Effect of Solvent Medium on the Photoreduction of Cobalt(III) Complexes

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The photochemical behaviour at 365 nm of $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(N_3)]^{2+}$ has been investigated in aqueous media containing added hydroxylic solvents to examine the role of solvent viscosity in determining the extent of radical breakdown, Φ(redox) (and also, in the case of the nitro-complex, linkage isomerization). In agreement with earlier findings, Φ(redox) decreases by >30% on addition of glycerol or ethylene glycol, but to interpret this effect as purely due to changing viscosity is an oversimplification, for the addition of cyclohexanol to give the same relative viscosity leaves Φ(redox) unchanged. Evidently a more specific role exists for the added solvent. The effect of adding synthetic polymers to give high viscosities again leaves Φ(redox) unaffected, but this may simply reflect the heterogeneous nature of polymer solutions.

COBALT(III) ammine complexes undergo redox reaction on irradiation in the charge-transfer bands and the mechanism of the photochemical reaction has been investigated in considerable detail.[1,2] Until recently, photoreactions of cobalt(III) complexes were studied mainly in acidic aqueous solutions in which these complexes are soluble. Studies of such reactions of ammineaniono-complexes of Co^{III} in solvents containing water and alcohol have indicated a variation of the quantum yield for Co^{II} with the bulk viscosity of the solvent, and a mechanism involving a solvent cage was envisaged.[3-5] The following general reaction scheme was proposed. Species (I) is a geminate pair of radicals,

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[1] V. Balzani and V. Carassiti, 'Photochemistry of Coordination Compounds,' Academic Press, New York, 1970.

[2] J. F. Endicott in 'Concepts in Inorganic Photochemistry,' eds. A. W. Adamson and P. D. Fleisauer, Wiley, New York, 1975.

[3] F. Scandola, C. Bartocci, and M. A. Scandola, *J. Amer. Chem. Soc.*, 1973, **95**, 7898.

[4] J. F. Endicott, G. J. Ferraudi, and J. R. Barber, *J. Amer. Chem. Soc.*, 1975, **97**, 219.

[5] P. Natarajan, *J.C.S. Chem. Comm.*, 1975, 26.

having some interactions between them, trapped in a solvent cage and the rate of separation of the radicals from each other is proportional to their rates of diffusion. Such an explanation is in line with the one proposed by Noyes[6] to explain the homolytic photolysis reactions of organic molecules in non-aqueous solvents. Since diffusion of the radicals from the cage is dependent on the microscopic viscosity of the solvent cage, predominance of reaction (2) or (3) strongly depends on the solvent medium. In more viscous solutions, recombination of the radicals to give the cobalt(III) complex is more favourable than the reaction to give net photoreduction. Endicott *et al.*[4] extensively investigated the photochemistry of penta-ammineanionocobalt(III) complexes in different solvent mixtures using light of different wavelengths, and observed a number of trends which conform to various mechanisms depending on the complex under study. From thermodynamic arguments it was proposed[7] that the recombination of the geminate radicals to give the original complex is feasible.

$$[\mathrm{Co^{III}(NH_3)_5X}]^{2+} \xrightarrow{h\nu} \underset{\text{(I)}}{[\mathrm{Co^{II}(NH_3)_5{\cdot}X}]^{2+}} \qquad (1)$$

$$\text{(I)} \longrightarrow [\mathrm{Co^{III}(NH_3)_5X}]^{2+} \qquad (2)$$

$$\text{(I)} \longrightarrow \mathrm{Co^{II}} + 5\mathrm{NH_3} + \mathrm{X^{\bullet}} \qquad (3)$$

An earlier communication from this laboratory[5] focused attention on the photolysis of cobalt(III) complexes in highly viscous solutions of macromolecules and concluded that macroscopic viscosity is not an important factor in determining the product yields. In the present study, it has been found that even in solvent mixtures the final product yield does not always depend on the viscosity of the medium, which indicates that solvent interactions with the radical pair or the thermally equilibrated excited state determine the net redox quantum yields.

EXPERIMENTAL

A sample of poly(vinylpyrrolidone) was obtained from SDS Lab. Chem. Industry. The complexes used, $[\mathrm{Co(NH_3)_5(NO_2)}][\mathrm{NO_3}]_2$ and $[\mathrm{Co(NH_3)_5(N_3)}][\mathrm{ClO_4}]_2$, were prepared by methods described in the literature.[8-10] The irradiation set-up consisted of a General Electric high-pressure mercury-vapour lamp (box-type), lenses to collimate the light beam, glass filters to obtain a light beam of desired wavelength, and a thermostatted vessel in which the irradiation cell was kept. All the experiments were carried out at 30 ± 0.5 °C and the light intensity was measured using ferrioxalate actinometry. The viscosity of the solutions relative to that of water was determined using a suspended-level dilution viscometer (Ubbelohe type, D 445-467). The amount of $\mathrm{Co^{II}}$ produced during irradiation was determined by the ammonium thiocyanate method,[11] immediately after irradiation. The concentration of $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ used in the irradiations was always $>10^{-3}$ mol dm^{-3} and the extent of decomposition of the complex never exceeded 7%. In solutions containing macromolecules the amount of light scattered was less than 1% of that absorbed by the complex ion, as determined approximately from the optical density of the polymer solution at the irradiating wavelength, a correction being made to the total light absorbed by the irradiated solution. The amount of the nitrito-isomer produced on photolyzing $[\mathrm{Co(NH_3)_5(NO_2)}]^{2+}$ was determined by a differential spectrophotometric method.[12] Solvents and other reagents used were of analytical reagent grade.

RESULTS

Photolysis of $[\mathrm{Co(NH_3)_5(NO_2)}]^{2+}$ *and* $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ *Ions in Aqueous Polymer Solutions.*—Irradiation of a solution of $[\mathrm{Co(NH_3)_5(NO_2)}]^{2+}$ ion in 0.1 mol dm^{-3} $\mathrm{HClO_4}$ at 365 nm produced $\mathrm{Co^{II}}$ and the linkage isomer $[\mathrm{Co(NH_3)_5(ONO)}]^{2+}$. There was no photoaquation leading to the formation of $[\mathrm{Co(NH_3)_5(OH_2)}]^{3+}$, at least up to 10% decomposition of the original complex. The viscosity of the solutions was increased by dissolving various concentrations of synthetic high polymer. Irradiation of these viscous solutions was carried out at 365 nm and the quantum yields for $\mathrm{Co^{II}}$ and the linkage isomer $[\mathrm{Co(NH_3)_5(ONO)}]^{2+}$ were determined. At high concentration of the polymer the solution viscosity was very high and the viscosity measurements could not be made with capillary viscometers. The results are summarized in the Table.

Photolysis of $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ ion at 365 nm in acidic aqueous medium produced $\mathrm{Co^{II}}$ and the photoaquation product $[\mathrm{Co(NH_3)_5(OH_2)}]^{3+}$. The present investigations were limited to the determination of the photoredox quantum yields. Ferraudi *et. al.*[13] recently investigated the photochemistry of this complex in great detail, and following their suggestions I carried out studies to exclude any complications due to the secondary reactions. The results of the photolysis of $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ ion in aqueous acidic solutions of poly(vinylpyrrolidone) are given in the Table.

Product quantum yields[a] for the photolysis of $[\mathrm{Co(NH_3)_5(NO_2)}]^{2+}$ and $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ ions in solutions of poly(vinylpyrrolidone)

[Polymer][b]	Φ/Φ_0[c]		
wt. %	$\mathrm{Co^{II}(NO_2)}$	l.i.$(\mathrm{NO_3})$	$\mathrm{Co^{II}(N_3)}$
1.0 (1.01)	1.02	1.01	0.98
2.0 (9.1)	0.97	1.07	0.95
4.0 (22.3)	0.99	1.03	1.0
6.0 (45.0)	1.05	0.98	1.0

[a] Φ_0 = Quantum yield in aqueous solution; Φ = quantum yield in polymer solution. [b] The relative viscosity is given in parentheses. [c] $\mathrm{Co^{II}(NO_2)}$ and $\mathrm{Co^{II}(N_3)}$ represent quantum-yield ratios of $\mathrm{Co^{II}}$ for the complexes $[\mathrm{Co(NH_3)_5(NO_2)}]^{2+}$ and $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ respectively; l.i.$(\mathrm{NO_2})$ is the quantum-yield ratio for linkage isomerization of $[\mathrm{Co(NH_3)_5(NO_2)}]^{2+}$.

Photolysis of $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ *Ion in Water–Alcohol Solvent Mixtures.*—Photolysis of $[\mathrm{Co(NH_3)_5(N_3)}]^{2+}$ ion was carried out at 365 nm in aqueous solutions containing glycerol, ethylene glycol, and cyclohexanol. Since cyclohexanol is only slightly miscible with water, the minimum amount of ethanol was added to increase the miscibility. Irradiations were carried out in 0.01 mol dm^{-3} perchloric

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[6] R. M. Noyes, *Progr. Reaction Kinetics*, 1961, **1**, 128.

[7] J. F. Endicott, *Inorg. Chem.*, 1975, **14**, 448.

[8] M. Linhard and M. Weigel, *Z. anorg. Chem.*, 1950, **267**, 328.

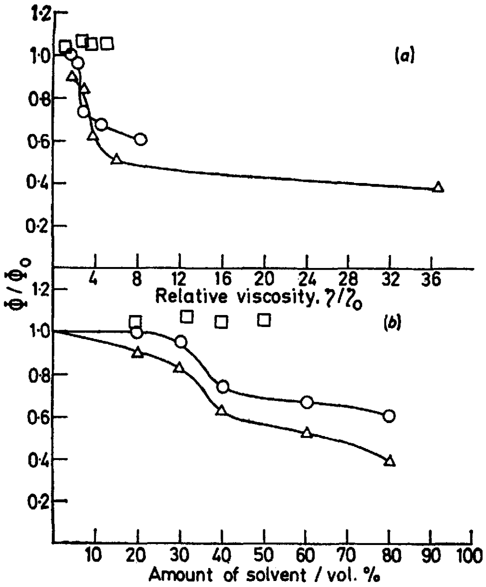
[9] J. F. Endicott, M. Z. Hoffman, and L. S. Beres, *J. Phys. Chem.*, 1970, **74**, 1021.

[10] M. Linhard and H. Flygare, *Z. anorg. Chem.*, 1950, **267**, 328.

[11] R. E. Kitson, *Analyt. Chem.*, 1959, **22**, 664.

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

acid containing different amounts of solvents. Variation of the solvent composition changes the viscosity of the irradiated solution, and the quantum yields for Co^{II} were determined as a function of the viscosity of the medium in each solvent (Figure).



Quantum yields of Co^{II} on irradiation of $[Co(NH_3)_5(N_3)]^{2+}$ in solution (Φ_0) and in solvent mixtures (Φ): (△) water–glycerol; (○) water–ethylene glycol; (□) water–ethanol–cyclohexanol

DISCUSSION

There is considerable uncertainty regarding the nature of the species that gives rise to the final products in the photolysis of these complex ions. The question of whether

$$[Co(NH_3)_5X]^{2+} \xrightarrow{h\nu} Co^{II} + X^{\bullet} + 5NH_3 \qquad (4)$$

the initial excited state relaxes to a lower-lying state responsible for the photoreduction or whether a radical pair is directly produced from the initial excited state cannot be definitely answered yet. In fact a very clear distinction between a lower-lying state in equilibrium with the solvent and a geminate radical pair having strong interactions is not possible and there seems to be some confusion in the literature on this aspect.[1,2] Scandola *et al.*[3] reported a photochemical study of $[Co(NH_3)_5(NO_2)]^{2+}$ ion in water–glycerol mixtures where the quantum yields for the two processes, reduction of the metal centre and linkage isomerization, varied in opposite directions with changing viscosity of the medium. The results have led to the suggestion that radical pairs are involved in the primary photochemical reaction and which combine to give the linkage isomer predominantly when the viscosity of the medium is increased. Such a situation results in a decrease in the quantum yield for Co^{II}, and the combined yield for Co^{II} and linkage isomerization was practically constant at different viscosities. The observations have been explained in terms of the reactions (5). Later, Ferraudi *et al.*[13] made a more complete study with a number of ammineaniono-complexes of Co^{III} at different energies of irradiation and in a number of mixed solvents. A radical-recombination process was invoked as a

$$[Co^{II}(NH_3)_5\cdots NO_2] \longrightarrow Co^{2+} + 5NH_3 + NO_2 \not\longrightarrow [Co(NH_3)_5(ONO)]^{2+} \qquad (5)$$

general feature of the photochemical redox behaviour of cobalt(III) complexes. Addition of polymers leaves Φ(redox) unchanged even at high macroscopic viscosities. This does not imply, however, that radical-pair separation is not influenced by a prevailing high viscosity, for in such solutions the complex is probably located in a solvent environment (as an island between the polymer network) and will simply undergo aqueous photochemistry.

The photochemical behaviour of the complex ions in mixed solvents requires a very different explanation. The ions $[Co(NH_3)_5(N_3)]^{2+}$ and $[Co(NH_3)_5(NO_2)]^{2+}$ are not soluble in the solvents used, except in water, and the latter ion is much less soluble in mixed solvents. In such solvents the complex ion is to a great extent solvated by water which is surrounded by the other solvent. The viscosity of the solvent around the metal ion should not be very different from that of the bulk solution as in the case of polymer solutions. Whereas the high viscosity of glycerol and ethylene glycol is due to the multicentre hydrogen bonding between the molecules,[14] that of cyclohexanol should be due to factors other than hydrogen bonding alone, namely the friction encountered by the molecular motion involving the CH_2 groups in the ring. If the diffusion of the photolyzed fragments is an important factor in the product distribution, quantum yields for Co^{II} in water–cyclohexanol should vary as in the case of water–glycerol. Even in the presence of 50% cyclohexanol ($\eta/\eta_0 = 5.1$) the quantum yield for Co^{II} is practically unaffected. These results thus cannot be explained in terms of the rate of diffusion of radicals in a viscous medium.

The first step in the light-absorption process for these complexes is excitation to the Franck–Condon state which is accompanied by the chemical reaction (6).

$$[Co(NH_3)_5X]^{2+} \xrightarrow{h\nu} {}^1CT \dashrightarrow {}^3CT \dashrightarrow [Co^{II}(NH_3)_5{\cdot}X]^{2+} \longrightarrow \text{Products} \qquad (6)$$

The involvement of the triplet state in the photochemical reaction is not well established for the pentaammineanionocobalt(III) complexes. Since the excited state of the complex does not emit light, the information on the photochemically active state can be inferred only from the photochemical studies. In solvent mixtures containing cyclohexanol, the microscopic viscosity should be approximately the same as the macroscopic viscosity. The variation of the cobalt(II) quantum yield in multicentre hydrogen-bonding solvents

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[13] G. J. Ferraudi, J. F. Endicott, and J. R. Barber, *J. Amer. Chem. Soc.*, 1975, **97**, 6406.

[14] G. C. Pimental and A. L. McClellan, 'The Hydrogen Bond,' W. H. Freeman, San Francisco, 1960.

should be based on the solvent environment around the radical pair. Interaction of solvent molecules with excited states is well known from the study of organic molecules,[15] and the mode of relaxation of excited states in different solvents is known to depend on properties such as solvent polarity and temperature.[16] Ultraviolet-absorption spectra of the complex are influenced by the solvent, as seen in this work and in the work of Ferraudi *et al.* The solvent relaxation time is of the order of 10^{-9}—10^{-10} s and the solvent interaction with the excited state or radical pair depends on the solvent composition. At high glycerol and ethylene glycol concentrations the hydrogen-bonding interaction of water with the excited state (radical pair) is minimal. Consequently, the cobalt(II) yield is less than in the pure aqueous medium. In alcohols such as ethanol and cyclohexanol the water–water and water–alcohol interactions are similar and so the cobalt(II) yield is not different in these solvents.

Evidence for the radical pair giving the original complex as proposed by Scandola [3] and other workers is mainly derived from the dependence of the cobalt(II) yield on the viscosity of the solvent. The explanation offered is an oversimplification of the real situation, and the viscosity effect on the quantum yield for Co^{II} is to be attributed to the interaction of the added solvent with the solvation sphere of the complex ion. There does not seem to be any compelling evidence for the recombination of the primary radicals from the viscosity effect on the quantum yield for the products. Simic and Lilie [17] reported that three ammonia ligands separate from the reduced cobalt(III) centre of a $[Co(NH_3)_5X]^{2+}$ complex in less than 0.1 μs, which is the shortest time they had access to. The first ammonia probably dissociates within the lifetime of the radical pair without forming the starting material by recombination. It is also known that the photoaquation process is not coupled with the redox reaction in the case of $[Co(NH_3)_5(N_3)]^{2+}$ ion.[13] Under these conditions it is very unlikely that recombination of radicals occurs in the photoreaction. My experiments with $[Co(NH_3)_5(NO_2)]^{2+}$ were unsuccessful due to the lack of solubility in the solvent mixtures.

In conclusion, the photoreduction of azidopenta-amminecobalt(III) is a strongly solvent(water)-coupled reaction, and the interaction of water with an excited state of the complex ion decreases in the presence of multicentre hydrogen-bonding solvents.

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[15] N. Mataga and T. Kubota, 'Molecular Interactions and Electronic Spectra,' Marcel Dekkar, New York, 1970.

[16] M. Ottolenghi, *Accounts Chem. Res.*, 1973, **6**, 153.

[17] M. Simic and J. Lilie, *J. Amer. Chem. Soc.*, 1974, **96**, 291.