Reactions of CHF_2^+ with n-Donor Bases by Ion Cyclotron Resonance Spectroscopy. The Proton Affinity of Difluorocarbene

Jürgen Vogt[1] and J. L. Beauchamp*[2]

Contribution No. 5073 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received March 10, 1975*

Abstract: The gas-phase ion-molecule reactions of CHF_2^+ with n-donor bases have been investigated using the techniques of ion cyclotron resonance spectroscopy. CHF_2^+ reacts only by proton transfer with CH_3CN, CH_3CHO, CH_3OH, AsH_3, and CH_2O. While CHF_2^+ with excess translational and internal energy undergoes proton transfer to HCN, ground state CHF_2^+ does not react. CHF_2^+ is also unreactive with H_2O. Rate constants for ion-molecule reactions in the pure systems and for the proton transfer reactions are reported. The proton affinity of difluorocarbene is determined to be 172 ± 2 kcal/mol, which is 7 kcal/mol lower than calculated from previously reported thermodynamic data. The possible use of CHF_2^+ as a reagent ion for chemical ionization is discussed, and some reservations are noted.

The ion-molecule reactions of fluoromethyl cations are of particular interest, for they are the simplest substituted carbonium ions and fluorine is unique in its ability as a substituent to modify molecular properties and reactivity. It is possible to generate CH_2F^+, CHF_2^+, and CF_3^+ under conditions such that they do not react with their precursors. The reaction of CH_3^+ with CH_4 is rapid and to our knowledge CH_3^+ reacts with all neutrals from which it can be derived as a fragment ion. In contrast, the ions CH_2F^+ from CH_3F or CH_2F_2,[3a] CHF_2^+ from CHF_3, and CF_3^+ from CF_4 derived either by electron impact or ion-molecule reaction sequences do not react with the respective fluoromethane neutrals.[3b]

While the gas-phase ion chemistry of the fluoromethanes themselves has been the subject of several investigations,[3b,4] the reactions of fluoromethyl cations with organic molecules have not been examined in detail.[5] A point of considerable interest is the possible use of these species as reagent ions in chemical ionization studies, which in the case of CF_3^+ has already been explored by Munson.[6]

We wish to report the ion-molecule reactions of the difluoromethyl cation with the n-donor bases CH_3CN, CH_3CHO, CH_3OH, AsH_3, CH_2O, HCN, and H_2O. Being considered as protonated difluorocarbene, the reactions of CHF_2^+ provide interesting insight into the molecular properties of difluorocarbene, CF_2.

Experimental Section

The theory, techniques, and instrumentation of ICR spectroscopy have been previously described in detail.[7-9] The instrument used was built in these laboratories, incorporating a 15-in. magnet and specially designed circuitry for performing trapped-ion experiments as described by McMahon and Beauchamp.[9]

Experiments reported herein were generally performed in the pressure range 10^{-7}–10^{-5} Torr. To measure absolute pressures, a Schulz-Phelps[10] gauge installed adjacent to the ICR cell in the magnetic field is calibrated for a given emission current and magnetic field (usually 5 μA and 6 kG, respectively) against an MKS Instrument Baratron Model 90 Hl-E capacitance manometer. A linear variation of ion gauge current with pressure is observed over three decades (10^{-6}–10^{-3} Torr). The major error in rate constants of ±10% arises from uncertainties in absolute pressure determination. Gas mixtures were prepared directly in the instrument using two sample inlets and the calibrated Schulz-Phelps gauge. Except as noted in the reported experiments, the primary ions were generated with a 25 eV electron beam pulse of 10 msec duration.

All chemicals were obtained from commercial sources and used as supplied except for removal of non-condensable gases using freeze-pump-thaw cycles. No impurities were detected by mass spectrometric analysis of samples prior to use.

Results

Fluoroform ionized by electron impact provides a convenient source of CHF_2^+ ions. The most abundant primary ions are CF_3^+ and CHF_2^+, the former being converted to the latter by the fluoride transfer reaction 1. The difluoromethyl cation is unreactive toward CHF_3. The rate con-

$$CF_3^+ + CHF_3 \longrightarrow CHF_2^+ + CF_4 \tag{1}$$

stant for reaction 1 is determined to be 5.5 × 10^{-10} cm^3 $molecule^{-1}$ sec^{-1} in pure CHF_3 and in mixtures of CHF_3 with gases toward which CF_3^+ is unreactive. This value is in agreement with 5.9 × 10^{-10} cm^3 $molecule^{-1}$ sec^{-1} reported by McAskill[4d] and 5.3 × 10^{-10} cm^3 $molecule^{-1}$ sec^{-1} as measured by Miasek,[11] but significantly higher than the value 2.1 × 10^{-10} cm^3 $molecule^{-1}$ sec^{-1} reported in earlier studies from our laboratory.[3b] The origin of this discrepancy has not been ascertained.

Acetonitrile, acetaldehyde, methanol, arsine, formaldehyde, hydrogen cyanide, and water were chosen as neutral molecules, covering a range of base strengths and expected reactivity. Total rate constants determined in this work for the principal ions formed in the pure systems are listed in Table I and compared with previously reported data. The results for the individual systems are discussed in order of decreasing base strength of the n-donor bases.

CH_3CN. The principal primary ions from acetonitrile at 25 eV electron energy include CH_3CN^+ (42%), CH_2CN^+ (34%), and $CHCN^+$ (24%). Observed processes include reaction 2 yielding the protonated parent ion and the condensation reaction 3 which have been previously discussed in detail.[12]

$$CH_3CN^+ + CH_3CN \longrightarrow CH_3CNH^+ + CH_2CN \tag{2}$$

$$CH_2CN^+ + CH_3CN \longrightarrow C_3H_4N^+ + HCN \tag{3}$$

CH_3CN-CHF_3. In addition to the expected ion-molecule reactions of the components the proton transfer reaction 4 is observed in a mixture of acetonitrile and fluoroform. Double resonance experiments confirm that only reaction 4 accounts for the disappearance of CHF_2^+ ions in this mixture.

$$CHF_2^+ + CH_3CN \longrightarrow CH_3CNH^+ + CF_2 \tag{4}$$

CH_3CHO. In acetaldehyde at 25 eV electron energy, the abundant primary ions include CH_3CHO^+ (40%), CH_3CO^+ (28%), and CHO^+ (32%). While CH_3CO^+ is unreactive with the parent neutral, both CH_3CHO^+ and CHO^+ react to form CH_3CHOH^+.

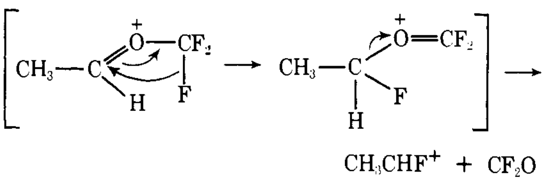
Table I. Total Rate Constants for the Reaction of Parent and Some Fragment Ions in the Pure Reactant Gases

Neutral	Ion	Total rate constant^{a} This work^{b}	Total rate constant^{a} Literature
HCN	HCN^+	21.2	6.0^{c}
			35^{d}
			12^{e}
CH_2O	CH_2O^+	17.7	19.3^{f,g}
	CHO^+	16.3	20.0^{g,h}
			17.9^{f,g}
			20.6^{g,h}
CH_3OH	$CH_3OH_2{}^+$	0.8	1.5^{i}
	CH_3OH^+	18.6	25.3^{j}
			20.0^{k}
			24.5^{l}
	CH_2OH^+	18.0	21.1^{j}
	CHO^+	16.1	19.0^{j,f}
CH_3CHO	CH_3CHO^+	19.9	19.1^{g}
			24.9^{m}
	CHO^+	19.9	25.3^{m}
CH_3CN	CH_3CN^+	20.9	19.6^{j}
			22.7^{f,j}
			35.0^{d}
	CH_2CN^+	9.7	
	$CHCN^+$	35.4	

[a] Rate constants in 10^{-10} cm^3 molecule^{-1} sec^{-1}. [b] Measured at 25 eV electron energy. Rate constants are from limiting slopes of trapped-ion decay curves, and are appropriate for thermal ion energies. [c] High-pressure MS: A. G. Harrison and J. C. J. Thynne, *Can. J. Chem.*, 45, 1321 (1967). This value is most probably too low as was stated later in footnote *j*. [d] High-pressure MS: T. W. Martin and C. E. Melton, *J. Chem. Phys.*, 32, 700 (1960). [e] M. Inoué and M. Cottin, *Adv. Mass Spectrom.*, 3, 339 (1966). [f] At 3.4 eV ion energy. [g] H. Pritchard and A. G. Harrison, *J. Chem. Phys.*, 48, 5623 (1968). [h] At 2.4 eV ion energy. [i] T. B. McMahon, Ph.D. Thesis, California Institute of Technology, 1973. [j] High-pressure MS: S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, 45, 3107 (1967). [k] D. J. Hyatt, E. A. Dodman, and M. J. Henchman, *Adv. Chem. Ser.*, 58, 131 (1966). [l] K. R. Ryan, L. Sieck, and J. H. Futrell, *J. Chem. Phys.*, 41, 111 (1964). [m] A. S. Blair and A. G. Harrison, *Can. J. Chem.*, 51, 703 (1973).

CH_3CHO–CHF_3. In addition to the ion–molecule reactions observed in acetaldehyde and fluoroform alone, several additional reactions occur in the mixture. Besides reacting with CHF_3 to form $CHF_2{}^+$, $CF_3{}^+$ also reacts with CH_3CHO in accordance with reaction 5. This reaction,

$$CF_3{}^+ + CH_3CHO \longrightarrow$$



$$CH_3CHF^+ + CF_2O \quad (5)$$

leading to the formation of CH_3CHF^+, is analogous to the reaction of $CF_3{}^+$ with various organic compounds containing a carbonyl functional group as reported by Eyler et al.[13] The product $C_2H_4F^+$ can be regarded as protonated vinyl fluoride, which has a proton affinity of 173 kcal/mol.[14] It is thus not surprising that $C_2H_4F^+$ undergoes the exothermic proton transfer reaction 6 with CH_3CHO. In contrast to

$$CH_3CHF^+ + CH_3CHO \longrightarrow CH_3CHOH^+ + C_2H_3F \quad (6)$$

$CF_3{}^+$, the $CHF_2{}^+$ ions react with CH_3CHO only in the proton transfer process 7. The proposed reaction scheme ac-

$$CHF_2{}^+ + CH_3CHO \longrightarrow CH_3CHOH^+ + CF_2 \quad (7)$$

counts for the variation of ion abundance with time as illustrated in Figure 1. It is of interest that a process analogous to reaction 5, in which CHFO is the neutral product, does not occur with $CHF_2{}^+$. It is estimated that such a process would be exothermic by 28 kcal/mol.[15]

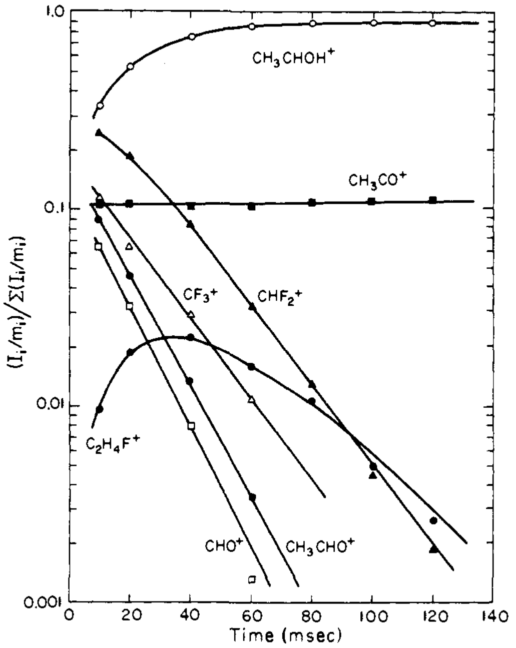


Figure 1. Variation of ion abundance with time for a 1:3.1 mixture of CH_3CHO and CHF_3 at 25 eV and a total pressure of 3.4×10^{-6} Torr.

CH_3OH. The ion–molecule chemistry of methanol is straightforward, the three primary ions CH_3OH^+ (28%), CH_2OH^+ (55%), and CHO^+ (17%) reacting to yield protonated methanol, $CH_3OH_2{}^+$, which in turn reacts slowly with methanol to form protonated dimethyl ether (reaction 8). For this process the rate constant was determined to be 0.8×10^{-10} cm^3 molecule^{-1} sec^{-1}.

$$CH_3OH_2{}^+ + CH_3OH \longrightarrow (CH_3)_2OH^+ + H_2O \quad (8)$$

CH_3OH–CHF_3. Again, in addition to the expected reactions of the two components, the proton transfer reaction 9

$$CHF_2{}^+ + CH_3OH \longrightarrow CH_3OH_2{}^+ + CF_2 \quad (9)$$

from $CHF_2{}^+$ to neutral methanol is observed in a mixture of methanol and fluoroform.

CH_2O. Both primary ions CH_2O^+ (66%) and CHO^+ (34%) formed by 25 eV electron impact in formaldehyde react with the neutral CH_2O to yield CH_2OH^+.

CH_2O–CHF_3. The only additional reaction observed in a mixture of formaldehyde and fluoroform is the proton transfer reaction 10. It is evident from the variation of ion

$$CHF_2{}^+ + CH_2O \longrightarrow CH_2OH^+ + CF_2 \quad (10)$$

abundance with time (Figure 2) that this reaction is much slower than the proton transfer process involving more basic neutrals (Table II). A process analogous to reaction 5 involving $CF_3{}^+$ and CH_2O was not observed, although the reaction is calculated to be exothermic by 24 kcal/mol.[15]

HCN. At 25 eV electron energy only HCN^+ is formed in abundance from hydrogen cyanide. This ion reacts rapidly with the neutral to form protonated hydrogen cyanide.

HCN–CHF_3. The data in Figure 3 illustrate the variation of ion abundance with time in a mixture of fluoroform and hydrogen cyanide. Both $CHF_2{}^+$ and $HCNH^+$ persist as abundant ions at long times. Also shown in Figure 3 is the observed decrease in the abundance of $HCNH^+$ when $CHF_2{}^+$ is continuously ejected during the trapped ion experiment. These results indicate that the proton transfer reaction 11 occurs only for a fraction (15%) of the initially

$$CHF_2{}^+ + HCN \longrightarrow HCNH^+ + CF_2 \quad (11)$$

formed $CHF_2{}^+$ ions. Since structural isomerization does not seem likely, the only reasonable suggestion to offer for these

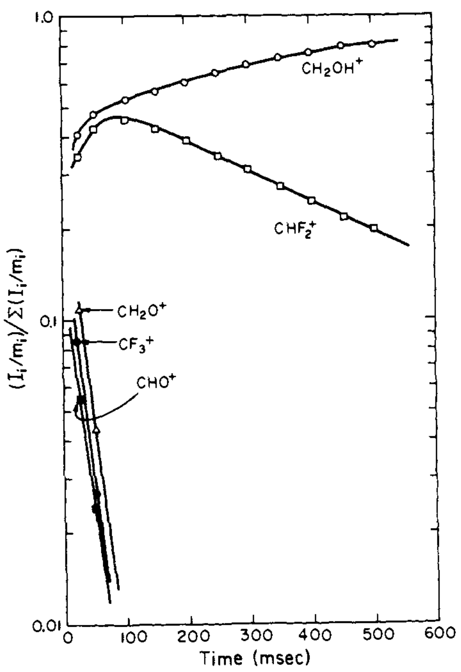


Figure 2. Variation of ion abundance with time for a 1:1.9 mixture of CH_2O and CHF_3 at 25 eV and a total pressure of 2.9×10^{-6} Torr.

Table II. Rates of Proton Transfer from CHF_2^+ to *n*-Donor Bases

Base	k^a	PA^b
CH_3CN	14.6	189^d
CH_3CHO	16.6	187^c
CH_3OH	10.4	184^d
AsH_3	2.2	175^e
CH_2O	0.73	172^c
HCN	$\leq 0.01^f$	171.6^d
H_2O	≤ 0.01	167.5^d

[a] Rate constants in 10^{-10} cm^3 molecule^{-1} sec^{-1}. [b] Proton affinities in kcal/mol. [c] Recent photoionization studies of aliphatic alcohols in our laboratory yield $\Delta H_f(CH_2OH^+) = 167 \pm 1$ kcal/mol and $\Delta H_f(CH_3CHOH^+) = 139 \pm 1$ kcal/mol, corresponding to PA(CH_2O) = 172 ± 1 kcal/mol and PA(CH_3CHO) = 187 ± 1 kcal/mol. These results do not differ significantly from those reported by K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, 48, 5205 (1968). [d] PA(CH_3CN) and PA(CH_3OH) are relative to PA(CH_3CHO) = 187 kcal/mol; PA(HCN) and PA(H_2O) are relative to PA(CH_2O) = 172 kcal/mol (R. H. Staley and J. L. Beauchamp, unpublished studies of proton transfer equilibria). [e] R. H. Wyatt, D. Holtz, T. B. McMahon, and J. L. Beauchamp, *Inorg. Chem.*, 13, 1511 (1974). [f] Proton transfer from vibrationally excited CHF_2^+ to HCN was observed (see text).

observations is that reaction 11 is endothermic and occurs only for CHF_2^+ possessing excess internal and/or translational excitation.

H_2O-CHF_3 and AsH_3-CHF_3. Due to difficulties associated with handling water, the ion-molecule reactions in a mixture of water with fluoroform were only investigated in a qualitative manner. Double resonance experiments indicated that the proton transfer reaction 12 does not occur,

$$CHF_2^+ + H_2O \not\rightarrow H_3O^+ + CF_2 \qquad (12)$$

and no competing processes were observed which would have obscured this reaction.

To further bracket the proton affinity of CF_2, the reactions occurring in a mixture of arsine and fluoroform were studied. The proton transfer reaction 13 occurs fairly rapidly,

$$CHF_2^+ + AsH_3 \longrightarrow AsH_4^+ + CF_2 \qquad (13)$$

accounting for the disappearance of CHF_2^+ in the mixture. Other reactions in this mixture were not examined in detail, owing to the complexity of the reaction scheme involving AsH_3.[16]

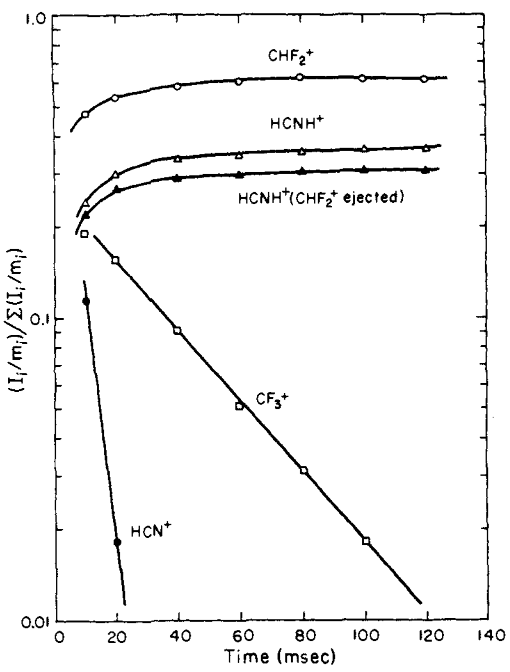


Figure 3. Variation of ion abundance with time for a 1:1.6 mixture of HCN and CHF_3 at 25 eV and a total pressure of 3.5×10^{-6} Torr. Also shown is the decrease in $HCNH^+$ abundance when CHF_2^+ is continuously ejected (see text for discussion).

Discussion

The only observed reaction of CHF_2^+ with the *n*-donor bases considered in this investigation involves proton transfer to species more basic than formaldehyde. With formaldehyde the proton transfer is slow, suggesting that this process is very nearly thermoneutral. From these results, the proton affinity of difluorocarbene is taken to be 172 ± 2 kcal/mol, approximately equal to formaldehyde, higher than HCN (171.6 kcal/mol), and lower than AsH_3 (175 kcal/mol). The measured proton affinity of CF_2 is significantly less than that calculated[15] for CHF (195.4 kcal/mol) and CH_2 (196.9 kcal/mol). This is generally consistent with the fact that CF_2 is considered to be the most stable of the three carbenes.

Thus, the difluoromethyl cation or, more appropriately, protonated difluorocarbene is observed to be a reasonably good Brönsted acid (proton donor) rather than reacting as a Lewis acid (electron acceptor). The latter behavior is appropriate for describing the reactions of CF_3^+ with aldehydes and ketones[13] (e.g., reaction 5). This behavior can be explained in part by considering the calculated net charges on the carbon atom in the different fluoromethyl cations. The higher positive charge on the C atom in CF_3^+ makes it a better electrophile compared to CHF_2^+ (Table III). The calculated charge distributions in the fluoromethyl cations suggest CH_2F^+ to be even less electrophilic than CHF_2^+.

The observed reactivity of CHF_2^+ indicates possible applications as a reagent ion for chemical ionization studies. The proton affinity of CF_2 is only slightly higher than H_2O. In certain applications CHF_2^+ might be preferred to H_3O^+, for the latter tends to form clusters with the molecules under study and its precursor, H_2O. Preliminary experiments[5] dealing with the reaction of CHF_2^+ with π-donor bases in part limit this perspective. In these experiments it is observed that CHF_2^+ reacts with ethylene or benzene primarily by addition followed by elimination of HF. Conse-

Table III. Calculated Charge Distribution in Fluoro-Substituted Methyl Cations

Charge on atom	CH_2F^+ *a*	CH_2F^+ *b*	CHF_2^+ *a*	CHF_2^+ *b*	CF_3^+ *a*	CF_3^+ *b*
C	+0.346	+0.659	+0.516	+0.862		+1.095
H	+0.254	+0.141	+0.272	+0.146		
F	+0.146	+0.059	+0.106	−0.004		−0.028

[a] STO-3G-minimal basis set ab initio calculation: N. C. Baird and R. K. Datta, *Can. J. Chem.*, 49, 3708 (1971). [b] INDO calculation: L. D. Kispert et al., *J. Am. Chem. Soc.*, 94, 5979 (1972).

Table IV. The Heat of Formation of CF_2[a]

ΔH_f, kcal/mol	Method	Ref
−44.5 ± 0.4	Equilibrium $CF_2{=}CF_2 \rightleftharpoons 2CF_2$	*b*
−46.4 ± 2.0	Equilibrium $CHF_2Br \rightleftharpoons CF_2 + HBr$	*c*
−41.6 ± 1.8	Photoionization threshold $CF_2{=}CF_2 \rightarrow CF_2^+ + CF_2$	*d*
	and IP(CF_2) = 11.42 eV	*e*
−43.2 ± 3.0	Photoionization threshold $C_6H_5CF_3 \rightarrow C_6H_5F^+ + CF_2$	*f*

[a] Older values ranging from −6.3 to −50 kcal/mol are discussed by J. Heicklen, *Adv. Photochem.*, 7, (1969). [b] G. A. Carlson, *J. Phys. Chem.*, 75, 1625 (1971). [c] E. N. Okafo and E. Whittle, *J. Chem. Soc., Faraday Trans 1*, 70, 1366 (1974). [d] T. A. Walter, C. Lifshitz, W. A. Chupka, and J. Berkowitz, *J. Chem. Phys.*, 51, 3531 (1969). [e] J. M. Dyke, L. Golob, N. Jonathan, A. Morris, and M. Okuda, *J. Chem, Soc., Faraday Trans. 2*, 11, 1828 (1974). [f] B. S. Freiser and J. L. Beauchamp, unpublished photoionization studies.

quently the assumption that an observed peak represents a protonated species would be unwarranted in the analysis of an unknown sample.

The value of 172 kcal/mol determined in this work for the proton affinity of difluorocarbene has some interesting thermochemical implications. The heat of formation of CF_2, a subject of considerable controversy, has recently been determined by Carlson[17] from the dissociation of tetrafluoroethylene to be ΔH_f (CF_2) = −44.5 ± 0.4 kcal/mol, which is in good agreement with data obtained by independent methods (Table IV). Combining this value with the determined proton affinity of CF_2 gives ΔH_f (CHF_2^+) = 149.2 kcal/mol which is inconsistent with the previously accepted value of 142.4 kcal/mol.[3b] Alternatively, assuming the previous value for ΔH_f (CHF_2^+), the heat of formation of CF_2 is calculated to be −51.3 kcal/mol, which in turn differs by about 7 kcal/mol from newer experimental data (Table IV). It is our suspicion that the discrepancy is in the heat of formation of CHF_2^+ and results from uncertainties in the heats of formation of several fluorinated methanes, on which the calculations are based. For example, the heat of formation of methyl fluoride has never been measured and the "accepted" value is an estimate.[18]

Acknowledgment. This work was supported in part by the Energy Research and Development Administration under Grant No. AT(04-3)767-8. The instrument used in these studies was funded by the National Science Foundation under Grant No. NSF-GP-18383. One of us (J.V.) thanks the Kanton Basel-Stadt, Switzerland, for a paid leave of absence.

References and Notes

(1) Postdoctoral Fellow 1974–1975, on leave from Physikalisch Chemisches Institut der Universität Basel, Switzerland.
(2) Camille and Henry Dreyfus Teacher–Scholar 1971–1976.
(3) (a) CH_2F^+ reacts very slowly with CH_2F_2 to form CHF_2^+ and CH_3F; for details see ref 3b; (b) R. J. Blint, T. B. MaMahon, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 1269 (1974).
(4) (a) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Am. Chem. Soc.*, **94**, 2798 (1972); (b) A. G. Marshall and S. G. Buttrill, Jr., *J. Chem. Phys.*, **52**, 2752 (1970); (c) A. A. Herod, A. G. Harrison, and N. A. McAskill, *Can. J. Chem.*, **49**, 2217 (1971); (d) N. A. McAskill, *Aust. J. Chem.*, **23**, 2301 (1970).
(5) R. J. Blint, Ph.D. Thesis, California Institute of Technology, 1972.
(6) N. Einolf and B. Munson, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 141 (1972).
(7) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).
(8) J. M. S. Henis, "Ion Molecule Reactions", Vol. II, J. L. Franklin, Ed., Plenum Press, New York, N.Y., 1972.
(9) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).
(10) G. J. Schulz and A. V. Phelps, *Rev. Sci. Instrum.*, **28**, 1051 (1957).
(11) P. G. Miasek, Ph.D. Thesis, California Institute of Technology, 1973.
(12) G. A. Gray, *J. Am. Chem. Soc.*, **90**, 2177 (1968); *ibid.*, **90**, 6002 (1968).
(13) J. R. Eyler, P. Ausloos, and S. G. Lias, *J. Am. Chem. Soc.*, **96**, 3673 (1974).
(14) A. D. Williamson and J. L. Beauchamp, unpublished photoionization studies.
(15) Thermodynamic data used were taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 26** (1969); JANAF Thermochemical Tables, *ibid.*, **No. 37** (1971), and from ref 3b.
(16) R. H. Wyatt, D. Holtz, T. B. McMahon, and J. L. Beauchamp, *Inorg. Chem.*, **13**, 1511 (1974).
(17) G. A. Carlson, *J. Phys. Chem.*, 7**5**, 1625 (1971).
(18) A. S. Rodgers, J. Chao, R. C. Wilhoit, and B. J. Zwolinski, *J. Phys. Chem. Ref. Data*, **3**, 117 (1974).

Tetrahedral Intermediates in Gas Phase Ionic Displacement Reactions at Carbonyl Carbon

Olabode I. Asubiojo, Larry K. Blair, and John I. Brauman*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received February 6, 1975*

Abstract: Making use of ion cyclotron resonance spectroscopy, we have identified adducts of negative halide ions and acyl halides ($RCOX_2^-$). Using double resonance, we have established that the adducts have structurally equivalent halides, indicating a tetrahedral structure.

Nucleophilic displacements at the carbonyl carbon have long been an area of active investigation.[1] Among other reasons, interest in this area arises from its relevance to the action of enzymes in catalysis of reactions of carboxylic acid derivatives.

The formation of tetrahedral intermediates is considered