

case, the τ 8.12 (8.15) peak was absent, and the peak at τ 8.46 sharpened to a singlet. After separate treatment of each labeled ketone with acid as above, the recovered ketone showed return of 1.5 H at τ 8.12 (8.15) and a decrease in the intensity of the τ 8.78 peak to 1.5 H.^{11,12}

These experiments establish that equilibrations of the type $1a \rightleftharpoons 1b \rightleftharpoons 1b' \rightleftharpoons 1a'$ occur without interchange in the positions of substituents at C_6 ; the endo group remains endo, and the exo group remains exo. The result can be rationalized readily in terms of the Woodward-Hoffmann rules for sigmatropic rearrangements;¹³ inversion occurs at C_6 as the bond to C_5 is displaced by one to C_2 , etc. The chemical evidence presented here is consistent with the conclusion⁷ based on nmr evidence.^{14,15}

(11) Control experiments showed that vpc purification was without effect on label distribution.

(12) With 6, integration of the τ 8.78 peak was unambiguous and gave the result described. With 7 the τ 8.78 peak overlapped those of the propyl methylenes (Table I). The entire peak was integrated and showed a decrease from 7.0 to 5.5 H; we assume the deuterium entered the C_5 methyl.

(13) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(14) We are indebted to the National Science Foundation for financial support of this research.

(15) After this paper was submitted, two related papers appeared in which similar stereochemical conclusions were reached. The reactions involved a single migration of C_6 , under conditions which are probably not equilibrating. See H. E. Zimmerman and D. S. Crumrine, *J. Am. Chem. Soc.*, **90**, 5612 (1968); T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968).

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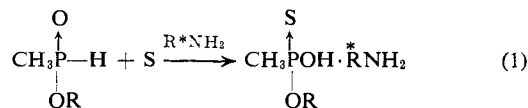
Received October 12, 1968

Evidence of Phosphino Radical from Alkyl Alkylphosphinates

Sir:

The addition of elemental sulfur to trivalent phosphorus compounds has been studied previously and has been considered to proceed *via* an ionic mechanism.¹ We wish to report a sulfur addition to pentavalent phosphorus which appears to proceed by a predominantly radical mechanism.

During the investigation of sulfur addition to alkyl methylphosphinates in the presence of an optically active base, *d*- or *l*- α -methylbenzylamine (eq 1), the

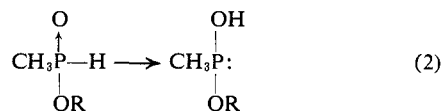


racemic acid obtained and the facile manner under which this reaction took place could not be readily explained by a simple prototropy to an "enol" form² as shown in eq 2.

Evidence of a radical mechanism was first noted by the inhibition of the above sulfur addition when 1

(1) P. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956); P. Bartlett, E. Cox, and R. Davis, *ibid.*, **83**, 103 (1961).

(2) A. Kirby and S. Warren, "The Organic Chemistry of Phosphorus," Elsevier Publishing New York, N. Y., 1967, pp 21-23.



equiv of hydroquinone was added. In the absence of hydroquinone the above reaction was rapid and highly exothermic. In the presence of hydroquinone the reaction was essentially inhibited.

The presence of radicals in mixtures of certain amines with elemental sulfur has been studied previously by Hodgson, *et al.*,³ and Poziomek⁴ using esr technique. They believe the radical present to be the result of homolytic scission of N,N' -polythiobisamine with localization of the odd electron around the terminal sulfur atom with $g = 2.030$.

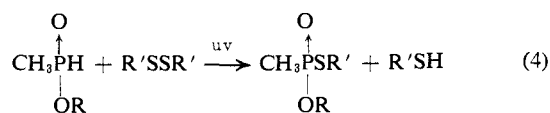
When a mixture of excess α -methylbenzylamine and elemental sulfur in a quartz tube was placed in a Varian 4500 esr instrument, no evidence of radicals was found. One drop of alkyl methylphosphinate was added to this mixture, resulting in a deep red coloration, and radicals were detected with approximate concentration of 5×10^{-4} spin/mol and a g value of 2.0289.

It is clear from the behavior of all possible combinations of the reagents in the esr that it is necessary to have all three components, phosphorus acid, amine, and elemental sulfur, present to produce the stable free radicals.

In order to obtain additional support for the radical mechanism of this reaction, advantage was taken of the alkyl and aryl disulfide radical reaction with trialkyl phosphites induced by ultraviolet light, as studied by Walling, *et al.*⁵ (eq 3).



When a neat sample of alkyl methylphosphinate and phenyl disulfide was exposed to ultraviolet light and distillation, a 63% yield of *S*-phenyl isopropyl methylphosphonothiolate was obtained with 45% of phenyl mercaptan (eq 4). A 0.2 *M* solution of this reaction



mixture in spectral grade benzene was studied under the influence of uv radiation using a uranyl oxalate actinometer.⁶ A quantum yield of 18.6 was obtained, indicating a relatively short chain length. The yield of phenyl mercaptan after 5 hr with uv light was 27.5%; bp 95-97° (0.10mm) (lit.⁷ 78° (0.010 mm)); ir (film on CsI), no P-H at 4.2-4.4, 6.32 (Ar), 7.7 (CH_3 -P), 8.11 (P-O), 10.1 (P-O-R), 18.6 μ (P-S-Ar) (the ir is consistent with the ir of the corresponding ethoxy compound); nmr (neat), σ 1.27 (m, 3, $J = 6$ Hz, CCH_3), 1.37 (m, 3, $J = 6$ Hz, CCH_3), 1.63 (d, 3, $J = 16$ Hz,

(3) W. Hodgson, S. Buckler, and E. Peters, *J. Amer. Chem. Soc.*, **85**, 543 (1963).

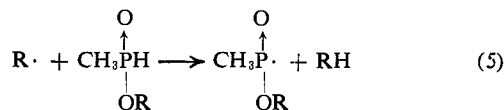
(4) E. Poziomek, *Chemist-Analyst*, **55**, 78 (1966).

(5) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957); **81**, 1243 (1959).

(6) A. Weissenberger, "Techniques of Organic Chemistry," Vol. II, Interscience Publishing Co., New York, N. Y., 1948, p 105.

(7) G. Schrader, Farbenfabriken Bayer AG., U. S. Patent 3,032,580 (May 1, 1962).

CH_3P), 4.93 (m, 1, $J = 6$ Hz, CH), 7.53 (m, 5, Ar). *Anal.* Calcd for $\text{C}_{10}\text{H}_{15}\text{PO}_2\text{S}$: C, 52.16; H, 6.57; P, 13.45; O, 13.90; S, 13.93. Found: C, 52.0; H, 6.5; P, 13.4; S, 15.4. This experiment would lead to the conclusion that in the presence of a source of radicals, a phosphino radical with seven electrons in the valence shell of the phosphorus atom is formed by the abstraction of a hydrogen atom from phosphinate (eq 5).



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Received September 23, 1968

Intraconfigurational Spin-Forbidden Transitions in Chromium(III), Manganese(II), and Nickel(II) Complexes in Aqueous Glass Solutions at 77°K¹

Sir:

The spin-forbidden, Laporte-forbidden intraconfigurational transitions of transition metal ions in complexes constitute the weakest light absorption processes in such ions. Such weak bands are usually obscured by stronger and more diffuse absorption bands of the ion. In a few cases they have been observed as narrow shoulders on broader bands, or occasionally have been studied in low-temperature crystal spectra as very sharp weak bands.

We have found that 77°K aqueous glasses are suitable as a medium for a spectral resolution of these transitions. Inorganic salts in water afforded a very suitable medium for the formation of aqueous glasses; e.g., $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}/\text{H}_2\text{O}$ in weight ratio 0.9/1 constitutes one of our most useful solutions. Solubility of metal ion complexes is favored in these over that in traditional organic solvent glass solutions, as is the possibility of using perdeuterated solvent. In a few cases we utilized ethylene glycol/water in a 1/2 volume ratio.

We have studied the low-temperature (77°K) aqueous glass solution absorption spectra of some first series transition metal ions in a variety of ligand environments. However, some intraconfigurational spin-forbidden transitions should be nearly independent of ligand field,² and in most cases very narrow bands have been observed and found to occur at wavelengths only slightly affected by the ligand.

Cr(III) (d^3) in an octahedral field has a ${}^4\text{A}_{2g}$ (t_{2g}^3) ground state, with intraconfigurational transitions to ${}^2\text{E}_g$, ${}^2\text{T}_{1g}$, and ${}^2\text{T}_{2g}$ states. In the 15,000- cm^{-1} region in room-temperature aqueous solutions of Cr(III) complexes, some very weak poorly resolved peaks are observed, e.g., in $\text{Cr}(\text{en})_3^{3+}$ (en = ethylenediamine). However, 77°K absorption and emission studies³ of

(1) This work was supported by a contract between the Division of Biology and Medicine, U. S. Atomic Energy Commission and the Florida State University.

(2) Cf. L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," John Wiley & Sons, Inc., New York, N. Y., 1961.

(3) G. E. Porter, and H. L. Schäfer, *Z. Physik. Chem.* (Frankfurt), 40, 280 (1964).

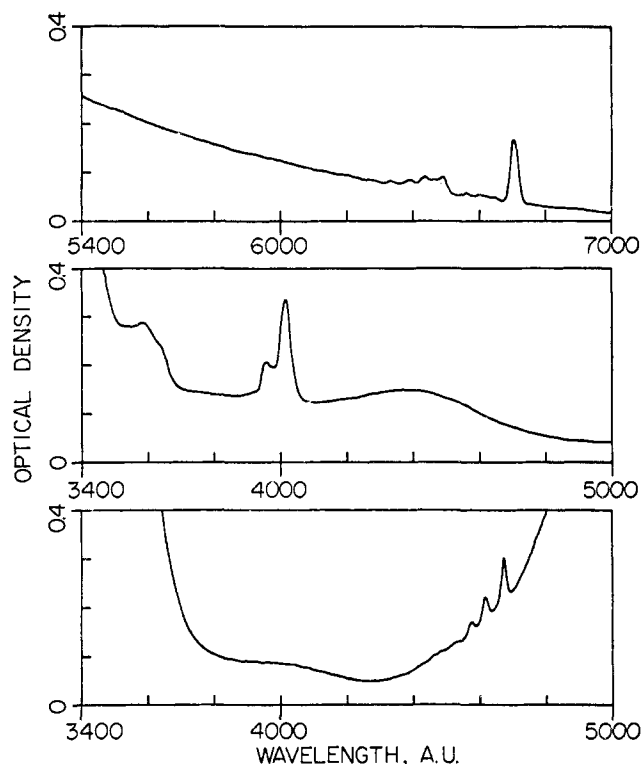


Figure 1. Intraconfigurational spin-forbidden transitions in Cr(III), Mn(II), and Ni(II) complexes in aqueous glass solutions at 77°K: (top) $\text{Cr}(\text{en})_3^{3+}$ in $\text{MgCl}_2\text{-H}_2\text{O}$ glass; (middle) $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ in ethylene glycol- H_2O glass; (bottom) $\text{Ni}(\text{en})_3^{2+}$ in $\text{MgCl}_2\text{-H}_2\text{O}$ glass (Cary 14 spectrometer).

this complex have yielded a very sharp though weak band at this position, assigned as the ${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$ transition, accompanied by considerable vibrational structure (partially resolved). Our studies of $\text{Cr}(\text{en})_3^{3+}$ in $\text{MgCl}_2\text{-H}_2\text{O}$ glass shown in Figure 1 (top) essentially duplicate these results, with the principal peak at 14,907 cm^{-1} identified as the ${}^4\text{A}_{2g} \rightarrow {}^2\text{E}_g$ intraconfigurational electronic transition. The Cr(III) case is the easiest to study since the intraconfigurational transition is in a long-wavelength region clear of other bands. In $\text{Cr}(\text{ox})_3^{3-}$ in $\text{MgCl}_2\text{-water}$ glass at 77°K transitions from ${}^4\text{A}_{2g}$ to ${}^2\text{E}_g$ (14,357 cm^{-1}), ${}^2\text{T}_{1g}$ (15,082 cm^{-1}), and ${}^2\text{T}_{2g}$ (20,512 cm^{-1}) states are observed as resolved peaks.

Mn(II) (d^5) in an octahedral environment has a ${}^6\text{A}_{1g}$ ($t_{2g}^3e_g^2$) ground state, with low-lying intraconfigurational transitions to ${}^4\text{A}_{1g}$ and ${}^4\text{E}_g$ states. These transitions have also been observed previously,⁴⁻⁶ with the ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ transition appearing as a scarcely resolved shoulder in the room-temperature spectra (but as well-resolved peaks in a 20°K MnF_2 crystal⁵). Our spectrum of $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ in ethylene glycol-water glass at 77°K (Figure 1, center) shows two clearly resolved peaks, the ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ absorption appearing at 24,876 cm^{-1} and the ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ absorption at 25,242 cm^{-1} . Also there appears a poorly resolved absorption peak at 27,861 cm^{-1} (ascribed⁵ to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$) with a shoulder at 27,450 cm^{-1} .

Ni(II) (d^8) in an octahedral environment has a ${}^3\text{A}_{2g}$

(4) C. K. Jørgensen, *Acta Chem. Scand.*, 8, 1505 (1954).

(5) J. W. Stout, *J. Chem. Phys.*, 31, 709 (1959).

(6) L. J. Heidt, G. F. Koster, and A. M. Johnson, *J. Am. Chem. Soc.*, 80, 6471 (1958).