correlation is the recognition of a difference between cations and anions. Thus, both B and $1/\epsilon_{\text{eff}}^2$ increase with an increase of anionic crystallographic radius, and both B and $1/\epsilon_{\text{eff}}^2$ increase with a decrease of cationic crystallographic radius.

A further possible relationship between B and ion-solvent interactions can be seen by noting that $(-\delta B/\delta T)$ (ref 3) is either positive or slightly negative for those univalent salts which contain ions that are considered "structure makers" (H^+, Li^+, F^-) and much more negative for univalent salts which contain ions that are considered to be "structure breakers".[24] A reexamination of heats of dilution for 2:1 electrolytes using the field-dielectric-gradient model should shed further light on this observation.

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Gas Phase Proton Affinities of Several Fluoroethylenes

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Received December 27, 1974

Abstract: Determinations of the proton affinities of C_2H_3F, CH_2CF_2, *cis-* and *trans*-CHFCHF, and C_2HF_3 using ion cyclotron resonance techniques are reported. The proton affinities are found to be 168 ± 1, 177 ± 3, 164 ± 2, 165 ± 2, and 167 ± 1 kcal/mol, respectively. The heats of formation of the protonated species derived from the proton affinities are compared with heats of formation of fluoroethyl cations derived in other ways. It is concluded that the most probable structures for the protonated species are CH_3CHF^+, $CH_3CF_2^+$, CH_2FCHF^+, and $CH_2FCF_2^+$. Limits on the previously unknown heats of formation of the 1,2-difluoroethylenes are determined from the proton affinities.

The enthalpy change for reaction 1 is a direct measure of the relative stabilities of alkyl cations R_1^+ and R_2^+. Recent

$$R_1^+ + R_2X \rightarrow R_2^+ + R_1X \qquad (1)$$

measurements of the gas phase equilibrium constants for reactions of this type have provided relative heats of formation of alkyl cations.[1-3] Another direct measure of relative alkyl cation stability is the enthalpy change for reaction 2

$$AH^+ + B \rightarrow BH^+ + A \qquad (2)$$

where A and B are olefins. The protonated olefins are, of course, alkyl cations. The complexity of the gas phase ion chemistry of mixtures of olefins in most cases prevents the direct measurement of equilibrium constants for reaction 2.[4-10] The proton affinities[11] of olefins can be determined using ion cyclotron double resonance,[12,13] however, and provide equivalent information since the enthalpy change for reaction 2 is the difference between the proton affinities of A and B.

The object of the present study is to determine the proton affinities of several fluoroethylenes. Some information about the stabilities of the corresponding fluoroethyl cations is available from study of fluoride transfer reactions analogous to reaction 1.[2,3] Heats of formation derived from mass spectrometric appearance potentials have been reported for several of the fluoroethyl cations.[14-16] Discrepancies between the various mass spectral measurements are to some extent resolved by the fluoride transfer reaction study, but the fluoroethylene proton affinities provide an indispensable addition to the available data on fluoroethyl cations.

There is some ambiguity in the structure of some of the fluoroethyl cations. The structure of $C_2H_4F^+$ has been the subject of a recent study.[17] The difluoro- and trifluoroethyl cations each have several possible isomers. The proton affinities of the fluoroethylenes indicate which fluoroethyl cations have stable isomers.

An interesting application of the proton affinity data arises in the case of the 1,2-difluoroethylenes. The heats of formation of the neutrals are not well known, but limits on the heat of formation of the 1,2-difluoroethyl cation have been established.[2,3] Limits on the neutral heats of formation of the 1,2-difluoroethylenes can therefore be deduced from the proton affinities.

The theory of ion cyclotron double resonance and its application to the determination of proton affinities has been discussed.[12,13] It has been generally established that if the single resonance signal intensity of ion A decreases when ion B is irradiated at its cyclotron frequency, then B reacts to form A at a rate that decreases with increasing ion kinetic energy. At the neutral pressures ($\sim 10^{-5}$ Torr) and drift times (~10^{-3} sec) used in the present study only reactions that proceed on nearly every collision are observable by double resonance. Thus, we assume that any reaction so observed is thermoneutral or exothermic and without activation energy. Precautions must, of course, be taken to preclude reactions of excited ions if we wish to infer thermodynamic properties of ground state ions from our observations. The ultimate test of the efficacy of such precautions is the consistency of the thermodynamic implications of the results. The implications must be both self-consistent and consistent with other measurements on the same systems.

The reactions relevant to the proton affinities of the fluoroethylenes are proton transfer reactions between the fluoroethylenes and reference bases whose proton affinities have been reported. Double resonance identifies those proton transfer reactions which are exothermic and thus establishes limits on the proton affinities of the fluoroethylenes. Examination of each fluoroethylene with a number of reference bases minimizes the possibility of being misled by reactions of excited ions.

Experimental Section

All experiments were performed on an ion cyclotron resonance instrument of conventional design built at the Ford Scientific Research Staff Laboratories and at the University of Delaware. The marginal oscillator detector is a solid state design described elsewhere.[18,19] The cell is 1.1 cm × 2.5 cm × 11.5 cm. The source region is 1 cm long and the analyzer region is 10.5 cm long. All experiments were done in the normal drift mode using trapping voltage modulation and phase sensitive detection.[20] The double resonance experiments were done with a Wavetek Model 144 HF Sweep Generator using signals with amplitudes between 25 and 500 mV.

Samples of vinyl fluoride, 1,1-difluoroethylene, *cis*-1,2-difluoroethylene, *trans*-1,2-difluoroethylene, trifluoroethylene, and ethyl fluoride were obtained from Peninsular Chemical Research and were used as supplied. Methane, methyl bromide, and hydrogen sulfide were supplied by Matheson and had a stated purity greater than 99.5%. Reagent grade methanol and ethyl iodide were obtained from Fisher and Baker, respectively. Formaldehyde vapor was obtained by heating paraformaldehyde under a vacuum. The paraformaldehyde was obtained from Mallinkrodt. CD_3Cl was prepared by reacting CD_3OD with $SOCl_2$ at 0°C. The product was collected in a trap at −78°C. After degassing in a vacuum manifold the product was frozen at −196°C into a tube containing solid $Ca(OH)_2$. This procedure was found to remove SO_2 from the product. The only product detected in the mass spectrum was CD_3Cl.

The ion cyclotron resonance instrument has two inlet systems and both a diffusion pump and an ion pump. Approximate pressures may be determined from the ion pump current. Accurate measurements of pressures above 2×10^{-5} Torr are made with an MKS Baratron Capacitance Manometer. Baratron readings can be extrapolated to lower pressures by monitoring the total ion current as the pressure is decreased. With the normal configuration of fields the ion collection efficiency does not depend on pressure so that the total ion current can be considered proportional to pressure.

In a typical experiment an ethylene was admitted to a pressure of approximately 10^{-6} Torr. Through the other inlet the reference base was admitted to approximately the same pressure. The total pressure was controlled by partially closing the valves between the pumps and the system. The ratio of the neutral pressures was controlled by regulating the leak rates from the inlets. Single resonance spectra were taken under a variety of pressure conditions. When conditions were found at which the concentrations of both protonated parents were maximized, double resonance spectra were taken. The energy of the ionizing electron beam was generally 15 eV or less to minimize reactions of excited species.

Results

Vinyl Fluoride. In a mixture consisting of approximately equal parts of C_2H_3F and CH_2O, the only peaks at 11.5 eV ionizing energy (nominal) at low pressure correspond to the two parent ions and CHO^+. At higher pressures, double resonance indicates reactions 3–6 proceed with significant

$$C_2H_3F^+ + CH_2O \rightarrow CH_2OH^+ + C_2H_2F \qquad (3)$$

$$CH_2O^+ + C_2H_3F \rightarrow C_2H_4F^+ + CHO \qquad (4)$$

$$CHO^+ + C_2H_3F \rightarrow C_2H_4F^+ + CO \qquad (5)$$

$$C_2H_4F^+ + CH_2O \rightarrow CH_2OH^+ + C_2H_3F \qquad (6)$$

rate constants producing the protonated parents, CH_2OH^+ and $C_2H_3F^+$. In each case the reactant ion signal decreases when the product is irradiated. The protonated vinyl fluoride reacts further with vinyl fluoride as indicated in reaction 7.[5] Also observed is an ion at *m/e* 77 ($C_3H_3F_2^+$) which

$$C_2H_4F^+ + C_2H_3F \rightarrow C_4H_6F^+ + HF \qquad (7)$$

has been previously identified as a product of reaction between $C_2H_3F^+$ and C_2H_3F.[5] In a mixture of H_2S and C_2H_3F the protonated parents and the $C_4H_6F^+$ and $C_3H_3F_2^+$ ions appear at higher pressures. The proton transfer reaction 8 gives a negative double resonance response in

$$C_2H_4F^+ + H_2S \rightleftarrows H_3S^+ + C_2H_3F \qquad (8)$$

both directions. That is, the signal of either ion decreases when the other ion is irradiated. In a mixture of H_2O and C_2H_3F the proton transfer reaction 9 gives a negative double resonance response. The chemistry of the mixture is otherwise analogous to that of the other mixtures. The order of proton affinities assigned on the basis of these results is $H_2O \leq C_2H_3F \simeq H_2S \leq CH_2O$.

$$H_3O^+ + C_2H_3F \rightarrow C_2H_4F^+ + H_2O \qquad (9)$$

1,1-Difluoroethylene. In mixtures of CH_2CF_2 with H_2O, H_2S, CH_2O, C_2H_5I, and CH_3OH the only products detected are the protonated parents and species previously identified as products of reactions in the pure gases.[6,13,21,22] The proton transfer reactions 10–14 all give negative double resonance responses. The order of proton affinities assigned on the basis of these results is H_2O, H_2S, CH_2O, $C_2H_5I \leq CH_2CF_2 \leq CH_3OH$.

$$H_3O^+ + CH_2CF_2 \rightarrow C_2H_3F_2^+ + H_2O \qquad (10)$$

$$H_3S^+ + CH_2CF_2 \rightarrow C_2H_3F_2^+ + H_2S \qquad (11)$$

$$CH_2OH^+ + CH_2CF_2 \rightarrow C_2H_3F_2^+ + CH_2O \qquad (12)$$

$$C_2H_5IH^+ + CH_2CF_2 \rightarrow C_2H_3F_2^+ + C_2H_5I \qquad (13)$$

$$C_2H_3F_2^+ + CH_3OH \rightarrow CH_3OH_2^+ + CH_2CF_2 \qquad (14)$$

As an indication of the stability of the protonated ethylene to loss of a proton to H_2O, the variation of relative ion concentration with pressure in the H_2O-CH_2CF_2 mixture is illustrated in Figure 1. The concentrations plotted are those of the only species whose concentrations depend on the partial pressure of H_2O.

1,2-Difluoroethylene. Both *cis*- and *trans*-CHFCHF react similarly with the reference bases used. In mixtures with methane reaction 15 gives a negative double resonance

$$C_2H_5^+ + CHFCHF \rightarrow C_2H_3F_2^+ + C_2H_4 \qquad (15)$$

response. The $C_2H_5^+$ ion is formed by the familiar reaction of CH_3^+ with methane.[20] Reactions in methyl chloride produce $CH_3ClCH_3^+$ [21] which has the same mass as protonated CHFCHF so CD_3Cl was used as the reference base. In CD_3Cl mixture reaction 16 gives a negative double resonance response. In mixtures with ethyl fluoride the concentrations of protonated parents are insufficient to allow un-

$$CD_3ClD^+ + CHFCHF \rightarrow C_2H_2DF_2^+ + CD_3Cl \qquad (16)$$

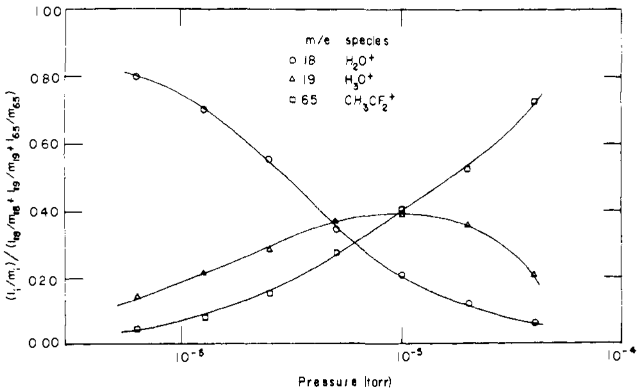

Figure 1. The variation of the relative concentrations of the mass 18, 19, and 65 ions in a 1:1 mixture of CH_2CF_2 and H_2O. The ionizing energy is 13.9 eV. The 18, 19, and 65 mass ions are the only ions whose relative concentrations change when H_2O is added to CH_2CF_2. The parameter I_i/m_i is approximately proportional to ion concentration (see S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968)).

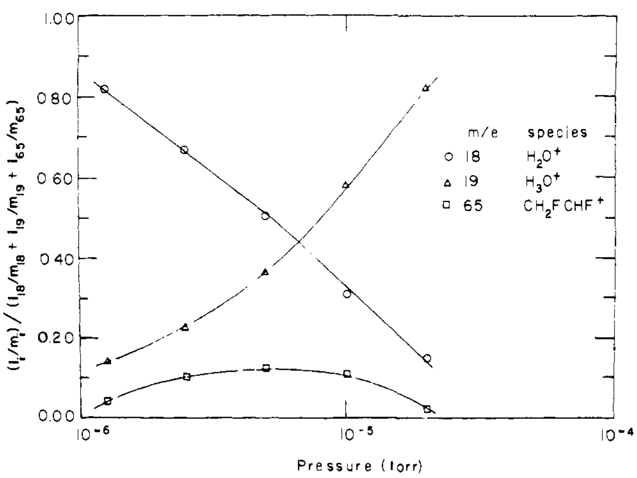

Figure 2. The variation of the relative concentration of the mass 18, 19, and 65 ions in a 1:1 mixture of CHFCHF and H_2O. The ionizing energy is 13.9 eV. The 18, 19, and 65 mass ions are the only ions whose relative concentrations change when H_2O is added to CHFCHF. The parameter I_i/m_i is approximately proportional to ion concentration (see S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968)).

equivocal double resonance results. Ethyl iodide, hydrogen iodide, and methane were therefore added to the mixtures as protonating agents. Reactions of ions generated from the protonating agents enhance the concentrations of the protonated difluoroethylene and ethyl fluoride. Reaction 17

$$C_2H_5FH^+ + CHFCHF \rightarrow C_2H_3F_2^+ + C_2H_5F \quad (17)$$

gives a negative double resonance response for isomers of CHFCHF. The chemistry of mixtures of CH_3Br with the 1,2-difluoroethylenes is complicated by rapid charge exchange between CH_3Br^+ and the ethylenes. The protonated parents are not observed in sufficient concentrations to do unequivocal double resonance.

The single resonance spectrum of CHFCHF is unchanged when H_2O is added except for the appearance of H_2O^+, H_3O^+, and protonated CHFCHF. The variation of the concentrations of these ions with pressure in the H_2O mixture is illustrated in Figure 2 as an indication of the stability of the protonated CHFCHF to rearrangement. Reaction 18 evidently proceeds to the right with a significant rate constant. This is confirmed by double resonance results. The order of proton affinities assigned is C_2H_4, CD_3Cl, $C_2H_5F < CHFCHF < H_2O$.

$$C_2H_3F_2^+ + H_2O \rightarrow H_3O^+ + C_2H_2F_2 \quad (18)$$

Trifluoroethylene. Reactions 19–21 give negative double resonance responses in the appropriate mixtures. In each instance only the protonated parents and species observed in the pure gases appear as reaction products. The assigned order of proton affinities is $H_2O < C_2HF_3 < H_2S$, CH_2O.

$$H_3O^+ + C_2HF_3 \rightarrow C_2H_2F_3^+ + H_2O \quad (19)$$

$$C_2H_2F_3^+ + H_2S \rightarrow H_3S^+ + C_2HF_3 \quad (20)$$

$$C_2H_2F_3^+ + CH_2O \rightarrow CH_2OH^+ + C_2HF_3 \quad (21)$$

Discussion

The overall order of the proton affinities of the fluoroethylenes and the reference bases is given in Table I. Values of the proton affinities of the reference bases from the literature are also given. Where several values of the proton affinity of a reference base have been reported, a value consistent with a preponderance of the data has been chosen. Values assigned to the proton affinities of the fluoroethylenes are also listed. The difference between the proton affinities assigned to *cis*- and *trans*-CHFCHF is the difference between the neutral heats of formation.[23] No difference was observed in the chemistry of the two species. Heats of formation of the fluoroethylenes and fluoroethanes used in subsequent calculations are included in Table II. Results of the studies of fluoride transfer reactions involving fluoroethyl cations[1-3] are summarized in Table III. Finally, heats of formation of fluoroethyl cations determined from the proton affinities and heats of formation of the fluoroethylenes are contained in Table IV.

The proton affinities of the 1,2-difluoroethylenes combined with the results of the fluoride transfer studies give a limit for the previously unknown heats of formation of the 1,2-difluoroethylenes. The limit on the enthalpy change for reaction 22 given in Table III limits the heat of formation

$$CH_2FCHF^+ + CHF_2CH_3 \rightleftarrows CH_3CHF^+ + CH_2FCHF_2 \quad (22)$$

of the CH_2FCHF^+ ion as indicated in Table IV. The proton affinity of CHFCHF combined with this limit on $\Delta H_f(CH_2FCHF^+)$ gives the limits on the CHFCHF heats of formation in Table II. These limits are consistent with an extended Hückel MO calculation which indicates the 1,2 isomers to be 10 kcal/mol less stable than the 1,1 isomer.[24] Benson's group equivalents method, on the other hand, predicts that the 1,2 isomers are more stable than the 1,1 isomer.[25] Fluorine is evidently not a well-behaved substituent in a group equivalent sense. As indicated in Table II the limit is also consistent with a limit inferred from ion molecule reactions observed in a mixture of ethylene and CHFCHF.[8]

No evidence was obtained for thermochemically distinct isomers of CH_3CHF^+. The available evidence indicates that α-fluorine substitution stabilizes an alkyl cation and β substitution is destabilizing[17,26,27] so that the monofluoroethyl cation is assumed to be α substituted. The possibility of fluorine protonation is not eliminated by the present results. As discussed below, however, both protonation of vinyl fluoride and fluoride abstraction from CH_3CHF_2 appear to give species with the same heat of formation. Electron impact on CH_3CHF_2 produced a CH_3CHF^+ ion, but the fragmentation process is probably nonadiabatic so that the appearance potential gives a heat of formation too large as indicated in Table IV. A similar mechanism may be operative in the electron impact induced fragmentation of CH_3CF_3 to give $CH_3CF_2^+$. The appearance potential of

Table I. Order of Proton Affinities of Fluoroethylenes and Reference Bases

Species (in order of decreasing proton affinity)	Reported proton affinities of ref bases, kcal/mol	Selected proton affinities of ref bases and fluoroethylenes, kcal/mol
CH_3OH	182 ± 3,[a] 180 ± 3,[b] 180[c]	180
CH_2CF_2		177 ± 3
C_2H_5I	175[d]	175
CH_2O	168 ± 1,[e] 166[c]	169
H_2S, C_2H_3F	170 ± 3[a]	168, 168 ± 1
CF_2CHF		167 ± 1
H_2O	165 ± 3[a], 164 ± 4,[b] 168 ± 3[f]	166
trans-CHFCHF		165 ± 2
cis-CHFCHF		164 ± 2
C_2H_5F	163[d]	163
CD_3Cl	160[d]	160
C_2H_4	159[g]	159

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Table II. Heats of Formation of Fluorohydrocarbons

Species	ΔH°_{f298}	Species	ΔH°_{f298}
CH_2CHF	−33.2 ± 0.4[a]	$CHFCF_2$	−118.5 ± 0.7[b]
CH_2CF_2	−82.5 ± 2.4[b]	CH_3CHF_2	−118 ± 1[b]
cis-CHFCHF	>−81[d], >−75 ± 3[c]	CH_3CF_3	−178.2 ± 0.4[b]
trans-CHFCHF	>−80[d], >−74 ± 3[c]	CH_2FCHF_2	−158.9 ± 1[b]

[a] V. P. Kolesov and T. S. Papina, *Russ. J. Phys. Chem. (Engl. Transl.)*, 44, 611 (1970). (Corrected for the improved value of ΔH°_{f298} [HF, 40 H_2O] given in (b) so that the heats of formation are at least internally consistent. [b] J. R. Lacher and H. A. Skinner, *J. Chem. Soc. A*, 1034, (1968). [c] Determined in the present study using the differences in the stabilities of the cis and trans species, reported in ref 23. [d] Reference 8.

Table III. Enthalpy Changes for Fluoride Transfer Reactions

Reaction	ΔH°_{298}, kcal/mol
(22) $CH_2FCHF^+ + CHF_2CH_3 \rightleftarrows CH_3CHF^+ + CHF_2CH_2F$	−1.4 ± 0.2,[a] <0,[b] −1 ± 3[c]
(24) $CH_3CF_2^+ + CH_3CHF_2 \rightleftarrows CH_3CHF^+ + CH_3CF_3$	<−2.3[a]

[a] From measurements of the equilibrium constants of the reactions. Reference 3. [b] Reference 2. [c] Present results.

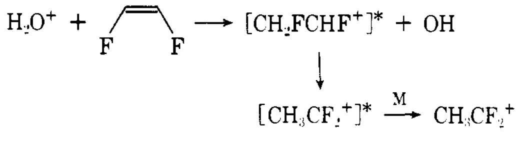
Table IV. Heats of Formation of Fluoroethyl Cations

	ΔH°_{f298} (R^+)		
	From appearance potentials		
R^+	From RH	From RF	Present results
CH_3CHF^+		206.7 ± 1,[a] 204.4 ± 1[b]	166 ± 1
$CH_3CF_2^+$	114.1[c]	152.1,[d] 146.5 ± 4.6[e]	107 ± 3
CH_2FCHF^+			>127 ± 1
$CH_2FCF_2^+$			81 ± 1

[a] Reference 14. [b] Reference 15. [c] Reference 14. [d] Reference 15. [e] Reference 16.

this latter process also apparently gives a heat formation for the fragment ion that is too large. The appearance potential of $CH_3CF_2^+$ from CH_3CHF_2, on the other hand, gives a heat of formation in reasonably good agreement with that determined from the proton affinity of CH_2CF_2.

The 1,1- and 1,2-difluoroethyl cations seem to be distinct, stable species. As indicated in Figure 1, protonated 1,1-difluoroethylene does not transfer a proton to H_2O. If protonated 1,2-difluoroethylene rearranged to a 1,1-difluoroethyl cation some of the *m/e* 65 ions should be stable at high pressures in the H_2O-CHFCHF mixture. The mechanism for producing such stable species is indicated in reaction 23. As shown in Figure 2, however, all the *m/e* 65



(23)

species disappears at high pressure, indicating that no rearrangement occurs. It is not surprising that CH_2FCHF^+ is stable since rearrangement to $CH_3CF_2^+$ involves exchanging a hydrogen and a fluorine between the carbon atoms. In contrast, the unstable β-fluoroethyl cation can be converted to the α-substituted cation by a simple hydride shift. Again, the present results do not exclude the possibility of fluorine protonation, but protonation of CH_2CF_2 and fluoride abstraction from CH_3CF_3 appear thermochemically to give the same species as discussed below.

The measured ionization potential of the CH_2CF_3 radical[26] implies a heat of formation for $CF_3CH_2^+$ of 114.1 kcal/mol. The protonated $CHFCF_2$ has a heat of formation of 81 ± 1 kcal/mol and is evidently not $CF_3CH_2^+$. Either $CH_2FCF_2^+$ or CHF_2CHF^+ is consistent with the present results. Since α fluorines are in general stabilizing and β fluorines are destabilizing, $CH_2FCF_2^+$ is the more probable structure, assuming that the $CHFCF_2$ is not fluorine protonated.

The enthalpy change for reaction 24 derived from measurement of the equilibrium constant[3] provides a particularly satisfactory test for the proton affinities obtained in the present studies. The enthalpy change calculated for reaction 24 from the ionic heats of formation determined in the present study agrees remarkably well with the directly measured enthalpy change as indicated in Table III. The agreement is striking in view of the variety of data involved in the calculated enthalpy change and is the most convincing evidence that the inferences from the double resonance results are correct.

$$CH_3CF_2^+ + CH_3CHF_2 \rightleftharpoons CH_3CHF^+ + CH_3CF_3 \quad (24)$$

Further substantiation of the present results comes from the photoionization of 2,2-difluoropropanes. Both $CH_3CF_2^+$ and $CH_2CF_2^+$ are products of photoinduced decomposition of $CH_3CF_2CH_3$. From the threshold energies for these processes and from the ionization potential of CH_2CF_2 the proton affinity of CH_2CF_2 is determined to be 174 kcal/mol.[28] The agreement with the number in Table I is satisfactory.

Acknowledgment. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the University of Delaware Research Foundation for partial support of this research. The assistance of B. Weinstock and H. Niki of the Ford Scientific Research Staff in obtaining use of instrumentation for this work was invaluable. The assistance of R. Dianich in synthesizing the CD_3Cl is also gratefully acknowledged.

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The Gas Phase Addition of Hydrogen Chloride to Propylene[1]

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Received January 13, 1975

Abstract: The neat gas phase addition of hydrogen chloride to propylene in mixtures containing up to 25 atm of hydrogen chloride and 5 atm of propylene has been examined at temperatures between 19 and 70°C. The reaction, in which the only detectable product is 2-chloropropane, was continuously monitored by gas phase proton magnetic resonance (^{1}H NMR) in glass-, quartz-, and Teflon-lined NMR tubes. Trace quantities of polar molecules (e.g., water and nitrogen oxides) appear to serve as homogeneous catalysts. Removal of the catalysts by repetitive vacuum distillation of both reagents permitted observation of the surface catalyzed process. Both homogeneous catalyzed and surface catalyzed processes are best fit by kinetic expressions first order in propylene and third order in hydrogen chloride, and the rates of both are attended by an inverse temperature dependence. A reaction scheme is proposed that includes a six-center intermediate.

The addition of hydrogen halides to olefins has been explored extensively and has played a fundamental role in the microscopic models used to explain chemical reactivity of organic molecules. For the generalized addition of hydrogen halide to olefin, three distinct pathways, not all of which are available to all alkenes and all hydrogen halides, are recognized. The first, ionic (Markovnikov) addition, takes place in polar solvents, presumably through protonation to yield a carbonium (carbenium) ion, which then goes on to product.[2] The second, free radical (anti-Markovnikov) addition, extensively studied by Kharasch and coworkers,[3] and useful for only hydrogen bromide,[4] occurs in both the gas phase and in solution. The third is the direct bimolecular addition which occurs in the gas phase and has been examined in detail by Benson and coworkers for the case of hydrogen iodide.[5] The latter is an example of the microscopic reverse of the thermal elimination of hydrogen halide from alkyl halides. Many such elimination studies have been undertaken.[6]

No gas phase reactions of hydrogen chloride with olefins have been reported. Maass and Sivertz[7] mixed hydrogen chloride and propylene at 1 atm total pressure and, after 400 days, they could observe no reaction. Kistiakowsky and Stauffer[8] measured the rate of elimination of hydrogen chloride from *tert*-butyl chloride and the equilibrium constant attending that elimination and suggested that the bimolecular addition of hydrogen chloride to alkenes has too high an activation energy to be observed at room temperature in any reasonable time. At sufficiently high temperatures for a reasonable addition rate, the equilibrium strongly favors elimination. Using the data from Benson's report,[5] which includes the Kistiakowsky and Stauffer[8] data, the time for 1% reaction of hydrogen chloride and propylene *via* the direct bimolecular addition at 20° and 1 atm each is 2.8×10^{11} days!

Maass and Sivertz[7] did observe a reaction between hydrogen chloride and propylene in the neat liquid phase, giving 2-chloropropane and a "chlorohexane" in a 2:1 ratio. In this reaction, it appeared that a high order in hydrogen chloride was necessary to account for the rapid reaction and the authors suggested that the reaction was "hydrogen chloride catalyzed". The rate was orders of magnitude faster than extrapolation from the gas phase results would give and thus it was suggested[8] that a different mechanism obtained in the liquid phase and that it might well occur through an HCl–alkene complex. Maass and Wright[9] interpreted melting point data of hydrogen chloride–alkene mixtures in terms of such complexes.

Mayo and Katz,[10] some years later, also obtained 2-chloropropane and the "chlorohexane" from the reaction of hydrogen chloride with propylene in heptane solution. Their results, while incomplete, suggested that the reaction was first order in propylene and roughly third order in hydrogen chloride. They also found evidence for complexes between hydrogen chloride and alkene.

Finally, recent observations by King, Dixon, and Hersch-