decision as to whether these observations are due to a kinetic factor[15] or whether an actual *structurally rigid* intermediate is involved would be somewhat premature at this time. Suffice it to say that, by all analogy presently available on kinetic secondary deuterium isotope effects, (2 + 2) cycloadditions of allene, *including dimerizations*, appear to proceed *via* nonsynchronous pathways.

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(15) Nonbonded interactions in possible diradical intermediates might very well slow down bond rotations drastically within the intermediates and thus allow ring closures to be relatively quite rapid.

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Excited States in the Ultraviolet Photochemistry of Cobalt(III) Complexes. Evidence from Chemical Scavenger Studies of $Co(NH_3)_5O_2CCH_3{}^{2+}$ at 254 nm[1]

Sir:

Most of the ultraviolet photochemistry of cobalt(III) complexes arises from the irradiation of absorption bands possessing charge-transfer (CT) character and results in oxidation–reduction processes and, to a lesser extent, ligand-exchange reactions.[2-6] Although radical transients have been observed under flash photolysis conditions,[7,8] the precursors of these radicals appear to be so short-lived as to preclude direct observation or to affect the formation kinetics of the observable transients.[8] Thus, it has been difficult to provide evidence which can distinguish between the radical pair[2] and excited-state[3,4] mechanisms that have been proposed to account for the photochemistry of cobalt(III) complexes. One potentially powerful technique which has not been exploited to any great extent in the photochemistry of complex ions is the use of nonabsorbing reactive chemical scavengers to distinguish between the mechanistic possibilities. We wish to describe the investigation of short-lived intermediates using chemical scavenging techniques.

Although it is possible to alter the distribution and yields of oxidized products,[2,3,7-10] it has proven very difficult to find nonabsorbing scavengers which can alter the primary quantum yield of Co^{2+} formation, $\phi_{Co^{2+}}$. We have found[3] that $\phi_{Co^{2+}}$ is often a function of [H+], implying that excited-state intermediates have acidities different than those of the ground-state com-

(1) This work was supported by the National Science Foundation under Grants GP 7048 and GP 11213.
(2) A. W. Adamson, *Discuss. Faraday Soc.*, 29, 163 (1960).
(3) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 87, 3348 (1965).
(4) V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta Rev.*, 1, 7 (1967).
(5) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 68, 541 (1968).
(6) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 90, 4740 (1968).
(7) S. A. Penkett and A. W. Adamson, *ibid.*, 87, 2514 (1965).
(8) G. Caspari, J. F. Endicott, and M. Z. Hoffman, unpublished observations.
(9) R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *Chem. Commun.*, 195 (1969).
(10) J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, 74, 1021 (1970).

Table I. Quantum Yields of Products[a]

Product	ϕ	Product	ϕ
Co^{2+}	0.190 ± 0.007^b	C_2H_6	0.07 ± 0.02^c
CO_2	0.15 ± 0.02^c	H_2	Trace
CH_4	0.008 ± 0.002^c	N_2	Not detectable

[a] $[Co(NH_3)_5O_2CCH_3{}^{2+}] = 5.0 \times 10^{-3}$ M; $[HClO_4] = 0.1$ M; $25°$. [b] $I_a \simeq 5.5 \times 10^{-4}$ einstein l.$^{-1}$ min^{-1}. Error limits are the average deviations of four determinations. [c] $I_a \simeq 6.5 \times 10^{-3}$ einstein l.$^{-1}$ min^{-1}. Error limits are the average deviations of eight determinations. The ratio $\phi_{CH_4}/\phi_{C_2H_6}$ decreases with increased light intensity but the sum ($\phi_{CH_4} + 2\phi_{C_2H_6}$) does not vary significantly with I_a.

plexes. Our observation[11] that the addition of [CH₃OH] ≥ 5 M to $Co(NH_3)_5Cl^{2+}$ increases $\phi_{Co^{2+}}$ nearly threefold has led us to apply the use of such nonabsorbing scavengers to systems where the photochemistry is relatively straightforward.

$[Co(NH_3)_5O_2CCH_3](ClO_4)_2$ was prepared as described in the literature[12] and was recrystallized until the absorption spectrum agreed with that in the literature. Solutions were prepared with distilled water and reagent grade chemicals. The photochemical techniques employed have already been described.[3,9,10] Product gases were identified mass spectrometrically and yields were determined by quantitative vpc (molecular sieve column and thermal conductivity detection).

Table I summarizes our determinations of the quantum yields of product formation in the absence of scavengers.[13] These yields are not noticeably dependent on [H+]. Note that $\phi_{Co^{2+}} \simeq \phi_{CO_2} \simeq (\phi_{CH_4} + 2\phi_{C_2H_6})$, indicating the accountability of all electron equivalents. $\phi_{Co^{2+}}$ is unaffected by [CH₃OH] $\leq$ 2.5 M but is increased in the presence of 2-propanol, reaching a limiting value of ~0.4 at high concentrations (Figure 1). ϕ_{CO_2} is not significantly affected by the presence of either alcohol and, although ϕ_{CH_4} is increased and $\phi_{C_2H_6}$ is decreased as [alcohol] is raised, $\phi_{CH_4} + 2\phi_{C_2H_6}$ remains relatively unchanged (Figure 2). Spectral and ion-exchange analyses of irradiated solutions have shown no evidence for photoaquation products.

The stoichiometry demonstrates that the only photoredox process occurring involves the acetate ligand and the cobalt center.

$$Co(NH_3)_5O_2CCH_3{}^{2+} \xrightarrow[h\nu]{H^+} Co^{2+} + 5NH_4^+ + CH_3CO_2\cdot$$

$\longrightarrow$ gaseous products
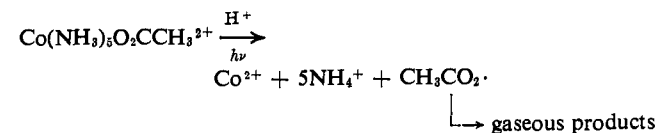
Furthermore, it is clear that the precursor excited states (or, alternatively, radical pairs) leading to the formation of CO_2, CH_4, and C_2H_6 are not scavengeable by either alcohol. It must be concluded, therefore, that absorption of 2537-Å radiation by $Co(NH_3)_5O_2CCH_3{}^{2+}$ leads to two chemically distinguishable intermediates: X*, which is not scavengeable and leads to the gaseous products of the reaction, and Y*, which normally re-

(11) G. Caspari, R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, manuscript in preparation.
(12) D. K. Sebera and H. Taube, *J. Amer. Chem. Soc.*, 83, 1785 (1961); L. M. Jackman, R. M. Scott, and R. H. Portman, *Chem. Commun.*, 1338 (1968).
(13) In addition to the equality of $\phi_{Co^{2+}}$ and ϕ_{CO_2} reported here, the fact that no N_2 generation in the photolysis of $Co(NH_3)_5O_2CCH_3{}^{2+}$ at 254 nm is observed eliminates any photoredox process leading to N_2 (from NH_2) and CH_3COOH as a mechanistic possibility and negates the recent proposal of such a step: A. W. Adamson, A. Vogler, and I. Lantzke, *J. Phys. Chem.*, 73, 4183 (1969).
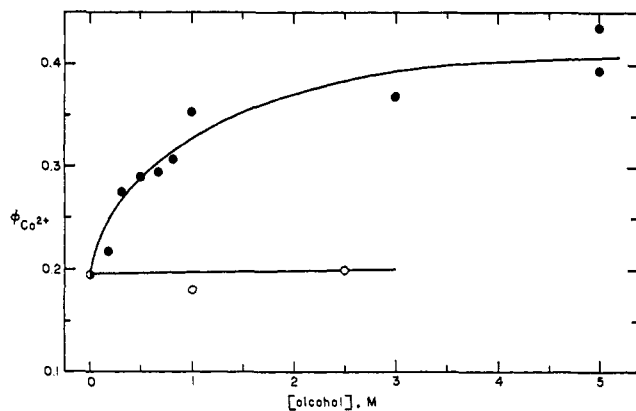
Figure 1. Dependence of $\phi_{Co^{2+}}$ on [alcohol]: $[Co(NH_3)_5O_2CCH_3{}^{2+}]$ = 5.0 × 10⁻³ M; [H⁺] = 0.1 M; $I_a \cong$ 6.5 × 10⁻³ einstein l.⁻¹ min⁻¹. Methanol, O; 2-propanol, ●.
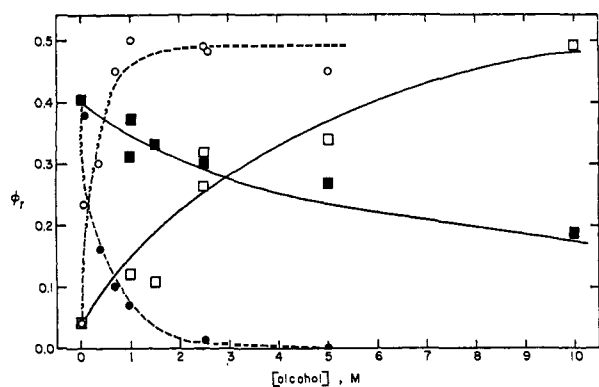

Figure 2. Dependence of the yields of CH₄ and C₂H₆ on [alcohol]: $\phi_r = \phi_{CH_4}/\phi_{Co^{2+}}$ or $\phi_{C_2H_6}/\phi_{Co^{2+}}$; $[Co(NH_3)_5O_2CCH_3{}^{2+}]$ = 5.0 × 10⁻³ M; [H⁺] = 0.1 M; $I_a \cong$ 6.5 × 10⁻³ einstein l.⁻¹ min⁻¹. When alcohol = methanol, ———; CH₄ = □, C₂H₆ = ■. When alcohol = 2-propanol, ------; CH₄ = O, C₂H₆ = ●.

turns to the ground state and has a sufficiently long lifetime to be reduced by the alcohols. The independence of the equivalent yields of gaseous product on [alcohol] shows that these two intermediate species are not interconvertible.
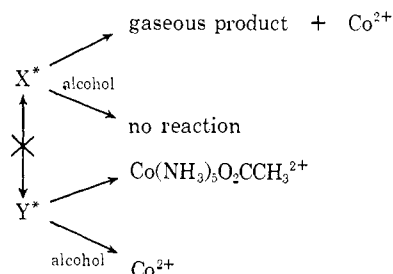
The intermediate leading to the gaseous products may well be a radical pair; if so, its lifetime is so short that it is not significantly scavenged by [alcohol] ≤ 10 M. Any precursor to this intermediate could not be scavenged without affecting the gas yields. Although the chemically important intermediates X* and Y* could derive from a common excited state, it is not unreasonable in this case to postulate that they arise from different excited states. In $Co(NH_3)_5O_2CCH_3{}^{2+}$ the carbonyl and the acetate → cobalt CT absorptions would be expected to occur in the same general spectral regions. Since the e_g acceptor orbital at the cobalt(III) center has approximately σ symmetry, interconversions between carbonyl and CT excited states would be symmetry forbidden.

These results represent the first unequivocal demonstration of the generation of more than one intermediate in the photochemistry of a cobalt(III) complex. It seems clear that the excited states populated do determine the course of reaction and must be taken into consideration in any mechanistic speculation.

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Conformational Influences on Antihistamine Activity. The Crystal Structure of 2-[(2)-Dimethylaminoethyl)-2-thenylamino]pyridine Hydrochloride, an Antihistamine

Sir:

Antihistamines are believed to compete with histamine for an ill-defined receptor site.[1] One of the requirements for antihistamine activity was assumed to be a conformational similarity with histamine. However, no structural data have been available to test this hypothesis. We have completed the first crystal structure study of an antihistamine, 2-[(2)-dimethylaminoethyl)-2-thenylamino]pyridine hydrochloride, Histadyl,[2] and have found a conformation similar to that observed recently in the histamine cation.[3]
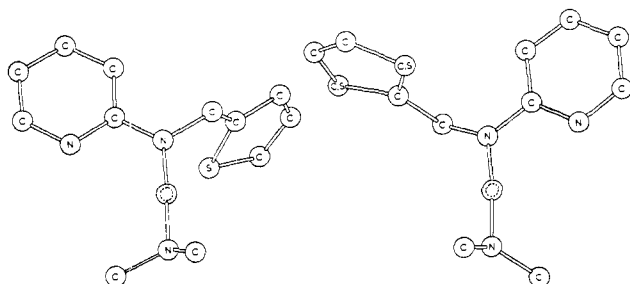

Figure 1. A view down the C-C bond of the dimethylaminoethyl group in the two molecules in the asymmetric unit. The disordered thiophene ring atoms are labeled C,S.

Histadyl was reported to crystallize in the monoclinic space group P2₁/n with cell dimensions of a = 27.35, b = 10.38, c = 10.96 Å, and β = 96°.[4] The density calculated for eight molecules (mol wt = 297.85) per unit cell is 1.281 g/cm³ and the observed density is 1.273 g/cm³. We used the standard setting P2₁/c with a = 10.936 ± 0.003, b = 10.417 + 0.003, c = 28.256 ± 0.008 Å, and β = 106.21 ± 0.02°. The intensity data were measured using the stationary crystal–stationary counter method with a G.E. automatic diffractometer. A total of 3023 nonzero reflections with $2\theta \leq 135°$ (Cu radiation) were used in the analysis.

(1) (a) R. E. Wilhelm, *Med. Clin. N. Amer.*, 45, 887 (1961); (b) C. Botré, M. Marchetti, C. Del Vecchio, G. Lionetti, and A. Memoli, *J. Med. Chem.*, 12, 832 (1969).

(2) Histadyl is the registered trade name of Eli Lilly and Co. for the compound 2-[(2-dimethylaminoethyl)-2-thenylamino]pyridine hydrochloride.

(3) M. V. Veidis and G. J. Palenik, *Chem. Commun.*, 196 (1969).

(4) H. A. Rose and J. G. Williams, *J. Amer. Pharm. Assoc.*, 48, 487 (1959).