Ion–Molecule Reactions in Methyl Halides.
The Behavior of Methyl Cations and Halide Transfer Reactions[1]

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Abstract: Apparent halide transfer is shown to be the major reaction of CD_3^+ with methyl fluoride, chloride, and bromide. Rate constants greater than 10^{-9} cm³ molecule sec⁻¹ are observed in each case. Also, in each case the product ion is a thermal methyl ion. Methyl iodide is comparatively unreactive toward methyl cations. The reactivities are analyzed in terms of the expected charge redistribution during reaction and it is shown that the reactive systems would be expected to undergo much less redistribution of charge during the reaction than would methyl iodide. The kinetic energy dependence of the reactions is qualitatively analyzed using phase space considerations. The rate constant of the thermoneutral halide transfer reactions relative to the total rate constants is shown to increase with increasing kinetic energy. The extent of the increase appears to be related to the degree of exothermicity associated with the hydride transfer reaction.

An analysis of gas phase ion–molecule reactions in chemical systems can provide useful information about those properties of the neutral molecules governing the observed kinetics and about the intrinsic properties of the neutral molecules themselves. It has been possible, due to the extensive development of ion cyclotron resonance spectroscopy, along with several other mass spectrometric techniques, to evaluate in much greater detail than was previously possible the gas phase[3] acidities and basicities and proton, hydride, and electron affinities of organic molecules,[3–5] as well as their inherent reactivities. In addition, ionic heats of formation can be obtained by straightforward analysis of equilibrium ion–molecule reactions[6] and by distinguishing between exo- and endoergic ion transfer reactions of various types of nonequilibrium systems.

The analysis of ion–molecule reaction dynamics is generally difficult because there is no unified theory which permits one to predict which products in a system will be favored, or what kinetic energy dependence to expect for several different products from the same reactants. Furthermore, those theories which have been developed can generally be rigorously applied to systems containing only three or four atoms at most. Thus, while it is possible to obtain thermochemical information, it is more difficult to usefully analyze or to predict dynamic behavior in reacting systems.

In this study we examine the extent of, and the energy dependence of, hydride, halide, and atom transfer reactions in the methyl halides and mixtures of CD_4 with the methyl halides to shed some light on the detailed mechanisms by which these reactions may be proceeding. The extent and magnitude of the reactions are analyzed in terms of the electron density descriptions of ion–molecule reactions.[7–10] The kinetic energy dependence of these reactions is also examined and discussed qualitatively in terms of the phase space theory[11–13] of chemical reactions.

In particular, we emphasize the reactions of the deuterated methyl cation CD_3^+ with the methyl halides. CD_3^+ is shown to participate in several reactions including what we shall call a "quasi-resonant" reaction. Because of their form, such reactions are particularly amenable to analysis by the electron density description.

For the purpose of this study, we define a quasi-resonant ion–molecule reaction as

$$A^+ + XA' \longrightarrow AX + A'^+ \tag{1}$$

where A^+ and A'^+ are equivalent functional groups, isotopically labeled so that they may be distinguished mass spectrometrically. In this work halide transfer is represented by reaction 2, where X represents the halide atom.

$$CD_3^+ + CH_3X \longrightarrow CH_3^+ + CD_3X \tag{2}$$
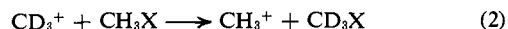
In previous studies of the methyl halides,[14–17] this reaction has not been reported, but we find that it is the most important reaction involving the methyl cation in three of the four systems studied.

Experimental Section

The procedures used for obtaining thermal rate constants, and for determining the kinetic energy dependences of rate constants, are exactly as described in earlier studies on ion–molecule reactions

(1) This work was supported in part by NIH Grant No. HL 13851-10.
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(5) (a) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 6561 (1968); (b) *ibid.*, **90**, 5636 (1968); (c) *ibid.*, **91**, 2126 (1969); (d) J. I. Brauman and R. C. Symth, *ibid.*, **91**, 7778 (1969).
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(16) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Platt, *J. Amer. Chem. Soc.*, **94**, 2798 (1972).
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Table I. Rate Constants for Reactions between CD_3^+ and Methyl Halides

Reactants	Intermediate	Products	Apparent transferred specie	k, cm³ molecule⁻¹ sec⁻¹ × 10⁹ This study[a]	Previously reported
(A) $CD_3^+ + CH_3F \rightarrow$	$CD_3FCH_3^+ \rightarrow$	$CH_3^+ + CD_3F$	F^-	$k_1 = 0.8 \pm 0.1$	
		$\rightarrow CH_2F^+ + CD_3H$	H^-	$k_2 = 0.13 \pm 0.02$	1.02^b
(B) $CD_3^+ + CH_3Cl \rightarrow$	$CD_3ClCH_3^+ \rightarrow$	$CH_3^+ + CD_3Cl$	Cl^-	$k_1 = 1.2 \pm 0.1$	
		$\rightarrow CH_2Cl^+ + CD_3H$	H^-	$k_2 = 0.11 \pm 0.02$	0.9^c
(C) $CD_3^+ + CH_3Br \rightarrow$	$CD_3BrCH_3^+ \rightarrow$	$CH_3^+ + CD_3Br$	Br^-	$k_1 = 1.9 \pm 0.2$	
		$\rightarrow CH_2Br^+ + CD_3H$	H^-	$k_2 = 0.05 \pm 0.01$	
(D) $CD_3^+ + CH_3I \rightarrow$	$CD_3ICH_3^+ \rightarrow$	$CH_2I^+ + CD_3H$	H^-	$k_1 = 0.07 \pm 0.03$	
		$\rightarrow CD_3I^+ + CH_3$	$I\cdot$	$k_2 = 0.04 \pm 0.02$	

[a] Absolute rate constants were obtained in equimolar mixtures of CD_4 and the corresponding methyl halide by comparing relative rate constants to the known rate constant for proton transfer in methane. [b] Reference 16. [c] Reference 14.
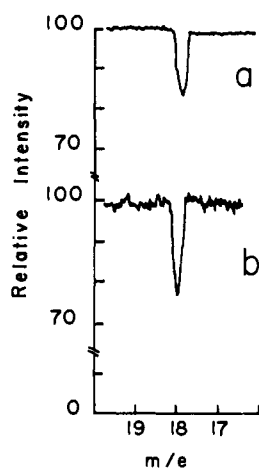

Figure 1. (a) Double resonance spectrum of m/e 15 in a CH_3F-CD_4 mixture: pressure, 8×10^{-6} Torr; electron energy, 16 eV; double resonance field strength, 0.24 V/cm. (b) Double resonance spectrum of m/e 15 in a CH_3Cl-CD_4 mixture: pressure, 5×10^{-6} Torr; electron energy, 16 eV; double resonance field strength, 0.24 V/cm.

Figure 2. Kinetic energy dependence of relative (100 corresponds to the thermal rate constant measured for each reaction (1.2 × 10^{-9} cm³/molecule⁻¹ sec⁻¹ for Cl^- transfer, 0.11 × 10^{-9} cm³ molecule⁻¹ sec⁻¹ for H^- transfer)) rate constants for chloride and hydride transfer in methyl chloride: (●) $CD_3^+ + CH_3Cl \rightarrow CH_3^+ + CD_3Cl$, (■) $CD_3^+ + CH_3Cl \rightarrow CH_2Cl^+ + CD_3H$.

in silanes.[6] In the kinetic energy experiments the primary ions are accelerated by a radiofrequency electric field in the source region so that the energy acquired and reported is actually the maximum kinetic energy the ion can acquire before reacting.[6c] All thermal rate constants are obtained relative to the $CD_4^+ \rightarrow CD_5^+$ proton transfer reaction[6c] and should be accurate to ±10%.

For reaction 2 double resonance experiments show that CH_3^+ in each system is produced only by reaction of CD_3^+. Two methods are used to obtain the product CH_3^+ intensities used for determining rate constants. In a strong field double resonance experiment the product CH_3^+ ions may be essentially eliminated[4,6] and decrease in CH_3^+ when CD_3^+ is irradiated may be taken as the total product intensity for the halide transfer reaction. In addition, since it is determined that the CH_3^+ is produced only by CD_3^+, it is possible to assume that the observed increase in CH_3^+ with increasing pressure relative to other primary ions which do not react is due only to reaction 2. Therefore, the total observed increase in CH_3^+ over and above the primary CH_3^+ can be used to calculate rate constants. In all experiments it was found that both methods gave essentially equivalent results within experimental error.

The methyl halides were purified in a vacuum line employing freeze–pump techniques. CD_4 was obtained from Merck Sharp and Dohme. The purity of all compounds was verified by low-pressure icr measurements. In all experiments, methyl halides and CD_4 were used in one to one mixtures.

Results

Table I lists the reactions observed for the deuterated methyl cation (CD_3^+) in each of the systems studied. For all reactions, rate constants have been cited and compared to previously reported values where possible. For those exothermic or thermoneutral reactions which
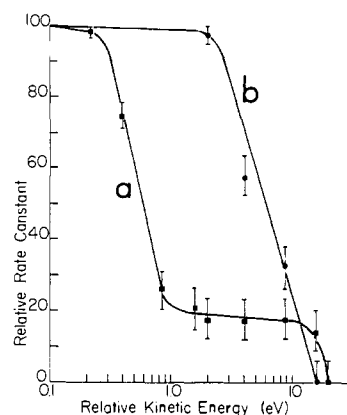
were not observed in this study, upper limits to the possible rate constants are estimated. Endothermic reactions were not expected to be observed at thermal kinetic energy and their rate constants were given as zero if they were not detected.

Figures 1a and 1b show the double resonance curve for CH_3^+ in methyl fluoride and methyl chloride. It is clear that in both cases CD_3^+ (m/e 18) is the principal reacting ion. Figure 2a shows the kinetic energy dependence of reaction 2 in methyl chloride. It is observed that the rate for halide transfer stays relatively constant up to ~2 eV and decreases at higher kinetic energies.

Figure 2b shows the kinetic energy dependence of the hydride transfer reaction for CD_3^+ reacting with methyl chloride. As seen from Table I, rate constants for all of the hydride transfer reactions are much smaller than those for the corresponding halide transfer at low kinetic energies, and Figure 2 shows that initially they also appear to decrease more rapidly with increasing kinetic energy.

The relative behavior of hydride vs. halide transfer in each system is shown in Figure 3. In each case it is clear that halide transfer becomes relatively more important with increasing kinetic energy even at very low kinetic energies. This detailed behavior is significant in terms of the reaction mechanism and is discussed in detail below. Figures 3–7 show the rate constants as a function of kinetic energy for each of the important reactions occurring within each system. Also shown

Table II. Comparison of Reaction Rates in the $CD_3{}^+ + CH_3F$ System

| | | | | Rate constants, cm³ molecule⁻¹ sec⁻¹ × 10⁹ | | | |
| | | | | This study | | Theoretical | |
Reactants	Intermediate	Products	ΔH^a	Obsd	Inferred	$k_L{}^{b,d}$	$k_{LD}{}^{c,d}$
(A) $CD_3{}^+ + CH_3F \rightarrow CD_3FCH_3{}^+ \rightarrow$		$CH_3{}^+ + CD_3F$	0	0.8 ± 0.1			
(B)		$\rightarrow CD_3{}^+ + CH_3F$	0		0.8 ± 0.1		
(C)		$\rightarrow CD_3F^+ + CH_3$	+69	0			
(D)		$\rightarrow CH_3F^+ + CD_3$	+69	0			
(E)		$\rightarrow CH_2F^+ + CD_3H$	-2	0.13 ± 0.02			
(F)		$\rightarrow CD_2F^+ + CH_3D$	-2	0.13 ± 0.02			
(G)		$\rightarrow CD_3H^+ + CH_2F$	+74	0			
(H)		$\rightarrow CH_3D^+ + CD_2F$	+74	0			
		Total rate constant			1.86 ± 0.24	1.41	3.8

^{a} All thermochemical data in kcal/mol at 298°K. ^{b} The Langevin or Gioumousis and Stevenson theoretical model gives $k_L = 2\pi e(\alpha/\mu)^{1/2}$ where e is the electronic charge, α is the polarizability of the neutral molecule, and μ is the reduced mass of the collision pair. ^{c} The locked dipole model gives $k_{LD} = k_L + 2\pi e\mu_D(2/\mu\pi kT)^{1/2}$ where μ_D is the permanent dipole moment of the neutral. ^{d} Dipole moments and polarizabilities were taken from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963.

Table III. Comparison of Reaction Rates in the $CD_3{}^+ + CH_3Cl$ System^a

| | | | | Rate constant, cm³ molecule⁻¹ sec⁻¹ × 10⁹ | | | |
| | | | | This study | | Theoretical | |
Reactants	Intermediate	Products	ΔH	Obsd	Inferred	k_L	k_{LD}
(A) $CD_3{}^+ + CH_3Cl \rightarrow CD_3ClCH_3{}^+ \rightarrow$		$CH_3{}^+ + CD_3Cl$	0	1.2 ± 0.1			
(B)		$\rightarrow CD_3{}^+ + CH_3Cl$	0		1.2 ± 0.1		
(C)		$\rightarrow CD_3Cl^+ + CH_3$	+31	0			
(D)		$\rightarrow CH_3Cl^+ + CD_3$	+31	0			
(E)		$\rightarrow CH_2Cl^+ + CD_3H$	-15	0.11 ± 0.02			
(F)		$\rightarrow CD_2Cl^+ + CH_3D$	-15	0.11 ± 0.02			
(G)		$\rightarrow CD_3H^+ + CH_2Cl$	+62	0			
(H)		$\rightarrow CH_3D^+ + CD_2Cl$	+62	0			
		Total rate constant			2.62 ± 0.22	1.36	4.0

^{a} All footnotes to Table II applicable to Table III.

are several reference reactions involving the same neutral molecules. Again it is clear that halide transfer becomes relatively more important in each system with increasing kinetic energy at very low kinetic energies. It is also evident from Figure 3 that the effect is smallest in the fluoride and largest in the chloride. This behavior is qualitatively interpreted according to phase space theory below. Figure 7 shows the reaction probability for all four systems plotted vs. the difference in electronegativity between the C and X atom in the neutral. Two approaches are used to predict the theoretical limit to the total reaction rate constant, and the ratio of measured to theoretical rate constant is taken as the reaction probability. The significance of this plot is related to the electron density description of ion–molecule reactions and is also discussed below.

Discussion

The Production of Unexcited Methyl Ions by Halide Transfer. Although much recent work has been carried out on alkyl halides,[14–17] the halide ion transfer reaction discussed here (reaction 2) has not been previously reported. However, Beauchamp, et al., have pointed out[16] that the pressure dependence of $CH_3{}^+$ in methyl fluoride is not typical of primary ions and have discussed possible reasons which could account for its behavior. From the double resonance experiment shown in Figures 1a and 1b for $CH_3{}^+$, it seems clear that $CH_3{}^+$ is being produced by $CD_3{}^+$ in a reaction which has the appearance of being an X^- transfer reaction. The results obtained in this study (as illustrated in Figure 1) indicate that this reaction is very important in the fluoride, chloride, and bromide systems, and it is sug-
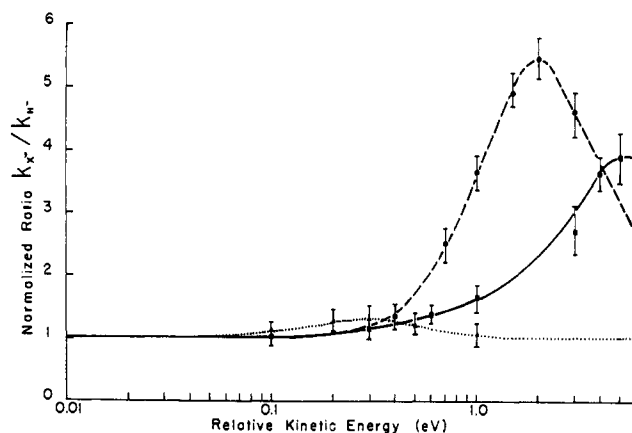

Figure 3. Variation k_X-/k_H- with energy: (▲) CH_3F, (●) CH_3Cl. (■) CH_3Br. The ratio for each system is normalized to 1 at thermal kinetic energy.

gested that it may be responsible for the odd pressure dependence observed for $CH_3{}^+$ in reference 17.

These observed rate constants are summarized in Table I for all of the systems. The rate constants are broken down in greater detail in Tables II through V. If the thermal rate constants for H^- and X^- transfer reported in Tables II–V are summed for each system, it is seen that the total approaches the theoretical rate constant for $CH_3{}^+$ reaction (Table II) obtained using either the locked dipole[18] model or the Gioumousis–Stevenson[19] ion induced dipole model. It is not clear which

(18) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).
(19) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

Table IV. Comparison of Reaction Rates in the CD_3^+ + CH_3Br System[a]

				Rate constant, cm^3 molecule^{-1} sec^{-1} $\times$ 10^9					
				This study				Theoretical	
				k(thermal)		k(1 eV)[b]			
Reactants	Intermediate	Products	ΔH	Obsd	Inferred	Obsd	Inferred	k_L	k_{LD}
(A) CD_3^+ + CH_3Br → $CD_3BrCH_3^+$ →		CH_3^+ + CD_3Br	0	1.9 ± 0.2		1.8 ± 0.2			
(B)		→ CD_3^+ + CH_3Br	0		1.9 ± 0.2		1.8 ± 0.2		
(C)		→ CD_3Br^+ + CH_3	+15	0		0			
(D)		→ CH_3Br^+ + CD_3	+15	0		0			
(E)		→ CH_2Br^+ + CD_3H	−12	0.05 ± 0.01		0.03 ± 0.01			
(F)		→ CD_2Br^+ + CH_3D	−12	0.05 ± 0.01		0.03 ± 0.01			
(G)		→ CD_3H^+ + CH_2Br	+12	0		0			
(H)		→ CH_3D^+ + CD_2Br	+12	0		0			
		Total rate constant		3.9 ± 0.42		3.66 ± 0.42		1.41	3.9

[a] All footnotes to Table II applicable to Table IV. [b] Relative energy in center of mass coordinate system.

Table V. Comparison of Reaction Rates in the CD_3^+ + CH_3I System[a]

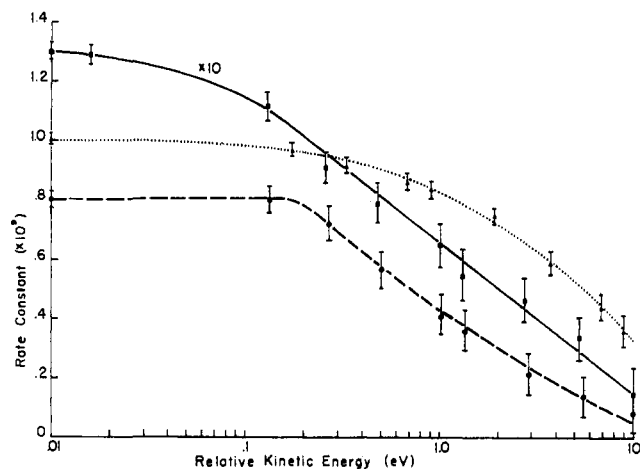| | | | | Rate constant, cm^3 molecule^{-1} sec^{-1} $\times$ 10^9 | | | |
| | | | | This study | | Theoretical | |
Reactants	Intermediate	Products	ΔH	Obsd	Inferred	k_L	k_{LD}
(A) CD_3^+ + CH_3I → $CD_3ICH_3^+$ →		CH_3^+ + CD_3I	0	0			
(B)		→ CD_3^+ + CH_3I	0		0		
(C)		→ CD_3I^+ + CH_3	−7	0.04 ± 0.02			
(D)		→ CH_3I^+ + CD_3	−7		0.04 ± 0.02		
(E)		→ CH_2I^+ + CD_3H	−14	0.07 ± 0.03			
(F)		→ CD_2I^+ + CH_3D	−14	0.07 ± 0.03			
(G)		→ CD_3H^+ + CH_2I	0	0			
(H)		→ CH_3D^+ + CD_2I	0	0			
		Total rate constant			0.22 ± 0.10	1.56	3.6

[a] All footnotes to Table II applicable to Table V.

Figure 4. Kinetic energy dependence of absolute rate constants in the CD_4-CH_3F system: (●) CD_3^+ + CH_3F → CH_3^+ + CD_3F, (■) CD_3^+ + CH_3F → CH_2F^+ + CD_3H, (▲) CD_4^+ + CD_4 → CD_5^+ + CD_3.

Figure 5. Kinetic energy dependence of absolute rate constants in the CD_4-CH_3Cl system: (●) CD_3^+ + CH_3Cl → CH_3^+ + CD_3Cl, (■) CD_3^+ + CH_3Cl → CH_2Cl^+ + CD_3H, (▲) CD_4^+ + CD_4 → CD_5^+ + CD_3.

model will better represent any given system, though in general the locked dipole model is used to account for rate constants larger than would be expected from the Gioumousis–Stevenson model. The point to emphasize is that regardless of which model is used, the total measured reaction rate constant is a very significant fraction of (or even greater than) the expected total rate constant from either model for the fluoride, chloride, and bromide systems. That the measured rate constant for each of these three systems is greater than the calculated Gioumousis–Stevenson rate constant unity suggests that the locked dipole model has at least some applicability.

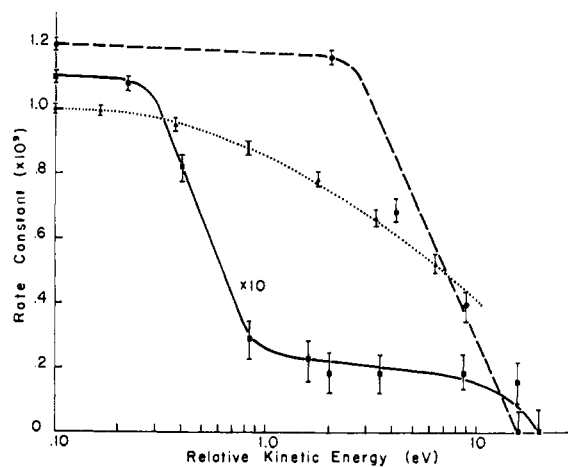It is also seen that for methyl fluoride the total rate

constant (sum of F^- + H^- transfer) is very close to that reported for H^- transfer alone in ref 17. Since the rate constant for H^- transfer in ref 17 was obtained from the log of CH_3^+ disappearance with time, and by assuming that CH_3^+ reacted to give CH_2^+F exclusively (i.e., H^- transfer), we believe that the results of the two studies are, in fact, quite consistent (i.e., if we were to interpret our results in terms of a reaction rate constant for the initial CH_3^+ primary ions, the results of the two studies would agree closely). In a system where no labeled CD_3^+ was present, CH_3^+ would react to yield principally CH_3^+, and it would not be possible to distinguish the product from the reactant. However, the product would very likely be a low kinetic energy, unexcited
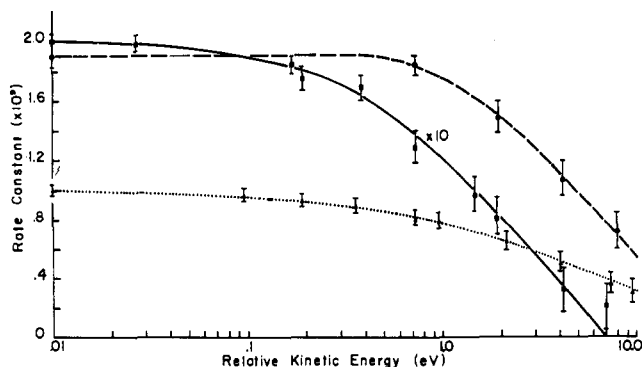
Figure 6. Kinetic energy dependence of absolute rate constants in the CD_4-CH_3Br system: (●) $CD_3^+ + CH_3Br \rightarrow CH_3^+ + CD_3Br$, (■) $CD_3^+ + CH_3Br \rightarrow CH_2Br^+ + CD_3H$, (▲) $CD_4^+ + CD_4 \rightarrow CD_5^+ + CD_3$.

CH_3^+ ion whose reaction properties and behavior could be very different from the primary CH_3^+ ion produced by electron impact. Indeed, such a reaction would be a very efficient mechanism for producing thermal, unexcited methyl cations. Whereas Beauchamp, et al.,[17] have concluded that collisional deactivation of CH_3^+ first occurs followed by a fast reaction to yield CH_2F^+, our results indicate that a reaction 2 occurs rapidly, producing "new" unexcited ions, followed by a much slower H^- transfer reaction yielding CH_2F^+. From the relative rates of the two reactions, it appears that reaction 2 can occur many times before a CH_2F^+ ion is produced by reaction 3.

Production of a Symmetrical Intermediate. It has been previously concluded[17] that the reactions in these systems proceed through a symmetrical intermediate of the type shown in Table I. It can be seen from Tables II–V that only two exothermic reaction channels are available at thermal kinetic energy for the fluoride, chloride, and bromide systems, but that for methyl iodide, four channels are either exothermic or thermoneutral. However, if a symmetrical intermediate is produced, there would be two possible sets of products from each reaction channel, depending upon which C–X bond is broken when the intermediate fragments (e.g., the apparent halide transfer reaction would have to be accompanied by an equivalent amount of back reaction from such an intermediate). These product pairs, along with the apparent transferred specie, are listed together in Tables II–V. Denoting such reactions as halide or atom transfer can be misleading even though the observed products would appear to indicate that that is what happened.

For the halide transfer channel, it is not possible to observe both sets of products directly. We assumed that the rate constant for the unobservable channel (back reaction) is equal to that for the forward reaction. For other channels (hydride transfer), both sets of products can be observed. The rate constants in Tables II–V are listed as either observed directly or inferred, depending upon our ability to detect both channels directly. The hydride transfer reactions provide good supportive evidence that a symmetrical intermediate is formed. Both sets of products can be observed and double resonance experiments show approximately equal rate constants for H^- transfer yielding CH_2X^+ and CD_2X^+ ions. This is only reasonable if the reaction does proceed through a symmetrical intermediate.
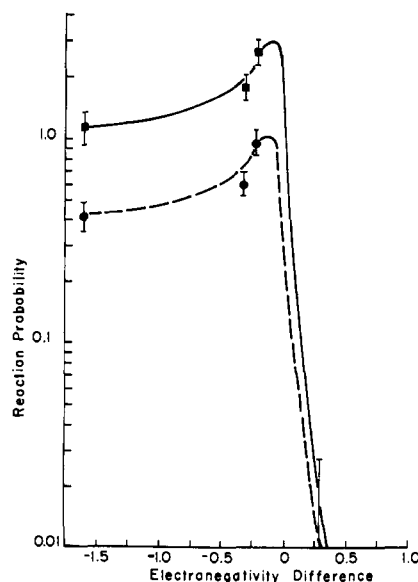

Figure 7. Reaction probability vs. electronegativity difference. Reaction probability is defined as the ratio of the rate constant for the observed plus inferred halide ion transfer to the total theoretical rate constant: (■) reaction probability determined by Gioumousis and Stevenson model, (●) reaction probability determined by locked dipole model. The electronegativity difference is defined as the difference in electronegativity between the carbon and the halogen with the carbon atom more electronegative than the halogen being assigned a positive value. Electronegativity differences are determined using the Allred-Rochow formula, ref 21.

Mechanism of the Halide Transfer Reactions. Although one of the two channels associated with halide transfer cannot be observed, these reactions nevertheless provide valuable evidence regarding mechanism. There are two aspects of the halide transfer reactions which should be emphasized in this respect. The first is the striking difference in the reaction probability between the fluorides, chlorides, and bromides on the one hand and the iodide on the other. The second is the variation of rate constant with kinetic energy for each system.

The behavior of each system with respect to the kinetic energy of the reactants is qualitatively amenable to a phase space analysis. However, no attempt is made to predict absolute rate constants for these reactions from phase space theory. Indeed, it has been well documented that the application of phase space theory for predicting rate constants (even in three-atom systems) has met with limited success[20] at best.

It is noted that the hydride ion transfer rate constant falls off much more rapidly with increasing kinetic energy than does the halide ion transfer rate constant (Figures 4–7).

The relative behavior of the two reactions for each system is shown in Figure 3 and is qualitatively similar in all three cases (i.e., the halide transfer reaction becomes relatively more probable with increasing energy in each case rather than the hydride transfer). It is also evident that the magnitude of the effect is largest for the bromide and smallest for the fluoride. The increase in halide vs. hydride transfer is qualitatively predicted by phase space theory, as is the order of the observed effect for the three systems. Consider the following.

(20) M. Henchman, "Ion Molecule Reactions," Vol. I, J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1971, Chapter 5.
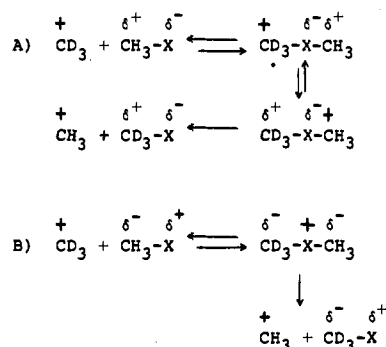
A)
$$CH_3^+ + CH_3\text{-}X \overset{\delta^+ \ \delta^-}{\underset{}{\rightleftharpoons}} CH_3\text{-}X\text{-}CH_3^{\delta^-\delta^+}$$

$$CH_3^+ + CD_3\text{-}X \overset{\delta^+ \ \delta^-}{\underset{}{\longleftarrow}} CD_3\text{-}X\text{-}CH_3^{\delta^+ \ \delta^-+}$$

B)
$$CD_3^+ + CH_3\text{-}X \overset{\delta^- \ \delta^+}{\underset{}{\rightleftharpoons}} CD_3\text{-}X\text{-}CH_3^{\delta^- + \delta^-}$$

$$CH_3^+ + CD_3\text{-}X^{\delta^- \ \delta^+}$$

Figure 8. Schematic of charge redistribution in the intermediate: $(+)$ indicates major positive charge density, (δ^+) indicates minor positive charge density, (δ^-) indicates minor negative charge density. Charge distributions are determined using Alfred–Rochow values, ref 21.

For the fluoride, chloride, and bromide, there are two possible reactions at thermal kinetic energy. Halide transfer in each case is quasi resonant and thermoneutral. Hydride transfer is exothermic by 2, 15, and 12 kcal/mol, respectively. For halide transfer, products can be produced only in their ground states at low kinetic energy, but as the kinetic energy of the reactants is increased, phase space theory would predict that more channels for halide transfer would be available and excited products could be produced. A phase space treatment would, therefore, predict that halide transfer should contribute more to the overall measured rate constant at higher kinetic energy.

If we consider the exothermicity of the hydride transfer reactions, it is easily understood why the magnitude of the increase for halide transfer, relative to hydride transfer, is so much less for the fluoride than it is for the bromide or the chloride. Since hydride transfer in the fluoride is only 2 kcal/mol exothermic, phase space theory would lead one to conclude that almost as many additional channels would be made available for that reaction by increasing the kinetic energy of the reactants as would be made available for halide transfer. Furthermore, one would expect to see an increase in fluoride transfer, if it did occur, only at very low kinetic energies. This is just what is observed. On the other hand, the chloride and bromide systems show much larger increases in halide transfer relative to hydride transfer at high kinetic energies. This also is to be expected since the hydride transfer reactions are fairly exothermic in those systems, and presumably most of the participating channels for hydride transfer would be available at thermal kinetic energy, whereas those for halide transfer would not.

It might be argued that the decrease in relative probability of the hydride transfer reactions at higher kinetic energy is due to the expected shorter lifetime of a higher energy intermediate. In such a case it might be argued that the extensive bond rearrangement required for hydride transfer would become relatively more probable. However, in Figure 3 it is seen that the ratio of halide to hydride transfer eventually begins to decrease with higher kinetic energy above a certain point which is inconsistent with a lifetime argument. We believe that the kinetic energy behavior can best be accounted for by the phase space arguments set forth above.

Such an analysis does not explain why halide transfer

is so much more probable than hydride transfer, even though it is limited in its contribution by being thermoneutral in each case. Another question to be answered is why the iodide system is so unreactive in comparison to the other three systems, and why is I⁻ transfer not observed at all?

These features of the reaction can be explained by the electron density redistribution model of ion–molecule reactions.

Reaction Probability. It has been previously shown[7] that the qualitative probability of occurrence for simple ion–molecule reactions involving N, C, and O atoms could be predicted by using as a guide the expected redistribution of charge density which must accompany the reaction. The treatment was later shown to predict the major reactions in systems containing S and F atoms.[9]

The initial model is generalized[10] to include many additional reactions which involve functional groups instead of atoms. The reaction types which can be treated and the correlation which exists are discussed in some detail in ref 10. As it applies to all systems including the halides, the model's validity depends upon the assumptions that (1) the bond-making process is nonadiabatic, (2) the details of intimate collisions are less important than are large changes in charge density in determining overall reaction probability, and (3) any intermediate produced must be similar to the reactants in its electronic character.

In ref 7, it was suggested that the reaction will have a large probability if ψ_1 and ψ_2 (the wave functions representing the initial and final states of the system) are electronically similar to each other and that the reaction will have a small probability if they are electronically very different. It was also suggested in ref 7 that for ion–molecule reactions the most useful measure of electronic similarity or dissimilarity was the amount of rearrangement of charge density which could be expected to occur in proceeding from one state to the other as determined by differences in the electronegativity between the central atoms.

If reaction 1 is taken as the model, A and A' are CH_3 and CD_3 functional groups, respectively, and X is the halogen. Only the properties of the C and X atoms are taken to be important as a first approximation.[10] Direct reactions involving hydrogen atoms and proton or hydride transfer are explicitly excluded[7] due to the gross electronic dissimilarity of hydrogen and other atoms involved, such as carbon, nitrogen, or the halogens. We can legitimately discuss hydride transfer here only as it may involve the breaking of additional bonds in an intermediate (see below), but otherwise the hydrogen atoms bonded to the central atoms involved in the reaction are ignored, and predictions regarding their behavior are not made.

The expected change in charge distribution during the reaction is evaluated as in Figure 8. Since such reactions are known to proceed through long-lived intermediates, the overall reaction is considered as two separate steps. In terms of this description presented in ref 7 the reactants and the stable intermediate would be represented by ψ_1 and ψ_2, and the intermediate decomposing to give the final products would be represented by ψ_2 and ψ_3.

It is reasonable to presume that the carbon atom in

the methyl cation is initially electron deficient to a large extent, since the entire specie is positively charged.

Using the known electronegativities for C, F, Cl, Br, and I,[21] it is also reasonable to presume that the carbon atoms in the neutral methyl fluoride, chloride, and bromide are electron deficient and that the halide has some negative character in each case. For these three systems it is expected that sequence A in Figure 8 would be appropriate (*i.e.*, the charge distribution in the initial reactants and final products would be the same). In addition, and more importantly, the change in distribution in proceeding from the initial to the final state would not be very great.

In the intermediate it is expected that the carbon atoms would also be significantly electron deficient and that the halide atom would still be electron rich. According to the electron density description, the halide transfer reaction shown in Figure 8, sequence A, should proceed (and the production of the intermediate shown should proceed) with high probability.

On the other hand, scheme B in Figure 8 shows the expected behavior for the iodide system. Iodine is less electronegative than carbon and hence the carbon atom should be electron rich in methyl iodide and the dimethyl halonium ion but electron deficient in the reacting methyl ion. As shown in Figure 8, sequence B, this would result in an intermediate structure in which the positive carbon from the methyl cation would have to become negative. As this would involve a very substantial rearrangement of charge density, the electron density model would prohibit the reaction.

The scale chosen to measure electronegativity is not very significant in terms of the overall correlation between charge redistribution and reaction probability.[10] In the case of iodine, for example, one scale may show iodine to be more electronegative than carbon, while another shows it to be slightly less electronegative than carbon. The point is that iodine is very much less electronegative than fluorine, and hence one would expect a much greater charge redistribution in the iodide system than in the fluoride system. Figures 8A and 8B are intended merely to show the limiting cases rather than the absolute charge distribution for each case.

The major problem which arises in considering gas phase intermediates such as the dimethyl halonium ions shown in Figure 8 is that we know even less about their physical properties than we do about the initial reactants or final products. Intuition must play a role in deciding what they would look like and how charge would be distributed in them. The electron density description provides that intermediates cannot be formed if they are electronically dissimilar from the reactants. Hence, the same predictions will always be made if the intermediate is ignored, and only the charge distribution in reactants and products is considered. In this way the role of intuition may be reduced in deciding which reactions will be allowed and which will be prohibited.

If we choose to describe the reaction without considering the intermediate directly, it is seen that the transfer of a halide ion from the neutral to the methyl

ion will be favorable for the F, Cl, and Br systems, because the halogen atom is already negatively charged and the methyl group positively charged in both reactants and products. The same reaction would be unfavorable for the iodide because the iodine atom starts out with a small net positive charge in the neutral, while the carbon atom in the methyl cation is substantially positively charged. For the reaction to proceed the carbon in the methyl ion would have to become net negatively charged. The experimental behavior is shown in Figure 7 where the probability of reaction is plotted *vs.* the difference in electronegativity between the central atoms. It is seen that as long as the halide atom in the neutral is significantly more electronegative than the carbon atom, a large halide transfer reaction is observed, but when the situation is reversed, no reaction is observed.

In spite of a general desire to avoid speculation on the structure of the intermediate, it is often useful to consider it because very often several different products can result from the fragmentation of a single intermediate. Table I shows that for methyl iodide four pathways are accessible at thermal kinetic energy. However, in the previous discussion it was suggested that production of the proposed intermediate in the iodide system should not occur with high probability. Hence, it would be expected that all of the products resulting from the fragmentation of the intermediate should be observed (if at all) with small rate constants. In line with this, we observe a relatively small rate constant for all of the products in the iodide system.

As a further test of the electron density distribution model, we consider the behavior of the bromide and chloride systems at greater than thermal kinetic energies. In the bromide system Br and H transfer are only about 0.5 eV endothermic, so that at 1 eV relative kinetic energy all four pathways should be accessible. However, the transfer of a Br atom from an intermediate such as shown in Figure 8a would require more total redistribution of charge than would Br^- transfer. It would therefore be expected that Br atom transfer would be less favorable than Br^- transfer, even when the reaction is thermochemically possible. Table II lists the rate constants for the four reactions at 1 eV in the bromide system, and it is seen that only Br^- transfer is significant. The same general results were obtained for the chloride system, but quantification of the results was more difficult due to the presence of two stable Cl isotopes.

In summary, it may be stated that a consideration of charge redistribution during the reaction of methyl ions with methyl halides predicts that proceeding to an intermediate for the iodide should be difficult and that even though there are four available exothermic channels, methyl iodide should be relatively unreactive toward methyl cations.

The same treatment predicts that formation of a symmetrical complex will be favorable for the fluoride, chloride, and bromide systems and further predicts that halide transfer would involve the least redistribution of charge density during the reaction. Hence, halide transfer is expected to be the major reaction observed in each of these systems. For the four systems studied here, the results are as expected without exception.

(21) A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).