Orme-Johnson, and H. Beinert, *Proc. Natl. Acad. Sci. U.S.A.*, **66**, 1157–1163 (1970). (b) J. D. Lipscomb, Ph.D. Thesis, University of Illinois, 1974; *Biochemistry*, in press.

(13) The details of our X-band EPR–ENDOR spectrometer are given elsewhere.[15] The measurements were made at liquid helium temperatures with EPR in the 9.1–9.2-GHz range. For both EPR and ENDOR we used 100-KHz field modulation with amplitude ~1 G peak to peak for the ^{14}N and ^{1}H ENDOR of Figures 1 and 2, and for Figure 3 ~0.3 G for the weakly coupled ^{1}H's. The amplitude of the radiofrequency power used for ENDOR was ~0.5 G peak to peak with the microwave power of ~10 μW.

(14) Cytochrome $P450_{CAM}$ was isolated in the m^{os} state from *P. putida* (ATCC 29607) by established procedures;[3] for m^{o}, camphor was removed by the two-step gel filtration technique.[3] H/D exchanged samples were prepared by dialysis vs. H or D solvents (10:1, v/v), with multiple changes over 24 h in sealed chambers. Solutes for deuterated buffers were exchanged with D_2O (99.98%) prior to dialysis.

(15) (a) C. P. Scholes, R. A. Isaacson, and G. Feher, *Biochim. Biophys. Acta*, **263**, 448–452(1972); (b) H. L. Van Camp, C. P. Scholes, and R. A. Isaacson, *Rev. Sci. Instrum.*, **47**, 516–517 (1976); (c) H. L. Van Camp, C. P. Scholes, C. F. Mulks, and W. S. Caughey, *J. Am. Chem. Soc.*, **99**, 8283–8290 (1977); (d) C. F. Mulks, C. P. Scholes, L. C. Dickinson, and A. Lapidot, *ibid.*, **101**, 1645–1654 (1979).

(16) (a) G. A. Helcké, D. J. E. Ingram, and E. F. Slade, *Proc. R. Soc. London, Ser. B.*, **169**, 275–288 (1968); (b) C. Mailer and C. P. S. Taylor, *Can. J. Biochem.*, **50**, 1048–1055 (1972); (c) H. Hori, *Biochim. Biophys. Acta*, **251**, 227–235 (1971).

(17) A detailed study of proton resonances in m^{o} with weak couplings, within ±1 MHz of the free proton frequency, shows an exchangeable proton with a hyperfine coupling of ~1.3 MHz.

(18) (a) J. E. Bennett, J. F. Gibson, D. J. E. Ingram, T. M. Haughton, G. A. Kerkut, and K. A. Munday, *Proc. R. Soc. London, Ser. A*, **262**, 395–408 (1961); (b) M. Kotani and H. Morimoto in "Magnetic Resonance in Biological Systems", A. Ehrenberg, G. B. Malmström, and T. Vänngard, Eds., Pergamon Press, Oxford, 1967, pp135–140.

(19) As reported in ref 15c, we found that weakly liganding solvent molecules like THF (tetrahydrofuran) and Me_2SO (dimethyl sulfoxide) can act as sixth ligands for high-spin ferric hemes. ENDOR was observed from protons on THF and Me_2SO, and the heme meso proton splittings in the presence of these solvents were remarkably similar to the splittings for six-coordinate heme proteins.

(20) Proto- and deuterohemin esters were studied[15c] as the five-coordinate, axially liganded derivatives. To prevent aggregation, a solvent mixture containing $CHCl_3$–CH_2Cl_2 plus diamagnetic mesoporphyrin ester was used. With the corresponding ferric derivatives of octaethylporphyrin, $CHCl_3$–CH_2Cl_2 alone will suffice to prevent aggregation, and the meso proton couplings observed are identical to within 0.02 MHz with those from the respective five-coordinate proto- and deuterohemins.

Russell LoBrutto, Charles P. Scholes*
Department of Physics and
Center for Biological Macromolecules
State University of New York at Albany
Albany, New York 12222

Gerald C. Wagner, I. C. Gunsalus
Department of Biochemistry, University of Illinois
Urbana, Illinois 61801

Peter G. Debrunner
Department of Physics, University of Illinois
Urbana, Illinois 61801

Received September 20, 1979

Applications of Light-Induced Electron-Transfer Reactions: Generation and Reaction of Ag^0 in Solution via Visible Light Photolysis of $Ru(bpy)_3{}^{2+}$

Sir:

Several investigations have shown that the effective oxidizing and reducing power of excited states of a wide variety of compounds including aromatic hydrocarbons, dyes, and transition-metal complexes is increased upon electronic excitation by an amount effectively equal to the relaxed excited-state energy.[1-5] Thus for excited states of a complex such as the much investigated tris(2,2′-bipyridine)ruthenium(II)$^{2+}$, $Ru(bpy)_3{}^{2+}$, reduction of substrates having potentials $E_{1/2}[S^{n+/(n-1)+}] \geq -0.81$ V is energetically favorable and generally extremely rapid with typical rates near the diffusion controlled limit.[3] Examination of polarographic data suggests that Ag^+ might be expected to be a good substrate for oxidative quenching of $Ru(bpy)_3{}^{2+*}$ since its half-wave reduction potential is in the range of +0.4 to +0.8 V[6] where rapid and efficient reduction is expected. However, measured reduction potentials for Ag^+ link the cation and metallic solid; when the reduction is carried out in dilute homogeneous solution, the initial species generated should be atomic silver which is clearly of much higher energy and likely of different reactivity than the metal. In the present paper, we report a study of quenching of $Ru(bpy)_3{}^{2+*}$ by Ag^+ in acetonitrile and aqueous solution. Our results indicate that effective quenching does occur but with much lower rates than predicted by reduction potentials. The results further indicate that the reduced silver species generated is extremely reactive and suggest that the techniques used can be extended for the generation and study of dispersed reactive atomic species by oxidation or reduction of other soluble ions.

Irradiation of solutions containing $Ru(bpy)_3{}^{2+}$ and $AgNO_3$, $AgClO_4$, or $Ag(bpy)_2{}^+$ in acetonitrile or water with visible or near-UV light results in quenching of the strong $Ru(bpy)_3{}^{2+}$ luminescence but no permanent chemistry.[7,8] For both solvent systems, linear Stern–Volmer plots are obtained with low to moderate concentrations of Ag^+. However, in aqueous solution there is a positive deviation with Ag^+ concentrations >1.5 M which suggests some ground-state complex formation at these levels.[9] Quenching constants obtained are 1.1×10^5 M^{-1} s^{-1} for both $AgNO_3$ and $AgClO_4$ in acetonitrile and 3.5×10^6 M^{-1} s^{-1} for $AgClO_4$ in water. The silver(I) complex, $Ag(bpy)_2{}^+$, is a somewhat better quencher in acetonitrile giving $k_q = 1.5 \times 10^6$ M^{-1} s^{-1}. Although no permanent products are formed at high Ag^+ concentrations, flash photolysis indicates a transient bleaching of the $Ru(bpy)_3{}^{2+}$ consistent with that observed in other cases where oxidative quenching occurs;[3,11] the regeneration of the spectrum follows equal concentration second-order kinetics giving $k_r = 5.5 \times 10^9$ and 1.2×10^{10} M^{-1} s^{-1} for $AgNO_3$-acetonitrile and $AgClO_4$-water, respectively. While no permanent products are produced in these cases, addition of low concentrations (1×10^{-2} M) of triethylamine [in the range where quenching of $Ru(bpy)_3{}^{2+*}$ by triethylamine is negligible][12] to solutions containing $Ru(bpy)_3{}^{2+}$ and $AgNO_3$ or $AgClO_4$ in acetonitrile results in the formation of colloidal silver or silver mirrors upon irradiation with visible-near-UV light. A study of the irradiation of acetonitrile solutions of $Ru(bpy)_3{}^{2+}/AgNO_3$ in an ESR cavity at 25 °C led to no detectable signals either in the absence or presence of triethylamine.

The results are most consistent with a transient reduction of Ag^+ ions by the excited complex, $Ru(bpy)_3{}^{2+*}$, as outlined in eq 1-6. Reaction 2 has been previously studied via pulse radiolysis techniques and found to have a rate constant of $k_2 = 5.9 \times 10^9$ M^{-1} s^{-1};[13] thus, under conditions used in the present study, conversion of Ag^0 to $Ag_2{}^+$ should dominate all other reactions and the observed back-reaction most likely is that given by eq 3. Addition of triethylamine has been previously shown to scavenge the oxidized complex, $Ru(bpy)_3{}^{3+}$, in competition with the normal back-electron transfer (eq 3 and 4);[14] in this case the use of the scavenger permits $Ag_2{}^+$ to survive long enough for agglomeration or aging processes leading to metallic silver to occur.

$$Ru(bpy)_3{}^{2+*} + Ag^+ \rightarrow Ru(bpy)_3{}^{3+} + Ag^0 \tag{1}$$

$$Ag^0 + Ag^+ \rightarrow Ag_2{}^+ \tag{2}$$

$$Ag_2{}^+ + Ru(bpy)_3{}^{3+} \rightarrow Ru(bpy)_3{}^{2+} + 2Ag^+ \tag{3}$$

$$Ru(bpy)_3{}^{3+} + Et_3N\colon \rightarrow Ru(bpy)_3{}^{2+} + Et_3N^+ \tag{4}$$

$$Et_3N^+\cdot \rightarrow \text{products} \tag{5}$$

$$Ag_2{}^+ \rightarrow \rightarrow Ag_{(s)} \tag{6}$$

0002-7863/80/1502-1170$01.00/0

The rapid rates of back electron transfer indicate the Ag^0 and Ag_2^+ species generated via electron transfer in solutions are extremely reactive reagents which should be capable of reacting with a variety of substrates that are either inert or sluggishly reactive toward metallic silver. The measured quenching rates permit an assessment of the energetics of the silver ion reduction if we assume that the retardation of the rate below the diffusion controlled limit is attributable to a free energy of activation equal to the endoergonicity of the quenching step (eq 1).[15-17] Thus for the reduction (eq 7) we

$$Ag_{(solv)}^+ + e \rightarrow Ag_{(solv)}^0 \qquad (7)$$

obtain potentials of −1.05 to −1.11 V in acetonitrile and −0.96 to −1.02 V in water.[15] Comparing these values to the measured Ag^+ metal reduction potentials indicates that the metal is more stable than the reduced soluble species by 31-44 kcal/mol. The values thus estimated are considerably below the sublimation energy of ~60 kcal/mol[18,19] indicating that solvation by water or acetonitrile stabilizes the metal atom to at least some extent.[20] Interestingly, related experiments on the photoinduced reduction of complexed Ag^+ ions suggest that the stability of Ag^0 complexes can cause profound changes in its redox reactivity toward reagents such as $Ru(bpy)_3^{3+}$.[21]

The results obtained in the photolysis study are somewhat related to recent investigations of silver ion reduction in solution initiated by pulse radiolysis (γ-radiation or electrons).[13,18,22] However, in the present study the reduced silver species can be generated under very mild conditions and in the presence of reagents which might not survive in radiolysis experiments. The use of scavengers to avert the back-reaction provides the possibility of increasing the lifetime of the reactive reduced species and to allow its interception by other substrates. The utility of reactive metal species in a number of synthetic applications has been demonstrated by Rieke,[23] Skell,[24] and Klabunde[25] using very different methods of generation. The general techniques used in the present study should be useful for reducing a number of monovalent metal ions to reactive atomic or subaggregate species, including those from copper, thallium, and mercury.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 7823126) for support of this work. Photochemical ESR studies at the CNRS Laboratories in Gif-sur-Yvette, France, were made possible via a NATO award.

References and Notes

(1) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).
(2) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
(3) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 2909 (1978).
(4) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, **99**, 241 (1977).
(5) R. Ballardini, G. Varani, M. T. Indelli, F. Scandola, and V. Balzani, *J. Am. Chem. Soc.*, **100**, 7219 (1978).
(6) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, 1970, p 479.
(7) Some substitution is observed on long-term irradiation. The mechanism of this process is under investigation.
(8) The $Ru(bpy)_3^{2+}$ concentration used in these studies was ~2 × 10^{-5} M.
(9) Ground-state complex formation is much more prominent with neutral complexes such as $Ru(bpy)_2(CN)_2$; the chemistry of these luminescent complexes with Ag^+ is under investigation.[10]
(10) M. Kinnaird, unpublished results.
(11) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974).
(12) P. J. Delaive, B. P. Sullivan, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **101**, 4007 (1979).
(13) J. Pukies, W. Roekke, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **72**, 842 (1968)
(14) P. J. DeLaive, C. Giannotti, and D. G. Whitten, *J. Am. Chem. Soc.*, **100**, 7413 (1978).
(15) The Sandros equation[16] $\Delta \log k = -\Delta E_{1/2}/2.3RT$ was used to calculate the $E_{1/2}$ values, assuming that $k_{lim} \approx 5 \times 10^9\ M^{-1}\ s^{-1}$ and $E_{1/2}$ for the couple $Ru^{3+/2+} = -0.81$ V.[11] The values obtained are therefore lower limits for the potentials.
(16) K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964).
(17) A study of the quenching of $Ru(bpy)_3^{2+*}$ in water over the temperature range 23-50 °C indicates a very low Arrhenius activation energy (~0.6 kcal/mol) suggesting that the quenching is entropically controlled.
(18) A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **81**, 556 (1977).
(19) W. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions", Prentice-Hall, Englewood Cliffs, N.J., 1952, p 190.
(20) This is probably a lower limit on the stabilization obtained, since the above calculation would give a potential for reaction 7 too high if an extra activation energy is involved.
(21) M. Grätzel, private communication. We thank Professor Grätzel for information about his study.
(22) M. C. R. Symons, D. R. Brown, and G. W. Eastland, *Chem. Phys. Lett.*, **61**, 92 (1979).
(23) R. D. Rieke, *Top. Curr. Chem.*, **59**, 1 (1975); R. D. Rieke, W. T. Wolf, N. Kujandzic, and A. V. Kavaliunas, *J. Am. Chem. Soc.*, **99**, 4159 (1977).
(24) P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein, and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 2829 (1965); P. S. Sekll and M. J. McGlinchey, *Angew. Chem.*, **87**, 215 (1975).
(25) K. J. Klabunde, J. Y. F. Low, and H. F. Efner, *J. Am. Chem. Soc.*, **96**, 1984 (1974).
(26) Institut de Chimie des Substances Naturelles, 91190 Gif-sur-Yvette, France.

Thomas K. Foreman, C. Giannotti,[26] David G. Whitten*
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received July 25, 1979

Photochemical or Photomimetic Fossil Triterpenoids in Sediments and Petroleum

Sir:

During a study of the sediments deposited in the delta of the Mahakam river, off the east coast of Borneo, we have encountered a series of fossil triterpenoids, the nature of which discloses the operation of a novel mechanism of early geochemical maturation: decay of excited ketones.

Precise structural characterization of products of the transformation or degradation of biological molecules has proven quite useful in the elucidation of the origin of the geological organic matter and of the (geo)chemical processes occurring in sediments at various stages of their maturation.[1,2] These processes, which start in the recent sediment, lead over geological periods to the formation of fossil energy sources, such as petroleum, gas, and coal.[3,4]

Most of the complex alicyclic molecular fossils identified so far in sediments (including petroleums, coals, shales etc.) are derivatives of the 3-deoxyhopane triterpene family, of microbiological origin.[5] Other triterpenoids, derived from 3-hydroxy constituents of higher plants, are sometimes found, and are considered as indicators of continental influences.[6,7] One such derivative of β-amyrin (**1**) has recently been identified in several recent and ancient sediments and crude oils.[8] The process leading to the loss of ring A, in **1**, was mysterious. Results described below appear to explain it.

Off the coast of as densely forested an island as Borneo, in the deltaic recent sediments (2-30% organic carbon) of a large river, dating from the present to a few thousand years at the most, continental impact should be large, and this is reflected by the isolation of a series of triterpene ketones in the nonpolar neutral fraction by our standard procedure.[9] Friedelin, α-amyrenone, β-amyrenone, and lupenone are frequent constituents of higher plants, notably of tree barks, or could have been formed by trivial oxidation of the corresponding 3-alcohols, ubiquitous in green plants. However, these ketones are accompanied, in particular in the same fraction or in the acidic and hydrocarbon fractions, by a homogeneous genetic family of products, *obtainable by photochemical decomposition of the 3-ketones*[10,11] (Figure 1). Indeed this is the way we have prepared most of the authentic reference samples to identify these products (Figure 2). A quantitative comparison of the results of the photochemical reaction with the relative abundance of the fossil substances is, in this case, meaningless, as