where R = NH_2, NHCH, NHC_6H_5, or OC_2H_5. Carbanilide and tetramethylurea may not produce the cyanato complex either because steric interactions make formation of the N-bonded complex very unfavorable or because it would be necessary for phenyl or methyl groups to migrate. The fact that the O-bonded isomer of urea has been isolated and does not seem to isomerize in solution or in the solid state indicates that O- to N-linkage isomerism is more likely to proceed by dissociation, as implied in the above reaction scheme, and not by intramolecular rearrangement.

The reactions outlined above may provide a model for metal ion catalyzed decomposition of urea. The crucial feature is the formation of the N-bonded urea complex which then forms the conjugate base of urea because the metal ion greatly increases the acidity of the coordinated $-NH_2$ protons.[15] The conjugate base of urea then easily decomposes to cyanate and ammonia.

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Electron Spin Resonance Spectra of Transition Metal Ions in Oxidation–Reduction Systems

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When solutions of $TiCl_3$ and H_2O_2 were mixed in an esr cavity, Dixon and Norman[3] observed a narrow singlet spectrum, line width 1 G, which they attributed to the $\cdot$OH radical. Other workers[4-15] have reported similar esr spectra for this system. Also, for this system an esr spectrum with two narrow lines, spaced a few gauss apart, has been reported[8,11,13] These lines have been assigned (1) to $\cdot$OH radicals and $\cdot$OOH radicals complexed with Ti^{4+} ions,[8] (2) to $\cdot$OOH radicals and $\cdot$OH or $\cdot$OOH radicals associated with titanium,[11] and (3) to $\cdot$OH radicals and $\cdot$OH radicals complexed with Ti^{4+} ions.[13]

When, in a similar manner, H_2O_2 and Ce^{4+}, Fe^{2+}, or Fe^{3+} ions were mixed in an esr cavity, no esr spectra with narrow line widths were observed, although the formation of $\cdot$OH and $\cdot$OOH radicals should occur. However, when Ti^{4+} ions were added to the Ce^{4+}–H_2O_2, Fe^{2+}–H_2O_2, and Fe^{3+}–H_2O_2 systems, esr spectra similar to that generated by the Ti^{3+}–H_2O_2 system[3] were observed.[4,6] The intensity of the signal was dependent on and proportional to the concentration of Ti^{4+} ions added. This dependence indicated that there was a greater concentration of free radicals formed in the systems than was being detected by esr spectroscopy. If Ti^{4+} ions were not added to the systems, esr spectra with line widths of about 1 G were not observed for these systems.[6] Oxyvanadium (V) ions also interacted with free radicals, formed in these systems, to generate esr spectra.[5]

We have observed that when transition metal ions, such as ZrO^{2+}, Hf^{4+}, Th^{4+}, and UO_2^{2+} ions, were added to these oxidation–reduction systems, esr spectra, similar to those generated when Ti^{4+} ions were added to these systems, were recorded.[4,6] The *g* values and line widths for the esr spectra generated in oxidation–reduction systems containing certain transition metal ions are shown in Table I. With Hf^{4+} ions, changing the experimental conditions did not alter the relative intensities of the two absorption bands which probably indicated that some hyperfine interaction split the line. The addition of $Ce_2(SO_4)_3$, $La(NO_3)_3$, H_2MoO_4, $(NH_4)_2MoO_4$, $NbCl_5$, $ScCl_3$, $TaCl_5$, H_2WO_4, or YCl_3 to these oxidation–reduction systems did not result in the formation of any complexes with the free radical species in these systems which generated esr spectra.

TABLE I

LINE WIDTHS AND *g* VALUES OF THE HYPERFINE COMPONENTS OF THE ESR SPECTRA GENERATED BY OXIDATION–REDUCTION SYSTEMS CONTAINING TRANSITION METAL IONS AT 22°

Metal ion	*g* value	Line width, G	Metal ion	*g* value	Line width, G
Ti^{4+}	2.0129[a]	0.95	Hf^{4+}	2.0141[b]	1.20
Ti^{4+}	2.0115[b]	0.75	Th^{4+}	2.0177	1.25
ZrO^{2+}	2.0141	2.10	UO_2^{2+}	2.0217	1.50
Hf^{4+}	2.0154[a]	1.30			

[a] Low field. [b] High field.

From these data, it would appear that some transition metal ions in their highest stable oxidation state form complexes with the free-radical species in oxidation–reduction systems to generate characteristic esr spectra. The Sc group of metals do not form stable peroxy compounds, so that any complexes formed by these metals with the free radical species in the

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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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