₁	Rate constant ratio		Arrhenius parameters (E ₂ - E ₁), kcal. mole ⁻¹	
	300°K.	195°K.	A ₂ /A ₁	
HBr-HCl	9 ± 2	3 ± 4	0.81 (0.93) ^b	-1.5
HI-HBr	4 ± 2	...	(1.03) ^b	(-0.8) ^c
HI-HCl	50 ± 15	...	(0.96) ^b	(-2.3) ^c

^a These experiments were done with a tenfold excess of CF₄ to hydrogen halide; since the limiting reactant is CH₂N₂, this is really a 1:30 mixture of CF₄ to reacted hydrogen halide. ^b A₂/A₁ calculated from collision theory with collision cross sections⁸ for HCl, HBr, HI, and CH₂N₂ of 3.3, 3.7, 4.1, and 4.2 Å., respectively. ^c (E₂ - E₁) calculated from A₂/A₁ and the 300°K. result.

of Table I show that the reaction is quantitative for HCl, HBr, and at high pressures for HI. The reaction with HI differs from the other two cases because the methyl iodide is formed with sufficient energy that decomposition may occur unless the molecules deactivated by collisions. This is discussed in detail below. At this point, it is sufficient to note that within the limited accuracy of our measurements the reaction between HI and CH₂N₂ is quantitative at high pressures. The failure to achieve 100% yield with experiment 5 of Table I is attributed to incomplete collisional quenching of the decomposition reaction of methyl iodide.

It should be noted that reaction 1 provides a quick method for the quantitative measurement of small gaseous samples of HCl and HBr. G.l.p.c. analysis of the resulting methyl halides by the method described in the Experimental section is convenient and reliable. Due to the necessity of high pressure, this method is not convenient for HI.

It proved impossible to show with equal precision that the yields were also quantitative with respect to diazomethane, since diazomethane reacts with even a well-seasoned glass surface to some extent and prevents

precision measurements or quantitative transfers. A typical result is entry 6 of Table I. Within our experimental error, the reaction is quantitative with respect to diazomethane as well as with respect to HCl and HBr and could be used as a technique for measuring small gas phase quantities of CH₂N₂.

The results of entries 3, 4, and 5 of Table I (the high-pressure condition applies to CH₃I) show that reaction 1 is not sensitive to oxygen even in relatively large quantities; therefore, the reaction between the hydrogen halides and diazomethane cannot involve significant quantities of free radicals.

Entry 7 of Table I compared to Table II also demonstrates that a large increase of surface area of the reaction flask had no influence on the ratio of reaction rates between HCl and HBr. If the entire reaction occurred on the surface, increasing the surface would not be a test for heterogeneity. The quenching of explosions by an inert gas and the occurrence of the pressure effect upon CH₃I yields, which is discussed in a later section, strongly indicate that reaction 1 is, at least in part, a gas phase reaction. Therefore entry 7 can be used to establish that the surface is relatively unimportant for reaction 1.

A few experiments were done with HCN and CH₂N₂. Reaction 1 does take place to give methyl cyanide and nitrogen and is again very rapid. However, some type of secondary reaction seemed to occur and the maximum yield of methyl cyanide was about 50%.

In order to obtain relative Arrhenius parameters, the product ratios were measured at 300 and 195°K., Table II. These experiments were done by expanding diazomethane into an excess of the HX₁-HX₂ mixture diluted with CF₄. Owing to the necessity of using pressures above 400 cm., it was difficult to obtain reliable ratios with HI as a reactant. The ratios for HI were measured at 400 cm. pressure and then corrected for the less than 100% yield of CH₃I (Table I, entry 5) under these conditions. Attempted runs at 195°K. were unsatisfactory

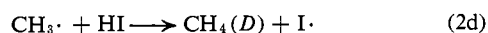
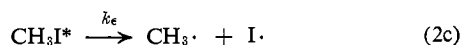
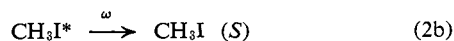
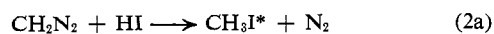
presumably owing to changing per cent yield for CH₃I relative to the room temperature results. The possibility of heating and consequent change in temperature of the bath as a result of the exothermic nature of reaction 1 was investigated by varying the ratio of CF₄ to the reacted products from 30:1 up to 150:1. No trend in the CH₂Br-CH₃Cl yields was discernible. Such effects would be more important for CH₃I since it is the fastest reaction. The scatter of the results could have masked a trend for this case. Although these results have limitations, we have taken the wall temperatures to be equal to the bath temperatures for the calculations of Table II.

The ratio of Arrhenius pre-exponential factors and the difference in activation energies were calculated from the HBr-HCl ratios at 300 and 195°K. The pre-exponential ratio obtained from simple collision theory and standard collision cross sections⁸ is in agreement with the measured values. For HI the ratios of pre-exponential factors were calculated and the activation energy differences were then obtained from the room temperature rate ratios. It is evident that the principal effect for the hydrogen halide series in an increase in the activation energy in proceeding from HI to HCl.

Attempts were made to quench the HCl reaction at 195°K. before the reaction was complete. This proved impossible with our experimental arrangement and the reaction must be essentially complete within 1 min. Since the HI reaction is roughly 60 times faster (Table II), it must be complete within 1 sec. Using conservative estimates of 50% reaction in 1 sec. at 195°K. and a collision efficiency of 1×10^{-2} , an upper limit of 6 kcal. mole⁻¹ is obtained for the activation energy of the HI reaction.

Unimolecular Decomposition of the Methyl Halides. The heats of formation for the pairs HCl-CH₃Cl (-22.1 and -19.6),⁹ HBr-CH₃Br (-8.7 and -8.5),⁹ and HI-CH₃I (6.2⁹ and 2.3¹⁰) show that reaction 1 is exothermic to the extent of the ΔH_f of diazomethane which is not known accurately but lies in the range⁵ 31-104 kcal. mole⁻¹. The activation energy for the decomposition of CH₃X (X = Cl, Br, I) can be set equal to the bond dissociation energies which are 80,⁹ 67,⁹ and 54¹⁰ kcal. mole⁻¹, respectively. Depending upon the magnitude of the $\Delta H_f(\text{CH}_2\text{N}_2)$, the activation energy for reaction 1, and the way in which the energy is partitioned among the degrees of freedom of the reaction products, the methyl halides may be formed in an energy state that is favorable for decomposition. This possibility was investigated in two ways.

One method used excess HI as a scavenger for the methyl radicals. Reactions 2a-d, where an asterisk signifies a vibrationally excited molecule capable of undergoing unimolecular decomposition, summarize



(8) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, N. Y., 1954.

(9) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500, U. S. Government Printing Office, Washington, D. C.

(10) M. C. Flowers and S. W. Benson, *J. Chem. Phys.*, **38**, 882 (1963).

this approach. The excited molecule may either be collisionally stabilized (2b) where ω is the collision frequency, or it may decompose (2c) where k_ϵ is the specific rate constant for unimolecular decomposition at energy ϵ . S and D are the quantities of methyl iodide stabilized and decomposed, respectively. Reaction 2d is quite rapid,¹⁰ and, since the reactions were run with excess HI, the methyl radicals should be quantitatively converted to methane. The results of these experiments, which are shown in Table III, conclusively demonstrate the presence of methane.

Table III. CH₃I Decomposition by Methane Analysis

Pressure, cm.	Products ^b		Rate constant, ^{a,c} $k_a \times 10^{-9}$, sec. ⁻¹
	CH ₄ (D)	N ₂ - CH ₄ (S)	
13	170	72	1.9
16	154	150	1.1
18	129	110	1.1
23	113	267	0.5
25	52	46	1.8
27	53	145	0.6
34	66	149	0.9
38	100	113	1.8
47	25	127	0.5
60	12	38	1.1
61	26	69	1.4
61	144	282	1.9
66	30	148	0.8
Average $k_a = 1.2 \times 10^9$ sec. ⁻¹			

^a The ratio of bath molecules (C₄F₈ and HI in approximately equal proportions) to reacted molecules was 100:1. C₄F₈ was also added to the CH₂N₂ to give a 5:1 mixture prior to expansion into HI-C₄F₈ in order to prevent the heating discussed in the text. ^b CH₄ and N₂ - CH₄ are given in arbitrary units. ^c Collision cross sections used to calculate ω were 4.0, 5.9, and 4.1 Å. for CH₃I, C₄F₈, and HI, respectively. The rate constants are defined (see ref. 12) as $k_a = \omega(D/S)$.

A second method used to confirm the results of Table III employed O₂ as a scavenger for the methyl radicals.¹¹ The reactions which summarize this approach are 2a, 2b, 2c, and 3a. It will first be assumed that CH₃O₂



eventually forms stable products without removal of either CH₃I or HI.^{11c} The consequences of this assumption are examined later. In this method, a known quantity of HI was treated with an excess of diazomethane in the presence of O₂, and the absolute yield of CH₃I was measured. This value was taken as the methyl iodide stabilized by collision; the quantity decomposed was taken equal to the difference of this quantity and the HI added to the reaction flask. A 10:1 excess of O₂ to HI was maintained to prevent the possibility of recombination 3a dominated over 2d. The results are shown in Table IV. It is evident that the yields are a function of pressure and that methyl iodide does decompose.

Using the two techniques previously described for methyl iodide, no decomposition of CH₃Br was found down to the lowest pressures studied, which were about 2 mm. for the CH₄-N₂ technique, and ca. 2 cm. for

(11) (a) M. Barber, J. Farren, and J. W. Linnett, *Proc. Roy. Soc. (London)*, **A274**, 306 (1963); (b) J. Heicklen and H. S. Johnston, *J. Am. Chem. Soc.*, **84**, 4030 (1962); (c) for a summary, see D. E. Hoare, and G. S. Pearson, *Advan. Photochem.*, **3**, 83 (1964).

Table IV. CH₃I Decomposition by Yield Analysis

Pressure, cm.	Yield, % (S)	D/S	Rate constant, ^{a,b} $k_a \times 10^{-9}$, sec. ⁻¹
20	25	3.0	4.1
21	34	1.9	3.0
21	30	2.3	4.2
24	25	3.0	4.7
33	28	2.6	5.5
49	45	1.2	3.8
61	48	1.1	4.4
110	48	1.1	7.8
240	86	0.2	3.1
240	74	0.4	6.1
400	76	0.3	7.7
400	88	0.1	2.6

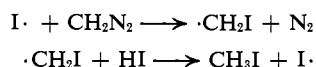
Average $k_a = 4.8 \times 10^9 \text{ sec.}^{-1}$

^a The rate constants are defined¹² as $k_a = \omega(D/S)$. The inert gas was CF₄; the total ratio of bath molecules (essentially 20% O₂ and 80% CF₄) to reacted molecules was greater than 100:1. CF₄ was also added to the CH₂N₂. ^b The collision cross sections that were used for the calculation are 4.0, 4.6, and 3.4 Å. for CH₃I, CF₄, and O₂, respectively.

absolute yield analysis (see footnote e, Table I). This indicates that methyl bromide is not formed in an energy state that is capable of decomposing. Since the activation energy for methyl chloride decomposition is even higher than for methyl bromide, it was not investigated. The calculated rate constants in Figure 1 for CH₃Br decomposition show that, at the pressures mentioned above, the CH₃Br should decompose if it was formed at an energy above the activation energy (67 kcal. mole⁻¹).

Rate Constants for CH₃I Decomposition. The rate constants for a chemical activation system⁴ such as eq. 2a-c have been defined^{12a} as $k_a = \omega(D/S)$. This formulation assumes unit collisional deactivation which should be valid¹³ for collisions of polyatomic molecules with methyl iodide which is only a few kcal. mole⁻¹ above its critical energy.

The values of k_a obtained from nitrogen-methane analysis are shown in Table III; the average value is $1.2 \times 10^9 \text{ sec.}^{-1}$. In this system there is the possibility that I atoms can set off a chain reaction.^{14a} Such



free-radical reactions with diazomethane have been found under some conditions.^{14b} The O₂ results of Table IV indicate this to be an unimportant factor^{14a}; however, it may contribute to the scatter of the data. If effective to a small extent, these reactions would increase the N₂ yield and make the 1.2×10^9 value a lower limit. Since some diazomethane decomposes on glass surfaces to yield N₂, and since CH₄ was not recovered with perfect efficiency, these effects also tend to make this a lower limit to the true rate constant. The scatter of the data is not surprising in view of these experimental difficulties.

(12) (a) B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959); (b) for a summary of notation 1 see B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

(13) (a) G. Kohlmaier and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 1692, 1709 (1963); (b) D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *ibid.*, **40**, 1751 (1964); **41**, 800 (1964).

(14) (a) We thank a referee for pointing out this possibility; (b) W. H. Urry and N. Bilow, *J. Am. Chem. Soc.*, **86**, 1815 (1964).

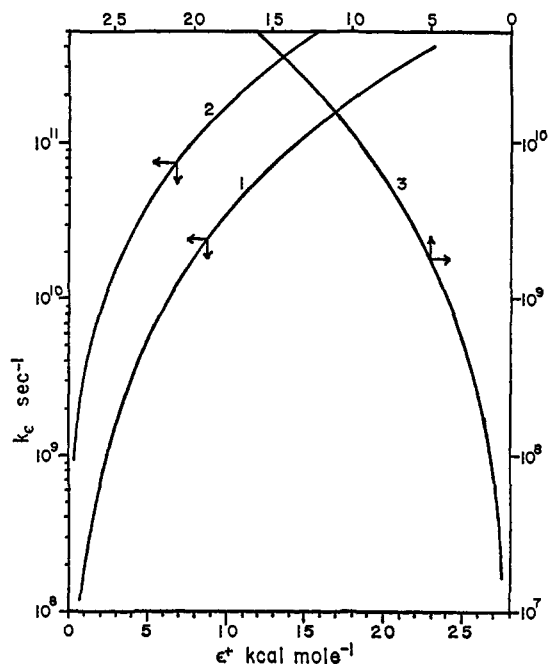


Figure 1. Plot of the specific rate constants for CH₃Br and CH₃I as a function of energy. 1 and 2 refer to complexes I and II for CH₃I; the $\epsilon^+ = 0$ intercepts are 1.02×10^7 and $5.39 \times 10^7 \text{ sec.}^{-1}$, respectively; $\epsilon_0 = 54 \text{ kcal. mole}^{-1}$. 3 refers to CH₃Br, the $\epsilon^+ = 0$ intercept = $5.2 \times 10^6 \text{ sec.}^{-1}$; $\epsilon_0 = 67 \text{ kcal. mole}^{-1}$.

Values of k_a from the O₂ scavenger technique are shown in Table IV; they were based upon the assumption that CH₃O₂ (eq. 3a) does not remove either HI or CH₃I in reaching stable products. The average from these results is $4.8 \times 10^9 \text{ sec.}^{-1}$. The reactions that describe the oxidation of CH₃ with O₂ are extremely complex.^{11c} Some recent results^{11a} indicate that an



important reaction when HI is present is eq. 3b. If this reaction competes effectively with CH₃N₂ for the HI, then the values of k_a in Table IV are too high. On this basis, $4.8 \times 10^9 \text{ sec.}^{-1}$ is an upper limit to k_a . The maximum correction is to assume that reaction 3b is very fast and every CH₃O₂ reacts with HI. Applying this correction, which decreases the values of D by a factor of two, gives $k_a = 2.4 \times 10^9 \text{ sec.}^{-1}$.

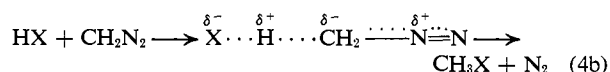
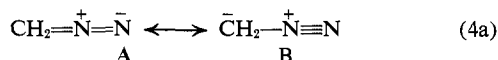
As will become apparent in the Discussion section, the exact value of k_a is not critical. The correct value must lie between 1.2 and $4.8 \times 10^9 \text{ sec.}^{-1}$ and we will arbitrarily choose a value of $3 \times 10^9 \text{ sec.}^{-1}$ for further discussion.

Discussion

"Semi-ionic" Transition State in the Reaction of HX with CH₂N₂. Reaction 1 has been shown to be a rapid homogeneous bimolecular reaction. During the reaction, two bonds (C-N and H-Cl) are broken and two more formed (C-H and C-Cl). It is unusual that such extreme rearrangement of structure should accompany a reaction of such low activation energy. A possible explanation may be the unusual structure of diazomethane which favors the formation of a polar transition state (eq. 4b). Diazomethane can be well represented by the resonance forms¹⁵ A and B with contribu-

(15) C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, **40**, 1529 (1964), and references therein.

tions of 70 and 30%, respectively. The transition state emphasizes the importance of structure B.



A method of estimating the activation energies of polar transition states has been proposed by Benson.^{2b} Using Benson's eq. 11, modified to the geometry of our proposed complex,¹⁶ with very crude approximations to the parameters, surprisingly good qualitative agreement is obtained with our estimated activation energies. However, in addition to the calculated values being too high, the change in E_a for the series HI to HCl was underestimated. Arbitrary adjustment of parameters to correct these items would seem to have little, if any, real meaning. Nevertheless, the calculations may be judged to support the concept of a quite polar transition state for this gas phase reaction.

An alternative mechanism could be the simultaneous bonding of the carbon to the H and Cl of HCl. Such a mechanism, which is similar to carbene insertion, would also emphasize the contribution of structure B.

Models for the Unimolecular Decomposition of Methyl Iodide. In order to determine the energy content of the energized methyl iodide, a model which permits calculation of the specific rate constant as a function of energy is necessary. We will use the RRKM^{12b,17} theory which gives the specific rate constant as

$$k_\epsilon = \frac{1}{h} \frac{Z_1^+}{Z_1^*} \frac{\Sigma P(\epsilon_{vr}^+)}{N^*(\epsilon_{vr})} \quad (5)$$

where Z_1^+ and Z_1^* are the products of the partition functions of the adiabatic degrees of freedom of the activated complex and molecule, respectively. $\Sigma P(\epsilon_{vr}^+)$ is the total sum of the degeneracies of all the possible energy eigenstates of the active degrees of freedom of the complex at total energy ϵ_{vr}^+ ; $N^*(\epsilon_{vr})$ is the number of eigenstates per unit energy of the active degrees of freedom for the molecule at energy ϵ_{vr} ; h is Planck's constant; ϵ_0 is the minimum energy necessary for reaction and $\epsilon_{vr}^+ = \epsilon_{vr} - \epsilon_0$. It should be noted that the first application of the RRKM theory of unimolecular reactions was to methyl iodide.^{17a} The calculations that are presented here follow the original approach.^{17a} The major improvement is that accurate and convenient methods for evaluating the $\Sigma P(\epsilon_{vr}^+)$ and $N^*(\epsilon_{vr})$ terms¹² permit more detailed models of the activated complex to be investigated. Further comparison of the work of Marcus and Rice with the present calculations are given in Appendix I.

The unimolecular decomposition of CH_3I occurs with rupture of the C-I bond to form methyl radicals and iodine atoms. According to microscopic reversibility, the transition state must be identical with that of

(16) We assumed end-on approach, which doubles the dipole-dipole term. The distance between the H of HCl and C of CH_2 was set at 1.5 Å. The parameters used were $\delta_{\text{HX}} = \delta_{\text{DM}} = 0.5$; $r_{\text{DM}} = 1.3$ Å; $\alpha_{\text{DM}} = 10$ Å.³/molecule; $r_{\text{HX}} = 1.54, 1.70, 1.93$ Å; $\alpha_{\text{HX}} = 3.13, 4.23, 6.58$ Å.³/molecule; $r_a = 1/2(r_{\text{DM}} + r_{\text{HX}}) + 1.5$. The results were $E_a = 9.1, 8.8, 8.3$ kcal./mole⁻¹. Where three values are given for a quantity, they are for HCl, HBr, and HI, respectively. Changing the approach from end-on to an angle of 45° increases the activation energy uniformly by 0.7 kcal. mole⁻¹.

(17) (a) R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, **55**, 894 (1951); (b) R. A. Marcus, *J. Chem. Phys.*, **20**, 352, 359 (1952).

the reverse (combination) reaction. Since the rate constants for combination of methyl and halogen atoms are very large ($10^{14.6}$ cc. sec.⁻¹ mole⁻¹ for $\text{CH}_3 + \text{Cl}$),^{18a} a loose complex is needed. The Gorin¹⁸ type, with free tumbling of the methyl group, is the upper limit to the loose transition state^{12b} (Appendix I, model II). For such a model of the complex, all vibrations and rotations of the methyl group are included as active degrees of freedom; the two over-all rotations perpendicular to the symmetry axis were assumed adiabatic. For the molecule the symmetry axis rotation and all vibrations were considered active; the rotations perpendicular to the symmetry axis were taken as adiabatic.^{12b,19}

Model II is an extreme case representing the upper limit for k_ϵ . A somewhat more rigid complex would be more realistic. Model I (see Appendix I) of the activated complex was chosen by arbitrarily lowering the C-I bending frequencies of the molecule from 880 to 150 cm.⁻¹. By analogy with model II, the symmetry axis rotation and the rotations perpendicular to the symmetry axis were taken as active and adiabatic, respectively, for both the molecule and complex.¹⁹ Model I gives a frequency factor of 8.6×10^{13} sec.⁻¹ for thermal decomposition at 500°K. and in the high-pressure limit²⁰; the Gorin-type complex gave 7.4×10^{14} sec.⁻¹ at the same temperature.

The model of the activated complex for the analogous decomposition of CH_3Br was chosen by lowering the C-Br bending frequencies of the molecule by the same proportion as model I of CH_3I .

Calculated specific rate constants are shown in Figure 1. The actual rate constant for methyl iodide must surely lie between models I and II. Since they differ only by a factor of ten at energies of *ca.* 2 kcal. mole⁻¹ and a factor of 5 at higher energies, discussion will be based on model I and should be adequate for our purposes.

Appendix II contains a summary of calculated rate constants based upon model I for different experimental situations in which unimolecular reaction of CH_3I might be important.

Energy Partitioning in the Reaction of HX with Diazo-methane. The observed rate constant of 3×10^9 sec.⁻¹ for methyl iodide decomposition corresponds to an energy of about 4 kcal. mole⁻¹ above ϵ_0 . Owing to the extreme sensitivity of k_ϵ to the energy in this region, a factor of two in the rate constant changes the energy by only 1 kcal. mole⁻¹. Thus our large experimental error is not especially critical for fixing the energy content of the molecule. The energy in the active degrees of freedom^{12,17} of CH_3I formed by reaction 1 can be assigned as 58 ± 2 kcal. mole⁻¹ based upon these calculations.

The thermochemistry of reaction 1 gives the active energy of the CH_3X as

$$E(\text{CH}_3\text{X}) = \Delta H_f(\text{CH}_3\text{X}) - \Delta H_f(\text{HX}) - \Delta H_f(\text{CH}_2\text{N}_2) - E_a + E_t \quad (6)$$

(18) (a) H. S. Johnston and P. Goldfinger, *J. Chem. Phys.*, **37**, 700 (1962); (b) E. Gorin, *Acta Physicochim. URSS*, **6**, 691 (1938); (c) Marcus and Rice^{17a} also explicitly discuss loose and tight complexes for this type of reaction.

(19) J. H. Current and B. S. Rabinovitch, *J. Chem. Phys.*, **38**, 783, 1967 (1963). These authors discuss separation of over-all rotations into active and adiabatic classifications.

(20) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

where E_a is the activation energy of reaction 1 and E_T is the sum of the energy in the adiabatic degrees of freedom of the CH_3X molecule (translation and rotations perpendicular to the symmetry axis) and in the degrees of freedom of N_2 . A more detailed treatment would include the energy distributions accompanying the quantities of eq. 6. Their average values are sufficient for our purpose.

The right-hand side of eq. 6 is equal to $-9.9 - \Delta H_f(\text{CH}_2\text{N}_2) + E_T$ for HI as reactant (E_a is taken as the upper limit of 6 kcal. mole⁻¹). Since $E(\text{CH}_3\text{X})$ is around 58 kcal. mole⁻¹, any reasonable assumption for $\Delta H_f(\text{CH}_2\text{N}_2)$ requires that a large fraction of the energy reside in the active degrees of freedom of the methyl halide. The N_2 would not be expected to contain much vibrational energy²¹ since the nitrogen internuclear distance changes only from 1.18 Å. in CH_2N_2 ²² to 1.09 Å. in N_2 .²³ In such a complex molecular rearrangement as reaction 1, it might have been expected that a large fraction of the energy would have appeared in the translational and rotational degrees of freedom of the products. Apparently this is not the case.

Bauer and co-workers²⁴ have recently proposed a four-center exchange reaction between NH_3 and D_2 that is effective when sufficient vibrational excitation is present within the D_2 . Suggestions have also been made⁶ that O_2 at bath temperatures near 25° may react with highly vibrationally excited hydrocarbon-type molecules that have energies near 100 kcal. mole⁻¹. By analogy with methyl iodide, methyl chloride and bromide should be produced with an internal energy content of about 60 kcal. mole⁻¹, plus some additional energy as rotation and translation which is estimated in the next section to be perhaps 10 kcal. mole⁻¹. Experiments 3 and 4 of Table I clearly show that these vibrationally excited molecules do not react with O_2 .

The anticipated reaction between O_2 and CH_3X would be H abstraction. The activation energy of this reaction would be ≥ 51 kcal. mole⁻¹.²⁵ Since the vibrational energy is only 9 and the total energy probably only 19 kcal. mole⁻¹ above the minimum activation energy, these particular molecules are unfortunately not a conclusive test for the abstraction reaction of O_2 with highly excited hydrocarbon-type molecules.^{25b} However, the data may be taken as tentative evidence against such a reaction, as well as showing that no unusual exchange reactions take place.

Heat of Formation of Diazomethane. The heat of formation of diazomethane has been much discussed.⁵ Paulett and Ettinger^{5b} published a value of 49 kcal. mole⁻¹ for $\Delta H_f(\text{CH}_2\text{N}_2)$ derived from mass spectral data. Bell,^{5a} assuming that excited states of CH_2^+ are involved in the electron impact results, recalculated Paulett and Ettinger's data to obtain 71 kcal. mole⁻¹; they^{5b} then re-examined their data on a different basis to obtain 103 kcal. mole⁻¹, although they favored their first value of 49 kcal. mole⁻¹. Setser and Rabinovitch,²⁶

(21) J. C. Polyani, *J. Chem. Phys.*, **31**, 1338 (1959).

(22) B. L. Crawford and W. H. Fletcher, *ibid.*, **19**, 406 (1951).

(23) J. T. Vanderslice, E. A. Mason, and E. R. Lippincott, *ibid.*, **30**, 129 (1959).

(24) A. Lifshitz, C. Lifshitz, and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 143 (1965).

(25) (a) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **36**, 2681 (1962). (b) We thank the referee for this observation.

(26) D. W. Setser and B. S. Rabinovitch, *Can. J. Chem.*, **40**, 1425 (1962).

from kinetic data, indicated a lower limit to $\Delta H_f(\text{CH}_2\text{N}_2)$ of 67 kcal. mole⁻¹.

The fact that CH_3I formed in (1) decomposes, while CH_3Br does not, establishes $E(\text{CH}_3\text{X})$ to be above 54 kcal. mole⁻¹ for CH_3I and below 67 kcal. mole⁻¹ for CH_3Br , respectively. The above limits on $E(\text{CH}_3\text{X})$ give $(44 + E_T) \leq \Delta H_f(\text{CH}_2\text{N}_2) \leq (57 + E_T)$ kcal. mole⁻¹.

A lower limit to the range is obtained if E_T is set equal to zero. Since $E(\text{CH}_3\text{I})$ is actually 58 ± 2 instead of 54 kcal. mole⁻¹, 48 ± 2 kcal. mole⁻¹ is the lower limit to $\Delta H_f(\text{CH}_2\text{N}_2)$ on the basis of our data.

It seems quite unreasonable for E_T to be zero. It is difficult to estimate how much energy may be in these degrees of freedom, but there is certainly precedent for large quantities of energy appearing in rotational or translational degrees of freedom.²⁷ Our estimation which is admittedly speculation proceeds in the following way. The difference in $R(\text{N}-\text{N})$ between CH_2N_2 and N_2 is small (0.09 Å.) and would correspond to excitation to the first vibrational level^{21,23} (3.5 kcal. mole⁻¹). Since extension of $R(\text{N}-\text{N})$ during the course of the reaction is not expected, 3.5 kcal. mole⁻¹ can be assigned as the average vibrational energy of N_2 . For the rotational energy we will assume an average excitation to $J = 30$ for the four rotational degrees of freedom (two for N_2 and two adiabatic rotations of CH_3I). This is a contribution of 6 kcal. mole⁻¹. If we further assume a translational energy of 10 kcal. mole⁻¹, the total for E_T is 20 kcal. mole⁻¹ and $64 \leq \Delta H_f(\text{CH}_2\text{N}_2) \leq 77$ kcal. mole⁻¹.

These seem "reasonable" estimates. Since $E(\text{CH}_3\text{I})$ was placed at 58 kcal. mole⁻¹, a 20-kcal. mole⁻¹ quantity for E_T gives $\Delta H_f(\text{CH}_2\text{N}_2) \geq 68$ kcal. mole⁻¹. This work thus supports the value of 71 kcal. mole⁻¹ obtained by Bell for the heat of formation diazomethane rather than a lower or upper extreme.^{5a}

Acknowledgments. We wish to thank Professor B. S. Rabinovitch, University of Washington, for the generous loan of computer programs which were used in this work. D. W. S. also wishes to thank Professor Rabinovitch for advice and encouragement offered on numerous occasions.

Appendix I

The models used for computing the RRKM¹⁷ specific rate constants are listed below. The harmonic sums and densities of the active vibrational rotational energy states were evaluated either by direct count^{12b} or by the Haarhoff approximation method.²⁸ The

Table V

CH ₃ I		CH ₃ Br	
Frequencies, cm. ⁻¹	Moments of inertia, a.m.u.	Frequencies, cm. ⁻¹	Moments of inertia, a.m.u.
3030 (3)	3.32 (1)	3028 (3)	3.23 (1)
1349 (3)	(Active)	1396 (3)	(Active)
880 (2)	60.2 (2)	952 (2)	54.2 (2)
524 (1)	(Adiabatic)	611 (1)	(Adiabatic)

(27) (a) J. R. Airey, R. R. Getty, J. C. Polyani, and D. R. Snelling, *J. Chem. Phys.*, **41**, 3255 (1964); (b) F. P. DelGreco and F. Kaufman, *Discussions Faraday Soc.*, **33**, 128 (1962).

(28) P. C. Haarhoff, *J. Mol. Phys.*, **6**, 337 (1963); **7**, 101 (1963).

Table VI

CH ₃ I complex				CH ₃ Br complex	
Model I		Model II		Model I	
Frequencies, cm. ⁻¹	Moments of inertia, a.m.u.	Frequencies, cm. ⁻¹	Moments of inertia, a.m.u.	Frequencies, cm. ⁻¹	Moments of inertia, a.m.u.
3023 (3)	3.53 (1)	3023 (3)	3.53 (1)	3023 (3)	3.53 (1)
1420 (2)	(Active)	1420 (2)	(Active)	1420 (2)	(Active)
950 (1)	86.7 (2)	950 (1)	1.75 (2)	950 (1)	78.0 (2)
150 (2)	(Adiabatic)		(Active)	175 (2)	(Adiabatic)
			335.4 (2)		
			(Adiabatic)		

Table VII. Calculated Rates for Methyl Iodide Decomposition, CH₃I* → CH₃ + I

Activation process	Temp., °K.	⟨ε ⁺ ⟩, ^a kcal. mole ⁻¹	Rate constants, sec. ⁻¹ k/e ^{-ε₀/RT}		Pressure, cm.						
					10 ⁵	10 ⁴	10 ³	10 ² k/k _∞	10 ¹	1.0	0.10
ω → CH ₃ I	600	1.4	1.19 × 10 ¹⁴	1.0	0.98	0.90	0.60	0.22	0.044	0.0057	
	1000	2.5	2.49 × 10 ¹⁴	0.99	0.91	0.63	0.26	0.061	0.0091	0.0010	
			k _∞	k ₀			S/D				
CH ₃ + I → CH ₃ I	298	1.7	9.6 × 10 ⁸	2.0 × 10 ⁸	...	800	82	9.4	1.4	0.25	0.036
	600	4.4	7.9 × 10 ⁹	9.2 × 10 ⁸	680	71	8.8	1.5	0.28	0.046	0.0057
	1000	9.0	5.4 × 10 ¹⁰	3.9 × 10 ⁹	80	9.8	1.7	0.35	0.064	0.009	...

^a Refers to the average energy of the system above ε₀. The total energy is ε₀ + ε⁺.

latter was used at the higher range of energies only after comparison to the direct count sums at intermediate energies ensured its validity.

As discussed in the text, the twelve internal degrees of freedom of the methyl halide molecule were divided into ten active and two adiabatic degrees of freedom. The vibrational frequencies²⁹ were grouped in the usual way.¹² Bond dissociation energies were used for ε₀; $D(\text{CH}_3\text{-I})^{10} = 54$ and $D(\text{CH}_3\text{-Br})^9 = 67$ kcal. mole⁻¹ (Table V).

Two models of the decomposition activated complex were used in these computations. Complex II is of a Gorin type¹⁹ and has free rotation of the methyl group. The moments of inertia are those of a free methyl group and of over-all rotation of the complex which were calculated for a diatomic rotor with point masses of 15 and 127 a.m.u. separated by 5 Å. Methyl radical frequencies were taken from Rabinovitch and Setser.^{12b} Complex I, which is preferred, contains an active symmetry axis rotation and two low bending frequencies rather than free rotation. The moments of inertia of complex I were obtained from the methyl iodide molecule with the C-I bond extended to 2.54 Å. (Table VI). It is interesting to note that the methyl iodide high-pressure thermal unimolecular rate constants are $k = 8.6 \times 10^{13} \exp(-54,000/RT)$ and $7.4 \times 10^{14} \exp(-54,000/RT)$ sec.⁻¹ at 500°K. for models I and II, respectively.

The models described above can be compared to those used by Marcus and Rice.^{17a} Their model for the molecule is identical with the one above except that they considered the rotation along the symmetry axis to be adiabatic, whereas we have taken it to be active.¹⁹ Marcus and Rice used both a loose and a tight complex. Their loose complex is similar to model II except that the rotation about the symmetry axis was adiabatic. Their tight complex was identical with their model of the

molecule except that the C-I stretching frequency was allowed to be the reaction coordinate. This is a much tighter model than our complex I.

The calculations of Marcus and Rice^{17a} are not in a form that permit ready comparison of magnitudes of k_c . However it is known from previous calculations^{12b,19} that converting one rotation from active to adiabatic in both the complex and molecule increases the magnitude of k_c . This is not a large effect (about a factor of two for ethyl radicals¹⁹) and relative to the accuracy of our data cannot be considered significant.

In their very useful paper Marcus and Rice^{17a} tentatively favored the more rigid complex on the basis of the experimental data available at that time. The more recent data (discussed in the text and ref. 12b) indicate that the complex must be of the loose type although exact description is still not yet possible.

Appendix II

The decomposition rates for methyl iodide activated by different processes can be calculated from the models of the molecule and activated complex (model I) that were used in this work. Of the possible cases, two of the more probable are thermal collisional activation and the combination of methyl radicals and iodide atoms. The equations that apply to these two experimental situations are adequately described elsewhere.^{12b} We have used unit collisional deactivation for both cases. The equations were numerically integrated on the IBM 1410; the results are shown in Table VII for several temperatures.

To our knowledge no detailed data exist for comparison with these calculated results, although the recombination of CH₃ and I has been suggested in some recent flash photolysis work.³⁰ The results of the calculations are included here for the convenience of

(29) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 315.

(30) (a) R. T. Meyer; Abstracts of Papers, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; (b) D. Lewis and G. J. Mains, *ibid.*

future workers who may study such systems. It is worth noting that in order to stabilize approximately one-half of the methyl iodide resulting from the association of $\text{CH}_3 + \text{I}$ at 600°K ., about 1 atm. pressure is

required. Similar calculations^{12b} have been done for methane formed by $\text{H} + \text{CH}_3$ which satisfied the existing experimental data and predicted that $S/D = 1$ at a pressure of about 400 cm. at 673°K .

Pulse Radiolysis of Gaseous Argon–Oxygen Solutions. Rate Constant for the Ozone Formation Reaction^{1a}

Myran C. Sauer, Jr., and Leon M. Dorfman^{1b}

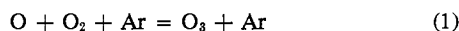
Contribution from Argonne National Laboratory, Argonne, Illinois.

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The pulse-radiolysis method has been used to study the kinetics of ozone formation in gaseous argon–oxygen solutions. The absolute rate constant for the reaction $\text{O} + \text{O}_2 + \text{Ar} = \text{O}_3 + \text{Ar}$ was found to be $(0.83 \pm 0.08) \times 10^8 \text{ M}^{-2} \text{ sec}^{-1}$ at 23° .

Introduction

The extension of the technique of pulse radiolysis² to the gas phase has been described in a preliminary report.³ In this paper we present the details of the experimental determination of the rate constant of the reaction 1 by direct observation of the ozone formation curve in the pulse radiolysis of gaseous argon–oxygen solutions.



The reaction of oxygen atoms with molecular oxygen has been the subject of numerous investigations,⁴ often producing conflicting values of k_1 . These values, obtained by a variety of methods, range over very nearly an order of magnitude. Because of its importance in the chemistry of the atmosphere, the ozone formation reaction continues to be a subject of investigation.^{5–8} The reaction is also of importance in the radiation chemistry of oxygen and oxygen-containing systems.⁹

The value of k_1 is determined here by a fast reaction method in which the reaction is initiated by a short-lived perturbation of the system. The method is direct, involving fast optical detection of ozone formation in a homogeneous system. The use of probes or any heterogeneity associated with phase discontinuity is

avoided. The result provides a useful addition to the current literature on this reaction.

Experimental

Pulse Irradiation. A 12- to 15-Mev. electron beam from the linear accelerator was used. The maximum current at the cell window was about 80 to 100 ma. The diameter of the electron beam at the cell window was about 15 mm. The pulse duration was generally 1.0 or 0.4 μsec ., although a 5- μsec . pulse was used occasionally. General aspects of the experimental arrangement have been described previously.¹⁰

Irradiation Vessels. The vessels used in this work were designed for the collinear entry of the electron beam at the front window and the analyzing light beam at the rear window. A diagram of the cell is shown in Figure 1 and a photograph in Figure 2. The cell body was made of 304 stainless steel, and the valves were 0.25-in. "speed valves" with "ermeto" connections from Autoclave Engineers Inc. The gasketing arrangement for the aluminum electron beam-window and the quartz light beam-window was similar to that in vessels used in a pulse radiolysis study¹¹ in which high pressures of hydrogen were needed over a liquid sample. The cell was hydrostatically tested at 200 atm. and was used up to 100 atm. of gas pressure. The cell volume was about 50 cc., of which the pressure gauge section made up 3 cc. and the cold-finger 7 cc.

Spectrophotometry. The technique of spectrophotometric observation of transients was in general the same as described previously.^{10,12} An Osram xenon lamp, Type XBO 450W, was used as the source of continuum. Ozone formation was monitored at 2600 \AA .^{13,14} using a 1P28 photomultiplier. A Bausch and Lomb grating monochromator, Type 33-86-25, f/3.5, was used with grating No. 33-86-01 and a band width of 24 to 70 \AA . The light beam passed through the irradiation vessel twice, giving an optical path length of 26 cm. A schematic diagram of the optical system is given in Figure 3. The amplification of the signal from the 1P28 photomultiplier and its display on an

(1) (a) Based on work performed under the auspices of the U. S. Atomic Energy Commission; (b) to whom correspondence should be addressed at the Chemistry Department, The Ohio State University, Columbus, Ohio.

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(4) For a survey see F. Kaufman, *Progr. Reaction Kinetics*, **1**, 1 (1961).

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(8) F. Kaufman and J. R. Kelso, *Discussions Faraday Soc.*, **37**, 26 (1964).

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(11) J. Rabani and M. S. Matheson, *J. Phys. Chem.*, **69**, 1324 (1965).

(12) G. Czapski and L. M. Dorfman, *ibid.*, **68**, 1169 (1964).

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