Photolysis of Cobalt(III) Complexes in Highly Viscous Polymer Solutions

By P. Natarajan

(*Department of Physical Chemistry, University of Madras, A. C. College Campus, Madras* 600 025, *India*)

Summary Photolysis of cobalt(III) complexes in high polymer solutions indicates that the viscosity of the medium has no significant effect on the product yields.

The photochemical behaviour of complexes of cobalt(III) as well as those of chromium(III) has been studied extensively. Cobalt(III) complexes undergo photolabilization as well as photoredox reactions giving rise to cobalt(II).[1] Although it used to be assumed that the nature of the solvent did not play an important role in determining the fate of excited states, recent observations have indicated the significance of coupling of the excited-states with the solvent media.[2,3] Scandola *et al.*[2] have proposed that during the photolysis of the $[Co(NH_3)_5NO_2]^{2+}$ ion, geminate radical recombination occurs in the solvent cage which leads to a decrease in the quantum yield for cobalt(II) formation with increasing viscosity of the medium. In contrast, for $[Co(NH_3)_5SCN]^{2+}$ [3] the quantum yield for cobalt(II) formation increased with solvent viscosity under certain conditions and it was proposed that the excited state of the complex specifically interacts with the solvent medium thereby determining the product distribution.

We have investigated the photoredox behaviour of cobalt(III) complexes in acidic aqueous solutions containing poly(acrylamide) at various concentrations. Poly(acrylamide) was prepared by radical-induced polymerization of recrystallized acrylamide and the sample was purified by repeatedly dissolving in water and reprecipitating in methanol. A 10% (by weight) solution of the polymer is highly viscous and its viscosity could not be determined by capillary viscometers. The $[Co(NH_3)_5NO_2]^{2+}$ ion in 0·1M $HClO_4$ containing various amounts of poly(acrylamide) was irradiated at 30 °C using 365 nm light from a high-pressure mercury vapour lamp. Quantum yields for the formation of cobalt(II) and $[Co(NH_3)_5ONO]^{2+}$ were determined by well known methods[4] after approximate corrections (usually small) for the light scattered by the macromolecules. For each experiment a blank run without polymer was carried out. The results are given in the Table. The results indicate clearly that the increase in the viscosity of the photolysis medium does not have a noticeable effect on the product distribution. Even in a 10% polymer solution which is highly viscous the ratio of cobalt(II) to the nitrito linkage isomer formed is the same as that obtained in less viscous aqueous media.

TABLE

Product yields from the photolysis of $[Co(NH_3)_5NO_2]^{2+}$ and $[Co(NH_3)_5N_3]^{2+}$ ions in polymer solutions.

		Φ/Φ_0[a]		
[Polymer] (% w/w)	Relative viscosity, η/η_0	Co^{II}	Linkage isomer	Φ_{AZ}[b]
1·0	1·0	1·0	1·0	0·24
2·0	7·15	1·06	0·95	0·25
4·0	20·80	1·05	1·09	0·24
7·0	102	1·12	1·09	0·24
8·0	c	—	—	0·24
10·0	c	1·0	1·07	—

[a] Ratio of quantum yields for $[Co(NH_3)_5NO_2]^{2+}$ in water (Φ_0) and in polymer solution (Φ). [b] Φ_{AZ} = quantum yield of Co^{II} for $[Co(NH_3)_5N_3]^{2+}$ ion. [c] Viscosity was too high to be measurable.

The high viscosity of the polymer solution is due to the solvation of the polymer molecule, which affects the mobility of the solvent water.[5] Bulk water is expected to be present between the complex ion and the polymer chain. The difference in the photochemical behaviour of the $[Co(NH_3)_5NO_2]^{2+}$ ion in water–glycerol[2] and in polymer solution media must be due to something other than the viscosity effect alone. Experiments with the $[Co(NH_3)_5N_3]^{2+}$ ion show similar quantitative behaviour in aqueous media and in polymer solution (see Table).

Recent studies[6] on the influence of solvent media on the photochemical behaviour of cobalt(III) complexes show that the solvent structure determines the product distribution of the photoredox reactions. The high viscosity of glycerol and ethyleneglycol is due to multicentre hydrogen bonding leading to a solvent structure with large aggregates of the monomeric species. The polar solvent structure couples with the highly polar excited state of the molecule. Relaxation from the excited state depends intimately on the interaction of the solvent structure around the solute species with the solute.[8] Chemical reaction from the excited[7] state thus occurs in competition with non-radiative decay aided by the medium. Light-induced linkage isomerisation and photoreduction of the $[Co(NH_3)_5NO_2]^{2+}$ ion occur from an excited state, A*, coupled to the solvent structure. A* is considerably different from the Franck–Condon excited state and its structure is such that it does not return to the nitro-isomer (ground state) directly. Experiments using the water-soluble polymer poly(vinylpyrrolidone) show the same general behaviour as described here indicating that the nature of the polymer does not alter the general behaviour of these complexes.

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