Details of the wave functions and monopole charges for benzene, phenol, imidazole, and indole are given in ref 62.

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Communications to the Editor

Photochemistry of Cobalt(III) Complexes. I. A Complication Due to Thermal Reduction of $Co(NH_3)_5OCOCH_3^{2+}$ by Ketyl Radicals

Sir:

We wish to report our results on the study of the photolysis of $Co(NH_3)_5OCOCH_3^{2+}$ (**1**) in aqueous alcoholic solutions. The photoreduction of Co(III) salts is one of the most intensively studied areas of inorganic photochemistry,[1] yet the nature of the excited state(s) involved has not been resolved. It is clear that there are radical products of the photolysis, and both radical-pair[2] and "excited-state"[1d,3] mechanisms have been invoked. The situation is further complicated by the fact that even proponents of the excited-state mechanism are forced to discuss the details of the reaction in terms of radicals and charge-transfer states.[4,5]

A recent communication[5] describes the photolysis of **1** in aqueous alcohol and interprets the results by invoking a complicated mechanism involving two excited states. The second excited state was postulated to explain the increase of $\varphi_{Co^{2+}}$ with [*i*-PrOH], and the authors claimed to have demonstrated a solvent effect on the primary quantum yield.

Our conclusions, based on data qualitatively in agreement with those presented by Kantrowitz, *et al.*,[5] are as follows. (1) The increase in $\varphi_{Co^{2+}}$ is due to a secondary *thermal* reduction reaction of **1**. (2) [*i*-PrOH] has no effect on the *primary* quantum yield. (3) There is no need to postulate a second excited state.

The compound $[Co(NH_3)_5OCOCH_3](ClO_4)_2$ was prepared and purified by previously described procedures.[6] The absorption agreed with that in the literature,[7] and a satisfactory chemical analysis was obtained.

The photolyses were carried out with a Bausch and Lomb high-intensity SP200 mercury arc and high-intensity monochromator by using conventional techniques. Irradiations were performed at 250 ± 10 nm. Quantum yields were determined using ferrioxalate actinometry and modifications of previously described methods for determination of Co(II)[8] and acetone.[9] Degassing was accomplished by three freeze–thaw cycles. Our results are presented in Table I.

Table I. Quantum Yields of Products[a]

System	Nondegassed		Degassed	
	$\varphi_{Co^{2+}}$[b]	$\varphi_{acetone}$[c]	$\varphi_{Co^{2+}}$[b]	$\varphi_{acetone}$[c]
H_2O	0.29		0.29	
5 *M* MeOH–H_2O	0.30		0.31	
5 *M* *i*-PrOH–H_2O	0.29	0.3	0.55	0.3

[a] $[Co(NH_3)_5O_2CCH_3]^{2+} = 10^{-2}$ *M*; $HClO_4 = 10^{-2}$ *M*; temperature = 23°; $I_a \simeq 10^{-7}$ einstein/min. Values for $\varphi_{Co^{2+}}$ listed are the averages of two or more determinations and agree within ±5%. Kantrowitz,[5] *et al.*, obtained $\varphi_{Co^{2+}}(H_2O) = 0.19$; $\varphi_{Co^{2+}}$(5 *M* MeOH) = 0.21; $\varphi_{Co^{2+}}$(5*M* *i*-PrOH) = 0.40. These values are substantially different from ours; however, we believe that both sets of values are internally consistent. [b] Zero-order kinetics were observed for 0.03–30% photodecomposition of the complex. [c] Quantum yield determinations at $I_a \simeq 10^{-5}$ einstein/min.

We find that $\varphi_{Co^{2+}}$ is 0.29 in both pure water and 5 *M* aqueous methanol. Degassing these systems has little effect. In 5 *M* aqueous isopropyl alcohol, undegassed, $\varphi_{Co^{2+}}$ is also 0.29. However, degassing this system causes a twofold increase in $\varphi_{Co^{2+}}$ with the concurrent formation of acetone; $\varphi_{acetone} = {}^1/_2\varphi_{Co^{2+}}$ (degassed) = $\varphi_{Co^{2+}}$(nondegassed).

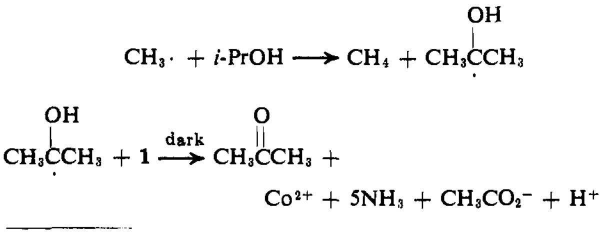
These data can readily be accommodated by the following scheme.

$$\mathbf{1} \xrightarrow[250\ \text{nm}]{h\nu} \mathbf{1}^* \qquad (1)$$

$$\mathbf{1}^* \longrightarrow Co(NH_3)_5^{2+} + CH_3CO_2\cdot \qquad (2)$$

$$CH_3CO_2\cdot \longrightarrow CH_3\cdot + CO_2 \qquad (3)$$

$$2CH_3\cdot \longrightarrow CH_3CH_3 \qquad (4)$$



$$CH_3\cdot + i\text{-PrOH} \longrightarrow CH_4 + CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\cdot}{C}}CH_3 \qquad (5)$$

$$CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\cdot}{C}}CH_3 + \mathbf{1} \xrightarrow{\text{dark}} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + Co^{2+} + 5NH_3 + CH_3CO_2^- + H^+ \qquad (6)$$

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(1) Recent reviews of this subject include (a) A. Adamson, W. Waltz, E. Zinato, D. Watts, P. Fleischauer, and R. Lindholm, *Chem. Rev.*, **68**, 541 (1968); (b) D. Valentine, Jr., *Advan. Photochem.*, **6**, 123 (1968); (c) E. Wehry, *Quart. Rev., Chem. Soc.*, 21, 213 (1967); (d) V. Balzani, L. Moggi, F. Scandola, and V. Corassiti, *Inorg. Chim. Acta Rev.*, **1**, 7 (1967).

(2) A. Adamson, *Discuss. Faraday Soc.*, **29**, 163 (1960).

(3) J. Endicott and M. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965).

(4) G. Caspari, R. Hughes, J. Endicott, and M. Hoffman, *ibid.*, **92**, 6801 (1970).

(5) E. Kantrowitz, J. Endicott, and M. Hoffman, *ibid.*, **92**, 1776 (1970).

(6) L. Jackman, R. Scott, and R. Portman, *Chem. Commun.*, 1339 (1968).

(7) D. Sebera and H. Taube, *J. Amer. Chem. Soc.*, **83**, 1785 (1961).

(8) R. Püschel, E. Lassner, and K. Katzengruber, *Z. Anal. Chem.*, 221, 132 (1966).

(9) (a) S. Berntsson, *Anal. Chem.*, **28**, 1337 (1956); (b) gas chromatography with an ionization detector.

This rationale is similar to those invoked by others to explain the photo and thermal decarboxylation of acids in the presence of Ce(IV)[10] and Pb(IV),[11] and it is consistent with Adamson's radical-pair hypothesis[2] and with the mechanism invoked by Haim and Taube[12] to explain the photolysis of $Co(NH_3)_5I^{2+}$ ion.

Reactions 5 and 6 readily account for the doubling of $\varphi_{Co^{2+}}$ in degassed 5 M isopropyl alcohol. Thus, the primary quantum yield for Co^{2+} production is not changed by the addition of isopropyl alcohol. Ketyl radicals,[13] as well as simple alkyl radicals,[14] are known to be efficient reducing agents for many metal ions. Oxidized ketyl radicals (in reaction 6) would deprotonate to form acetone. The ketyl radical is probably also formed in the nondegassed isopropyl alcohol system, but it is efficiently trapped by dissolved oxygen, thus effectively preventing the doubling of $\varphi_{Co^{2+}}$ according to reaction 6.

Furthermore, we would predict, using our scheme, the constancy in $\varphi_{Co^{2+}}$ and the increase in CH_4/C_2H_6 which were observed by Kantrowitz,[5] *et al.*, as [isopropyl alcohol] was increased. Above 1 M *i*-PrOH, CH_4 was the only hydrocarbon product, with $\varphi_{CH_4} = {}^1/_2\varphi_{Co^{2+}}$(degassed) $= \varphi_{Co^{2+}}$(nondegassed).

Thus, it is unnecessary to postulate two different excited states. The *apparent* quantum yield is changed by solvent, as found by Kantrowitz,[5] *et al.*, but there is no evidence to support their claim that the primary quantum yield is affected. The overall photoreduction is explained by a two-step sequence involving a primary photoreduction and a secondary thermal reduction of the substrate.

However, it should be noted that for complex **1** the product analysis requires the intermediacy of acetoxy radical, and this strongly suggests that **1*** is either a radical pair or a charge-transfer excited state with radical character (which ultimately undergoes facile homolytic cleavage). Therefore, we maintain that until unambiguous evidence to the contrary is obtained, the radical-pair mechanism serves as an adequate model to explain the known behavior of Co(III) complexes.

One should also note that this reaction provides a convenient preparation of ketyl radicals from alcohols in aqueous medium.

Acknowledgment. We wish to thank Dr. David A. Loeliger of Kodak Research Laboratories for many valuable discussions.

(10) (a) R. Sheldon and J. Kochi, *J. Amer. Chem. Soc.*, **90**, 6688 (1968); (b) D. Greatorex and T. Kemp, *Chem. Commun.*, 383 (1969).

(11) (a) J. Kochi, R. Sheldon, and S. Lande, *Tetrahedron*, **25**, 1197 (1969); (b) K. Heusler, H. Labhart, and H. Loeliger, *Tetrahedron Lett.*, 2847 (1965), and papers cited therein.

(12) A. Haim and H. Taube, *J. Amer. Chem. Soc.*, **85**, 499 (1963).

(13) K. Takeda and Y. Iwakura, *Bull. Chem. Soc. Jap.*, **41**, 268 (1968).

(14) J. Kochi, A. Bemis, and C. Jenkins, *J. Amer. Chem. Soc.*, **90**, 4616 (1968), and references cited therein.

Robert D. Lindholm*
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

Thomas K. Hall
Department of Chemistry, Rochester Institute of Technology
Rochester, New York 14623

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Transition Metal Promoted Organic Reactions as Models for Nitrogenase Behavior

Sir:

In both enzymic and nonenzymic reactions of nitrogen (N_2), a central role is ascribed to transition metal species.[1] The principal property of the enzyme nitrogenase, which contains iron and molybdenum, is its remarkable reductive action on not only N_2, but also substitute, organic substrates, including acetylenes, cyanide ion, nitriles, and isonitriles. We report herein the simulation of such enzymic organic reactions by various reducing agent–transition metal combinations *also* recognized for their pronounced nonenzymic N_2-fixing properties, thus supporting the assigned role of transition metals in biological N_2 fixation reactions, permitting comprehension of the chemical behavior described, and helping pave the way for further understanding of the enzymic phenomena.

Past efforts have demonstrated that nitrogenase brings about the reduction of: (1) alkyl cyanides to the corresponding hydrocarbons,[2,3] (2) hydrogen cyanide or cyanide ion to primarily methane and ammonia,[4,5] in addition to some methylamine and traces of ethane and ethylene,[6] and (3) isonitriles to methane, the major hydrocarbon product, and the corresponding amine, accompanied by higher hydrocarbons (*e.g.*, ethane and ethylene in the methylisonitrile or ethylisonitrile case[1a,2,6]), findings that reveal a marked propensity for complete reductive cleavage of triple bonds, as in the N_2 case. In addition, alkynes are converted to alkenes.[2,4,7] In relation to these biological reactions, our studies have involved (Table I) three transition metals, molybdenum, iron, and—as an example of a nonbiological element—titanium,[8] all of which fix nitrogen under mild, abiological conditions. By comparison, methane and various amounts of ethane and ethylene are formed from potassium cyanide through the action of Fe(III)- and Ti(IV)-naphthalenide combinations.[9] In the case of cyclohexylisonitrile, $FeCl_3$–Mg and $TiCl_3$–Mg produced methane, cyclohexane, and trace amounts of ethane, and ethylene, with no detectable amounts of cyclohexylamine, while Mo(acac)$_3$– and Fe(acac)$_3$–naphthalenide promoted formation of cyclohexane alone. The combinations $MoCl_5$–Mg[10] and $FeCl_3$–Mg[9] effected formation of hexene-1 from hexyne-1, although further reduction to hexane was also involved. The laboratory, transition metal

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(1) For pertinent reviews, see (a) R. W. F. Hardy and R. C. Burns, *Annu. Rev. Biochem.*, **37**, 331 (1968), and (b) R. Murray and D. C. Smith, *Coord. Chem. Rev.*, **3**, 429 (1968).

(2) R. W. F. Hardy and E. K. Jackson, *Fed. Proc., Fed. Amer. Soc. Exp. Biol.*, **26**, 725 (1967).

(3) See footnote 12 in ref 1a (p 349).

(4) R. W. F. Hardy, E. Knight, Jr., and E. K. Jackson, *Biochem. Biophys. Acta*, **139**, 69 (1967).

(5) R. W. F. Hardy and E. Knight, Jr., *Biochem. Biophys. Res. Commun.*, **23**, 409 (1966).

(6) M. Kelly, J. R. Postgate, and R. L. Richards, *Biochem. J.*, **102**, 1c (1967).

(7) M. J. Dilworth, *Biochem. Biophys. Acta*, **127**, 285 (1966).

(8) E. E. van Tamelen, *Accounts Chem. Res.*, **3**, 361 (1970).

(9) For reduction of cyanide or alkyne by Fe(II) complex–borohydride or dithionite combinations, see W. E. Newton, J. L. Corbin, P. W. Schneider, and W. A. Bulen, *J. Amer. Chem. Soc.*, **93**, 268 (1971); 5% yields of ammonia from N_2 were realized in these systems.

(10) For conversion of alkynes to alkenes by Mo complexes and borohydride or dithionite, see G. N. Schrauzer and G. Schlesinger, *ibid.*, **92**, 1808 (1970); G. N. Schrauzer and P. A. Doemeny, *ibid.*, **93**, 1608 (1971). Ammonia yields $\leq 0.1\%$ from N_2 (2000 psi) were observed after 5 days reaction at room temperature.