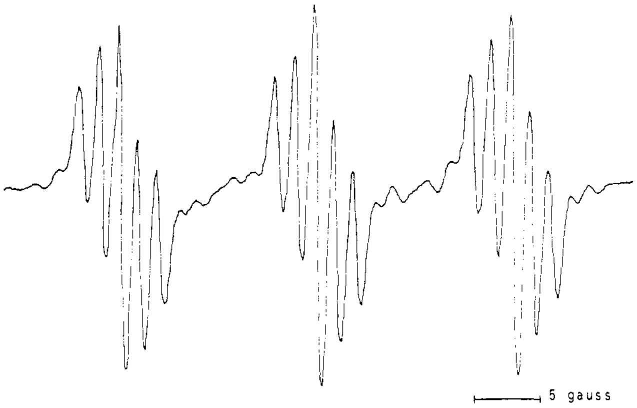
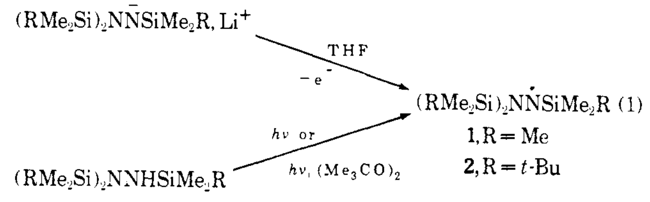
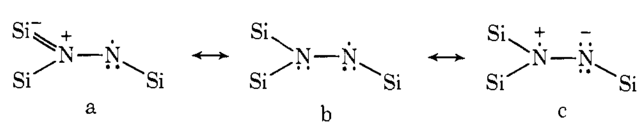


Figure 1. Esr spectrum of new radical from photolysis of tris(trimethylsilyl)hydrazine, believed to be tetrakis(trimethylsilyl)triazyl, $(Me_3Si)_2N\dot{N}N(SiMe_3)_2$.

methylsilyl)hydrazyl (**2**) were obtained[4] by two general methods: (1) electrolytic oxidation of a dilute solution of the lithium salt of the parent hydrazine in THF, and (2) ultraviolet photolysis of the parent hydrazine,[5] with or without the assistance of di-*tert*-butyl peroxide[6] (eq 1). Hydrazyls **1** and **2** are far more stable than the alkylhydrazyls. Apparent half-times for decomposition, which is approximately first order for several lifetimes, are 25 min for **1** and 30 hr for **2**, at 30°.



The esr spectrum of **1** consists of nine lines attributed to interaction of the unpaired electron with two nonequivalent nitrogens, with a_N values of 11.1 and 4.2 G. The spectrum of **2** is almost identical with a_N values of 11.2 and 4.3 G. The large difference between the a_N values is unprecedented (compare DPPH, a_N = 9.65 and 8.03 G,[7] and other data in ref 2) and suggests marked restriction of the spin density to one nitrogen (we believe to the monosubstituted nitrogen). Such localization of spin could result from lone-pair delocalization from the disubstituted nitrogen onto silicon through dative bonding, as proposed earlier to explain the unusual esr spectra of organometal-substituted nitroxides.[8] In valence bond notation, this would be represented by a significant contribution of canonical forms like a to the resonance hybrid.



Photolysis of tris(trimethylsilyl)hydrazine (**3**) for an extended period in the presence of di-*tert*-butyl peroxide led also to the formation of secondary radical products. When **3** was photolyzed for 1 hr and then allowed to stand in the dark for 10 hr to permit decay of **1**, the esr spectrum shown in Figure 1 was obtained. The spectrum shows coupling of the unpaired electron with two equivalent and one unique nitrogen atoms (a_N = 14.6 and 1.48 G). Side bands attributable to hyperfine interaction with ^{29}Si are also observed; these have the proper intensity for coupling with *four* equivalent silicon atoms. The new spectrum is tentatively assigned to the tetrakis(trimethylsilyl)triazyl radical, $(Me_3Si)_2N\dot{N}N(SiMe_3)_2$; if this assignment is correct this is the first triazyl radical to be observed.[9] Our continuing research will examine the reasons for the relative stability of these radical systems and explore for other new organometallic hydrazyls.[10]

---

(4) All experiments were carried out after extensive degassing of the sample by the freeze-thaw method utilizing a high vacuum system.

(5) (a) U. Wannagat and H. Niederprüm, *Z. Anorg. Allg. Chem.*, 310, 32 (1961). (b) Satisfactory elemental analyses and nmr, ir, and mass spectra were obtained for the new compound tris(*tert*-butyldimethylsilyl)hydrazine.

(6) The hydrazines were photolyzed with a General Electric 100-W mercury spot lamp focused on a Suprasil quartz tube esr cell. Radical 1 was generated from a neat or di-*tert*-butyl peroxide (DTBP) solution of the parent hydrazine; radical 2 was generated either from hydrocarbon solution with or without the aid of DTBP or from DTBP solution.

(7) Yu. M. Ryzhmanov, Yu. V. Yablokov, B. M. Kozyrev, R. O. Matevosyan, and L. I. Stashkov, *Dokl. Akad. Nauk SSSR*, **156**, 106 (1964).

(8) R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, **93**, 5901 (1971).

(9) Triazyl radicals have, however, been proposed as reaction intermediates. See L. Holleck and G. Kazemifrad, *Monatsh. Chem.*, **103**, 1427 (1972); J. Hollaender, W. P. Neumann, and G. Alester, *Chem. Ber.*, 105, 1540 (1972).

(10) Note Added in Proof. Very recently bicyclic hydrazyls have been reported (S. F. Nelson and R. T. R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 6454 (1973)), and 1,1-dialkylhydrazyls have been detected in solution by esr (V. Malatesta and K. U. Ingold, *ibid.*, **95**, 6110 (1973)).

Robert West,* Blake Bichlmeir
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received June 22, 1973

Viscosity Dependence of the Nitropentaamminecobalt(III) Photochemistry. Evidence for Radical Cage Recombination

Sir:

The photochemistry of Co(III) complexes is characterized by the extensive occurrence of redox decomposition reactions.[1-3] It is now generally agreed that the redox decomposition arises from a homolytic metal–ligand bond fission occurring in excited states of ligand-to-metal charge transfer (LMCT) character. However, since the earlier investigations in this field, there has been some dispute on the mechanism of the redox decomposition process.[3-10] Although the terms of the dispute have often been ambiguously stated,[11] it

---

(1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y, 1970.

(2) V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta Rev.*, 1, 7 (1967).

(3) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

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

(5) J. F. Endicott, *Isr. J. Chem.*, **8**, 209 (1970).

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

(7) R. D. Lindholm and T. K. Hall, *J. Amer. Chem. Soc.*, **93**, 3525 (1971).

(8) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970).

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

(10) D. Valentine, *Advan. Photochem.*, **6**, 186 (1968).

(11) Most of the ambiguity stems from the fact the term "radical pair mechanism" has assumed a dual meaning, *i.e.*, that (i) all LMCT states of Co(III) complexes quantitatively dissociate to give a radical pair (in other words, a LMCT state is just equivalent to a radical pair) and (ii) the radical pair formed from bond homolysis of a LMCT state can undergo radical cage recombination and/or back electron transfer. Actually, the two points are quite independent from one another, and separate criticisms are needed in any discussion of this mechanism.

seems that the most controversial point concerns whether[6,8] or not[5,10] the radical pair generated by the excited-state homolytic bond fission can undergo geminate recombination or back electron transfer during the solvent cage lifetime.

In most Co(III) complexes, the occurrence of a radical geminate recombination process would only have the effect of lowering the observed redox quantum yields with respect to the (unknown) primary dissociation yields. In Co(III) complexes containing ligands which can bind to the metal through two different donor atoms (ambidentate ligands), however, a radical geminate recombination could also have qualitative consequences, *i.e.*, it could provide a route to linkage photoisomerization. As a matter of fact, simultaneous redox decomposition and nitro–nitrito linkage isomerization were observed following irradiation of $Co(NH_3)_5NO_2^{2+}$ in aqueous solution.[9] This behavior was explained assuming that homolytic $Co-NO_2$ bond fission in a LMCT excited state was the common primary photoprocess for both photoreactions and that redox decomposition arose because of the diffusion apart of the primary radical pair, while linkage isomerization was the result of a geminate recombination process occurring through the oxygen atom of the NO_2 radical.[9,12] A rather similar behavior was observed by Hoffman and coworkers for the isoelectronic $Co(NH_3)_5O_2CH^{2+}$ ion.[13,14] In this case, however, a different mechanism was proposed which considered redox decomposition and O-bonded to C-bonded linkage isomerization of the formato ligand essentially as uncoupled processes arising from different excited states of the complex (LMCT and ligand-centered excited states, respectively).[13,14]

In the course of mechanistic studies of homolytic organic reactions (both thermal and photochemical), the effect of solvent viscosity on reaction rates has often been a useful tool in order to establish the presence of a cage recombination effect.[15,16] It seems likely that similar studies can be valuable to establish whether cage recombination can take place in the photochemistry of Co(III) complexes. We wish to report here the results of a viscosity dependence investigation carried out on the $Co(NH_3)_5NO_2^{2+}$ ion.

The quantum yields of redox decomposition and of linkage isomerization have been determined[17] in various water–glycerol solvent mixtures using 365-nm exciting radiations. The results obtained are shown in Figure 1. The increase in the glycerol content of the irradiated solutions brings about an evident increase in the photoisomerization quantum yields and a corresponding decrease in the redox quantum yields. It does not seem plausible to ascribe the observed behavior to any specific chemical effect of glycerol on the photoreactions. It should be noticed that a change of solvent from water to 50% water–ethanol only causes a small *increase* (about 20%) in the photoredox quantum yields of $Co(NH_3)_5NO_2^{2+}$.[12] On the other hand, physical effects of the solvent composition on excited-state lifetimes of the complex cannot be responsible for the observed behavior, since opposite dependencies are found for the two photoprocesses. Thus, it seems safe to conclude that the observed trend in photoredox and photoisomerization quantum yields is the result of viscosity effects alone.

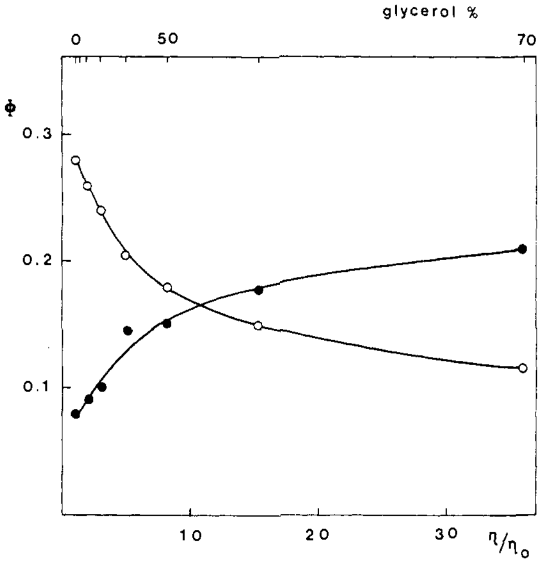


Figure 1. Effect of the solvent on the photoredox (○) and photoisomerization (●) quantum yields of $Co(NH_3)_5NO_2^{2+}$: upper scale, volume per cent of glycerol in the glycerol–water solvent system; lower scale, viscosity of the solvent relative to that of pure water.

Likely mechanistic implications of the viscosity dependence shown in Figure 1 are the following: (i) redox decomposition competes with cage recombination of the radical pair generated by the primary homolytic bond splitting, (ii) linkage isomerization is the result of a geminate recombination process between two primarily produced species, (iii) the two processes directly compete with one another. Thus, it is to be concluded that redox decomposition and linkage isomerization are coupled processes which most probably follow a primary homolytic $Co-NO_2$ bond splitting occurring in a LMCT state of $Co(NH_3)_5NO_2^{2+}$. Diffusion apart of the resulting radical pair gives rise to redox decomposition, while cage recombination accounts for the linkage isomerization process. The experimental results clearly rule out in this case a mechanism in which the two photoprocesses are independently generated by different excited states of the complex.

No attempt has been performed to fit the observed viscosity dependence to any one of the existing cage effect theories.[16] In the present case, no good agreement should be expected with theoretical models because of the preferential solvation of the complex ions by water in the mixed solvent system used. This effect would make the solvent very inhomogeneous in the

---

[12] F. Scandola, C. Bartocci, and M. A. Scandola, submitted for publication.

[13] A. D. Vaudo, E. R. Kantrowitz, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **93**, 6698 (1971).

[14] E. R. Kantrowitz, M. Z. Hoffman, and K. M. Schilling, *J. Phys. Chem.*, **76**, 2492 (1972).

[15] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

[16] J. P. Lorand in "Inorganic Reaction Mechanisms," J. O. Edwards, Ed., Interscience, New York, N. Y., 1972, p 207.

[17] For details of experimental procedures and product analyses, see ref 9 and 12. The irradiated solutions always contained 10^{-3} *M* $[Co(NH_3)_5NO_2](NO_3)_2$ and 10^{-2} *M* $HClO_4$. The solutions were thermostated at 20° during irradiation. The calibration plots for Co^{2+} analyses were always measured in the same experimental conditions used for photochemical experiments. Particular care was used to ensure efficient stirring of the irradiated solutions with a vigorous stream of pure nitrogen.

immediate neighborhood of the complex ions with microscopic viscosity values lower than the macroscopic mean one and dependent on the distance from the complex. For this very reason, the observed results cannot be used to test the earlier proposal[9,12] that the cage recombination is in this case a "secondary" rather than a "primary" [16] one.

The results of this work show that cage recombination of the radical pair generated by excited-state bond homolysis is important in the photochemistry of $Co(NH_3)_5NO_2^{2+}$. Of course, the observed behavior is not meant to be a general rule for all Co(III) complexes. It might well be that in other complexes, especially in those where LMCT excited states are not dissociative with respect to one metal–ligand coordinate, radical recombination is unimportant. In any case, it seems likely that the study of the dependence of photoreaction quantum yields on solvent viscosity, if properly separated from other possible accompanying effects, could be of considerable diagnostic value.

Acknowledgment. We wish to thank Professor V. Balzani of the University of Bologna and Professor V. Carassiti of this Institute for helpful discussions and criticism.

Franco Scandola,* Carlo Bartocci, Maria Anita Scandola
Istituto Chimico dell' Università
Centro di Studio sulla Fotochimica e Reattività degli Stati
Eccitati dei Composti di Coordinazione del C.N.R.
Ferrara, Italy

Received July 31, 1973

Additional Channel for Singlet–Triplet Intersystem Crossing in Unsaturated Aldehydes. 5-Hexenal[1]

Sir:

Primary photochemical processes of unconjugated olefinic aldehydes have been little studied,[2] although those of conjugated aldehydes, such as acrolein[3] and crotonaldehyde,[4] have been much studied in detail. In the former classes of simple aldehydes, there are two seemingly isolated, potentially reactive sites as well as two low-lying triplet states, the $^3(n,\pi^*)$ state of the carbonyl group and $^3(\pi,\pi^*)$ state of the olefinic group. This interesting molecular electronic feature led us to study the primary photochemical transformation mechanism of 5-hexenal which would reflect the difference in the probabilities of populating the two triplet states and that in chemical reactivities of the two triplet states. The experiments were carried out in the gas phase at low pressures in order to minimize the collisional effects on the product formation yields.

5-Hexenal has an allylic γ hydrogen, and therefore it is expected to undergo an efficient Norrish type II process, as numerous carbonyl compounds do. At 312 nm, the type II photoelimination product quantum yield of 1-butene from *n*-hexanal is 0.23 ± 0.03, whereas that of 1,3-butadiene from 5-hexenal is 0.36 ± 0.03 of which 0.23 ± 0.03 is attributable to the singlet yield and 0.13 ± 0.02 to the triplet yield. At 254 nm, the yields of 1-butene and 1,3-butadiene are 0.26 ± 0.03 and 0.35 ± 0.03, respectively, indicating little change if any. The yield of propylene (and acrolein) from 5-hexenal is 0.25 ± 0.05 at 312 nm and 0.22 at 254 nm. The triplet benzene ($^3B_{1u}$, 84.4 kcal/mol) sensitized decomposition of 5-hexenal gives the following quantum efficiency[5] values: propylene = 0.09 ± 0.01 and 1,3-butadiene = 0.72 ± 0.07.

Fluorescence quantum yields, Φ_F, and fluorescence decay times, τ_F, obtained for *n*-hexanal and 5-hexenal are shown in Table I. For 5-hexenal, values of τ_F at wavelengths less than 330 nm were too short (<1.5 nsec) to be measured directly. However, if it is assumed that the radiative rate constant, k_F, varies little throughout the $\pi^* \leftarrow n$ absorption band, then the value of τ_F at 312 nm may be estimated as 6×10^{-10} sec, where $\tau_F(312 \text{ nm}) = \Phi_F(312 \text{ nm})/k_F$ and $k_F = \Phi_F(330 \text{ nm})/\tau_F(330 \text{ nm})$.

Table I. Fluorescence Properties[a]

Aldehyde	λ_{ex}, nm	$10^{-4}\Phi_F$	τ_F, nsec
n-Hexanal	330	(4 ± 1)	3.3 ± 0.3
	312	(1.8 ± 0.2)	2.2 ± 0.3
5-Hexenal	330	(3 ± 1)	2.4 ± 0.3
	312	(0.8 ± 0.1)	

[a] 10 Torr aldehyde plus 2 Torr oxygen.

Knowledge of τ_F and Φ_{II}^s, the singlet type II quantum yield, allows the calculation of the rate constants for the singlet type II process, $k_{II}^s(312 \text{ nm}) = \Phi_{II}^s(312 \text{ nm})/\tau_F(312 \text{ nm})$: 3.7×10^8 sec^{-1} for 5-hexenal, and 1.0×10^8 sec^{-1} for *n*-hexanal. The four times faster rate constant for 5-hexenal may be rationalized in terms of a more facile γ-hydrogen abstraction since the bond energy of an allylic C–H is ~6 kcal/mol less than that of a secondary C–H bond.[6]

Whether or not the enhanced type II reactivity of 5-hexenal is solely responsible for its factor of 2 smaller fluorescence quantum yield relative to *n*-hexanal over the wavelength interval studied may be examined in the following way. The fluorescence quantum yield may be defined as

$$\Phi_F = k_F/(k_F + k_{II}^s + k_\alpha^s + k_{ISC} + k_{IC}) \qquad (1)$$

where the expected predominant reactive pathways are represented by the rate constants k_α^s, for α cleavage, and k_{II}^s. Rates of unimolecular nonradiative processes are given by k_{ISC} for intersystem crossing and k_{IC} for internal conversion. Substituting the known values of Φ_F, k_F, and k_{II}^s for 5-hexenal and *n*-hexanal at 312 nm into eq 1 yields the value of $(k_\alpha^s + k_{ISC} + k_{IC})$ to be $\sim 13 \times 10^8$ sec^{-1} for 5-hexenal and $\sim 4 \times 10^8$ sec^{-1} for *n*-hexanal.

Because the terminal olefinic group of 5-hexenal

---

[1] This research has been supported by National Science Foundation Grant GP 28010X.

[2] (a) J. N. Butler, A. T. Drake, J. C. Mitchell, and P. Singh, *Can. J. Chem.*, 41, 2704 (1963); (b) R. F. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *ibid.*, 43, 1934 (1965); (c) N. E. Lee and E. K. C. Lee, *J. Phys. Chem.*, 71, 1167 (1967).

[3] (a) J. W. Coomber and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, 91, 547 (1969); (b) R. S. Becker, K. Inozuka, and J. King, *J. Chem. Phys.*, 52, 5164 (1970).

[4] (a) E. R. Allen and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, 91, 3135 (1969); (b) J. W. Coomber and J. N. Pitts, Jr., 91, 4955 (1969).

[5] E. K. C. Lee in "Excited State Chemistry, A Symposium," J. N. Pitts, Jr., Ed., Gordon and Breach, New York, N. Y., 1970, p 59.

[6] (a) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, 91, 2136 (1969); (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967, Table A-5.