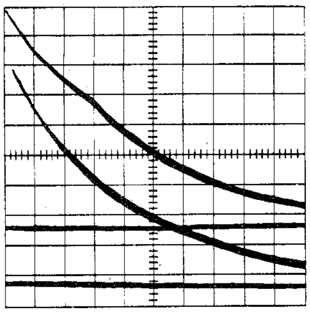

Figure 1. Reaction between Np(VI) and thiomalic acid, followed on a Durrum Model D-110 stopped-flow spectrophotometer. The upper trace was obtained using air-saturated solutions; the lower trace was obtained under anaerobic conditions. Conditions: 25°, λ 3400 Å, I = [$HClO_4$] = 2.00 F, [Np(VI)]$_0$ = 1.065 × 10^{-3} F, [thiomalic acid]$_0$ = 7.20 × 10^{-2} F, vertical scale = 0.02 optical density unit/division, and horizontal scale = 0.50 sec/division.

at constant initial concentration of oxidant, [oxidant]$_0$. (5) The extent of overoxidation is a function of the nature of the thiol. For the thiols studied, the susceptibility to overoxidation increases in the order cysteamine < cysteine < thioglycolic acid < thiomalic acid for Np(VI) as the oxidant and cysteamine ≃ thioglycolic acid < thiomalic acid for Ce(IV) as oxidant. Again, these results are in general agreement with Danehy's observation that thiols containing a β-carboxylate function are most susceptible to overoxidation.[4] (6) For thioglycolic acid and thiomalic acid, there does not seem to be much difference in the extent of overoxidation caused by Np(VI) or Ce(IV). However, cysteamine hydrochloride is more susceptible to overoxidation by Ce(IV) than by Np(VI). (7) When Np(VI) oxidizes thiomalic acid in the presence of molecular oxygen, the reaction stoichiometry drops to less than 1 mol of oxidant consumed for every mole of thiol oxidized (compare experiments 12 and 13). This implies that molecular oxygen is effecting net oxidation of thiol during the reaction (note that, under the conditions of these reactions, molecular oxygen normally does not oxidize thiols at an appreciable rate).

Further evidence that molecular oxygen severely interferes with the normal course of thiol oxidation by 1-equiv oxidants is provided by Figure 1 wherein two stopped-flow traces of the reaction between Np(VI) and thiomalic acid are reproduced. The conditions under which these traces were obtained are exactly identical (see caption: at this wavelength the trace is monitoring the concentration of Np(VI)) except that the lower trace was obtained under anaerobic conditions. It is easily seen that the presence of molecular oxygen inhibits the rate of disappearance of Np(VI) in the early part of the reaction, an effect which could readily be mistaken for the formation of a neptunium-thiol intermediate.

The results reported in this work may be qualitatively explained by a mechanism analogous to that proposed by Danehy.[4] Within the systems we have considered, this scheme postulates a sequence of 1-equiv oxidation reactions to generate first a free radical RS· and then a reactive intermediate sulfenium ion, RS^+. Competing reactions of RS^+ with RSH and H_2O and the reaction of RS· with oxygen allow a facile rationalization of our observations. In the case of thiomalic acid, the reaction of RS^+ with water may be assisted by the presence of the β-carboxylate function.[4]

To summarize, in the reactions of the 1-equiv oxidants Np(VI) and Ce(IV) with thiols, the stoichiometry depends upon the initial concentration of thiol and the presence of β-carboxylate functions in the thiol. The presence of molecular oxygen in the solutions has an effect on both the dynamic and thermodynamic aspects of these reactions. These observations should be taken into consideration in any further work in this field.

Registry No. Neptunium, 7439-99-8; cerium, 7440-45-1; thiomalic acid, 70-49-5; thioglycolic acid, 68-11-1; cysteine, 4371-52-2; cysteamine, 60-23-1; oxygen, 7782-44-7.

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Contribution from the Chemistry Department,
Edinburgh University, Edinburgh, Scotland

Dissociation and Ionization of Difluorocyanophosphine

P. W. Harland, D. W. H. Rankin, and J. C. J. Thynne*[1]

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Although the chemistry of the fluorophosphines has received much attention recently,[2] there has been only a limited study[3] of the results of electron impact on these molecules and in particular no studies of negative ion formation. We have accordingly measured positive—and negative—ion formation by difluorocyanophosphine.

Experimental Section

The experiments were performed using a Bendix time-of-flight mass spectrometer, Model 3015. The technique employed has been described previously.[4-6]

Difluorocyanophosphine was prepared by passing gaseous difluorobromophosphine over solid silver cyanide at 300°K, the product being condensed at 177°K. After vacuum distillation several times the product showed no traces of impurity when analyzed by infrared spectrometry.

Results and Discussion

(1) Positive Ion Formation. The principal ions observed in the positive ion mass spectrum of PF_2CN are PF_2CN^+ (22), $PFCN^+$ (9.1), PF_2^+ (100), PF^+ (9.2), and CN^+ (3.3); their relative intensities at 70 eV are shown in parentheses.

In Table I are shown the measured appearance potential data for these ions.

(i) PF_2^+. This ion is presumably formed by reaction 1

$$PF_2CN + e \rightarrow PF_2^+ + CN + 2e \qquad (1)$$

at the energy shown in Table I. No value has been reported for the ionization potential of PF_2. A reasonably reliable value may be estimated as follows *via* a value of 15.4 ± 0.2 eV which we have measured in this laboratory for $A(PF_2^+)$ from phosphorus trifluoride: the energy of decomposition of gaseous PF_3, $PF_3(g) \rightarrow P(g) + 3F(g)$, may be calculated to

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[1] To whom correspondence should be addressed at the Department of Trade and Industry, Shell Mex House, Strand, London W.C.2, England.

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Table I. Appearance Potential Data (in eV) for the Positive Ions Formed by PF_2CN

Ion (X^+)	$A(X^+)$	Ion (X^+)	$A(X^+)$
PF_2CN^+	11.7 ± 0.2	PF^+	19.1 ± 0.2
$PFCN^+$	15.7 ± 0.2	CN^+	19.8 ± 0.3
PF_2^+	13.4 ± 0.2		

be 15.4 ± 0.1 eV. Since $D(\mathrm{P-F}) = 4.5 \pm 0.1$ eV;[7,8] hence $D(\mathrm{PF_2-F}) + D(\mathrm{PF-F}) = 10.9 \pm 0.2$ eV. If we assume both bonds to have similar energies, then $D(\mathrm{PF_2-F}) = 5.4 \pm 0.1$ eV, and since $D(\mathrm{PF_2-F}) \leqslant A(\mathrm{PF_2^+}) - I(\mathrm{PF_2})$, we may estimate that $I(\mathrm{PF_2}) \leqslant 10.0 \pm 0.3$ eV. Substitution of this value for $I(\mathrm{PF_2})$ in $D(\mathrm{PF_2-CN}) \leqslant A(\mathrm{PF_2^+}) - I(\mathrm{PF_2})$ leads to a value of $\leqslant 3.4 \pm 0.5$ eV for $D(\mathrm{PF_2-CN})$. No other value has been reported for this bond dissociation energy from which the heat of formation of the fluorocyanide molecule may be calculated to be ~−4.1 ± 0.6 eV.

(ii) CN^+

$$\mathrm{PF_2CN + e \rightarrow CN^+ + PF_2 + 2e} \qquad (2)$$

If the absence of excess energy in reactions 1 and 2 is assumed, then

$$A(\mathrm{PF_2^+}) - I(\mathrm{PF_2}) = A(\mathrm{CN^+}) - I(\mathrm{CN}) \qquad \mathrm{(I)}$$

From expression I a value of 16.4 ± 0.7 eV may be obtained for the ionization potential of the cyanide radical. This is in poor agreement with the reported value of 14.03 eV.[9] Application of Stevenson's rule[10] to reactions 1 and 2 would however suggest that the CN^+ ion is produced with excess kinetic energy and so expression I is invalid.

(2) Negative Ion Formation. The principal negative ions observed at 70 eV are PF_2CN^- (6.4), PF_2^- (10), FCN^- (1), F_2^- (1), CN^- (1000), and F^- (47); their relative intensities are shown in parentheses. The presence of F_2^- and FCN^- in the mass spectrum indicates the occurrence of rearrangement reactions, the ions presumably being formed by F atom migration.

In common with the formation of several ions in the PF_3 system[11] it was found that at relatively low electron energies the F^-, CN^-, FCN^-, and PF_2^- resonances at ~4 eV exhibited a vertical rise to their maximum cross section at threshold. This was shown by comparison of the ionization efficiency curves for these ions with that for O^--CO which is known[12] to exhibit the vertical onset effect. This result is interpreted to indicate that ion formation at this energy is due to the multichannel decay of an unstable excited state of the parent ion, *i.e.*

$$\mathrm{PF_2CN + e \rightarrow [PF_2CN^{-*}] \rightarrow PF_2^-, CN^-,\ etc.}$$

A similar explanation has been advanced to account for ion formation in perfluoroolefins.[13]

(i) CN^-. This ion was formed abundantly particularly at ~0 eV. The major resonance peak onsets at 0.0 ± 0.1 eV; minor resonances were observed at 4.6 ± 0.1, 5.9 ± 0.2, and ~9 eV which have cross sections of 0.15, 0.07, and 0.10, respectively, relative to that of the initial resonance. The formation of CN^- is *via*

$$\mathrm{PF_2CN + e \rightarrow CN^- + PF_2} \qquad (3)$$

$D(\mathrm{PF_2-CN}) \leqslant A(\mathrm{CN^-}) + E(\mathrm{CN})$, where $E(\mathrm{CN})$ is the electron affinity of the nitrile radical. Since $A(\mathrm{CN^-}) = 0.0 \pm 0.1$ eV, then $D(\mathrm{PF_2-CN}) \leqslant E(\mathrm{CN})$. A recent value of 3.8 ± 0.05 eV has been reported[9] for $E(\mathrm{CN})$, suggesting that $D(\mathrm{PF_2-CN}) \leqslant 3.8 \pm 0.05$ eV. This bond strength is in reasonable accord with the value of $\leqslant 3.4 \pm 0.05$ eV deduced above in the positive ion study of the fluorocyanide.

(ii) PF_2^-

$$\mathrm{PF_2CN + e \rightarrow PF_2^- + CN} \qquad (4)$$

$A(\mathrm{PF_2^-}) = 4.6 \pm 0.1$ eV. The minimum enthalpy requirement for reaction 4 is $3.4 \pm 0.5\ \mathrm{eV} - E(\mathrm{PF_2})$; since no ions are formed below 4.6 eV, clearly there is at least 1.2 eV of excess kinetic and/or excitation energy associated with reaction 4. We cannot attribute the reaction energy more specifically since we know of no reported value for the electron affinity of PF_2.

(3) Thermochemical Data. The following values for the heats of formation (in eV) at 298°K have been used in this paper: F, 0.8; P, 3.3; PF_2, −5.1 ± 0.1 (calculated from $D(\mathrm{PF_2-F}) = 5.4 \pm 0.1$ eV); PF_3, −9.7; CN, 4.4.[14] Except where indicated all values have been taken from ref 15.

Registry No. PF_2Br, 15597-40-7; AgCN, 506-64-9; PF_2CN, 14118-40-2.

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Contribution from the Department of Physical Chemistry,
University of Melbourne, Parkville, Victoria, Australia 3052, and
the Division of Chemical Physics, CSIRO, Clayton,
Victoria, Australia 3168

Vaporization of Tin(II) Halides. I. Stannous Chloride and Stannous Bromide

S. Ciach,[1a] D. J. Knowles,[1a] A. J. C. Nicholson,*[1b] and D. L. Swingler[1b]

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As part of a study of the reactions of tin halides with gases it was necessary to determine the composition of the gas in equilibrium with the molten salt. Brewer[2] has suggested on the basis of radius-ratio considerations that the dihalides of germanium and tin could be expected to dimerize in the gas phase. Vapor density measurements on stannous halides made without identifying the vapor species[3,4] show that at pressures in the 20–600 Torr range (1 Torr = 133.3 N m^{-2}) the number of molecules in the gas phase decreases and this effect has always been interpreted as a dimerization. Uy, *et al.*,[5] established that at the pressures used in Knudsen cell

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[1] (a) University of Melbourne. (b) CSIRO.

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