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Properties and Reactions of Phosphorus Trifluoride in the Gas Phase by Ion Cyclotron Resonance Spectroscopy. Energetics of Formation of PF_2^+ , PF_4^+ , HPF_3^+ , and CH_3PF_3^+

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The techniques of ion cyclotron resonance spectroscopy are used to examine the gas-phase ion chemistry of PF_3 . The gas-phase basicity, or proton affinity, of PF_3 is determined to be 160 ± 5 kcal/mol, which leads directly to a homolytic bond dissociation energy $D(\text{PF}_3^+-\text{H}) = 113.2$ kcal/mol. The proton affinities and homolytic bond dissociation energies for NH_3 , NF_3 , PH_3 , and PF_3 and bond strengths $D(\text{B}-\text{H})$ for isoelectronic neutral congeners to BH^+ are compared and discussed in terms of contributions from inductive and hyperconjugative interactions involving $p_\pi-d_\pi$ bonding of HPF_3^+ . Ion-molecule reactions of PF_3 in mixtures with SiF_4 , BF_3 , SF_6 , NF_3 , CH_3F , and $(\text{CH}_3)_2\text{CO}$ are briefly considered. The CH_3PF_3^+ ion is produced in a mixture of PF_3 and CH_3F ; various thermochemical considerations give $\Delta H_f(\text{CH}_3\text{PF}_3^+) = -8.5 \pm 5$ kcal/mol. The reaction of PF_3^+ with NF_3 leads to formation of PF_4^+ as an abundant species. When a trace of acetone is added to a mixture of PF_3 and NF_3 , the $(\text{CH}_3)_2\text{CF}^+$ ion is produced in a four-center reaction in which the carbonyl oxygen exchanges with F^+ in PF_3^+ and PF_4^+ . Limits on $\Delta H_f(\text{PF}_4^+)$ are discussed and compared with literature estimates. Fluoride-transfer reactions observed in mixtures of PF_3 with SiF_4 , BF_3 , SF_6 , and NF_3 lead directly to $D(\text{PF}_2^+-\text{F}^-) = 281.4 \pm 6.1$ kcal/mol, confirming the available literature data.

Introduction

The techniques of ion cyclotron resonance spectroscopy¹⁻³ (ICR) are especially suited for the quantitative determination of gas-phase thermochemical quantities such as the proton basicity⁴⁻¹⁵ and acidity^{16,17} of molecules. Our recent studies extending these techniques to the measurement of metal-ligand bond dissociation energies of the transition metal ions ($\eta^5\text{-C}_5\text{H}_5$) Ni^{18} and ($\eta^5\text{-C}_5\text{H}_5$) Co^{19} to various ligands have prompted, in part, our interest in trifluorophosphine, PF_3 . While PF_3 is known to be an excellent π -acceptor ligand,^{20,21} little quantitative information which relates to its σ -donor ability toward different acids is available.^{22,23}

Also of interest are the effects of alkyl and fluoroalkyl substitution on the heterolytic and homolytic bond dissociation energies of protonated phosphorus bases,⁸ as much less is known about such effects for phosphorus than for nitrogen bases.¹⁵ In addition to an examination of the ion chemistry of PF_3 alone and in several mixtures, the present work reports the quantitative determination of the gas-phase proton affinity (basicity) and homolytic bond dissociation energy, $D(\text{B}^+-\text{H})$, of PF_3 using the ICR techniques.²⁴ Studies of the He I photoelectron spectrum of PF_3 ,²⁵⁻²⁸ ab initio calculations of the electronic structure of PF_3 ,^{28,29} and appearance potential measurements of ions derived from PF_3 ³⁰⁻³² are useful in interpreting the present results.

Experimental Section

The theory and instrumentation of ICR mass spectrometry have been previously described.^{1-3,33} This work employed an instrument constructed at Caltech equipped with a 15-in. electromagnet capable of a maximum field strength of 23.4 kG. All chemicals used in this study were obtained commercially and used without further purification. Before use, each sample was degassed by repeated freeze-pump-thaw cycles. All experiments were performed at ambient temperature ($\sim 25^\circ\text{C}$).

Results and Discussion

Mass Spectrum and Positive Ion Chemistry of PF_3 . The 70-eV ICR single-resonance spectrum of PF_3 at 4.8×10^{-7} Torr is in good agreement with previously reported mass spectra.³⁰⁻³² The ions observed and their relative abundances are PF_3^+ (35%), PF_2^+ (60%), and PF^+ (5%). At electron energies ≤ 15 eV, only the molecular ion is observed, consistent with a previous measurement of the appearance potential of PF_2^+ , $\text{AP}(\text{PF}_2^+) = 15.5 \pm 0.2$ eV.³⁰ The temporal variation of relative ion abundance for PF_3 at 1.0×10^{-6} Torr following a 70-eV, 10-ms electron beam pulse is shown in Figure 1. The single ion-molecule process observed in PF_3 is reaction 1,

$$\text{PF}^+ + \text{PF}_3 \rightarrow \text{PF}_2^+ + \text{PF}_2 \quad (1)$$

Table I. Proton-Transfer Reactions Involving PF_3

Reacn obsd	PA(PF_3) ^a
$\text{CH}_5^+ + \text{PF}_3 \rightarrow \text{HPF}_3^+ + \text{CH}_4$	$>128^b$
$\text{HCO}^+ + \text{PF}_3 \rightarrow \text{HPF}_3^+ + \text{CO}$	$>143^b$
$\text{CH}_3\text{FH}^+ + \text{PF}_3 \rightarrow \text{HPF}_3^+ + \text{CH}_3\text{F}$	$>151^b$
$\text{HNF}_3^+ + \text{PF}_3 \rightarrow \text{HPF}_3^+ + \text{NF}_3$	$>151^c$
$\text{CH}_3\text{ClH}^+ + \text{PF}_3 \rightleftharpoons \text{HPF}_3^+ + \text{CH}_3\text{Cl}$	$\sim 160^b$
$\text{HPF}_3^+ + (\text{CF}_3)_2\text{CO} \rightarrow (\text{CF}_3)_2\text{COH}^+ + \text{PF}_3$	$<164.7^d$
$\text{HPF}_3^+ + \text{CF}_3\text{CHO} \rightarrow \text{CF}_3\text{CHOH}^+ + \text{PF}_3$	$<165.7^d$
$\text{HPF}_3^+ + \text{CF}_3\text{CN} \rightarrow \text{CF}_3\text{CNH}^+ + \text{PF}_3$	$<166.7^d$
$\text{HPF}_3^+ + \text{CF}_3\text{CH}_2\text{OH} \rightarrow \text{CF}_3\text{CH}_2\text{OH}_2^+ + \text{PF}_3$	$<172.2^d$
$\text{HPF}_3^+ + \text{H}_2\text{S} \rightarrow \text{H}_3\text{S}^+ + \text{PF}_3$	$<173.9^e$

^a All values in kcal/mol. ^b J. L. Beauchamp in "Interactions between Ions and Molecules", P. Ausloos, Ed., Plenum Press, New York, N.Y., 1975, pp 413-444. ^c Reference 14. ^d I. Koppel and R. W. Taft, unpublished results. ^e Reference 11.

producing PF_2^+ ($k = 3.2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹; $\Delta H = -15 \pm 13$ kcal/mol^{34,35}). Reaction 1 may involve either fluoride-ion or fluorine-atom transfer as the two processes are indistinguishable. The slight decrease of PF_3^+ ion abundance with a concomitant increase in PF_2^+ abundance suggests that some fraction of the PF_3^+ formed by electron impact is vibrationally excited and collisionally dissociates to PF_2^+ . Both PF_3^+ and PF_2^+ are unreactive toward PF_3 .

Gas-Phase Basicity of PF_3 . Mixtures of PF_3 with molecules having a range of base strengths were examined to determine the preferred direction of proton transfer. Proton-transfer reactions from CH_5^+ , HCO^+ , CH_3FH^+ , and HNF_3^+ were confirmed by double-resonance techniques^{1,2} to produce HPF_3^+ . With CH_3Cl , reversible proton transfer (eq 2) was

$$\text{CH}_3\text{ClH}^+ + \text{PF}_3 \rightleftharpoons \text{HPF}_3^+ + \text{CH}_3\text{Cl} \quad (2)$$

observed and verified by double resonance.^{1,2} For $\text{B} = (\text{CF}_3)_2\text{CO}$, CF_3CHO , CF_3CN , $\text{CF}_3\text{CH}_2\text{OH}$, and H_2S , no evidence for the formation of HPF_3^+ from BH^+ is observed and is taken to indicate that proton transfer from BH^+ to PF_3 is endothermic for these molecules. For each mixture examined, proton-transfer reactions involving PF_3 are observed to be slow ($k < 10^{-10}$ cm³ molecule⁻¹ s⁻¹), which precludes accurate measurement of an equilibrium constant for reaction 2 [which is also complicated by the formation of $(\text{CH}_3)_2\text{Cl}^+$ by reaction of CH_3ClH^+ with methyl chloride³⁶] and necessitates the use of double-resonance techniques^{1,2} to bracket the proton affinity between upper and lower bounds.³⁷ Thermochemical data relevant to the present results are given in Table I, from which the proton affinity of PF_3 is established as 160 ± 5 kcal/mol, corresponding to $\Delta H_f(\text{HPF}_3^+) = -18 \pm 5$ kcal/mol.³⁴

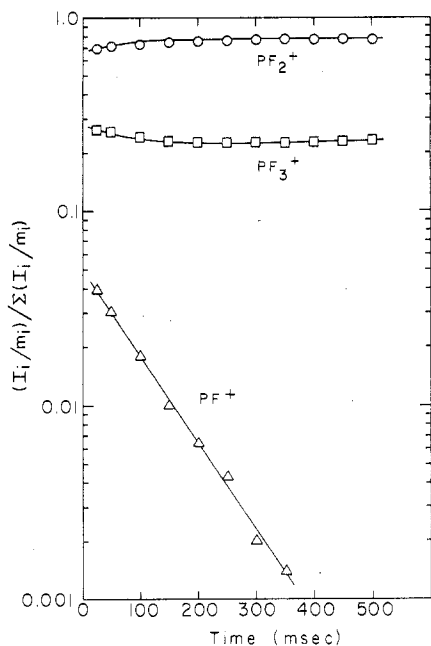


Figure 1. Temporal variation of relative ion abundance in PF_3 at 1.0×10^{-6} Torr following a 70-eV, 10-ms electron beam pulse.

Table II. Thermochemical Data Related to Base Strengths of Group 5 Hydrides and Fluorides

B	PA(B) ^{a,b}	IP(B) ^a	$D(\text{B}^+-\text{H})^a$	Isoelec- tronic neutral RH	$D(\text{R}-\text{H})^{a,c}$
NH_3	202.3	234.5 (10.17)	123.1	CH_4	104.0
NF_3	151 ^d	300.0 (13.00) ^e	137	CF_3H	106.2
PH_3	187.3	229.7 (9.96) ^f	103.4	SiH_4	89.5
PF_3	160 ^g	266.8 (11.57) ^f	113.2	SiF_3H	85.1

^a All data in kcal/mol except values quoted in parentheses for ionization potentials which are in electron volts. ^b Proton affinities relative to $\text{PA}(\text{NH}_3) = 202.3$ kcal/mol; ref 11. ^c M. K. Murphy and J. L. Beauchamp, submitted for publication in *J. Am. Chem. Soc.* ^d Reference 14. ^e V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, **8**, 1728 (1969). ^f Reference 25. ^g Present work.

The homolytic bond dissociation energy, $D(\text{M}^+-\text{H})$, is defined as the enthalpy change for the reaction $\text{MH}^+ \rightarrow \text{M}^+ + \text{H}$ and is related to the proton affinity of M by eq 3, where $\text{PA}(\text{M}) - D(\text{M}^+-\text{H}) = \text{IP}(\text{H}) - \text{IP}(\text{M})$ (3)

the indicated ionization potentials refer to the adiabatic values. Homolytic bond energies are useful for correlating gas-phase basicities because they generally remain constant for a homologous series, yielding a linear relationship between $\text{PA}(\text{M})$ and $\text{IP}(\text{M})$.^{1,6,8,15} The He I photoelectron spectrum of PF_3 reveals the first adiabatic IP at 11.57 ± 0.01 eV.²⁵ Combining this value with $\text{PA}(\text{PF}_3) = 160 \pm 5$ kcal/mol measured in this study gives $D(\text{PF}_3^+-\text{H}) = 113.2 \pm 5$ kcal/mol.

Table II presents the proton affinities, adiabatic ionization potentials, and homolytic bond dissociation energies, $D(\text{B}^+-\text{H})$, for several group 5 hydrides and fluorides. Included for comparison are the bond strengths $D(\text{R}-\text{H})$ for the group 4 molecules isoelectronic with the protonated nitrogen and phosphorus bases BH^+ . Fluorine substituted directly on nitrogen or phosphorus causes a significant decrease in $\text{PA}(\text{B})$ and a somewhat smaller increase in $D(\text{B}^+-\text{H})$. The greater decreases in proton affinity are attributed to the electron-withdrawing effects of fluorine relative to hydrogen, whereby fluorine destabilizes positive charge development at nitrogen or phosphorus.¹⁵ The smaller effect of fluorine substitution on PF_3 [$\text{PA}(\text{PH}_3) - \text{PA}(\text{PF}_3) = 27.3$ kcal/mol while $\text{PA}(\text{NH}_3)$

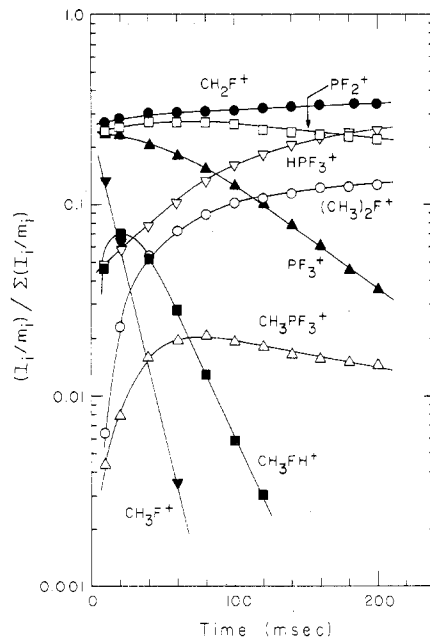
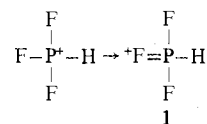


Figure 2. Temporal variation of relative ion abundance in a 1:1 mixture of PF_3 and CH_3F at 1.6×10^{-6} Torr total pressure following a 20-eV, 10-ms electron beam pulse.

– $\text{PA}(\text{NF}_3) = 51.3$ kcal/mol] may be due to the increased importance of structures of type **1** which involve donation from



filled p_π orbitals of fluorine into empty phosphorus d_π orbitals.²⁴ Since these structures stabilize the conjugate acid of PF_3 , they lead to smaller fluorine substituent effects on $\text{PA}(\text{B})$ and $D(\text{B}^+-\text{H})$ for PF_3 relative to NF_3 , for which structures of type **1** are not expected to be important. Additionally, the ion of structure **1** is isoelectronic with HF_2PO , for which ab initio calculations show appreciable charge transfer from the filled fluorine p_π orbitals into the empty phosphorus d_π orbitals.³⁸ As expected, the homolytic B–H bond strengths (Table II) increase upon proceeding to the isoelectronic ion; an increase of 20–30 kcal/mol has been previously noted for other systems.^{1,13,14} An alternative explanation not invoking the participation of d orbitals may involve F–P–F bond angles being smaller than F–N–F bond angles, lending stability to the HPF_3^+ species due to increased p character in the PF bonding orbitals.

In previous studies of the ion chemistry of mixtures of $(\eta^5\text{-C}_5\text{H}_5)\text{NiNO}$ and PF_3 ,^{18,39} it has been observed that PF_3 is incapable of displacing NO from CpNiNO^+ (reaction 4). $\text{CpNiNO}^+ + \text{PF}_3 \rightarrow \text{CpNiPF}_3^+ + \text{NO}$ (4)

Using the value for $\text{PA}(\text{PF}_3) = 160$ kcal/mol measured in this study and the previously determined linear relationship between $D(\text{B}-\text{H}^+)$ and $D(\text{B}-\text{CpNi}^+)$,¹⁸ the value of $D(\text{PF}_3-\text{CpNi}^+) = 39.3 \pm 5$ kcal/mol is calculated. This value is substantially less than the dissociative bond energy of NO to CpNi^+ , $D(\text{NO}-\text{CpNi}^+) = 45.9 \pm 1.0$ kcal/mol,¹⁸ and corroborates the observation that PF_3 does not displace NO from CpNiNO^+ (eq 4).

Formation of CH_3PF_3^+ . A mixture of CH_3F and PF_3 exhibits several interesting reactions in addition to those observed in CH_3F ³⁶ and PF_3 (Figure 1) alone. Figure 2 presents the temporal variation of relative ion abundance in a 1:1 mixture of PF_3 and CH_3F at 1.6×10^{-6} Torr total

Table III. Thermochemical Data for Inorganic Fluorides^a

M	$\Delta H_f(M)$	$\Delta H_f(M^+)$	$\Delta H_f(MF)$	$D(M-F)$	$D(M^+-F^-)$
BF ₂	-141.0	77.1	-271.7	149.4	287.4
CF ₃	-112.2 ^b	100.6	-223.0	129.5	262.6
SiF ₃	-250.0 ^c	-22.7 ^c	-386.0	154.7	347.6
NF ₂	+10.1	278.1 ^d	-31.4	60.2	248.5
PF ₂	-105.0	117.6 ^e	-224.9	138.6	281.4
SF ₅	-218.0 ^f	42.0 ^g	-291.8	92.6	272.8
UF ₅	-455.0 ^h	-209.0 ^h	-511.0 ^h	74.7	241.0
WF ₅	-309.1 ⁱ	-78.8 ⁱ	-411.5	121.0	271.7

^a All values in kcal/mol, from ref 34 and M. W. Chase, J. L. Curnott, A. T. Hu, H. Prophet, A. N. Syverud, and L. C. Walker, *J. Phys. Chem. Ref. Data*, 3, 311 (1974), unless otherwise noted. ^b F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, 48, 955 (1970). ^c M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, 99, 2085 (1977). ^d A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *J. Chem. Phys.*, 54, 1872 (1971). ^e Reference 30. ^f J. L. Lyman, *J. Chem. Phys.*, 67, 1868 (1977). ^g V. H. Dibeler and J. A. Walker, *J. Chem. Phys.*, 44, 4405 (1966). ^h J. L. Beauchamp, *ibid.*, 64, 718 (1976). ⁱ D. L. Hildenbrand, *ibid.*, 62, 3074 (1975).

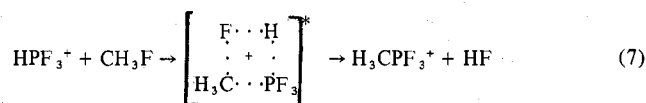
pressure following a 20-eV, 10-ms electron beam pulse. Lower limits to $D(\text{PF}_3^+-\text{H})$ and $\text{PA}(\text{PF}_3)$ are established by observation of reaction 5, a hydrogen-atom transfer from CH_3F

$$\text{PF}_3^+ + \text{CH}_3\text{F} \rightarrow \text{HPF}_3^+ + \text{CH}_2\text{F} \quad (5)$$

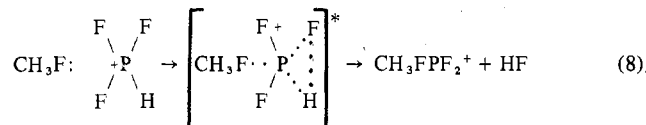
to PF_3^+ . For process 5 to be exothermic requires that $D(\text{PF}_3^+-\text{H}) > D(\text{CH}_2\text{F}-\text{H}) = 101 \text{ kcal/mol}$,⁴⁰ from which $\text{PA}(\text{PF}_3) > 148 \text{ kcal/mol}$ is directly inferred (eq 3). HPF_3^+ reacts further with CH_3F in reaction 6 to produce CH_3PF_3^+

$$\text{HPF}_3^+ + \text{CH}_3\text{F} \rightarrow \text{CH}_3\text{PF}_3^+ + \text{HF} \quad (6)$$

and eliminate HF. Reaction 7 presents a mechanism for the



formation of the protonated methylene phosphorane product ion,¹⁴ CH_3PF_3^+ , which involves the four-center elimination of HF from the activated complex. An alternative mechanism involving nucleophilic attack by CH_3F on the phosphonium center is also possible (eq 8). In this case, the (difluoro-



phosphine)methylfluoronium ion may result, which appears unusual at first but is isoelectronic with CH_3OPF_2 .⁴² At long ion trapping times ($t > 10 \text{ ms}$), CH_3PF_3^+ slowly reacts with the neutral CH_3F present to produce the dimethylfluoronium ion (eq 9; $k = 1.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). By assuming

$$\text{CH}_3\text{PF}_3^+ + \text{CH}_3\text{F} \rightarrow (\text{CH}_3)_2\text{F}^+ + \text{PF}_3 \quad (9)$$

that both reactions 6 and 9 are exothermic or thermoneutral, upper and lower limits, respectively, of $\Delta H_f(\text{CH}_3\text{PF}_3^+)$ may be calculated and give an average value of $\Delta H_f(\text{CH}_3\text{PF}_3^+) = -8.5 \pm 5 \text{ kcal/mol}$, which leads directly to $D(\text{CH}_3^+-\text{PF}_3) = 44 \pm 5 \text{ kcal/mol}$.

Fluorine Atom Transfer Reactions Leading to PF_4^+ . In a mixture of PF_3 and NF_3 , fluorine-atom transfer from neutral NF_3 to PF_3^+ is observed (eq 10) and indicates that $D(\text{PF}_3^+-\text{F})$

$$\text{PF}_3^+ + \text{NF}_3 \rightarrow \text{PF}_4^+ + \text{NF}_2 \quad (10)$$

$> D(\text{NF}_2-\text{F}) = 60.2 \text{ kcal/mol}$ (Table III). This process is observed only with NF_3 as a neutral reactant.

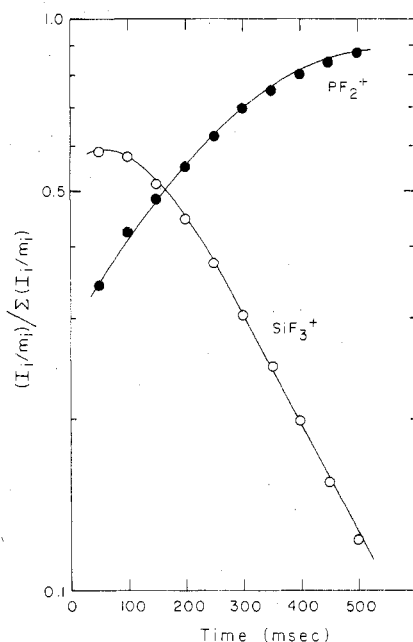
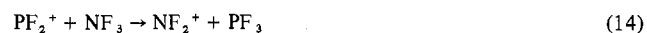


Figure 3. Temporal variation of relative ion abundance in a 9.6:1 mixture of SiF_4 and PF_3 at a total pressure of 2.2×10^{-6} Torr following an 18-eV, 10-ms electron beam pulse.

Fluoride-Transfer Reactions Involving PF_2^+ . The ion chemistry of mixtures of PF_3 with a variety of inorganic fluorides including SiF_4 , BF_3 , SF_6 , CF_4 , and NF_3 was examined. The SiF_3^+ and BF_2^+ ions produced by electron impact ionization of SiF_4 and BF_3 , respectively, abstract F^- from neutral PF_3 (eq 11 and 12). Figure 3 presents the temporal



variation of relative ion abundance in a 9.6:1 mixture of SiF_4 and PF_3 at a total pressure of 2.2×10^{-6} Torr following an 18-eV, 10-ms electron beam pulse. Reaction 11 is the only ion-molecule reaction observed in this system under these conditions. From the linear portion of the decrease in SiF_3^+ relative abundance ($t > 200 \text{ ms}$), $k = 6.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is calculated. PF_2^+ reacts with SF_6 and NF_3 , on the other hand, to produce SF_5^+ (eq 13) and NF_2^+ (eq 14).



Fluoride ion transfer reactions cannot be observed in mixtures of PF_3 and CF_4 since the reactant and product ions, PF_2^+ and CF_3^+ , have the same mass. From these results, the heterolytic bond dissociation energy $D(\text{PF}_2^+-\text{F}^-)$ is less than $D(\text{SiF}_3^+-\text{F}^-)$ and $D(\text{BF}_2^+-\text{F}^-)$ and greater than $D(\text{SF}_5^+-\text{F}^-)$ and $D(\text{NF}_2^+-\text{F}^-)$. The thermochemical changes associated with these reactions can be inferred from the data presented in Table III, which are entirely consistent with the derived order. These experiments thus confirm available data which yield $D(\text{PF}_2^+-\text{F}^-) = 281.4 \pm 6.1 \text{ kcal/mol}$ (Table III). With a larger number of fluorides, it would be possible to accurately establish relative heterolytic bond dissociation energies for species such as those listed in Table III. In most cases there are no competing reactions which would interfere with the examination of halide-transfer equilibria.⁴³

Reactions of PF_3^+ and PF_4^+ with Acetone. When a trace of acetone (3×10^{-8} Torr) is added to a mixture of NF_3 and PF_3 , several new ionic species result. Figure 4 presents the temporal variation of relative ion abundance for a 53:20:1 mixture of NF_3 , PF_3 , and $(\text{CH}_3)_2\text{CO}$ at a total pressure of 2.7×10^{-6} Torr [excluding ions observed in $(\text{CH}_3)_2\text{CO}$ alone⁴⁴],

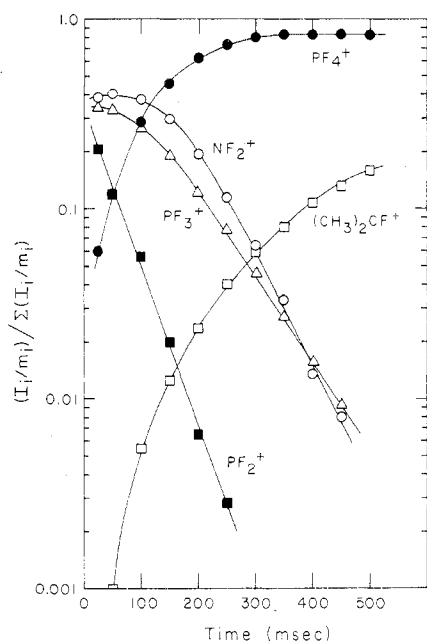
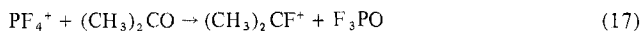
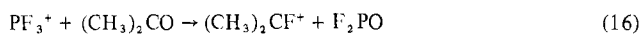
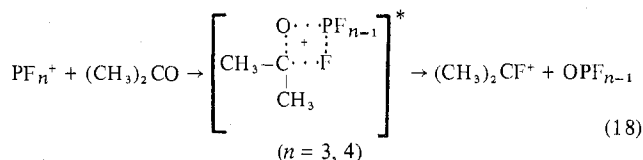


Figure 4. Temporal variation of relative ion abundance in a 53:20:1 mixture of NF_3 , PF_3 , and $(\text{CH}_3)_2\text{CO}$ at 2.7×10^{-6} Torr total pressure following a 20-eV, 10-ms electron beam pulse. The normalized data excludes ions from acetone alone.⁴⁴

following a 20-eV, 10-ms electron beam pulse. In addition to the fluorine atom transfer reaction 10, the sequence of reactions 14–17 describe the ion–molecule processes which



occur in this system. Reaction 14 (discussed in greater detail above) is a fluoride transfer from NF_3 to PF_2^+ ($k = 3.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and indicates that $D(\text{PF}_2^+ - \text{F}^-) > D(\text{NF}_2^+ - \text{F}^-) = 248.5 \text{ kcal/mol}$ (Table III). The NF_2^+ formed in eq 14 reacts further to produce PF_3^+ by charge exchange (reaction 15; $k = 5.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Particularly interesting, however, are reactions 16 and 17, in which the carbonyl oxygen exchanges with F^+ in PF_3^+ and PF_4^+ . Analogous reactions have been observed by Ausloos et al. in mixtures of aldehydes, ketones, esters, acids, and acetic anhydride with CX_3^+ ions ($\text{X} = \text{F}$ or Cl).⁴⁵ Their results demonstrate that a four-center reaction mechanism resulting in the formation of a monohalogenated carbonium ion predominates.⁴⁵ An analogous mechanism for reaction 16 and 17 is presented in equation 18.



Reaction 17 indicates $\Delta H_f(\text{PF}_4^+) \geq -106 \text{ kcal/mol}$, to be compared with the limit $\Delta H_f(\text{PF}_4^+) \leq 0.4 \text{ kcal/mol}$ inferred from observation of reaction 10. These rather wide limits are consistent with estimates of -94 and -77 kcal/mol derived from core binding energy data.⁴⁶ If the latter estimates are correct, then processes analogous to reaction 10 with other neutrals (e.g., SF_6) would be substantially exothermic. As noted above these reactions were not observed.

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Registry No. PF_3 , 7783-55-3; PF_4^+ , 29075-80-7; PF_2^+ , 37366-67-9; HPF_3^+ , 62779-06-0; CH_3PF_3^+ , 66057-03-2.

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