in Chart I rationalizes the information[9] that the triplet excited state[10] of product is not reached.

Acknowledgment. Support of this research by a National Science Foundation Predoctoral Fellowship for J. O. G. and by an Army Research Office (Durham) grant is gratefully acknowledged.

---

[9] The demotion is shown as occurring just subsequent to internal three-ring bond fission with 2* pictured as a discrete species; this is a convenience. Thus 2* may not be an energy minimum, and demotion may occur by crossing or close approach of potential energy surfaces[2] and change in configuration at a slightly earlier or later point in the transformation.

[10] The intervention of the triplet in the phenol-forming reactions is suggested by the formation of the same products in the photosensitized runs as in the direct runs and by analogy to the diphenyl analog[3] where the phenolic product was shown to arise from the triplet and the acidic product from triplet and singlet.

Howard E. Zimmerman, Joan O. Grunewald
Chemistry Department, University of Wisconsin
Madison Wisconsin

Received April 7, 1967

Molecular and Electronic Structure of Pentacyanocobaltate[1]

Sir:

The complex $Co(CN)_5{}^{3-}$ has occasioned a good deal of interest in late years. Its action as a hydrogenation catalyst[2] for certain unsaturated organic molecules and the kinetics of its free-radical type reactions with some organic halides[3,4] have been subjects of recent investigation. Esr and optical spectral studies[5,6] of oxidation products of $Co(CN)_5{}^{3-}$ have also been carried out.

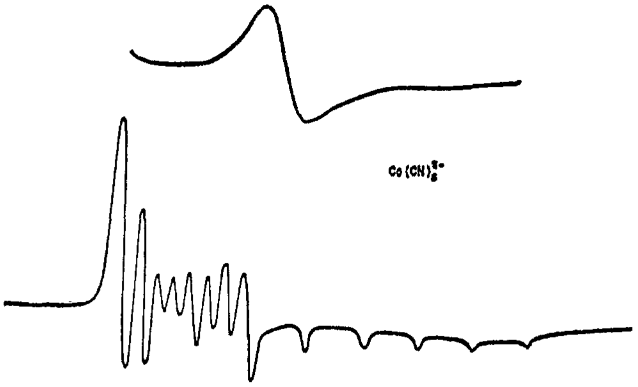


Figure 1. Electron spin resonance spectra for $Co(CN)_5{}^{3-}$ in 2:1 ethylene glycol–water: upper curve, 300°K; lower curve, 77°K in frozen solution. Spectra in pure ethylene glycol are not significantly different.

Up to now, the geometry of $Co(CN)_5{}^{3-}$ in solution has been unknown; supposing it to be five-coordinate, the two most likely idealized spatial arrangements are the trigonal bipyramid (of D_{3h} symmetry) and the square pyramid (of C_{4v} symmetry). (This latter symmetry would also hold if weak axial solvation made the complex six-coordinate.)

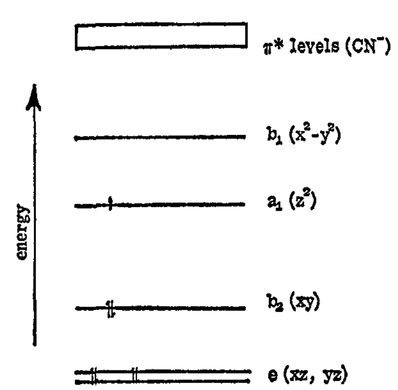


Figure 2. Partial diagram of electronic energy levels and suggested ground state for square-pyramidal $Co(CN)_5{}^{3-}$.

We have measured optical and esr spectra of pentacyanocobaltate(II) under a variety of conditions; here we show how the data from these experiments point to an idealized square-pyramidal ground-state geometry for this system.

Solutions for esr spectra were prepared by dissolving $K_6Co_2(CN)_{10} \cdot 4H_2O$[7] in 2:1 ethylene glycol–water and in pure ethylene glycol. Examination of the optical spectra of these solutions at 300°K and frozen at 77°K reveals the absorption pattern characteristic of the paramagnetic ($S = {}^1/_2$), monomeric $Co(CN)_5{}^{3-}$ species.[8] In particular, the intensity of the band peaking at 10,350 cm^{-1} shows $Co(CN)_5{}^{3-}$ to be the predominant species under the conditions of our experiment at 77°K. Confirmation of the existence of $Co(CN)_5{}^{3-}$ in the frozen solutions was necessary in light of results which indicate that dimerization and oxidation may readily occur under these conditions.[5,6]

Figure 1 shows esr spectra for $Co(CN)_5{}^{3-}$ at 300 and 77°K. At 300°K, a broad resonance lacking hyperfine structure and centered at $g = 2.11 \pm 0.01$ is seen. On freezing the solution at the lower temperature, the pattern observed is a 16-line resonance expected from an axially symmetric ^{59}Co ($I = {}^7/_2$) species, with two of the $g_{||}$ lines hidden under the second and fifth lines of the $g_{\perp}$ pattern. Analysis of this spectrum gives $g_{||} = 1.992 \pm 0.005$, $g_{\perp} = 2.157 \pm 0.005$, and hyperfine tensor components $A = 87 \pm 2$ and $B = 28 \pm 2$ gauss.

The axial symmetry of the g tensor combined with the value of 1.992 for $g_{||}$ strongly suggest a square-pyramidal structure for $Co(CN)_5{}^{3-}$ with the unpaired electron placed in an orbital of d_{z^2} symmetry ($^2A_1$ ground state). This is nicely compatible with the electronic energy levels expected for a square-pyramidal pentacyano complex (Figure 2). The ground state in a d^7 case would be $(e)^4(b_2)^2(a_1)^1 = {}^2A_1$. Furthermore, none of the ground-state possibilities in a trigonal-bipyramidal geometry is consistent with the esr results.[9]

The electronic spectrum of $Co(CN)_5{}^{3-}$ in aqueous solution shows[8] bands at 10,350 cm^{-1} (ϵ 233), 16,200 (7), 23,300 (65), 31,700 (527), 35,700 (4030), 38,100 (980 sh), and 43,300 (6500). The rich pattern of weak-

---

[1] This research was supported by the National Science Foundation.

[2] J. Kwiatek, I. L. Mader, and J. K. Seyler, Advances in Chemistry Series, No. 37, American Chemistry Society Washington, D. C., 1963, p 201.

[3] J. Halpern, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

[4] (a) J. Halpern and S. Nakamura, *ibid.*, **87**, 3002 (1965); (b) J. Halpern and P. J. Maher, **87**, 5361 (1965).

[5] J. H. Bayston, F. D. Looney, and M. E. Winfield, *Australian J. Chem.*, **16**, 557 (1963).

[6] J. H. Bayston, R. N. Beale, N. K. King, and M. E. Winfield, *ibid.*, **16**, 954 (1963).

[7] A. W. Adamson, *J. Am. Chem. Soc.*, **73**, 5710 (1951).

[8] Our electronic spectral measurements are in essential agreement with those reported by N. K. King and M. E. Winfield, *ibid.*, **73**, 3366 (1951).

[9] The ground state $(e'')^4(e')^3 = {}^2E'$ expected for D_{3h} $Co(CN)_5{}^{3-}$ should give $g_{||} \gg 2.0$. The fact that a slight Jahn-Teller distortion would be expected does not affect this conclusion.

and medium-intensity absorptions, especially in the 10,000–25,000-cm^{-1} range, again points to a system of electronic levels appropriate for a square-pyramidal Co(CN)$_5{}^{3-}$. At least two reasonable assignment schemes exist based on the splitting diagram shown in Figure 2.[10] Contrariwise, simple extrapolation of electronic levels from analogous trigonal bipyramidal complexes indicates that an approximately D_{3h} Co(CN)$_5{}^{3-}$ would not exhibit electronic bands between 8000 and 20,000 cm^{-1}.[11] Thus, the combined esr and optical spectral data require a square-pyramidal structure for Co(CN)$_5{}^{3-}$ in solution.

(10) We tentatively suggest the following assignments: 10,350 cm^{-1}, $^2A_1 \rightarrow {}^2B_1$ ($z^2 \rightarrow x^2 - y^2$); 16,200 cm^{-1}, doublet → quartet; 23,300 cm^{-1}, $^2A_1 \rightarrow {}^2B_2$ ($xy \rightarrow z^2$); 31,700 cm^{-1}, $^2A_1 \rightarrow {}^2A_2$ ($xy \rightarrow x^2 - y^2$). The intense bands at 35,700 and 43,300 cm^{-1} probably represent allowed M → π^*(CN$^-$) transitions.

(11) The observed ligand field bands in trigonal bypyramidal Ni-[PPh(OR)$_2$]$_3$(CN)$_2$ complexes (B. B. Chastain, R. Pruett, E. A. Rick, and H. B. Gray, to be published) are at approximately 25,000 and 29,000 cm^{-1}. In addition, there is very little difference in the positions of the lowest ligand-field bands in Ni(CN)$_4{}^{2-}$ and Ni[PPh$_2$(OR)]$_2$(CN)$_2$. Thus, we may expect a trigonal bypyramidal Co(CN)$_5{}^{3-}$ to have an $e'' \rightarrow e'$ band below 8000 cm^{-1} and an $e' \rightarrow a_1'$ band at about 25,000 cm^{-1}.

(12) National Science Foundation Predoctoral Fellow, 1964–1966.

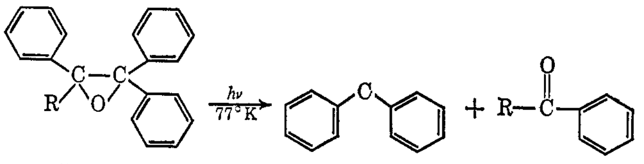
John J. Alexander[12]
Department of Chemistry, Columbia University
New York, New York 10027
Harry B. Gray
Contribution No. 3522
Gates and Crellin Laboratories of Chemistry
California Institute of Technology, Pasadena, California 91109
Received May 3, 1967

Direct Evidence for the Formation of Diphenylmethylene in the Photolysis of Triphenyl- and Tetraphenyloxirane

Sir:

Recent studies have shown that the photolytic reactions of oxiranes can give rise to products which have been interpreted in terms of carbene (methylene) intermediates.[1] We wish to report *convincing* direct evidence for the formation of diphenylmethylene (III) in the photolysis of triphenyloxirane (I) and of tetraphenyloxirane (II) (Scheme I).

Scheme I



I, R = H
II, R = C$_6$H$_5$
III
IV, R = H
V, R = C$_6$H$_5$

Irradiations were carried out in methylcyclohexane glass at 77°K. Typically, a solution (10^{-4} *M*) of the oxirane was irradiated[2] with 2537-A light for 5–30 sec. The photolysis products were identified by a combination of epr and luminescence techniques.

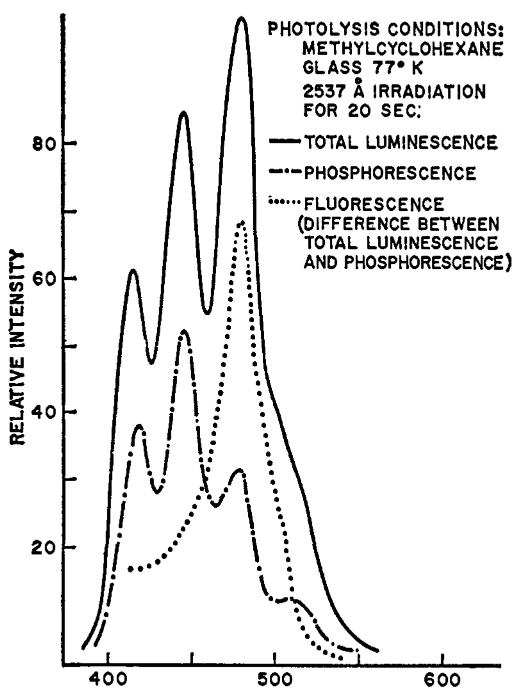


Figure 1. Photolysis of tetraphenyloxirane: luminescence of products.

The total luminescence spectrum[3] obtained after II was irradiated is shown in Figure 1. By use of a phosphoroscope it was possible to show that part of this luminescence was phosphorescence which corresponded closely with that of benzophenone, and the remaining luminescence was identified as the *fluorescence* previously reported for diphenylmethylene (III).[4]

Further confirmation for the presence of III was obtained from epr studies. The epr absorption spectrum of the same photolyzed solution which had been used in the luminescence measurements was attributed to a ground-state triplet molecule with zero-field parameters D/hc = 0.4053 cm^{-1}, E/hc = 0.0190 cm^{-1}. The comparable values for these parameters which had been obtained for III (in benzophenone) are: (a) randomly oriented sample:[5] D/hc = 0.4055 cm^{-1}, E/hc = 0.0194 cm^{-1}; and (b) single crystal:[6] D/hc = 0.40505 cm^{-1}, E/hc = 0.01918 cm^{-1}.

When a solution of I was photolyzed, the phosphorescence of benzaldehyde was detected as well as the fluorescence of III. The epr of III was detected with zero field parameters D/hc = 0.4056 cm^{-1}, E/hc = 0.0188 cm^{-1}. However, no epr absorption signals corresponding to those of phenylmethylene[7] were detected and no phosphorescence which could be ascribed to benzophenone was observed. This is to be contrasted with the results obtained in solution where products which could be derived from both phenyl- and diphenylcarbene were observed.[1a]

---

(1) (a) H. Kristinnson and G. W. Griffin, *Angew. Chem. Intern. Ed. Engl.*, **4**, 868 (1965); *Angew. Chem.*, **77**, 859 (1965); (b) H. Kristinnson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966); (c) H. Kristinnson, *Tetrahedron Letters*, 2343 (1966); (d) H. Kristinnson, R. A. Mateer, and G. W. Griffin, *Chem. Commun.*, 415 (1966); (e) G. W. Griffin and co-workers, unpublished work.

(2) An air-cooled Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) was used as the light source equipped with 16 8-w low-pressure mercury lamps.

(3) The luminescence spectra were recorded on an Aminco-Kiers spectrophotofluorometer (American Instrument Co., Silver Spring, Md.).

(4) (a) W. A. Gibbons and A. M. Trozzolo, *J. Am. Chem. Soc.*, **88**, 172 (1966); (b) A. M. Trozzolo and W. A. Gibbons, *ibid.*, **89**, 239, (1967).

(5) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys.*, **61**, 1663 (1964); E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964).

(6) R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *ibid.*, **37**, 1878 (1962); R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, *ibid.*, **43**, 2006 (1965).

(7) A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).