photooxidation. We are currently exploring this possibility by use of cation-exchange techniques.

Photooxidation of Ru(II) necessitates the corresponding reduction of some solution species. Sigwart and Spence[1] suggest the reduction of coordinated N_2 in the photolysis of Ru(II)–N_2 complexes since mass spectrometer experiments did not reveal H_2 as a reaction product. However, in photolysis of argon-deaerated $Ru(NH_3)_6{}^{2+}$ and $Ru(NH_3)_5H_2O^{2+}$ solutions, H_3O^+ or H_2O appears to be the most likely oxidant. We have demonstrated in nonquantitative mass spectrometer experiments that the full-beam photolysis of $Ru(NH_3)_5$py^{2+} ($\sim 4 \times 10^{-3}$ M, $BF_4{}^-$ salt) does produce H_2 in easily detectible quantities. Whether the formation of H_2 is a minor or major pathway in the photolysis of this ion and of the other Ru(II) ammines shall be elucidated by more quantitative experiments which are being initiated. Despite the care taken in deaerating the solution, we have not excluded the possibility of trace quantities of O_2 also acting as the electron acceptor. Nevertheless, the reproducibility of the photooxidation yields and the stability in the dark of $Ru(NH_3)_5H_2O^{2+}$ solutions (which are sensitive to O_2) argue against this suggestion.

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Difluorophosphoryl-μ-oxo-difluorophosphine.
A Novel Mixed Valence Phosphorus Oxyfluoride

Sir:

The recent mention of compounds containing phosphorus in two valence states[1] prompts us to report our work on the preparation of $F_2POP(O)F_2$. We have prepared the compound in 40% yield by the photolysis of $P(O)F_2Br$ in the presence of mercury at 23°.
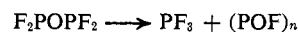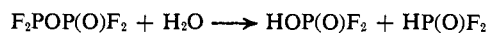
$$2P(O)F_2Br + \text{excess Hg} \xrightarrow{2537\,\text{Å}} F_2POP(O)F_2 + Hg_2Br_2$$
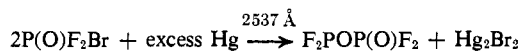
Other products formed include POF_3, F_2POPF_2, $P_2O_3F_4$, PF_3, and unidentified colored solids. Purification of $F_2POP(O)F_2$ was accomplished by fractionation through traps of -78 and $-195°$. The product and a small amount of $P_2O_3F_4$ were retained in the $-78°$ trap.

Difluorophosphoryl-μ-oxo-difluorophosphine is a colorless liquid [mp $-31°$, bp 48°, vapor density molecular weight 174 (calcd for $P_2O_2F_4$, 170.0)] which decomposes slowly at 23°. The ^{19}F nmr, infrared, and chemical reactivity are all consistent with the presence

(1) R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, Chem. Commun., 434 (1969).

of both trivalent and pentavalent phosphorus atoms. The ^{19}F nmr spectrum obtained in 25% $CFCl_3$ at 34.5° showed two doublets of equal area centered at φ 38.3 (F_2PO) and 81.2 ($OP(O)F_2$) with $J_{PF} = 1412$ and 1033 Hz, respectively.[2,3] The resonance attributed to $OP(O)F_2$ was slightly broadened at 34.5°. On cooling to $-26°$ (at lower temperatures the sample froze), a symmetrical complex multiplet of the type A_2B_2XX' was formed. The F_2PO resonance, however, remained sharp at this temperature. The infrared spectrum of $F_2POP(O)F_2$ contained absorptions at (cm^{-1}): 1385 (s), $P{=}O$; 1024 (vs), P–O–P; 975 (s), P–F; 910 (w); 868 (s), P–F; 721 (m); 510 (m); 445 (w). The assignments are based on comparison with F_2POPF_2[4] and $F_2P(O)OP(O)F_2$.[5] Further proof of the unsymmetrical structure of $F_2POP(O)F_2$ was obtained by reaction with HCl. Stoichiometric amounts reacted nearly quantitatively at 23° forming $HOP(O)F_2$ and PF_2Cl.

The decomposition of $F_2POP(O)F_2$ appeared to be catalyzed by impurities, and considerable decomposition was often observed in the vacuum system. However, a 2-mmole sample was kept for 2 weeks in a sealed 100-ml Pyrex bulb without complete decomposition. The compound was extremely sensitive to traces of water and some $HOP(O)F_2$ was almost always observed along with PF_3 and F_2POPF_2. The effect of impurities and exact stoichiometry are not yet known, but our results to date are consistent with the following equations and previously reported instability of F_2POPF_2[4] and $HP(O)F_2$.[6,7]

$$2F_2POP(O)F_2 \longrightarrow F_2POPF_2 + F_2P(O)OP(O)F_2$$

$$F_2POP(O)F_2 + H_2O \longrightarrow HOP(O)F_2 + HP(O)F_2$$

$$HP(O)F_2 + F_2POP(O)F_2 \longrightarrow F_2POPF_2 + HOP(O)F_2$$

$$F_2POPF_2 \longrightarrow PF_3 + (POF)_n$$

Further studies of the decomposition and other chemical reactions of $F_2POP(O)F_2$ are in progress along with a detailed analysis of the temperature-dependent nmr.

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A Molecular Orbital Correlation of the Rates of Formation of Arylmethyl Radicals

Sir:

In the past decade attempts to correlate the rates of formation of arylmethyl carbonium ions and carban-