Photosensitization of Superoxo-bridged Dicobalt(III) Cations by Tris-(2,2′-bipyridyl)ruthenium(II) in the Excited State

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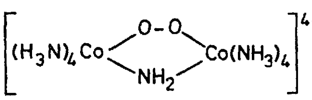
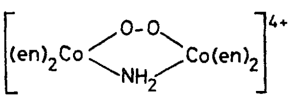
Summary The charge-transfer excited state of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridyl) is quenched by superoxo-bridged dicobalt(III) cations by the excited-state electron transfer mechanism.

Reactivity and structural aspects of bridged binuclear complexes of cobalt(III) are well documented.[1] In the dibridged complexes of the types (I) and (II), one-electron


(I)

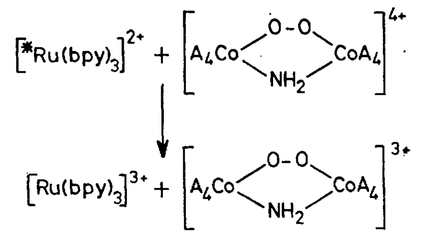

(II)

en = ethylenediamine

reduction produces the peroxo-analogue which is stable for several days in solution.[2] The reduction potential of (II) is *ca.* 1 V and the reduced peroxo-bridge is protonated readily.[3]

We report the photosensitization of (I) and (II) by the excited state of tris(2,2′-bipyridyl)ruthenium(II), $[^*Ru(bpy)_3]^{2+}$, in hydrochloric acid solution. $[^*Ru(bpy)_3]^{2+}$ is effectively quenched by (I) and (II) and the bimolecular quenching constant was determined by emission intensity and life-time measurements of the sensitizer. The life-time of $[^*Ru(bpy)_3]^{2+}$ was measured in the presence and in the absence of the quenchers and the data are presented in the Figure (a). Excitation of $[Ru(bpy)_3]^{2+}$ was carried out by a 530 nm laser pulse of *ca.* 20 ns width and the life-time of the excited state was monitored by observing the luminescence decay at 610 nm. Bimolecular quenching constants, k_q, calculated from the Stern–Volmer plot in the Figure (a) using the equation $\tau_0/\tau = 1 + k_q\tau_0$ [Q] are $2{\cdot}0 \pm 0{\cdot}2 \times 10^9$ and $2{\cdot}2 \pm 0{\cdot}15 \times 10^9$ l mol^{-1} s^{-1} for (I) and (II), respectively. Since the quenchers absorb a part of both the exciting and emitting light, emission quenching data do not give a good Stern–Volmer plot. Suitable corrections[4] were made for the intensity of emitted light and the quenching constant† observed was $4 \pm 1{\cdot}5 \times 10^9$ l mol^{-1} s^{-1}. Flashing a solution of $[Ru(bpy)_3]^{2+}$ ($7{\cdot}5 \times 10^{-5}$ mol l^{-1}) and (I) (2×10^{-3} mol l^{-1}) with a 460 nm dye laser pulse (width *ca.* 0·6 μs) causes instant bleaching of the $[Ru(bpy)_3]^{2+}$ absorption at 450 nm which is regenerated following the initial bleaching. Reappearance of $[Ru(bpy)_3]^{2+}$ absorption follows equal-concentration second-order kinetics and the bimolecular rate constant obtained for the reaction from the Figure (b) was $0{\cdot}9 \pm 0{\cdot}2 \times 10^6$ l mol^{-1} s^{-1} in 1N HCl.

Results obtained on the quenching of $[^*Ru(bpy)_3]^{2+}$ by (I) and (II) and the flash photolysis experiments clearly indicate a predominant excited state electron transfer process shown in the Scheme where A is the ammine.



Scheme

$[^*Ru(bpy)_3]^{2+}$ sensitized reactions of cobalt(III) compounds are believed[5] to proceed by an excited-state energy-transfer process or by an excited-state electron-transfer process. In the present case the predominant excited state reaction of $[^*Ru(bpy)_3]^{2+}$ is unambiguously one of electron transfer and this is the first report on the back thermal electron transfer process of a cobalt(III) complex and $[Ru(bpy)_3]^{3+}$ ion. However, the excited state electron transfer in the present systems occurs to the superoxide group rather than to the cobalt(III) centre‡ while the $[Ru(bpy)_3]^{2+}$ sensitized reduction of cobalt(III) monomeric complexes is believed to involve direct reduction of the metal centre.§

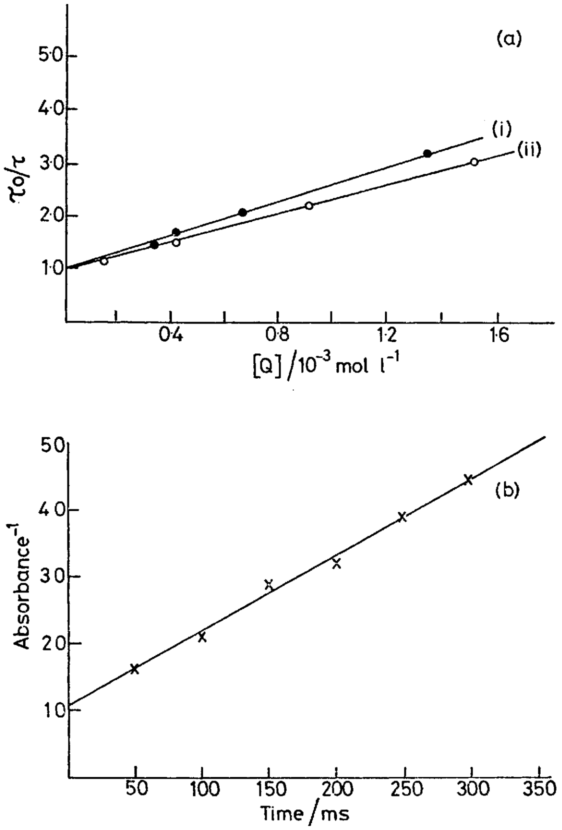


Figure. (a) Stern–Volmer plot for $[^*Ru(bpy)_3]^{2+}$–(I) (i) and $[^*Ru(bpy)_3]^{2+}$–(II) (ii). τ_0 and τ are life-times of $[^*Ru(bpy)_3]^{2+}$ in the absence and in presence, respectively, of the quencher, Q. (b) Flash photolysis of $[Ru(bpy)_3]^{2+}$–(I) in solution: equal-concentration second-order plot of absorbance^{-1} at 460 nm *vs.* time.

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† Higher value for the quenching constant from luminescence measurements may be partly due to some ion-pairing.

‡ Sykes (ref. 1b) has shown that even with powerful reducing agents the electron is transferred to the superoxo group rather than to the cobalt(III) centre. It is very unlikely that the electron is initially transferred to the metal centre with the subsequent reduction of the superoxo bridge since the life-time of the cobalt(II) centre is very short, at least with ammonia ligands.

§ Cobalt(II) is produced even in this system with low yields [ϕ (Co^{II}) varies from 0·008 to 0·02] which could occur from the inefficient energy transfer pathway where a charge transfer excited state of the dicobalt(III) ion is populated by $[^*Ru(bpy)_3{}^{2+}]$.

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