oxidation–reduction systems may be too short-lived to be detected by esr spectroscopy at 22°. As reported, oxyvanadium(V) ions do form short-lived complexes detectable by esr spectroscopy.[5] The characteristic esr spectra were not obtained with Ce^{4+} ions, probably because Ce^{4+} ions are not stable in the presence of H_2O_2, being reduced to Ce^{3+} ions. Apparently, neither Ce^{4+} or Ce^{3+} ions (or Fe^{3+} ions formed in the Fe^{2+}–H_2O_2 system) form complexes with free-radical species in oxidation–reduction systems detectable by esr spectroscopy at 22°.

Experimental Section

A Varian 4502-15 epr spectrometer system, operating at 100-kcps field modulation and using an aqueous flow cell at 22°, was used. The flow rate of mixing of the oxidation–reduction systems was varied, in the usual way, by pressurizing the two solution reservoirs with nitrogen (0.5 atm), by adjusting a clip on the exit line, and by measuring the rates of flow by meters inserted on the inlet sides of the mixing chamber to the aqueous cell.[3,5]

The compositions of the solutions, usually being mixed in equal volumes, were: (1) Fe^{2+} (0.01 *M*)–H_2SO_4 (9 ml of concentrated l.$^{-1}$) and $UO_2(NO_3)_2$ (0.01 *M*)–H_2O_2 (0.1 *M*)–H_2SO_4 (9 ml of concentrated l.$^{-1}$); (2) Ce^{4+} (0.001 *M*)–H_2SO_4 (9 ml of concentrated l.$^{-1}$) and $UO_2(NO_3)_2$ (0.02 *M*)–H_2O_2 (0.1 *M*)–H_2SO_4 (9 ml of concentrated l.$^{-1}$); (3) Ce^{4+} (0.001 *M*)–$Th(NO_3)_4$ (0.005 *M*)–H_2SO_4 (7.5 ml of concentrated l.$^{-1}$) and H_2O_2 (0.1 *M*)–H_2SO_4 (7.5 ml of concentrated l.$^{-1}$); (4) Ce^{4+} (0.001 *M*)–H_2SO_4 (9 ml of concentrated l.$^{-1}$) and H_2O_2 (0.1 *M*)–$ZrO(NO_3)_2$ (0.01 *M*)–H_2SO_4 (9 ml of concentrated l.$^{-1}$); (5) Fe^{2+} (0.01 *M*)–H_2SO_4 (9 ml of concentrated l.$^{-1}$) and H_2O_2 (0.1 *M*)–$ZrO(NO_3)_2$ (0.01 *M*)–H_2SO_4 (9 ml of concentrated l.$^{-1}$); (6) Ce^{4+} (0.001 *M*)–H_2SO_4 (7.5 ml of concentrated l.$^{-1}$) and H_2O_2 (0.1 *M*)–$HfCl_4$ (0.01 *M*)–H_2SO_4 (7.5 ml of concentrated l.$^{-1}$).

The esr spectrum of the mixed solutions was recorded at 22° after equilibrium for a given flow rate was reached; that is, the intensity of the esr spectrum became constant. *g* values and line widths of the esr spectra were determined at a relatively slow scan rate for the magnetic field and a relatively high speed for the chart. DPPH was used as a standard. Chemicals used were reagent grade; solutions were prepared with oxygen-free distilled water.

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Reaction of Difluorophosphines with Pseudohalogen Halides

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Although it has been well established that phosphoranes can be obtained by oxidizing phosphines with halogens,[1-3] the only pseudohalogen halide which has been reported to act as an oxidizing agent with phosphines is cyanogen bromide. Specifically, it has been observed that BrCN would interact with $(CH_3)_2NPF_2$ to give $(CH_3)_2NPF_3(CN)$ and $(CH_3)_2NPFBr$ as products, although BrCN does not interact with PF_3.[4] In this paper, the results of a series of studies of the reactions of difluorophosphines with BrCN and ClCN are reported.

Methyltetrafluorophosphorane, dicyanomethylphosphine, dibromomethylphosphine, and the previously unreported $CH_3PBr(CN)$ were obtained when CH_3PF_2 was allowed to interact with BrCN. In contrast, no evidence that any reaction occurred was obtained when ClCN was allowed to interact with PF_3, CH_3PF_2, or $(CH_3)_2NPF_2$. These compounds were identified by infrared, nmr, mass spectral, and elemental analyses. $CH_3PBr(CN)$ was also prepared by the direct interaction of CH_3PBr_2 and $CH_3P(CN)_2$.

These reactions of pseudohalogen halides with phosphines appear to depend on two factors. First, as the strength of the carbon–halogen bond increases, the reactivity of the pseudohalogen halide appears to decrease. ClCN does not react, although BrCN does. Second, the reactivity of the phosphine appears to depend on the relative electronegativity of the phosphorus atom. When electron-releasing groups are attached to phosphorus (*i.e.*, $(CH_3)_2N$ or CH_3), the phosphine is reactive. PF_3 is not reactive. The factors which influence the amounts and nature of the products are not well understood.

Experimental Section

Apparatus.—Standard high-vacuum techniques were used throughout. Proton and fluorine nmr spectra were obtained on a Varian Model 56/60 nuclear magnetic resonance spectrometer operating at 60.0 Mc for the proton and 56.4 Mc for fluorine. For the proton spectra, tetramethylsilane and methylene chloride were used as external standards. For fluorine magnetic resonances, fluorotrichloromethane was used as an external reference, by the tube-interchange technique. Whenever possible, samples were run as neat liquids. Phosphorus nmr absorptions were obtained on a Varian Model DA 60 spectrometer operating at 24.3 Mc. Phosphoric acid (85%) was used as an external reference.

An F & M 810 research chromatograph was used, with helium as the carrier gas and a flame ionization detector. Glpc analyses of the products were performed on a 0.125 in. × 20 ft stainless steel column packed with 20% silicon gum rubber SE 30 on Chromosorb W. The column was operated at 70°. The infrared spectra were obtained on a Perkin-Elmer 457 grating infrared spectrometer. For volatile materials a gas cell with a 7.5-cm path length and CsI windows was used. Nonvolatile materials were examined as smears between CsI plates. All mass spectra were obtained on a Perkin-Elmer Hitachi RMU-6E mass spectrometer operating with an ionization potential of 70 eV.

Materials and Analyses.—Cyanogen bromide (Aldrich Chemical Co.) was dried before use by distilling it *in vacuo* at 23° through two traps filled with phosphorus pentoxide suspended on asbestos. Cyanogen chloride was prepared from sodium cyanide and chlorine;[5] mp −5.1° (lit.[5] mp −5 to −6°). Dimethylaminodifluorophosphine was prepared by a previously described method.[6] The identity of the phosphine was established by comparison of its infrared spectrum with a previously reported spectrum[7] and by a vapor pressure of 93.7 mm at 0° (lit.[6] pressure 93.4 mm). Phosphorus trifluoride (Ozark Mahoning Co.) was bubbled through water at 0° and dried by passing the gas

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through 0 to −78 to −196° traps. The −78° fraction was discarded. The purity of the sample thus obtained was established by a vapor pressure of 114.4 mm at −126.0° (lit.[8] pressure 113.9 mm). Methyldifluorophosphine was prepared by allowing CH_3PCl_2 to interact with SbF_3 suspended in pyridine.[9] The infrared, proton, and fluorine nmr spectra of CH_3PF_2 prepared in this manner were identical with previously reported spectra;[10] mp −112° (lit.[10] mp −110°).

All analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Attempted Reactions of Difluorophosphines with Cyanogen Chloride.—In a typical reaction ClCN (2.06 mmol) was condensed at −196° *in vacuo* into a 340-ml reaction tube equipped with a stopcock and a standard taper joint. While the tube was maintained at −196°, 3.29 mmol of PF_3 was distilled *in vacuo* onto solid ClCN.

The mixture was allowed to warm to 25° for 1 hr. After this time, the gaseous mixture was heated to 75° for 5 hr by immersion of the reaction tube in a heated oil bath. After heating, the reaction mixture was passed through traps held at 0, −78, and −196°. A 3.26-mmol sample of unreacted PF_3 was recovered from the −196° trap, indicating no reaction occurred. The PF_3 thus recovered was identified by its infrared and mass spectra, which were identical with those of a sample of authentic PF_3.

Methyldifluorophosphine and dimethylaminodifluorophosphine also were allowed to interact with ClCN in a similar manner. No evidence that any reaction occurred was obtained.

Reaction of CH_3PF_2 with BrCN.—In a typical experiment a sample of cyanogen bromide (11.1 mmol) was distilled *in vacuo* into a 25-ml glass reaction tube maintained at −196°. The tube was equipped with a standard taper joint and a glass Teflon high-vacuum stopcock (Ace, Catalog No. 8194). Methyldifluorophosphine (11.1 mmol) was then distilled *in vacuo* into the same tube. The reaction mixture was warmed to −20° by placing the reaction tube in a bath of salt and ice. The colorless reaction mixture turned amber within about 10 min. After the color change, the mixture was cooled again to −196°. The mixture was then allowed to warm to 23° over a period of 2.3 hr. During this time, the volatile products were removed by distillation *in vacuo*. These products were passed through a trap filled with molecular sieves (previously dried at 550° under a stream of nitrogen for 2 hr) and then through traps held at −12, −90, and −196°. A 2.7-mmol sample of $CH_3P(CN)_2$ was recovered from the −12° trap. The −90° trap contained 2.8 mmol of a mixture of about 90% CH_3PBr_2, about 9% $CH_3PBr(CN)$, and about 1% $CH_3P(CN)_2$.[11] A pure sample of CH_3PBr_2 was obtained from this mixture by passing the mixture through traps held at −45 and −196°; the CH_3PBr_2 was retained in the −196° trap. Identification of these products is described in subsequent portions of this paper.

The −196° trap used in the original distillation contained a 5.3-mmol sample of CH_3PF_4, identified by its mass spectrum which was identical with a previously reported spectrum[12] and by a vapor pressure of 752 mm at 10° (lit.[12] bp 10°).

Characterization of CH_3PBr_2 and $CH_3P(CN)_2$.—The proton and phosphorus nmr data are presented in Table I. The chemical shifts and coupling constants of the absorptions are consistent with the proposed formulations. The ^{31}P chemical shifts obtained for CH_3PBr_2 (δ −184.1 ppm) and $CH_3P(CN)_2$ (δ +80.3 ppm) are almost identical with previously reported values (lit.[13] $\delta(CH_3PBr_2)$ −184.0 ppm; lit.[14] $\delta(CH_3P(CN)_2$ +81.4 ppm). The position and intensity of ir absorptions are identical with previously reported data.[13,14]

Table I

Proton and Phosphorus Nmr Data for Methylphosphines

Compound	^1H nmr		^{31}P nmr	
	δ, ppm	J_{PH}, cps	δ, ppm	J_{PH}, cps
CH_3PBr_2	−2.66[c]	19.9	−184.1[a,d]	19.6
$CH_3PBr(CN)$	−2.20[c]	13.1	−23.6[d]	13.9
$CH_3P(CN)_2$	−1.88[c]	7.7	+80.3[b,d]	7.5

[a] Lit.[13] −184.0 ppm. [b] Lit.[14] +81.4 ppm. [c] 1:1 doublet. [d] 1:3:3:1 quartet.

The mass spectrum of CH_3PBr_2 shows peaks attributed to the following positive ions, *m/e*, relative intensity: $CH_3P^{81}Br_2$, 208, 31; $CH_3P^{79}Br^{81}Br$, 206, 64; $CH_3P^{79}Br_2$, 204, 32; $P^{81}Br_2$, 193, 13; $P^{79}Br^{81}Br$, 191, 28; $P^{79}Br_2$, 189, 13; ?, 162, 2; ?, 160, 2; ?, 147, 2; ?, 145, 2; $CH_3P^{81}Br$, 127, 69; $CH_2P^{81}Br$, 121, 4; $CH_3P^{79}Br$ and $CHP^{81}Br$, 125, 73; $CH_2P^{79}Br$, 124, 4; $CHP^{79}Br$, 123, 3; $P^{81}Br$, 112, 7; $P^{79}Br$, 110, 7; $H^{81}Br$, 82, 9; ^{81}Br and ?, 81, 16; $H^{79}Br$, 80, 9; ^{79}Br, 79, 9; CH_3P, 46, 6; CH_2P, 45, 78; CHP, 44, 27; CP, 43, 6; O_2, 32, 20; N_2, 28, 100; H_2O, 18, 20; HO, 17, 19; CH_3, 15, 3.

The mass spectrum of $CH_3P(CN)_2$ shows peaks attributed to the following positive ions: $CH_3P(CN)_2$, 98, 25; $P(CN)_2$, 83, 4; ?, 73, 6; CH_3PCN, 72, 4; CH_2PCN, 71, 36; CHPCN, 70, 10; CPCN, 69, 4; HPCN, 58, 3; PCN, 57, 31; CH_3P, 46, 24; CH_2P, 45, 13; CHP, 44, 15; CP, 43, 3; ?, 40, 3; ?, 39, 5; O_2, 32, 65; P, 31, 8; N_2, 28, 80; HCN, 27, 100; CN, 40, 35; H_2O, 18, 32; HO, 17, 7; O, 16, 4; CH_3, 15, 10; N, 14, 10.

The large amount of HCN which appears is apparently formed by hydrolysis of $CH_3P(CN)_2$ at the injection point of the mass spectrometer.

Anal. Calcd for CH_3PBr_2: C, 5.83; H, 1.47; Br, 77.65. Found: C, 6.03; H, 1.55; Br, 77.42.

Characterization of $CH_3P(CN)Br$.—The ^{31}P and ^1H nmr of the material recovered from the −90° trap suggested it was a mixture. It was impossible to separate this mixture using trap-to-trap distillation. In a separate experiment we were also unable to separate this mixture by glpc, although several columns with different packings were employed. The mass spectrum of the mixture showed peaks, together with appropriate isotopic intensity distributions, corresponding to $CH_3PBr_2^+$, PBr_2^+, $CH_3P(CN)_2^+$, $P(CN)_2^+$, $CH_3PBr(CN)^+$, CH_3PBr^+, $CH_3P(CN)^+$, CH_3PBr^+, CH_3PCN^+, CH_3P^+, Br^+, CN^+, and CH_3^+. The observation of a peak corresponding to $CH_3PBr(CN)^+$ as well as fragments which would arise from this molecule suggested the presence of $(CH_3)PBr(CN)$ in the mixture. The ^1H nmr (Table I) showed that a doublet was observed whose chemical shift and coupling constants were between those of CH_3PBr_2 and $CH_3P(CN)_2$. Additional support for the existence of $CH_3PBr(CN)$ is obtained from the ^{31}P nmr spectrum, where a peak is observed whose chemical shifts, splitting pattern, and coupling constants are consistent with $CH_3PBr(CN)$.

In a separate experiment a sample (1.2 mmol) of pure $CH_3P(CN)_2$ and a sample (1.2 mmol) of pure CH_3PBr_2 were mixed and allowed to equilibrate for 48 hr at 24°. At the end of this time the ^{31}P and ^1H nmr indicated the presence of a new compound whose identity was the same as that obtained from the interaction of CH_3PF_2 and BrCN. Ligand-exchange reactions between PX_3 (where X is any halogen except F) and PZ_3 (where Z is a pseudohalogen such as NCS, NCO, SCN, and OCN) are well known,[15] so it is expected that the interaction of CH_3PBr_2 and $CH_3P(CN)_2$ would produce $CH_3P(CN)Br$.

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