# ION CYCLOTRON RESONANCE INVESTIGATIONS
# OF NEGATIVE ION-MOLECULE REACTIONS

Thesis by

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For Mom - a beautiful lady, who deserves the best.

## Acknowledgment

## Abstract

### Chapter I

Ion cyclotron resonance techniques are employed in the examination of the gas phase reactions of $PF_3$ and $OPF_3$ with anionic bases, including $NH_2^-$, $OH^-$, $CH_3CH_2O^-$, $HNO^-$, $HS^-$, $SF_6^-$, and $SF_5^-$. Evidence is presented which suggests that all reactions proceed by initial attack at phosphorous, with products resulting from decomposition of chemically activated intermediates. The energetics of intermediates inferred in these processes are related to the Lewis acidities of $OPF_3$ and $PF_3$. With fluoride ion as a reference base, $OPF_3$ is found to be more acidic than $PF_3$, with $D(OPF_3-F^-) = 58.9 \pm 0.4$ kcal/mole and $D(PF_3-F^-) = 50 \pm 5$ kcal/mol.

### Chapter II

Ion cyclotron resonance techniques are employed to determine the gas phase Brönsted and Lewis acidities as well as the Brönsted basicity of 1-methyl-1,4 dihydroborabenzene, $CH_3BC_5H_6$. The ring proton is found to be highly acidic with $PA(CH_3BC_5H_5) = 337 \pm 3$ kcal/mol. This acidity results from the formation of $6\pi$ electron aromatic anion $CH_3BC_5H_5^-$, which is isoelectronic with toluene. Both the Lewis acidity and proton basicity of the parent molecule suggest that there is little interaction between the diene $\pi$ system and the electron deficient boron. This is further confirmed by the similarity of both negative and positive ion chemistry of the borabenzene to that of aliphatic boranes.

## Chapter III

Ion cyclotron resonance techniques are employed in the investigation of positive and negative ion formation and ion molecule reactions in sulfuryl halides $SO_2XY(X, Y = Cl, F)$. Positive ion reactivity is discussed in terms of the relative Cl and F bond strengths in these species and possible structures of ionic intermediates and products. Electron attachment processes generate halide ion donors such as $F_2^-$, $Cl_2^-$, $SO_2F^-$ and $SO_2Cl^-$ from sulfuryl halides. Negative ion reactivity is dominated by halide transfer reactions. Halide transfer reactions in mixtures with HCN and HCl are examined in an attempt to quantify $D(SO_2-F^-)$ and $D(SO_2-Cl^-)$.

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## Introduction

Ionic species have long been postulated as reaction intermediates in solution.[1] Consequently, reactivity is often described in terms of the stabilities and charge distributions of such intermediates. There is much evidence that solution effects may strongly modify the properties of these species. For this reason, ion cyclotron resonance techniques have been a valuable tool in the investigation of intrinsic molecular properties and reactivity.[2]

A broad and important class of solution reactions initiated by nucleophilic attack are proposed to proceed through anionic intermediates.[1] Gas phase anion reactions not only provide models for solution reactions but provide thermochemical properties (proton and Lewis acidities) which are not modified by solvation effects. In part because of the difficulties in generation of ionic reagents, anionic reactions have not been studied as extensively as positive ion reactivity. Gas phase studies performed relate to the interaction of bases with acidic protons,[4,5,6] anionic nucleophilic attack[7,8,9] and anion exchange reactions.[10,11]

The predominant reaction of an anionic base with an acidic neutral is simple proton transfer. Gas phase proton acidities are inversely related to the proton affinities of the anionic conjugate bases $(B^-)$. The proton affinity $PA(B^-)$ is defined as the enthalpy for reaction 1. Relative proton affinities are measured by determining the

$$BH \longrightarrow B^- + H^+ \qquad\qquad (1)$$

preferred direction of proton transfer (eq 2) in mixtures of neutrals.[2]

$$B^- + AH \;\rightleftharpoons\; A^- + BH \qquad\qquad (2)$$

Ion cyclotron resonance techniques are particularly useful in this regard.[2] Quantitative relative proton affinities result from measurements of $K_{eq}$ (eq 2) using either icr trapping studies[12] or high pressure mass spectrometry.[13] Appendix III provides several tables of relative gas phase acidities of representative compounds including carbon, oxygen and inorganic acids. References included in this appendix provide both discussions of trends in acidities and comparisons to solution results. An interesting reversal is found in the acidities of alcohols. In solution, the acidities of alkyl alcohols generally decrease with increased alkylation $CH_3OH > CH_3CH_2OH > t\text{-}C_4H_9OH$.[1] This is explained in terms of increasing electron donation by the alkyl group.[1,14] The gas phase ordering $tC_4H_9OH > C_7H_5OH > CH_3OH$[14,15] suggests induced dipole effects (which increase with the polarizability of the alkyl group) provide anion stabilization.[14] Comparisons of gas phase and solution acidities provide information on both intrinsic molecular properties and solvation effects.

Strong hydrogen bonds may result from interaction of anionic bases with acidic species. For example, the interaction of alkoxide ions with fluoroalkanes[5,6,7] results in energetic hydrogen bonded intermediates which decompose resulting in proton transfer or HF elimination as in Scheme 1 for $CH_3O^-$ with $CH_3CH_2F$. The energy to

eliminate HF from the alkane is provided by the formation of the hydrogen bond ($\sim 40$ kcal mole$^{-1}$) in the intermediate. There is a general trend favoring elimination as base strength decreases.

Scheme 1

$$CD_3O^- + CFH_2CH_3 \longrightarrow$$



$$CFH_2CH_2^- + CD_3OH$$

$$CD_3OHF^- + CH_2CH_2$$
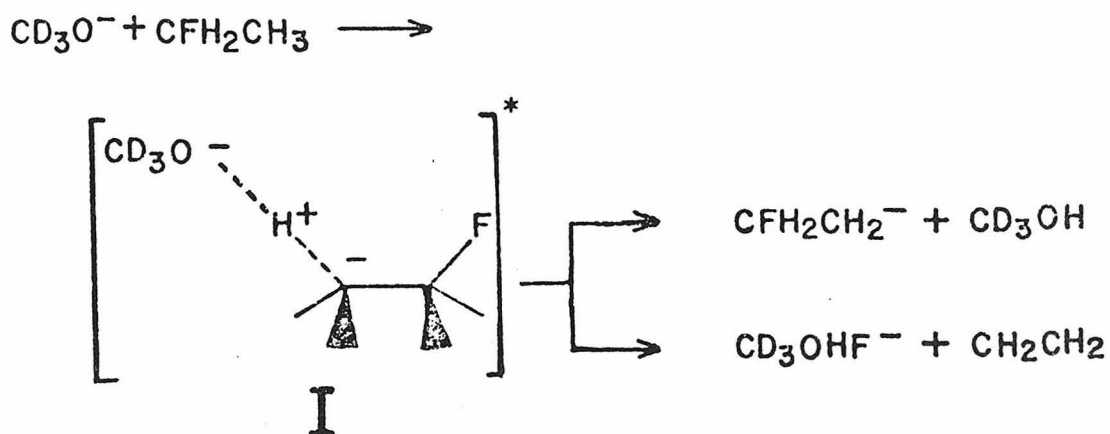
Although the formation of the hydrogen bound anion $CH_3OHF^-$ suggests a $\underline{cis}$ HF elimination from the energetic intermediate (Scheme I), the reactions of fluoroethylenes with gas phase bases suggest a more complicated mechanism.[7] When both $\underline{cis}$ 1,2-difluoro-ethylene and $\underline{trans}$ 1,2-difluoroethylene were treated with $CH_3O^-$, elimination of HF was observed $\underline{only}$ from the $\underline{cis}$ olefin (eq 3).

$$CH_3O^- + \underline{cis}\text{-CFHCFH} \rightarrow CH_3OHF^- + CFCH \qquad (3)$$
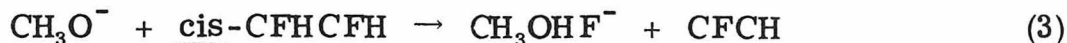
Although there is no thermochemical basis for a differences in reactivity of the isomers, solution results suggest that the F $\underline{trans}$ to the site of negative charge will have a larger portion of distributed electron density.[16] In this case, the formation of $CH_3OHF^-$ is facilitated by the stronger interaction of ions with polar molecules.[17] Such interactions may result in multiple encounters, which would explain formation of $CH_3OHF^-$ through an apparent $\underline{trans}$-elimination.

Nucleophilic anionic attack results in direct substitution reactions (eq 4, for $Cl^-$ with $CH_3Cl$) and more complicated rearrangement processes, exemplified by the generation of the fluoroenolate anion $OCFCF_2^-$ on reaction of $CH_3O^-$ with $CF_2CF_2$ (eq 5).[7] Since a compre-

$$F^- + CH_3Cl \rightarrow F^- \text{---} \overset{\overset{\displaystyle H \quad H}{\diagdown \; \diagup}}{\underset{\displaystyle H}{C}} \text{---} Cl^- \rightarrow CFH_3 + Cl^- \qquad (4)$$

$$CH_3O^- + CF_2CF_2 \rightarrow \quad \underset{\displaystyle \underset{F \diagup \; \diagdown F}{C}}{\overset{\displaystyle \overset{CH_3}{O}}{\underset{\displaystyle F}{\overset{\diagup}{\diagdown}} \; F}} \rightarrow OCFCF_2^- + CH_3F \qquad (5)$$

I
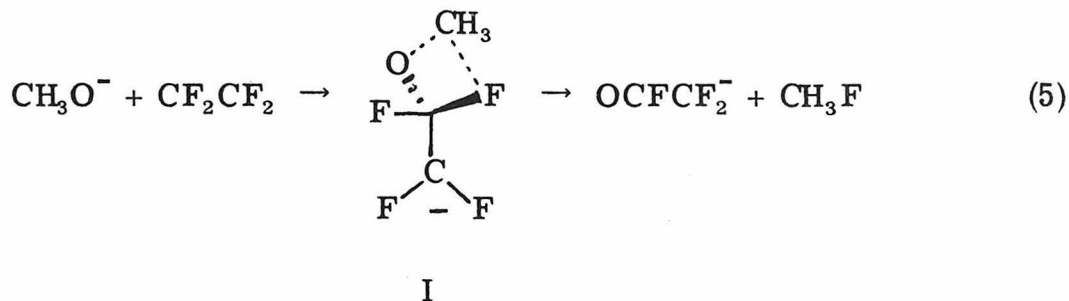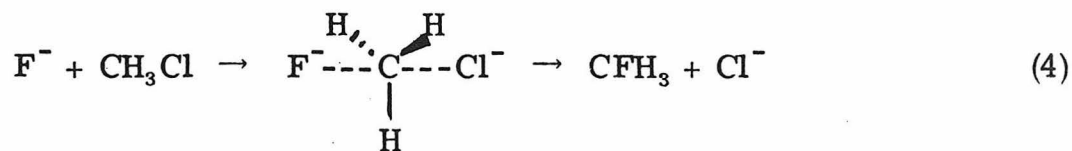
hensive discussion of the mechanism of nucleophilic substitution reactions has been provided recently by Olmstead and Brauman,[18] these reactions will not be discussed further.
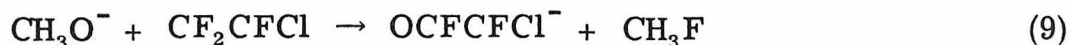
Reaction (4) exemplifies what now appears to be a general reaction of negative ions with a variety of substrates. In this reaction, products apparently result from initial attack at the electropositive carbon (as in I), followed by a 4-center rearrangement to lose $CH_3F$. A similar mechanism is suggested for alkoxide attack on fluorobenzenes.[8] The formation of the same ionic product on reaction of $F^-$ with the pentafluoro anisole (eq 6)[8] and reaction of $CH_3O^-$ with pentafluorobenzene (eq 7),[7] indicates that species II is intermediate



$$CH_3O^- + C_6F_6 \qquad (6)$$

$$\longrightarrow C_6F_5O^- + CH_3F$$

$$F^- + C_6F_5OCH_3 \qquad (7)$$

II
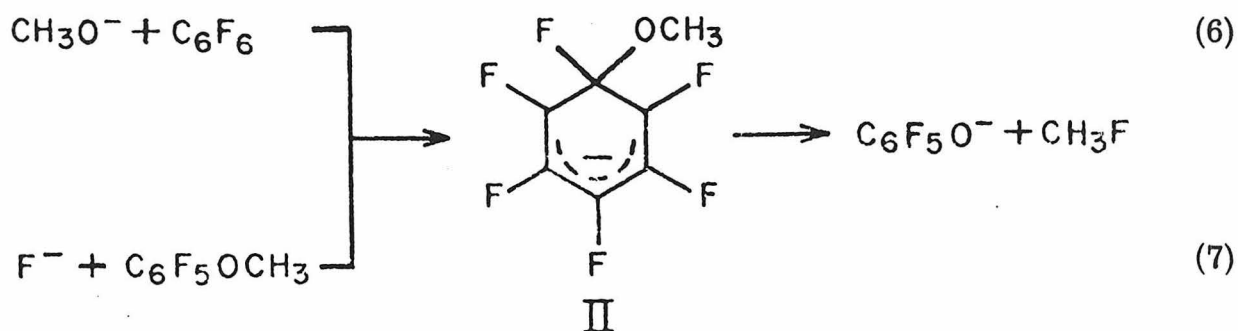
in both cases. Rate measurements of the reactions of $F^-$ with alkyl formates $HCO_2R$ (eq 8, $R = C_2H_5$) as a function of R group, indicate



$$F^- + HCOCH_2CH_3 \longrightarrow \longrightarrow HCO_2^- + CH_2CH_2 \qquad (8)$$
$$+ HF$$
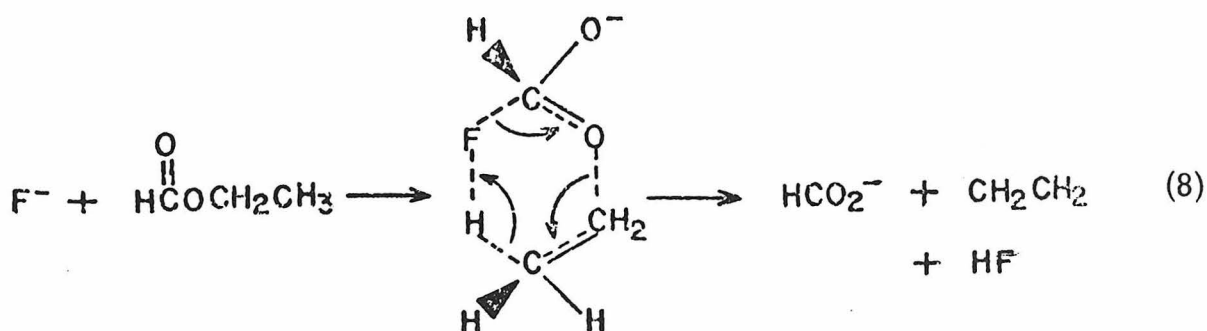
that reaction results from the decomposition of a 6-center intermediate to form HF and olefin.[9] In all of the above reactions direct elimination of the basic $F^-$ or $OR^-$ anions does not occur. Rearrangements proceed to eliminate an energetically favorable neutral (HF or $CH_3F$). It might be expected that elimination of a good leaving group ($Cl^-$, $Br^-$) might predominate over this rearrangement process. Interestingly, the only products observed on reaction of $CF_2CFCl$ and $CF_2CFBr$ with $CH_3O^-$ are the chloro and bromoenolate anions (eq 9, 10).[7] Reactions of this

$$CH_3O^- + CF_2CFCl \rightarrow OCFCFCl^- + CH_3F \qquad (9)$$

$$CH_3O^- + CF_2CFBr \rightarrow OCFCFBr^- + CH_3F \qquad (10)$$

type also occur with $NH_2^-$ and $OH^-$ with $CF_2CF_2$ (eq 11 and 12).[7] In the

$$NH_2^- + CF_2CF_2 \rightarrow CNCF_2^- + 2HF \qquad (11)$$

$$OH^- + CF_2CF_2 \rightarrow OCFCF_2^- + HF \qquad (12)$$
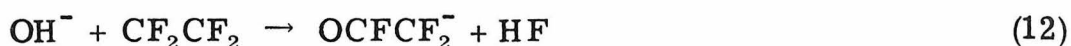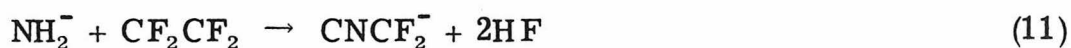
latter case loss of 2HF occurs directly, with no detection of $HNCFCF_2^-$.

Investigations of anion transfer reactions have provided relative gas phase Lewis acidities,[10,11] and hydrogen bond strengths in proton-bound anionic[19] species. As for gas phase proton acidities, Lewis acidities of neutrals toward an anionic base can be determined by examination of the preferred direction of anion transfer (eq 13).

$$B + AF^- \rightleftharpoons BF^- + A \qquad (13)$$

At present, $F^-$ transfers have been the most extensively investigated. Murphy and Beauchamp have examined $F^-$ transfers to determine the relative Lewis acidities of a variety of boron[10,11] and silicon compounds.[11] For example, the Lewis acidities of alkyl boranes are found to increase with alkylation $(CH_3)_3B < (CH_3CH_2)_3B < (i-C_3H_7)_3B$. This suggests, as with the acidities of alcohols, that the increased polarizability of the larger alkyl groups allows better anion stabilization. It is well known from solution studies that relative Lewis acidities are dependent on the reference base, for this reason further investigation of other anion adducts is important.

Bihalide ions, with unusually strong hydrogen bonds $(XHY^-)$ can be produced by elimination reactions[6] or by halide transfer to hydrogen halides[10] (eq 14). Yamdagni and Kebarle have proposed that the

$$SO_2F^- + HCl \rightarrow FHCl^- + SO_2 \qquad (14)$$

hydrogen bonds $D(XH-Y^-)$ will increase with the acidity of XH and the basicity $Y^-$.[20] These trends have been confirmed by icr investigations of halide[19] transfer reactions. Quantitative values for these bond strengths may eventually be available from these studies by comparisons to reference anions (i.e., $F_2^-$, $Cl_2^-$ or $FHF^-$).

This thesis describes further investigations of negative ion chemistry related to nucleophilic reactivity, acidity studies and halide transfer reactions. Chapter I deals with nucleophilic attack at phosphorous in $OPF_3$ and $PF_3$. Rearrangements to lose HF, similar to those noted above, predominate. In Chapter II the acid-base

properties of methyl 1,4-dihydroborabenzene are discussed. Using acidity measurements the resonance energy of the $6\pi$ aromatic anion formed by proton abstraction from the borabenzene is determined. Finally, Chapter III describes the positive and negative ion chemistry of sulfuryl halides. The most important feature of these investigations is the copious formation of $SO_2F^-$ in low pressures of $SO_2FCl$. This ion has been shown to be a good $F^-$ donor, so that $SO_2FCl$ appears to be an excellent reagent for negative chemical ionization spectroscopy.

References

1. See discussions in J. March "Advanced Organic Chemistry: Reactions, Mechanisms and Structure," McGraw-Hill, New York, N.Y., 1968.

2. J. L. Beauchamp, Ann. Rev. Phys. Chem., 22, 527 (1972) and J. L. Beauchamp "Reaction Mechanisms of Organic and Inorganic Ions in the Gas Phase," in Interactions Between Ions and Molecules, P. Ausloos, Ed., Plenum Press, New York, 1975, p. 413.

3. A review of negative ion generation is provided in J. G. Dillard, Chem. Rev., 73, 589 (1973).

4. See Appendix III for references to gas phase acidity measurements.

5. D. P. Ridge and J. L. Beauchamp, J. Amer. Chem. Soc., 96, 637 (1974) and D. P. Ridge and J. L. Beauchamp, ibid., 3595 (1974).

6. S. A. Sullivan and J. L. Beauchamp, J. Amer. Chem. Soc., 98, 1060 (1976).

7. S. A. Sullivan and J. L. Beauchamp, J. Amer. Chem. Soc., accepted for publication and unpublished results.

8. S. M. Jose Briscese and J. M. Riveros, J. Amer. Chem. Soc., 97, 230 (1975).

9. J. F. G. Fargle, P. C. Isolani and J. M. Riveros, J. Amer. Chem. Soc., 98, 2049 (1976) and S. M. Jose and J. M. Riveros, Nouveau J. Chimie, 1, 113 (1977).

References (continued)

10. M. K. Murphy and J. L. Beauchamp, J. Amer. Chem. Soc.,
    98, 1433 (1976).

11. M. K. Murphy and J. L. Beauchamp, submitted for publication.

12. For example, see R. T. McIver, Jr., and J. H. Silvers,
    J. Amer. Chem. Soc., 95, 8462 (1973).

13. T. B. McMahon and P. Kebarle, J. Amer. Chem. Soc., 98,
    3399 (1976).

14. J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 90,
    6561 (1968).

15. J. S. Miller and R. T. McIver, Jr., J. Amer. Chem. Soc.,
    96, 4323 (1974).

16. S. Y. Delavarenne and H. G. Vielhe, "Abstracts, Fourth Int.
    Symp on Fluorine Chemistry," Estes Park (Am. Chem. Soc.),
    1967, p. 122.

17. J. V. Dugan, Jr., J. H. Rice and J. L. Magee, Chem. Phys.
    Lett., 3, 323 (1969).

18. W. H. Olmstead and J. I. Brauman, J. Amer. Chem. Soc.,
    99, 4219 (1977).

19. M. S. Foster and J. L. Beauchamp, submitted for publication.

20. R. Yamdagni and P. Kebarle, J. Amer. Chem. Soc., 93,
    7139 (1971).

# CHAPTER I

Nucleophilic Reactions of Anions with $PF_3$ and $OPF_3$ in the
Gas Phase Using Ion Cyclotron Resonance Spectroscopy.
Mechanism and Energetics of Anionic
Adduct ($OPF_4^-$ and $PF_4^-$) Formation.
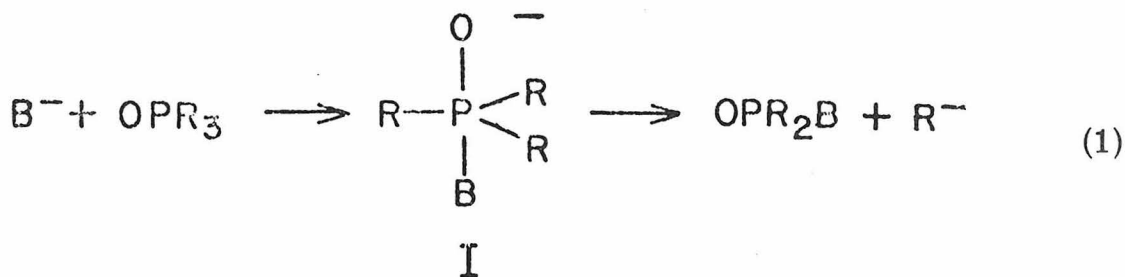
S. A. Sullivan and J. L. Beauchamp

## ABSTRACT

Ion cyclotron resonance techniques are employed in the examination of the gas phase reactions of $PF_3$ and $OPF_3$ with anionic bases, including $NH_2^-$, $OH^-$, $CH_3CH_2O^-$, $HNO^-$, $HS^-$, $SF_6^-$, and $SF_5^-$. Evidence is presented which suggests that all reactions proceed by initial attack at phosphorous, with products resulting from decomposition of chemically activated intermediates. The energetics of intermediates inferred in these processes are related to the Lewis acidities of $OPF_3$ and $PF_3$. With fluoride ion as a reference base, $OPF_3$ is found to be more acidic than $PF_3$, with $D(OPF_3-F^-) = 58.9 \pm 0.4$ kcal/mol and $D(PF_3-F^-) = 50 \pm 5$ kcal/mol.

## Introduction

Phosphorous, like other second row elements, is capable of hypervalent bonding[1] as shown by the existence of pentavalent phosphoranes $PR_5$ and phosphoryl compounds $OPR_3$ in addition to the expected trivalent phosphines $PR_3$. Many studies of these compounds have focussed on processes involving nucleophilic attack at phosphorous.[1, 2ab] Both P(III) and P(V) are susceptible to nucleophilic attack in solution. The reactions of tetracoordinate P(V) compounds, phosphate esters in particular, have been examined more extensively because of their relationship to processes in biological systems.[3]
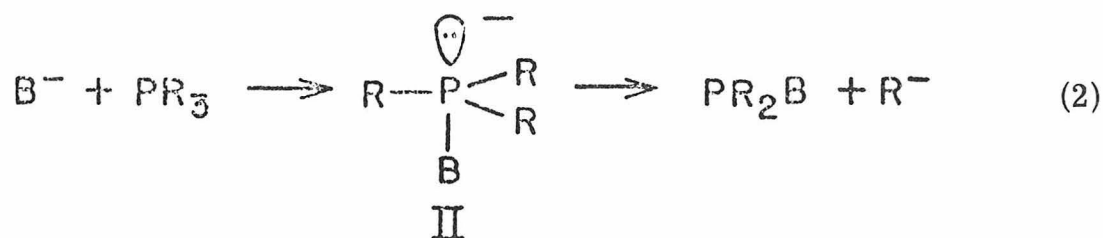
A somewhat complex situation is suggested by mechanistic studies of nucleophilic substitution at P(V). Isotopic exchange during hydrolysis of alkyl phosphoryl compounds by bases $B^-$ implicates the formation of pentavalent P(V) anionic intermediates[1, 4] (I). Similar experiments, with phosphorous bearing more electronegative
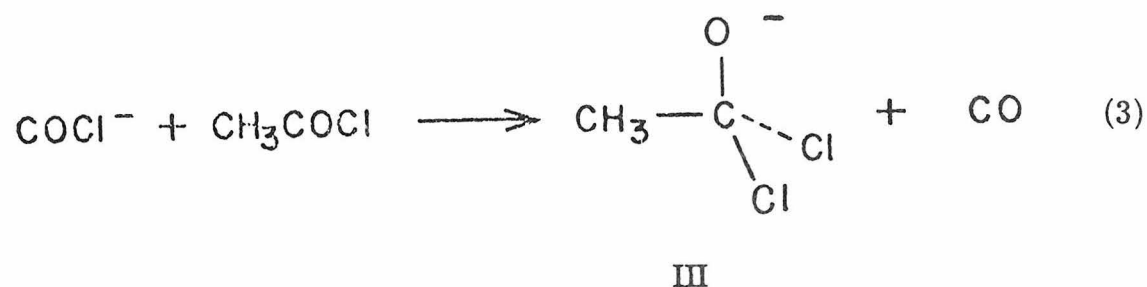
$$B^- + OPR_3 \longrightarrow R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle I}{B}}{P}}{\overset{R}{<}}{\underset{R}{}} \longrightarrow OPR_2B + R^- \tag{1}$$

substituents (e.g., $R = CH_3O$, Cl), are consistent with a direct displacement mechanism through a transition state like I.[1, 5] The inference of reaction mechanisms in these systems is complicated[6] by the presence of two distinct ligand sites in the proposed intermediates. Analogous to $PF_5$,[7] the intermediates are expected to have trigonal

bipyramidal structure, with a preference for axial binding of electro-negative substituents.[1] Structures and the mode of decomposition of reaction intermediates or transition states may thus be strongly moderated by the substituents on phosphorous.

Direct displacement mechanisms involving tetracoordinate transition states (II) have been proposed for nucleophilic attack at P(III) (eq 2). Recent results indicating complete inversion at P(III) on nucleophilic attack are consistent with a direct displacement.[8]

$$B^- + PR_3 \longrightarrow R\!-\!\!\overset{\displaystyle \overset{\text{\LARGE $\ominus$}}{|}}{\underset{\displaystyle B}{P}}\!\!\overset{R}{\underset{R}{<}} \longrightarrow PR_2B + R^- \qquad (2)$$

II

Recent ion cyclotron resonance (ICR) studies have considered gas phase reactions of anionic bases with fluorinated alkenes,[9] alkyl formates[10] and other halogenated carbonyls.[11] Observed products are rationalized as the results of multiple bond rearrangements and dissociation of chemically activated anionic intermediates. Often it is possible to separately study the energetics of the reaction intermediates in these processes. For example, the tetrahedral adduct III is formed in eq 3 by chloride transfer.[12]

$$COCl^- + CH_3COCl \longrightarrow CH_3\!-\!\!\overset{\displaystyle \overset{O^-}{|}}{\underset{\displaystyle Cl}{C}}\!\!\cdots Cl \ + \ CO \qquad (3)$$

III

In this laboratory we are extending our continuing investigation of negative ion reaction mechanisms by examining the interaction of anions with phosphorous compounds. Preliminary studies of the reactions of strong bases with trimethylphosphate[13] indicate that reaction 4 is the major process    with $CD_3O^-$. The absence of

$$CD_3O^- + OP(CH_3)_3 \rightarrow O_2P(OCH_3)_2^- + CH_3OCD_3 \qquad (4)$$

deuterium incorporation into the ionic product in reaction 4 suggests that nucleophilic attack occurs at carbon rather than phosphorous. This somewhat surprising result is in contrast to solution reactions in which strong bases preferentially attack phosphorous.[14]

By analogy with the gas phase reactions of fluoroalkyl silanes (i.e., $CH_3SiF_3$) in mixtures with $SF_6$,[15] it was expected that $F^-$ transfer adducts could also be formed with phosphate esters by transfer from $F^-$ donors, for example, eq 5. Formation of such adducts may be

$$SF_5^- + OP(OR)_3 \rightarrow OP(OR)_3F^- + SF_4 \qquad (5)$$
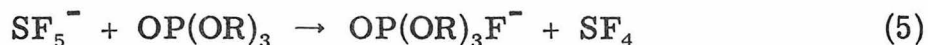
important as a method of soft ionization useful in chemical ionization mass spectrometry.[16] All attempts to form $F^-$ adducts with phosphate esters have failed.[13] This suggests that these compounds are very weak Lewis acids.

In the present study we have examined the nucleophilic reactions of anionic bases including $NH_2^-$, $OH^-$, $CH_3CH_2O^-$, $HNO^-$, and $HS^-$, with $OPF_3$ and $PF_3$. The electronegative fluorine ligands should decrease electron density at phosphorous significantly enhancing its

susceptibility to nucleophilic attack. Similarly, the stability of fluoride adducts $OPF_4^-$ and $PF_4^-$ should be considerably greater compared to adducts of phosphorous esters.

## Experimental

Experiments were performed using an ICR spectrometer built in this laboratory, incorporating a 15' magnetic capable of observing up to $\underline{m/e}$ 800. Instrumentation and experimental techniques of icr spectroscopy have been described in detail previously.[17, 18] Pressure was measured using a Schulz-Phelp ion gauge calibrated against a MKS Baratron Model 90-H1 capacitance manometer at higher pressures. Pressure measurements are the major source of error (± 20%) in reaction rate constants.

Negative ion trapping techniques have been described elsewhere.[19] In a typical trapped ion experiment, the precursor to the reagent base was admitted to the analyzer, followed by addition of one or two other compounds to be investigated. Independent pressure control allows for variation of the partial pressures of each component. Total pressures normally were below $5 \times 10^{-6}$ torr, to minimize ion loss. Reaction rate constants are determined from limiting slopes for the disappearance of reactant ions in semi-log plots of the variation of ion abundance with time.

Reactivity of ions in mixtures of neutrals may also be examined by observation of the variation of single resonance ion intensities as a function of component partial pressure. Analytical methods for the

calculation of reaction rates using icr pressure studies have been described.[20]

The major ions produced by thermalized electron attachment in $SF_6$ are $SF_6^-$ (95%) and $SF_5^-$ (5%). Both ions are unreactive toward $SF_6$.[21] In a similar manner, the alkoxide ion $C_2H_5O^-$ is produced in $CH_3CH_2ONO$.[22] Primary ions $CH_2CHO^-$ (17%) and $HNO^-$ (10%) are also formed by electron attachment. The only reaction product ion detected is $NO_2^-$, which is formed on reaction of $CH_3CH_2O^-$ with the precursor nitrite. This reaction is minimized by maintaining low partial pressure of nitrites.

Reagent negative ions $NH_2^-$, $HO^-$ and $HS^-$ are formed in $NH_3$, $H_2O$ and $H_2S$, respectively.[23, 24] Resonance electron capture processes (4.0-6.0 eV) initiate $NH_2^-$ and $OH^-$ formation. Near zero energy electrons are required for formation of $HS^-$. In all three cases, high pressures ($\sim 10^{-5}$ torr) of precursor were necessary to produce reagent negative ion intensities adequate for study. Only drift mode studies were performed in these cases.

Nitrites were prepared from $CD_3OD$ and $C_2H_5OH$ using standard methods.[25] Both $PF_3$ and $OPF_3$ were obtained from PCR. An impurity found in $OPF_3$ at m/e 155 was removed by trap-to-trap vacuum distillation. All other compounds used in these studies were obtained from commercial sources and used without further purification except for repeated freeze-pump-thaw cycles to remove noncondensible impurities.

## Results

Negative Ions in $OPF_3$ and $PF_3$. In $OPF_3$ at low pressures $(10^{-6}$ torr) the negative ions $O^-$, $F^-$ and a small amount of $OPF_2^-$ have been observed in previous studies.[26] These ions are formed by dissociative electron attachment processes, with resonance maxima between 10-15 eV electron energy. Similarly, the ions $F^-$, $F_2^-$, $PF^-$, and $PF_2^-$ have been produced in $PF_3$ at electron energies above 10 eV.[27] In both cases, cross sections for negative ion formation are small. With pressure, emission current, and electron energy conditions used in experiments described below, the negative ions noted above are not observed in samples of $OPF_3$ and $PF_3$.

Only in the case of $OPF_3$ at pressures above $10^{-5}$ torr was the negative ion $O_2PF_2^-$ (m/e 101) observed with a resonance maxima for ion formation at 7.2 eV electron energy. No other ions are detected with increased pressure. Mass spectral analysis indicates the presence of no other neutrals in the $OPF_3$.[28]

In mixtures of $OPF_3$ and $PF_3$ with both $H_2O$ and $NH_3$, ions are produced which show no double resonance from $OH^-$ and $NH_2^-$. These ions ($PF_2^-$ in $PF_3$ and $OPF_2^-$ in $OPF_3$) are formed only in the presence of the second neutral. Double resonance results eliminate the possibility of ion generation from ion molecule reactions.[29] Surface reactions[28] or reactions on the electron filament[30] are possible. Neither of these ions is included in the figures presented.

Reactions of Nucleophiles with $OPF_3$. Figure 1 presents the variation of normalized ion intensity as a function of $OPF_3$ pressure

FIGURE 1

Variation of normalized negative ion intensity as a function of the partial pressure of $OPF_3$ in a mixture with $10^{-5}$ torr $NH_3$ at 4.8 eV electron energy.

Partial Pressure of $OPF_3$ (torr)
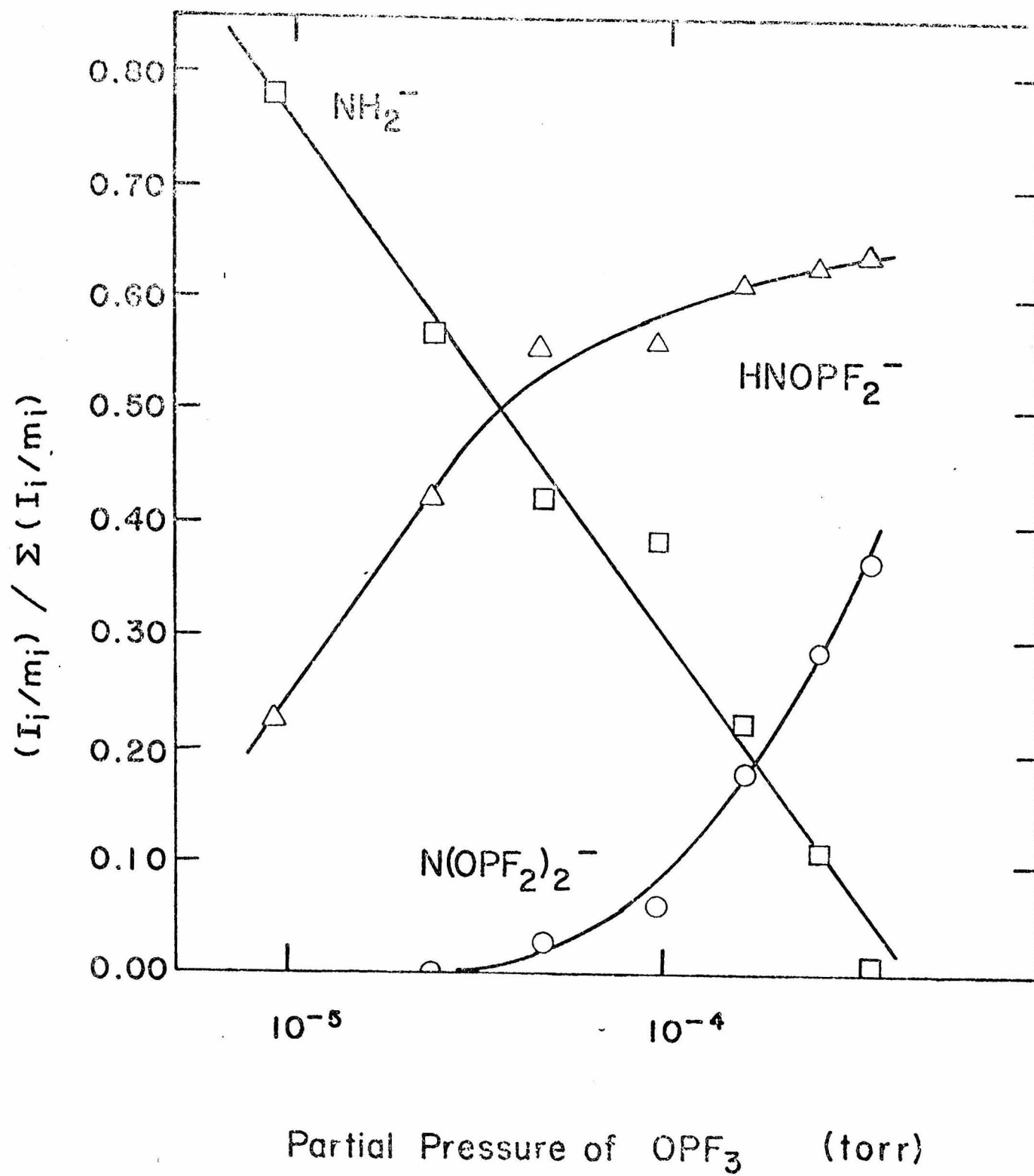
in a mixture with $10^{-5}$ torr $NH_3$. As $NH_2^-$ ($\underline{m/e}$ 16) decreases, ions appear corresponding to $NHOPF_2^-$ ($\underline{m/e}$ 100) and $N(OPF_2)_2^-$ ($\underline{m/e}$ 185). As noted above $OPF_2^-$ ($\underline{m/e}$ 85) is also detected in this mixture. Since it is not formed by reaction of $NH_2^-$, it is not included in Figure 1. Double resonance experiments indicate that $NH_2^-$ is the precursor to both product ions and further that $HNOPF_2^-$ reacts to form $N(OPF_2)_2^-$. There is no indication that $HNOPF_2^-$ and $OPF_2^-$ are reactively coupled. Reactions 6 and 7 are consistent with these results.

$$NH_2^- + OPF_3 \rightarrow HNOPF_2^- + HF \qquad (6)$$

$$HNOPF_2^- + OPF_3 \rightarrow N(OPF_2)_2^- + HF \qquad (7)$$
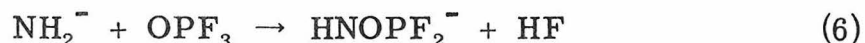
Analogous nucleophilic reactions occur in mixtures of $H_2O$, (eq 8) and $H_2S$ (eq 9) with $OPF_3$. Although, as noted above, $O_2PF_2^-$ is

$$OH^- + OPF_3 \rightarrow O_2PF_2^- + HF \qquad (8)$$

$$SH^- + OPF_3 \rightarrow OSPF_2^- + HF \qquad (9)$$
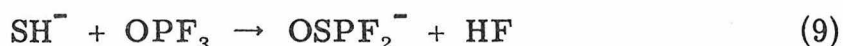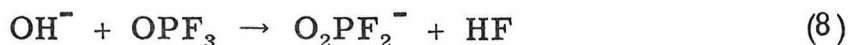
formed in $OPF_3$ alone, double resonance indicates the ~ 30% of the observed $O_2PF_2^-$ is formed by reaction with $OH^-$. Neither of the product ions react further with the neutrals present. Rates for reactions 6, 7, and 9, determined from single resonance pressure studies are presented in Table I. Because of complications due to other sources of $O_2PF_2^-$, a reaction rate for eq 8 could not be measured.

Figure 2 presents the temporal variation of ion intensity as a function of reaction time in a mixture of $1 \times 10^{-7}$ torr, $CH_3CH_2ONO$ with $1.76 \times 10^{-6}$ torr $OPF_3$. Product ions $OPF_2^-$ ($\underline{m/e}$ 85), $O_2PF_2^-$

Table I. Summary of Gas Phase Nucleophilic Reactions of $OPF_3$ and $PF_3$

| Reaction | Equation Number | $k_{ex}{}^a$ | $k_{ado}{}^b$ | $k_{ex}{}^c/k_{ado}$ |
|---|---|---|---|---|
| $NH_2^- + OPF_3 \rightarrow NHOPF_2^- + HF$ | 6 | 16.5 | 20.6 | 0.80 |
| $NHOPF_2^- + OPF_3 \rightarrow N(POF_2)_2^- + HF$ | 7 | 2.0 | 10.8 | 0.19 |
| $OH^- + OPF_3 \rightarrow O_2PF_2^- + HF$ | 8 | -- | 20.0 | -- |
| $CH_3CH_2O^- + OPF_3 \rightarrow O_2PF_2^- + CH_3CH_2F$ | 10 | 11.6 | 13.7 | 0.85 |
| $HNO^- + OPF_3 \rightarrow OPF_2^- + HF + NO$ | 11 | 11.9 | 15.7 | 0.76 |
| $CH_2CHO^- + OPF_3 \rightarrow C_2H_2OPF_2^- + HF$ | 12 | 5.0 | 13.9 | 0.36 |
| $SH^- + OPF_3 \rightarrow OSPF_2^- + HF$ | 9 | 1.2 | 15.4 | 0.08 |
| $NH_2^- + PF_3 \rightarrow NHPF_2^- + HF$ | 13 | 7.9 | 15.1 | 0.96 |
| $NH_2^- + PF_3 \rightarrow NPF^- + 2HF$ | 14 | 6.6 | | |
| $OH^- + PF_3 \rightarrow OPF_2^- + HF$ | 15 | -- | 14.8 | -- |
| $CH_3CH_2O^- + PF_3 \rightarrow OPF_2^- + CH_3CH_2F$ | 17 | 5.6 | 9.2 | 0.61 |
| $HNO^- + PF_3 \rightarrow NOPF_2^- + HF$ | 18 | 5.0 | 11.8 | 0.42 |
| $PF_2^- + H_2O \rightarrow OPF_2^- + OH$ | 16 | -- | 18.0 | -- |

[a] Experimental rate is determined as noted in text; in units $10^{-10}$ $cm^3$ $mol^{-1}$ $sec^{-1}$.

[b] Rate, in units $10^{-10}$ $cm^3$ $mol^{-1}$ $sec^{-1}$ is calculated using the average dipole orientation model.

Table I – Continued

equation:

$$k_{ado} = [2\pi e/\mu^{\frac{1}{2}}][\alpha^{\frac{1}{2}} + c\mu_d (2/\pi kT)^{\frac{1}{2}}]$$

in which $\mu$ = reduced mass of the ion molecule collision pair, $\alpha$ = polarizability of the neutral, $\mu_d$ = dipole moment of the neutral and c = constant estimated as noted in reference 36. Polarizabilities for $OPF_3$ and $PF_3$ are taken as 33.0 and $29.0 \times 10^{-25}$ $cm^3$, respectively, see reference 41. Dipole moments for $OPF_3$ and $PF_3$ are taken as 1.74 D and 1.03 D, respectively, from R. R. C. Carlson and D. W. Meck, Inorg. Chem., 13, 1941 (1974).

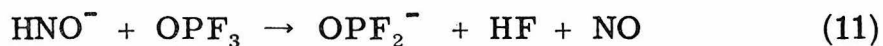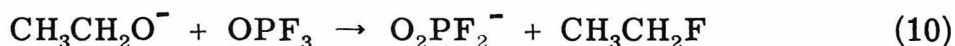[c]In those cases where two reaction pathways occur, the total rate is compared to the ADO rate.

FIGURE 2

Temporal variation of normalized negative ion intensity in a mixture of $CH_3CH_2ONO$ ($1.00 \times 10^{-7}$ torr) and $OPF_3$ ($1.76 \times 10^{-6}$ torr) at 20.0 eV electron energy.

TIME (msec)
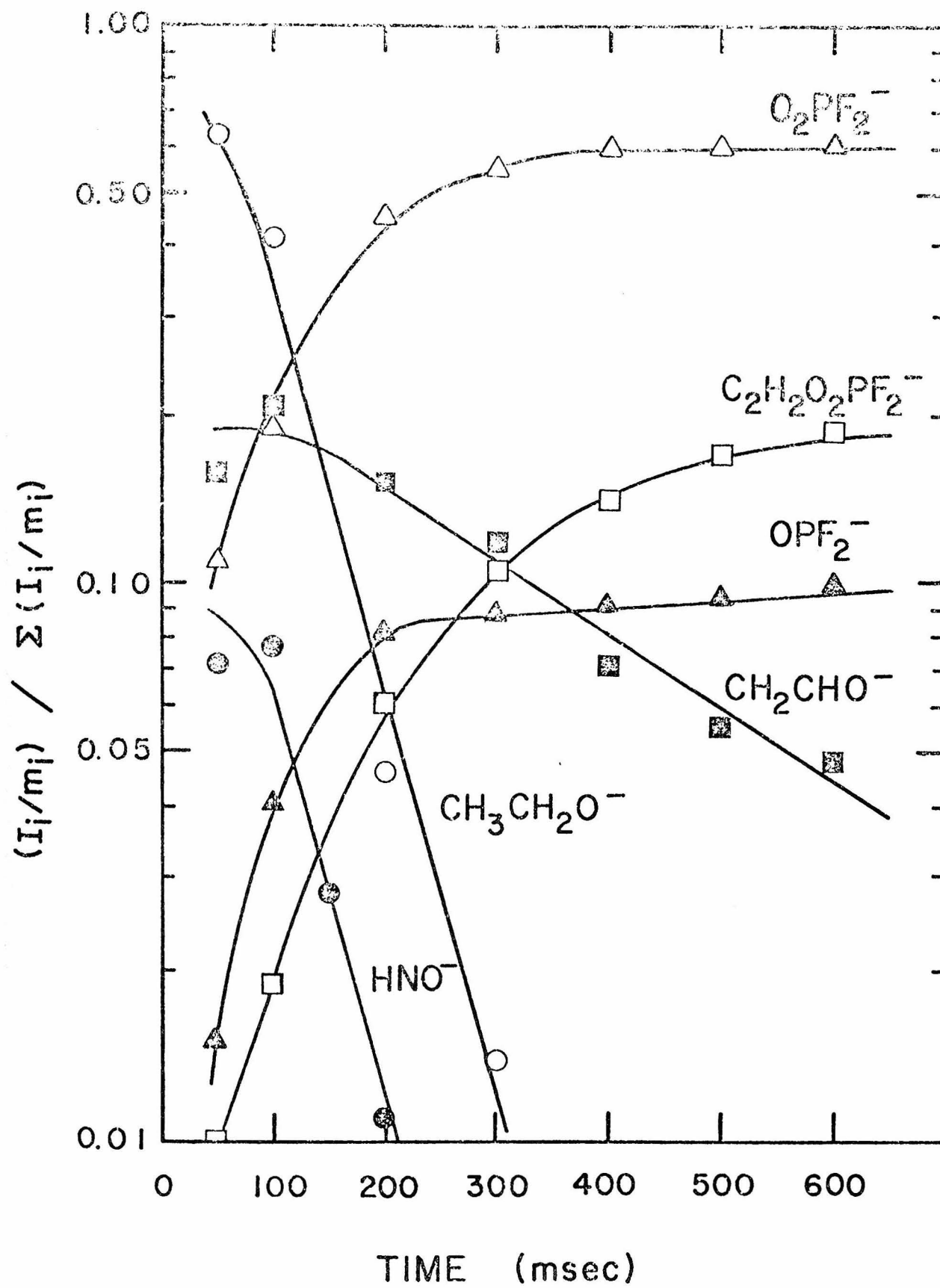
($\underline{m/e}$ 101) and $C_2H_2OPF_2^-$ ($\underline{m/e}$ 127)[31] appear as a function of time. Double resonance experiments confirm that $CH_3CH_2O^-$ reacts to produce $O_2PF_2^-$ (eq 10). It should be noted that at low pressures and 20 eV electron energy no $O_2PF_2^-$ is generated in $OPF_3$ alone. The complete disappearance of $OPF_2^-$ and $C_2H_2OPF_2^-$ on double resonance irradiation of $HNO^-$ and $CH_2CHO^-$, respectively, indicate reactions 11 and 12 rates

$$CH_3CH_2O^- + OPF_3 \rightarrow O_2PF_2^- + CH_3CH_2F \qquad (10)$$

$$HNO^- + OPF_3 \rightarrow OPF_2^- + HF + NO \qquad (11)$$

$$CH_2CHO^- + OPF_3 \rightarrow C_2H_2OPF_2^- + HF \qquad (12)$$

for reactions 10-12 as determined from trapping studies are listed in Table I.

Reactions of Nucleophiles with $PF_3$. On addition of $PF_3$ to $1 \times 10^{-5}$ torr $NH_3$ at 4.8 eV electron energy, ions are detected at $NH_2^-$ ($\underline{m/e}$ 16), $NPF^-$ ($\underline{m/e}$ 64), $PF_2^-$ ($\underline{m/e}$ 69), and $HNPF_2^-$ ($\underline{m/e}$ 84). As noted above, $PF_2^-$ is not formed by reaction of $NH_2^-$. Double resonance experiments confirm that $NH_2^-$ reacts to form both $HNPF_2^-$ and $NPF^-$ as in eqs 13 and 14. No further reactions of these species are observed
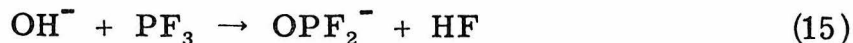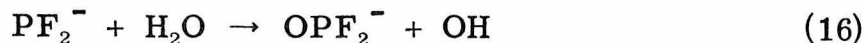
$$NH_2^- + PF_3 \begin{cases} \rightarrow HNPF_2^- + HF & (13) \\ \rightarrow NPF^- + 2HF & (14) \end{cases}$$
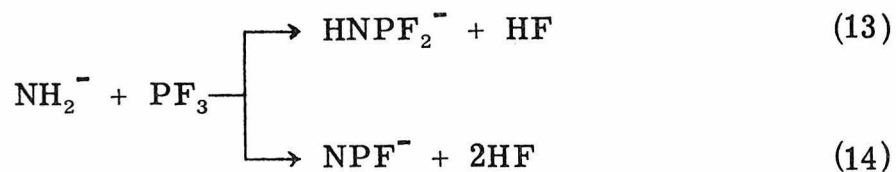
with the neutrals present.

Ions $PF_2^-$ ($\underline{m/e}$ 69) and $OPF_2^-$ ($\underline{m/e}$ 85) appear as $PF_3$ is added to a sample of $H_2O$ ($2 \times 10^{-5}$ torr). Only the latter ion $OPF_2^-$ is

formed by reaction of $PF_3$ with $OH^-$ (eq 15). Double resonance also

$$OH^- + PF_3 \rightarrow OPF_2^- + HF \tag{15}$$

indicates that $PF_2^-$ reacts to form $OPF_2^-$, possibly as in eq 16.

$$PF_2^- + H_2O \rightarrow OPF_2^- + OH \tag{16}$$

The temporal variation of ion intensity in a mixture of $CH_3CH_2ONO$ ($1.20 \times 10^{-7}$ torr) and $PF_3$ ($2.44 \times 10^{-7}$ torr) is presented in Figure 3. Product ions $OPF_2^-$ ($m/e$ 85) and $NOPF_2^-$ ($m/e$ 99) appear at longer times. Reactions 17 and 18 are consistent with double

$$CH_3CH_2O^- + PF_3 \rightarrow OPF_2^- + CH_3CH_2F \tag{17}$$
$$HNO^- + PF_3 \rightarrow NOPF_2^- + HF \tag{18}$$
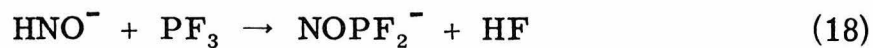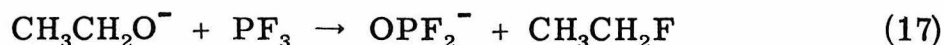
resonance experiments, $CH_3CH_2O^-$ and $HNO^-$ being the sold precursors of $OPF_2^-$ and $NOPF_2^-$, respectively. The ion $CH_2CHO^-$ ($m/e$ 43) is unreactive in this mixture. Rates for reactions 13-18 are listed in Table I.

Fluoride Transfer Reactions and Lewis Acidity of $OPF_3$.
Figure 4 presents the temporal variation of normalized ion intensity in a mixture of $3.50 \times 10^{-7}$ torr $OPF_3$ with a trace amount ($< 10^{-7}$ torr) of $SF_6$. Both primary ions $SF_6^-$ ($m/e$ 146) and $SF_5^-$ ($m/e$ 127) decrease as a product ion $OPF_4^-$ ($m/e$ 123) appears. Double resonance experiments link production of $OPF_4^-$ directly to $SF_6^-$ (eq 19). A slower $F^-$ transfer from $SF_5^-$ also occurs (eq 20).
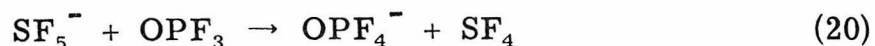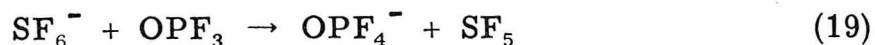
$$SF_6^- + OPF_3 \rightarrow OPF_4^- + SF_5 \tag{19}$$
$$SF_5^- + OPF_3 \rightarrow OPF_4^- + SF_4 \tag{20}$$

FIGURE 3

Temporal variation of normalized negative ion intensity in a mixture of $CH_3CH_2ONO$ ($1.20 \times 10^{-7}$ torr) and $PF_3$ ($2.44 \times 10^{-7}$ torr) at 20.0 eV electron energy.
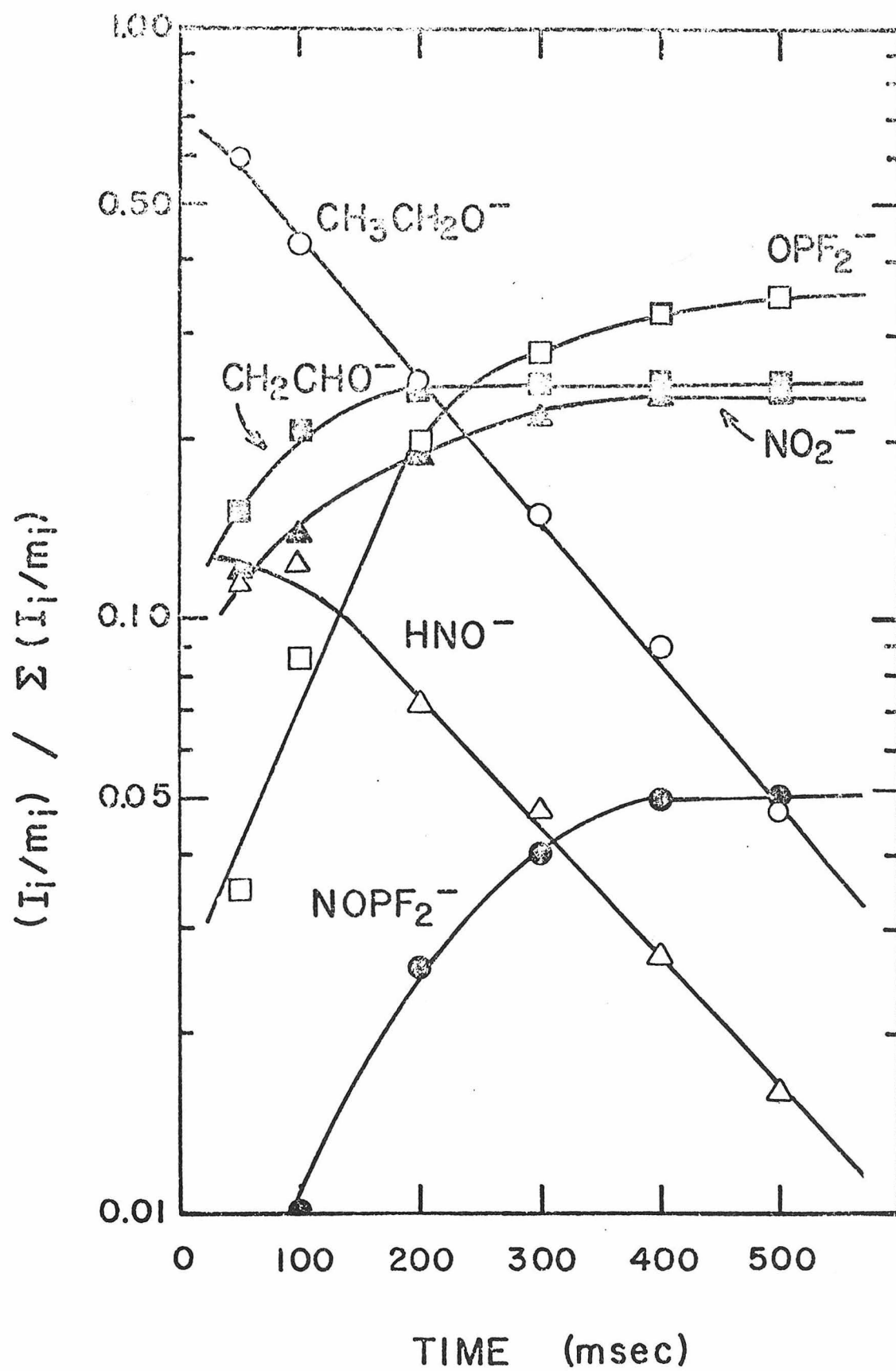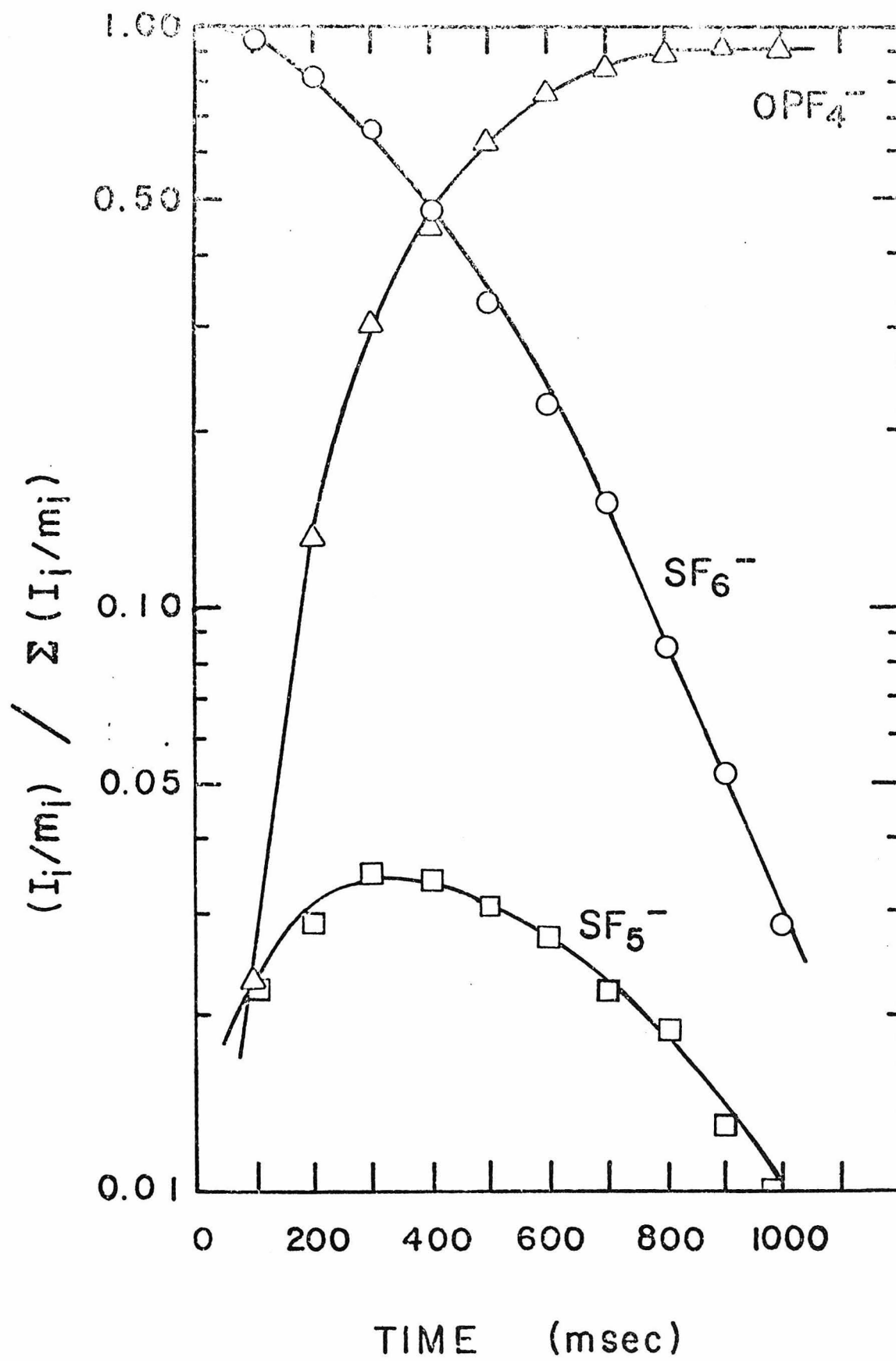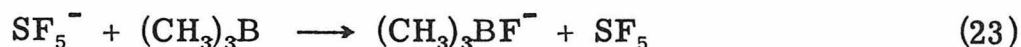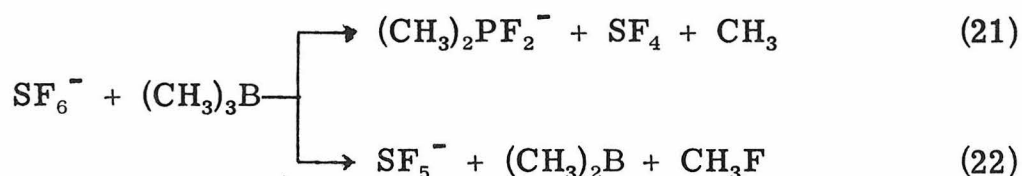
FIGURE 4

Temporal variation of normalized negative ion intensity in a mixture of $OPF_3$ ($3.50 \times 10^{-7}$ torr) with a trace of $SF_6$ at 20.0 eV.

Temporal variation of normalized ion intensity in a (1:1.9)
mixture of $OPF_3$ and $(CH_3)_3B$ is presented in Figure 5. Ions
$(CH_3)_3BF^-$ ($\underline{m/e}$ 75), $(CH_3)_2BF_2^-$ ($\underline{m/e}$ 79), $OPF_4^-$ ($\underline{m/e}$ 123) and $SF_5^-$
($\underline{m/e}$ 127) appear and increase as $SF_6^-$ ($\underline{m/e}$ 146) decays with time.
Reactions 21-23 in addition to reactions 16 and 17, are consistent with
observed double resonance. Reactions 21-23 have been investigated

$$SF_6^- + (CH_3)_3B \begin{cases} \longrightarrow (CH_3)_2PF_2^- + SF_4 + CH_3 & (21) \\ \\ \longrightarrow SF_5^- + (CH_3)_2B + CH_3F & (22) \end{cases}$$

$$SF_5^- + (CH_3)_3B \longrightarrow (CH_3)_3BF^- + SF_5 \qquad (23)$$

previously.[32] At long times equilibrium fluoride transfer occurs
between $OPF_4^-$ and $(CH_3)_3BF^-$ (eq 24). The equilibrium constant $(K_{eq})$

$$(CH_3)_3BF^- + OPF_3 \rightleftharpoons OPF_4^- + (CH_3)_3B \qquad (24)$$
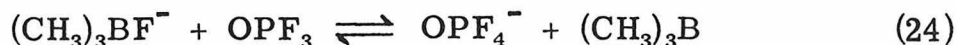
for reaction 21 as written is determined to be $1.9 \pm 0.4$. Ion ejection
techniques,[33] which allow measurement of the forward and reverse
rate constants of reaction 24 (Table I), confirm this value for $K_{eq}$.
Entropy contributions will be negligible,[34] so that $\Delta H \sim \Delta G$ and
$D(OPF_3-F^-) - D[(CH_3)_3B-F^-] = 0.38 \pm 0.14$ kcal/mol. Using the
estimated value of $58.5 \pm 0.4$ kcal/mol for the bond strength
$D[(CH_3)_3B-F^-]$ (Table II). $D(OPF_3-F^-)$ is calculated as $58.9 \pm 0.4$
kcal/mol.

In the mixture of $(CH_3)_3B$ and $OPF_3$, fluoride transfer does not
occur from $(CH_3)_2BF_2^-$ to $OPF_3$ (Figure 5). Further, $(CH_3)_2SiF_3^-$

FIGURE 5

Temporal variation of normalized ion intensity in a
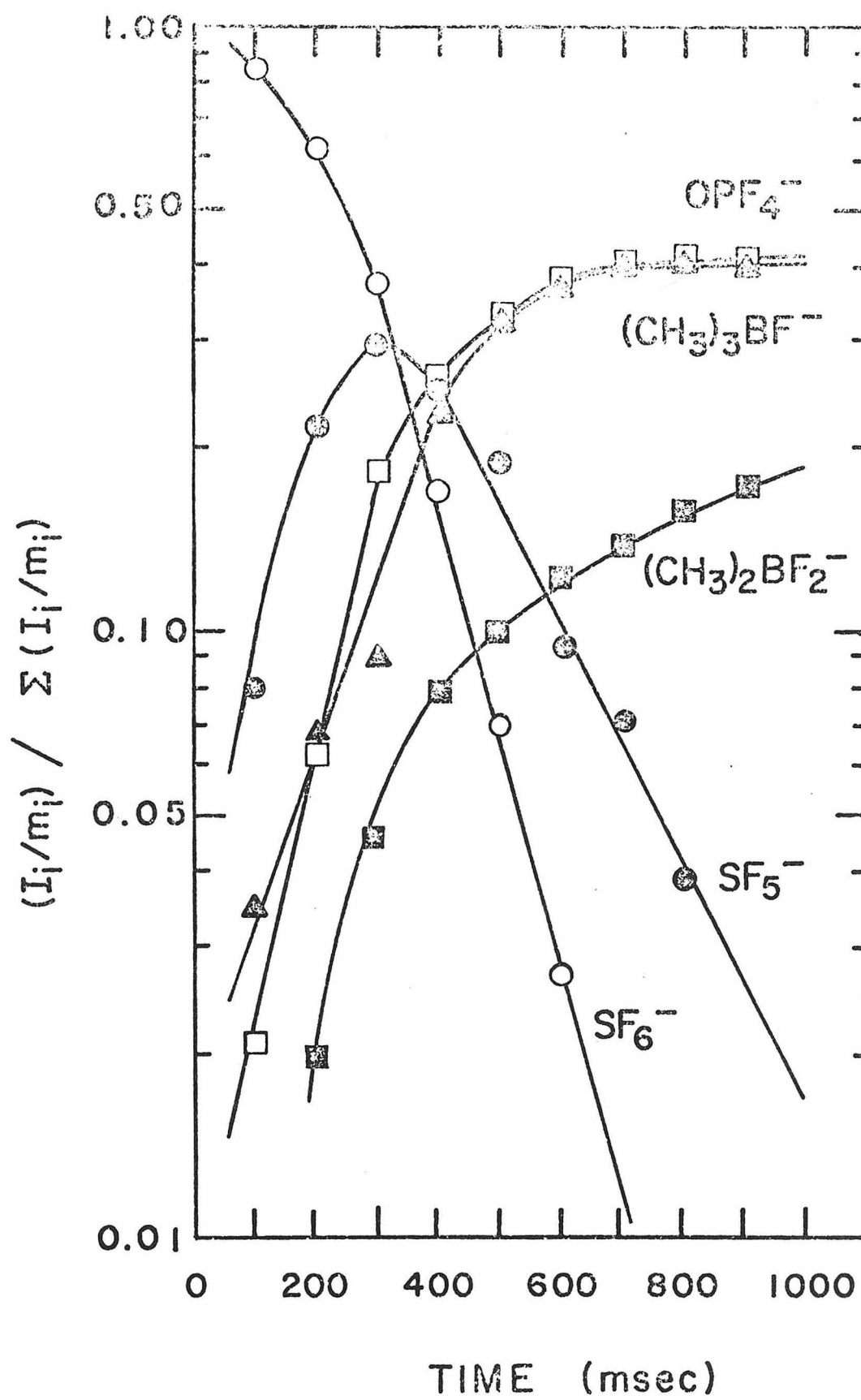(1:1.9) mixture of $OPF_3$ and $(CH_3)_3B$ at total pressure
$6.6 \times 10^{-7}$ torr.

Table II. Fluoride Bond Strengths[a]

| M | $D(M-F^-)$[b] |
| --- | --- |
| $PF_5$ | $> 71$[c] |
| $BF_3$ | $71$[c] |
| $SiF_4$ | $< 71$[c] |
| $(CH_3)_2BF$ | $61.8$ |
| $OPF_3$ | $58.9$[d] |
| $(CH_3)_3B$ | $58.5$ |
| $(CH_3)_2SiF_2$ | $55.5$ |
| $SF_4$ | $54 \pm 12$[e] |
| $(CH_3)_3SiF$ | $50 \pm 10$ |
| $PF_3$ | $50 \pm 5$[d] |
| $HCN$ | $47 \pm 3$[f] |
| $SO_2$ | $< 45$[f] |
| $F$ | $29 \pm 3.0$[g] |
| $SF_5$ | $11 \pm 8$[e] |

[a]All values in kcal/mol at 298°K.

[b]Binding energies of $F^-$ to boron and silicon compounds are taken from reference 32 and 15, respectively.

[c]J. C. Haartz and D. H. McDaniel, J. Amer. Chem. Soc., 95, 3562 (1973).
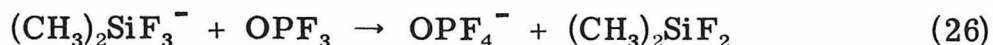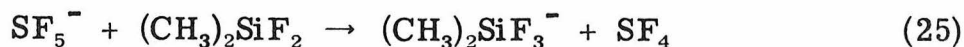
[d]Present study.

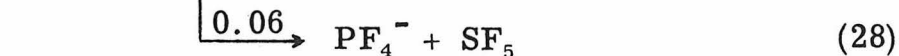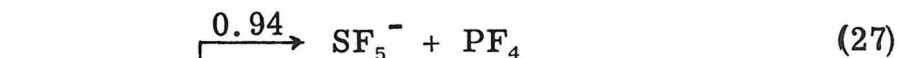[e]Reference 19.

[f]Reference 35.

[g]Calculated using $EA(F_2) = 3.09 \pm 0.1$ eV from W. A. Chupka, J. Berkowitz, and D. Gutman, J. Chem. Phys., 55, 2724 (1971).

produced in a mixture of $(CH_3)_2SiF_2$ and $SF_6$ by reaction 25 reacts with $OPF_3$ to form $OPF_4^-$ (eq 26). These results indicate limits for the

$$SF_5^- + (CH_3)_2SiF_2 \rightarrow (CH_3)_2SiF_3^- + SF_4 \tag{25}$$

$$(CH_3)_2SiF_3^- + OPF_3 \rightarrow OPF_4^- + (CH_3)_2SiF_2 \tag{26}$$

bonds strength in $OPF_4^-$, 61.8 kcal/mol > $D(OPF_3-F^-)$ > 55.5 kcal/mol, consistent with the measured bond strength noted above. Rates for $F^-$ transfer reactions to $OPF_3$ are summarized in Table III.

Fluoride Transfer Reactions and Lewis Acidity of $PF_3$. In Figure 6, the temporal variation of ion intensity in a mixture of $7.2 \times 10^{-7}$ torr $PF_3$ with a trace of $SF_6$ is presented. As a function of reaction time, $SF_6^-$ ($\underline{m/e}$ 146) decays as $SF_5^-$ ($\underline{m/e}$ 127) and $PF_4^-$ ($\underline{m/e}$ 107) appear. Reactions 27 and 28 are confirmed by double

$$SF_6^- \; PF_3 \begin{cases} \xrightarrow{0.94} SF_5^- + PF_4 & (27) \\ \xrightarrow{0.06} PF_4^- + SF_5 & (28) \end{cases}$$

resonance experiments. Fluoride transfer reaction 29 is effected by

$$SF_5^- + PF_3 \rightarrow PF_4^- + SF_4 \tag{29}$$

irradiating $SF_5^-$ in double resonance experiments, suggesting that this process is endothermic. In mixtures of $OPF_3$, $PF_3$ and a trace of $SF_6$, no $PF_4^-$ is observed, due to the competing and much faster process 19.

Negative ions $F^-$ ($\underline{m/e}$ 19, 60%), $F_2^-$ ($\underline{m/e}$ 38, 11%) and $SO_2F^-$ ($\underline{m/e}$ 85, 29%) are generated by electron impact in moderate pressures

**Table III. Summary of Fluoride Transfer Reactions**

| Reaction | Equation Number | $k_{ex}$ [a] | $k_{ado}$ [b] | $k_{ex}/k_{ado}$ [c] | Thermochemical Inference |
|---|---|---|---|---|---|
| $SF_6^- + OPF_3 \rightarrow OPF_4^- + SF_5$ | 20 | 3.1 | 9.8 | 0.32 | $D(SF_5-F^-) < D(OPF_3-F^-)$ |
| $SF_5^- + OPF_3 \rightarrow OPF_4^- + SF_4$ | 20 | 2.1 | 10.4 | 0.20 | $D(SF_4^+\,F^-) < D(OPF_3-F^-)$ |
| $SF_6^- + (CH_3)_3B \rightarrow (CH_3)_2BF_2^- + SF_4 + CH_3$ | 21 | 1.4 | 10.4 | 0.49 | |
| $\rightarrow SF_5^- + (CH_3)_2B + CH_3F$ | 22 | 3.7 | | | |
| $SF_5^- + (CH_3)_3B \rightarrow (CH_3)_3BF^- + SF_4$ | 23 | 2.8 | 10.6 | 0.26 | |
| $(CH_3)_3BF^- + OPF_3 \rightarrow OPF_4^- + (CH_3)_3B$ | 24f | 3.1 | 11.7 | 0.26 | $D(OPF_3-F^-) =$ |
| $OPF_4^- + (CH_3)_3B \rightarrow (CH_3)_3BF^- + OPF_3$ | 24r | 1.7 | 10.7 | 0.16 | $58.9 \pm 0.4$ kcal/mol |
| $(CH_3)_2SiF_3^- + OPF_3 \rightarrow OPF_4^- + (CH_3)_2SiF_2$ | 26 | 2.87 | 10.4 | 0.27 | $D[(CH_3)_2SiF_2-F^-] < D(OPF_3-F^-)$ |
| $SF_6^- + PF_3 \rightarrow SF_5^- + PF_4$ | 27 | 0.95 | 7.7 | 0.13 | $D(SF_5-F^-) < D(PF_3-F^-)$ |
| $\rightarrow PF_4^- + SF_5$ | 28 | 0.04 | | | |
| $F_2^- + PF_3 \rightarrow PF_4^- + F$ | 30 | -- | -- | -- | $D(F-F^-) < D(PF_3-F^-)$ |
| $SO_2F^- + PF_3 \rightarrow PF_4^- + SO_2$ | 31 | -- | -- | -- | $D(SO_2-F^-) < D(PF_3-F^-)$ |

Table III. Continued

| Reaction | Equation Number | $k_{ex}$[a] | $k_{ado}$[b] | $k_{ex}/k_{ado}$[c] | Thermochemical Inference |
|---|---|---|---|---|---|
| $PF_4^- + OPF_3 \rightarrow OPF_4^- + PF_3$ | 32 | -- | -- | -- | $D(PF_3-F^-) < D(OPF_3-F^-)$ |
| $(CH_3)_3SiF_2^- + PF_3 \rightarrow PF_4^- + (CH_3)_3SiF$ | 33 | -- | -- | -- | $D[(CH_3)_3SiF-F^-] < D(PF_3-F^-)$ |
| $FHCN^- + PF_3 \rightarrow PF_4^- + HCN$ | 34 | -- | -- | -- | $D(CNH-F^-) < D(PF_3-F^-)$ |

[a] Experimental rate is determined as noted in the text; in units of $cm^3 mol^{-1} sec^{-1}$.

[b] In units $cm^3 mol^{-1} sec^{-1}$; calculated as noted in Table I. The Langevain rate equation is used for nonpolar molecules $[k_L = 2\pi e(\alpha/\mu)^{\frac{1}{2}}]$, $\alpha[(CH_3)_3B]$ was taken from reference 32.
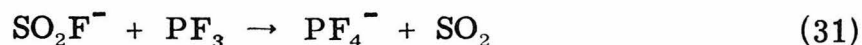
[c] In those cases in which two reaction pathways occur, the total rate is compared to the calculated rate.

FIGURE 6

Temporal variation of normalized ion intensity in a mixture of $PF_3$ ($9.74 \times 10^{-7}$ torr) with a trace of $SF_6$ at 20.0 eV.
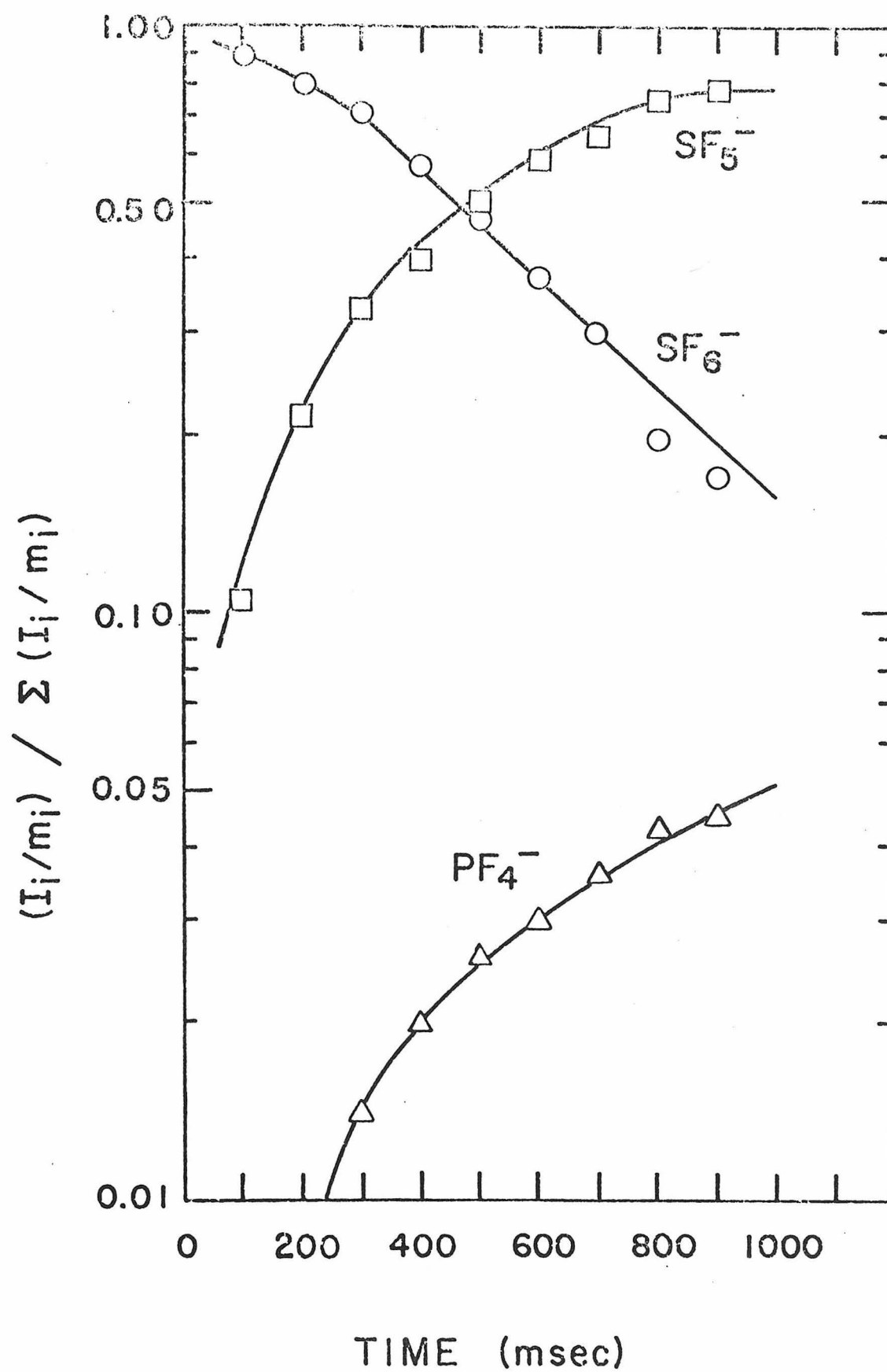
$(5 \times 10^{-6}$ torr) of $SO_2F_2.$[19] In a mixture of $PF_3$ with $SO_2F_2,$ $PF_4^-$ ($\underline{m/e}$ 107) is produced by $F^-$ transfer from $F_2^-$ (eq 30) and $SO_2F^-$ (eq 31).

$$F_2^- + PF_3 \rightarrow PF_4^- + F \tag{30}$$

$$SO_2F^- + PF_3 \rightarrow PF_4^- + SO_2 \tag{31}$$

On addition of $OPF_3$ and $PF_3$ to $SO_2F_2,$ $OPF_4^-$ and $PF_4^-$ can be observed. Double resonance confirms that $F^-$ transfer occurs only from $PF_4^-$ to $OPF_3$ (eq 32). In similar experiments using mixtures of $SO_2F_2$

$$PF_4^- + OPF_3 \rightarrow OPF_4^- + PF_3 \tag{32}$$

with $(CH_3)_3SiF$ and HCN, $F^-$ transfer processes generate $(CH_3)_3SiF_2^-$ ($\underline{m/e}$ 111) and $FHCN^-$ ($\underline{m/e}$ 46), respectively. Both of these ions transfer $F^-$ to $PF_3$ (eq 33 and 34). An ordering of $F^-$ bond strengths

$$(CH_3)_3SiF_2^- + PF_3 \rightarrow PF_4^- + (CH_3)_3SiF \tag{33}$$

$$FHCN^- + PF_3 \rightarrow PF_4^- + HCN \tag{34}$$
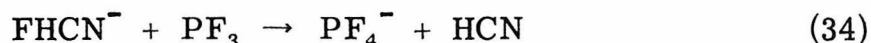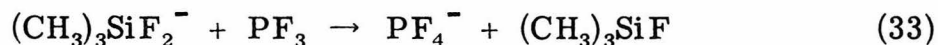
$D(SO_2-F^-) < D(CNH-F^-) < D(PF_3-F^-) < D(SF_4-F^-)$ is consistent with these results. Although $D(SO_2-F^-)$ and $D(CNH-F^-)$ are not well known, estimates[35] lead to limits of 45 kcal/mol $< D(PF_3-F^-) < 54$ kcal/mol. Fluoride transfer reactions are summarized in Table II.

## Discussion

Nucleophilic Reactivity. In Table I, rate constants for reactions of $OPF_3$ and $PF_3$ with gas phase bases are summarized. Experimental rates are compared to collision rates, calculated using the average dipole orientation (ADO) model[36] to account for the dipole moment of

the neutral reactants. There is a general trend of increased rate with increased base strength.

The reactions of $OPF_3$ and $PF_3$ with anionic bases can be described as the result of the decomposition of penta and tetra coordinate intermediates. In the reaction of $NH_2^-$ with $OPF_3$ (Scheme I) the
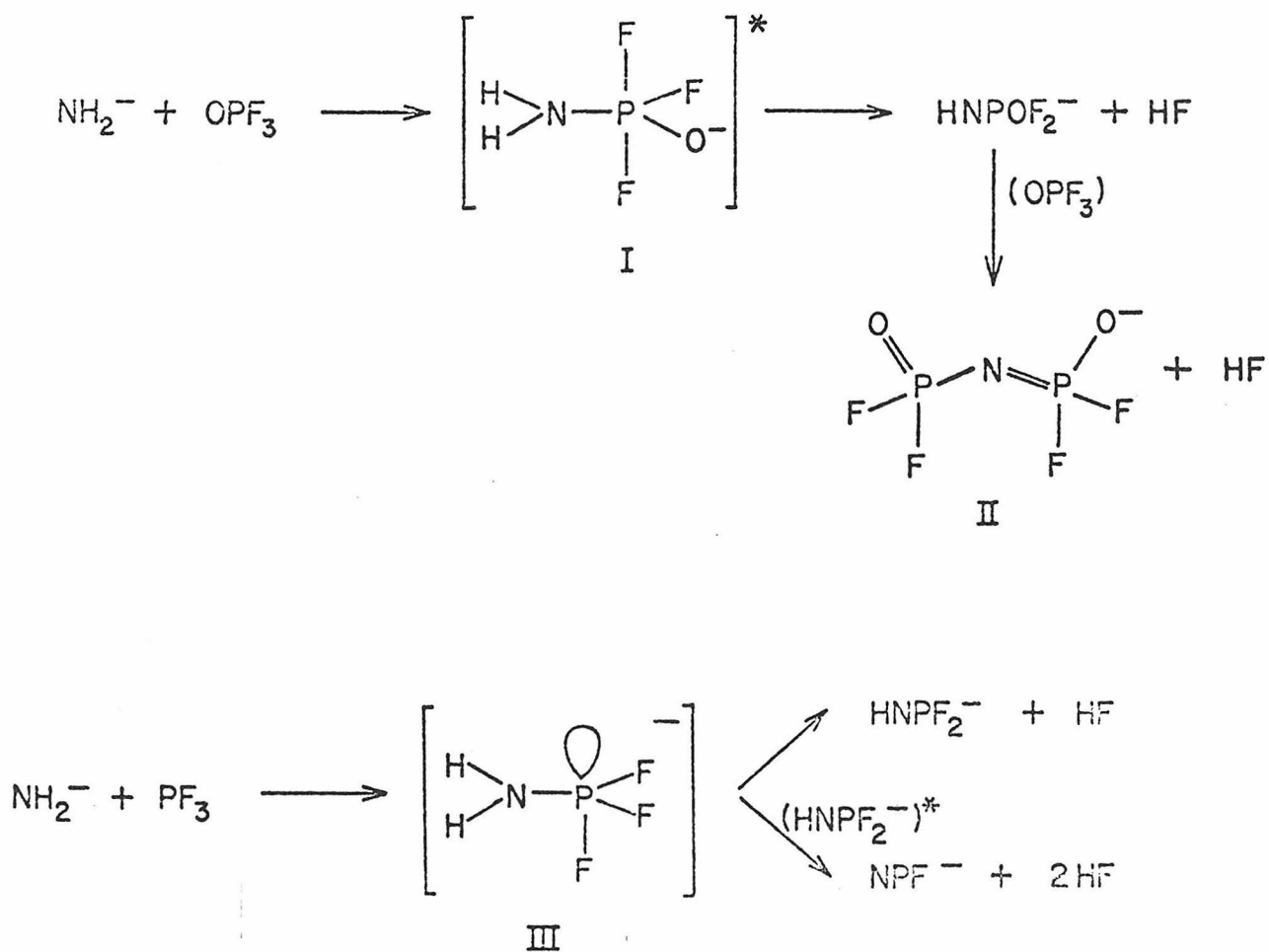


Scheme I

penta coordinate intermediate I dissociates by elimination of HF. The initial product $HNOPF_2^-$ reacts further with $OPF_3$ to form $N(OPF_2)_2^-$, presumably a nitrogen bridged anion (II). In contrast, the reaction of $NH_2^-$ with $PF_3$ results in two products $HNPF_2^-$ and $NPF^-$ (Scheme I). The intermediate in this case, III, also dissociates by elimination of HF. The product $HNPF_2^-$ may be formed with sufficient internal excitation for further decomposition to occur leading to $NPF^-$.

In the present study, $O_2PF_2^-$, $OSPF_2^-$, and $OPF_2^-$ do not react further with the neutrals examined. In solution these ions are weakly nucleophilic, displacing halides from phosphoryl and carbonyl compounds.[1] Direct displacement of $F^-$ in gas phase ion molecule reactions is very slow ($k \sim 10^{-12}$ cm$^3$mol$^{-1}$s$^{-1}$).[37] Since the phosphorous anions noted above do not contain H or alkyl group to form an energetically favorable neutral leaving group (HF or RF), they are unreactive in these systems.

There are several interesting mechanistic possibilities for the reactions of $HNO^-$ with $OPF_3$ and $PF_3$ (Scheme II). In reactions with alkyl boranes, for example with $(CH_3)_3B$ (eq 35), $HNO^-$ acts as a hydride donor. With stronger acids such as $HCO_2H$, an apparent proton transfer occurs[38] (eq 36) with $H_2$ and NO assumed to be the neutral products.

$$HNO^- + (CH_3)_3B \rightarrow (CH_3)_3BH^- + NO \qquad (35)$$

$$HNO^- + HCO_2H \rightarrow HCO_2^- + H_2 + NO \qquad (36)$$
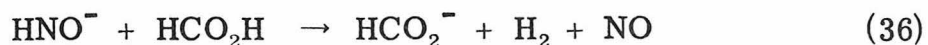
Reaction 36 could proceed as a proton transfer or by decomposition of a chemically activated hydride transfer product $[CH_3O^-]^*$. In reaction
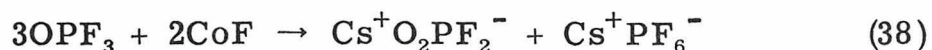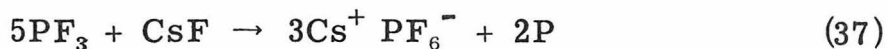
of $OPF_3$ with $HNO^-$, proton transfer is impossible. The formation of
an energetic hydride transfer intermediate IV as in Scheme II is
feasible however. This intermediate would then decompose by elimina-
tion of HF, as proposed for the intermediates in Scheme I. The for-
mation of $NOPF_2^-$ by reaction of $HNO^-$ with $PF_3$ suggests a more
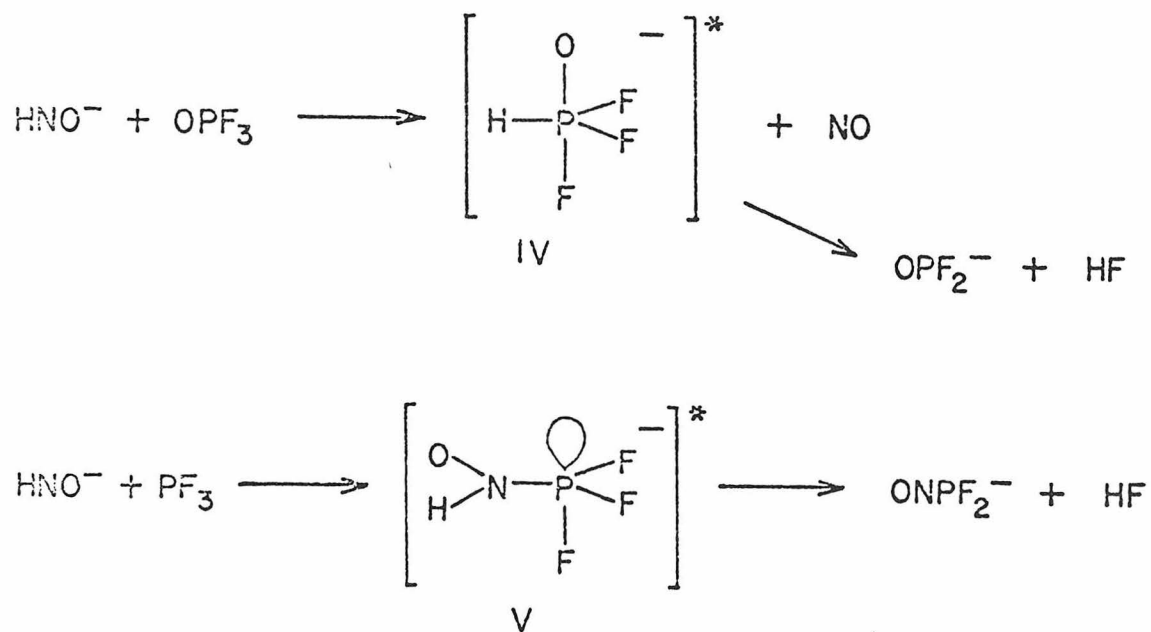


Scheme II

complicated process. Direct complexation of HNO$^-$ to PF$_3$ as in intermediate V in Scheme II, followed by elimination of HF is a possible pathway to the observed ionic product.

Fluoride Transfer Reactions and Lewis Acidities. In solution, relative Lewis acidities are determined by measurement of the dissociation energies of acid–base complexes, such as R$_3$B–NR$_3$. A wide range of such complexes are formed with PF$_5$ acting as an acid. Trivalent phosphorus (III) compounds are generally considered as electron donors, but weakly bound complexes of PF$_3$ with tertiary amines have been reported.[39] Only acid–base complexes in which OPF$_3$ behaves as a base, with bonding through oxygen, have been observed.[40] A comparison of the relative abilities of OPF$_3$, PF$_3$ and PF$_5$ to bind F$^-$ is seen in their reaction with CsF in solution.[41] With PF$_5$, the salt Cs$^+$PF$_6^-$ is readily produced on treatment of PF$_5$ with CsF. The species Cs$^+$OPF$_4^-$ and Cs$^+$PF$_4^-$ have not been observed under similar conditions with OPF$_3$ and PF$_3$. In these cases, more complicated reactions occur to form the more stable Cs$^+$PF$_6^-$ (eq 37) and Cs$^+$O$_2$PF$_2^-$ (eq 38). These

$$5PF_3 + CsF \rightarrow 3Cs^+\,PF_6^- + 2P \qquad (37)$$

$$3OPF_3 + 2CoF \rightarrow Cs^+O_2PF_2^- + Cs^+PF_6^- \qquad (38)$$

solution results indicate that Lewis acidity should decrease in the order PF$_5$ $\gg$ PF$_3$ > OPF$_3$.

Gas phase Lewis acidities toward F$^-$, as measured using icr techniques, decrease in the somewhat different order PF$_5$ > OPF$_3$ > PF$_3$ (Table III).[42] The susceptibility of OPF$_3$ to nucleophilic attack is strong evidence that OPF$_3$ acts as an electron acceptor, consistent with the present results. Kinetic instability

rather than thermodynamic instability may prevent the observation of base complexes with $OPF_3$ in solution. Alternatively, differential solvation effects may cause the inversion of acidities in solution.

The relative acidities of $PF_5$, $OPF_3$ and $PF_3$ toward $F^-$ as a reference base reflect the decreasing electron density at phosphorous. The ordering observed in this study parallels the increase in Lewis acidities of fluorinated methyl silanes with increased number of fluorine ligands $(CH_3)_3SiF < (CH_3)_2SiF_2 < CH_3SiF_3$[15] (Table II). The failure to observe $F^-$ adduct formation with alkyl phosphate esters and the predominance of nucleophilic attack at carbon in these compounds, is then consistent with the lower electronegativity of alkoxide groups compared to fluorine. These results suggest that fluorinated phosphate esters (i.e., $OPF(OCH_3)_2$) may have moderate gas phase Lewis acidities toward $F^-$ as a base. If this is true, anionic fluorine transfer will be a useful method for chemical ionization detection[16] of these compounds.[43]

In conclusion, anionic nucleophilic attack on $OPF_3$ and $PF_3$ occurs at phosphorous with anionic products the result of HF elimination from tetra and penta coordinated intermediates. Reaction is enhanced with increased basicity of the attacking anion. This is in contrast to the reactivity of alkyl phosphate esters, in which anionic attack occurs preferentially at carbon. Fluoride transfer reactions suggest that $OPF_3$ and $PF_3$ are considerably stronger Lewis acids than phosphorous esters. Both of these differences appear to be a consequence of the decreased electron density at phosphorous in $OPF_3$ and $PF_3$ which is imposed by the electronegative fluorine ligands.

References and Notes

(1) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorous", Elsevier, Amsterdam, 1967.

(2) (a) G. M. Kosolapoff and L. Maier, "Organic Phosphorous Compounds", Wiley Interscience, New York, N.Y., 1972; (b) J. R. Van Wazer, "Phosphorous and Its Compounds", Interscience, New York, N.Y., 1958.

(3) Attack and displacement at phosphoryl groups is important in biological energy transfer processes, see reference 2b.

(4) D. B. Denny, A. K. Tsolis, and K. Mislow, J. Amer. Chem. Soc., 84, 4486 (1964).

(5) I. Dostrovsky and M. Halmann, J. Chem. Soc., 1004 (1956).

(6) D. Samuel and B. L. Silver, Adv. in Phys. Org. Chem., 3, 123 (1965).

(7) K. W. Hausen and L. S. Bartell, Inorg. Chem., 4, 1775 (1965).

(8) E. R. Kyba, J. Amer. Chem. Soc., 97, 2554 (1976).

(9) S. A. Sullivan and J. L. Beauchamp, J. Amer. Chem. Soc., accepted for publication.

(10) J. F. G. Faigle, P. C. Isolaini, and S. M. Riveros, J. Amer. Chem. Soc., 98, 2049 (1976).

(11) J. A. Bowie and B. D. Williams, Aust. J. Chem., 27, 1923 (1974).

(12) O. I. Asubiojo, L. K. Blair, and J. I. Brauman, J. Amer. Chem. Soc., 97, 6685 (1975).

(13) R. V. Hodges, S. A. Sullivan, and J. L. Beauchamp, unpublished results.

(14) N. T. Thuong, Bull. Soc. Chim. France, 928 (1971).

(15) M. K. Murphy and J. L. Beauchamp, Inorg. Chem., accepted for publication.

(16) See for example, H. P. Tannenbaum, J. D. Roberts, and R. C. Dougherty, Analytical Chem., 47, 49 (1975).

(17) J. L. Beauchamp, Ann. Rev. Phys. Chem., 22, 527 (1972).

(18) T. B. McMahon and J. L. Beauchamp, Rev. Sci. Instrum., 43, 509 (1972).

(19) M. S. Foster and J. L. Beauchamp, unpublished results.

(20) A. G. Marshall and S. E. Buttrill, Jr., J. Chem. Phys., 52, 2750 (1970) and T. B. McMahon, Ph.D. Thesis, California Institute of Technology, Pasadena, 1973, Chapter V.

(21) R. W. Odom, D. L. Smith, and J. H. Futrell, Chem. Phys. Lett., 24, 227 (1974) and M. S. Foster and J. L. Beauchamp, Chem. Phys. Lett., 31, 482 (1975).

(22) K. Jaeger and A. Heinglein, Z. Naturforsch A., 222, 700 (1967).

(23) J. G. Dillard, Chem. Rev., 73, 590 (1973).

(24) G. E. Melton and G. A. Neece, J. Amer. Chem. Soc., 93, 6757 (1971).

(25) W. A. Noyes, Org. Synthesis, 2, 108 (1943).

(26) T. C. Rhyne and J. G. Dillard, Int. J. Mass Spectrom. Ion Phys., 7, 371 (1971).

(27) K. A. G. MacNeil and J. C. J. Thynne, J. Phys. Chem., 74, 2257 (1970).

(28) These ionic species may be formed by electron attachment to trace impurities or neutral products of surface reactions. Similar processes may generate $Cl_2^-$ in $CF_2CFCl$. See, S. A. Sullivan and J. L. Beauchamp, <u>Chem. Phys. Lett.</u>, <u>48</u>, 294 (1977).

(29) Since $OH^-$ is generated by a very fast reaction of $H^-$ with $H_2O$, $H^- + H_2O \rightarrow OH^- + HO$ (see reference 24). Similar processes (i.e., $H^- + PF_3 \rightarrow PF_2^- + HF$) are possible in these systems. Double resonance experiments eliminate this possibility.

(30) J. L. Beauchamp, <u>J. Chem. Phys.</u>, <u>64</u>, 929 (1976).

(31) The chemical formula of this ion is inferred from its mass and precursor. The ion structure has not been established.

(32) M. K. Murphy and J. L. Beauchamp, <u>J. Amer. Chem. Soc.</u>, <u>98</u>, 1433 (1976).

(33) B. S. Freiser, T. B. McMahon, and J. L. Beauchamp, <u>Int. J. Mass Spectrom. Ion Phys.</u>, <u>12</u>, 249 (1973).

(34) Entropy effects in equilibrium reaction 21 are estimated to be negligible by comparison of $\Delta S_{298}$ of $OPF_3$, $(CH_3)_3B$, $PF_5$, and $(CH_3)_3CF$. The latter two species are isoelectronic with the reactant ions $OPF_4^-$ and $(CH_3)_3BF^-$, respectively. See S. W. Benson, "Thermochemical Kinetics", 2nd Ed., Wiley and Sons, New York, N.Y., 1976.

(35) S. A. Sullivan and J. L. Beauchamp, "Positive and Negation Ion Chemistry of Sulfuryl Halides", Chapter III of this thesis.

(36) L. Bass, T. Su, W. J. Chesnavich, and M. T. Bowers, <u>Chem. Phys. Lett.</u>, <u>34</u>, 119 (1975).

(37) D. K. Bohme, G. J. Mackay, and J. D. Payzant, J. Amer. Chem. Soc., 96, 4027 (1974).

(38) S. A. Sullivan and J. L. Beauchamp, unpublished results (see Appendix II of this thesis).

(39) R. R. Holmes, W. P. Gallagher, and R. P. Carter, Jr., Inorg. Chem., 2, 437 (1963), and E. L. Muetterties and W. Mahler, Inorg. Chem., 4, 119 (1965).

(40) R. R. Holmes and J. A. Forstner, Inorg. Chem., 2, 380 (1963), and R. R. Holmes, J. Amer. Chem. Soc., 82, 5285 (1960).

(41) M. Lustig and J. K. Ruff, Inorg. Chem., 6, 2115 (1967).

(42) A previous gas phase study suggests the relative $F^-$ binding energies decrease $PF_5^- > PF_4^- > OPF_4^-$. T. C. Rhyne and J. G. Dillard, J. Amer. Chem. Soc., 91, 6521 (1969) and T. C. Rhyne and J. G. Dillard, Inorg. Chem., 10, 730 (1971). This ordering is based on relative cross sections for $F^-$ transfer from $SF_6^-$. Rates do not necessarily reflect thermochemistry. See J. C. Haartz and D. H. McDaniel, J. Amer. Chem. Soc., 95, 3562 (1973).

(43) Fluorophosphonates are used widely as pesticides. The high human toxcities of some of these compounds necessitates the development of sensitive and specific methods of detection. See, R. D. O'Brien "Toxic Phosphorous Esters: Chemistry, Metabolism and Biological Effects", Academic Press, New York, N.Y., 1960.

CHAPTER II

Acid-Base Properties of 1-Methyl-1, 4
Dihydroborabenzene, $CH_3BC_5H_6$

S. A. Sullivan, H. Sanford, J. L. Beauchamp, and A. J. Ashe III

## ABSTRACT

Ion cyclotron resonance techniques are employed to determine the gas phase Brönsted and Lewis acidities as well as the Brönsted basicity of 1-methyl-1,4 dihydroborabenzene, $CH_3BC_5H_6$. The ring proton is found to be highly acidic with $PA(CH_3BC_5H_5) = 337 \pm 3$ kcal/mol. This acidity results from the formation of a $6\pi$ electron aromatic anion $CH_3BC_5H_5^-$, which is isoelectronic with toluene. Both the Lewis acidity and proton basicity of the parent molecule suggest that there is little interaction between the diene $\pi$ system and the electron deficient boron. This is further confirmed by the similarity of both negative and positive ion chemistry of the borabenzene to that of aliphatic boranes.

## Introduction

Ionic $6\pi$ electron aromatic compounds isoelectronic with ben-
zene can be generated and studied in the gas phase where their intrinsic
properties and reactivities can be probed without interference from
solvent effects. For example, on protonation of pyridine to form
$C_5H_6N^+$ (Scheme I), the cation retains the aromatic properties of
neutral pyridine. The low solution basicity of pyridine compared to
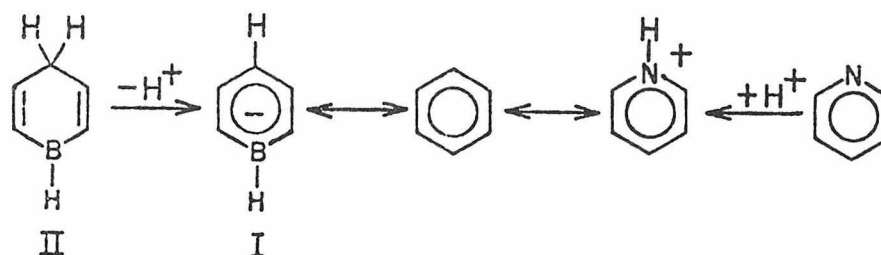


Scheme I

aliphatic amines has been interpreted as the result of increased s
character in the nitrogen lone pair. This hybridization change is the
result of the involvement of nitrogen in the planar $\pi$ system. Ion
cyclotron resonance measurements indicate that the gas phase basicity
of pyridine is significantly greater than that of $NH_3$ and comparable to
aliphate amines.[1] Differential solvation is responsible for the dis-
crepancy between gas phase and solution results.

An anionic analog of benzene can be generated by proton
abstraction from dihydroborobenzene (II) (Scheme I). If boron

participates effectively in $\pi$ bonding, the anion I will be resonance stabilized, imposing a high acidity on the ring protons of the conjugate acid precursor. Not surprisingly, solution studies in THF indicate that the methyl substituted 1,4-dihydroborabenzene (eq 1) (III)[2] is a very strong acid, considerably stronger than cyclopentadiene under the same

$$\text{III} \longrightarrow \text{IV} + H^+ \tag{1}$$
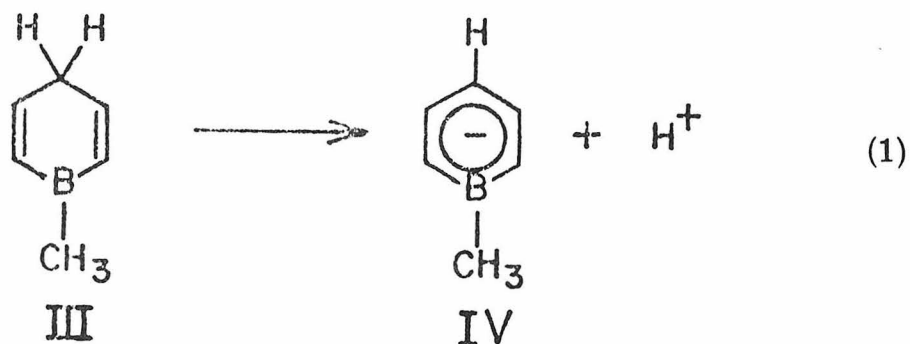
conditions.[3]

As with proton basicities, gas phase studies indicate that molecular acidities are strongly moderated by solvation effects. For example, the lower solution acidity of fluorene (pK 23) compared to cyclopentadiene (pK 14-15) has been explained as the result of decreased availability of the electrons to the five-membered ring (annellation) in the fluorenyl anion.[4] In the gas phase, fluorene is slightly more acidic than cyclopentadiene (Table I).[5] The solution acidities are apparently strongly moderated by decreased solvation of the larger fluorenyl anion.

In addition to extensive $\pi$ delocalization in the anion (IV), it is possible that the electron rich diene system may donate electron density into the deficient boron in the neutral borane. The question of $\pi$

Table I. Gas Phase Acidities of Selected Compounds[a]

| MH | PA(M⁻) | D(M−H) | EA(M) |
|---|---|---|---|
| $CH_3CHCH_2$ | 388[b, c] | 87[g] | 12.7[j] |
| (1,4-pentadiene structure) | 359.7 ± 0.4[d] | 67[b] | 20.4 ± 0.3[j] |
| (cyclopentadiene structure) | 352.7 ± 0.2[d] | 81.2[h] | 42.4 ± 0.7[k] |
| (fluorene structure) | 348.5[d] | - - | - - |
| (borabenzene structure) | 335 ± 2.0[e] | (74)[i] | (53)[b, i] |
| (dimethyl borabenzene structure) | 363[e] | - - | - - |
| $(CH_3)_3B$ | 365 ± 5[f] | - - | - - |

[a] All values in kcal/mol at 298°K.

[b] Calculated using data in this table.

[c] J. H. Richardson, L. M. Stephenson, and J. I. Brauman, J. Chem. Phys., 59, 5068 (1973).

[d] Reference 5.

[e] This study.

[f] Reference 17.

[g] S. W. Benson, "Thermochemical Kinetics", Wiley Interscience, New York, N.Y., 1976.

[h] S. Furuyama, D. M. Golden, and S. W. Benson, Int. J. Chem. Kinetics, 3, 237 (1971).

[i] Estimated as the bond strength in cyclohexadiene, Reference 20.

[j] J. I. Brauman, private communication.

delocalization in vinyl boranes has been examined by several spectro-scopic techniques including uv,[6] nmr,[7] and photoelectron spectros-copy (PES).[8] It has been reported that the photoelectron spectra of vinyl borane indicates little or no delocalization into the boron orbital.[8] On the other hand, both ultraviolet[6] spectra and nmr studies[7] have been interpreted in terms of this delocalization. For example, a recent $^{13}$C-nmr study relates the large deshielding of the terminal carbons in vinyl boranes to $\pi$ interactions with boron.[7] This deshielding was considerably decreased in the Lewis acid-base com-plexes of the vinyl boranes, in which the boron orbital is bonded to a substituent base. By similar reasoning it is expected that the availa-bility of the boron orbital for bonding to a base would be directly effected by $\pi$ delocalization in the neutral.

Gas phase Lewis acidities of neutrals are determined by measuring bond strengths of neutrals to reference anionic bases such as $F^-$.[9] Ion cyclotron resonance studies have provided Lewis acidities of a variety of S, Si, and B compounds toward $F^-$ as a reference base (Table II).

In this study we have investigated the gas phase acid-base properties of $CH_3BC_5H_6$. The proton acidity as well as the Lewis acidity and proton basicity have been determined. By comparisons with appropriate model compounds the present results provide information relating to the degree of resonance stabilization in the anion and $\pi$ delocalization in the neutral.

Table II. Gas Phase Fluoride Bond Strengths[a]

| M | D(M−F)[b] |
|---|---|
| $BF_3$ | 71[c] |
| $SiF_4$ | < 71[c] |
| $(C_2H_5)_2FB$ | 64.0 |
| $(C_2H_5)_3B$ | 62.0 |
| $(CH_3)_2FB$ | 61.8 |
| $CH_3SiF_3$ | 60.2[d] |
| $CH_3BC_5H_6$ | ∼ 59[e] |
| $(CH_3)_3B$ | 58.5 |
| $(CH_3)_2SiF_2$ | 56[d] |
| $SF_4$ | 54 ± 12[f] |
| $SF_5$ | 11 ± 8[f] |

[a]All values in kcal/mol at 298°K, listed in order of decreasing bond strengths.

[b]Bond strengths to boron species from M. K. Murphy and J. L. Beauchamp, Inorg. Chem., in press, and Reference 17.

[c]J. C. Haartz and D. M. McDaniel, J. Amer. Chem. Soc., 95, 8562 (1973).

[d]Estimates based on order of strengths in Reference 9.

[e]This study.

[f]M. S. Foster and J. L. Beauchamp, submitted for publication.

## Experimental

ICR instrumentation and techniques have been detailed pre-viously.[10,11] All experiments were performed on a spectrometer built in this laboratory, incorporating a 15" magnet capable of observing up to $m/e$ 800. Pressure was measured using a Schulz–Phelp ion gauge, calibrated at higher pressures against an MKS Model 90-H1 baratron capacitance manometer. Pressure measurements are the major source of error ($\pm$ 20%) in reported reaction rate constants.

Double resonance techniques were employed to determine the preferred direction of proton transfer reactions in mixtures. Relative proton basicities and acidities result from these data. In acidity studies, the anionic conjugate bases of the neutrals to be compared were generated in proton abstraction reactions of the strong gas phase base $CD_3O^-$. In a similar manner, relative Lewis acidities toward the reference base $F^-$ were determined in mixtures with $SF_6$, in which fluoride donors are produced by electron attachment.

Near thermal electron attachment produces $CD_3O^-$ (75%) and $HNO^-$ (25%) in $CD_3ONO$.[12] The deuterated nitrite is used to distinguish between $CH_3O^-$ and $HNO^-$ which both appear at $m/e$ 31. At moderate pressures of nitrite ($5 \times 10^{-5}$ torr), $NO_2^-$ is formed on reaction of $CD_3O^-$ with the nitrite. By variation of the partial pressures of the components of mixtures, $NO_2^-$ can be generated in amounts adequate for study of its reactions. Electron attachment processes in $SF_6$ result in formation of $SF_6^-$ (95%) and $SF_5^-$ (5%).[13] $F^-$ is similarly generated from $NF_3$.[14]

The methods of synthesis of the boron compounds used in this study have been described previously.[2] The purity and identities of $CH_3BC_5H_6$ and the dimethyl analog $CH_3BC_5H_4(CH_3)_2$ were checked by H-nmr and mass spectral analysis. The latter sample contained ~ 5% of an unidentified boron species at $\underline{m/e}$ 124-126. Since relative proton acidity studies were not affected by the impurity, no attempt was made to purify the sample. No trace of isotopic impurity was detected in the H-nmr or mass spectrum of the deuterated borabenzene $CD_3BC_5H_6$.

Preparation and use of alkyl nitrites has been described previously.[15] All other compounds used in these experiments were from commercial sources and used without further purification except for repeated freeze-pump-thaw cycles to remove noncondensible impurities.
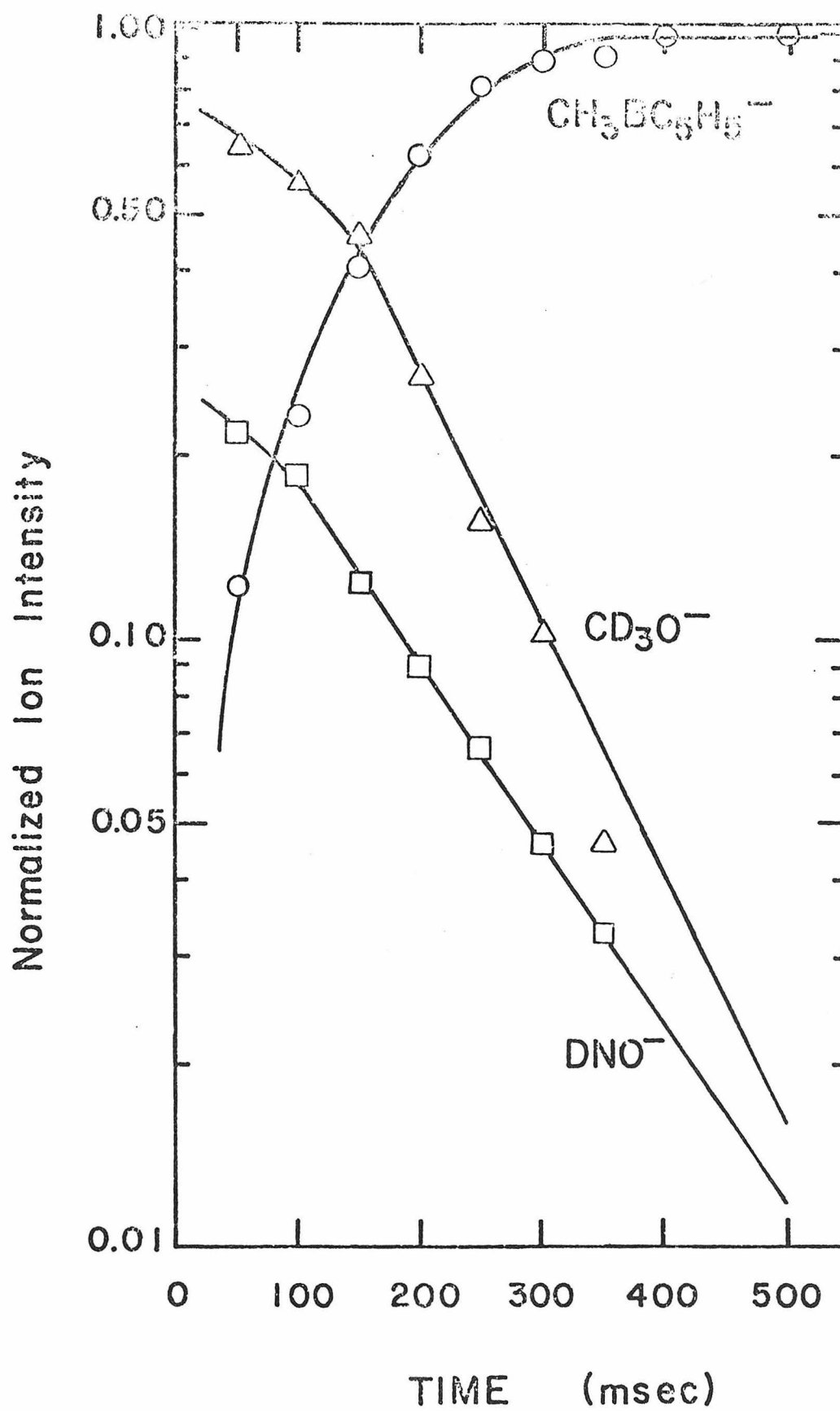
Normalized intensities of boron ions reported in tables and figures are the sum of $^{10}B$ and $^{11}B$ isotope intensities. In all cases, the naturally occurring isotope ratios were observed ($^{10}B$, 19.9% and $^{11}B$, 80.1%). For simplicity, only the mass of the more abundant $^{11}B$ isotopes are included in the text and figures.

Results

Proton Acidity of $CH_3BC_5H_6$. Figure 1 presents the temporal variation of normalized ion intensity in a (1.3:1) mixture of $CH_3BC_5H_6$ and $CD_3ONO$ at a total pressure of $8.0 \times 10^{-7}$ torr. Double resonance experiments confirm that both $CD_3O^-$ ($\underline{m/e}$ 34) and $DNO^-$ ($\underline{m/e}$ 32) react with $CH_3BC_5H_6$ by proton transfer to form $CH_3BC_5B_5^-$ ($\underline{m/e}$ 91),
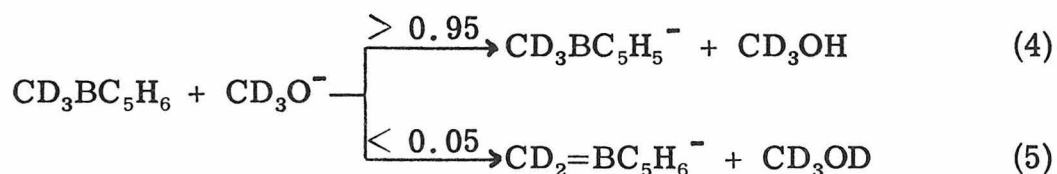
FIGURE 1

Temporal variation of normalized negative ion intensity in a (1.3:1) mixture of $CH_3BC_5H_6$ and $CD_3ONO$ at total pressure $8.0 \times 10^{-7}$ torr.

$$CD_3O^- + CH_3BC_5H_6 \rightarrow CH_3BC_5H_5^- + CD_3OH \qquad (2)$$

$$DNO^- + CH_3BC_5H_6 \rightarrow CH_3BC_5H_5^- + DH + NO \qquad (3)$$

as in eqs 2 and 3, where neutrals are assumed. The ring proton is more acidic, as shown by the predominance of $CD_3BC_5H_5^-$ ($\underline{m/e}$ 94) in the reaction of $CD_3O^-$ with $CD_3BC_5H_6$ as seen in eqs 4 and 5. Rates of

$$CD_3BC_5H_6 + CD_3O^- \begin{cases} \xrightarrow{>0.95} CD_3BC_5H_5^- + CD_3OH \qquad (4) \\ \xrightarrow{<0.05} CD_2{=}BC_5H_6^- + CD_3OD \qquad (5) \end{cases}$$

reactions 2 and 3 are listed in Table III.

Proton transfer processes were further examined in mixtures of $CD_3ONO$, $(CH_3)_3B$, $HCO_2H$, $HCN$, $HCl$, $C_6H_5OH$ and $C_6H_5CO_2H$ with $CH_3BC_5H_6$ to determine the acidity of the latter species. In each case, $CD_3ONO$ was added to insure the formation of both anionic species, by reaction of the strong base $CD_3O^-$. The preferred direction of proton transfer in these mixtures was determined using double resonance techniques. Proton transfer reaction 6 is observed only in the direction noted with $B^- = (CH_3)_2B{=}CH_2^-$, $CN^-$, $HCO_2^-$ and $NO_2^-$. In contrast,

$$B^- + CH_3BC_5H_6 \rightarrow CH_3BC_5H_5^- + HB \qquad (6)$$

$CH_3BC_5H_5$ reacts with HCl to form $Cl^-$ (eq 7). Double resonance

$$CH_3BC_5H_5^- + HCl \rightarrow Cl^- + CH_3BC_5H_6 \qquad (7)$$
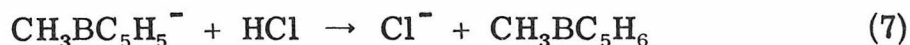
irradiation of $Cl^-$ results in a slight decrease in $CH_3BC_5H_5^-$ ion intensity, suggesting that reaction 7 may also occur in the reverse direction.

Table III. Summary of Measured Reaction Rates

| Reaction | $k_{ex}$ [a] |
|---|---|
| $CD_3O^- + CH_3BC_5H_6 \longrightarrow CH_3BC_5H_5^- + CD_3OH$ | 11.1 |
| $DNO^- + CH_3BC_5H_6 \longrightarrow CH_3BC_5H_5^- + DH + NO$ | 3.2 |
| $SF_6^- + CH_3BC_5H_6 \xrightarrow{0.75} SF_5^- + HF + CH_3BC_5H_5$ | 1.25 |
| $\xrightarrow{0.25} F_2BC_5H_6^- + CH_3 + SF_4$ | 0.22 |
| $SF_5^- + CH_3BC_5H_6 \longrightarrow F(CH_3)BC_5H_6^- + SF_4$ | 0.56 |
| $SF_6^- + (CH_3)_3B \longrightarrow SF_5^- + HF + (CH_3)_2BCH_2$ | 3.7 |
| $\longrightarrow F_2B(CH_3)_2^- + SF_4 + CH_3$ | 1.4 |
| $SF_5^- + (CH_3)_3B \longrightarrow FB(CH_3)_2^- + SF_4$ | 2.8 |

[a] $k_{ex}$ in units of $10^{-10}$ $cm^3 mol^{-1} sec^{-1}$.

However, equilibrium could not be achieved in this mixture by variation of the relative pressures of the neutrals. In mixtures of $C_6H_5OH$ and $C_6H_5CO_2H$ with $CH_3BC_5H_6$, the conjugate bases were formed in abundance by proton transfer to $CD_3O^-$. In each case, no reactive coupling of the anions was detected by double resonance. This is not very surprising considering that reactions of conjugated anions are generally very slow.[16] These experiments combined with literature data suggest that acidity increases in the order $(CH_3)_3B > HCO_2H > HCN > HNO_2 > CH_3BC_5H_6 > HCl$. The acidities of the reference compounds have been determined previously as listed in Table IV. Using these data, $PA(CH_3BC_5H_5^-)$ is estimated as $335 \pm 2$ kcal/mol.

Lewis Acidity of $CH_3BC_5H_6$. The bond strength $D(M-F^-)$ is a measure of the Lewis acidity of the species M. Relative fluoride bond strengths to a variety of neutrals have been measured previously and are listed in Table II. The acidity of a compound toward fluoride ion as a reference base can be measured by determining the preferred direction of $F^-$ transfer in mixtures with neutrals of known acidity.[9] Anionic $F^-$ adducts are formed in these experiments by reactions of $SF_6^-$ and/or $SF_5^-$.

Temporal variation of normalized ion intensity in a mixture of $CH_3BC_5H_6$ ($7.16 \times 10^{-7}$ torr) with a trace amount ($< 10^{-7}$ torr) of $SF_6$ is presented in Figure 2. Ionic products $SF_5^-$ (m/e 127), $F(CH_3)BC_5H_6^-$ (m/e 111) and $F_2BC_5H_6^-$ (m/e 115) increase as $SF_6^-$ (m/e 146) decays with time. Double resonance confirms that $SF_6^-$ reacts to form $SF_5^-$ (eq 8) and $F_2BC_5H_6^-$ (eq 9). The $F^-$ adduct $F(CH_3)BC_5H_6^-$ is formed only

Table IV. Gas Phase Acidities of Selected Reference Acids[a]

| MH | PA(M⁻) |
|---|---|
| $CD_3OH$ | 378.4[b] |
| HF | 371.3[c] |
| $CF_3CH_2OH$ | 364 ± 5[d] |
| $AsH_3$ | 360 ± 10[e] |
| HCN | 348.9[c] |
| $C_6H_5OH$ | 346.9[f] |
| $HCO_2H$ | 342.2[g] |
| $C_6H_5CO_2H$ | 336.7[g] |
| HCl | 333.3[c] |

[a]All values in kcal/mol at 298°K. Unless otherwise noted, error limits are ± 0.5 or less.

[b]R. T. McIver, Jr. and J. S. Miller, J. Amer. Chem. Soc., 96, 4323 (1974) and J. E. Bartness and R. T. McIver, Jr., J. Amer. Chem. Soc., 99, 4163 (1977).

[c]Calculated using thermochemical data from D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd edition, U. S. Government Printing Office, Washington, D.C., 1971.

[d]B. S. Freiser and J. L. Beauchamp, unpublished results.

[e]R. H. Wyatt, D. Holtz, T. B. McMahon, and J. L. Beauchamp, Inorg. Chem., 13, 1511 (1974).

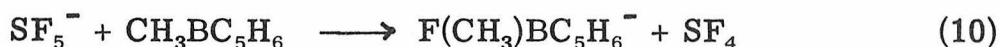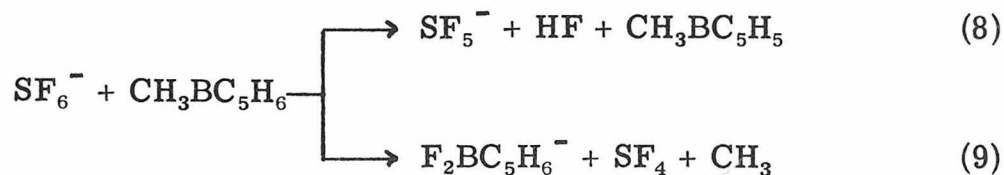[f]R. T. McIver, Jr. and J. H. Silvers, J. Amer. Chem. Soc., 95, 8462 (1973).

[g]T. B. McMahon and P. Kebarle, J. Amer. Chem. Soc., 99, 2222 (1977) and references contained therein.
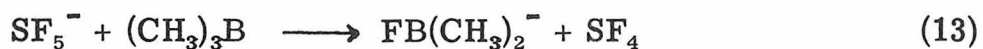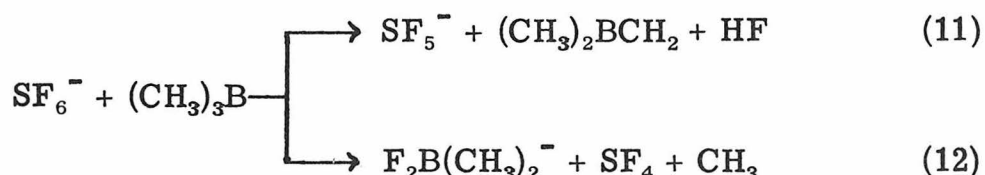
FIGURE 2

Temporal variation of normalized negative ion intensity in a mixture of $7.16 \times 10^{-7}$ torr $CH_3BC_5H_6$ with a trace amount of $SF_6$.
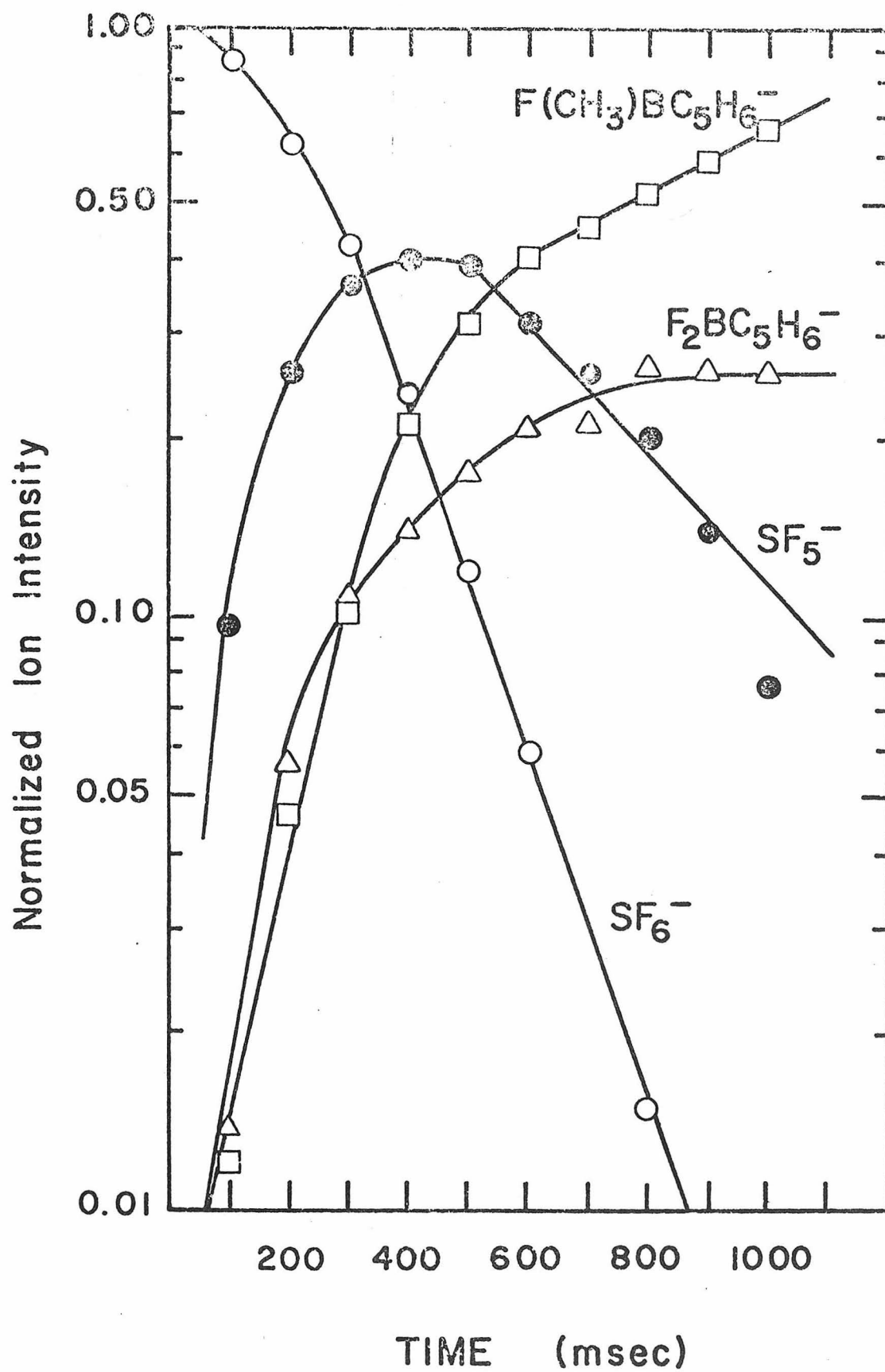
by reaction of $SF_5^-$ (eq 10). Rates for these reactions (eqs 7-10) are summarized in Table III.

$$SF_6^- + CH_3BC_5H_6 \longrightarrow \begin{cases} SF_5^- + HF + CH_3BC_5H_5 & (8) \\ \\ F_2BC_5H_6^- + SF_4 + CH_3 & (9) \end{cases}$$

$$SF_5^- + CH_3BC_5H_6 \longrightarrow F(CH_3)BC_5H_6^- + SF_4 \tag{10}$$

Fluoride transfers were examined in mixtures of $(CH_3)_3B$ and $(CH_3)_2SiF_2$ with $CH_3BC_5H_6$ and a trace amount of $SF_6$. When $(CH_3)_3B$ is added to $SF_6$,[17] product ions $(CH_3)_3BF^-$ ($\underline{m/e}$ 75) and $(CH_3)_2BF_2^-$ ($\underline{m/e}$ 79) and $SF_5^-$ ($\underline{m/e}$ 127) result in reactions 11-13 analogous to

$$SF_6^- + (CH_3)_3B \longrightarrow \begin{cases} SF_5^- + (CH_3)_2BCH_2 + HF & (11) \\ \\ F_2B(CH_3)_2^- + SF_4 + CH_3 & (12) \end{cases}$$

$$SF_5^- + (CH_3)_3B \longrightarrow FB(CH_3)_2^- + SF_4 \tag{13}$$

processes 8-10. These reactions are summarized in Table III with rates included for comparison to reactions of $CH_3BC_5H_6$. With addition of $CH_3BC_5H_6$, double resonance indicates that $(CH_3)_3BF^-$ reacts to form $F(CH_3)BC_5H_6^-$ (eq 14). Although there is some indication

$$(CH_3)_3BF^- + CH_3BC_5H_6 \rightarrow F(CH_3)BC_5H_6^- + (CH_3)_3B \tag{14}$$
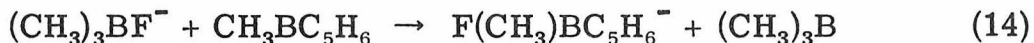
that the reverse reaction occurs, the slow rate of formation of $F(CH_3)BC_5H_6^-$ from $SF_5^-$ hinders quantitative measurement of the equilibrium constant for $F^-$ transfer in this reaction. The difluoride

ion $(CH_3)_2BF_2^-$ does not contribute to the formation of $F(CH_3)BC_5H_6^-$ suggesting that reaction 15 is endothermic.

$$(CH_3)_2BF_2^- + CH_3BC_5H_6 \longrightarrow F(CH_3)BC_5H_6^- + (CH_3)_2BF \qquad (15)$$
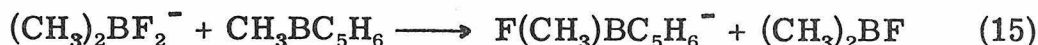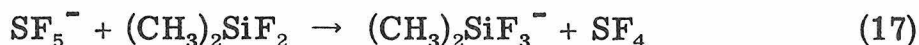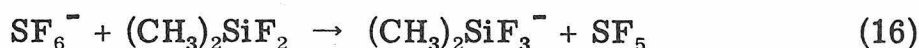
Both $SF_6^-$ (eq 16) and $SF_5^-$ (eq 17) react to form $(CH_3)_2SiF_3^-$ ($\underline{m/e}$ 115) on electron impact of a mixture of $(CH_3)_2SiF_2$ and $SF_6$.[9]

$$SF_6^- + (CH_3)_2SiF_2 \rightarrow (CH_3)_2SiF_3^- + SF_5 \qquad (16)$$

$$SF_5^- + (CH_3)_2SiF_2 \rightarrow (CH_3)_2SiF_3^- + SF_4 \qquad (17)$$

On addition of $CH_3BC_5H_6$, double resonance indicates that $(CH_3)_2SiF_3^-$ transfers $F^-$ to $CH_3BC_5H_6$ (eq 18). These results suggest the Lewis

$$(CH_3)_2SiF_3^- + CH_3BC_5H_6 \rightarrow F(CH_3)BC_5H_6^- + (CH_3)_2SiF_2 \qquad (18)$$

acidities increase $SF_5 < (CH_3)_2SiF_2 < (CH_3)_3B \sim CH_3BC_5H_6 < (CH_3)_2BF$. A value of 59 kcal/mol for $D(CH_3BC_5H_6 - F^-)$ is estimated from $F^-$ bond strengths in Table II.

$\underline{\text{Proton Affinity of } CH_3BC_5H_6}$. Proton transfer reactions were examined in mixtures of $CH_3BC_5H_6$ with $CH_4$, $(CH_3)_2CHCH_2$, $CH_3CHCH_2$, $c-C_6H_{10}$ and $CH_3COCH_3$ to determine the basicity of the borabenzene. Protonation of $CH_3BC_5H_6$ to form $CH_3BC_5H_7^+$ ($\underline{m/e}$ 93) occurs with proton donors ($MH^+ = CH_5^+$, $C_2H_5^+$ and $(CH_3)_3C^+$) as in reaction 19.

$$MH^+ + CH_3BC_5H_6 \rightarrow CH_3BC_5H_7^+ + M \qquad (19)$$

Double resonance indicates that reaction occurs in both directions with

M = isobutene. Failure to observe equilibrium in this case suggests that deprotination of $CH_3BC_5H_7^+$ is slow.

Conclusive results were not obtained in other mixtures. In mixtures of $CH_3BC_5H_6$ with $c$-$C_6H_{10}$ and $CH_3CHCH_3$, the boron compound is preferentially protonated by the parent and fragment ions of the alkenes. In both cases, little or no protonated alkene is observed. The reverse situation obtains in mixtures of $CH_3BC_5H_6$ with $CH_3COCH_3$, in which protonation of acetone predominates and proton transfer from this species to the neutral borane is not observed. These results suggest that proton affinities increase $CH_4 < C_2H_4 < CH_3CHCH_2 < (CH_3)_2CCH_2 \sim CH_3BC_5H_6 < CH_3COCH_3$, with $PA(CH_3BC_5H_6)$ estimated as 195 kcal/mol (Table V). From a limiting value for the ionization potential $IP(CH_3BC_5H_6) < 9.0 \pm 0.50$ eV obtained from appearance potential measurements,[19] a hydrogen affinity[10] $HA(CH_3BC_5H_6^+)$ = $89 \pm 11$ kcal/mol is estimated, somewhat higher than expected by analogy to trans-2-butene (Table V).

Positive Ion Chemistry of $CH_3BC_5H_6$. Three major ions represent $\sim 95\%$ of total ionization in the 70.0 eV electron impact mass spectrum of $CH_3BC_5H_6$, the parent ion $CH_3BC_5H_6^+$ (m/e 92, 12%), loss of methyl to give $BC_5H_6^+$ (m/e 77, 22%) and loss of hydrogen to yield $CH_3BC_5H_5^+$ (m/e 91, 61%). The latter ion, first detected at electron energies $\sim 0.50$ eV higher than the $IP(CH_3BC_5H_6)$,[19] becomes the most abundant fragment above 10.0 eV. These three ions are unreactive with $CH_3BC_5H_6$. In particular, double resonance of the boron isotopes of $BC_5H_6^+$ indicate that the thermoneutral $CH_3^-$ transfer (eq 20) does

Table V. Gas Phase Proton Affinities, Hydrogen Affinities, and Ionization Potentials of Selected Alkenes[a]

| M | PA(M)[b] | HA(M$^+$)[b] | IP(M) | $\Delta H_f$(MH$^+$) |
|---|---|---|---|---|
| CH$_2$CH$_2$ | 161 | 89 | 242.4 | 219 |
| CH$_3$CHCH$_2$ | 181 | 92 | 224.6 | 191 |
| (structure) | 181 | 78 | 210.5 | 183 |
| (structure) | 182 | 79 | 210.5 | 183 |
| (structure) | 196 | 95 | 212.8 | 167 |
| (structure) | 200 | 84 | 197.6 | 199[c] |
| (structure) | 178 | 72 | 207.7 | 197[c] |
| (structure, B) | 195 | 88[d] | $< 207 \pm 12$[d] | - - |

[a]All values in kcal/mol at 298°K. Unless otherwise noted, IP(M) and $\Delta H_f$(MH$^+$) are taken from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. and Chem. Ref. Data, 6, Supplement 1 (1977).

[b]Calculated from thermochemical data listed in this table.

[c]Calculated using data in F. P. Lossing and J. C. Traeger, J. Amer. Chem. Soc., 97, 1579 (1975).

[d]See text.

not occur in contrast to reactions in $(CH_3)_3B$.[17]

$$^{10}BC_5H_6^+ + CH_3{}^{11}BC_5H_6 \;\;\cancel{\rightleftharpoons}\;\; {}^{11}BC_5H_6^+ + CH_3{}^{10}BC_5H_6 \qquad (20)$$
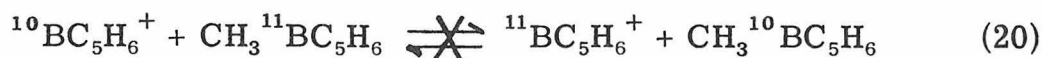
Positive Ion Chemistry in Mixtures of $(CH_3)_3B$ and $CH_4$ with $CH_3BC_5H_6$. In trapped ion studies of mixtures of $CH_3BC_5H_6$ and $(CH_3)B$, double resonance confirms that the major fragment ion of $(CH_3)_3B$, $(CH_3)_2B^+$, reacts with $CH_3BC_5H_6$ to form $CH_3BC_5H_5^+$ (eq 21) and $BC_5H_6^+$ (eq 22).

$$(CH_3)_2B^+ + CH_3BC_5H_6 \begin{cases} \xrightarrow{0.66} CH_3BC_5H_5^+ + (CH_3)_2BH & (21) \\[2ex] \xrightarrow{0.33} BC_5H_6^+ + (CH_3)_3B & (22) \end{cases}$$
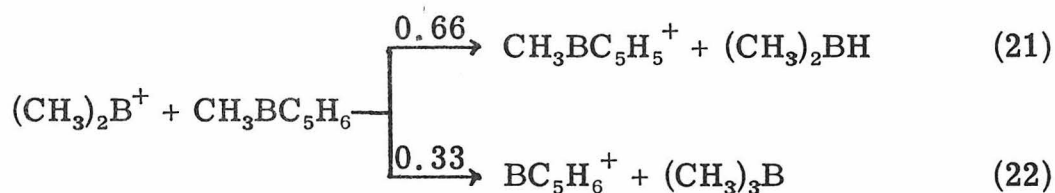
As described above, proton transfer reactions in mixtures of $CH_3BC_5H_6$ with a variety of proton donors were examined. With $CH_4$, the reactivity of $CH_5^+$ and $C_2H_5^+$ were studied in more detail. In addition to proton transfer reactions (eq 5), both $CH_5^+$ (eq 23) and $C_2H_5^+$ (eq 24) react with $CH_3BC_5H_6$ to form $BC_5H_6^+$. $CH_5^+$ also contributes to the formation of $CH_3BC_5H_5^+$ (eq 25). This reaction involves cleavage of the ring hydrogen, as determined by reaction with $CD_3BC_5H_6$ (eq 26).

$$CH_5^+ + CH_3BC_5H_6 \begin{cases} \longrightarrow BC_5H_6^+ + 2CH_4 & (23) \\[2ex] \longrightarrow CH_3BC_5H_5^+ + H_2 + CH_4 & (24) \end{cases}$$

$$C_2H_5^+ + CH_3BC_5H_6 \longrightarrow BC_5H_6^+ + C_3H_8 \qquad (25)$$

$$CH_5^+ + CD_3BC_5H_6 \longrightarrow CD_3BC_5H_5^+ + H_2 + CH_4 \qquad (26)$$
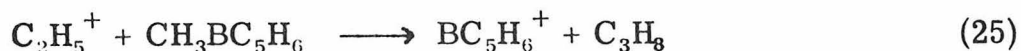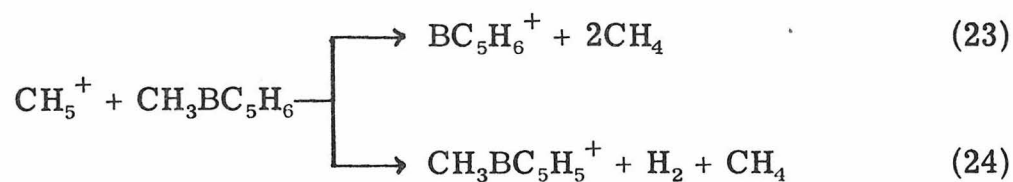
Negative Ion Chemistry. Proton transfer processes dominate the negative ion chemistry of $CH_3BC_5H_6$. To probe the interaction of negative ions with the vinyl borane moiety, chemistry in mixtures with $CH_3BC_5H_5(CH_3)_2$ (V) was examined. These studies also provide a

$$\underset{\text{V}}{\text{[structure: 6-membered ring with B at bottom bearing CH}_3\text{, and a carbon bearing two CH}_3\text{ groups]}}$$
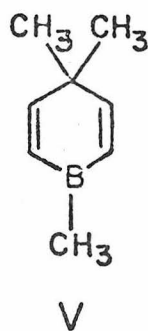
qualitative measure of the proton acidity of the boron methyl.

In a mixture of V with $CD_3ONO$, anionic products $CH_2{=}BC_5H_4(CH_3)_2^-$ ($\underline{m/e}$ 119), $CD_3O(CH_3)BC_5H_4(CH_3)_3^-$ ($\underline{m/e}$ 154) and $D(CH_3)BC_5H_4(CH_3)_2^-$ ($\underline{m/e}$ 122) appear. Double resonance indicates that $CD_3O^-$ reacts with V by proton transfer (eq 27) and direct anion addition (28). Product distributions in eqs 27 and 28 are determined

$$CD_3O^- + CH_3BC_5H_4(CH_3)_2 \overset{0.48}{\underset{0.52}{\rightarrow}}
\begin{cases}
CH_2{=}BC_5H_4(CH_3)_2^- + CD_3OH & (27)\\[1em]
CD_3O(CH_3)BC_5H_4(CH_3)_2^- & (28)
\end{cases}$$
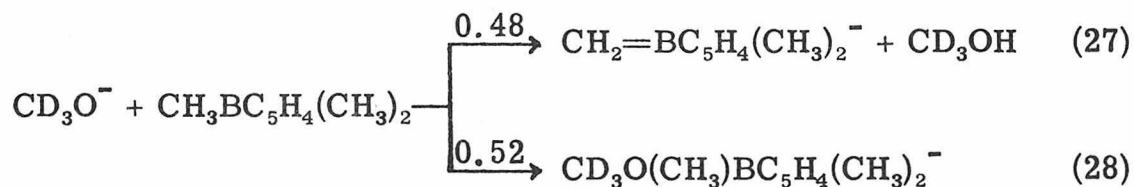
from drift mode single resonance ion intensities at $1 \times 10^{-5}$ torr of borane. The anion addition product (eq 28) increases markedly relative to proton transfer, as the borane pressure is increased. This is consistent with increased collisional stabilization of the adduct ion at higher pressures. In contrast to reactivity in $CH_3BC_5H_6$, $DNO^-$ reacts with V to form only $D(CH_3)BC_5H_4(CH_3)_2^-$ by deutride transfer (eq 29).

$$DNO^- + (CH_3)BC_5H_4(CH_3)_2 \rightarrow D(CH_3)BC_5H_4(CH_3)_2^- + NO \qquad (29)$$
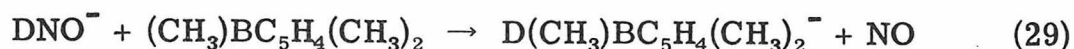
Direct formation of anionic adducts (eq 30) is observed with anions $X^- = CD_3O^-$, $NO_2^-$, and $Cl^-$. In contrast, $F^-$ reacts with V only by proton transfer (eq 31).

$$X^- + (CH_3)BC_5H_4(CH_3)_2 \rightarrow X(CH_3)BC_5H_4(CH_3)_2^- \qquad (30)$$

$$F^- + (CH_3)BC_5H_4(CH_3)_2 \rightarrow CH_2{=}BC_5H_4(CH_3)_2^- + HF \qquad (31)$$
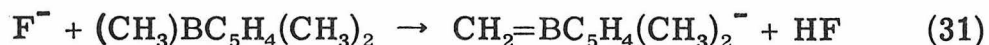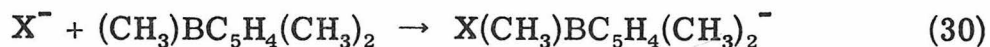
Attempts were made to determine the preferred direction of proton transfer in mixtures of V with $AsH_3$ and $CF_3CH_2OH$. Although the anionic conjugate bases were formed by proton transfer to $CD_3O^-$ in both bases, no reactive coupling of $AsH_2^-$ and $CF_3CH_2O^-$ with $CH_2{=}BC_5H_4(CH_3)_2^-$ was observed. Only rough limits $\sim 365$ kcal/mol $<$ $PA(CH_2BC_5H_4(CH_3)_2^-) < 370$ kcal/mol are suggested by reaction 30 and the failure to observe proton transfer to $DNO^-$ (Table IV).[18] The proton affinity $PA[(CH_3)_2B{=}CH_2^-]$ was determined previously in a similar manner to be $365 \pm 5$ kcal/mol.[19]

## Discussion

The acid–base properties of $CH_3BC_5H_6$ reflect the degree of interaction of the diene $\pi$ system with the empty B orbital in both the neutral and conjugate base. The unusually high acidity of $CH_3BC_5H_6$, comparable to HCl, indicates that the anion is resonance stabilized with participation of the boron orbital to form a $6\pi$ aromatic anion. In contrast, no evidence is found for $\pi$ delocalization in $CH_3BC_5H_6$.

Delocalization of $\pi$ electron density into the B orbital in the neutral would be expected to decrease its availability for bonding, i.e.,

result in a low Lewis acidity or electron acceptor ability. There is no significant decrease in Lewis acidity of $CH_3BC_5H_6$ compared to $(CH_3)_3B$ or $(C_2H_5)_3B$ (Table II). Similarly, the basicity of the ring in $CH_3BC_5H_6$ is expected to be decreased if a favorable $\pi$ interaction is disrupted by protonation. Although proton affinities vary significantly with substitution for homologous series, hydrogen affinities of the cations (homolytic bond dissociation energies) appear to be representative of the site of protonation (Table V).[10] As noted above, the thermochemical properties derived for $CH_3BC_5H_6$ and the protonated species $CH_3BC_5H_7^+$, are consistant with protonation of an unperturbed alkene (Table V). Finally, both positive and negative ion reactions involving the boron moiety in $CH_3BC_5H_6$ are similar to those observed with alkyl boranes. The Lewis acidity proton affinity and ion chemistry of $CH_3BC_5H_6$ are all consistent with PES results,[8] indicating that there is little interaction of the diene $\pi$ system with boron.

Delocalization in Aromatic Anions. The proton affinity of an anion $B^-$, $PA(B^-)$, is related to the homolytic bond energy $D(BH)$ and the electron affinity $EA(B)$ by eq 32, in which the ionization potential of

$$PA(B^-) = D(B{-}H) - EA(B) + IP(H) \qquad (32)$$

H, $IP(H) = 313.6$ kcal/mol. Relative proton affinities or acidities are the result of differences in bond strength and electron affinities, which reflect the stability of the radical B and the anion $B^-$, respectively. If two of the quantities in eq 32 are known, it is possible to assess how differences in radical and anion stabilities affect the acidity of a species.

By comparison to appropriate model compounds with known acidities, it is possible to quantify the resonance energy of aromatic anions. For example, in the gas phase $c$-$C_5H_6$ is only 7 kcal/mol more acidic than the open chain 1, 4-pentadiene, $C_5H_8$ (Table I). Cyclopentadienyl radical has an electron affinity 22 kcal/mol higher than the open chain diene. The 15 kcal/mol higher bond strength in $c$-$C_5H_6$ compared to 1, 4-pentadiene is responsible for the small acidity difference in the two dienes. This change in bond strength can be attributed for the most part to ring strain in the radical $c$-$C_5H_5$. The difference in electron affinities $EA(c\text{-}C_5H_5) - EA(C_5H_7)$ does not directly measure the delocalization energy in $c$-$C_5H_6$, since it ignores structural changes required to form the strained planar anion. If it is assumed that the strain in the anion is equal to that in the radical, 15 kcal/mol, a delocalization energy of 37 kcal/mol is calculated for $c$-$C_5H_5^-$.

Neither the electron affinity of the borabenzene radical $EA(CH_3BC_5H_5)$ nor the strength of the ring $C-H$ bond in the neutral have been measured. An $EA(CH_3BC_5H_5) = 58$ kcal/mol is estimated, however, by assuming that the $C-H$ bond strength is equal to that in 1, 4-cyclohexadiene (74 kcal/mol).[20] The delocalization energy is the quantity needed for comparison to other aromatic systems. By the same analysis used for cyclopentadienyl anion, comparisons of relative bond strengths and electron affinities of $CH_3BC_5H_6$ and 1, 4-pentadiene yield a delocalization or resonance energy of 40 kcal/mol for $CH_3BC_5H_5^-$. Although admittedly dependent on the assumptions made, this indicates little difference in delocalization energies of the 5-center $6\pi$-electron cyclopentadienyl anion and the 6-center $6\pi$-electron

dihydroborabenzene anion. Interestingly, the delocalization energies in both anions is approximately equivalent to that generally accepted for benzene which is determined (36 kcal/mol) from heats of hydrogenation. Simple Hückle molecular orbital theory[21] predicts the equivalence of resonance energy in benzene and cyclopentadienyl anion. However, the extension of these principles to borabenzene anion is not straightforward. These results indicate that the presence of the heteroatom boron has little effect on $\pi$ delocalization in the 6-member ring.

## References and Notes

(1) M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, J. Amer. Chem. Soc., 95, 1369 (1972).

(2) A. J. Ashe III, E. Meyers, P. Shu, T. von Lehmann, and J. Bastide, J. Amer. Chem. Soc., 97, 6865 (1975).

(3) A. J. Ashe III, private communication.

(4) See discussion in J. March, "Advances in Organic Chemistry Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, Chapter 8.

(5) T. B. McMahon and P. Kebarle, J. Amer. Chem. Soc., 98, 3399 (1976).

(6) J. R. Durig, R. O. Carter, and J. D. Odom, Inorg. Chem., 13, 701 (1974).

(7) L. W. Hall, J. D. Odom, and P. D. Ellis, J. Amer. Chem. Soc., 97, 4527 (1975).

(8) A. K. Holliday, W. Reade, K. R. Seddon, and I. A. Steer, J. Organomet. Chem., 67, 1 (1974).

(9) M. K. Murphy and J. L. Beauchamp, J. Amer. Chem. Soc., in press.

(10) J. L. Beauchamp, Ann. Rev. Phys. Chem., 22, 527 (1971).

(11) T. B. McMahon and J. L. Beauchamp, Rev. Sci. Instrum., 43, 509 (1972).

(12) K. Jaeger and A. Heinglein, Z. Naturforsch A, 222, 700 (1967).

(13) R. W. Odom, D. L. Smith, and J. H. Futrell, <u>Chem. Phys. Lett.</u>, <u>24</u>, 227 (1974) and M. S. Foster and J. L. Beauchamp, <u>Chem. Phys. Lett.</u>, <u>31</u>, 482 (1975).

(14) A review of electron attachment processes is given in J. G. Dillard, <u>Chem. Ref.</u>, <u>73</u>, 641 (1973).

(15) S. A. Sullivan and J. L. Beauchamp, <u>J. Amer. Chem. Soc.</u>, <u>98</u>, 1061 (1976).

(16) W. E. Farneth and J. I. Brauman, <u>J. Amer. Chem. Soc.</u>, <u>98</u>, 7891 (1976).

(17) M. K. Murphy and J. L. Beauchamp, <u>J. Amer. Chem. Soc.</u>, <u>98</u>, 1433 (1976).

(18) Proton transfer reactions observed in mixtures of moderate acids with $CD_3ONO$ suggest $PA(DNO^-) \cong 365 \pm 5$ kcal/mol (see Appendix II).

(19) Since other measurements are not available, $IP(CH_3BC_5H_6) < 9.0 \pm 0.5$ eV is used, determined from $CH_3BC_5H_6^+$ intensity as a function of electron energy. In a similar way the appearance potential of the loss of hydrogen fragment $AP(CH_3BC_5H_5^+)$ was determined as $\sim 9.5 \pm 0.5$ eV.

(20) S. W. Benson, <u>J. Chem. Ed.</u>, <u>42</u>, 503 (1965).

(21) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory", Benjamin, New York, N.Y., 1964 and J. D. Roberts, A. Streitweiser, Jr. and C. M. Regan, <u>J. Amer. Chem. Soc.</u>, <u>74</u>, 4579 (1952).

# CHAPTER III

Positive and Negative Ion Chemistry
of Sulfuryl Halides

S. A. Sullivan and J. L. Beauchamp

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## ABSTRACT

Ion cyclotron resonance techniques are employed in the investigation of positive and negative ion formation and ion molecule reactions in sulfuryl halides $SO_2XY$ (X, Y = Cl, F). Positive ion reactivity is discussed in terms of the relative Cl and F bond strengths in these species and possible structures of ionic intermediates and products. Electron attachment processes generate halide ion donors such as $F_2^-$, $Cl_2^-$, $SO_2F^-$ and $SO_2Cl^-$ from sulfuryl halides. Negative ion reactivity is dominated by halide transfer reactions. Halide transfer reactions in mixtures with HCN and HCl are examined in an attempt to quantify $D(SO_2-F^-)$ and $D(SO_2-Cl^-)$.

## INTRODUCTION

Electron attachment processes generate fluoride ion donors $SO_2F^-$ and $F_2^-$ in $SO_2F_2$ and chloride ion donors $SO_2Cl^-$ and $Cl_2^-$ in $SO_2Cl_2$ [1]. Facile halide transfers from these ions to a variety of neutrals have been observed. Reactions of this type have been employed to quantify Lewis acidities [2] and hydrogen bond strengths [1] in proton bound dimer ions, i.e., $ClHF^-$. In addition, halide transfer reactions may result in generation of unusual ions such as $CH_3COCl_2^-$ which model solution reaction intermediates [3]. Halide donor ions may also be important for use in negative chemical ionization techniques to provide methods of soft ionization [4]. The characterization of negative ion chemistry in sulfuryl halides is important in relation to these applications. Negative ion formation in $SO_2ClF$ has not been previously examined.

Other uses of sulfuryl halides are related to the relatively weak halide bonds in the neutral. There has been some interest recently in these species as possible reactants for rare gas halide excimer lasers [5]. Laser activity is generally induced by electron beam pumping [6] or electrical discharge [7]. Under such conditions, gaseous mixtures are highly ionized. Consequently, positive and negative ion processes may significantly modify the species present, and thereby affect lasing efficiency.

The present study describes positive and negative ion formation and ion molecule reactions in sulfuryl halides as determined by ion cyclotron resonance spectroscopy. Previous investigations have

considered only the electron impact ionization of $SO_2F_2$ [8] and negative ion generation from $SO_2F_2$ and $SO_2Cl_2$ [1]. In an attempt to quantify the halide bond strengths in $SO_2F^-$ and $SO_2Cl^-$, halide ion transfers are examined in mixtures with HCN and HCl, for which halide binding energies are known [1, 9].

## EXPERIMENTAL

Experiments were performed employing an ICR spectrometer built in this laboratory incorporating a 15" magnet, capable of observing up to $\underline{m/e}$ 800. Instrumentation and experimental techniques of ICR spectroscopy have been described in detail [10, 11]. Pressure measurements were made using a Schulz-Phelp ion gauge, calibrated against an MKS Baratron, Model 90-H1 capacitance manometer, at higher pressures.

Positive ion appearance potentials were estimated using the vanishing current method from the variation of ion intensity as a function of electron energy. The energy scale was calibrated using the known ionization potential of $SO_2F_2$ from photoelectron spectra [12]. These data can only be considered accurate to $\pm 0.5$ eV [13]. All compounds were obtained from commercial sources and used without further purification except for multiple freeze-pump-thaw cycles to remove noncondensible impurities. Sulfuryl chloride decomposes readily on introduction into the ICR inlet system to produce $SO_2$ and presumably $Cl_2$. The amount of $SO_2$ impurity was minimized by repeated flushing of the inlet system with $SO_2Cl_2$. Large drifts in $SO_2Cl_2$ pressure prevented trapping studies and decreased the reliability of pressure studies of this molecule.

For simplicity, only the mass of the most abundant isotopic ion is included in figures and tables. In all cases, the expected natural abundance isotopic ratios were observed. Calculated ion intensities consider isotopic contributions.

## RESULTS

### Electron Impact Mass Spectra and Positive Ion Chemistry

$SO_2F_2$. Table 1 lists normalized relative intensities of fragment ions produced on 70.0 eV electron impact on $SO_2F_2$ ($1 \times 10^{-6}$ torr). The good agreement between these results and previous mass spectra measured under different conditions [8, 14] indicates that $SO_2F_2$ does not decompose in the ICR inlet. As $SO_2F_2$ pressure is raised to $\sim 10^{-4}$ torr and 30.0 eV electron energy, no other ions appear and the relative intensities of the initial fragment ions remain unchanged. Double resonance experiments indicate that no ion molecule reactions occur, in particular $SO_2^+$ does not react to form $SO_2F_2^+$.

$SO_2Cl_2$. The decomposition of $SO_2Cl_2$ is reflected by the variation of $SO_2^+$ intensity with $SO_2Cl_2$ sample age and the length of time that the sample is exposed to the inlet system. Decomposition is minimized by repeated flushing of the inlet system with $SO_2Cl_2$. The 70.0 eV electron impact mass spectrum of $SO_2Cl_2$ described in Table 1, represents a sample in which a minimum amount of decomposition ($\sim$ 15-20%) occurs. As $SO_2Cl_2$ pressure is increased, product ions $(SO_2)_2Cl^+$ ($\underline{m/e}$ 163), $SO_2Cl_3^+$ ($\underline{m/e}$ 169) and $(SO_2Cl_2)SO_2Cl^+$ ($\underline{m/e}$ 233)

TABLE 1

Electron Impact (70.0 eV) Mass Spectra of Sulfuryl Halides

| Ion | $SO_2Cl_2$[a] | | $SO_2FCl$ | | $SO_2F_2$ | | |
|-----|-----------------------|-------------------|-----------------------|----------------|---------------|-------------------|----------------|
| | Relative Intensity | IP or AP[b] | Relative Intensity | IP or AP[b] | Relative Intensity | | IP or AP[b] |
| | | | | | This Study | Previous Studies[f] | |
| parent | 19.7 | 12.05[c,d] 11.4[e] | 90.8 | 12.3[e] | 77.1 | 74 | 13.0[c,d] 13.3[f] |
| loss of Cl | 100.0 | 11.8[e] | 100.0 | 13.0[e] | -- | -- | |
| loss of F | -- | -- | 13.7 | -- | 100.0 | 100 | 14.8[e] 15.1[f] |
| $SOCl^+$ | 4.5 | -- | -- | -- | -- | -- | |
| $SOF^+$ | -- | -- | 23.5 | -- | 25.9 | 30 | |
| $SO_2^+$ | 29.5 | -- | 19.5 | -- | 11.2 | 4 | |
| $SO^+$ | 10.5 | -- | 12.4 | -- | 5.7 | 9 | |

[a]Some decomposition of $SO_2Cl_2$ occurs, resulting in larger amounts of $SO_2^+$ and $SO^+$. Decomposition is estimated as ~ 20%, see text.

[b]Ionization potentials and appearance potentials in eV at 298°C.

[c]IP($SO_2Cl_2$) and IP($SO_2F_2$) taken from ref. 12.

TABLE 1 – Continued

[d]For IP($SO_2Cl_2$) in ref. 12, the vertical ionization potential is assigned a value (12.45 eV) equal to the peak maximum of the broad first band of the pes spectrum. This band represents ionization out of at least three orbitals. The band onset is taken as the adiabatic ionization potential.

[e]Ionization and appearance potentials measured from the variation of ion intensity as a function of electron energy. The electron energy scale is calibrated using IP($SO_2F_2$) = 13.0 eV from ref. 12. Values measured in this way can be considered accurate only to ± 0.5 eV.

[f]From ref. 8. The mass spectrum is also consistent with that presented in ref. 14.

appear. Double resonance experiments indicate that $SO_2Cl_2^+$ reacts with $SO_2Cl_2$ to form each of these ions, eqn. (1-3). Product

$$SO_2Cl_2^+ + SO_2Cl_2 \begin{cases} \xrightarrow{0.16} (SO_2)_2Cl^+ + Cl_2 + Cl & (1) \\ \xrightarrow{0.16} SO_2Cl_3^+ + SO_2Cl & (2) \\ \xrightarrow{0.68} (SO_2Cl_2)SO_2Cl^+ + Cl & (3) \end{cases}$$
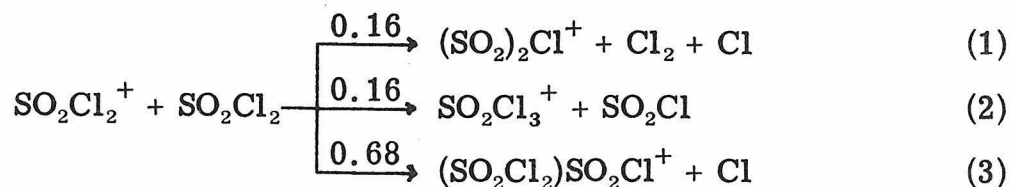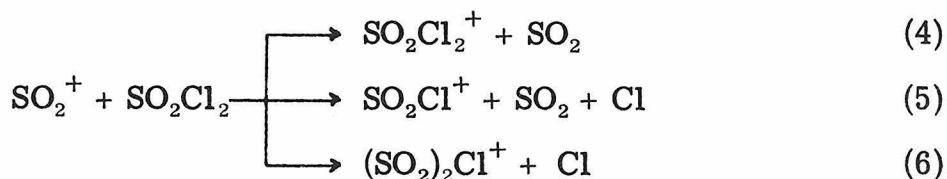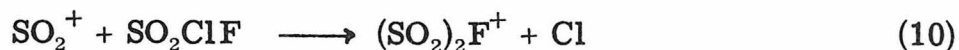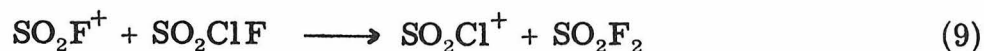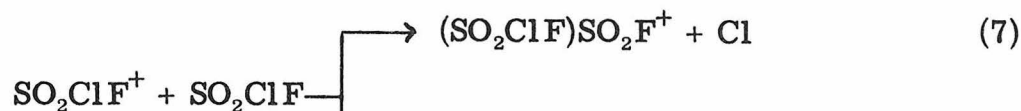
distributions are determined from relative ion intensities at $1.0 \times 10^{-4}$ torr $SO_2Cl_2$. At this pressure, ionic products represent only 11% of total ionization, indicating moderately slow reactions ($\sim 5 \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$). Double resonance further indicates that $SO_2^+$ reacts to produce both $SO_2Cl_2^+$, eqn. (4), and $SO_2Cl^+$, eqn. (5). The enhanced intensity of $(SO_2)_2Cl^+$ only when large amounts of $SO_2^+$ are present suggest that reaction 6 occurs but must proceed quite slowly.

$$SO_2^+ + SO_2Cl_2 \begin{cases} \longrightarrow SO_2Cl_2^+ + SO_2 & (4) \\ \longrightarrow SO_2Cl^+ + SO_2 + Cl & (5) \\ \longrightarrow (SO_2)_2Cl^+ + Cl & (6) \end{cases}$$

$\underline{SO_2ClF}$. Table 1 presents the 70.0 eV electron impact mass spectrum of $SO_2ClF$. Cleavage of the S—Cl bond to form $SO_2F^+$ predominates over formation of $SO_2Cl^+$. Although $SO_2ClF$ samples decompose slowly over several weeks, there is no indication that rapid decomposition occurs on addition of the sample to the inlet system. As $SO_2ClF$ pressure is increased at 30.0 eV electron energy, $SO_2Cl^+$ ($\underline{m/e}$ 99), $(SO_2)_2F^+$ ($\underline{m/e}$ 147) and $(SO_2ClF)SO_2F^+$ ($\underline{m/e}$ 201) increase in intensity as $SO_2F^+$ ($\underline{m/e}$ 83) and $SO_2ClF^+$ ($\underline{m/e}$ 118) decrease. Reactions 7-10, are consistent with observed double resonance spectra. A small

$$\text{SO}_2\text{ClF}^+ + \text{SO}_2\text{ClF} \begin{cases} \longrightarrow (\text{SO}_2\text{ClF})\text{SO}_2\text{F}^+ + \text{Cl} & (7) \\ \\ \longrightarrow (\text{SO}_2)_2\text{F}^+ + \text{Cl}_2 + \text{F} & (8) \end{cases}$$

$$\text{SO}_2\text{F}^+ + \text{SO}_2\text{ClF} \longrightarrow \text{SO}_2\text{Cl}^+ + \text{SO}_2\text{F}_2 \qquad (9)$$

$$\text{SO}_2^+ + \text{SO}_2\text{ClF} \longrightarrow (\text{SO}_2)_2\text{F}^+ + \text{Cl} \qquad (10)$$

contribution of $\text{SO}_2\text{ClF}^+$ to the formation of $(\text{SO}_2)_2\text{F}^+$ suggests a some-what slow reaction 8.

Figure 1 presents the temporal variation of normalized positive ion intensity in $\text{SO}_2\text{ClF}$ at $1.68 \times 10^{-6}$ torr (30.0 eV). Rates for reactions 7, 9 and 10 are determined (Table 2) from semilog plots of normalized ion intensity, by neglecting the contribution of reaction 8.

$\underline{\text{SO}_2\text{F}_2/\text{SO}_2\text{ClF} \text{ and } \text{SO}_2\text{F}_2/\text{SO}_2\text{Cl}_2 \text{ Mixtures.}}$ The reactions of $\text{SO}_2\text{F}_2^+$ with $\text{SO}_2\text{ClF}$ were examined by increasing $\text{SO}_2\text{ClF}$ pressure in a mixture with $1.5 \times 10^{-6}$ torr $\text{SO}_2\text{F}_2$. Reactions 11 and 12 are

$$\text{SO}_2\text{F}_2^+ + \text{SO}_2\text{ClF} \begin{cases} \longrightarrow (\text{SO}_2\text{ClF})\,\text{SO}_2\text{F}^+ + \text{F} & (11) \\ \\ \longrightarrow \text{SO}_2\text{ClF}^+ + \text{SO}_2\text{F}_2 & (12) \end{cases}$$
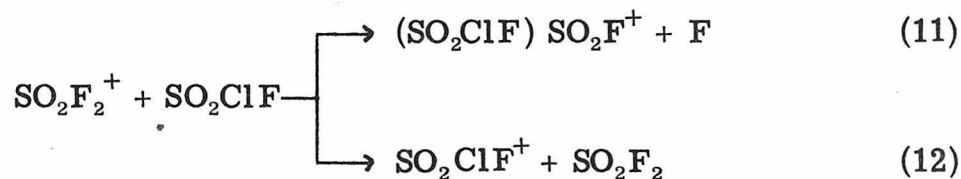
consistent with double resonance experiments.

Similar reactions of $\text{SO}_2\text{F}_2^+$ are observed in mixtures with $\text{SO}_2\text{Cl}_2$, eqn. (13, 14). The molecular ion $\text{SO}_2\text{ClF}^+$ reacts with $\text{SO}_2\text{F}_2$ to

$$\text{SO}_2\text{F}_2^+ + \text{SO}_2\text{Cl}_2 \begin{cases} \longrightarrow (\text{SO}_2\text{Cl}_2)\text{SO}_2\text{F}^+ + \text{F} & (13) \\ \\ \longrightarrow \text{SO}_2\text{Cl}_2^+ + \text{SO}_2\text{F}_2 & (14) \end{cases}$$
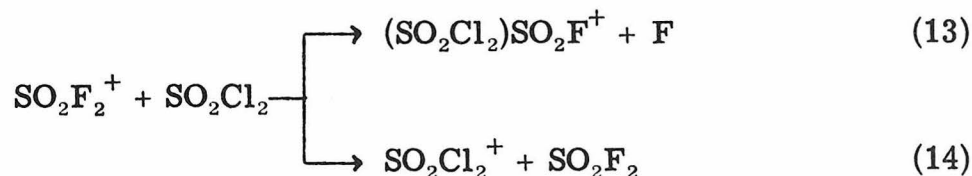
FIGURE 1

Temporal variation of normalized positive ion intensity
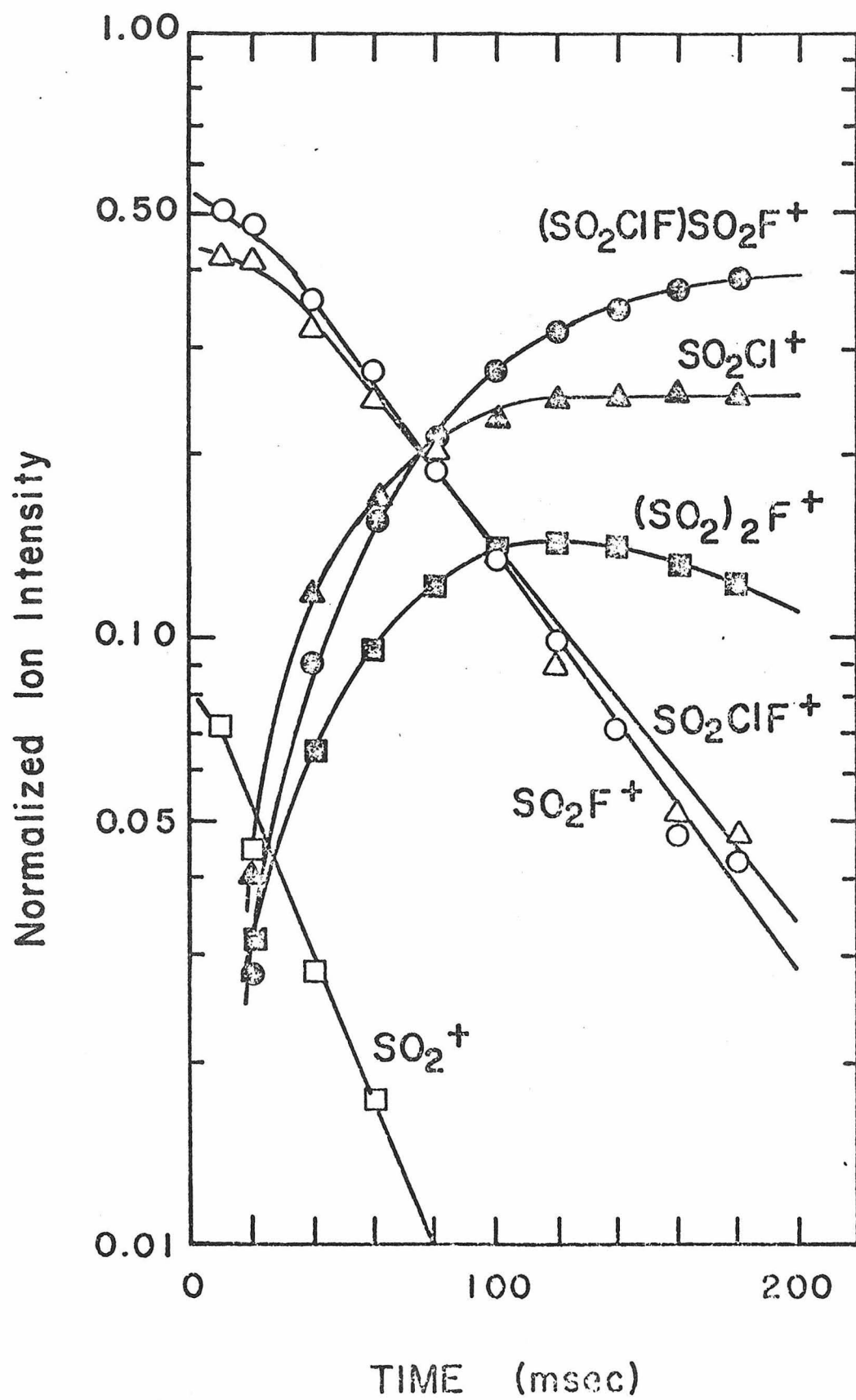in $1.68 \times 10^{-6}$ torr of $SO_2ClF$ at 30.0 eV electron energy.

TABLE 2

Summary of the Ion Molecule Reactions of Sulfuryl Halides

| | $k_{ex}^{a}$ | Thermochemical Inferences, $\Delta H_{reaction}^{b}$ |
|---|---|---|

Positive Ion Reactions

$SO_2Cl_2^+ + SO_2Cl_2$
- $\xrightarrow{0.16} (SO_2)_2Cl^+ + Cl_2 + Cl$ — $\Delta H_f[(SO_2)_2Cl^+] < 79.2$
- $\xrightarrow{0.16} SO_2Cl_3^+ + SO_2Cl$ — $D(SO_2Cl_2^+ - Cl) < D(SO_2Cl-Cl)$
- $\xrightarrow{0.68} (SO_2Cl_2)SO_2Cl^+ + Cl$ — $\Delta H_f[(SO_2Cl_2)SO_2Cl^+] < 79.2$

$SO_2^+ + SO_2Cl_2$
- $\longrightarrow SO_2Cl_2^+ + SO_2$ — $-7$
- $\longrightarrow SO_2Cl^+ + SO_2 + Cl$ — $\Delta H_f[(SO_2)_2Cl^+] < 100$
- $\longrightarrow (SO_2)_2Cl^+ + Cl$ — $-13$

$SO_2ClF^+ + SO_2ClF$
- $\xrightarrow{2.98^c} (SO_2ClF)SO_2F^+ + Cl$ — $\Delta H_f[(SO_2ClF)SO_2F^+] < -10.9$

$SO_2F^+ + SO_2ClF$
- $\xrightarrow{2.59} (SO_2)_2F^+ + Cl_2 + F$ — $\Delta H_f[(SO_2)_2F^+] < 0$
- $\longrightarrow SO_2Cl^+ + SO_2F_2$ — $-31$

$SO_2^+ + SO_2ClF$
- $\longrightarrow (SO_2)_2F^+ + Cl$ — $\Delta H_f[(SO_2)_2F^+] < 52$

$SO_2F_2^+ + SO_2ClF$
- $\longrightarrow (SO_2ClF)SO_2F^+ + F$ — $\Delta H_f[(SO_2ClF)SO_2F^+] < -33$
- $\longrightarrow SO_2FCl^+ + SO_2F_2$ — $\sim -16$

TABLE 2 – Continued

| Reaction | $k_{ex}^a$ | Thermochemical Inferences, $\Delta H_{reaction}^b$ |
|---|---|---|
| $SO_2F_2^+ + SO_2Cl_2 \longrightarrow (SO_2Cl_2)SO_2F^+ + F$ | | $\Delta H_f[(SO_2Cl_2)SO_2F^+] < 15$ |
| $\quad\quad\quad\longrightarrow SO_2Cl_2^+ + SO_2F_2$ | | $\sim -22$ |
| $SO_2ClF^+ + SO_2F_2 \longrightarrow (SO_2F_2)SO_2F^+ + Cl$ | | $\Delta H_f[(SO_2F_2)SO_2F^+] < -59$ |

Negative Ion Reactions

| Reaction | $k_{ex}^a$ | Thermochemical Inferences, $\Delta H_{reaction}^b$ |
|---|---|---|
| $SO_2F^- + SO_2ClF \longrightarrow SO_2Cl^- + SO_2F_2$ | $\sim 0.1$ | $\sim -22$ |
| $Cl^- + SO_2ClF \longrightarrow SO_2F^- + CL_2$ | $1.05$ | $\sim 12$ |
| $SO_2F^- + HCl \longrightarrow SO_2Cl^- + HF$ | $\sim 1.5^d$ | $\sim -13$ |

Halide Transfer Reactions

| Reaction | $k_{ex}^a$ | Thermochemical Inferences, $\Delta H_{reaction}^b$ |
|---|---|---|
| $SO_2F^- + HCl \longrightarrow FHCl^- + SO_2$ | $\sim 1.5^d$ | $D(SO_2-F^-) < D(HCl-F^-)$ |
| $SO_2F^- + HCN \longrightarrow FHCN^- + SO_2$ | | $D(SO_2-F^-) < D(HCN-F^-)$ |
| $SO_2Cl^- + HCl \longrightarrow ClHCl^- + SO_2$ | $1.64$ | $D(SO_2-Cl^-) < D(ClH-Cl^-)$ |
| $FHCl^- + HCl \longrightarrow ClHCl^- + HF$ | $1.40$ | $D(FH-Cl^-) < D(ClH-Cl^-)$ |
| $FHCN^- + HCl \longrightarrow CNHCl^- + HF$ | | $D(FHCN^-) < D(ClH-CN^-)$ |
| $FHCN^- + HCN \longrightarrow CNHCN^- + HF$ | | $D(FH-CN^-) < D(CNH-CN^-)$ |
| $CNHCl + HCl \longrightarrow ClHCl^- + HCN$ | | $D(CNHCl^-) < D(ClH-Cl^-)$ |

TABLE 2 - Continued

[a] $k_{ex}$ in units $10^{-10} cm^3 molecule^{-1} s^{-1}$ .

[b] Based on heats of formation in Table 3. All values in kcal/mol at 298°K.

[c] Calculated assuming that concomitant reaction 8 is slow.

[d] Total rate of decay of $SO_2F^-$ in reaction with HCl is $3 \times 10^{-10}$ cc/molecule sec. Rates noted in table are approximate since product distribution could not be accurately determined.

form $(SO_2F_2)SO_2F^+$ as in eqn. (15). Reactions 11-15 are moderately

$$SO_2ClF^+ + SO_2F_2 \rightarrow (SO_2F_2)SO_2F^+ + Cl \tag{15}$$
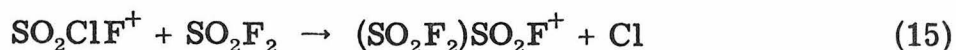
slow($< 10^{-10}$ cm$^3$molecule$^{-1}$s$^{-1}$) with product ions detected only at higher pressures ($> 5 \times 10^{-5}$ torr).

## Negative Ion Chemistry

$\underline{SO_2F_2}$. The generation and reactivity of negative ions have been examined previously in $SO_2F_2$ and $SO_2Cl_2$ [1]. Negative ions are formed by attachment of scattered thermalized electrons provided by impact of a 70.0 eV electron beam. The ions $F^-$ (60%), $F_2^-$ (11%), and $SO_2F^-$ (29%) are formed by electron attachment to $SO_2F_2$ at moderate pressures ($\sim 10^{-5}$ torr). Small amounts of $SO_2F_2^-$, presumably formed by similar processes, appear at high pressures ($\sim 10^{-4}$ torr) of $SO_2F_2$. The only observed reaction is $F^-$ transfer from $F_2^-$ to $SO_2F_2$, eqn. (16).

$$F_2^- + SO_2F_2 \rightarrow SO_2F_3^- + F^- \tag{16}$$
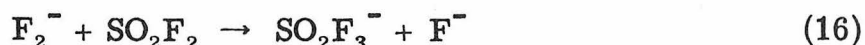
$\underline{SO_2Cl_2}$. Attachment processes from $Cl^-$ (49%), $Cl_2^-$ (8%), and $SO_2Cl^-$ (43%) from $SO_2Cl_2$. Reaction of $Cl^-$ with $SO_2Cl_2$ occurs forming $SO_2Cl^-$, eqn. 17, which further reacts to generate $SO_2Cl_3^-$, eqn. (18).

$$Cl^- + SO_2Cl_2 \rightarrow SO_2Cl^- + Cl_2 \tag{17}$$
$$SO_2Cl^- + SO_2Cl_2 \rightarrow SO_2Cl_3^- + SO_2 \tag{18}$$
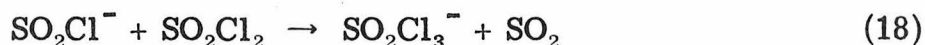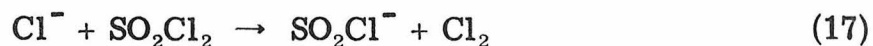
$\underline{SO_2ClF}$. Negative ions $Cl^-$ (16%) and $SO_2F^-$ (84%) are produced by electron attachment to $SO_2ClF$ at 70 eV electron energy. No other

abundant negative ions, in particular $ClF^-$, were detected. As $SO_2ClF$ pressure is raised to $1.74 \times 10^{-4}$ torr, no reactions are apparent. However, trapped ion studies of $SO_2ClF$ (Fig. 2) reveal the very slow reaction of $SO_2F^-$ to form $SO_2Cl^-$, eqn (19), with $k \simeq 1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$s$^{-1}$. A somewhat faster reaction of $Cl^-$ with $SO_2ClF$ to form $SO_2F^-$, eqn (20) is also observed with $k = 1.05 \times 10^{-10}$ cm$^3$molecule$^{-1}$s$^{-1}$.

$$SO_2F^- + SO_2ClF \rightarrow SO_2Cl^- + SO_2F_2 \tag{19}$$

$$Cl^- + SO_2ClF \rightarrow SO_2F^- + Cl_2 \tag{20}$$
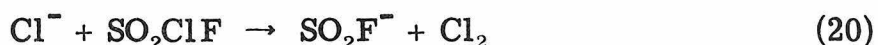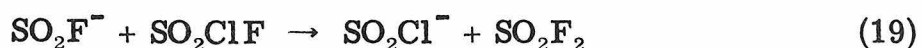
$\underline{SO_2ClF/HCl \text{ Mixture.}}$ Temporal variation of normalized negative ion intensity in a mixture of $6.98 \times 10^{-7}$ torr $SO_2Cl$ and $1.66 \times 10^{-6}$ torr HCl is presented in Fig. 3. Ions $FHCl^-$ ($\underline{m/e}$ 55), $ClHCl^-$ ($\underline{m/e}$ 71) $SO_2Cl^-$ ($\underline{m/e}$ 99) appear as $SO_2F^-$ ($\underline{m/e}$ 83) decays with time. Initially formed $Cl^-$ reacts away very slowly. The larger amount of $SO_2Cl^-$ produced in this mixture compared to that generated in $SO_2ClF$ by reaction 19, suggests that another mechanism is responsible for its formation. Double resonance experiments indicate that $SO_2F^-$ is the only precursor to $SO_2Cl^-$, therefore reaction 21 must occur. Concomitant $F^-$ transfer to HCl, eqn. (22), is also confirmed by double

$$SO_2F^- + HCl \begin{cases} \rightarrow SO_2Cl^- + HF & (21) \\ \rightarrow FHCl^- + SO_2 & (22) \end{cases}$$
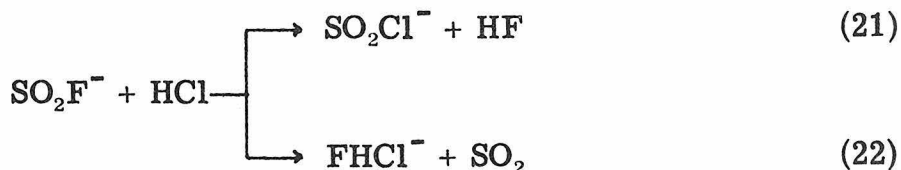
resonance results. Both $SO_2Cl^-$, eqn. (23) and $FHCl^-$, eqn. (24) further react with HCl to form $ClHCl^-$. Rates of reactions 21 and 22 are summarized in Table 2.

FIGURE 2

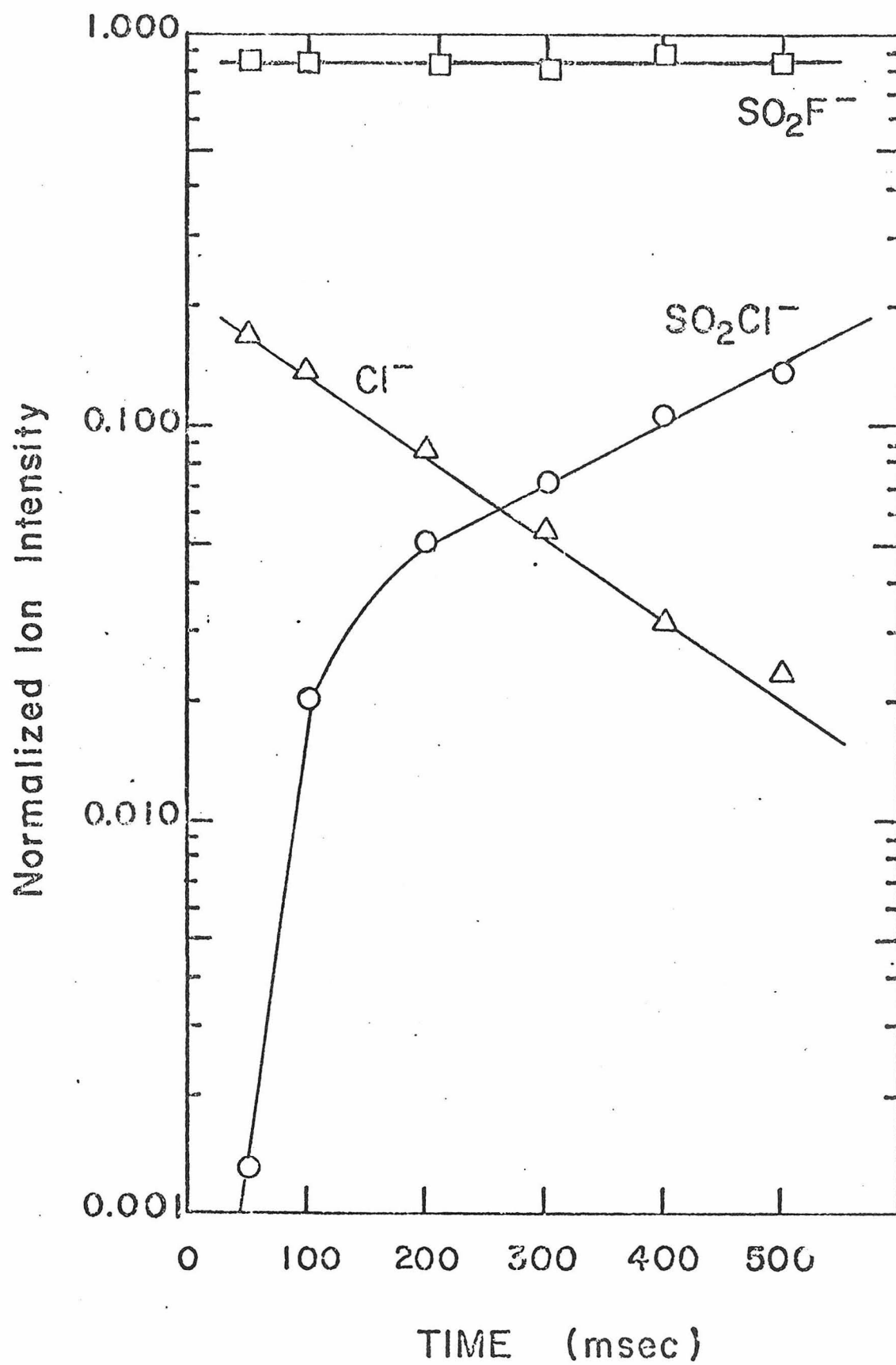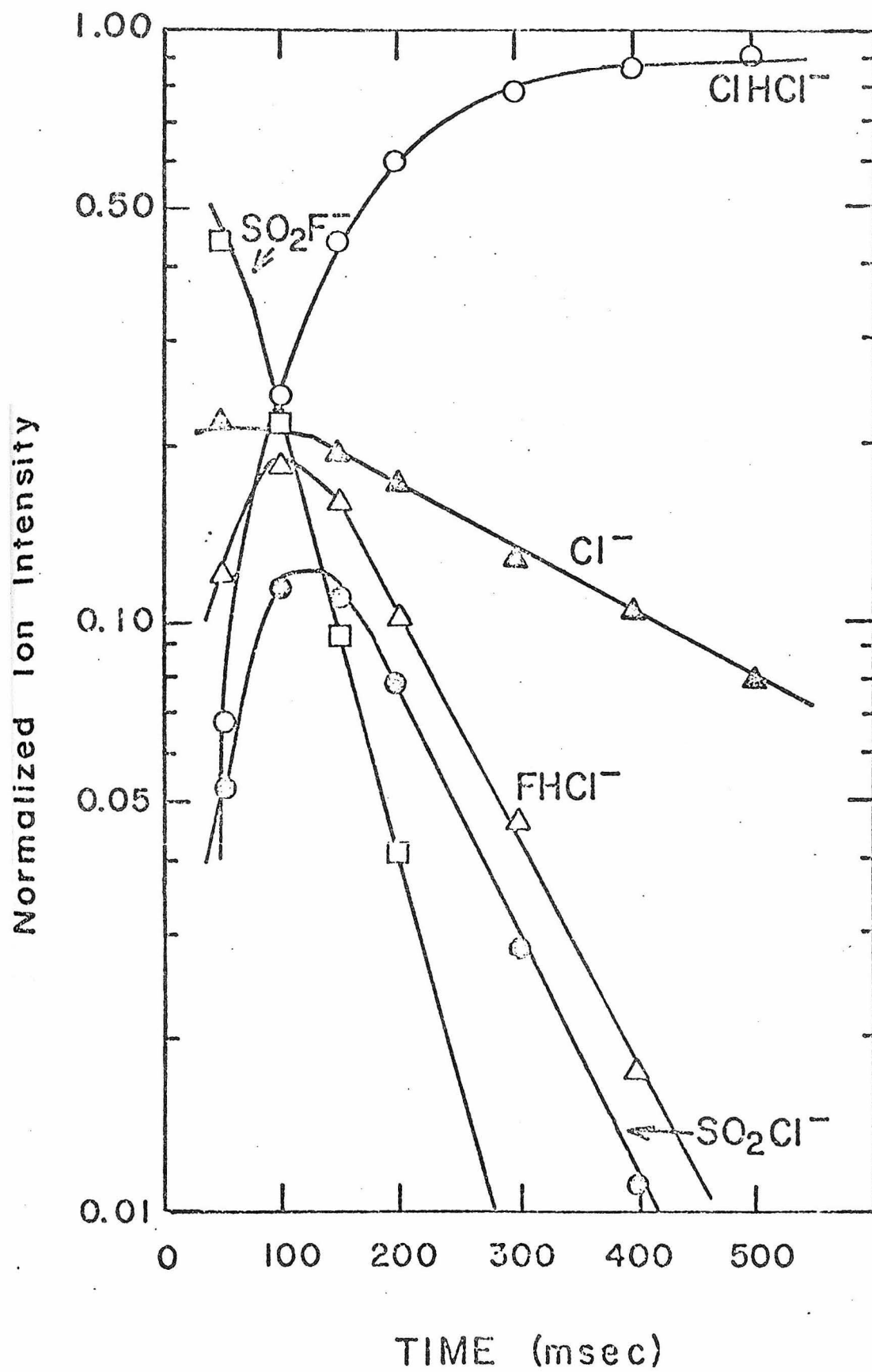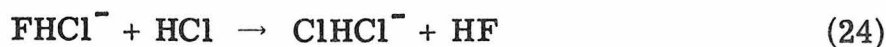Temporal variation of normalized negative ion intensity in $1.40 \times 10^{-6}$ torr $SO_2ClF$ at 70.0 eV electron energy.
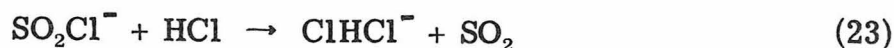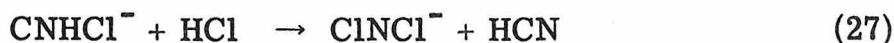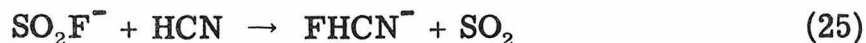
FIGURE 3

Temporal variation of normalized negative ion intensity in a mixture of $6.98 \times 10^{-7}$ torr $SO_2ClF$ with $1.66 \times 10^{-6}$ torr HCl at 70.0 eV electron energy.

$$SO_2Cl^- + HCl \rightarrow ClHCl^- + SO_2 \qquad (23)$$

$$FHCl^- + HCl \rightarrow ClHCl^- + HF \qquad (24)$$

$\underline{SO_2ClF/HCN\ Mixture.}$ In a mixture of $3.49 \times 10^{-7}$ torr, $SO_2ClF$ and $2.35 \times 10^{-6}$ torr HCN, ions $FHCN^-$ ($\underline{m/e}$ 46), $CNHCl^-$ ($\underline{m/e}$ 62) and $ClHCl^-$ ($\underline{m/e}$ 71) appear as $SO_2F^-$ decays with time. The sole precursor to $FHCN^-$ is $SO_2F^-$, presumably through $F^-$ transfer, eqn. (25). The production of $CNHCl^-$ from $FHCN^-$, eqn. (26) and its further reaction, eqn. (27), to form $ClHCl^-$ can be explained only by

$$SO_2F^- + HCN \rightarrow FHCN^- + SO_2 \qquad (25)$$

$$FHCN^- + HCl \rightarrow CNHCl^- + HF \qquad (26)$$

$$CNHCl^- + HCl \rightarrow ClNCl^- + HCN \qquad (27)$$

the presence of HCl impurities. Although not directly detected under these conditions, double resonance of $ClHCl^-$ indicates the presence of $FHCl^-$ in this mixture, possibly formed by reaction 22. At lower pressures of HCN, $FHCl^-$ is directly detected. On initial addition of HCN to the ICR spectrometer, the positive ion mass spectrum indicates less than 2% HCl impurity. However, HCl signal increases with exposure of the HCN sample to the inlet system. A similar problem results on addition of HBr to the inlet system. Since the amount of HCl present cannot be accurately determined, rate measurements are not possible in this mixture. The predominance of chlorinated products does indicate that $Cl^-$ and $CN^-$ transfer reactions to HCl are very fast relative to transfer to HCN. Small amounts of $CNHCN^-$ produced by reaction 28 are detected at low pressures of $SO_2ClF$ and HCN. No

double resonance was observed between $CNHCN^-$ and $ClHCN^-$.

$$FHCN^- + HCN \rightarrow CNHCN^- + HF \qquad (28)$$

## Thermochemical Considerations

Ionization potentials for the sulfuryl halides are listed in Table 1. While acknowledging the inaccuracies in their measurement, ionization potentials derived in this study are consistent with those for $SO_2F_2$ and $SO_2Cl_2$ derived from photoelectron spectra [12]. The electron impact $IP(SO_2ClF) = 12.4 \pm 0.5$ eV noted in Table 1 is intermediate between those of the other halides as expected from previous studies of the effects of chlorine and fluorine substitution on ionization potentials [15]. Data listed in Table 1 have been used to calculate heats of formation of some of the positive ions involved in ion molecule reactions (Table 3). Where possible heats of reaction have been calculated (Table 2) using these thermochemical data. In all cases, the observed reactions are predicted to be exothermic. For other reactions the assumption that only exothermic reactions will be observed allows upper limits to be set for $\Delta H_{f298}°$ of positive ions as noted in Table 2.

Observed $F^-$ transfer reactions indicate that $D(SO_2-F^-) < D(FH-F^-) \sim 45 \pm 5$ kcal/mol and $D(SO_2-Cl^-) < D(ClH-Cl^-) \sim 24$ kcal/mol [1]. Estimates of $\Delta H_{f298}° (SO_2F^-)$ and $\Delta H_{f298}° (SO_2Cl^-)$ derived from these limits (Table 3) are consistent with other negative ion reactions observed in $SO_2ClF$, eqn. (19-21), Table 2. It is further possible to limit $EA(SO_2F) < 2.34$ eV and $EA(SO_2Cl) < 3.17$ eV using data in Table 3.

TABLE 3

Thermochemical Properties of Sulfuryl Halides[a]

| | $\Delta H_f(M)$ | $\Delta H_f(M^+)$[b] | $\Delta H_f(M^-)$ |
|---|---|---|---|
| $SO_2F_2$ | -181.3 | 118.5 | - - |
| $SO_2Cl_2$ | - 84.9 | 193.0 | - - |
| $SO_2FCl$ | $\leqslant -133$[c] | $\geqslant 151$ | - - |
| $SO_2F$ | -122.2[d] | 141 (138) | > -177[e] |
| $SO_2Cl$ | - 77.8[d] | 158 | > -151[e] |
| $SO_2$ | - 70.9 | 214 | - - |
| SO | 1.17 | 246 | - - |
| Cl | 28.9 | - - | - 55.9 |
| F | 18.86 | - - | - 61.0 |

[a]All values in kcal/mol at 298°K. Unless otherwise noted, all values taken from D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", U.S. Printing Office, Washington, D.C., 1971.

[b]Calculated using appearance potentials in Table 1 and ref. 8.

[c]Estimate assuming that $D(SO_2F-Cl)$ and $D(SO_2Cl-F)$ are equal to those in $SO_2F_2$ and $SO_2Cl_2$. This study indicates that $D(SO_2F-Cl) >$ $D(SO_2Cl-Cl)$, see text.

[d]Calculated using average bond strengths $D(SO_2F-F) = 74$ kcal/mol, $D(SO_2Cl-Cl) = 36$ kcal/mol, which are derived from the heats of formation in this table.

[e]Estimates based on observed halide transfers using $D(FH-F^-) \sim$ $45 \pm 5$ kcal/mol and $D(ClH-Cl^-) \cong 24$ kcal/mol. See S. A. Sullivan and J. L. Beauchamp, J. Amer. Chem. Soc., 98 (1976) 1160 and ref. 9.

DISCUSSION

Positive Ion Chemistry

Positive ion reactions of sulfuryl halides can be classified as charge transfer processes, halogen atom, or anion transfer reactions and condensation reactions which are generalized in eqn. (29) for

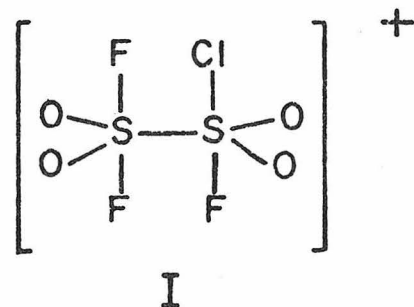$$SO_2X_2^+ + SO_2X_2 \rightarrow (SO_2X_2)SO_2X + X \qquad (29)$$

X = Cl or F. As noted above, and shown in Table 2, the observed charge transfer reactions are consistent with the relative ionization potentials of the neutrals involved.
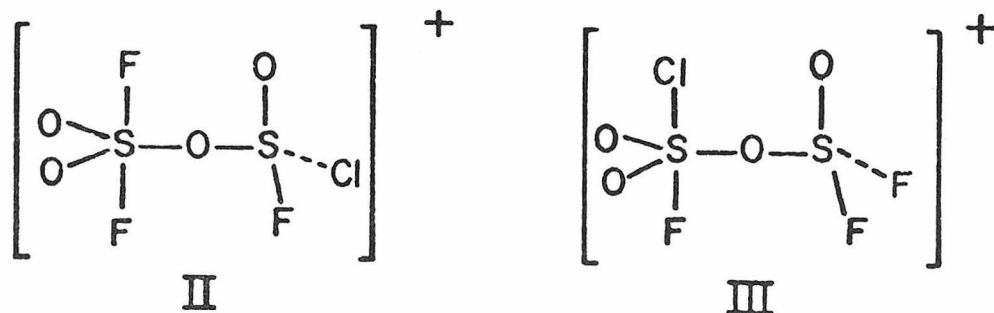
The chlorine transfer reaction 2 indicates that $D(SO_2Cl_2^+-Cl) > D(SO_2Cl-Cl) = 36$ kcal/mol (Table 3). In contrast, $SO_2FCl^+$ does not transfer Cl to the neutral $SO_2FCl$, suggesting that $D(SO_2ClF^+-Cl) < D(SO_2F-Cl)$. This may result from an increase in $D(SO_2F-Cl)$ compared to $D(SO_2Cl-Cl)$. Qualitative theoretical descriptions of bonding in hypervalent sulfur indicate that the more electronegative F should contract the sulfur d orbitals allowing better overlap and stronger bonds [12, 16]. This idea is consistent with the observed shortening of O–S bonds in $SO_2F_2$ compared to $SO_2Cl_2$ [17].

Parent ions $SO_2F_2^+$, $SO_2ClF^+$ and $SO_2Cl_2^+$ each react with the neutral sulfuryl halides by eqn. (29). Only in the case of $SO_2F_2^+$ reacting with $SO_2F_2$ is this process not observed. Preferential loss of Cl is observed on reaction of $SO_2ClF^+$ with $SO_2F_2$ for which the only product of reaction 29 is $(SO_2F_2)SO_2F^+$, eqn. 15. This is consistent with the weaker S–Cl bond. Interestingly when $SO_2F_2^+$ reacts with

$SO_2ClF$, exclusive cleavage of the S–F bond produces $(SO_2FCl)SO_2F^+$, eqn. (11). The formation of a symmetric ionic reaction intermediate as in I for both reaction 11 and 15, should result in identical ionic

$$\left[\begin{array}{c} \underset{\underset{F}{|}}{\overset{\overset{F}{|}}{O\diagdown\underset{O\diagup}{S}}}-\underset{\underset{F}{|}}{\overset{\overset{Cl}{|}}{S\diagup^{O}_{\diagdown O}}} \end{array}\right]^{+}$$

I

products. The observation of different reaction products suggests that attack may occur at oxygen, as in II and III, for reactions 11 and 15, respectively. Loss of the more weakly bonded halogen from the penta coordinate sulfur may then predominate.

$$\left[\begin{array}{c} \overset{\overset{F}{|}}{O\diagdown\underset{O\diagup}{\underset{|}{S}}}-O-\overset{\overset{O}{||}}{\underset{|}{S}}\cdots Cl \\ F \quad\quad F \end{array}\right]^{+} \quad\quad \left[\begin{array}{c} \overset{\overset{Cl}{|}}{O\diagdown\underset{O\diagup}{\underset{|}{S}}}-O-\overset{\overset{O}{||}}{\underset{|}{S}}\cdots F \\ F \quad\quad F \end{array}\right]^{+}$$

II                                III

## Negative Ion Chemistry and Halide Binding Energies

The negative ions $SO_2F^-$ and $SO_2Cl^-$ formed in sulfuryl halides are unreactive or react only slowly with their neutral precursors. Chloride transfer from $SO_2Cl^-$ to $SO_2Cl_2$ suggests that $D(SO_2-Cl^-) < D(SO_2Cl_2-Cl^-)$. In contrast, $SO_2F^-$ does not transfer $F^-$ to $SO_2ClF$, suggesting $D(SO_2-F^-) > D(SO_2ClF-F^-)$. This ion reacts only very slowly with $SO_2ClF$ to form $SO_2Cl^-$, eqn. (19). Similarly, $Cl^-$ reacts

with $SO_2ClF$ and $SO_2Cl_2$ to form $SO_2F^-$, eqn. (20), and $SO_2Cl^-$, eqn. (17), respectively.

In mixtures of HCN and HCl with $SO_2ClF$, $SO_2F^-$ transfers $F^-$ to form the hydrogen bonded anions $FHCN^-$ and $FHCl^-$. The further transfers of $CN^-$, $Cl^-$ and $F^-$ in these mixtures allow the ordering of anion binding energies in Table 2. This order is consistent with that in Table 4 which had been proposed by Yamdagni and Kebarle [9]. Anion binding energies $D(YH-X^-)$ increase with gas phase acidity of HY and the gas phase basicity of $X^-$.

In conclusion, the generation of large amounts of $SO_2F^-$ by electron attachment in low pressures of $SO_2FCl$ and the inertness of the ion toward the precursor halide, suggest that these compound would be a good reagent for negative chemical ionization. The mixed sulfuryl halide also appears to be an excellent choice for further study in excimer laser investigations because of the expected weakness of the chloride bond and the chemical inertness of the neutral compared to other halogen atom donors.

## ACKNOWLEDGMENTS

TABLE 4

Anion Bond Energies in Proton Bound Ions[a]

---

$D(FH-F^-) \sim 45$ kcal/mol[b] $< D(CNH-F^-) < D(ClH-F^-) \sim 50$ kcal/mol[c]

$\vee$                $\vee$          $\vee$

$D(FH-CN^-)$         $< D(CNH-CN^-) < D(ClH-CN^-)$

$\vee$                $\vee$          $\vee$

$D(FH-Cl^-) \sim 13$ kcal/mol[d] $< D(CNH-Cl^-) < D(ClH-Cl^-) \sim 24$ kcal/mol[c]

---

[a]Ordering based on halide and anion transfers in references 1 and 9.

[b]S. A. Sullivan and J. L. Beauchamp, J. Amer. Chem. Soc., 98,
(1975) 1066.

[c]Reference 9.

[d]Calculated from $D(ClH-F^-)$.

# REFERENCES

1 M. S. Foster and J. L. Beauchamp, Inorg. Chem., to be published.

2 M. K. Murphy and J. L. Beauchamp, J. Amer. Chem. Soc., 98 (1976) 1433; M. K. Murphy and J. L. Beauchamp, Inorg. Chem., submitted for publication.

3 O. I. Asubiojo, L. K. Blair and J. I. Brauman, J. Amer. Chem. Soc., 97 (1975) 6685; W. N. Olmstead and J. I. Brauman, J. Amer. Chem. Soc., 99 (1977) 4219.

4 H. P. Tannenbaum, J. D. Roberts and R. C. Dougherty, Anal. Chem., 47 (1975) 49.

5 J. E. Velazco, J. H. Kolts and D. W. Setser, J. Chem. Phys., 65 (1976) 3498.

6 J. J. Ewing and C. A. Brau, Appl. Phys. Lett., 27 (1975) 350; E. R. Ault, R. S. Bradford and M. L. Bhaumik, Appl. Phys. Lett., 27 (1975) 413.

7 D. G. Dutton, S. H. Suchard, O. L. Gibb and C. P. Wang, Appl. Phys. Lett, 28 (1976) 522.

8 R. M. Reese, V. H. Diebler and J. L. Franklin, J. Chem. Phys., 29 (1958) 880.

9 R. Yamdagni and P. Kebarle, J. Amer. Chem. Soc., 93 (1971) 7139.

10 J. L. Beauchamp, Ann. Rev. Phys. Chem., 22 (1972) 527.

11 T. B. McMahon and J. L. Beauchamp, Rev. Sci. Inst., 43 (1972) 509.

12 D. Chadwick, D. C. Frost, F. G. Herring, A. Katrib, C. A. McDowell and R. A. N. McLean, Can. J. Chem., 51 (1975) 1893.
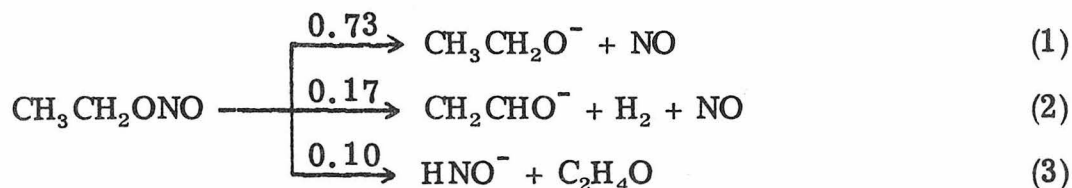
13  H. M. Rosenstock, Int. J. Mass Spectrom. Ion Phys., 20 (1976) 139.

14  W. H. Beattie, Appl. Spectrosc., 29 (1975) 334.

15  M. R. Litrow and T. R. Spalding, Mass Spectrometry of Inorganic and Organometallic Compounds, Elsevier, New York, 1973.

16  There is much controversy as to the role of d orbitals in bonding of hypervalent sulfur.  None of the theoretical treatments adequately describes reactivity.  I. H. Hillier and V. R. Saunders, J. Chem. Soc. D, 1183 (1970); I. H. Hillier and M. F. Guest, Int. J. Quant. Chem., 6 (1972) 967; P. J. Hay, J. Amer. Chem. Soc., 99 (1977) 1003.

17  R. M. Fristrom, J. Chem. Phys., 20 (1952) 1; I. Hargittai, Acta Chem. Acad. Sci. Hung., 57 (1968) 403.

Appendix I

Negative Ion Formation and Ion-Molecule Reactions in Alkyl Nitrites

Alkyl nitrites have been used extensively in recent gas phase studies[1] as an abundant source of alkoxide ions. These species are useful in the determination of gas phase acidites and in the investigation of negative ion-molecule reaction mechanisms. It is therefore important that negative ion generation and reactivity with the precursor nitrites are well understood. For this reason, we have examined negative ion formation and reactivity in $CD_3ONO$, $CH_3CH_2ONO$, $iC_3H_7ONO$ and $tC_4H_9ONO$ employing ion cyclotron resonance spectroscopy.[2]

Negative Ion Generation. Negative ion generation in alkyl nitrites can be summarized by the electron attachment processes observed in $CH_3CH_2ONO$. Thermalized electron attachment to $CH_3CH_2ONO$ results in $CH_3CH_2O^-$ (eq 1), $CH_2CHO^-$ (eq 2) and $HNO^-$ (eq 3).[3] The major

$$CH_3CH_2ONO \left\{ \begin{array}{ll} \xrightarrow{0.73} & CH_3CH_2O^- + NO \qquad (1) \\ \xrightarrow{0.17} & CH_2CHO^- + H_2 + NO \qquad (2) \\ \xrightarrow{0.10} & HNO^- + C_2H_4O \qquad (3) \end{array} \right.$$

process (1) results from dissociation of the very weak O-NO bond. Alkoxide formation is the major process observed for each of the alkyl nitrites examined as seen in Table 1. Enolate anion formation, process (2), is observed only in $CH_3CH_2ONO$ and $iC_3H_7ONO$. Only 3% of $CH_3CH_2CO^-$ (m/e 57) is observed in $iC_3H_7ONO$, consistent with the

Table I.  Negative Ion Formation in Alkyl Nitrites[a]

|  | Electron Attachment Product Distribution | | |
| Nitrite | Alkoxide | Enolate | HNO$^-$ |
| --- | --- | --- | --- |
| CD$_3$ONO | 0.75 | -- | 0.25 |
| CH$_3$CH$_2$ONO | 0.73 | 0.17 | 0.10 |
| i-C$_3$H$_7$ONO | 0.91 | 0.03 | 0.07 |
| t-C$_4$H$_9$ONO | 1.00 | -- | -- |

[a]Negative ions are formed by attachment of thermalized electrons provided by impact of a 70.0 eV electron beam.  In each case, product distributions were determined, after the Shulz-Phelp gauge was turned off and allowed to cool (see text).

greater energy required to eliminate $H_2$ from $iC_3H_7O^-$ ($\Delta H_{elim} \cong$ 9 kcal mole$^{-1}$) than $CH_3CH_2O^-$ ($\Delta H_{elim} \cong 1$ kcal mole$^{-1}$). Formation of $HNO^-$ apparently results from cleavage of the $\alpha$-H in the nitrite, since no $HNO^-$ is detected in $t$-$C_4H_9ONO$ (Table 1).

Negative Ion Reactions in Alkyl Nitrites.

$CD_3ONO$. The deuterated nitrite is employed to distinguish between $HNO^-$ and $CH_3O^-$ both appearing at m/e 31. Figure 1 presents the temporal variation of ion intensity in $3.7 \times 10^{-6}$ torr of $CD_3ONO$. The product ion $NO_2^-$ (m/e 46) appears as both $CD_3O^-$ (m/e 34) and $DNO^-$ (m/e 32) decrease with time. Double resonance links production of $NO_2^-$ to $CD_3O^-$ (eq 4) and indicates that $DNO^-$ reacts to form $CD_3O^-$ (eq 5).[4,5] Rates determined from semilog plots of the disappearance

$$CD_3O^- + CD_3ONO \rightarrow NO_2^- + CD_3OCD_3 \tag{4}$$

$$DNO^- + CD_3ONO \rightarrow CD_3O^- + DNO + NO \tag{5}$$
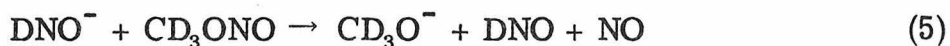
of $CD_3O^-$ and $DNO^-$ are listed in Table 2.

$CH_3CH_2ONO$. The temporal variation of ion intensity in $2.0 \times 10^{-6}$ torr $CH_3CH_2ONO$ is presented in Figure 2. As initially formed $CH_3CH_2O^-$ (m/e 45) and $HNO^-$ (m/e 31) decrease, $NO_2^-$ (m/e 46) appears and there is a small increase (9%) in $CH_2CHO^-$ (m/e 43). Double resonance confirms that $NO_2^-$ is formed by reaction of $CH_3CH_2O^-$ (eq 6). As discussed below, the increase in $CH_2CHO^-$ may result from the reaction of $CH_3CH_2O^-$ with the pyrolysis impurity $CH_3CHO$ or from reaction (7) with the nitrite. Data presented in Figure 2 were obtained with the ion pressure gauge off to avoid pyrolysis. Reaction products of $HNO^-$

Figure 1

Temporal variation of normalized ion
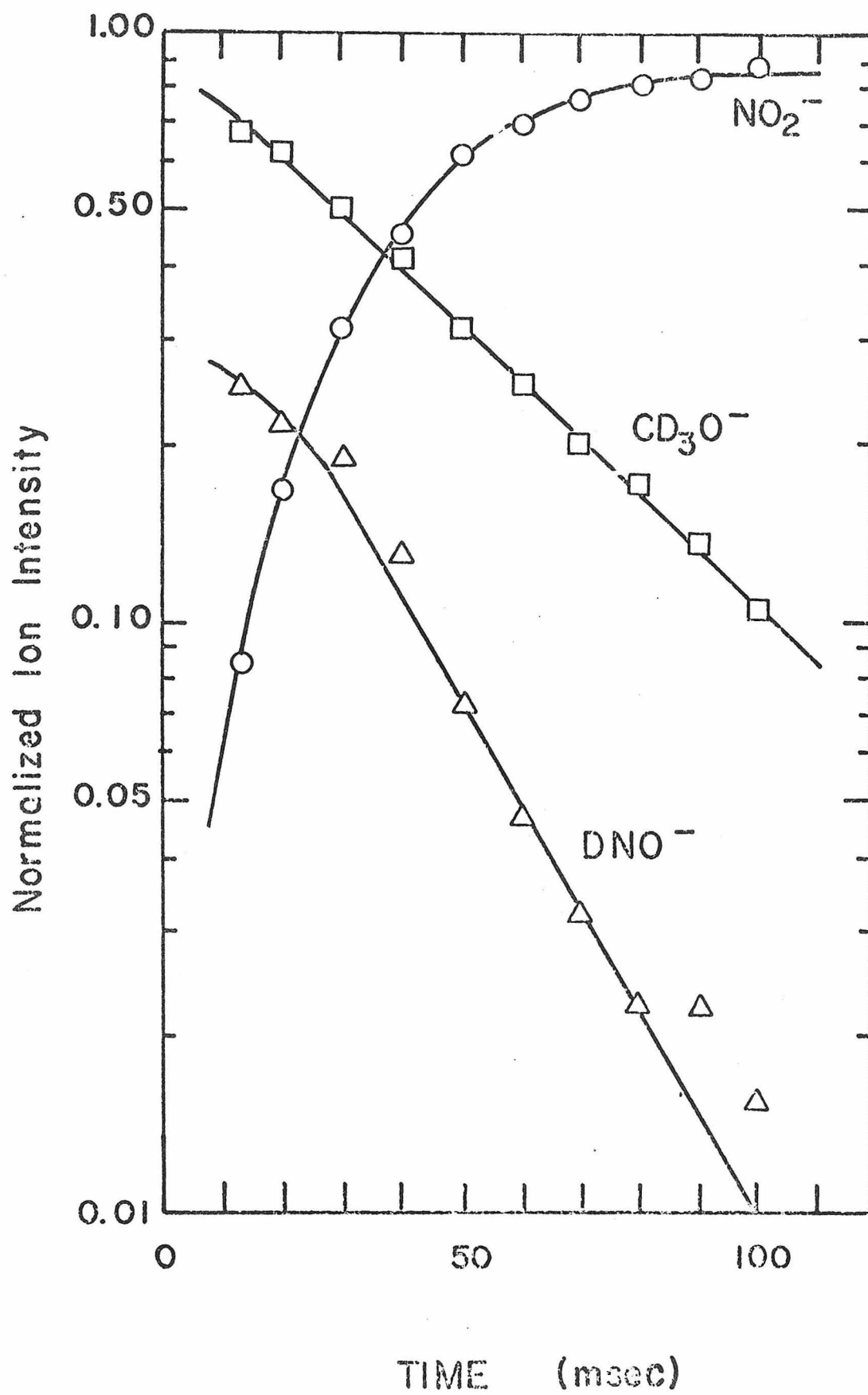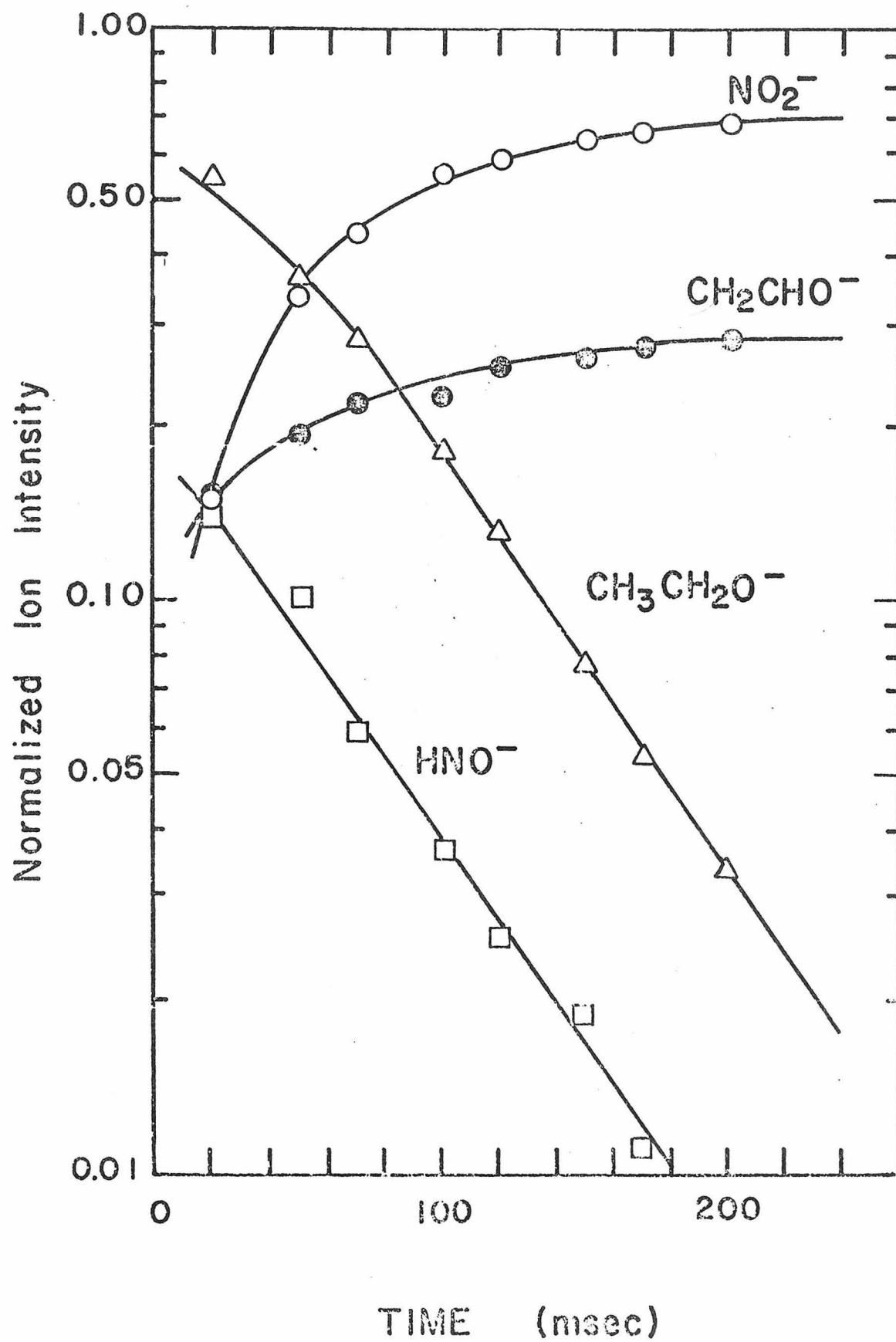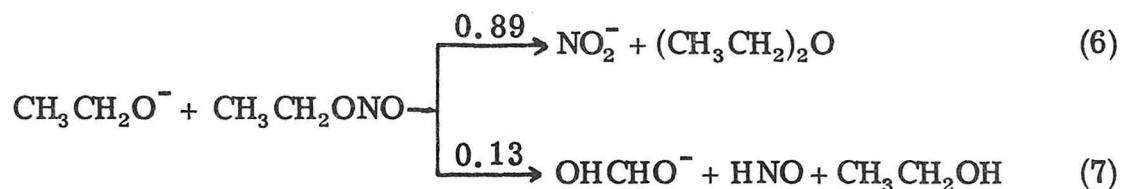intensity in $3.7 \times 10^{-6}$ torr of $CD_3ONO$.

TIME (msec)

Figure 2

Temporal variation of normalized ion
intensity in $2.0 \times 10^{-6}$ torr of $CH_3CH_2ONO$.

$$CH_3CH_2O^- + CH_3CH_2ONO \begin{array}{c} \xrightarrow{0.89} NO_2^- + (CH_3CH_2)_2O \qquad (6) \\ \\ \xrightarrow{0.13} OHCHO^- + HNO + CH_3CH_2OH \qquad (7) \end{array}$$

could not be identified by double resonance.[5] The ion, $HNO^-$ may react with $CH_3CH_2ONO$ forming $CH_3CH_2O^-$ (eq 8), analogous to reaction (5). Rates listed in Table 2 were calculated assuming that $CH_2CHO^-$ is produced only by reaction (7) and that $HNO^-$ reacts only through process (8).

$$HNO^- + CH_3CH_2ONO \rightarrow CH_3CH_2O^- + HNO + NO \qquad (8)$$

$\underset{\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim\sim}{iC_3H_7ONO \text{ and } tC_4H_9ONO.}$ Isopropoxide reacts to form both $NO_2^-$ and $CH_3CHCHO^-$ (m/e 57), presumably by reactions (9) and (10). Reaction

$$iC_3H_7O^- + iC_3H_7ONO \rightarrow NO_2^- + (iC_3H_7)_2O \qquad (9)$$

$$iC_3H_7O^- + CH_3CH_2CHO \rightarrow CH_3CH_2CO^- + iC_3H_7OH \qquad (10)$$
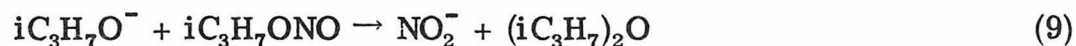
(10) is indicated by a large decrease in the intensity of $CH_3CHCHO^-$ relative to $NO_2^-$ when the S-P pressure gauge is turned off. Reaction to form $CH_3CH_2CO^-$ is negligible under these conditions, suggesting that reaction (11) does not occur or is very slow. The rate for

$$iC_3H_7O^- + iC_3H_7ONO \xrightarrow{\;\times\;} CH_3CH_2CO^- + HNO + iC_3H_7OH \qquad (11)$$

reaction (9) is determined with minimum pyrolysis of the nitrite. Again double resonance cannot identify the fate of $HNO^-$.[5] By analogy with reaction (5), $iC_3H_7O^-$ may be formed (eq 12).

$$HNO^- + iC_3H_7ONO \rightarrow iC_3H_7O^- + HNO + NO \qquad (12)$$

The only reaction detected in $tC_4H_9ONO$, is formation of $NO_2^-$ from $tC_4H_9O^-$ (eq 13).

$$tC_4H_9O^- + tC_4H_9ONO \rightarrow NO_2^- + (tC_4H_9O)_2O \qquad (13)$$

Reactions are summarized in Table 2 along with rates determined under conditions of minimum pyrolysis. Since the extent of pyrolysis has not been determined, rates of reactions of $HNO^{-4}$ and reaction (7) may be effected by the presence of impurities. Formation of $NO_2^-$ is not subject to these problems.

Pyrolysis of Alkyl Nitrites. It is well established that alkyl nitrites are easily decomposed by heating[6-8] or photolysis.[9] The initial step in the pyrolysis is cleavage of the weak $\sim 40$ kcal mole$^{-1}$ O—NO bond, to form alkoxy radicals (RO$\cdot$). Neutral products then result from radical decomposition.[7,8] For example, $CH_3CH_2O\cdot$ produced in the pyrolysis of $CH_3CH_2ONO$ (eq 14), will lose $CH_3$ to form $CH_2O$ (eq 15).

$$CH_3CH_2ONO \rightarrow CH_3CH_2O\cdot + NO \qquad (14)$$

$$CH_3CH_2O\cdot \rightarrow CH_2O + CH_3\cdot \qquad (15)$$

Similarly, $CH_3CH_2CHO$ is formed in pyrolysis of $i\text{-}C_3H_7ONO$.

It has recently been determined[8] that an elimination of HNO from all nitrites except $t\text{-}C_4H_9ONO$ occurs in competition with RO$\cdot$ formation. For example, $CH_3CH_2ONO$ decomposed to HNO and $CH_3CH_2O$ (eq 16).

Table 2. Summary of Reactions and Rates

| Reaction | $k^a$ | $\Delta H^b$ |
|---|---|---|
| $CD_3O^- + CD_3ONO \rightarrow NO_2^- + (CD_3)_2O$ | 1.90 | -40 |
| $CH_3CH_2O^- + CH_3CH_2ONO \rightarrow NO_2^- + (CH_3CH_2)_2O$ | 2.24 | -39 |
| $iC_3H_7O^- + iC_3H_7ONO \rightarrow NO_2^- + (i\text{-}C_3H_7)_2O$ | 1.82 | -33 |
| $tC_4H_9O^- + tC_4H_9ONO \rightarrow NO_2^- + (t\text{-}C_4H_9)_2O$ | 1.47 | -24 |
| $HNO^- + CH_3ONO \rightarrow CD_3O^- + HNO + NO$ | 4.5 | $\sim 0$ |
| $HNO^- + CH_3CH_2ONO \rightarrow CH_3CH_2O^- + HNO + NO$ | 3.9 | -4 |
| $HNO^- + iC_3H_7ONO \rightarrow iC_3H_7O^- + HNO + NO$ | 2.1 | -5 |
| $CH_3CH_2O^- + CH_3CH_2ONO \rightarrow CH_2CHO^- + CH_3CH_2OH + HNO$ | 0.50 | -9 |
| $iC_3H_7O^- + iC_3H_7ONO \rightarrow CH_3CHCHO^- + iC_3H_7OH + HNO$ | -- | -2 |

[a]Experimental rates in units $10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$.

[b]Heats of reactions in kcal mole$^{-1}$ at 298°K, calculated using heats of formation in Table 3.

Table 3. Thermochemical Data of Anions and Neutrals Involved in Nitrite Reactions[a]

| Anion | $\Delta H_f 298°$ [b] | Neutral | $\Delta H_f 298°$ [c] |
|---|---|---|---|
| $CD_3O^-$ | -36.9 | NO | $21.58 \pm 0.04$ |
| $CH_3CH_2O^-$ | -48.0 | HNO | 23.8 |
| $i\text{-}C_3H_7O^-$ | -58.8 | $CH_3ONO$ | $-15.79 \pm 0.25$ |
| $t\text{-}C_4H_9O^-$ | -69.2 | $CH_3CH_2ONO$ | $-22.3 \pm 0.50$ |
| $CH_2CHO^-$ | $-47 \pm 5.0$ [c] | $i\text{-}C_3H_7ONO$ | $-32.7 \pm 0.50$ |
| $CH_3CHCHO^-$ | $-52 \pm 5.0$ [c] | $t\text{-}C_4H_9ONO$ | $-42.4 \pm 0.50$ |
| $NO_2^-$ | -48.45 | $(CH_3)_2O$ | $-43.99 \pm 0.12$ |
| $HNO^-$ | 24 [d] | $(CH_3CH_2)_2O$ | $-60.62 \pm 0.19$ |
| | | $(i\text{-}C_3H_7)_2O$ | $-76.20 \pm 0.59$ |
| | | $(t\text{-}C_4H_9)_2O$ | $-87.1 \pm 0.40$ |
| | | $CH_3OH$ | $-48.07 \pm 0.05$ |
| | | $CH_3CH_2OH$ | $-56.24 \pm 0.07$ |
| | | $i\text{-}C_3H_7OH$ | $-65.5 \pm 0.50$ [f] |
| | | $t\text{-}C_4H_9OH$ | $-75.1 \pm 0.50$ [f] |

[a] Unless otherwise noted, values are in kcal mole$^{-1}$ at 298°C and are taken from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970 and D. R. Stull and H. Prophet, "JANAF Thermochemical Tables" NSRDS-NBS37, 1971.

[b] Alkoxide ion $\Delta H_f$ are calculated using PA(RO$^-$) from J. S. Miller and R. T. McIver, J. Amer. Chem. Soc., 96, 4323 (1974), with correc-

Table 3 (continued)

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tions to original data, J. S. Miller, private communication.

[c]See reference 10.

[d]See Appendix II.

[e]$\Delta H_f$ 298° for nitrites are calculated using Benson's group additivities and by comparison to known $\Delta H_f$ of alkyl nitro compounds. See S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1976. See also reference 2.

[f]Estimated using group additivities, see ref. e.

$$CH_3CH_2ONO \rightarrow HNO \cdot + CH_3CHO \qquad (16)$$

Kinetic studies indicate that for the most part, these eliminations result from heterogeneous surface reactions (pyrex vessel). In only one case, $CH_3CH_2ONO$, was homogeneous elimination expected to contribute significantly to the products formed.

The pyrolysis of nitrites is important to ion-molecule chemistry because of the presence of heated surfaces within the icr cell. Both the heated electron filament and the Schulz-Phelp gauge filament and its shield may induce nitrite decomposition. In $CH_3CH_2ONO$ and $iC_3H_7ONO$, it was found that the amount of enolate anion formed is greatly decreased when the pressure gauge filament is turned off and allowed to cool. Since both $CH_3CHO$ and $CH_3CH_2CHO$ are more acidic than the alcohols,[10] alkoxide ions are expected to abstract protons from them to form the corresponding enolate anions.

In conclusion, the observed reactivity of the nitrites especially $CH_3CH_2ONO$ and $iC_3H_7ONO$ are strongly moderated by concomitant neutrals reactions. Recent results[11] suggest that the generation and reactions of negative ions in other systems may also be affected by surface processes of the neutrals present. Since neutral products can not be routinely detected under icr conditions, such processes are not readily detectible. Therefore care must be taken to consider the possibility of such interfering reactions when ion-molecule chemistry is investigated.

References

1. S. A. Sullivan and J. L. Beauchamp, J. Amer. Chem. Soc., 98, 1066 (1976). S. M. J. Briscese and J. M. Riveros, J. Amer. Chem. Soc., 97, 230 (1975), and J. S. Miller and R. T. McIver, J. Amer. Chem. Soc., 96, 4323 (1974).

2. Techniques of icr spectroscopy are detailed in J. L. Beauchamp, Ann. Rev. of Phys. Chem., 22, 527 (1972).

3. K. Jaeger and A. Heinglein, Z. Naturforsch A, 222, 700 (1967).

4. It should be noted that $HNO^-$ may react with the possible pyrolysis products to form alkoxides. For example:

$$HNO^- + CH_2O \rightarrow CH_3O^- + NO$$
$$HNO^- + CH_3CH_2CHO \rightarrow i\text{-}C_3H_7O^- + NO$$
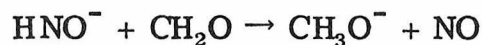
5. A number of processes may be responsible for decay of $HNO^-$. Recent studies suggest that $EA(HNO) \sim 0$, so that electron transfer (a), collisional detachment (b) and associative detachment (c) may all be favorable.

    a) $HNO^- + M \rightarrow M^- + HNO$
    b) $HNO^- + M \rightarrow M + HNO + e^-$
    c) $HNO^- + M \rightarrow MH + NO + e^-$
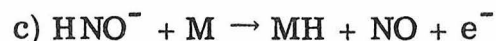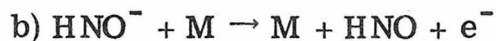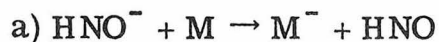
These processes are discussed by F. H. Paulson in "Ion-Molecule Reactions", Vol. 1, J. L. Franklin, ed., Plenum Press, New York, 1972, p. 77. See also Appendix II.

6. J. B. Levy, J. Amer. Chem. Soc., 78, 1780 (1956) and references therein.

References (continued)

7. L. Batt, K. Christie, R. T. Milne and A. J. Summers, Inter. J. Chem. Kinetics, 6, 877 (1974).

8. L. Batt, R. D. McCullock and R. T. Milne, Inter J. Chem. Kinetics, 1st Symposium, 441 (1975).

9. For example, P. Kabasakalian and E. R. Townley, J. Amer. Chem. Soc., 84, 2711 (1962).

10. $PA(CH_3CHCHO^-)$ and $PA(CH_2CHO^-)$ are both estimated at $\sim 360 \pm 5$ kcal/mole, B. S. Freiser, unpublished results.

11. S. A. Sullivan and J. L. Beauchamp, Chem. Phys. Lett., in press and this thesis, Chapter I.

Appendix II

## Reactions of HNO⁻

The unusual ion HNO⁻ (m/e 31) is generated by electron attachment in alkyl nitrites.[1] Two types of reactions of HNO⁻ are observed in mixtures of nitrites with neutrals, hydride transfer and apparent proton transfer. For example, HNO⁻ reacts to transfer H⁻ to $(CH_3)_3B$ (eq 1) while with $HCO_2H$, only $HCO_2^-$ (m/e 45) is observed. Reaction 2 may proceed directly or by energetic hydride transfer forming

$$HNO^- + (CH_3)_3B \rightarrow (CH_3)_3BH^- + NO \tag{1}$$

$$HNO^- + HCO_2H \rightarrow HCO_2^- + H_2 + NO \tag{2}$$
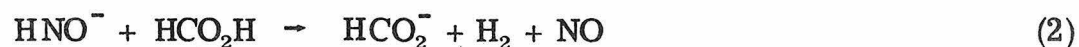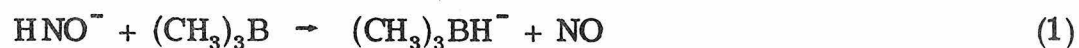
$[H_2CO_2H^-]^*$, which then decomposes to products. Observed reactions are summarized in Table 1 along with thermochemical inferences. In mixtures of $CD_3ONO$ and fluorinated alkanes and alkenes proton transfer to DNO⁻ is not observed. Considering the reactions listed in Table 1, HNO⁻ does not abstract a proton from species less acidic than $CF_3CH_2OH$. An approximate PA(HNO⁻) is then estimated as $365 \pm 5$ kcal/mole⁻¹. From this, $\Delta H_f(HNO^-) = 24 \pm 5$ kcal/mole⁻¹ is calculated, and the electron affinity EA(HNO) is estimated as ~ 0. Since HNO⁻ is involved in H⁻ transfers, the D(NO–H⁻) is of interest. The bond strength is calculated to be a quite weak 31 kcal mole⁻¹.

Table I.  Summary of the Reactions of $HNO^-$

| Reaction | Thermochemical References[f] |
|---|---|
| $HNO^- + (CH_3)_3B \rightarrow (CH_3)_3BH^- + NO$[a] | — |
| $HNO^- + CF_3CH_2OH \rightarrow CF_3CH_2O^- + H_2 + NO$[b] | $PA(HNO^-) \sim 365$ kcal mole$^{-1}$ |
| $HNO^- + AsH_3 \rightarrow AsH_2^- + H_2 + NO$[b] | $PA(HNO^-) > 356$ kcal mole$^{-1}$ |
| $HNO^- + HCO_2H \rightarrow HCO_2^- + H_2 + NO$[b] | $PA(HNO^-) > 342$ kcal mole$^{-1}$ |
| $HNO^- + CH_3BC_5H_6 \rightarrow CH_3BC_5H_5^- + H_2 + NO$[c] | $PA(HNO^-) > 337$ kcal mole$^{-1}$ |
| $HNO^- + CH_3ONO \rightarrow CH_3O^- + HNO + NO$[d] | $\Delta H_f(HNO^-) < 24.3$ kcal mole$^{-1}$ |
| $HNO^- + OPF_3 \rightarrow OPF_2^- + HF + NO$[e] | — |
| $HNO^- + PF_3 \rightarrow NOPF_2^- + HF$[e] | — |

[a] M. K. Murphy and J. L. Beauchamp, J. Amer. Chem. Soc., 98, 1433, 1976. $PA[(CH_3)_2BCH_2^-] \sim 365$ kcal mole$^{-1}$

[b] S. A. Sullivan and J. L. Beauchamp, unpublished results.

[c] See Chapter II.

[d] See Appendix I.

[e] See Chapter I.

[f] A table of acidities is given in Appendix III.

Appendix III

## Tables of Gas Phase Acidities

The following tables list gas phase proton affinities of anions, which are defined as the enthalpy for reaction 1 or the heterolytic

$$B^- + H^+ \rightarrow BH \tag{1}$$

bond dissociation energy. These values are inversely related to the acidity of BH. These tables present representative values, and as such are not comprehensive lists of all known gas phase proton affinities. The references following the tables represent major contributions to gas phase acidity measurements in the last few years.

Table 1      Hydrocarbons

Table 2      Substituted Alkanes

Table 3      Organic Oxygen Compounds

Table 4      Organic Nitrogen Compounds

Table 5      Inorganic Acids

Table 1. Gas Phase Proton Affinities - Hydrocarbon Acidities[a]

| MH | PA(M$^-$) | References |
|---|---|---|
| $CH_4$ | >403.8 | 12 |
| $CH_2CH_2$ | >403.8 | 12 |
| $C_6H_6$ | 395 ± 5 | 14, 12 |
| $CH_3CHCH_2$ | <390 | 14, 12 |
| $CH_3C_6H_4CH_3$ | 384 ± 7 | 15 |
| $C_6H_5CH_3$ | 373 ± 3[b] | 12 |
| $C_2H_2$ | 373.2 | 15, 12, 8 |
| $C_6H_5CH_2C_6H_5$ | 360.6 | 4 |
|  | 359.7 | 4 |
|  | 352.6 | 4, 5 |
|  | 348.5 | 4 |

[a]All values in kcal/mole at 298°K. Unless otherwise noted error limits can be considered ≤ ± 2.0 kcal/mole.

[b]Electron affinity measurements suggest PA($C_2H_5O^-$) > PA($C_6H_5CH_2^-$) > PA(t-$C_4H_9O^-$) see Table 3 and J. H. Richardson, L. M. Stephenson and J. I. Brauman, J. Chem. Phys., 63, 74 (1975).

Table 2.   Gas Phase Proton Affinities - Acidities of Substituted
Alkanes[a]

| MH | PA(M$^-$) | References |
|---|---|---|
| $CH_3F$ | $>390$[b] | – |
| $CH_2F_2$ | $384 \pm 7$[b] | – |
| $CHF_3$ | $377 \pm 3$[c] | – |
| $C_6H_5CH_3$ | $376 \pm 3$ | 12 |
| $CH_3CH_2F$ | $374 \pm 3$[d] | – |
| $CH_3CN$ | $366.3$[e] | 4 |
| $CHCl_3$ | $<363$ | 12 |
| $CH_2Cl_2$ | $>366.3$ | 12 |
| $CH_3NO_2$ | $>350$ | 12 |
| $CF_3\overset{\text{O}}{\overset{\|}{C}}CH_3$ | 347 | 4, 5 |
| $(CN)_2CH_2$ | 330.8 | 4 |

[a]All values in kcal/mole at 298°K.   Unless otherwise noted
error limits can be considered $\leq \pm 2.0$ kcal/mole.
[b]S. A. Sullivan and J. L. Beauchamp, unpublished results.
[c]B. S. Freiser and J. L. Beauchamp, unpublished results.
[d]S. A. Sullivan and J. L. Beauchamp, J. Amer. Chem. Soc.,
98. 1060 (1976).
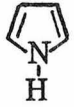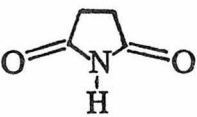[e]Note a footnote correction to PA(CH$_2$CN$^-$) in reference 4.

Table 3. Gas Phase Proton Affinities - Acidities of Organic
Oxygen Compounds[9]

| MH | PA(M⁻) | References |
|---|---|---|
| $H_2O$ | 390.7[b] | 13,12 |
| $H_2CO$ | >378.3[c] | |
| $CH_3OH$ | 378.3[d] | |
| $C_2H_5OH$ | 375.4 | |
| $i-C_3H_7OH$ | 373.5 | 16,8 |
| $t-C_4H_9OH$ | 372.7 | |
| $CH_3CHO$ | <370.1[c] | |
| $CH_3COCH_3$ | 363.6 | 4 |
| $C_6H_5OH$ | 347 | 10 |
| $CH_3CO_2H$ | 345.8 | 9 |
| $HCO_2H$ | 342.6 | 9 |
| $CH_3COCH_2COCH_3$ | 341.6 | 4 |
| $C_6H_5CO_2H$ | 337.1 | 7 |

[a]All values in kcal/mole at 298°K. Unless otherwise noted
error limits can be considered ≤ ± 2 kcal/mole.
[b]Calculated from electron affinity data, see Table 5.

Table 4.  Gas Phase Proton Affinities - Acidities of Organic

Nitrogen Compounds[a]

| MH | PA(M$^-$) | References |
|---|---|---|
| $NH_3$ | 403.8[b] | |
| $CH_3NH_2$ | 402 ± 3[c] | 15 |
| $(CH_3)_2NH$ | 395 ± 5[c] | 15 |
|  | 355.4 | 4, 5 |
| $CH_3CONHCOCH_3$ | 343.7 | 4, 5 |
|  | 341.3 | 4, 5 |

[a]All values in kcal/mole at 298°K.  Unless otherwise noted
error limits can be considered ≤ ± 2 kcal/mole.
[b]See Table 5.
[c]J. I. Brauman, private communication.

Table 5.  Gas Phase Proton Affinities - Acidities of Inorganic Hydrides[a]

| M | PA(M$^-$)[b] | References |
|---|---|---|
| NH$_3$ | 403.8 | 13, 12 |
| H$_2$ | 400 | |
| H$_2$O | 390.7 | 13, 12 |
| HF | 370.1 | 13 |
| PH$_3$ | 370[c] | 13 |
| HCN | 350.3 | |
| H$_2$S | 351 | 13 |
| H$_2$Se | 343[d] | |
| HNO$_2$ | 337 | |
| HCl | 333.3 | 13 |
| HNO$_3$ | 324.5 | |
| HBr | 323.6 | 13 |
| HI | 314.4 | 13 |

[a]All values in kcal/mole at 298°K.  Unless otherwise noted error limits can be considered $\leq \pm 2$ kcal/mole.

[b]Unless otherwise noted these values are calculated from data in D. R. Stull and H. Prophet "JANAF Thermochemical Tables" U.S. Government Printing Office, Washington, D.C., 1971.

[c]Private communication, J. S. Miller and R. T. McIver.

[d]Electron affinity EA(HSe) = 2.21 ± 0.03 eV from K. C. Smyth and J. I. Brauman, J. Chem. Phys., 56, 5993 (1972).

References

1. J. E. Bartmess, W. J. Hehre, R. T. McIver, Jr., and L. E. Overman, J. Amer. Chem. Soc., 99, 1976 (1977).

2. J. E. Bartmess and R. T. McIver, Jr., J. Amer. Chem. Soc., 99, 4163 (1977).

3. T. B. McMahon and P. Kebarle, J. Amer. Chem. Soc., 99, 2222 (1977).

4. T. B. McMahon and P. Kebarle, J. Amer. Chem. Soc., 98, 3399 (1976).

5. P. Kebarle, R. Yamdagni, K. Hiraoka and T. B. McMahon, Int. J. Mass Spectrom. Ion Physics, 19, 71 (1976).

6. R. Yamdagni and P. Kebarle, Can. J. Chem., 52, 861 (1974).

7. R. Yamdagni, T. B. McMahon and P. Kebarle, J. Amer. Chem. Soc., 96, 4035 (1974).

8. R. T. McIver and J. S. Miller, J. Amer. Chem. Soc., 96, 4323 (1974).

9. R. Yamdagni and P. Kebarle, J. Amer. Chem. Soc., 95, 4050 (1973).

10. R. T. McIver, Jr., and J. H. Silvers, J. Amer. Chem. Soc., 95, 8463 (1973).

11. K. Hiraoka, R. Yamdagni and P. Kebarle, J. Amer. Chem. Soc., 95, 6833 (1973).

12. D. K. Bohme, E. Lee Ruff and L. B. Young, J. Amer. Chem. Soc., 94, 5153 (1972).

References (continued)

13.  J. I. Brauman, J. R. Eyler, L. K. Blair, M. J. White, M. B. Comisarow and K. C. Smith, J. Amer. Chem. Soc., 93, 6360 (1971).

14.  D. K. Bohme and L. B. Young, Can. J. Chem., 49, 2918 (1971).

15.  J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 93, 3911 (1971).

16.  J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 93, 4315 (1971).

17.  J. I. Brauman and L. K. Blair, J. Amer. Chem. Soc., 92, 5986 (1970).