Tetrakis[tri(2-ethoxyhexyl) phosphite]nickel(0), white powder, m.p. 112–115°; 35% yield. *Anal.* Calcd. for $C_{96}H_{204}O_{24}P_4Ni$: Ni, 3.06. Found: Ni, 3.18.

Tetrakis[tri*p*(-tolyl) phosphite]nickel(0), white powder, m.p. 98–100°; 23% yield. *Anal.* Calcd. for $C_{84}H_{84}O_{12}P_4Ni$: Ni, 4.00. Found: Ni, 4.18.

Tetrakis[tri(2-ethylhexyl) phosphite]nickel(0), white powder, m.p. 112–115°; 48% yield. *Anal.* Calcd. for $C_{96}H_{204}O_{12}P_4Ni$: Ni, 3.4. Found: Ni, 3.3.

Acknowledgment.—We wish to thank Mr. C. D. Storrs for his help in conjunction with some of the experimental work.

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Photochemistry of Aqueous Octacyanomolybdate(IV) Ion, $Mo(CN)_8^{-4}$

BY ARTHUR W. ADAMSON AND JAYARAMA R. PERUMAREDDI[1]

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We report here the results of some investigations on the photolytic chemistry of aqueous $K_4Mo(CN)_8$ which seem to clarify some aspects of the rather complex behavior that is encountered. Earlier work in this laboratory[2] showed that exchange with $C^{14}N^-$, negligible in the dark, was strongly photocatalyzed. The quantum yield for the exchange was at least unity.[3] A later study[4] showed that irradiation produced free cyanide ion with a quantum yield at 370 mμ also of about unity. Low intensity irradiation eventually converted the yellow initial solution to one of a blue product, B, while tenfold higher intensities, of the order of 6 × 10^{-5} einstein/min. cm.^{2}, produced a transient red species, R. Subsequently Jakob and co-workers[5] have published a suggestion that R is the decacoordinated species $Mo(CN)_8(H_2O)_2^{-4}$. While our own studies were incomplete, they were extensive, and suggest a quite different formulation.

The preparation of $K_4Mo(CN)_8$ was as previously described.[2] The equipment and procedures for the photochemical work were also essentially the same as reported earlier.[4] The spectral changes that occur on irradiation of aqueous $Mo(CN)_8^{-4}$ ion using low light intensities are shown in Figure 1. Gaussian analysis[6] of the absorption spectrum of these solutions shows peaks at 510, 431, 368, 308, 267, and 240 mμ, of which the first two appear in Figure 1, and tentative assignments of these transitions have been made. Note that we find the third band at 368 mμ rather than at 376 mμ as reported by Jakob, *et al.*[5] The absorption spectrum of the blue product shows, in addition to the weak band at 615 mμ displayed in Figure 1, shoulders at 305 and 270 mμ, and a very high intensity peak at 223 mμ.

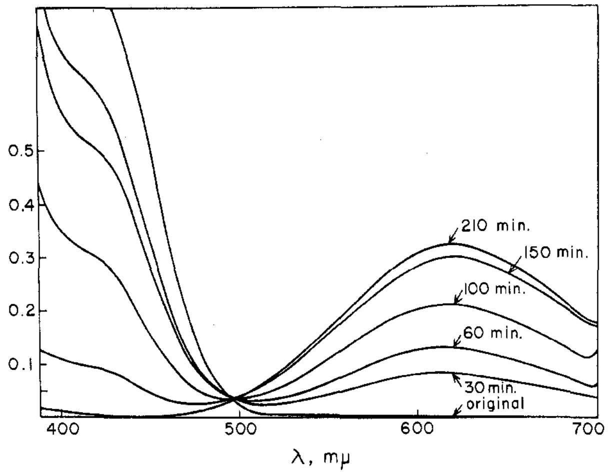

Figure 1.—Optical density for 1-cm. light path; solutions allowed to stand until red form had disappeared.

The terminal blue product, B, was isolated by fractional precipitation with ethanol and analyzed. *Anal.* Calcd. for $K_3Mo(CN)_4(OH)_3(H_2O)$[7]: C, 12.4; H, 1.3; K, 30.3; Mo, 24.8; N, 14.5, O, 16.6. Found: C, 11.5; H, 0.9; K, 29.4; Mo, 26.2; N, 14.7; O (by difference), 17.3. We thus disagree with Jakob, *et al.*,[5] who proposed $K_2Mo(CN)_4(OH)_2$. Not only are the analyses different (their formulation gives C, 15.4; H, 0.64; K, 25.0; Mo, 30.8; N, 17.9), but their species would presumably be octahedral in geometry and for a d^2 system, paramagnetism should be observed. We found B to be diamagnetic. Also, the intensity of the 610 mμ band (ϵ 35 l. mole^{-2} cm.$^{-1}$) indicates a spin-allowed transition, yet for an octahedral complex the first spin-allowed process should occur at a much higher energy. An illustration would be the case of trivalent vanadium.[6] We are agreed, however, that the terminal blue product has four cyanides per molybdenum; it is possible that conditions of isolation and drying, if sufficiently extreme, could lead to loss of KOH and water.

The quantum yield for production of B was determined as follows, for light of 363 mμ (±5 mμ window width of the interference filter). At this wave length B absorbs negligibly, but since the solution was optically dense with respect to $Mo(CN)_8^{-4}$, it was necessary to allow for the varying degree of absorption of incident light during the course of the photolysis. If the absorption coefficient, a, be defined as $I/I_0 = \exp(-aC)$, then, for a first-order photolysis reaction

$$a(C_0 - C) - \ln\left[\frac{1 - e^{-aC}}{1 - e^{-aC_0}}\right] = (\varphi I_0 a/V)t = k't \quad (1)$$

where φ is the quantum yield, V, the volume of solution,

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[1] This report is based on portions of the junior author's Ph.D. dissertation.

[2] A. W. Adamson, J. P. Welker, and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950).

[3] J. P. Welker, Ph.D. Dissertation, University of Southern California, 1950.

[4] A. W. Adamson and A. H. Sporer, *J. Am. Chem. Soc.*, **80**, 3865 (1958).

[5] W. Jakob, A. Sametus, and Z. Stasicka, Proceedings, 7th International Conference on Coordination Chemistry, Stockholm, June 1962; W. Jakob and Z. Jakob, *Roczniki Chem.*, **36**, 593 (1962).

[6] J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Am. Chem. Soc.*, **85**, 249 (1963).

[7] N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford Press, 1950, p. 1056.

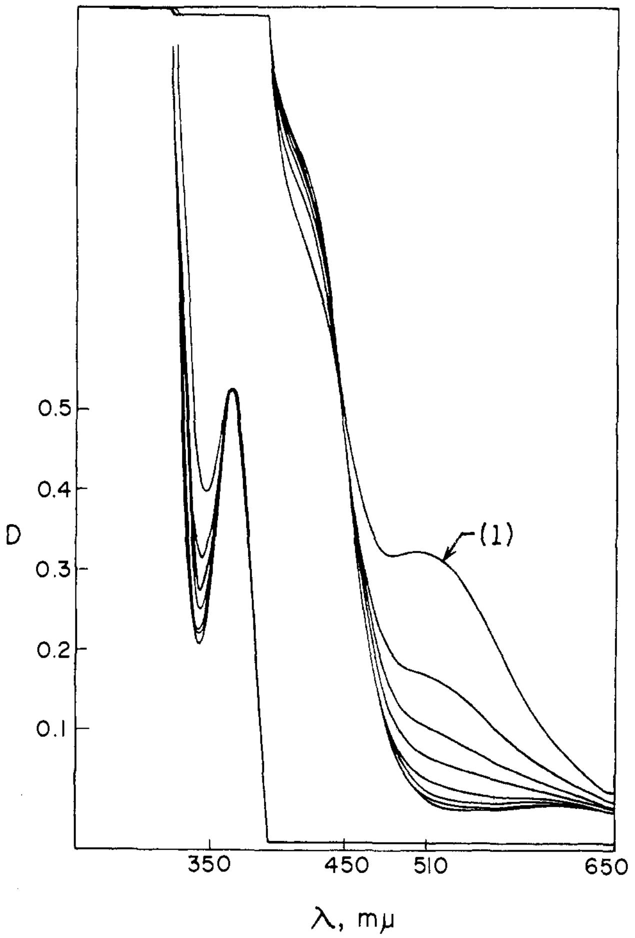

Figure 2.—Photolysis at 363 mμ of 0.01 *M* $Mo(CN)_8^{-4}$. The successive curves show the fading of the red form (510 mμ peak) on standing; the curve labeled 1 being that obtained (1-cm. light path) immediately after irradiation.

and I_0, the incident light intensity in einsteins per unit time. At I_0 values of about 6×10^{-6} einstein/min., the stationary state concentration of R is small, and eq. 1 was obeyed very well, with $\varphi = 0.14$ at 25°.

The spectrum of the transient species R is displayed in Figure 2, which also illustrates the few-minute order of magnitude of the half-life for its disappearance. If the optical density at 510 mμ, a nearly direct measure of R, is measured immediately after irradiation, its value is found to go through a maximum with increasing time of irradiation. Detailed analysis of such data is complicated by the difficulty of allowing for inner filter effects and by lack of knowledge of the photosensitivity of R itself, but the results fit qualitatively the mathematics of sequential first-order reactions. The times for reaching a maximum in R thus decreased with increasing light intensity; at an incident light intensity of 6.9×10^{-5} einstein/min. on a 1-cm. path length of 0.01 *M* $K_4Mo(CN)_8$, t_{max} was 2.5 min., corresponding to a photolytic half-life for $Mo(CN)_8^{-4}$ of 1.4 min.

A number of experiments were then carried out to determine the stoichiometry of the formation of R, and the kinetics of its disappearance; for most of these the above conditions of light intensity and irradiation time were used, so that at the end of the 2.5-min. irradiation of the solution about 70% of the original $Mo(CN)_8^{-4}$ had been photolyzed.

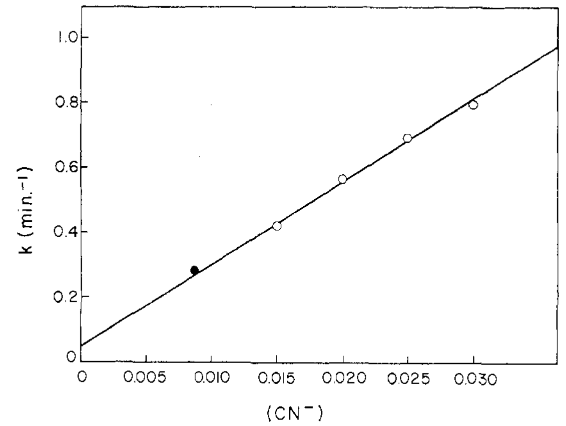

Figure 3.—Dependence of rate constant for the disappearance of R on cyanide concentration. Data for 0.01 *M* $Mo(CN)_8^{-4}$, pH 9.5 and 25°. Indicated concentrations of CN^- are those of KCN added immediately after irradiation, plus that estimated as produced in the photolysis. The run with no added KCN is given by the full circle.

While it was not possible to isolate R in pure form, it was determined that its production was accompanied by release of cyanide ion, and titration of free cyanide by iodine showed that it was present immediately at the end of the irradiation in about 1:1 mole ratio with complex photolyzed, although severe fading of the starch indicator made exact measurements difficult. There was no effect of deaerating the solutions nor of added I^- ion so it appears that the red form is an aquation and not an oxidation–reduction product (*e.g.*, $Mo(CN)_7^{-3}$, whose spectrum is reported to be similar to that of R[8]).

The rate of disappearance of R was then determined as a function of CN^- concentration, in acetate buffer at pH 9.5; as illustrated in Figure 3, the disappearance was first order and directly dependent on CN^-. The first-order specific rate constant, *k*, was given by

$$k\ (\text{sec.}^{-1}) = 8.3 \times 10^{-4} + 0.42(\text{CN}^-) \qquad (2)$$

The intercept at zero CN^- agreed reasonably well with the directly determined value from the iodine titration. In addition, the rate was found to be pH dependent, and for $(CN^-) = 0.007$, the behavior was given by

$$k\ (\text{sec.}^{-1}) = 0.005(\text{H}^+)/((\text{H}^+) + 0.6 \times 10^{-10}) \qquad (3)$$

Since the p*K* of HCN is about 10 for our conditions, it appears that the second-order term in eq. 2 probably involved the species HCN rather than CN^-. An additional, qualitative observation was that the production of blue final product was inhibited in the presence of added cyanide ion, and also at high light intensities and irradiation times such that rapid photolysis of most of the $Mo(CN)_8^{-4}$ occurred.

We therefore conclude that the photolysis of $Mo(CN)_8^{-4}$ proceeds according to a mechanism of the type

$$\text{Mo(CN)}_8^{-4} \xrightarrow{h\nu} \text{R} + \text{CN}^- \qquad (4)$$

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[8] R. C. Young, *J. Am. Chem. Soc.*, **54**, 1402 (1932).

$$\mathrm{R} + \mathrm{HCN} \rightleftharpoons \mathrm{Mo(CN)_8^{-4}} \quad (5)$$

$$\mathrm{R} \longrightarrow \text{final blue product} \quad (6)$$

The reverse of reaction 5 then accounts for the high quantum yield for photoinduced CN^- exchange. Since the aquo cyano complexes are weak acids, it is possible that at pH 9–10 the actual form of R is $Mo(CN)_7(OH)^{-4}$, and also that the observed pH dependence of reaction 5 is partly due to this acid–base equilibrium. We do conclude, however, that the transient red species is not decacoordinated and is probably a heptacyano complex.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF
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Solubility Studies on Substituted Ammonium Salts of Halide Complexes. IV. Tristetramethylammonium Enneachlorodiantimonate(III)[1]

BY G. P. HAIGHT, JR., AND BARBARA YODER ELLIS

Received September 3, 1964

Knowledge concerning halide complexes of antimony(III) has been extremely difficult to obtain because of the ease of hydrolysis, the irreversibility of antimony electrodes, and the fact that the complexes are weak. The ultraviolet absorption spectrum of antimony(III) is invariant from 6 to 12 *M* hydrochloric acid, indicating that a limiting coordination number with chloride ion is reached.[2] However, in more dilute acid the absorbance in the ultraviolet decreases generally without the appearance of new, distinctive bands for lower complexes and without the appearance of any crossing points. A limited polarographic study[3] indicated that the average ligand number was approximately four in solutions varying from 0.5 to 6.0 *M* hydrochloric acid. The present study is an attempt to ascertain the species of Sb(III) present in hydrochloric acid by means of a solubility study on a complex chloride of antimony(III).

Experimental

Preparation of Complex Salts. Tristetramethylammonium Enneachlorodiantimonate(III).—Antimony trichloride was dissolved in 3.0 to 4.0 *M* hydrochloric acid and treated with tetramethylammonium chloride in the same solvent. From 0.2 *M* solutions of the salts at 0° large hexagonal crystals were obtained in about 15% yield. The crystals were washed with 3 *M* hydrochloric acid and air dried in a desiccator over KOH. The salt may also be dried at 100° in air without decomposition. Larger yields may be obtained using more concentrated solutions.

Anal. Calcd. for $((CH_3)_4N)_3Sb_2Cl_9$: C, 18.35; H, 4.63; Sb, 31.00; Cl, 40.7. Found: C, 18.45; H, 4.25; Sb, 31.00; Cl, 40.33.

Tetraphenylarsonium Tetrachloroantimonate(III).—Tetraphenylarsonium ion gave much more insoluble precipitates of composition near that of $(C_6H_5)_4AsSbCl_4$ but the composition varied erratically with treatment and in subsequent solubility studies the saturated solutions never contained the same As:Sb ratio as the solid phase. It was thus necessary to use the tetramethylammonium salt, although its high solubility (0.05 to 0.07 *M*) made maintenance of constant ionic strength problematical, especially at high chloride ion concentration.

Analysis for antimony(III) in solution was made by titration with standard potassium bromate solution using methyl orange indicator. Analysis for chloride was made by potentiometric titration with standard silver nitrate solution. Analysis for carbon and hydrogen was performed by the Clark Microanalytical Laboratory, Urbana, Ill.

For solubility studies, solutions were saturated either by shaking an excess of salt with solvent in 50-ml. flasks in a thermostat at 25.0 ± 0.1° for 24–96 hr. or by using a Brønsted saturator,[4] one pass being sufficient for saturation. The concentration of antimony(III) was determined by titration with bromate. With 4 *M* sulfuric acid as the solvent the Sb:Cl mole ratio in solution was 2:9, indicating that the solid phase did not change composition during the study.

The solvent used was H_2SO_4 and HCl with $[H^+]$ maintained at 4.0 *M*. As in previous studies[5] H_2SO_4 is assumed to be a 1:1 electrolyte, and the ionic strength was essentially constant.

Results and Discussion

Analysis of data is based on the assumption of reactions 1 and 2 contributing to the solubility of the salt. A test was made for the presence of polynuclear complexes by substituting up to 0.15 *M* $(CH_3)_4NCl$ for HCl at 4.0 *M* Cl^-. The product $[(CH_3)_4N^+]^{3/2}\cdot[Sb(III)]$ was $7.24 \pm 0.30 \times 10^{-3}$ over a twofold variation in solubility (Table I). Its constancy indicates no significant concentration of polynuclear species.

$$[(CH_3)_4N]_3Sb_2Cl_9 \rightleftharpoons 3(CH_3)_4N^+ + 2SbCl_4^- + Cl^- \quad (1)$$

$$SbCl_4^- + (n-4)Cl \rightleftharpoons SbCl_n^{3-n} \quad (2)$$

TABLE I

TEST FOR POLYNUCLEAR COMPLEXES

$[HCl] + [(CH_3)_4NCl] = 4.0$

$[(CH_3)_4NCl]_0$, *M*	[Sb(III)], *M*	$[(CH_3)_4N^+]$, *M*	$10^3[Sb(III)]\cdot[(CH_3)_4N^+]^{3/2}$
0	0.1105	0.166	7.6
0.025	0.099	0.173	7.1
0.050	0.090	0.185	7.2
0.100	0.0725	0.209	6.9
0.150	0.0625	0.244	7.5

In the absence of polynuclear complexes the solubility data may be analyzed using the equations

$$S^{5/2}[Cl^-]^{1/2} = \frac{K_S^{1/2}\sum_{\Delta}^{n}\beta_n[Cl^-]^{n-4}}{10.4\beta_4} \quad (3)$$

$$[Cl^-] = [Cl^-]_0/(1 + 5dS/d[Cl^-]) \quad (4)$$

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(1) Presented in part at the 7th International Conference on Coordination Chemistry in Uppsala, Sweden, June 1962.

(2) N. A. Bonner and W. Goishi, *J. Am. Chem. Soc.*, **83**, 85 (1961).

(3) G. P. Haight, Jr., *ibid.*, **75**, 3843 (1953).

(4) F. J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961, p. 190.

(5) G. P. Haight, Jr., C. Springer, and O. J. Heilman, *Inorg. Chem.*, **3**, 195 (1964).