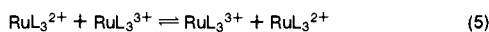


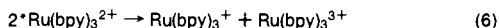
to be $1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ from a relative Marcus calculation using the $\text{Cr}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Ru}(\text{NH}_3)_6^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$ cross-reactions (ref 10b and 10c) and $4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ for the $\text{Ru}(\text{NH}_3)_6^{2+}/\text{Ru}(\text{NH}_3)_6^{3+}$ self-exchange rate constant (ref 10d), $3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ from a relative Marcus calculation using the $\text{Cr}(\text{bpy})_3^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{V}^{2+}/\text{Co}(\text{NH}_3)_6^{3+}$ (ref 10e) cross-reactions with $1.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for the $\text{V}^{2+}/\text{V}^{3+}$ self-exchange (ref 10f), and $10^7 \text{ M}^{-1} \text{ s}^{-1}$ from the $\text{Cr}(\text{bpy})_3^{3+}/\text{V}^{2+}$ cross-reaction for which $k = 4.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C and $\mu = 1.0 \text{ M}$ (ClO_4^-) (ref 10g). The E^0 values used for the Cr, Ru, and V couples are -0.25 , $+0.051$ (ref 10d), and -0.255 (ref 10h), respectively. (b) A. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **29**, 42 (1960). (c) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1886 (1964). (d) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968). (e) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). (f) K. V. Krishnamurthy and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958). (g) M. Chou, unpublished observations, Brookhaven National Laboratory, 1976. (h) W. M. Latimer, "Oxidation Potentials", 2d ed, Prentice-Hall, Englewood Cliffs, N.J., 1952.

- (11) For the $\text{Fe}(\text{phen})_3^{3+}$ exchange k_{11} has been reported to be $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in aqueous 1.84 M sodium sulfate at 25°C (I. Ruff and M. Zimonyi, *Electrochim. Acta*, **18**, 515 (1973)), M. Chan (M. Chan, Ph.D. Thesis, Washington University, 1974) has found k_{11} for $\text{Ru}(\text{bpy})_3^{3+}$ to be ~ 1.5 times that for $\text{Fe}(\text{phen})_3^{3+}$ and k_{11} for $\text{Os}(\text{bpy})_3^{3+}$ to be four times that for $\text{Fe}(\text{phen})_3^{3+}$ ($k_{11} = 6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) in acetonitrile at $\mu \sim 0.1 \text{ M}$ and 25°C . Thus $k_{11} \geq 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in aqueous solutions at 0.5 M ionic strength seems a reasonable value for the $\text{Os}(\text{bpy})_3^{3+}$ and RuL_3^{3+} systems, allowing that self-exchange may be somewhat faster for $\text{Os}(\text{III})$ than $\text{Ru}(\text{III})$.
- (12) Figure 2 depicts cross-sections of the reactant and product potential energy surfaces in the vicinity of the intersection region relevant to electron-transfer quenching of $^* \text{RuL}_3^{2+}$ by RuL_3^{3+} . The upper pair of intersecting curves are for self-exchange involving the excited ruthenium(II) complex (eq 3), while the lower set of intersecting curves are for the ground-state self-exchange (eq 5).



Because quenching according to eq 4 lies in the inverted region, the intersection of the excited-state reactant curve with the ground-state product curve occurs on the left-hand side of the excited-state reactant curve; similarly the intersection of the excited-state product curve with the ground-state reactant curve occurs on the right-hand side of the excited-state product curve. Focusing on the excited-state reactant curve, in order for electron-transfer quenching to occur it is necessary that the system move to the left-hand side where nonadiabatic electron-transfer forming the electronic ground-state species can occur. If, on the other hand, the system moves to the right there is no net change aside from excited-state self-exchange, but, by symmetry, once excited-state self-exchange has occurred, crossing to the "reactant" ground-state curve may occur if the system moves again to the right. Thus the excited-state exchange reaction has no effect on quenching via crossing to the ground-state surfaces since this crossing is equally probably from either of the upper intersecting curves, and the excited-state exchange reaction does not waste time or motion that would otherwise lead to quenching.

- (13) S. Efrima and M. Bixon, *Chem. Phys. Lett.*, **25**, 34 (1974).
 (14) W. Schmickler, *J. Chem. Soc., Faraday Trans. 2*, **72**, 307 (1976).
 (15) R. A. Marcus and N. Sutin, *Inorg. Chem.*, **14**, 213 (1975); N. Sutin, *Annu. Rev. Nucl. Chem.*, **12**, 285 (1962).
 (16) R. P. Van Duyne and S. F. Fischer, *Chem. Phys.*, **5**, 183 (1974).
 (17) Of course, electron transfer to produce electronically excited RuL_3^{3+} or ML_3^{2+} may offer another and distinctly different route leading eventually to ground-state RuL_3^{2+} and ML_3^{3+} .
 (18) Considerably more striking evidence for inverted behavior in systems of this kind is provided by the reaction



Preliminary flash-photolysis experiments in which the emission or solution absorbance was monitored at $^* \text{Ru}(\text{bpy})_3^{2+}$ levels $> 10^{-3} \text{ M}$ indicate an upper limit of $10^7 \text{ M}^{-1} \text{ s}^{-1}$ (25°C , $\mu = 0.5 \text{ M}$) for the rate constant for reaction 6. Since the reorganization energies for the $^* \text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^+$ and $^* \text{Ru}(\text{bpy})_3^{2+}/\text{Ru}(\text{bpy})_3^{3+}$ couples are small ($k_{11}, k_{22} \sim 10^{14} - 10^{18} \text{ M}^{-2} \text{ s}^{-2}$, ref 3 and H. E. Toma and C. Creutz, *Inorg. Chem.*, in press) and ΔE^0_{12} is 1.7 V, the very small value obtained for this rate constant suggests that the $^* \text{Ru}(\text{bpy})_3^{2+}$ disproportionation also manifests "inverted" behavior.

Carol Creutz,* Norman Sutin*

Chemistry Department, Brookhaven National Laboratory
 Upton, New York 11973
 Received August 18, 1976

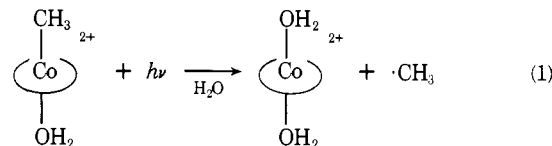
A Flash Photolytic Investigation of Low Energy Homolytic Processes in Methylcobalamin¹

Sir:

Coordination complexes containing alkyl-cobalt bonds have been the subject of much interest since the discovery of coenzyme B_{12} .² The nature of the cobalt-carbon bond is a fundamental concern, both from the point of view of basic chemistry

and as an aid in understanding the functioning of the coenzyme in protein substrates. The photochemistry of coenzyme B_{12} and related organocobalt complexes has been of continuing³⁻¹⁰ interest, no doubt because the susceptibility of these systems to photoinduced homolytic processes has seemed qualitatively pertinent to the nature of the cobalt-carbon bond. In fact the photochemically determined threshold energies for homolytic processes ($\text{M-X} \rightarrow \text{M} + \cdot \text{X}$) can be used as measures of M-X bond strength.¹⁰ We report here some pertinent, direct observations of homolytic processes in methylcobalamin and related compounds.

We have recently shown that cobalt-methyl homolysis (eq 1) occurs following relatively low energy irradiations of com-



plexes containing synthetic equatorial (N_4) ligands.^{11,12} For both $\text{Co}([\text{14}] \text{janeN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ and $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ the homolytic process (eq 1) occurs with large nearly wavelength independent quantum yields following monochromatic excitations in the visible absorption region.¹¹ A fairly well defined, low energy threshold (610 nm)^{11b} for homolysis in $\text{Co}([\text{14}] \text{tetraeneN}_4)(\text{OH}_2)\text{CH}_3^{2+}$ implies that the cobalt-methyl bond energy is relatively small: about 47 kcal mol⁻¹ assuming a bond of negligible polarity and similar energies of solvation for reactants and products.¹⁰

Our experience with homolysis in $\text{Co}^{\text{III}}\text{L}_5\text{X}$ systems^{10,13} is that differences in Co-X homolysis energies vary with changes in the ligand field stabilization energy of the CoL_5 fragment, and solvation energies, but that the apparent Co-X bond energies are not otherwise greatly dependent on L. Thus we would predict that homolysis should occur for low energy irradiations of methylcobalamin, in accord with the observations of Taylor et al.⁶ and of Pratt.^{7b} More recently Hogenkamp et al.⁵ have found that methylcobalamin is "... surprisingly resistant to ... photolysis ..." in the absence of oxygen. Since the products of homolysis of $\text{Co}(\text{N}_4)(\text{OH}_2)\text{CH}_3^{2+}$ complexes have been established to recombine at rates apparently limited only by the rates of Co-OH₂ bond breaking,^{14,15} and since the nonluminescent methylcobalamin excited states surely could not be sufficiently long lived to react directly with dissolved oxygen,¹⁶⁻²¹ we have undertaken a flash photolysis study of methylcobalamin with a view to identifying and directly observing the reactions of any transient species.

A sample of purified, solid methylcobalamin was generously donated to us by Professor C. P. Dunne. Solutions approximately $6 \times 10^{-6} \text{ M}$ in methylcobalamin were prepared in water and in 2 M 2-propanol. A filter solution of $\text{Ni}([\text{14}] \text{dieneN}_4)^{2+}$ ²² and FeCl_3 in 1 M HCl was prepared concentrated enough to transmit only light with $\lambda > 480 \text{ nm}$, and placed in a quartz jacket surrounding the sample cell. A stream of Cr^{2+} scrubbed nitrogen was passed through sample solutions for about 1 h when deaeration was necessary. All samples were handled in a darkened room and in shielded vessels. Standard flash photolysis techniques were employed.²³

In all samples of methylcobalamin flash photolyzed we observed the efficient generation of B_{12r} during the flash pulse (Figure 1b). The amount of B_{12r} generated was independent of medium conditions, i.e., we achieved about a micromolar yield of B_{12r} per $40 \times 10^{-6} \text{ s}$, 160 J flash in water (aerated or deaerated) or 2-propanol (aerated or deaerated). The generation of B_{12r} was accompanied by a decrease in concentration of substrate (methylcobalamin). In deaerated aqueous solution the initial generation of B_{12r} was followed by a rapid partial decay which also corresponded to a rapid partial regeneration

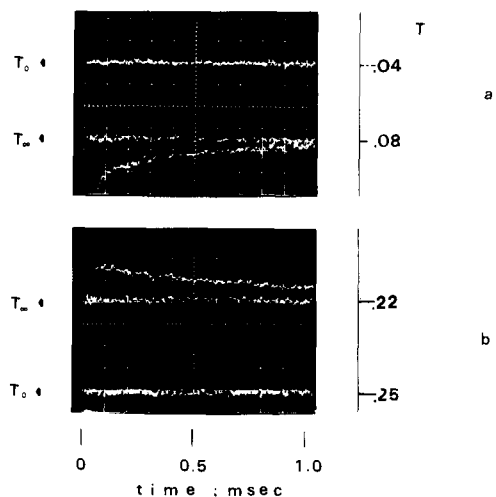


Figure 1. Transient absorbance changes following the flash photolysis of methylcobalamin. Vertical scale is the solution transmittance; T_0 = the transmittance of the unphotolyzed substrate; T_∞ = the final transmittance after the transient absorbance changes. Transmittances during the first 0.1 ms show very large contributions due to scattered light from the flash pulse. Changes in transmittance were monitored at the absorption maximum of methylcobalamin (λ_{\max} 520 nm; trace a) and at the absorption maximum of B_{12r} (λ_{\max} 470 nm; trace b). The optical path length was 20 cm.

of the methylcobalamin absorbance (Figure 1a). Thus the back-reaction (eq 2) is demonstrated to occur very rapidly, with $k_2 \sim 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (from a pseudo-first-order treatment of the decay in Figure 1a) or $k_2 \sim 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (from the initial decay in Figure 1b).

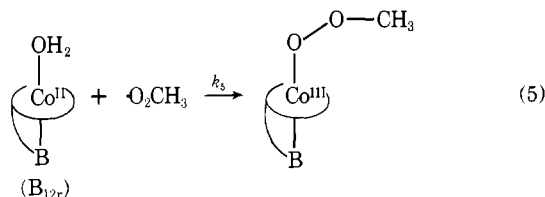


The decay of B_{12r} in deaerated solutions appeared to have two components, the second of which is no doubt a contribution due to the small amount ($[\text{O}_2] < 10^{-7} \text{ M}$) of oxygen not removed by our nitrogen purge (see below). Since the methyl radical decays (eq 3) rapidly ($k_3 \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$),²⁵ and since $[\cdot\text{CH}_3]$ is relatively large ($> 10^{-7} \text{ M}$) in the flash experiments, under our conditions most of the methyl radicals generated dimerize, and a relatively large net generation of B_{12r} is observed.



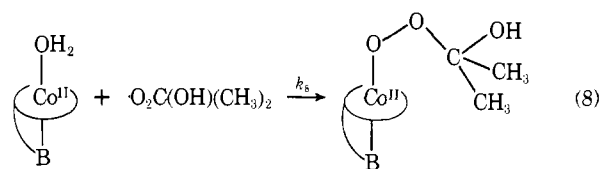
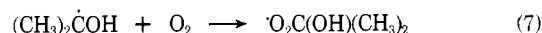
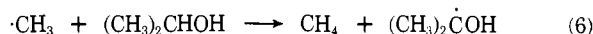
In a continuous photolysis experiment excitation intensities are orders of magnitude smaller and the stationary state concentrations of methyl radicals can rarely be as high as 10^{-8} M . Under these conditions $[B_{12r}]_{ss}$ would quickly become large enough (i.e., $[B_{12r}]_{ss} > \sim 10[\cdot\text{CH}_3]_{ss}$) that most of the methyl radicals generated in eq 1 would be scavenged by B_{12r} in eq 2 and very little net reaction would be observed. Similar inferences have been drawn by several investigators,^{4b,6,7} but direct observation of the transient behavior has not previously been reported.

In aerated solutions the initial B_{12r} absorbance decays rapidly and apparently completely in what appears to be a second-order process. We attribute this decay to the combination of reactions 4 and 5. Reaction 4 is well known and rapid ($k_4 = 4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$)²⁶ and eq 5 has considerable prece-



dent; e.g., $\cdot\text{O}_2\text{CH}_3$ has been shown to react rapidly with $\text{Co}([\text{14}]\text{tetraeneN}_4)^{2+}$.^{11b} From our observations, we estimate for eq 5 $k_5 \approx 2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Very similar observations have been made in aerated 2 M 2-propanol solutions, probably corresponding to some combination of reactions 4–8,^{27,28} with $k_8 \sim 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

The analogues of reactions 2, 5, and 8 for cobalt(II) complexes with synthetic macrocyclic ligands are believed to proceed at rates limited by substitution into the cobalt(II) coordination sphere.^{11,14,29} For these complexes the rate constants for reactions analogous to eq 2, 5 and 8 are approximately $10^8 \text{ M}^{-1} \text{ s}^{-1}$,^{11,14} an order of magnitude smaller than found here. This suggests that the water molecule replaced is more labile in B_{12r} than in many of the synthetic analogues. An exceptional lability of B_{12} derivatives has considerable precedent²



We have performed similar flash photolysis experiments on pyridinomethylbis(dimethylglyoximate)cobalt, $\text{Co}(\text{DMG})_2(\text{py})\text{CH}_3$, with very similar results. The cutoff filter used for these experiments transmitted only radiation with $\lambda \geq 380 \text{ nm}$. The formation of $\text{Co}^{\text{II}}(\text{DMG})_2$ ³⁰ occurred during the flash pulse, and decayed rapidly in accord with reactions 2 and 5 ($k_2' \sim 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; $k_5' \sim 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) in deaerated and aerated solutions, respectively.

Flash photolysis studies presented here directly confirm that cobalt–methyl bonds tend to undergo efficient homolysis at relatively low energy. In the sense of homolytic dissociation, the cobalt–carbon “ σ -bonds” must be regarded as significantly weaker than the usual “cobalt(III)–ligand” bonds.

Acknowledgment. We wish to thank Professor T. L. Brown for bringing to our attention some apparently contradictory reports of the photolysis of methylcobalamin. We are very grateful to Professor C. P. Dunne for the sample of methylcobalamin, for his helpful suggestions, and for a large number of useful details from his Ph.D. dissertation (Brandeis University, 1971).

References and Notes

- (1) Partial support of this research by the National Institutes of Health (AM 14341-08) is gratefully acknowledged.
- (2) For reviews see (a) G. N. Schrauzer, *Acc. Chem. Res.*, **1**, 97 (1968); (b) J. M. Pratt, “Inorganic Chemistry of Vitamin B_{12} ”, Academic Press, New York N.Y., 1972; (c) H. A. O. Hill in “Inorganic Biochemistry”, G. Eichhorn, Ed., Elsevier, New York, N.Y., 1973, Chapter 30, p 1067; (d) D. G. Brown, *Prog. Inorg. Chem.*, **18**, 177 (1973); (e) H. P. C. Hogenkamp in “Cobalamin”, Wiley, New York, N.Y., 1975, Chapter 1, p 21.
- (3) H. P. C. Hogenkamp, *Biochemistry*, **5**, 417 (1966).
- (4) (a) G. N. Schrauzer, J. W. Sibert, and R. J. Windgassen, *J. Am. Chem. Soc.*, **90**, 6681 (1968); (b) G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *ibid.*, **92**, 2997 (1970).
- (5) H. P. C. Hogenkamp, D. J. Vergamini, and N. A. Matwiyoff, *J. Chem. Soc., Dalton Trans.*, 2628 (1975).
- (6) R. T. Taylor, L. Smucker, M. L. Hanna, and J. Gill, *Arch. Biochem. Biophys.*, **156**, 521 (1973).
- (7) (a) J. M. Pratt, *J. Chem. Soc.*, 5152 (1964); (b) J. M. Pratt and B. R. D. Whitear, *ibid.*, 252 (1971).
- (8) E. Ochiai, K. M. Long, C. R. Sperati, and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 320 (1969).
- (9) (a) C. Giannotti and J. R. Bolton, *J. Organomet. Chem.*, **80**, 379 (1974); (b) C. Giannotti, G. Merle, C. Fontaine, and J. R. Bolton, *ibid.*, **91**, 357 (1975); (c) C. Giannotti, G. Merle, and J. R. Bolton, *ibid.*, **99**, 145 (1975); (d) C. Giannotti, C. Fontaine, and B. Septe, *ibid.*, **71**, 107 (1974); (e) C. Giannotti and J. R. Bolton, *ibid.*, **110**, 383 (1976).

- (10) J. F. Endicott, *Inorg. Chem.*, in press.
 (11) C. Y. Mok and J. F. Endicott, submitted.
 (12) The macrocyclic ligands employed were [14]aneN = 1,3,8,11-tetraazacyclotetradecane and [14]tetraeneN₄ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene.
 (13) (a) J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Phys. Chem.*, **79**, 630 (1975); (b) J. F. Endicott and G. J. Ferraudi, *Inorg. Chem.*, **14**, 3133 (1975); (c) J. F. Endicott in "Concepts in Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, Chapter 3, p 83.
 (14) (a) T. S. Roche and J. F. Endicott, *Inorg. Chem.*, **13**, 1575 (1974); (b) *J. Am. Chem. Soc.*, **13**, 1575 (1974).
 (15) A. M. Tait, M. Z. Hoffman, and E. Hayon, *J. Am. Chem. Soc.*, **98**, 86 (1976).
 (16) In order for dissolved O₂ in aerated solutions ([O₂] ~ 2 × 10⁻⁴ M) to react at a diffusion limited rate ($k \leq 10^{10} \text{M}^{-1} \text{s}^{-1}$) with an excited species, the lifetime of that species must exceed 5 × 10⁻⁷ s. Such an excited species would have to luminesce. However, no such luminescence has been detected for cobalt(III) complexes with excited states lower in energy than 1.5 μm⁻¹,¹⁷⁻²⁰ and there are reasons to believe that such cobalt excited states should be very short lived.¹⁷⁻²¹ It is further to be observed that the slow decay in Figure 1b may be used to set an upper limit of [O₂] ≤ 10⁻⁷ M in our experiments; under such conditions we would observe any and all reactions between dioxygen and photochemical intermediates or excited states. The homolysis reactions were observed to occur during the flash pulse and could not have been the result of reaction with O₂.
 (17) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970.
 (18) (a) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970); (b) P. D. Fleischauer, private communication.
 (19) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Prog. Inorg. Chem.*, **17**, 1 (1972).
 (20) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).
 (21) J. F. Endicott and G. J. Ferraudi, *J. Phys. Chem.*, **80**, 949 (1976).
 (22) The macrocyclic ligand abbreviated as [14]dieneN₄ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11⁴-diene. We have found Ni([14]dieneN₄) to be "photoinert" ($\phi < 10^{-4}$).
 (23) For descriptions of the techniques used see (a) T. L. Kelly and J. F. Endicott, *J. Am. Chem. Soc.*, **94**, 1797 (1972); (b) W. L. Wells and J. F. Endicott, *J. Phys. Chem.*, **75**, 3075 (1971); (c) G. J. Ferraudi and J. F. Endicott, *Inorg. Chem.*, **12**, 2389 (1973).
 (24) λ_{max} 470 nm, ε_{max} 9.4 × 10³ for B_{12r} and λ_{max} 520 nm, ε_{max} 9.8 × 10³ for Me-B₁₂; C. P. Dunne, Ph. D. dissertation, Brandeis University, 1971.
 (25) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966, p 161.
 (26) J. K. Thomas, *J. Phys. Chem.*, **71**, 1919 (1967).
 (27) E. R. Kantrowitz, M. Z. Hoffman, and J. F. Endicott, *J. Phys. Chem.*, **75**, 1914 (1971).
 (28) For examples of reactions analogous to eq 7 and 8 see J. Butler, G. G. Jayson, and A. J. Swallow, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1394 (1974).
 (29) (a) J. F. Endicott, J. Lillie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsees, M. G. Simic, M. D. Glick, and D. P. Rillema, *J. Am. Chem. Soc.*, in press; (b) B. Durham, D. P. Rillema, and J. F. Endicott, manuscript in preparation.
 (30) λ_{max} 460 nm, ε_{max} 3.84 × 10³; A. Adin and J. H. Espenson, *Inorg. Chem.*, **11**, 686 (1972).

John F. Endicott,* Guillermo J. Ferraudi

Department of Chemistry, Wayne State University
 Detroit, Michigan 48202

Received August 31, 1976

Photolysis of *tert*-Butyl Peroxylaurate

Sir:

It has been reported¹ that the photolysis of neat *tert*-butyl peroxycaprate and *tert*-butyl peroxylaurate produces high yields of the corresponding carboxylic acids, capric, and lauric acids. By reinvestigation² of the photolysis, using *tert*-butyl peroxylaurate as substrate, we have found that little or no carboxylic acid is formed.

The titration procedure used to determine the acid in the original work¹ was tested and found erroneous principally because the perester itself is saponified in the procedure. We then tried other methods of analysis and found them suitable for the detection of lauric acid in the presence of peroxylaurate. The methods employed thin-layer chromatography, and infrared and NMR spectroscopy. Using those methods, no lauric acid was detected in the photolyzed *tert*-butyl peroxylaurate.

We have also discovered some striking effects caused by a

small pyridine impurity such as was present in the peresters studied originally. Those peresters were prepared by the pyridine-acylation method of Silbert and Swern³ and the recrystallization procedure of that method does not remove the pyridine completely. When we came to suspect the effects of that slight impurity, we were able to remove it completely by chromatography on a silica gel column, using a 10% solution of diethyl ether in petroleum ether as eluting agent.⁴

The UV spectrum of *tert*-butyl peroxylaurate reported in the original work¹ showed a band at 2700 Å. That band is spurious and disappears when the perester is completely freed of pyridine. The highly purified perester has a structureless spectrum in the range 3000–2100 Å, the absorbance rising smoothly with decreasing wavelength. Pyridine has a strong band close to 2700 Å ($\epsilon \sim 3000$).⁵ The very strong absorption by the pyridine in that spectral region plays an important role when peresters are photolyzed with 2537-Å radiation.

The radiation photolyzes the pyridine as well as the perester and produces a coloration that progresses from yellow to reddish brown during the process. The strong absorption by the pyridine also diminishes the quantum yield of decomposition of the perester. The value of ϕ_D for the *tert*-butyl peroxylaurate was 1.76 in the original work¹ but rose to 7.0 at the same radiation intensity with the pyridine-free perester. In the absence of pyridine the photolyzed perester was colorless and the ϕ_D value was not lowered by saturation of the perester with oxygen gas.

The rate of photodecomposition of the chromatographed *tert*-butyl peroxylaurate followed a three-halves-order dependence on the perester concentration over times up to 3 h. Since that kinetic behavior and the high ϕ_D value indicated a chain reaction, EPR spectroscopy was used to detect any radicals produced during photolysis. The neat perester was photolyzed directly in the spectrometer cavity at 10 °C. A single-line spectrum was observed and the radical was apparently an alkyl peroxy radical ($g = 2.0150$, peak-to-peak width ~6 G). It was observed that if pyridine was present the signal was enhanced, showing a stabilization of the radical. Such stabilization might be expected to lower the induced decomposition of the perester.

References and Notes

- (1) W. H. Simpson and J. G. Miller, *J. Am. Chem. Soc.*, **90**, 4093 (1968).
 (2) Details of the reinvestigation are given in the Ph.D. Dissertation of John J. Davis, University of Pennsylvania, 1975.
 (3) L. S. Silbert and D. Swern, *J. Am. Chem. Soc.*, **81**, 2364 (1959).
 (4) We are grateful to L. S. Silbert for suggesting this method of pyridine removal.
 (5) A. Albert, "Heterocyclic Chemistry", 2nd ed, Athlone Press, London, 1968, pp 401, 415.

John J. Davis, John G. Miller*

Department of Chemistry, University of Pennsylvania
 Philadelphia, Pennsylvania 19174

Received September 28, 1976

Photolysis of Organopolysilanes. Formation and Reactions of Substituted 1-Silacyclopentene and 1-Sila-1,2-propadiene

Sir:

Despite widespread interest in the photochemical studies of the organopolysilanes,¹⁻⁵ there have been no reports of the photolysis of 1-alkynylpolysilanes. Recently we demonstrated that irradiation of vinylsilanes produces reactive silicon-carbon double-bonded intermediates in high yields via photorearrangement of a silyl group to the terminal carbon of a vinyl group.⁶ In this communication we report a novel photo-