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

Charge on atom	CH$_2$F$^+$		CHF$_2$$^+$		CF$_3$$^+$	
	a	b	a	b	a	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$_2$ ⇌ 2CF$_2$	b
−46.4 ± 2.0	Equilibrium CHF$_2$Br ⇌ CF$_2$ + HBr	c
−41.6 ± 1.8	Photoionization threshold CF$_2$=CF$_2$ → CF$_2$$^+$ + CF$_2$ and IP(CF$_2$) = 11.42 eV	d, e
−43.2 ± 3.0	Photoionization threshold C$_6$H$_5$CF$_3$ → C$_6$H$_5$F$^+$ + 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 ^{f}B. S. Freiser and J. L. Beauchamp, unpublished photoionization studies.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]

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$_2$F$^+$ reacts very slowly with CH$_2$F$_2$ to form CHF$_2$$^+$ and CH$_3$F; 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.*, **75**, 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

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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 ac-

tion of enzymes in catalysis of reactions of carboxylic acid derivatives.

The formation of tetrahedral intermediates is considered

very probable in carbonyl displacement reactions.[2-4] Consequently, there has been considerable interest in detecting such intermediates. Most of the evidence for the presence of intermediates comes from concurrent hydrolysis and isotopic oxygen exchange reactions[5-8] and breaks in pH rate profiles of amides[9a] and thio esters.[9b] Johnson[10] has presented kinetic evidence that an intermediate lies on the reaction path for carboxylic ester solvolysis. Finally, NMR observation of an adduct in the reaction of alkoxide ion with an amide has recently been reported.[11]

Because of the uncertainties and complications introduced by solvent effects into the understanding of the intrinsic reactivities of compounds studied in solution,[12] we thought it would be useful to attempt the formation of this mechanistically important intermediate under solvent-free conditions. Part of the problem encountered in detecting the addition complex in homogeneous solution is due to the stabilization of the uncomplexed esters, thio esters, amides, etc. This arises from the resonance contribution in these derivatives:

$$R-\underset{\underset{\displaystyle O}{\|}}{C}-Z \longleftrightarrow R-\underset{\underset{\displaystyle O^-}{|}}{C}=Z^+$$
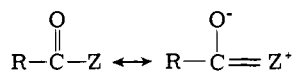
Evidence for such stabilization in esters and amides has been provided by dipole measurements,[13] thermochemical studies,[14] long-range spin coupling,[15] and other NMR techniques.[16] It would therefore be easier to form intermediates in cases where the extra resonance contribution is reduced or removed. In line with this argument, the relative degree of ground state stabilization of acyl derivatives would follow the order:[17]

$$NR_2 > OR > SR > \text{halide} > \text{alkyl}$$
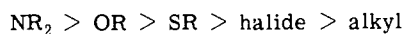
The presence of electron-withdrawing groups on the acyl part of the carboxylic acid derivatives would also be expected to enhance stabilization of the addition complex. In agreement with these predictions, intermediates have been directly detected in reactions of ketones;[18] in fact, addition complexes of some aldehydes and ketones are more stable than the parent.[19] In addition, it has been shown that ethyl trifluoroacetate and trifluoroacetamide form stable adducts.[20,21] It has also been reported that transients were detected during the reaction of acid chlorides with amines in alkane solvents.[22]

We report here on our studies of formation and structure of addition complexes of acyl halides in the gas phase utilizing ion cyclotron resonance spectroscopy (ICR).[23] While this manuscript was in preparation, Bowie and Williams[24] reported the formation of an adduct of trifluoroacetic anhydride by "collisional stabilization" in the gas phase.

In essence, we have attempted to observe the reaction: $A^- + BX \rightarrow ABX^-$. However, reaction of the ion A^- with the neutral molecule BX will produce a highly energized species ABX^-* which must be stabilized in order to be detected. Since we work at very low pressures ($< 10^{-4}$ Torr) and with relatively small molecules and ions, the complex will dissociate to reactants (or products) faster than it can collide and be stabilized. Hence we had to devise another means of stabilizing our adduct.

In their studies on the formation of chloride ion clusters in the gas phase, Riveros, Breda, and Blair[25] formed $COCl^-$ from phosgene and produced stable alkyl halide complexes from the reaction of this ion with alkyl halides: $COCl^- + RCl \rightarrow RCl_2^- + CO$. Earlier, we had produced Cl_2^- and $COCl^-$ from phosgene, and both of these ions were found to react with acyl halides to produce stable adducts.[26] In this work we have produced our halide sources from $COCl_2$, CF_3COCl (for Cl^- transfer), and SF_6 (for F^- transfer).

Experimental Section

Materials. Acetyl chloride (MCB) and propionyl chloride (Aldrich Chemical Co.) were purified by distillation at atmospheric pressure. Phosgene and sulfur hexafluoride (Matheson) were used without further purification. Trifluoroacetyl chloride (Peninsular Chem. Research Inc.) was used without further purification. All samples were prepared on a vacuum line. Two or three freeze-pump-thaw cycles were used to degas the samples followed by trap-to-trap distillation into a gas sample bulb for direct introduction into the unheated inlet of the ICR spectrometer.

Instrumentation. The basic ICR instrument used was the Syrotron mass spectrometer (Varian V-5900). The auxiliary equipment has been described previously.[12] Single resonance spectra were obtained by fixing the marginal oscillator frequency (112.0 kHz) and sweeping the magnetic field using a phase-sensitive detection scheme. The marginal oscillator frequency was fixed at 112.0 kHz instead of the conventional 153.5 kHz in order to observe ions up to m/e 170. The continuous double resonance technique[27,28] was used for all reaction studies. Typical rf amplitudes were 0.20–0.25 V (peak-to-peak measured externally at the base of the cell). Trapping voltages in the range 0.5–2.5 V were used. Analyzer drift voltages <0.10 V for both analyzer plates and source drift voltages <1.0 V for both source plates were typical.

With the exception of the SF_6-CF_3COCl system which was investigated at about 2.0×10^{-7} Torr and 0.9 eV electron energy, all single and double resonance spectra were obtained in the electron energy range 15–35 eV and pressure range 10^{-6}-10^{-4} Torr.
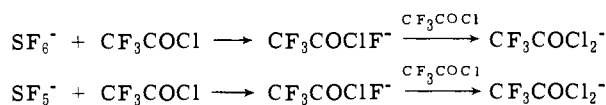
Results

Formation of Ions. In the ICR spectrometer, ions are generated by an electron beam in the source region of the ICR cell and are drifted into the analyzer region where they are detected.[29] With the exception of SF_6^-, which was formed via electron capture[30] by SF_6, all primary ions were formed by dissociative electron capture.[31] The primary ions are listed in Table I.

Ion–Molecule Reactions. All reactions reported in this work were verified by continuous double resonance experiments.[27,28] For a typical ion–molecule reaction $X^- + AB \rightarrow AX + B^-$, the product, B^-, is monitored at a fixed magnetic field strength, while a second oscillator is swept through the resonant frequencies associated with possible reactants, X^-. When any ion comes into resonance, it is accelerated, and in general, its *apparent* rate constant for reaction is altered. Thus, if the ion X^- is a precursor of B^-, a change in the abundance of B^- is observed when X^- is accelerated. As a general rule, B^- decreases when the reaction is exothermic.

Using this approach, we obtained the results shown in Table II. Since we were able to observe certain reactions, while other reactions differing only in isotopic label were not observable, we conclude that the nonoccurrence of these reactions is significant. For example, $CO^{35}Cl^-$ reacts with CH_3COCl to produce $CH_3COCl_2^-$ which contains at least one ^{35}Cl.

In addition to the results shown in Table II above, ejection of SF_6^- in the presence of CF_3COClF^- (m/e 151 and 153) caused a decrease in the signal intensities of $CF_3COCl_2^-$ (m/e 167, 169, and 171). The same result was obtained when SF_5^- was ejected. Thus evidence is furnished for the following sequence of reactions:

$$SF_6^- + CF_3COCl \longrightarrow CF_3COClF^- \xrightarrow{\text{CF}_3\text{COCl}} CF_3COCl_2^-$$

$$SF_5^- + CF_3COCl \longrightarrow CF_3COClF^- \xrightarrow{\text{CF}_3\text{COCl}} CF_3COCl_2^-$$

Discussion

Many chemical reactions involve two or more elementary steps,[32] the product species of one elementary step serving as the reacting species of a subsequent elementary step.

Table I. Formation of Primary Ions

Neutral	Primary ion	Electron energy,[a] eV
$COCl_2$	Cl^-	0–40
	$COCl^-$	15–35
	Cl_2^-	15–35
CF_3COCl	Cl^-	0–35
	CF_3Cl^-	20–35
	$COCl^-$	20–35
SF_6	SF_6^-	0.8–1.0
	SF_5^-	0.8–1.0
CH_3COCl	Cl^-	0–35

[a] Measured at the base of the cell, uncorrected for trapping voltages.

Table II. Reactions Observed by Double Resonance[a]

| Reactant ion (isotope)[b]	Neutral	Product ion (isotope)[b]
Cl^- (35)	RCOCl	Cl^- (37)
(37)	RCOCl	(35)
MCl^- (35)	RCOCl	$RCOCl_2^-$ (35,35)
		(35,37)
(37)		(35,37)
		(37,37)
Cl_2^- (35,35)	CH_3COCl	$CH_3COCl_2^-$ (35,35)
		(35,37)
(35,37)		(35,35)
		(35,37)
		(37,37)
(37,37)		(35,37)
		(37,37)
$CH_3COCl_2^-$ (35,35)	CF_3COCl	$CF_3COCl_2^-$ (35,35)
		(35,37)
(35,37)		(35,35)
		(35,37)
		(37,37)
$C_2H_5COCl_2^-$ (35,35)	CF_3COCl	$CF_3COCl_2^-$ (35,35)
		(35,37)
(35,37)		(35,35)
		(35,37)
		(37,37)
SF_6^-	CF_3COCl	CF_3COClF^- (35)
		(37)
		SF_5Cl^- (35)
		(37)
SF_5^-	CF_3COCl	CF_3COClF^- (35)
		(37)
		SF_4Cl^- (35)
		(37)
CF_3COClF^- (35)	CF_3COCl	$CF_3COCl_2^-$ (35,35)
		(35,37)
(37)		(35,37)
		(37,37)

[a] R = CF_3, CH_3, and C_2H_5. M = CO and CF_3. [b] Isotope(s) of Cl required to form the ions of observed m/e.

Such transient species, which are isolable in some but not in all cases, are known as intermediates in chemical reactions. To gain a full understanding of a particular reaction, the detailed elementary steps, and hence the intermediate species, must be known. However, direct detection of these intermediates is a very difficult task if they are short lived.

A typical exchange reaction can be represented as X^- + $AB \rightarrow [ABX]^- \rightarrow AX + B^-$. In general, because of polarization stabilization, the intermediate ion, which is larger, will be more stable than the reactants. This is likely to be true even if the intermediate is simply a solvated complex held together only by ion-induced dipole forces; it is even more likely to be true if "conventional" chemical bonds are formed. Since formation of the intermediate is an exoergic process, the intermediate will retain the excess energy as internal energy, and it must be stabilized or it will dissociate to reactants or products. This stabilization could be accomplished by working at sufficiently high pressures so that col-

lisions would be frequent enough to deactivate the energized species. Alternatively, for addition complexes made up of large groups of atoms, the complex has many internal degrees of freedom into which it can partition its excess energy. Such adducts have long lifetimes and collisions may be sufficiently frequent to deactivate the energized species.[33] Such appears to be the case recently reported by Bowie and Williams.[24] However, for adducts made up of small groups, a convenient way of stabilizing at low pressures is through a reaction of the type $MX^- + AB \rightarrow ABX^- + M$. Here, two product species are formed, providing a mechanism for dissipation of energy in the form of translational energy of the products. For our halide transfer reactions which involve small ions and molecules and which were investigated at very low pressures ($<10^{-4}$ Torr), we adopted this approach. Thus, for chloride transfer we made use of $COCl^-$ and Cl_2^- (from $COCl_2$), $COCl^-$ and CF_3Cl^- (from CF_3COCl), and for fluoride transfer we employed SF_6^- and SF_5^- (from SF_6).

As reported above, negative ion signals corresponding to the adduct $CH_3COCl_2^-$ were observed in a mixture of $COCl_2$ and CH_3COCl. Formation and stabilization of the adduct can be schematically represented as
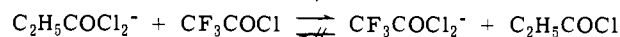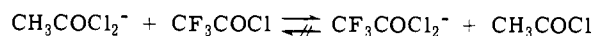
$$Cl_2^- + CH_3COCl \longrightarrow CH_3COCl_2^- + Cl$$

$$COCl^- + CH_3COCl \longrightarrow CH_3COCl_2^- + CO$$
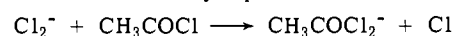
Here Cl and CO carry off the excess energy of the adduct. Similar results were observed for mixtures of CH_3COCl-CF_3COCl and CF_3COCl-CH_3CH_2COCl and for CF_3COCl.

$$CF_3Cl^- + RCOCl \longrightarrow RCOCl_2^- + CF_3$$

$$R = CH_3, C_2H_5, CF_3$$
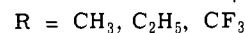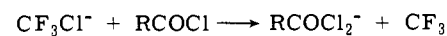
In a mixture of SF_6 and CF_3COCl, the energized chloride-fluoride adduct was also stabilized, with SF_5 and SF_4 acting as third bodies.

$$SF_6^- + CF_3COCl \longrightarrow CF_3COClF^- + SF_5$$

$$SF_5^- + CF_3COCl \longrightarrow CF_3COClF^- + SF_4$$
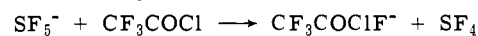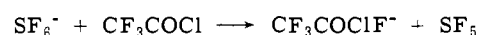
Our double resonance experiments provide evidence that both $CH_3COCl_2^-$ and $C_2H_5COCl_2^-$ transfer Cl^- to CF_3COCl, but $CF_3COCl_2^-$ does not transfer Cl^- to CH_3COCl or C_2H_5COCl.

$$CH_3COCl_2^- + CF_3COCl \overset{\longrightarrow}{\underset{\longleftarrow}{/\!\!/}} CF_3COCl_2^- + CH_3COCl$$

$$C_2H_5COCl_2^- + CF_3COCl \overset{\longrightarrow}{\underset{\longleftarrow}{/\!\!/}} CF_3COCl_2^- + C_2H_5COCl$$

Thus, $CF_3COCl_2^-$ is more stable than $CH_3COCl_2^-$ and $C_2H_5COCl_2^-$ relative to the respective neutrals. These results are consistent with electron-withdrawing substituents on the alkyl group leading to more stable adducts.

The results of chloride transfer from Cl_2^- to CH_3COCl indicate that only one of the chlorines in Cl_2^- is transferred. If the two chlorines in the complex $CH_3COCl_2^-$ were derived from Cl_2^-, ejection of m/e 70 ($^{35,35}Cl_2^-$) should have resulted in a decrease in the intensity of m/e 113 ($CH_3CO^{35,35}Cl_2^-$) only. However, ejection of m/e 70 ($^{35,35}Cl_2^-$) resulted in a decrease in the intensity of both m/e 113 and 115 ($CH_3CO^{35,37}Cl_2^-$) but not m/e 117. Also, m/e 72 ($^{35,37}Cl_2^-$) is coupled to all three isotopic fractions of $CH_3COCl_2^-$. These results clearly rule out a structure in which both chlorines in the adduct come from Cl_2^-.

At least two structures can be postulated for the adduct:

$$CH_3-\overset{O^-}{\underset{Cl}{\overset{|}{\underset{|}{C}}}}-Cl \qquad [CH_3\overset{O}{\overset{||}{C}}-Cl-Cl]^-$$
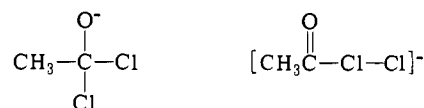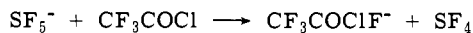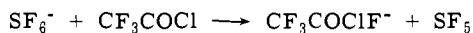
The work of Riveros, Breda, and Blair[25] suggests that alter-

native, unexpected products should be considered carefully.

As reported above, ions of m/e 151 and 153 (CF_3COClF^-) and 167, 169, and 171 ($CF_3COCl_2^-$) were observed in the mass spectrum of SF_6 and CF_3COCl. Our ion ejection experiments show that CF_3COClF^- transfers Cl^- to CF_3COCl.

$$CF_3COClF^- + CF_3COCl \longrightarrow CF_3COCl_2^- + CF_3COF$$
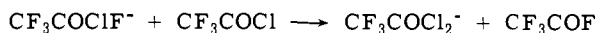
Since CF_3COClF^- itself comes from the transfer of F^- from SF_6^- and SF_5^- to CF_3COCl,

$$SF_6^- + CF_3COCl \longrightarrow CF_3COClF^- + SF_5$$
$$SF_5^- + CF_3COCl \longrightarrow CF_3COClF^- + SF_4$$

then CF_3COClF^- must have a tetrahedral structure. If it were simply a loose association complex of the type $[CF_3COClF]^-$, we would not have expected it to transfer Cl^- to neutral CF_3COCl. Further confirmation comes from the secondary coupling observed between the precursor ions of CF_3COClF^- (SF_6^- and SF_5^-) and $CF_3COCl_2^-$ as evidenced by the decrease in intensity of $CF_3COCl_2^-$ signals when SF_6^- and SF_5^- were ejected:

$$SF_6^- + CF_3COCl \longrightarrow CF_3COClF^- \xrightarrow{CF_3COCl} CF_3COCl_2^-$$

It is possible to deduce some thermochemical properties of these intermediates. Since acetyl chloride reacts with Cl_2^-, ΔH_f° for $CH_3COCl_2^-$ must be[34] ≤ -144 kcal/mol. This result is consistent with the tetrahedral intermediate occurring in the exchange reaction of acetyl chloride with Cl^-, since its formation would be at least 30 kcal/mol exothermic. If we assume that the neutral radical CH_3COCl_2 has a heat of formation which would be predicted by bond or group additivity, its electron affinity would have to be ≥ 104 kcal/mol (4.4 eV), an unusually high value for an alkoxy radical.[35] This may be a result of having two halogens on the α carbon.

The results then provide strong evidence for the existence of a secondary minimum on the potential surface by which acyl halides react with halide ions. The structure at this minimum is probably best described as a tetrahedral intermediate. Adducts have also been found in S_N2 reactions at saturated carbon.[25,36] There is some evidence that the halogens in such adducts are not symmetrical with respect to the carbon center.[25] As far as "intermediates" in the reactions of atomic halide ions with acetyl halides are concerned, although the surface has a minimum, the exothermicity of formation coupled with the small number of vibrational degrees of freedom may result in a lifetime sufficiently short to preclude conventional detection. Presumably, beam experiments with their shorter time scale could shed some light on this problem.

References and Notes

(1) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960), and references therein.
(2) T. C. Bruice and S. Benkovic, "Bioorganic Mechanisms", Vol. 1, W. A. Benjamin, New York, N.Y., 1966.
(3) S. L. Johnson, "Advances in Physical Organic Chemistry", Vol. 5, V. Gold, Ed., Academic Press, London, 1967, 1967, p 237.
(4) D. P. N. Satchell and R. S. Satchell, "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Interscience, London, 1969, Chapter 9.
(5) (a) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951); (b) M. L. Bender, R. D. Ginger, and K. C. Kemp, *ibid.*, **76**, 3350 (1954).
(6) (a) M. L. Bender, R. D. Ginger, and J. P. Unik, *J. Am. Chem. Soc.*, **80**, 1044 (1958); (b) M. L. Bender, H. Matsui, R. J. Thomas, and S. W. Tobey, *ibid.*, **83**, 4193 (1961).
(7) C. A. Bunton, T. A. Lewis, and D. H. Llewellyn, *Chem. Ind. (London)*, 1154 (1954).
(8) C. A. Bunton and D. N. Spatcher, *J. Chem. Soc.*, 1079 (1956).
(9) (a) B. Zerner and M. L. Bender, *J. Am. Chem. Soc.*, **83**, 2267 (1961); (b) L. R. Fedor and T. C. Bruice, *ibid.*, **87**, 4138 (1965); E. S. Hand and W. P. Jencks, *ibid.*, **84**, 3505 (1962).
(10) S. L. Johnson, *J. Am. Chem. Soc.*, **86**, 3819 (1964); *Tetrahedron Lett.*, 1481 (1964).
(11) G. Fraenkel and D. Watson, *J. Am. Chem. Soc.*, **97**, 231 (1975).
(12) For example, see: J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90**, 5636 (1968); **90**, 6561 (1968); **91**, 2126 (1969); **92**, 5986 (1970); **93**, 3911 (1971).
(13) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).
(14) G. W. Wheland, "Resonance in Organic Chemistry", Wiley, New York, N.Y., 1955, p 99.
(15) G. Fraenkel, *J. Chem. Phys.*, **34**, 1466 (1961).
(16) (a) W. D. Phillips, *J. Chem. Phys.*, **23**, 1363 (1955); (b) H. S. Gutowsky and C. H. Holm, *ibid.*, **25**, 1228 (1956).
(17) Cf. ref 3, p 226.
(18) H. E. Zaugg, V. Papendick, and R. J. Michaels, *J. Am. Chem. Soc.*, **86**, 1399 (1964).
(19) E.g., chloral.
(20) M. L. Bender, *J. Am. Chem. Soc.*, **75**, 5986 (1953).
(21) A. Moffatt and H. Hunt, *J. Am. Chem. Soc.*, **81**, 2082 (1959).
(22) S. G. Entelis and O. V. Nesterov, *Dokl. Chem. (Engl. Transl.)*, **148**, 174 (1963).
(23) (a) J. D. Baldeschwieler, *Science*, **159**, 263 (1968); (b) for a recent review, cf. C. J. Drewery, G. C. Goode, and K. R. Jennings, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One. 1972* (1972).
(24) J. H. Bowie and B. D. Williams, *Aust. J. Chem.*, **27**, 1923 (1974).
(25) J. M. Riveros, A. C. Breda, and L. K. Blair, *J. Am. Chem. Soc.*, **95**, 4066 (1973).
(26) L. K. Blair, Ph.D. Dissertation, Stanford University, 1970, and unpublished results.
(27) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).
(28) J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).
(29) (a) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **89**, 4569 (1967); (b) J. M. S. Henis, *ibid.*, **90**, 844 (1968).
(30) W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).
(31) J. G. Dillard, *Chem. Rev.*, **73**, 589 (1973).
(32) M. Boudart, "Kinetics of Chemical Processes", Prentice-Hall, Englewood Cliffs, N.J., 1968, Chapter 1.1.
(33) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968, p 108.
(34) $\Delta H_f^\circ(Cl_2^-) = -56.7$ kcal/mol [D. B. Dunkin, F. C. Fehsenfeld, and E. E. Ferguson, *Chem. Phys. Lett.*, **15**, 527 (1972)]. $\Delta H_f^\circ(CH_3COCl) = -58.9$ kcal/mol [D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969]. $\Delta H_f^\circ(Cl) = +29$ kcal/mol [*Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37** (1971)].
(35) K. J. Reed and J. I. Brauman, *J. Am. Chem. Soc.*, **97**, 1625 (1975).
(36) R. C. Dougherty, J. Dalton, and J. D. Roberts, *Org. Mass Spectrom.*, **8**, 77 (1974).