penhafer, and B. DuBeshter, *J. Am. Chem. Soc.*, **96**, 4283 (1974), and references cited therein; (c) H. J. Reich and D. A. Murcia, *ibid.*, **95**, 3418 (1973); (d) T. J. Pinnavaia, W. T. Collins, and J. J. Howe, *ibid.*, **92**, 4544 (1970); (e) A. J. Ashe III, *ibid.*, **92**, 1233 (1970); (f) A. G. Brook, D. M. MacRae, and W. W. Limburg, *ibid.*, **89**, 5493 (1967).

(4) This statement does not imply that there is necessarily any mechanistic analogy.

(5) (a) J. Tsuji, M. Hara, and K. Ohno, *Tetrahedron*, **30**, 2143 (1974); I. Ojima and M. Kumagai, *Tetrahedron Lett.*, 4005 (1974); (b) P. N. Rylander, "Organic Syntheses with Noble Metal Catalysts", Academic Press, New York, N.Y., 1973, pp 274–284.

(6) M. F. Lappert and H. Pyszora, *Adv. Inorg. Chem. Radiochem.*, **9**, 133 (1966); J. S. Thayer and R. West, *Adv. Organomet. Chem.*, **5**, 169 (1967).

(7) (a) D. A. Evans, J. M. Hoffman, and L. K. Truesdale, *J. Am. Chem. Soc.*, **95**, 582 (1973); (b) D. A. Evans, L. K. Truesdale, and G. L. Carroll, *J. Chem. Soc., Chem. Commun.*, **55** (1973); (c) D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.*, 4929 (1973); (d) H. R. Kricheldorf, *Synthesis*, 551 (1972); (e) S. S. Washburne and W. R. Peterson, *Synth. Commun.*, **2**, 227 (1972); (f) L. Birkofer, F. Muller, and W. Kaiser, *Tetrahedron Lett.*, 2781 (1967).

(8) (a) H. Sakurai, K. Nishiwaki, and M. Kira, *Tetrahedron Lett.*, 4193 (1973); H. Sakurai, A. Okadu, M. Kira, and K. Yonezwawa, *ibid.*, 1511 (1971); (b) P. F. Hudrlik and R. Feasley, *ibid.*, 1781 (1972); (c) Yu. K. Yur'ev and Z. V. Belyakova, *Russ. Chem. Rev.*, **29**, 383 (1960); (d) L. Birkofer and H. Dickopp, *Chem. Ber.*, **102**, 14 (1969); (e) L. Birkofer, A. Ritter, and H. Uhlenbrauch, *ibid.*, **96**, 3280 (1963); (f) L. Birkofer, A. Ritter, and H. Wieden, *ibid.*, **95**, 971 (1962).

(9) For a comprehensive review of the synthesis and properties of organo sulfur derivatives of the group 4 atoms see: E. W. Abel and D. A. Armitage, *Adv. Organomet. Chem.*, **5**, 2 (1967).

(10) (a) K. A. Hooten and A. L. Allred, *Inorg. Chem.*, **4**, 671 (1965); (b) E. W. Abel, D. A. Armitage, and D. B. Brady, *J. Organomet. Chem.*, **5**, 130 (1966); (c) I. Ojima, M. Nihonyangi, and T. Nagai *ibid.*, **50**, C26 (1973); (d) R. S. Glass, *ibid.*, **61**, 83 (1973).

(11) There is a disappointing lack of accurate bond energy data available for silicon derivatives: cf. E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements", Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N.Y., 1968, Chapter 1. Equilibration studies have suggested that the Si–S and C–S bond energies are comparable; M. Schmeisser and H. Muller, *Angew. Chem.*, **69**, 781 (1957).

(12) (a) I. Ojima and Y. Nagai, *J. Organomet. Chem.*, **57**, C42 (1973); (b) T. Mukaiyama, T. Takeda, and K. Atsumi, *Chem. Lett.*, 1013 (1974); (c) T. Mukaiyama, T. Takeda, and K. Atsumi, *ibid.*, 187 (1974); (d) E. W. Abel, D. J. Walker, and J. N. Wingfield, *J. Chem. Soc. A*, 1814 (1968); (e) E. W. Abel and D. J. Walker, *ibid.*, 2338 (1968); (f) K. Itoh, K. Matsuzaki, and Y. Ishii, *J. Chem. Soc., C*, 2709 (1968).

(13) For a brief description of related reversed polarity equivalents see: D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 5 (1974); D. A. Evans, G. C. Andrews, and B. Buckwalter, *J. Am. Chem. Soc.*, **96**, 5560 (1974).

(14) (a) D. A. Evans, L. K. Truesdale, and G. L. Carroll, *J. Chem. Soc., Chem. Commun.*, 55 (1973); (b) D. A. Evans, J. M. Hoffman, and L. K. Truesdale, *J. Am. Chem. Soc.*, **95**, 5822 (1973); (c) D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.*, 4929 (1973); (d) D. A. Evans, G. L. Carroll, and L. K. Truesdale, *J. Org. Chem.*, **39**, 914 (1974); (e) D. A. Evans, L. K. Truesdale, and K. G. Grimm, *ibid.*, **41**, 3335 (1976).

(15) D. A. Evans and K. M. Hurst, unpublished observations. The formation and synthetic utility of phosphonium salts will be published in due course.

(16) L. Birkofer, A. Ritter, and H. Wieden, *Chem. Ber.*, **95**, 971 (1962); L. Birkofer and H. Dickopp, *ibid.*, **101**, 3579 (1968).

(17) A. R. Norris, *Can. J. Chem.*, **45**, 2703 (1967).

(18) D. L. Fowler, W. V. Loebenstein, D. B. Pall, and C. A. Kraus, *J. Am. Chem. Soc.*, **62**, 1140 (1940).

(19) For a convenient synthesis of 18-crown-6 see: G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, *J. Org. Chem.*, **39**, 2445 (1974).

(20) T. Mukaiyama, K. Banno, and K. Narasaka, *J. Am. Chem. Soc.*, **96**, 7503 (1974); K. Narasuka, K. Soia, and T. Mukaiyama, *Chem. Lett.*, 1223 (1974); K. Banno and T. Mukaiyama, *ibid.*, 279 (1976).

(21) D. A. Evans, K. G. Grimm, and L. K. Truesdale, *J. Am. Chem. Soc.*, **97**, 3229 (1975).

(22) J. W. Ralls and B. Riegel, *J. Am. Chem. Soc.*, **76**, 4479 (1954). For a recent highly regioselective thioketalization of **50** see J. R. Williams and G. M. Sarkisian, *Synthesis*, 32 (1974).

(23) For recent innovations in the design of ketals which may be removed under nonacidic conditions see: E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 3775 (1975); J. L. Isidor and R. M. Carlson, *J. Org. Chem.*, **38**, 554 (1973); E. J. Corey and R. A. Ruden, *ibid.*, **38**, 834 (1973); J. Hebart and D. Gavel, *Can. J. Chem.*, **52**, 187 (1974).

(24) T. H. Chan and B. S. Ong, *Tetrahedron Lett.*, 319 (1976).

(25) As a cautionary note, in those thiosilane syntheses which involve amine-catalyzed thiol silylation (cf. ref 10d), trace amine contamination in the

$$2\ \mathrm{RSH} + (\mathrm{Me_3Si})_2\mathrm{NH} \xrightarrow{\text{imidazole}} 2\ \mathrm{RSSiMe_3} + \mathrm{NH_3}$$

product can lead to spurious results wherein *O*-silylhemithioketals are produced under attempted acid-catalyzed thioketalization.

(26) R. S. Glass, *Synth. Commun.*, **6**, 47 (1976). Professor Glass has kindly informed us that these thermal and imidazole-catalyzed thiosilane carbonyl insertion reactions do not appear to be general for ketonic substrates.

(27) Cf. M. F. Lappert and B. Prokai, *Adv. Organomet. Chem.*, **5**, 225 (1967).

(28) M. Rimpler, *Chem. Ber.*, **99**, 128 (1966).

(29) L. Wolinski, H. Tieckelman, and H. W. Post, *J. Org. Chem.*, **16**, 1134 (1951).

(30) Ethyl pentanoate shows no reaction with thiosilanes in the presence of zinc iodide (Et_2O, 25 °C) after 24 h.

(31) M. M. G. Dousse and J. Satge, *Recl. Trav. Chim. Pays-Bas*, **90**, 221 (1971).

(32) S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

(33) E. W. Abel, *J. Chem. Soc.*, 4406 (1960).

Reactions of Fluoroethylenes with Strong Bases in the Gas Phase

S. A. Sullivan and J. L. Beauchamp*[1]

Contribution No. 5468 from the Arthur Amos Noyes Laboratory of Chemical Physics,
California Institute of Technology, Pasadena, California 91125.

Received December 27, 1976

Abstract: Ion cyclotron resonance spectroscopy (ICR) has been used to examine reactions of fluoroethylenes with strong bases in the gas phase. Observed reaction types include proton transfer, elimination, and nucleophilic attack leading to substitution and elimination. The latter yields enolate anions as ionic products. Product distributions are determined for reactions of fluoroethylenes with CD_3O^-, $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, $(CH_3)_3CO^-$, and F^-. Acidities of fluoroolefins relative to alcohols and fluoroethanes are reported. Rates for the nucleophilic addition reaction of CF_2CF_2 with alkoxide ions have been measured. In addition, reactions of a series of perhalogenated chlorofluoro- and bromofluoroolefins with CD_3O^- have been studied. Probable mechanisms of the elimination and nucleophilic addition reactions are discussed in terms of observed reactivity.

Introduction

There is evidence for the intermediacy of charged species in many chemical transformations.[2] Accordingly, reactivity is often explained in terms of the thermodynamic stabilities and charge distributions of such intermediates. In solution, the medium of most ionic reactions, these properties are strongly moderated by solvation. Studies of gas phase ionic reactions allow a correlation between intrinsic molecular properties and reactivity. Ion cyclotron resonance spectroscopy (ICR) is well suited for such investigations.

Recently we examined gas phase reactions of fluoroethanes with strong bases such as NH_2^-, OH^-, F^-, and RO^- (R =

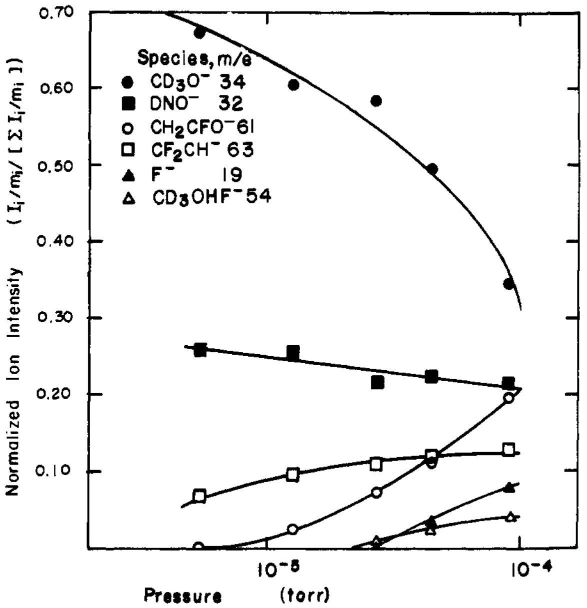
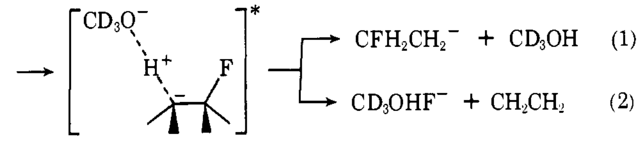


Figure 1. Variation of normalized ion intensity in a mixture of CD_3ONO (2×10^{-6} Torr) and CF_2CH_2, as a function of olefin pressure.

alkyl).[3,4] A competition between proton transfer (eq 1) and elimination of HF (eq 2) results from decomposition of the

$CD_3O^- + CFH_2CH_3$



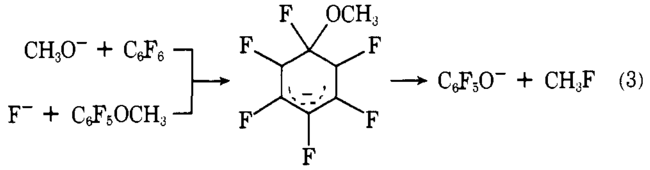
$$\rightarrow CFH_2CH_2^- + CD_3OH \quad (1)$$

$$\rightarrow CD_3OHF^- + CH_2CH_2 \quad (2)$$

I

chemically activated intermediate I formed by interaction of base with an acidic hydrogen of the fluoroethane. Product distributions are determined largely by relative acidities of the fluoroethanes and the conjugate acids of the reactant bases. Elimination becomes more important as attacking base strength decreases. The process leading to elimination (eq 2) is rendered exothermic by hydrogen bond formation between the alcohol and F^-. This bond strength increases as acidity of the alcohol increases.[5]

In a study of reactivity of alkoxide anions with fluorinated benzenes in the gas phase,[6] proton transfer products as well as fluorinated phenoxide ions (e.g., eq 3) were observed. The

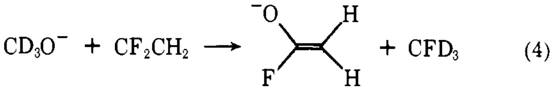


$$CH_3O^- + C_6F_6 \rightarrow \mathrm{II};\quad F^- + C_6F_5OCH_3 \rightarrow \mathrm{II};\quad \mathrm{II} \rightarrow C_6F_5O^- + CH_3F \quad (3)$$

II

latter reaction is apparently initiated by nucleophilic attack of base at carbon as in II. The observation of the same ionic product $C_6F_5O^-$ from reaction of F^- with pentafluoroanisole[7] (eq 3) suggests that II is intermediate in both instances.

The present report details a study of reactivity of strong bases with fluoroethylenes. In addition to expected proton transfer and elimination reactions, processes analogous to reaction 3 are observed, resulting in formation of fluoroenolate anions as indicated in eq 4 for reaction of CH_3O^- with CF_2CH_2.



$$CD_3O^- + CF_2CH_2 \rightarrow {}^-O(F)C{=}CH_2 + CFD_3 \quad (4)$$

Experimental Section

Experiments were performed using an ICR spectrometer, built in this laboratory, incorporating a 15-in. magnet. Instrumentation and techniques of ICR have been detailed elsewhere.[8]

Product distributions were obtained from drift mode experiments,[9] in which precursors of reagent bases were admitted to the analyzer and maintained at constant pressure ($\sim 10^{-6}$ Torr). This was followed by addition of fluoroethylene through another inlet. Ion intensities were then measured as a function of olefin pressure, which was varied between 10^{-6} and 10^{-4} Torr. Reported product distributions were measured at $\sim 10^{-4}$ Torr.

Relative acidities were determined using double resonance techniques,[10] which indicate the preferred direction of proton transfer. In these experiments the two neutrals to be compared and precursors of the reagent ions were admitted through three inlets with independent pressure control.

Trapped ion techniques[11] were used to determine reaction rates of the alkoxide ions with CF_2CF_2. The total pressure typically employed is 3×10^{-6} Torr. Alkoxide ions were produced from alkyl nitrites[12] by attachment of thermalized trapped electrons provided by impact of a 70-eV electron beam. Fluoride ion was similarly generated from NF_3. Since alkoxides react with the precursor nitrite,[3,4] the ratio of nitrite to CF_2CF_2 was kept low to minimize interfering reactions. Because of simultaneous production of HNO^- and CH_3O^-, both *m/e* 31, from CH_3ONO, CD_3ONO is employed to avoid attributing reactions of HNO^- to CH_3O^-.

Pressure measurements were made using a Schulz-Phelps ion gauge, calibrated against an MKS baratron Model 90H1-E capacitance manometer at higher pressures. Alkyl nitrites may be pyrolyzed on the heated gauge filament.[13] To minimize decomposition, the ion gauge was turned off and allowed to cool before spectra were taken.

Alkyl nitrites were prepared using standard methods.[14] All halogenated ethylenes except $CFHCH_2$ and CF_2CH_2 (Matheson) were obtained from PCR. Noncondensable impurities were removed by repeated freeze-pump-thaw cycles. Purities were found to be acceptable by mass spectral analysis. The isomeric purity and identities of the difluoroethylenes were checked by GLC analysis and ^1H nmr.[15]

Results

General Reactivity of Fluoroethylenes and Alkoxide Ions. Reactions of fluoroolefins with alkoxide ions are exemplified by considering the reactions of CF_2CH_2 with CD_3O^-. As CF_2CH_2 is added to CD_3ONO, the ions F^- (*m/e* 19), CD_3OHF^- (*m/e* 54), CH_2CFO^- (*m/e* 61), and CF_2CH^- (*m/e* 63) appear as the intensity of CD_3O^- (*m/e* 34) decreases (Figure 1). Double resonance indicates that CD_3O^- is the sole precursor of all product ions, suggesting reactions 5–8, where neutral products are assumed.

$$CF_2CH_2 + CD_3O^- \begin{cases} \xrightarrow{0.09} CD_3OH + CF_2CH^- & (5) \\ \xrightarrow{0.30} CFCH + CD_3OHF^- & (6) \\ \xrightarrow{0.08} CD_3OH + CFCH + F^- & (7) \\ \xrightarrow{0.53} CFD_3 + CH_2CFO^- & (8) \end{cases}$$

Reactions 5 and 6 correspond to proton transfer and elimination of HF, respectively. The production of F^- is shown as an elimination in reaction 7. Another possible neutral product, CD_3OCFCH_2, would be the result of a substitution mechanism.[3,4] Reaction 8 can be described as nucleophilic addition followed by loss of methyl fluoride. No further reactions of any product ions were observed. Product distributions for reactions of fluoroethylenes with CD_3O^-, $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, $(CH_3)_3CO^-$, and F^- are presented in Table I. A qualitative measure of relative rates is given in Table I as the conversion of ionic reactants to observed products at 10^{-4} Torr.

Only 20% conversion to products is observed in reaction of CD_3O^- which $CFHCH_2$, which does not react at all with weaker bases. All bases except CD_3O^- react with CF_2CH_2 exclusively by nucleophilic addition. With *cis*-CFHCFH

Table I. Product Distributions for Reactions of Bases with Fluoroethylenes[a]

Fluoroethylene	Base[b]	Double resonance[c]	Proton transfer	Elimination	Nucleophilic addition	% convrn[d]
$CFHCH_2$	CD_3O^{-}[e]	+	0.12	0.81		20
	$CH_3CH_2O^-$		No reaction			
	$(CH_3)_2CHO^-$		No reaction			
CF_2CH_2	CD_3O^{-}[e]	+	0.09	0.33	0.53	52
	$CH_3CH_2O^-$				1.00	14
	$(CH_3)_2CHO^-$				1.00	19
	$(CH_3)_3CO^-$				1.00	5
	F^-	+	1.00			3
cis-CFHCFH	CD_3O^-	−	1.00			70
	$CH_3CH_2O^-$	+	0.71	0.18	0.11	45
	$(CH_3)_2CHO^-$	+	0.33	0.51	0.16	15
	$(CH_3)_3CO^-$			1.00		3
	F^-	+	0.14	0.86		18
trans-CFHCFH	CD_3O^-	−	1.00			78
	$CH_3CH_2O^-$	+	1.00			24
	$(CH_3)_2CHO^-$	+	1.00			8
	$(CH_3)_3CO^-$	+	1.00			4
	F^-	+	1.00			11
CF_2CFH	CD_3O^-	−	1.00			78
	$CH_3CH_2O^-$	−	1.00			85
	$(CH_3)_2CHO^-$	−	1.00			70
	$(CH_3)_3CO^-$	−	1.00			78
	F^-	+	1.00			33

[a] Product ion abundance normalized to 1.00. [b] Bases listed in order of decreasing base strength. CD_3O^- was used to avoid interference from HNO^- (see text). [c] The sign of double resonance for the proton transfer reactions is indicated by + and −, indicating rates which increase and decrease, respectively, with increasing reactant ion kinetic energy. [d] Percent conversion of reactants to products, at 10^{-4} Torr. [e] F^- was observed as a minor product in reaction of $CD_3O^{-}\cdot$ with $CFHCH_2$ (0.07) and CF_2CH_2 (0.05).

proton transfer occurs in competition with elimination of HF and to a lesser extent nucleophilic addition. In contrast, CF_2CFH and *trans*-CFHCFH react only by proton transfer.

Acidities of Fluoroethylenes. Relative acidities of the fluoroolefins are presented in Table II. The order of acidities, which is determined by double resonance experiments in mixtures of olefins and alcohols is $H_2O < CFHCH_2 < CF_2CH_2 < CH_3OH <$ *cis*-CFHCFH, *trans*-CFHCFH $< CH_3CH_2OH < (CH_3)_3COH < CF_2CFH < HF$. This ordering of relative acidities predicts that certain of the observed proton transfer reactions, summarized in Table I, are endothermic. In all cases in which proton transfer reactions are predicted to be endothermic, an increase in product ion intensity is observed on an increase in reactant ion kinetic energy (positive double resonance[8,10]). In contrast, all other reactions observed in these systems show negative double resonance signals, indicating rate constants which decrease with increasing ion kinetic energy. For example, $(CH_3)_3CO^-$, generated from the alkyl nitrite, reacts with *trans*-CFHCFH by proton transfer. In a mixture of CD_3ONO, $(CH_3)_3COH$, and *trans*-CFHCFH, in which $(CH_3)_3CO^-$ and *trans*-$CFHCF^-$ are formed by reaction with CD_3O^-, *trans*-$CFHCF^-$ reacts with $(CH_3)_3COH$ by proton transfer with no reverse reaction of $(CH_3)_3CO^-$ with *trans*-CFHCFH observed. In this case reaction is indicated by a decrease in $(CH_3)_3CO^-$ ion intensity as the kinetic energy of *trans*-$CFHCF^-$ is increased. It appears that alkoxides and F^- generated from alkyl nitrites and NF_3, respectively, retain excess energy,[16] which is not effectively quenched in nonreactive collisions[17] with the neutrals present.

Nucleophilic Substitution Reactions of Perhalogenated Olefins with Alkoxide Ions. Alkoxide ions react with CF_2CF_2 only by nucleophilic substitution as in eq 9. Rates of these reactions are measured and presented in Table III along with calculated Langevin rates.[8,18] Reaction rates increase in the order $CD_3O^- < CH_3CH_2O^- < (CH_3)_2CHO^-$, with the reaction of $(CH_3)_2CHO^-$ proceeding at approximately the calculated collision rate. This trend does not continue for $(CH_3)_3CO^-$, which reacts somewhat slower than $(CH_3)_2CHO^-$.

$$RO^- + CF_2CF_2 \rightarrow CF_2CFO^- + RF \qquad (9)$$

$$R = CD_3, CH_3CH_2, (CH_3)_2CH, (CH_3)_3C$$

To further examine the mechanism of nucleophilic addition and determine if loss of RCl and RBr compete with loss of RF, a series of perhalogenated olefins were examined including CF_2CFCl (eq 10), CF_2CCl_2 (eq 11), cis/trans mixture of CFClCFCl (eq 12), and CF_2CFBr (eq 13). Loss of X^- (X = F, Cl, Br), resulting from simple nucleophilic substitution, is expected to be more favorable for Cl and Br compounds.[19] All of these compounds react with CD_3O^- to produce only enolate anions, resulting as noted from loss of CD_3F in eq 10-13. No reaction is observed with CCl_2CCl_2.

$$CF_2CFCl + CD_3O^- \rightarrow CFClCFO^- + CD_3F \qquad (10)$$

$$CF_2CCl_2 + CD_3O^- \rightarrow CCl_2CFO^- + CD_3F \qquad (11)$$

$$CFClCFCl + CD_3O^- \rightarrow CFClCClO^- + CD_3F \qquad (12)$$

$$CF_2CFBr + CD_3O^- \rightarrow CFBrCFO^- + CD_3F \qquad (13)$$

Discussion

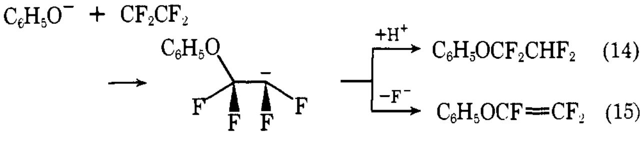
The position and number of substituent fluorines determines the reactivity of fluoroolefins. Base attack at the two favorable sites, which are the most acidic hydrogen or the more electropositive olefinic carbon, appears to be affected differently by substitution. By relating patterns of reactivity to the mode of fluorine substitution, it may be possible to define the stabilizing effect of F in anions and radicals and begin to understand mechanisms of these ion-molecule reactions.

Nucleophilic Substitution. It is known that fluoroethylenes are susceptible to nucleophilic attack in solution.[20-22] The observed products can be explained by the dissociation (eq 14)

Table II. Acidities of Fluoroethylenes[a]

BH	PA(B^-)[b]
H_2O	390.6 ± 1.0[c]
$CFHCH_2$, CF_2CH_2	380[d]
CH_3OH	378.3 ± 0.8
cis-CFHCFH, *trans*-CFHCFH	377[e]
CH_3CH_2OH	375.4 ± 0.7
CFH_2CH_3, CF_2HCH_3, CF_3CH_3	374[e]
$(CH_3)_2CHOH$	373.5 ± 0.7
$(CH_3)_3COH$	372.7 ± 0.6
CF_2HCFH_2	372
CF_2HCF_2H, CF_3CFH_2	372
CF_2CFH	372
CF_3CF_2H	372
HF	371.3 ± 0.5[c]

[a] The proton affinity (PA) of B^- is defined as the enthalpy for reaction BH → $B^- + H^+$. The acidity of BH increases as PA(B^-) decreases. [b] All values in kcal/mol at 298 K. The proton affinities of the alkoxides are from R. T. McIver and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 4323 (1974), with corrections to the original values from J. S. Miller, private communication. The ordering of fluoroethyl carbanions is taken from ref 3. Proton affinities of fluorovinyl carbanions are estimates based on the relative acidities of fluoroethylenes to alcohols and fluoroethanes (see text). [c] Calculated using thermochemical data from ref 27. The $\Delta H_f(F^-)$ has been corrected for a revised EA(F·) = 3.398 ± 0.002 eV, from R. Milstein and R. S. Berry, *J. Chem. Phys.*, **55**, 4146 (1971). [d] The observation of proton transfer from $CFHCH_2$ and CF_2H_2 to CD_3O^-, which is generated from CD_3ONO, suggests that the proton affinities of corresponding fluorovinyl carbanions are at most ~2–3 kcal/mol higher than PA(CH_3O^-). [e] The ordering of these compounds has not been established.



III

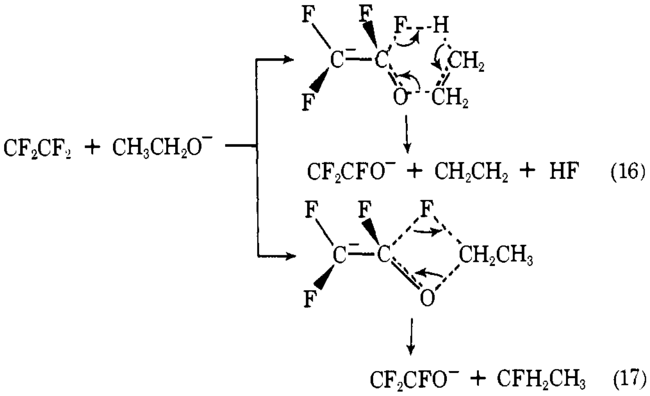
or further reaction (eq 15) of an intermediate anion formed as in II for the reaction $CF_2{=}CF_2$ with $C_6H_5O^-$.[21] The intermediacy of such anions is suggested by the parallel between reactivity and expected stability of the intermediate. In general, fluorinated olefins are more reactive toward nucleophiles than other halogenated olefins in solution. Attack occurs at the more electropositive carbon, which in most cases is a geminal difluoro carbon. Gas phase nucleophilic reactions of alkoxides with fluoroolefins resemble solution reactions. Products result from the rearrangement (eq 9) of intermediate anions similar to III. Preferential attack at the geminal difluoro group is suggested by the relative reactivities of difluoroethanes (CF_2CH_2 > *cis*-CFHCFH > *trans*-CFHCFH). The increased lability of the proton and the increase in the C-F bond strength explain the absence of nucleophilic reaction with CF_2CFH. Surprisingly, direct nucleophilic substitution, production of F^-, Cl^-, and Br^-, does not compete with the rearrangement and loss of RF for any perhalogenated olefins examined.

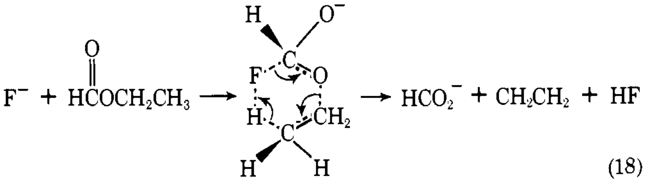
Table III. Rates for Reaction 9 of Alkoxide Ions with CF_2CF_2

Alkoxide	Experimental rate (k_e) × 10^{10} $cm^3\ mol^{-1}\ s^{-1}$	Collision rate (k_c)[a] × 10^{10} $cm^3\ mol^{-1}\ s^{-1}$	k_e/k_c
CD_3O^-	1.02 ± 0.22	9.52	0.11
$CH_3CH_2O^-$	2.72 ± 0.36	8.61	0.32
$CD_3CH_2O^-$	2.87 ± 0.54	8.42	0.34
$(CH_3)_2CHO^-$	7.51 ± 0.20	7.87	0.95
$(CH_3)_3CO^-$	2.93 ± 0.29	7.38	0.40

[a] The collision rate, k_c, is calculated using $k_c = 2\pi e(\alpha/\mu)^{1/2}$, where α is the polarizability of the neutral molecule and μ the reduced mass of reaction ion–molecule pair. A calculated value of 41.99 × 10^{-25} cm^3 was used for $\alpha(CF_2CF_2)$ from E. R. Lippincott, G. Nagarajan, and J. M. Stutman, *J. Phys. Chem.*, **70**, 78 (1966).

For bases other than CD_3O^-, there are two reasonable rearrangements of the intermediate leading to identical ionic products with different neutral products as in eq 16 (six-center rearrangement) and eq 17 (four-center rearrangement) for CF_2CF_2 with $CH_3CH_2O^-$. Reaction 17 is more exothermic than reaction 16 by the ΔH of elimination of HF from CFH_2CH_3 (12.5 kcal/mol).[23] However, a six-center rearrangement is likely to be more facile and has been suggested by rate measurements for the similar reactions of F^- with alkyl formates, for example, eq 18 with ethyl formate.[24] In these experiments a rate increase was seen as a function of the number of β hydrogens in the alkyl formate. Significantly, in the case of reaction 9, rate increases with increasing number of β hydrogens as expected for a six-center rearrangement. However, the rate of reaction of $(CH_3)_3CO^-$ with 9 β hydrogens drops sharply from that of $(CH_3)_2CHO^-$. In varying the number of β hydrogens by changing the alkyl group of the base, the base strength and size of the reactant is also changed. Both of these factors can influence reaction rate. The observation of significant reaction with CD_3O^- necessitates a four-center rearrangement mechanism. The rate determinations suggest that for higher alkyl substitution both mechanisms may occur.





Proton Transfer. The acidities of fluoroolefins have been compared to those of the fluoroethanes and alcohols in Table II. Substitution of F in CH_2CH_2 results in ≥24 kcal/mol increase in acidity for $CFHCH_2$ compared to CH_2CH_2.[25] Further F substitution increases acidity only slightly, with a range of 10 kcal/mol for all fluoroethylenes. Similarly, substitution of one F in CH_3CH_3 has the largest effect on acidity, with the range of proton affinities for all fluoroethyl anions being ~4 kcal/mol.

The proton affinity of an anion (B^-) is related to the homolytic bond energy D(BH) and the electron affinity EA(B^-) by eq 19 in which the ionization potential of H, IP(H)

$$PA(B^-) = D(B\text{-}H) - EA(B^-) + IP(H) \qquad (19)$$

= 313.6 kcal/mol. Relative proton affinities or acidities are the result of differences in bond strength and electron affinity, which reflect the stability of the radical B and the anion B^-, respectively. A weaker C-H bond strength and a higher electron affinity indicate increased stability of the radical and ion, respectively. The small differences in acidities of fluoroethanes

Table IV. Hydrogen Bond Strength in BHF^- [a]

BH	$D(BH\cdots F^-)$ limits[b] Lower	Upper	$D(B^-\cdots HF)$ limits[c] Lower	Upper
H_2O[d]	17	26	35.7	44.7
CH_3OH	30	39	37	46
CH_3CH_2OH	32	41	36.1	45
$(CH_3)_2CHOH$	33	42	35.2	44.2
$(CH_3)_3COH$	34	43	35.4	44.4
HF	44	50	44	50

[a] Bond strengths in kcal/mol at 298 K. [b] Limits from ref 3. [c] Calculated using $D(B^- - HF) = D(BH - F^-) + PA(B^-) - PA(F^-)$ with proton affinities from Table II. [d] Experimental values of $D(H_2O - F^-) = 23$ kcal/mol and $D(HF - OH^-) = 44$ kcal/mol are reported in ref 5.

Table V. Thermodynamic Properties of Fluoroethylenes and Acetylenes[a]

	ΔH_f[b]	ΔH elimination of HF[c]
$CFHCH_2$	-33.2 ± 0.4	22.3 ± 0.8
CF_2CH_2	-82.5 ± 2.4	47, 33[h]
cis-CFHCFH	>-81[d]	46, 32[h]
trans-CFHCFH	>-80[d]	45, 31[h]
CF_2CFH	-118.5 ± 0.7	58, 23[h]
CF_2CF_2	-157.6 ± 1.1	
CFCH	30 ± 15[e] (16.1)[f] (>28)[g]	
CFCF	5 ± 15[e] (−30.5)[f] (<1.6)[g]	

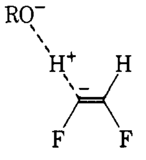
[a] All values in kcal/mol at 298 K. [b] Heats of formation for the fluoroethylenes are taken from J. R. Skinner and H. A. Lacher, *J. Chem. Soc. A*, 1034 (1968); D. P. Ridge, *J. Am. Chem. Soc.*, **97**, 5670 (1975), and references therein. [c] Enthalpy for removal of HF from fluoroethylenes, calculated using data in this table and $\Delta H_f(HF) = -65.14 \pm 0.2$ kcal/mol, $\Delta H_f(CHCH) = 54.19 \pm 0.19$ kcal/mol from ref 27. [d] Although ΔH_f are not well established, the difference in ΔH_f of the cis and trans isomers has been determined as 0.928 kcal/mol. See, N. C. Craig and E. A. Enteman, *J. Am. Chem. Soc.*, **83**, 3047 (1961). [e] Experimental values from ref 27. [f] Calculated values from ref 28. [g] Limits set by the present study (see text). [h] Computed using calculated values for ΔH_f of fluoroacetylenes.

appear to result from comparable but opposing changes in stabilities of both radicals and anions. For fluoroethanes, only $D(CF_3CH_2-H) = 106.7 \pm 1.1$ kcal/mol and $D(CF_3CF_2-H) = 103.0 \pm 1.0$ kcal/mol are available. Using the proton affinities in Table II, $EA(CF_3CH_2^-)$ is estimated to be 1.7 kcal/mol higher than $EA(CF_3CF_2^-)$. Fluoroethylenes are generally less acidic than fluoroethanes, with $PA(CFHCH^-)$ 6 kcal/mol greater than $PA(CFH_2CH_2^-)$. Using hybridization arguments, the C-H bond in $CFHCH_2$ is expected to be stronger than the C-H bond in CFH_2CH_3. An estimate of this difference is 10 kcal/mol $[D(CH_2CH-H) - D(CH_3CH_2-H)]$.[23] Again small changes both in radical and anion stabilities affect acidity. Unfortunately, bond strengths and electron affinities for fluoroethylenes and the other fluoroethanes are not known, making quantitative comparisons of the stabilizing effects of F in radicals and carbanions impossible at this time.

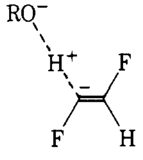
Elimination. Elimination of HF from fluoroethylenes by alkoxides and F^- results in formation of proton bound dimers $ROHF^-$ (R = alkyl) and FHF^-. Hydrogen bond strengths in these species have been estimated previously (Table IV). The heat of elimination of HF from each fluoroolefin has been determined from available thermochemical data and summarized in Table V. It should be noted that heats of formation of fluoroacetylenes, as well as several of the fluoroethylenes, are not well known. Comparison of the heats of elimination to the strength of the bond between HF and the base indicates that elimination of HF should be exothermic for all of the bases reacting with $CFHCH_2$. Considering the uncertainties in the thermochemical data, the difluoroolefins might all be expected to eliminate HF in these reactions. Elimination occurs from all olefins except CF_2CFH and *trans*-CFHCFH, which both react only by proton transfer. If it is assumed that the absence of elimination from CF_2CFH is due to the endothermicity of the process, a lower limit of 1.6 kcal/mol can be set for the heat of formation of CFCF. This can be compared to experimental[27] and calculated[28] values of 5 ± 15 and -30.5 kcal/mol. The observation of elimination from CF_2CH_2 sets an upper limit of 28 kcal/mol on the heat of formation of CFCH. This compares with experimental[27] and calculated[28] values of 30 ± 15 and 16.1 kcal/mol.

The surprising difference in reactivity of *cis*-CFHCFH and *trans*-CFHCFH cannot be rationalized on the basis of the thermochemistry of the reactants. The identities and purities of these olefins were carefully checked. In addition, the marked variation in reactivities of the two compounds precludes isomerization on the surfaces within the analyzer. The reactivity pattern suggests some fundamental difference in the interaction of *cis*-CFHCFH and *trans*-CFHCFH with anionic bases.

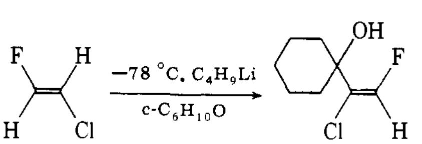
Elimination can be visualized as resulting from initial attack at the acidic hydrogen resulting in intermediates that will retain isomeric structure as in IV and V for the cis and trans isomers, respectively. To be consistent with results, a trans elimination of F is required from IV, whereas the apparently more facile cis elimination from V cannot occur. In these proton-bound dimer intermediates it is possible that the F trans to the site of base attack has a larger portion of the distributed negative charge, making it more labile than a cis F. Solution results[20,29] also reflect a difference in reactivity between fluorinated geometrical isomers. For example, under the same experimental conditions, metalation of *cis*-CFHCClH and *trans*-CFHCClH with C_4H_9Li followed by addition of cyclohexanone gave different final products. *trans*-CClHCFH with F cis to the labile hydrogen reacts only by addition of cyclohexanone (eq 20). In *cis*-CFHCClH the final product (eq 21) results from an intermediate elimination of F, suggesting a labilization of the trans F.



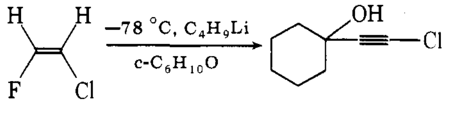
IV



V



(20)



(21)

A significant difference between the interaction of the *cis*-CFHCFH and *trans*-CFHCFH with ions is the polarity of the two neutrals.[30] Calculations by Dugan, Rice, and Magee[31] indicate that ion-polar molecule collision complexes have longer lifetimes than those of ion-nonpolar molecules. The dynamical constraints on dissociation of the ion-polar molecule complex are more severe and several secondary encounters may occur before the products separate. It is possible that for the *cis*-CFHCFH these secondary encounters allow F^- to be transferred to the alcohol, resulting in an apparent trans elimination of HF.

Acknowledgment. This research was supported in part by the Energy Research and Development Administration under Grant No. AT(04-3)767-8.

References and Notes

(1) Camille and Henry Dreyfus Teacher-Scholar, 1971-1976.
(2) For example, see J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure", McGraw-Hill, New York, N.Y., 1968, Chapter 7.
(3) S. A. Sullivan and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 1160 (1976).
(4) D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 3595 (1974).
(5) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **93**, 7139 (1971).
(6) S. M. J. Briscese and J. M. Riveros, *J. Am. Chem. Soc.*, **97**, 230 (1975).
(7) S. A. Sullivan and J. L. Beauchamp, unpublished results.
(8) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1972).
(9) In most cases, product distributions are determined by dividing ion intensity by ion mass (I_i/m_i), however, for low conversion to products it is necessary to divide intensity by ion mass squared (I_i/m_i^2), see D. Holtz, J. L. Beauchamp, and J. R. Eyler, *J. Am. Chem. Soc.*, **92**, 7045 (1970).
(10) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).
(11) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).
(12) K. Jaeger and A. Henglein, *Z. Naturforsch. A*, **222**, 700 (1967).
(13) J. B. Levy, *J. Am. Chem. Soc.*, **78**, 1780 (1956).
(14) W. A. Noyes, *Org. Synth.*, **2**, 108 (1943).
(15) G. W. Flynn, M. Matsushima, and J. D. Baldeschwieler, *J. Chem. Phys.*, **38**, 2295 (1963).
(16) Alkoxides generated from alkyl nitrites have previously been observed to undergo endothermic proton transfer reactions. See ref 6.
(17) V. G. Anicish and M. T. Bowers, *J. Am. Chem. Soc.*, **96**, 1279 (1974).
(18) E. W. McDaniel, "Collision Phenomenon in Ionized Gases", Wiley, New York, N.Y., 1964.
(19) Although $\Delta H_f(X^-)$ decreases slightly for the series Br > Cl > F, the large increase expected in D(C–X) for vinyl halides (Br < Cl < F) makes loss of X^- most probable from CH_2CHBr. $D(CH_2CH{-}Br)$, $D(CH_2CH{-}Cl)$, and $D(CH_2CH{-}F)$ have been calculated as 76, 88, and 119 kcal/mol, respectively, using thermochemical data in ref 23 and 27.
(20) Reactivity of fluoroolefins is summarized in R. D. Chambers, "Fluorine in Organic Chemistry", Wiley-Interscience, New York, N.Y., 1973 and W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969.
(21) D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **82**, 5116 (1960).
(22) J. D. Park, M. L. Sharrah, W. H. Breen, and J. R. Lacher, *J. Am. Chem. Soc.*, **73**, 1329 (1951).
(23) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
(24) J. F. G. Faigle, P. C. Isolani, and J. M. Riveros, *J. Am. Chem. Soc.*, **98**, 2049 (1976).
(25) Bohme reports that $C_2H_3^- + NH_3 \rightarrow NH_2^- + C_2H_4$ is the preferred direction for proton transfer, therefore, $PA(C_2H_3^-) \geq 404$ kcal/mol. See D. K. Bohme, E. Lee-Ruff, and L. B. Young, *J. Am. Chem. Soc.*, **94**, 5153 (1972).
(26) $D(CF_2CH_2{-}H)$ and $D(CF_3CF_2{-}H)$ have been determined in E. C. Wu and A. S. Rodgers, *J. Phys. Chem.*, **78**, 2315 (1974), and T. E. Basset and E. Whittle, *J. Chem. Soc., Faraday Trans. 1*, **68**, 492 (1972), respectively.
(27) D. R. Stull and H. Prophet, "JANAP Thermochemical Tables", 2nd ed, National Bureau of Standards, Washington, D.C., 1971.
(28) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1307 (1975).
(29) S. Y. Delavarenne and H. G. Viehe, Abstracts, Fourth International Symposium on Fluorine Chemistry, Estes Park (American Chemical Society), 1967, p 122.
(30) Dipole moments of CF_2CH_2, *cis*-CFHCFH, and *trans*-CFHCFH are 1.37, 2.42, and 0.00 D, respectively. See A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, Calif., 1963.
(31) J. V. Dugan, Jr., J. H. Rice, and J. L. Magee, *Chem. Phys. Lett.*, **3**, 323 (1969); see also, J. V. Dugan, Jr., and J. L. Magee, *J. Chem. Phys.*, **47**, 3103 (1967); P. P. Dymerski, R. C. Dunbar, and J. V. Dugan, Jr., *J. Chem. Phys.*, **61**, 298 (1974).

Aromatic Substitution in the Gas Phase. Ambident Behavior of Phenol toward t-$C_4H_9^+$ Cations

Marina Attinà, Fulvio Cacace,* Giovanna Ciranni, and Pierluigi Giacomello

Contribution from the University of Rome, 00100 Rome, Italy. *Received August 2, 1976*

Abstract: The reactivity of phenol toward t-$C_4H_9^+$ cations, obtained in the dilute gas state from the γ-radiolysis of neopentane, is characterized by a typical ambident behavior. The competition between the n-type and the π-type nucleophilic centers of the substrate is kinetically biased in favor of O-alkylation, leading to the predominant (ca. 8:1) formation of *tert*-butyl phenyl ether with respect to *tert*-butylphenols under conditions, i.e., high neopentane pressure and the presence of a gaseous base (NH_3), which favor kinetic control of products. Ring-alkylated arenium ions appear, however, to be more stable than the isomeric oxonium ion, as indicated by the higher yields of *tert*-butylphenols under conditions of increasing thermodynamic control of products, reaching a 4:1 excess over the ether at the lowest pressure investigated (20 Torr). The results of competition experiments show that phenol reacts faster than toluene with gaseous t-$C_4H_9^+$, the apparent $k_{\text{phenol}}:k_{\text{toluene}}$ ratio ranging from 2.0 to 4.4. The isomeric composition of ring-alkylated products underlines the electrophilic character and the remarkable *positional* selectivity of the t-$C_4H_9^+$ attack, yielding exclusively ortho- and para-substituted isomers, whose ratio depends on the pressure of the system and the presence of NH_3. Thus, the ortho:para ratio, that reaches a 0.4 value under conditions of kinetic control of products, decreases as the pressure is lowered, down to the 0.04 value measured at 20 Torr. The mechanism of the gas-phase alkylation, and of the subsequent isomerization processes that appear of intermolecular nature, are discussed and compared with those of related alkylation reactions, both in the gas phase and in solution.

Meaningful comparison of the *intrinsic* reactivity of the oxygen atom (n-type center) and of the ring (π-type center) of phenol and aromatic ethers toward charged electrophiles remains a difficult problem, despite extensive kinetic, spectroscopic, and NMR investigations concerning, in particular, protonation and alkylation.[1-7]

The major difficulty arises from the inherently close reactivity of the substituent group and of the ring, which makes their competition for the electrophile exceedingly sensitive to the reaction environment, especially to solvation and ion-pairing effects, preventing any generalization of the results concerning a specific reaction medium.

The problem of assessing the *intrinsic* reactivity scale of the nucleophilic centers of phenol and related compounds, i.e., of determining a kinetically significant reactivity ratio independent of any particular reaction environment, appears eminently suitable for exploitation of a recently developed technique,[8-10] that allows the study of aromatic substitutions by charged electrophiles in the dilute gas state, in the absence of solvation, counterions, etc., and further permits the direct determination of the *substrate* and *positional* selectivity of the attack.

The present paper deals with the gas-phase alkylation of phenol by the t-$C_4H_9^+$ cation, a relatively mild electrophile,