Thermochemical Properties and Ion–Molecule Reactions of the Alkyl Halides in the Gas Phase by Ion Cyclotron Resonance Spectroscopy

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Received April 27, 1971

Abstract: The gas-phase ion–molecule reactions of the methyl and ethyl halides both pure and in binary mixtures have been investigated by ion cyclotron resonance spectroscopy. Reaction pathways, product distributions, and rate constants have been determined for the majority of the fragment and parent ion species. Particular attention is given to processes possessing the character of gas-phase nucleophilic displacement reactions which result in the production of dialkylhalonium ions, $R_1XR_2^+$. Where possible, thermochemical data have been determined, including proton affinities (gas-phase basicities). Basicities decrease in the order RI > RBr > RCl > RF for a given alkyl group and $C_2H_5X > CH_3X$ for a given halogen. Significantly, even small differences in thermochemical properties are important in determining reactivity. The gas-phase ion chemistry of the alkyl halides is systematic and is remarkably similar to the corresponding solution chemistry of these species in strongly acidic media.

The systematic delineation of the ion–molecule chemistry of various functional groups is barely in its infancy. With few exceptions, comprehensive surveys of the reactivity of homologous series of compounds are lacking. Such studies are of interest in themselves, but more importantly they allow the determination of thermochemical data and the identification of general reaction processes. Few investigations of the gas-phase ion–molecule chemistry of the alkyl halides have been attempted.[2–8] We report here a detailed study of the ion–molecule chemistry of the methyl and ethyl halides employing the mass spectrometric technique of ion cyclotron resonance spectroscopy (icr). Included are the cataloging of reaction pathways, the determination of reaction rate constants, and the determination of thermochemical data including the proton affinities (gas-phase basicities) of these halides. Not surprisingly, many of the processes observed have analogies in solution chemistry. Of special interest is the observation of a reaction process of wide generality possessing the character of a gas-phase nucleophilic displacement reaction which results in the production of dialkylhalonium ions, $R_1XR_2^+$ (X represents a halogen atom and R_1 and R_2 are alkyl groups). Some preliminary aspects of this work have been previously reported.[9]

Experimental Section

The instrumentation and experimental techniques associated with ion cyclotron resonance spectroscopy have been previously described in detail.[10] All experiments were performed at ambient temperature. Reported single resonance intensities were summed for different isotopic species to obtain monoisotopic spectra with respect to Cl and Br. Product distributions in the present study were determined by the source ion ejection technique.[10,11] Reaction rate constants were calculated from single resonance intensities using the analysis of Buttrill and Marshall and are summarized in Tables I and II.[12,13] The analysis of Buttrill and Marshall treats power absorption as being limited by either the time an ion spends in the icr cell or the time between ion–neutral reactive encounters. This treatment is applicable only to fast processes, *i.e.*, reactions which occur on every collision. Several of the processes observed in the alkyl halides proceed with relatively slow rates in the range 10^{-10}–10^{-12} cm^3 molecule^{-1} sec^{-1}. For these reactions the data were analyzed by assuming that the power absorption is collision limited.[14,15] Rates obtained from this alternative treatment were within experimental error of the rates determined with the analysis of Buttrill and Marshall. Apparently the cumulative errors in the latter treatment tend to cancel for slow reactions.

Deuterium-labeled species, CD_4 and CD_3Cl, were obtained from Merck Sharp and Dohme of Canada. Methyl and ethyl fluoride were obtained from Peninsular Chemresearch, Inc. All other chemicals were reagent grade commercial samples. All samples were used as supplied except for degassing with multiple freeze–pump–thaw cycles. Purities as ascertained by mass spectrometric analysis were acceptable.

Results and Discussion

The ion–molecule chemistry of the methyl and ethyl halides was examined. Reaction sequences were formulated by observing changes in relative ion abundances as a function of neutral molecule pressure in the range 10^{-7}–10^{-3} Torr at several electron energies. Complementary and confirmatory information was obtained by means of ion cyclotron double resonance experiments and isotopic substitutions. Where possible, reaction rate constants were determined. These are summarized in Tables I and II.

Methyl Fluoride. The ion–molecule chemistry of methyl fluoride has been studied in detail by McAskill employing the technique of high-pressure mass spec-

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Table I. Rate Constants for Some Reactions of the Alkyl Halides

Reaction	Rate constants, cm³ molecule⁻¹ sec⁻¹ × 10¹⁰ Experimental[a]	k_L[b,d]	k_{LD}[c,d]
$CH_3F^+ + CH_3F \rightarrow CH_3FH^+ + CH_2F$	$k_1 = 12.8$[e]	9.07	49.44
$\rightarrow C_2H_4F^+ + HF + H$	$k_2 = 0.96$[e]		
$CH_3FH^+ + CH_3F \rightarrow (CH_3)_2F^+ + HF$	$k_3 = 7.1$[e]	9.00	49.09
$C_2H_5F^+ + C_2H_5F \rightarrow C_2H_5FH^+ + C_2H_4F$	$k_{15} = 15.0$	10.00	46.40
$C_2H_5FH^+ + C_2H_5F \rightarrow (C_2H_5)F^+ + HF$	$k_{16} = 14.0$	9.94	46.16
$CH_3Cl^+ + CH_3Cl \rightarrow CH_3ClH^+ + CH_2Cl$	$k_{22} = 12.5$[f]	9.79	45.10
$CH_3ClH^+ + CH_3Cl \rightarrow (CH_3)_2Cl^+ + HCl$	$k_{23} = 1.4$	9.74	44.91
$C_2H_5Cl^+ + C_2H_5Cl \rightarrow C_4H_8^+ + 2HCl$	$k_{26} = 0.70$	10.32	43.19
$\rightarrow C_4H_9^+ + HCl + Cl$	$k_{27} = 0.85$		
$\rightarrow C_2H_3Cl^+ + C_2H_5Cl + H_2$	$k_{28} = 4.0$		
$\rightarrow C_2H_5ClH^+ + C_2H_4Cl$	$k_{29} = 9.4$		
$C_2H_5ClH^+ + C_2H_5Cl \rightarrow (C_2H_5)_2Cl^+ + HCl$	$k_{30} = 5.5$	10.28	43.02
$C_2H_4^+ + C_2H_5Cl \rightarrow C_4H_8^+ + HCl$	$k_{31} = 0.83$	13.25	55.47
$\rightarrow C_4H_9^+ + Cl\cdot$	$k_{32} = 1.24$		
$\rightarrow C_2H_3Cl^+ + C_2H_6$	$k_{33} = 2.71$		
$\rightarrow C_2H_4Cl^+ + C_2H_5$	$k_{34} = 0.47$		
$CH_3Br^+ + CH_3Br \rightarrow (CH_3)_2Br^+ + Br\cdot$	$k_{39} = 0.55$	7.91	31.68
$C_2H_5Br^+ + C_2H_5Br \rightarrow (C_2H_5)_2Br^+ + Br\cdot$	$k_{46} = 0.56$	8.56	33.73
$C_2H_5BrH^+ + C_2H_5Br \rightarrow (C_2H_5)_2Br^+ + HBr$	$k_{51} \sim 0.5$	8.54	33.65
$CH_3I^+ + CH_3I \rightarrow (CH_3)_2I^+ + I\cdot$	$k_{52} = 0.055$	7.48	25.30
$C_2H_5I^+ + C_2H_5I \rightarrow (C_2H_5)_2I^+ + I\cdot$	$k_{55} = 0.16$	7.98	27.88

[a] Reaction rate constants were determined at an electron energy within 2 eV of the appearance potential of the reactant ion. [b] Langevin model, calculated by means of eq 78. [c] Locked dipole model, calculated by means of eq 79. [d] Dipole moments and polarizabilities used in calculating k_L and k_{LD} were taken from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman, San Francisco, Calif., 1963, and E. W. Rothe and R. B. Bernstein, *J. Chem. Phys.*, **31**, 1619 (1959). The polarizabilities of C_2H_5F and C_2H_5I were assumed to be 1.84 Å³ greater than the values reported for CH_3F and CH_3I. [e] Buttrill and Marshall, ref 13, employing icr methods, report values of 13.6, 0.96, and 8.0 for k_1, k_2, and k_3, respectively. McAskill, ref 8, employing a high-pressure mass spectrometer, reports a value of 22 for $-d(CH_3F)/dt$. [f] Several investigators employing a high-pressure mass spectrometer have reported values for k_{22} (ion exit energy in parentheses): 26.5 (thermal), 18.8 (3.7 eV), A. G. Harrison, and J. C. J. Thynne, *Trans. Faraday Soc.*, **64**, 1287 (1968); 17.0 (thermal), 12.1 (3.4 eV), S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, **45**, 3107 (1967); 19.4 (0.5–2.0 eV), McAskill, ref 7.

Table II. Total Reactivities of the Parent and Protonated Parent Ion of the Alkyl Halides[a]

Species	Rate constant, cm³ molecule⁻¹ sec⁻¹ × 10¹⁰ F	Cl	Br	I
CH_3X^+	13.8	12.5	0.55	0.06
$C_2H_5X^+$	15.0	15.0	0.56	0.16
CH_3XH^+	7.1[b]	1.4		
$C_2H_5XH^+$	14.0	5.5	~0.5	

[a] Data taken from Table I. [b] The actual reactivity of CH_3FH^+ is somewhat greater than indicated since a portion of the $(CH_3)_2F^+$ formed in reaction 3 decomposes to give CH_2F^+ and CH_4.

trometry.[8] Our results are in general agreement with his study.

The variation of single resonance intensities with pressure at 70 eV is illustrated in Figure 1. At 5 × 10⁻⁷ Torr only the CH_3F^+, CH_2F^+, and CH_3^+ ions are present. As the pressure is raised, the parent ion undergoes reactions 1 and 2. With increasing pressure the

$$CH_3F^+ + CH_3F \longrightarrow CH_3FH^+ + CH_3F \qquad (1)$$

$$CH_3F^+ + CH_3F \longrightarrow C_2H_4F^+ + HF + H \qquad (2)$$

protonated parent ion generated in reaction 1 undergoes reaction 3 to yield the dimethylfluoronium ion which

$$CH_3FH^+ + CH_3F \longrightarrow CH_3FCH_3^+ + HF \qquad (3)$$

does not react further with methyl fluoride. In a mixture containing CH_3F in excess D_2, CH_3FD^+ generated principally by reaction 4 undergoes the condensation reaction 5 with no incorporation of deuterium in the di-

$$D_3^+ + CH_3F \longrightarrow CH_3\overset{+}{F}D + D_2 \qquad (4)$$

$$CH_3FD^+ + CH_3F \longrightarrow CH_3\overset{+}{F}CH_3 + DF \qquad (5)$$

methylfluoronium ion product. Since the dimethylfluoronium ion is most probably formed by the direct displacement of HF by CH_3F (reaction 3), protonation on fluorine is suggested.

The CH_2F^+ ion, which is found to be unreactive toward methyl fluoride, exhibits a slight increase in intensity with the appearance of the dimethyl fluoronium ion. Partial decomposition of the initially formed excited dimethyl fluoronium ion accounts for the additional CH_2F^+ (reaction 6). Reaction 6 can in fact be collisionally induced.[16] The overall process, reaction 3 followed by reaction 6, is exothermic by 11 kcal/mol.[17]

$$[CH_3\overset{+}{F}CH_3]^* \longrightarrow CH_2F^+ + CH_4 \qquad (6)$$

The final ion, methyl cation, reacts at high pressure to yield CH_2F^+ (reaction 7). In a mixture of CD_4 with CH_3F, CD_3^+ reacts to produce nearly equal amounts of CH_2F^+ and CD_2F^+ suggesting a dimethylfluoronium ion intermediate for reactions 7 and 8.

$$CD_3^+ + CH_3F \longrightarrow$$

$$[CD_3\overset{+}{F}CH_3] \xrightarrow{53\%} CH_2F^+ + CD_3H \qquad (7)$$

$$\xrightarrow{47\%} CD_2F^+ + CH_3D \qquad (8)$$

The ion–molecule chemistry of CH_3F at 13 eV is similar to that described above except for the absence of the CH_3^+ ion and a diminution in the intensity of the CH_2F^+ ion.

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(16) The technique has been described in F. Kaplan, *J. Amer. Chem. Soc.*, **90**, 4483 (1968).

(17) The following heats of formation were used: $\Delta H_f(CH_2F^+)$ = 200 kcal/mol, M. Kraus, J. A. Walker, and V. H. Dibeler, *J. Res. Nat. Bur. Stands., Sect. A*, 72, 281 (1968); $\Delta H_f(CH_3F)$ = −56 kcal/mol, J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034 (1968); H. W. Chang and D. W. Setser, *J. Amer. Chem. Soc.*, **91**, 7648 (1969).

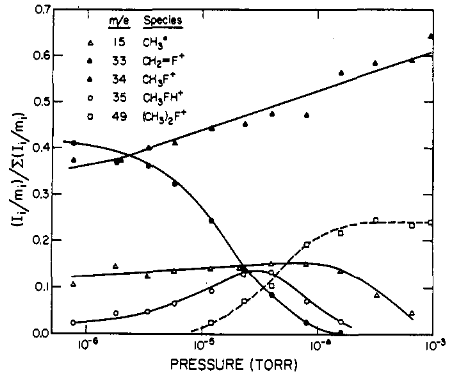


Figure 1. Variation of ion densities (reported as normalized mass corrected single-resonance intensities) with pressure for CH_3F at 70 eV.

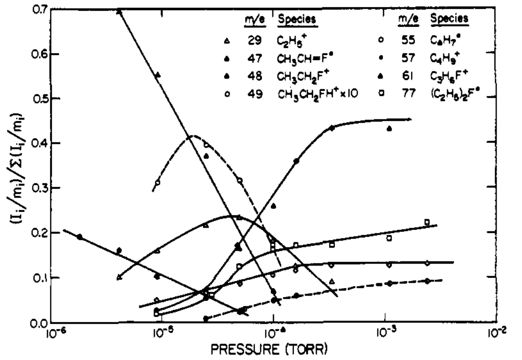
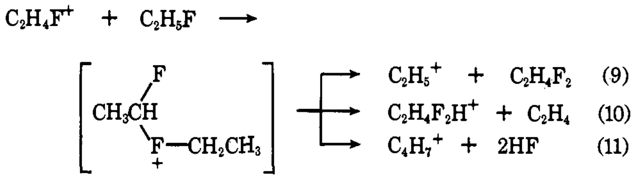


Figure 2. Variation of ion densities (reported as normalized mass corrected single-resonance intensities) with pressure for the major ionic species present in C_2H_5F at 13.4 eV.

Ethyl Fluoride. The variation with pressure of the single resonance intensities of the major ionic species present at 13.4 eV is illustrated in Figure 2. At 1 × 10^{-6} Torr only the parent ion, $C_2H_5F^+$, and the fragment ion, $C_2H_4F^+$, are present in a ratio of 1:4. With increasing pressure $C_2H_4F^+$ undergoes reactions 9–11



$$C_2H_4F^+ + C_2H_5F \longrightarrow$$

$$\longrightarrow C_2H_5^+ + C_2H_4F_2 \quad (9)$$

$$\longrightarrow C_2H_4F_2H^+ + C_2H_4 \quad (10)$$

$$\longrightarrow C_4H_7^+ + 2HF \quad (11)$$

I

generating the ions $C_2H_5^+$, $C_2H_5F_2^+$, and $C_4H_7^+$. The formation of the first two ions can be rationalized in terms of the intermediate reaction complex I which decomposes by direct bond cleavage (reaction 9) or rearrangement with loss of ethylene (reaction 10). The formation of $C_4H_7^+$ involves a more complicated rearrangement.

Of the ions generated in reactions 9–11 only $C_2H_5^+$ reacts further with C_2H_5F. Product ions corresponding to $C_2H_5FH^+$, $C_3H_5^+$, and $C_4H_9^+$ are generated (reactions 12–14). The protonated parent ion $C_2H_5FH^+$,

$$C_2H_5^+ + C_2H_5F \longrightarrow \begin{cases} C_2H_5FH^+ + C_2H_4 & (12) \\ C_3H_5^+ + CH_4 + HF & (13) \\ C_4H_9^+ + HF & (14) \end{cases}$$

also generated in reaction 15, undergoes reaction 16 to

$$C_2H_5F^+ + C_2H_5F \longrightarrow C_2H_5FH^+ + C_2H_4F \quad (15)$$

$$C_2H_5FH^+ + C_2H_5F \longrightarrow C_2H_5\overset{+}{F}C_2H_5 + HF \quad (16)$$

form the diethylfluoronium ion.[18] The $C_3H_5^+$ ion generated from $C_2H_5^+$ undergoes reaction 17 to form $C_3H_5FH^+$.

$$C_3H_5^+ + C_2H_5F \longrightarrow C_3H_5FH^+ + C_2H_4 \quad (17)$$

This reaction probably proceeds through a halonium ion intermediate similar to that suggested for reaction 10. The $C_4H^+_9$ ion generated from $C_2H_5^+$ does not react further with C_2H_5F.

The formation of $C_4H_9^+$ was briefly investigated. In a mixture of CD_4 with ethyl fluoride, $C_2D_5^+$, formed in the reaction of CD_3^+ with CD_4, reacts with C_2H_5F to give the isotopic product distribution indicated for reaction 18. The nearly equal loss of HF and DF suggests a

$$C_2D_5^+ + C_2H_5F \longrightarrow \begin{cases} \xrightarrow{57\%} C_4H_5D_4^+ + DF \\ \xrightarrow{43\%} C_4H_4D_5^+ + HF \end{cases} \quad (18)$$

symmetrical intermediate for reactions 14 and 18. Elimination of HF from the diethylfluoronium ion $(C_2H_5)_2F^+$ is one possible pathway for this reaction.

At 70 eV several additional primary ions are generated from ethyl fluoride. The most important of these are the $C_2H_3^+$ and CH_2F^+ species. The latter ion undergoes reaction 19 to yield $C_2H_5^+$. The analogy with

$$CH_2F^+ + C_2H_5F \longrightarrow C_2H_5^+ + CH_2F_2 \quad (19)$$

reaction 9 is evident. The reactivity of $C_2H_3^+$ toward the parent neutral is similar to that of $C_2H_5^+$. Reactions 20 and 21 give the protonated parent and a product

$$C_2H_3^+ + C_2H_5F \longrightarrow \begin{cases} C_2H_5FH^+ + C_2H_2 & (20) \\ C_4H_7^+ + HF & (21) \end{cases}$$

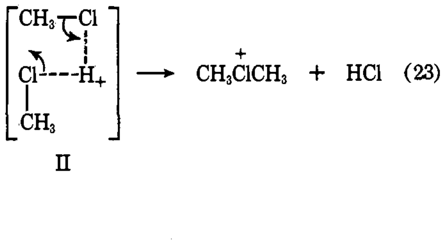
with empirical formula $C_4H_7^+$, respectively.

Methyl Chloride. The ion-molecule chemistry of methyl chloride has been studied in detail by McAskill employing the technique of high-pressure mass spectrometry.[7] Our results are in general agreement with his study.

The ion-molecule chemistry of methyl chloride is similar to that of methyl fluoride. Thus at 70 eV and 1 × 10^{-6} Torr only the CH_3Cl^+, CH_2Cl^+, and CH_3^+ ions are present. With increasing pressure the parent ion undergoes reaction 22 to form the protonated parent which at still higher pressure undergoes reaction 23 to

$$CH_3Cl^+ + CH_3Cl \longrightarrow CH_3ClH^+ + CH_2Cl \quad (22)$$

$$CH_3ClH^+ + CH_3Cl \longrightarrow$$



$$\longrightarrow CH_3\overset{+}{Cl}CH_3 + HCl \quad (23)$$

II

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[18] Determination of the rate constants for the above processes is complicated by the presence of primary through quaternary ion species, with two precursors contributing to the formation of the protonated parent ion. It is evident from Figure 2, however, that the diethylfluoronium ion intensity at high pressure is approximately equal to the parent ion intensity at low pressures. Consequently, the rates of reactions 15 and 16 were calculated by ignoring reaction 12. Similarly, reactions 12 and 13 were ignored in determining the rate constants for the sequence initiated by $C_2H_4F^+$. The rate constants are reported in Table I.

form the dimethylchloronium ion. Double resonance experiments indicate that for both reactions 22 and 23, the Cl atom in the product ion comes with *equal probability* from the ionic and neutral reactant species.[19] For reaction 22 this is probably the result of electron exchange during the formation of the ion–neutral reaction pair. For reaction 23 an intermediate such as II in which the proton is shared between the two reactant molecules is suggested.

The fragment ions CH_2Cl^+ and CH_3^+ have similar reactivity toward methyl chloride as do their fluorine counterparts toward methyl fluoride. Thus, the CH_2Cl^+ ion is generated from CH_3^+ in reaction 24 and is unreactive toward CH_3Cl. In a mixture of CD_4 with CH_3Cl, CD_3^+ reacts to produce nearly equal amounts of CH_2Cl^+ and CD_2Cl^+. This suggests, in analogy with reaction 8, that reactions 24 and 25 proceed not by simple

$$CH_3^+ + CH_3Cl \longrightarrow CH_2Cl^+ + CH_4 \qquad (24)$$

$$CD_3^+ + CH_3Cl \longrightarrow [CH_3\overset{+}{Cl}D_3] \begin{cases} \xrightarrow{58\%} CH_2Cl^+ + CD_3H \\ \xrightarrow{42\%} CD_2Cl^+ + CH_3D \end{cases} \qquad (25)$$

hydride abstraction, but rather through a dimethylchloronium ion intemediate.[20]

The ion–molecule chemistry of CH_3Cl at 13 eV is similar to that described above but simplified since at this electron energy the only ion formed by electron bombardment is the parent ion.

Ethyl Chloride. The ion–molecule chemistry of ethyl chloride has been studied in detail by Tiernan and Hughes using the combined techniques of high-pressure time of flight and tandem mass spectrometry.[6] Our results are in general agreement with their study.

The variation of single resonance intensities with pressure at 12.5 eV is illustrated in Figure 3. At 1 × 10^{-6} Torr only the parent ion, $C_2H_5Cl^+$, and one fragment ion, $C_2H_4^+$, are present. As the pressure is raised the parent ion undergoes reactions 26–29. With increasing pressure only the protonated parent ion reacts further, undergoing reaction 30 to generate the diethylchloronium ion. As was the case for the dimethylchloronium ion in reaction 23, double resonance experiments[19] indicate that the chlorine atom in the diethylchloronium ion comes with equal probability from the ionic and neutral reactants.

$$C_2H_5Cl^+ + C_2H_5Cl \begin{cases} \xrightarrow{5\%} C_4H_8^+ + 2HCl & (26) \\ \xrightarrow{6\%} C_4H_9^+ + HCl + Cl & (27) \\ \xrightarrow{26\%} C_2H_3Cl^+ + C_2H_5Cl + H_2 & (28) \\ \xrightarrow{63\%} C_2H_5ClH^+ + C_2H_4Cl & (29) \end{cases}$$

$$C_2H_5ClH^+ + C_2H_5Cl \longrightarrow C_2H_5\overset{+}{Cl}C_2H_5 + HCl \qquad (30)$$

The reaction of $C_2H_4^+$ with C_2H_5Cl leads to several of the same products (reactions 31–34) formed by reaction of the parent ion with C_2H_5Cl (reactions 26–29). None of the product ions formed in reactions 31–34 react further with C_2H_5Cl.

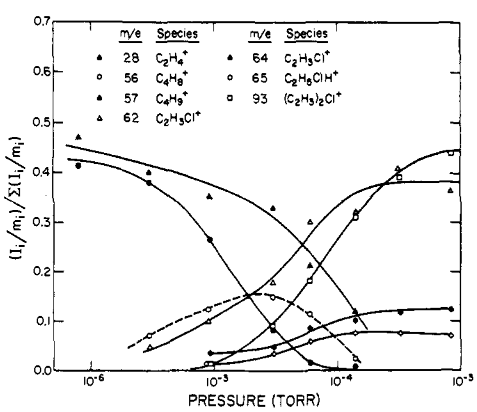


Figure 3. Variation of ion densities (reported as normalized mass corrected single-resonance intensities) with pressure for C_2H_5Cl at 12.5 eV.

$$C_2H_4^+ + C_2H_5Cl \begin{cases} \xrightarrow{16\%} C_4H_8^+ + HCl & (31) \\ \xrightarrow{24\%} C_4H_9^+ + Cl & (32) \\ \xrightarrow{51\%} C_2H_3Cl^+ + C_2H_6 & (33) \\ \xrightarrow{9\%} C_2H_4Cl^+ + C_2H_5 & (34) \end{cases}$$

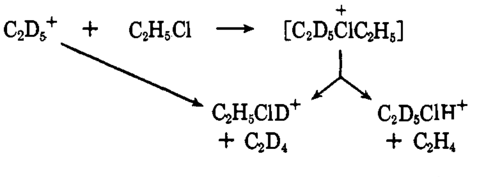
At 70 eV the additional primary ions that are generated are $C_2H_3^+$, $C_2H_5^+$, CH_2Cl^+, $C_2H_3Cl^+$, and $C_2H_4Cl^+$. The latter two species react slowly if at all with C_2H_5Cl. The CH_2Cl^+ ion reacts with C_2H_5Cl (reaction 35) to

$$CH_2Cl^+ + C_2H_5Cl \longrightarrow C_2H_5^+ + CH_2Cl_2 \qquad (35)$$

form $C_2H_5^+$ in analogy to the reaction of CH_2F^+ with C_2H_5F (reaction 19). The vinyl and ethyl cations react principally to form the protonated parent ion (reactions 36 and 37) and hence lead eventually to the diethylchloronium ion (reaction 30), which remains the major product ion at high pressure. In a mixture of CD_4 and C_2H_5Cl, the $C_2D_5^+$ ion, formed in the reaction of CD_3^+ with CD_4, participates in reaction 38 to produce $C_2H_5ClD^+$ and $C_2D_5ClH^+$ in the approximate ratio of 2:1.[21] The divergence of this ratio from unity indicates that protonated ethyl chloride is formed from ethyl cation by two mechanisms:[22] (1) direct proton transfer and (2) by means of the diethylchloronium ion (reaction 38).

$$C_2H_3^+ + C_2H_5Cl \longrightarrow C_2H_5ClH^+ + C_2H_2 \qquad (36)$$

$$C_2H_5^+ + C_2H_5Cl \longrightarrow C_2H_5ClH^+ + C_2H_4 \qquad (37)$$



$$C_2D_5^+ + C_2H_5Cl \longrightarrow [C_2D_5\overset{+}{Cl}C_2H_5] \longrightarrow C_2H_5ClD^+ + C_2D_4 \text{ or } C_2D_5ClH^+ + C_2H_4;\quad C_2D_5^+ + C_2H_5Cl \longrightarrow C_2H_5ClD^+ + C_2D_4 \qquad (38)$$

Methyl Bromide. Only the parent ion is present at 11.4 eV and 1 × 10^{-6} Torr. As the pressure is raised

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[19] Determination of the origin of the halogen atom retained in the product ion is possible whenever the halogen contains more than one isotope, *i.e.*, chlorine or bromine. The technique is described in J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

[20] T. O. Tiernan and B. M. Hughes,[6] using a tandem mass spectrometer, report a 55:45 product distribution ratio for reaction 25.

[21] The complexity of the reaction scheme prevented an accurate determination of the product distribution. Tiernan and Hughes[6] using a tandem mass spectrometer report a 7:3 product distribution ratio for reaction 38, to be compared with our estimate of 2:1.

[22] If reaction 38 proceeded entirely through a chloronium ion intermediate, isotope effects favoring production of $C_2D_5ClH^+$ would be expected, contrary to observation.

the parent ion undergoes reaction 39 to yield the dimethylbromonium ion.

$$CH_3Br^+ + CH_3Br \longrightarrow CH_3\overset{+}{Br}CH_3 + Br \qquad (39)$$

No other reaction products are observed. Double resonance experiments[19] indicate that the Br atom in the ionic product comes with equal probability from the ionic and neutral reactants. This can be rationalized by assuming that electron exchange occurs during the formation of the intermediate complex.

At 70 eV the additional primary ions generated are CH_3^+, Br^+, and CH_2Br^+. The latter species is produced from CH_3^+ in reaction 40 and is unreactive toward CH_4Br.

$$CH_3^+ + CH_3Br \longrightarrow CH_2Br^+ + CH_4 \qquad (40)$$

The ionization potential of atomic Br is 1.32 eV greater than the ionization potential of CH_3Br. The charge-transfer reaction 41 accounts for the disappearance of Br^+ as the pressure is raised.

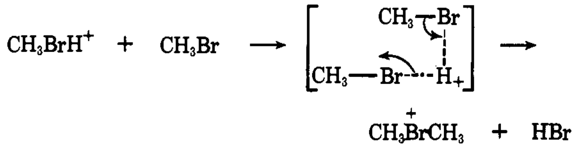
$$Br^+ + CH_3Br \longrightarrow CH_3Br^+ + Br \qquad (41)$$

Formation of the protonated parent ion is not observed. This is consistent with thermochemical considerations presented in the next section which indicate that the process leading to the formation of protonated parent ions in the case of the fluorides and chlorides (reactions 1 and 22) is endothermic in the case of methyl bromide (reaction 42). Addition of excess methane to CH_3Br provides, however, a means for generating the protonated parent through the exothermic reactions 43 and 44. Protonated methyl bromide thus formed undergoes the condensation reaction 45 to form the dimethylbromonium ion with expulsion of HBr.

$$CH_3Br^+ + CH_3Br \not\longrightarrow CH_3BrH^+ + CH_2Br \qquad (42)$$

$$CH_5^+ + CH_3Br \longrightarrow CH_3\overset{+}{Br}H + CH_4 \qquad (43)$$

$$C_2H_5^+ + CH_3Br \longrightarrow CH_3\overset{+}{Br}H + C_2H_4 \qquad (44)$$



(45)

The familiar intermediate postulated for reaction 45 is suggested from double resonance experiments[19] which indicate that the Br atom in the ionic product of reaction 46 comes with equal probability from the ionic and neutral reactants.

Ethyl Bromide.[23] At 12.0 eV only the parent ion is present. With increasing pressure the condensation reaction 46 occurs to form the diethylbromonium ion.

$$C_2H_5Br^+ + C_2H_5Br \longrightarrow C_2H_5\overset{+}{Br}C_2H_5 + Br \qquad (46)$$

The additional primary ions generated at 70 eV are $C_2H_3^+$, $C_2H_5^+$, Br^+, and CH_2Br^+. The CH_2Br^+ ion undergoes reaction 47 to form ethyl cation (compare reactions 19 and 35).

$$CH_2Br^+ + C_2H_5Br \longrightarrow C_2H_5^+ + CH_2Br_2 \qquad (47)$$

The charge-transfer reaction 48 consumes Br^+.

$$Br^+ + C_2H_5Br \longrightarrow C_2H_5Br^+ + Br \qquad (48)$$

The hydrocarbon ions $C_2H_3^+$ and $C_2H_5^+$ are sufficiently strong acids to protonate the parent neutral (reactions 49 and 50). The protonated ethyl bromide thus formed undergoes condensation reaction 51 to form the diethylbromonium ion.

$$C_2H_3^+ + C_2H_5Br \longrightarrow C_2H_5\overset{+}{Br}H + C_2H_2 \qquad (49)$$

$$C_2H_5^+ + C_2H_5Br \longrightarrow C_2H_5\overset{+}{Br}H + C_2H_4 \qquad (50)$$

$$C_2H_5\overset{+}{Br}H + C_2H_5Br \longrightarrow C_2H_5\overset{+}{Br}C_2H_5 + HBr \qquad (51)$$

As was the case for the dimethylbromonium ion in reaction 45, double resonance experiments[19] indicate that the bromine atom in the diethylbromonium ion originates with equal probability from the ionic and neutral reactants. Species containing two bromine atoms were not observed.[24]

Methyl Iodide.[23] The ion chemistry of methyl iodide is similar to that observed for methyl bromide. At 10.4 eV only the parent ion is generated, reacting to form the dimethyliodonium ion (reaction 52). At 70 eV the fragment ions I^+ and CH_3^+ appear. Reactions 53 and 54 account for the disappearance of I^+ and CH_3^+, respectively.

$$CH_3I^+ + CH_3I \longrightarrow CH_3\overset{+}{I}CH_3 + I \qquad (52)$$

$$I^+ + CH_3I \longrightarrow CH_3I^+ + I \qquad (53)$$

$$CH_3^+ + CH_3I \longrightarrow CH_2I^+ + CH_4 \qquad (54)$$

Species containing two iodine atoms were beyond the mass range of our instrument.[24]

Ethyl Iodide.[23] The ion chemistry of ethyl iodide is similar to that of ethyl bromide. At 10.9 eV only the parent ion is present, reacting to form the diethyliodonium ion (reaction 55).

$$C_2H_5I^+ + C_2H_5I \longrightarrow C_2H_5\overset{+}{I}C_2H_5 + I \qquad (55)$$

At 70 eV the fragment ions, CH_2I^+, I^+, and $C_2H_5^+$, are formed. Resolution problems make positive identification of reaction sequences difficult but presumably reactions 56 and 57 account for the disappearance of I^+ and CH_2I^+ and reactions 58 and 59 for the formation of the diethyliodonium ion.

$$I^+ + C_2H_5I \longrightarrow C_2H_5I^+ + I \qquad (56)$$

$$CH_2I^+ + C_2H_5I \longrightarrow C_2H_5^+ + CH_2I_2 \qquad (57)$$

$$C_2H_5^+ + C_2H_5I \longrightarrow C_2H_5IH^+ + C_2H_4 \qquad (58)$$

$$C_2H_5IH^+ + C_2H_5I \longrightarrow C_2H_5\overset{+}{I}C_2H_5 + HI \qquad (59)$$

Species containing two iodine atoms were beyond the mass range of our instrument.[24]

Binary Mixtures of the Alkyl Halides. The generality of the dialkylhalonium ions in the ion–molecule chemistry of the alkyl halides led us to investigate further the mechanism for the formation of these ions. For this purpose binary mixtures of $CH_3Cl(CD_3Cl)$ with CH_3F, C_2H_5F, and C_2H_5Cl were examined.

Methyl and Ethyl Chloride. The variation of single resonance intensities with pressure at 70 eV for a 4:1 mixture of CH_3Cl and C_2H_5Cl reveals the formation of the methyl ethylchloronium ion as the moxt abundant product at high pressures (Figure 4). Double resonance experiments indicate that both CH_3ClH^+ and C_2-

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(23) Some aspects of the ion–molecule chemistry of ethyl bromide,[4] methyl iodide,[3,5] and ethyl iodide[3] have been previously studied in a high-pressure mass spectrometer.

(24) Ionic dimers $(RX)_2^+$ for X = Cl, Br, and I have been reported in previous studies.[2-4] We did not observe these species or the proton bound dimers $(RX)_2H^+$ for X = F, Cl, and Br, and R = CH_3 and C_2H_5. Dimer species for X = I were beyond the mass range of our instrument.

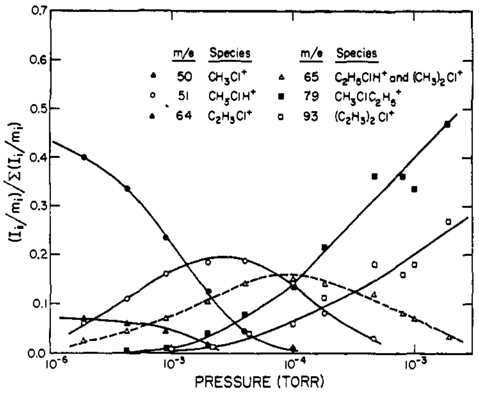
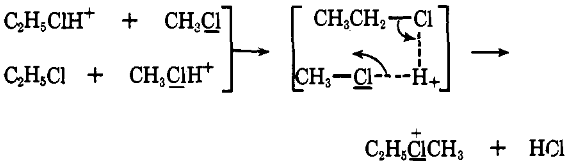


Figure 4. Variation of ion densities (reported as normalized mass corrected single-resonance intensities) with pressure for the major ionic species present in a 4:1 mixture of CH_3Cl and C_2H_5Cl at 70 eV.

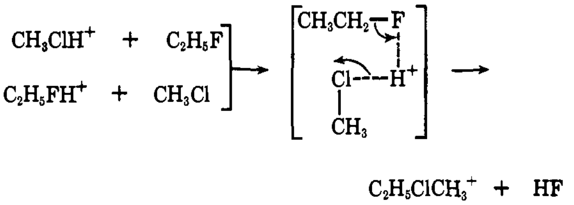
H_5ClH^+ contribute to the formation of the methyl ethylchloronium ion with the Cl atom retained in this product being that originally bound to the methyl group in the reactants.[19] This result suggests that the formation of the methyl ethylchloronium ion occurs by means of the intermediate suggested for reaction 60. The



$$\left.\begin{matrix} C_2H_5ClH^+ + CH_3\underline{Cl} \\ C_2H_5Cl + CH_3\underline{Cl}H^+ \end{matrix}\right] \longrightarrow \left[\begin{matrix} CH_3CH_2-Cl \\ CH_3-\underline{Cl}\cdots H^+ \end{matrix}\right] \longrightarrow C_2H_5\overset{+}{\underline{Cl}}CH_3 + HCl \qquad (60)$$

chlorine of ethyl chloride is more basic than that of methyl chloride and therefore preferentially binds the proton in this complex regardless of whether the proton was originally bound to methyl or ethyl chloride. Thus, in the formation of the reaction complex, proton transfer to ethyl chloride precedes condensation to the methyl ethylchloronium ion.

Methyl Chloride and Ethyl Fluoride. The variation of single resonance intensities with pressure at 15 eV for a 1.3:1 mixture of CH_3Cl and C_2H_5F indicates the formation of the methyl ethylchloronium ion as a major product at high pressure (Figure 5). Double resonance experiments indicate that this condensation product is formed from both CH_3ClH^+ and $C_2H_5FH^+$ (reaction 61). Significantly, the other possible cross-product



$$\left.\begin{matrix} CH_3ClH^+ + C_2H_5F \\ C_2H_5FH^+ + CH_3Cl \end{matrix}\right] \longrightarrow \left[\begin{matrix} CH_3CH_2-F \\ Cl\cdots H^+ \\ CH_3 \end{matrix}\right] \longrightarrow C_2H_5ClCH_3^+ + HF \qquad (61)$$

halonium ion $CH_3FC_2H_5^+$ is not formed.

Methyl Chloride and Methyl Fluoride. The variation of single resonance intensities with pressure at 15 eV for a 3.4:1 mixture of CH_3F and CD_3Cl is presented in Figure 6. In addition to products observed in an examination of the halides alone, reactions 62 and 63 are

$$CH_2F^+ + CD_3Cl \longrightarrow CD_2Cl^+ + CH_2DF \qquad (62)$$

$$CH_3FCH_3^+ + CD_3Cl \longrightarrow CD_3ClCH_3^+ + CH_3F \qquad (63)$$

observed. Double resonance experiments indicate that

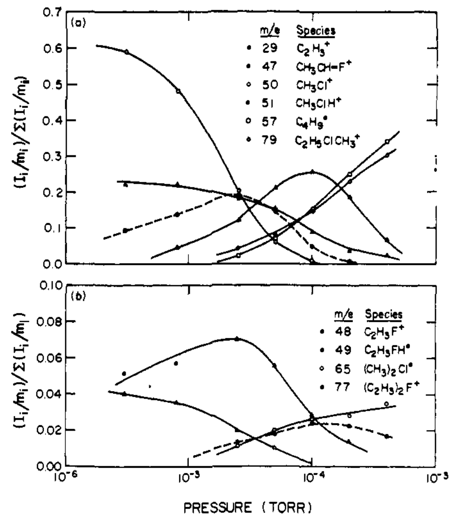


Figure 5. Variation of ion densities (reported as normalized mass corrected single-resonance intensities) with pressure for a 1.3:1 mixture of CH_3Cl and C_2H_5F at 15 eV: (a) major ions; (b) minor ions.

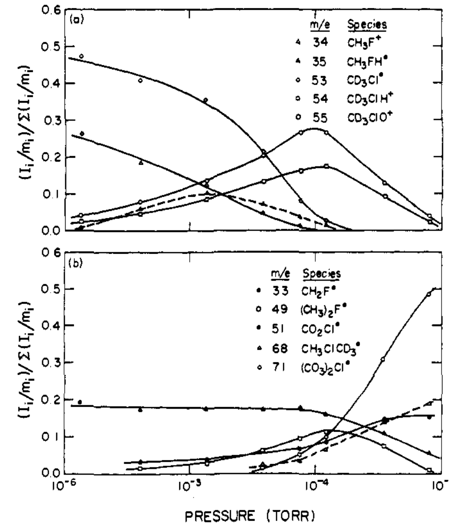


Figure 6. Variation of ion densities (reported as normalized mass corrected single-resonance intensities) with pressure for a 3.4:1 mixture of CH_3F and CD_3Cl at 15 eV.

the cross-product chloronium ion $CH_3ClCD_3^+$ is generated solely from $(CH_3)_2F^+$ (reaction 63) with no contribution from CH_3FH^+ (reaction 64). Significantly,

$$CH_3FH^+ + CD_3Cl \not\longrightarrow CD_3ClCH_3^+ + HF \qquad (64)$$

the cross-product fluoronium ion $CD_3FCH_3^+$ is not observed.

Proton Affinities of the Methyl and Ethyl Halides. The study of acid-base phenomena remains an important area of endeavor in chemistry. The alkyl halides are only weakly basic in solution and remain unprotonated in even 100% H_2SO_4.[25] The more strongly acidic HSO_3F-SbF_5 medium is required for ionization to occur.[26] Quantitative estimates of the solution basicities of the alkyl halides have been derived from hydrogen bonding studies and are contradictory even with regard to the relative basicities of the halogens.[25]

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[25] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

[26] G. A. Olah, *Science*, **168**, 1298 (1970).

We have thus, as part of our continuing program of determining proton affinities (basicities) in the gas phase,[10–14,27,28] determined the proton affinities of the methyl and ethyl halides. Since the formation and subsequent reactions of the protonated halide ions RXH^+ play an important role in the ion chemistry of the alkyl halides, a knowledge of the thermochemistry of these species is also important in understanding the processes observed. The proton affinity of the species RX, PA(RX), is the negative of the enthalpy change for reaction 65. The hydrogen affinity of the parent ion,

$$RX + H^+ \longrightarrow R\overset{+}{X}H \qquad (65)$$

$HA(RX^+)$, is similarly defined as the negative of the enthalpy change for reaction 66. Proton and hydrogen

$$RX^+ + H \longrightarrow R\overset{+}{X}H \qquad (66)$$

affinities are interrelated by eq 67 where IP(M) is the

$$PA(RX) - HA(RX^+) = IP(H) - IP(RX) \qquad (67)$$

adiabatic ionization potential of the species M.

Methods utilizing icr techniques to determine proton affinities are well established.[10,14] The species given in Table III are listed in decreasing order of proton affinity.

Table III. Relative Proton Affinities of the Alkyl Halides and Other Compounds[a]

Species	PA[b]
C_3H_6	179[c]
C_2H_5I	
CH_3I	
H_2S	170[d]
C_2H_5Br	
C_2H_5Cl	
H_2O	165[d]
C_2H_5F	
CH_3Br	
C_2H_4	160[c]
CH_3Cl	
C_2H_2	151[e]
CH_3F	
CO	142[d]
HCl	141[d]

[a] In descending order. Species in brackets have proton affinities which are experimentally indistinguishable to ±1 kcal/mol. [b] Proton affinity in kilocalories per mole. [c] F. P. Lossing and G. P. Semelnk, *Can. J. Chem.*, **48**, 955 (1970). [d] Haney and Franklin, ref 29. [e] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 26**, 36 (1969).

The braces indicate species whose proton affinities could not be distinguished. The order determined is in agreement with the less complete data reported by Haney and Franklin.[29] Assignment of numerical values to the proton affinities of those alkyl halides listed in Table III which are not well bracketed by standard compounds can be made by postulating that the hydrogen affinities of corresponding methyl and ethyl halides are equal. This is a reasonable assumption since hydrogen affinities have been found invariant to substituent changes for many other types of homologous series including alcohols, amines, ethers, aldehydes, and ketones.[28,30,31] The proton and hydrogen affinities of the methyl, ethyl, and hydrogen halides are summarized in Table IV along with the corresponding ionization potentials and related thermochemical properties.

Table IV. Proton and Hydrogen Affinities of the Alkyl Halides[a]

RX	IP(RX),[b,f] eV	PA(RX),[c] kcal/mol	$HA(RX^+)$,[d] kcal/mol	D(HX),[e,f] kcal/mol
CH_3F	12.50[g]	151	126	133[h]
C_2H_5F	12.00[i]	163	126	
CH_3Cl	11.28	160	107	103
C_2H_5Cl	10.97	167	107	
CH_3Br	10.53	163	93	88
C_2H_5Br	10.29	170	93	
CH_3I	9.54	170	77	72
C_2H_5I	9.33	175	77	

[a] PA and HA values from Table III using eq 67 and the assumption that the HA values are substituent invariant—see text. [b] Ionization potential. [c] Proton affinity. [d] Hydrogen affinity. [e] Bond dissociation energies for the hydrogen halides. [f] Except where noted values taken from Table III, footnote *e*. [g] M. Kraus, J. A. Walker, and V. H. Dibeler, *J. Res. Nat. Bur. Stand., Sect. A*, **72**, 281 (1968); J. A. Lacher and H. A. Skinner, *J. Chem. Soc., A*, 1034 (1968). [h] V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, **50**, 4592 (1969). [i] C. A. McDowell and B. G. Cox, *ibid.*, **22**, 946 (1954).

Inspection of Table IV indicates that for a given alkyl group, R, proton affinities decrease in the order RI > RBr > RCl > RF. Hydrogen affinities, on the other hand, decrease in the opposite order, paralleling the behavior of HX bond strengths. This correspondence is not surprising since, as indicated by reaction 66, the hydrogen affinity is the dissociation energy of the XH bond in the charged species, $D(RX^+–H)$. Consequently, for a given halogen, the change in proton affinities with alkyl substitution is fully accounted for, in accordance with eq 67, by the change in ionization potential.[28] For a given alkyl group, however, the variation of basicity with the halogen is seen to be determined by two factors which are mutually compensating in the case of the alkyl halides. These are the changes in the orbital ionization potentials (low-ionization potentials correspond to high basicities through increased *n*-donor ability) and the change in the $RX^+–H$ bond dissociation energies (higher bond dissociation energy corresponds to increased basicity). The variation in the former dominates the latter in the case of the alkyl halides, giving the observed order of basicities.

General Discussion

The chemistry of the alkyl halides delineated above is systematic. Even small differences in thermochemical properties, however, are important in determining the reactive behavior of these species. This is abundantly clear in considering the main ion–molecule reaction sequences involved in the generation of the protonated halides and dialkylhalonium ions.

Parent Ion Reactivity. The ion chemistry initiated by the parent ions of the alkyl fluorides and chlorides

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(27) D. Holtz and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5913 (1969).

(28) D. Holtz, J. L. Beauchamp, W. G. Henderson, and R. W. Taft, *Inorg. Chem.*, 10, 201 (1971).

(29) M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4329 (1969).

(30) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1967.

(31) J. L. Beauchamp and M. C. Caserio, *J. Amer. Chem. Soc.*, submitted for publication.

differs from that of the corresponding bromides and iodides. For the fluorides and chlorides, the parent ion reacts to form the protonated parent (reaction 68),

$$\mathrm{RX^+ + RX \longrightarrow RXH^+ + R'X} \qquad (68)$$

which subsequently reacts to form the dialkylhalonium ion (reaction 69). For the alkyl bromides and iodides,

$$\mathrm{RXH^+ + RX \longrightarrow RXR^+ + HX} \qquad (69)$$

however, the parent ion does not react to form the protonated parent, reacting instead at a relatively slow rate to form directly the dialkylhalonium ion (reaction 70). Reaction 70 may also occur in the case of the alkyl

$$\mathrm{RX^+ + RX \longrightarrow RXR^+ + X} \qquad (70)$$

fluorides and chlorides but is obscured by the more rapid processes 68 and 69.

An examination of the thermochemistry of reaction 68 is helpful in understanding these reactivity differences. With the exception of the alkyl fluorides, the parent ion of the alkyl halides is formed by removal of a nonbonding electron on halogen.[32] Such a species $\mathrm{RX^+}$ will probably react to form protonated parent $\mathrm{RXH^+}$ by means of hydrogen abstraction.[33] Therefore, formation of the protonated parent will only occur if the X–H bond formed in $\mathrm{RXH^+}$ is stronger than the bond broken, $\mathrm{H{-}C{<}}$. Inspection of the hydrogen affinities $\mathrm{HA(RX^+)}$ listed in Table IV indicates that hydrogen abstraction from a C–H bond of ~100 kcal/mol is not possible for the alkyl bromides or iodides but quite favorable for the alkyl fluorides and chlorides. The protonated parents of the alkyl bromides and iodides can, however, be generated by proton donation from a less basic species (*e.g.*, reactions 43, 44, 49, 50, and 58). Such protonated bromides and iodides react similarly to the analogous fluorides and chlorides (reaction 69). We see, therefore, that the ion–molecule reactivity of the alkyl parent ions is determined primarily by the X–H bond strengths in the species $\mathrm{RXH^+}$.

Dialkylhalonium Ion Formation–Nucleophilic Displacement Reaction. We have recently reported the occurrence of a gas-phase ionic process which has the character of a nucleophilic displacement reaction.[34] The displacement reaction proceeds through a four-center reaction complex such as represented in eq 60 in which proton attachment to the most basic site available precedes the displacement process. The fact that exclusive formation of specific dialkylhalonium ions is observed in mixtures of the alkyl halides is adequately rationalized by postulating that dialkylhalonium ion formation occurs by means of this nucleophilic displacement reaction.

For example, as noted above in a mixture of methyl chloride and ethyl fluoride, the methyl ethylfluoronium ion is not observed. Instead the methyl ethylchloronium ion is formed exclusively. This result is consistent with the formation of an intermediate complex in which the labile proton is always transferred to the more basic site (ethyl fluoride) prior to the formation of the product dialkylhalonium ion (reaction 61). It is reasonable that proton transfer reactions which involve a minimum of molecular rearrangement will, if thermodynamically feasible, be kinetically favored over more complicated reaction processes such as nucleophilic displacement.

Similar results have been obtained with methyl chloride, ethyl chloride, mixtures of the two chlorides, methyl bromide, and ethyl bromide.[30] Double resonance experiments which identify the origin of the Cl or Br atom retained in the product dialkylhalonium ions[19] indicate that proton transfer where thermodynamically feasible precedes halonium ion formation. Again the nucleophilic displacement mechanism is indicated.

A slightly more complicated situation occurs in a mixture of methyl fluoride and methyl chloride-d_3. Since the proton affinity of methyl chloride is greater than that of methyl fluoride the nucleophilic displacement reaction should lead to the exclusive formation of the cross-product halonium ion $\mathrm{CH_3FCD_3^+}$. However, $\mathrm{CH_3ClCD_3^+}$ is the only cross-product halonium ion observed (reaction 63). The reason that the expected cross-product ion $\mathrm{CH_3FCD_3^+}$ does not appear can be attributed to reaction 71 being endothermic. Reaction 71

$$\mathrm{CH_3F + CD_3ClH^+ \not\longrightarrow CD_3FCH_3^+ + HCl} \qquad (71)$$

does not proceed even with the additional internal energy available from proton transfer [in reaction 72, ~9 kcal/mol = $\mathrm{PA(CH_3Cl) - PA(CH_3F)}$]. Instead the competing proton transfer reaction 73 is observed.

$$\mathrm{CH_3FH^+ + CD_3Cl} \begin{cases} \not\longrightarrow \mathrm{CH_3FCD_3^+ + HCl} & (72) \\ \longrightarrow \mathrm{CD_3ClH^+ + CH_3F} & (73) \end{cases}$$

To summarize, the results indicating the exclusive formation of specific cross-product halonium ions in halide mixtures, as well as double-resonance results indicating the origin of halogen atoms in halonium ions containing chlorine and bromine, indicate that proton transfer between the reactant ion and neutral molecule precedes hydrogen halide elimination in forming the dialkylhalonium ion. These results are consistent with a postulated nucleophilic displacement mechanism[34] in which the formation of a proton-bound four-center intermediate precedes nucleophilic attack leading to the dialkylhalonium ion.

Thermochemistry. The relative nucleophilicity of molecules undergoing the general displacement reaction 74 has been quantified.[34] A useful thermochemical

$$\mathrm{N + CH_3MH^+ \longrightarrow CH_3N^+ + MH} \qquad (74)$$

quantity to employ in the description of these reactions is the methyl cation affinity (MCA) defined as the negative of the enthalpy change for attaching a methyl cation to a neutral molecule M as depicted in reaction 75. Es-

$$\mathrm{M + CH_3^+ \longrightarrow MCH_3^+} \qquad (75)$$

timates for the methyl cation affinities of the methyl and hydrogen halides as well as the halide radicals are presented in Table V. The observation of reaction 69 for all of the methyl halides indicates that for a given X, $\mathrm{MCA(CH_3X) \geq MCA(HX)}$. The occurrence of reaction 69 and nonoccurrence of reaction 64 for methyl fluoride brackets the methyl cation affinity of methyl fluoride as $\mathrm{MCA(CH_3F)} = 44 \pm 8$ kcal/mol. Upper limits for $\mathrm{MCA(CH_3X)}$ were not obtained for the other methyl halides.

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(32) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970, Chapter 8.

(33) The ensuing description of the thermochemistry associated with this reaction is correct irrespective of whether the actual reaction mechanism involves hydrogen abstraction or proton transfer.

(34) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, **92**, 7484 (1970).

Table V. Methyl Cation Affinities of Various Halide Species[a]

Species	MCA,[b] kcal/mol				Process
	F	Cl	Br	I	
X·	47	50	53	63	$CH_3X\cdot^+ \rightarrow CH_3^+ + X\cdot$
HX	36	51	56	67	$CH_3XH^+ \rightarrow CH_3^+ + HX$
CH_3X	44	≥ 51	≥ 56	≥ 67	$CH_3XCH_3^+ \rightarrow CH_3^+ + CH_3X$

[a] Thermochemical estimates for the halide radicals are from footnote *e*, Table III, for the hydrogen halides from Holtz, Beauchamp, and Woodgate, ref 34, and for the methylhalides from the occurrence of reaction 69. [b] Methyl cation affinity—defined in text.

The methyl cation affinity has thermochemical interest for the general theory of acids and bases beyond simply predicting the order of nucleophilic displacements. Pearson[35] has recently espoused an empirical theory of hard and soft acids and bases (HSAB) which, at least qualitatively, serves to rationalize large areas of chemical reactivity. The methyl cation affinity is a quantitative measure of the basicity of a given neutral M toward the soft acid CH_3^+, the proton affinity is a quantitative measure of the basicity of a given neutral M toward the soft acid CH_3^+, and the proton affinity is a quantitative measure of the basicity of a given neutral M toward the hard acid H^+. A quantitative measure of the difference in the behavior of the soft acid CH_3^+ from that of the hard acid H^+ is simply the difference in the methyl cation and proton affinities of M. Table VI lists several examples of neutrals whose relative basicities invert when the standard acid is changed from CH_3^+ to H^+. Although only lower limits are available for MCA(CH_3X) for X = Cl, Br, and I, it appears that the methyl halides have the same relative basicities I > Br > Cl > F toward the soft acid CH_3^+ (Table IV) as toward the hard acid H^+ (Table IV).

Table VI. Examples of Reversals in Relative Basicities toward Hard and Soft Acids[a]

Species	CO	> HI	> H_2O	> HCl	> CH_3F	> N_2	> HF
MCA[b]	82	67	66	51	44	42	36
Species	H_2O	> CH_3F	> HI	> CO	> HCl	> HF	> N_2
PA[c]	165	151	145	142	141	137	116

[a] All values are in kilocalories per mole and unless indicated otherwise are taken from Holtz, Beauchamp, and Woodgate, ref 34, and Tables III–V. [b] Methyl cation affinity—defined in text. [c] Proton affinity—defined in text.

Reactions of Methyl- and Ethylcarbonium Ions. The reactions of methyl- and ethylcarbonium ions with the alkyl halides are particularly interesting in that dialkylhalonium ions are postulated reaction intermediates which serve to rationalize many of the isotopic labeling experiments discussed above. Studies with isotopically labeled methyl cations (reactions 8 and 25) indicate that the methyl cation does not react by simple hydride abstraction with the neutral halide to yield methane and the halogen-substituted methyl cation. Rather, as generalized in reaction 76, a transient dimethylhalonium ion is formed which subsequently undergoes unimolecular decomposition to yield the observed products. A similar study with isotopically labeled ethyl cation (reaction 38) indicates that the reaction of this ion to form protonated alkyl halide proceeds in part by means of a dialkylhalonium ion (reaction 77). Clearly the dialkylhalonium ion is a keystone to understanding much of the ion–molecule chemistry of the alkyl halides.

$$CH_3^+ + CH_3X \longrightarrow [CH_3XCH_3^+] \longrightarrow CH_2X^+ + CH_4 \quad (76)$$

$$C_2H_5^+ + RX \longrightarrow [C_2H_5XR^+] \longrightarrow RXH^+ + C_2H_4 \quad (77)$$

The reaction of ethyl cation with ethyl fluoride results principally in the generation of the condensation product $C_4H_9^+$ (reaction 14). If, as suggested by the product distribution from reaction 18, this process involves a diethylhalonium ion intermediate, extensive rearrangement must occur if HF elimination is to result. The reactions of the methyl- and ethylcarbonium ions and their substituted analogs (reaction 62) with various other functional groups remains to be investigated in greater detail. The availability of reliable thermochemical data with which to analyze these processes would be of great value.

Reaction Rates. There are two basic treatments which may be considered for the calculation of ion–molecule rates. The Langevin or Gioumousis and Stevenson model[36,37] is based on a long-range ion-induced dipole polarization interaction which gives

$$k_L = 2\pi e(\alpha/\mu)^{1/2} \quad (78)$$

where e is the electronic charge, α is the angle-averaged polarizability of the neutral collision partner, and μ is the reduced mass of the collision pair. Experimental reaction rates for systems involving nonpolar neutral reactants are generally in good agreement with the predictions of eq 78.[38,39] The presence of a permanent dipole moment in the neutral reactant, however, frequently leads to reaction rates larger than predicted by eq 78. Several investigators have attempted to account for these effects by assuming that the permanent dipole in the neutral species locks to the orientational potential energy minimum. The rate constant for this thermally locked dipole model[40,41] is given by eq 79

$$k_{LD} = k_L + 2\pi e\mu_0(2/\mu\pi kT)^{1/2} \quad (79)$$

where μ_0 is the permanent dipole moment of the neutral, k is Boltzman's constant, and T is the temperature. Unlike the ion-induced dipole model, the locked dipole model predicts a temperature-dependent rate constant, or equivalently a rate that varies with ion velocity. It is well recognized that the rate constant predicted by eq 79 should be considered only as an upper limit to the true rate constant.[7,41,42]

Experimentally determined rate constants for some of the reaction processes of the methyl and ethyl halides along with k_L and k_{LD} for comparison are presented in Table I. It is apparent that the locked dipole model inaccurately represents the experimental results; the ion-induced dipole model seems to be a much better first approximation. The derivations of eq 78 and 79 assume that all collisions will be reactive. Clearly, this is not necessarily the case, a simple proton transfer or hy-

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(39) J. H. Futrell and T. O. Tiernan in "Fundamental Processes of Radiation Chemistry," P. Ausloos, Ed., Wiley, New York, N. Y., 1968.

(40) T. F. Moran and W. H. Hamill, *J. Chem. Phys.*, **39**, 1413 (1963).

(41) See Gupta, *et al.*, Table I, footnote *f*.

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drogen atom abstraction reaction being likely to occur with higher probability than a condensation reaction, where more intimate contact between ion and neutral is required. This may in part explain the rather low rate constants noted in Table I for several of the condensation processes.

The total reactivities of the methyl and ethyl halide parent ions, RX^+, and the corresponding protonated parent ions, RXH^+, are presented in Table II. There is a definite trend toward decreasing reactivity proceeding from fluorides to iodides, with rate constants varying over a range involving nearly three orders of magnitude. This difference may in part be attributed to the increasing charge localization on halogen to be expected in proceeding from fluorine to iodine. In methyl cation transfer processes, for example, increased initial charge density on the methyl group in the reactant ion will lower the energy of the intermediate through which the methyl cation is formally transferred from one center to another, thus facilitating the reaction.

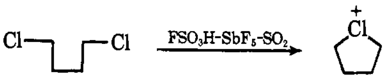
Comparison to Solution Chemistry. Although diphenyliodonium sulfate was isolated over 75 years ago[43] and halonium ions are frequently postulated as reaction intermediates,[44,45] it is only recently that investigations of Friedel–Crafts chemistry in solvents of low nucleophilicity have provded synthetic pathways to dialkylhalonium ions.[44–47] Methyl fluoride, for instance, forms a complex with antimony pentafluoride in SO_2 solution in accordance with reaction 80. This complex

$$CH_3F + SbF_5 \longrightarrow CH_3^+SbF_6^- \qquad (80)$$

reacts rapidly with other halides, RX, to generate a variety of dialkylhalonium ions (reaction 81). Dialkylhalonium ions generated by these and related reactions have been isolated and characterized as hexafluoroantimonate salts.[48] These salts have found synthetic utility as reagents for alkylation of heteroorganic compounds.[49] Studies of such reactions suggest that the alkylating ability of halonium ions decreases in the order Cl > Br > I.[48,49] This is in full accord with the observed gas-phase basicities of the alkyl halides toward both protons and methyl cations which decreases in the order I > Br > Cl > F. Olah and DeMember suggest that, due to the high electronegativity of fluorine, alkyl fluorides are not alkylated on the fluorine atom, with carbon alkylation occurring instead.[46] In contrast, alkylation on the halogen is a dominant feature of the gas-phase ion chemistry of all the alkyl halides, including fluorides.

$$RX + CH_3^+SbF_6^- \longrightarrow RXCH_3^+ + SbF_6^- \qquad (81)$$

Internal condensation reactions occur in solution which are similar in many respects to the bimolecular reactions forming halonium ions in the gas phase. For example, in strong acid solution, 1,4-dichlorobutane is converted to the tetramethylene chloronium ion (reaction 82).[45] The tetramethylenechloronium ion is subject to nucleophilic attack on the α carbon with resultant ring opening. Although not a concern of the present study, it should be straightforward to study these processes in the gas phase as well. Cyclic halonium ions can be generated either in processes analogous to the solution reactions or directly in mass spectral fragmentations.[50]



(82)

Conclusion

The gas-phase ion chemistry of the alkyl halides is entirely systematic. The correlation with solution chemistry in solvents of low nucleophilicity is interesting to note, particularly the observation of the same relative ordering of basicities.

The thermochemical properties of the alkyl halides, including both proton and methyl cation affinities, are important in predicting the course of reactions in both pure compounds and binary mixtures. Using the rules governing nucleophilic displacement reactions it is possible to use derived thermochemical data to predict a wide variety of reactions resulting in the formation of dialkylhalonium ions. The same rules apply as well to mixtures of alkyl halides with other *n*-donor bases.

The utility of ion cyclotron resonance spectroscopy for these studies is evident. The ability to follow the chemistry through several stages of reaction is an important feature of icr experiments. Reaction rate constants for sequential processes are derived without difficulty from single-resonance intensity data. Double-resonance experiments identify reactions, determine product distributions, and provide valuable information relating to reaction mechanisms, complementing information derived from isotopic labeling studies. The outlook is bright for the continued application of this new spectroscopy to the investigation of the chemistry of organic ions in the gas phase.

Acknowledgment. This work was supported in part by the United States Atomic Energy Commission under Grant No. AT(04-3) 767-8 awarded to J. L. Beauchamp (California Institute of Technology) and by the National Science Foundation under Grant No. NSF-GP-4924-X and the National Aeronautics and Space Administration under Grant No. NGL-02-020-S1 awarded to John D. Baldeschwieler (Stanford University), and by the Center for Materials Research (Stanford University).

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