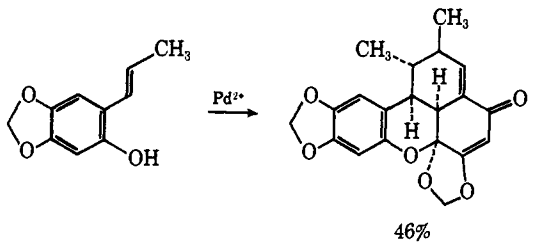

cules of carpanone and four molecules of carbon tetrachloride per unit cell (ρ_{calcd} = 1.51 g/cm^3). Diffractometer measured cell constants are a = 19.071 (5), b = 9.721 (5), c = 13.152 (5) Å, and β = 113.11 (5)°. All data in the hkl and $\bar{h}kl$ octants with $2\theta \leq 110°$ were recorded (2647 reflections) with filtered Cu Kα radiation (1.5418 Å). After correction for background, Lorentz, and polarization effects, 1727 reflections were judged observed. A Wilson plot was computed and normalized structure factors were derived in a standard fashion.[7] The 293 largest normalized structure factors were assigned phases by an iterative application of Sayre's equation.[8] All 31 nonhydrogen atoms were revealed in the subsequent E synthesis.[9] Full-matrix least-squares refinements with anisotropic temperature factors for all nonhydrogen atoms and isotropic temperatures factors for all hydrogens are currently at 11.6% for the observed reflections.[10] A computer-generated drawing of the final X-ray model is given in Figure 1.[11] There is no evidence that the carbon tetrachloride is disordered. The closest intermolecular contact is 2.90 Å between chlorine and oxygen. All bond distances and angles in the carpanone molecule agree well with generally accepted values.[12]

The introduction of five contiguous asymmetric centers with the correct stereochemistry in a single high-yield reaction suggests additional uses of palladium(II) in the synthesis of polyphenolic natural products which are now under investigation.

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[7] A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942); J. Karle and H. Hauptmann, *Acta Crystallogr.*, **9**, 635 (1956).

[8] R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.

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[10] W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least-Squares Program," U. S. Atomic Energy Commission Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

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[12] "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc. Spec. Publ.*, **No. 11** (1958).

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Photolytically Induced Oxygen→Carbon Linkage Isomerization in Formato- and Oxalatoamine Complexes of Cobalt(III)[1]

Sir:

The 254-nm continuous photolysis of $(NH_3)_5CoO_2CH^{2+}$ in $HClO_4$ solution produces Co^{2+}, H_2, and CO_2 with the yields affected by the presence of O_2, 2-propanol, and allyl alcohol; the formation of H atoms and their reaction with the substrate have been established.[2] The flash photolysis of this complex reveals two transients which absorb at λ < 320 nm, one short-lived (SL) and the other long-lived (LL). Because of the overlap of their spectra, it is not possible to discern whether LL arises from SL or whether they are independent species. However, the spectrum and decay kinetics of LL can be evaluated without any contribution from SL. Point-by-point determination of the absorption spectrum of LL shows a maximum at $\lambda \sim$ 268 nm. LL decays *via* first-order kinetics with the rate constant a function of pH as shown in Figure 1a. The activation energy for the decay process is 23 kcal mol^{-1} independent of pH. The amount of LL and its decay kinetics are independent of the presence of O_2, allyl alcohol, 2-propanol, and (except for the decay rate) H^+.

The 254-nm continuous photolysis of $(NH_3)_5CoO_2CCO_2H^{2+}$, $(NH_3)_4Co(C_2O_4)^+$, and $(en)_2Co(C_2O_4)^+$ in $HClO_4$ solution yields Co^{2+}, CO_2, and O_2-scavengeable radicals.[3] The flash photolysis of these complexes, in the presence or absence of O_2, likewise gives two discernible transients which are unaffected by the presence of alcohols or Cl^-. The pH dependences of the first-order decays of LL are shown in Figures 1a and 1b. The activation energy for these decays has the same value as quoted above within experimental error. The spectrum of LL for $(NH_3)_5CoO_2CCO_2H^{2+}$ is the same as that for $(NH_3)_5CoO_2CH^{2+}$. In 2 M $HClO_4$ the lifetime of LL for $(NH_3)_4Co(C_2O_4)^+$ is sufficiently long for a spectrum to be obtained by double beam spectrophotometry within 1 min of the flash. An absorption maximum at $\lambda \sim$ 265 nm is observed; the parent complex does not have an absorption maximum in that region. Intermediate LL for $(en)_2Co(C_2O_4)^+$ (en-LL) is so long lived[4] in highly acidic medium that it can be generated by continuous photolysis and separated from Co^{2+} and the substrate by ion-exchange chromatography.[5] Although we have been unable to isolate en-LL as a solid,[6] its spectrum in acidic solution has been characterized and is shown in Figure 2 in comparison with $(en)_2Co(C_2O_4)^+$. Intermediate en-LL decays quantitatively to Co^{2+} with a first-order rate constant identical with that seen from flash photolysis; CO_2 is also produced in this reaction. Intermediate en-LL undergoes base-catalyzed hydrolysis to yield $(en)_2Co(OH_2)_2{}^{3+}$.

The following facts are evident from the data: (1) the LL intermediate from the formato and monodentate

[1] Support by NSF Grant No. GP 11213 is gratefully acknowledged.

[2] E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, manuscript in preparation.

[3] A. F. Vaudo, E. R. Kantrowitz, M. Z. Hoffman, E. Papaconstantinou, and J. F. Endicott, manuscript in preparation.

[4] In highly acidic solution, $t_{1/2}$ of en-LL is about 2.5 hr.

[5] The ion-exchange behavior of en-LL shows that this intermediate has a 2+ charge in acidic solution.

[6] Anions used to attempt precipitation of en-LL include ClO_4^-, Cl^-, BF_4^-, $B(C_6H_5)_4^-$, and $F_3CSO_3^-$ and also various ethanol–ether mixtures.

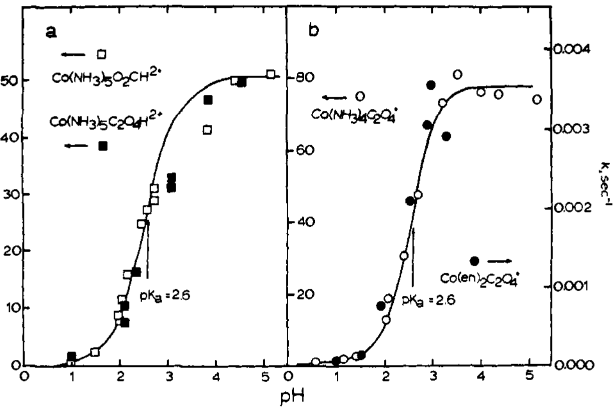


Figure 1. Rate constants for the decay of the long-lived intermediates as a function of pH (ClO_4^- medium): (a) [$(NH_3)_5CoO_2CH^{2+}$] or [$(NH_3)_5CoO_2CCO_2H^{2+}$] = 5×10^{-5} *M;* monitoring wavelength, 275 or 280 nm; (b) [$(NH_3)_4Co(C_2O_4)^+$] or [$(en)_2Co(C_2O_4)^+$] = $2\text{-}6 \times 10^{-5}$ *M*; monitoring wavelength, 280 nm. The rate constants were measured at ambient temperature with ±15–20% error.

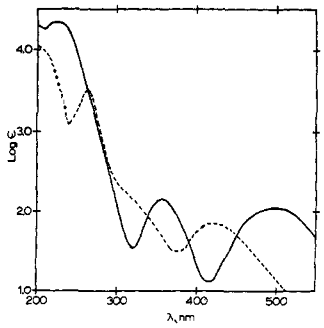
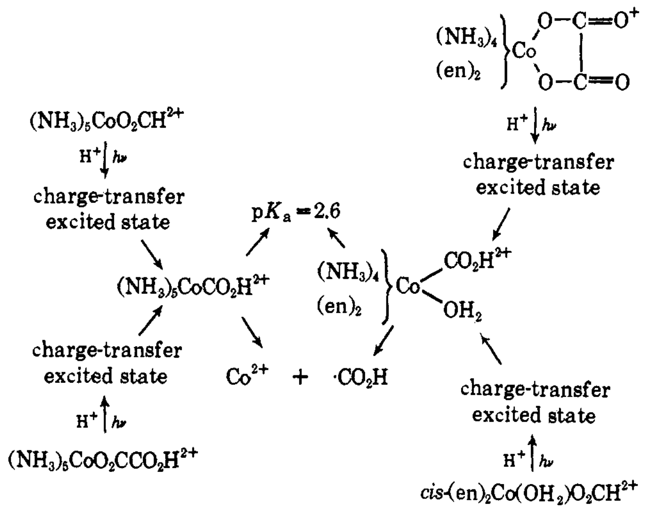


Figure 2. Spectra of $(en)_2Co(C_2O_4)^+$ (————) and en-LL = $(en)_2(H_2O)CoCO_2H^{2+}$ (– – – – – – – –).

oxalato complex are extremely similar if not identical; the differences in the rate constants of the bidentate oxalato compounds are consistent with the lower reactivity of en complexes;[7] (2) LL is *not* a free radical nor an excited state of Co^{2+} or the substrate;[8] (3) LL undergoes protonation–deprotonation with pK_a = 2.6 with the rate of decay to Co^{2+} dependent upon the state of protonation;[10] (4) the spectrum of en-LL, presumably representing the spectra of the other LL intermediates, strongly resembles that of a Co(III) complex with blue-shifted d–d bands and discernibly split charge-transfer bands; indeed, from the hydrolysis result there is no question that LL is a Co(III) complex.

We wish to propose that the ultraviolet photochemistry of $(NH_3)_5CoO_2CH^{2+}$ generates, in addition to Co^{2+} directly, the C-bonded formato linkage isomer, $(NH_3)_5CoCO_2H^{2+}$, which undergoes internal electron transfer to produce additional Co^{2+}. The formation of the isomer would arise *via* proton migration in the charge-transfer excited state of the complex coupled with rotation of the ligand. The intermediate from $(NH_3)_5CoO_2CCO_2H^{2+}$ would arise from heterolytic C–C bond scission, loss of CO_2, and oxygen → carbon linkage isomerization to give the same species as from the formato complex. For the bidentate oxalato complexes, charge-transfer excitation causes, in addition to the direct formation of Co^{2+}, loss of CO_2 and substitution of H_2O to produce the C-bonded formato intermediate, presumably in the cis aquo configuration. The decay of LL to Co^{2+} *via* intramolecular electron transfer is accompanied by the formation of the $\cdot CO_2H$ radical which either disproportionates to form CO_2 or reduces the complex and/or LL to give Co^{2+} and CO_2. Gas analysis of the continuous photolysis of these complexes supports this mechanism.[2,3] The fact that the flash photolysis of *cis*-$(en)_2Co(OH_2)O_2CH^{2+}$ gives an intermediate with identical characteristics as en-LL[11] establishes the identity of the C-bonded formato isomer with certainty. The pK_a of LL is 2.6. Although the pK_a of free formic acid is 3.8, the greater electron-withdrawing character of the 3+ metal center would strengthen the C-bonded acid and lower its pK_a. For a comparison, the pK_a of the free carboxylate end of $(NH_3)_5CoO_2CCO_2H^{2+}$ is 2.2.[12]



An examination of the spectrum of en-LL supports the correctness of this identification. The crystal-field splittings of O-bonded carboxylate–amine complexes are virtually identical giving these complexes very similar d–d spectra with absorption band maxima at ~360 and ~500 nm. The absorption bands of en-LL at ~320 and ~421 nm firmly establish that this intermediate is *not* an O-bonded carboxylate complex but rather contains a ligand that lies very high in the spectrochemical series, perhaps even higher than C-bonded cyanide which has the largest ligand field strength of common ligands. C-Bonded formate would be expected to have a larger ligand field strength than O-bonded formate inasmuch as the deprotonated formate carbon is a stronger Lewis base than is the carboxylate oxygen. It is this extremely low acidity of the carbon hydrogen which has rendered thermally induced oxygen→carbon linkage isomerization of formate unobservable. Finally, in support of our assignment of the nature of LL, it should be noted that

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(7) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N.Y., 1967, p 224.

(8) Although excited states are definitely implicated in Co(III) photochemistry, they have not been detected by flash photolysis to date; it should be noted that no transients are observed in the flash photolysis of $(NH_3)_5CoO_2CCH_3^{2+}$ in the absence of O_2.[9]

(9) E. R. Kantrowitz, M. Z. Hoffman, and J. F. Endicott, *J. Phys. Chem.*, 75, 1914 (1971).

(10) The parent complexes (except $(NH_3)_5CoO_2CCO_2H^{2+}$) do not have comparable acid–base properties.

(11) The quantum yield for the formation of LL from *cis*-$(en)_2Co(OH_2)O_2CH^{2+}$ is sufficiently low so that the intermediate could not be isolated by continuous photolysis.

(12) C. Andrade and H. Taube, *Inorg. Chem.*, 5, 1087 (1966).

the ultraviolet irradiation of $(NH_3)_5CoNO_2^{2+}$ results in the formation of the linkage isomer, $(NH_3)_5CoONO^{2+}$, in addition to the direct generation of Co^{2+};[13] formate, HCO_2^-, is isoelectronic with NO_2^-. N-Bonded nitrite has a higher ligand field strength than does the O-bonded isomer and shows blue-shifted d–d bands in a manner similar to that observed for LL.[13]

C-Bonded formate is apparently both thermodynamically and kinetically unstable with respect to Co^{2+} with protonation of the free carboxylate end serving to retard the rate of transfer of a ligand electron to the metal center; it should be noted that formate is a more powerful reducing agent than is formic acid.[14] It is clear that a facile pathway to Co^{2+} exists for these compounds that is not available for the usual Co(III)–amine complexes which are kinetically stable. It is not immediately clear what the structural parameter is which permits intramolecular electron transfer; unfortunately, the number of cases of simple Co(III) complexes in which such a process occurs is extremely limited. The activation energy of 23 kcal mol^{-1} for the formation of Co^{2+} can be viewed as the energy required to promote a ligand electron to a charge-transfer excited state of the complex and thence to an e_g orbital of the metal center. This thermal activation process is clearly independent of the state of protonation of the formate and the nature of the other ligands.

These results require that the mechanisms previously proposed[15] for the photolysis of oxalato complexes of Co(III) be reexamined, and that the implications to electron transfer processes involving Co(III) be explored.

Acknowledgment. The authors thank Professor J. N. Armor for assistance in the separation and characterization of en-LL and Dr. E. Rotlevi for his help in obtaining the data for $(NH_3)_5CoO_2CCO_2H^{2+}$.

[13] V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 7, 1398 (1968).

[14] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952, p 130.

[15] T. B. Copestake and N. Uri, *Proc. Roy. Soc., Ser. A*, **228**, 252 (1955); G. B. Porter, J. G. W. Doering, and S. Karanka, *J. Amer. Soc.*, **84**, 4027 (1962); H. Way and N. Filipescu, *Inorg. Chem.*, **8**, 1609 (1969).

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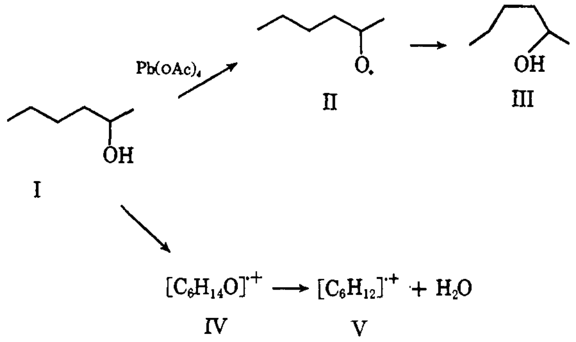
Electron Impact Induced 1,4 Elimination. The Barton Reaction in Disguise

Sir:

Transfer to oxygen of a hydrogen located on a carbon δ to the carbinol grouping (II → III and IV → V in Scheme I) characterize both the Barton reaction[1] and the mass spectral elimination of water[2,3] (Scheme I).

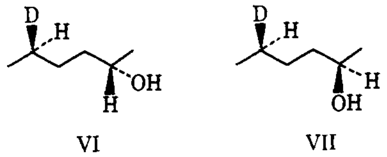
Scheme I[a]



[a] Various reagents will effect this reaction (I to II). Some of these go on to produce furans while others lead to differing final products. See ref 1.

Although the products of the Barton reaction are compelling evidence for the accepted gross structure of the intermediate II no such product information is at hand to assign structure to the species IV which lives for less than 1 μsec in the mass spectrometer. The comparative dynamic stereochemistry of the hydrogen transfer steps (II → III and IV → V), uncovered in the present work, provides strong evidence of similar structures for II and the previously inaccessible IV. The diastereomers exhibited in Chart I, with deuterium substituted in turn for the C-5 diastereotopic hydrogens of 2-hexanol, are the molecules necessary to effect such a stereochemical comparison. As outlined in Scheme II acetol and lactic acid served as effective precursors to put these molecules (VI and VII) and their enantiomers in hand.

Chart I



As shown (Scheme II), (*R*)-(−)-propylene glycol and its enantiomer were obtained from acetol[4] and (*S*)-(−)-ethyl lactate, respectively.[5] In each case, primary hydroxyl group tritylation[6] prior to tosylation[7] followed by lithium aluminum deuteride reduction yielded the labeled enantiomeric 1-propanols (IX, one enantiomer shown).[8,9] Alkylation of the derived bromide[10] yielded

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[1] M. Akhtar, *Advan. Photochem.*, 2, 263 (1964), is a general review of this reaction. Also see: K. Heusler and J. Kalvoda, *Angew. Chem., Int. Ed. Engl.*, 3, 525 (1964). For more recent papers with leading references see: M. LJ. Mihailović, Ž. Čeković, and J. Stanković, *Chem. Commun.*, 981 (1969); A. Deluzarche, A. Maillard, P. Rimmelin, F. Schue, and J. M. Sommer, *ibid.*, 976 (1970); A. C. Cope, M. A. McKervey, N. M. Weinshenker, and R. B. Kinnel, *J. Org. Chem.*, **35**, 2918 (1970); M. LJ. Mihailović and Ž. Čeković, *Synthesis*, 209 (1970).

[2] A recent comprehensive article containing leading references is: M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, *J. Amer. Chem. Soc.*, **92**, 3076 (1970).

[3] The highly site specific 1,4 abstraction is deduced from the products in the Barton reactions. See discussion and references in Akhtar's review article (ref 1 herein). In the mass spectrometer, deuterium labeling revealed the highly specific (>90%) 1,4 abstraction; see: W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 2375 (1964); S. Meyerson and L. C. Leitch, *ibid.*, **86**, 2555 (1964).

[4] P. A. Levene and A. Walti, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 545.

[5] J. Jacobus, Z. Majerski, K. Mislow, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1998 (1969).

[6] J. Jary and K. Kefurt, *Collect. Czech. Chem. Commun.*, **31**, 1803 (1966).

[7] L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967, p 1180.

[8] Lithium aluminum deuteride displacement of tosylate is known to proceed with inversion of configuration; see: G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, **22**, 479 (1957). Apparently the trityloxy group does not participate since the product trityl ether of 2-deuteriopropanol may be isolated. In addition no 2-propanol is obtained.

[9] All deuterated materials were shown to be identical with authentic protium compounds by vpc comparison.

[10] C. S. Marvel and F. D. Hager, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 248.