Inorganica Chimica Acta, 53 (1981) L23–L24

Chemiluminescence on Oxidation of Tris(2,2′-bipyridine)chromium(II): Chemical Generation of a Metal-Centered Excited State

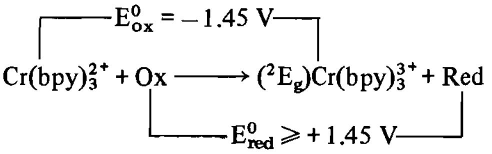
F. BOLLETTA*[a], A. ROSSI[a] and V. BALZANI[a,b]

Instituto Chimico "G. Ciamician" dell'Università, Bologna, Italy. Istituto di Fotochimica e Radiazioni d'Alta Energia del CNR, Bologna, Italy

Received September 9, 1980

Generation of electronically excited states by very exoergonic chemical reactions is a well known phenomenon in several fields of chemistry [1]. Such reactions are particularly important when they lead to the generation of luminescent excited states[†] because of their potential use in electronic display devices [2] and lasers [3]. In the field of coordination compounds there are few examples of chemiluminescent reactions [1c, 4–9]. Most of them involve the reduction of Ru(bpy)$_3^{3+}$ (bpy = 2,2′-bipyridine) generating the lowest (triplet metal-to-ligand charge transfer) excited state of Ru(bpy)$_3^{2+}$, (^{3}CT) [4–7]. The transient observed in the reduction of Co(bpy)$_3^{3+}$ by hydrated electrons, first claimed [10] to be a metal centered (MC) excited state of Co(bpy)$_3^{2+}$, has recently been shown to be the ground state Co(bpy)$_3^{2+}$ [11]. Thus, none of the known cases involves the generation of MC excited states of transition metal complexes. We report here the results concerning the chemical oxidation of Cr(bpy)$_3^{2+}$ by very powerful oxidants, showing the generation of a luminescent MC excited state of Cr(bpy)$_3^{3+}$.

Cr(bpy)$_3^{3+}$ is known to emit luminescence in fluid solution at room temperature [12, 13]. The emitting state is the lowest excited state, ^2E_g, which belongs to the same t_{2g}^3 electronic configuration as the $^4A_{2g}$ ground state. Spectroscopic measurements show that the ^2E_g emission band is very narrow with a peak at 727 nm, corresponding to a zero-zero spectroscopic energy of 1.71 eV [12–14]. Since the reduction potential of the Cr(bpy)$_3^{3+/2+}$ couple is –0.26 V *vs.* NHE in aqueous solutions [14], from the thermodynamic point of view the generation of (^2E_g)Cr(bpy)$_3^{3+}$ on Cr(bpy)$_3^{2+}$ oxidation requires the use of an oxidant having reduction potential more positive than +1.45 V (eqn. 1).



$$\overbrace{\mathrm{Cr(bpy)_3^{2+}} + \mathrm{Ox}}^{E^0_{ox} = -1.45\ \mathrm{V}} \longrightarrow \underbrace{(^2E_g)\mathrm{Cr(bpy)_3^{3+}} + \mathrm{Red}}_{E^0_{red} \geqslant +1.45\ \mathrm{V}} \qquad (1)$$

Potentially useful reactants for reaction 1 are $S_2O_8^{2-}$, H_2O_2 and Tl^{3+}. All these species are known to react according to a two-step one-electron mechanism (eqns. 2 and 3), where the reduction potential of the first step is rather low (≤0.6, ≤0.6 and 0.31 V for $S_2O_8^{2-}$ [15], H_2O_2 [15], and Tl^{3+} [18]) whereas the reduction potential of the second step is very high (3.4, 2.94, and 2.22 V for $S_2O_8^{2-}$ [15], H_2O_2 [15], and Tl^{3+} [16]).

$$\mathrm{Ox} + e^- \longrightarrow \mathrm{Ox}^- \qquad (2)$$

$$\mathrm{Ox}^- + e^- \longrightarrow \mathrm{Ox}^{2-} \qquad (3)$$

Freshly prepared deaerated solutions of Cr(bpy)$_3^{2+}$ (1–5 × 10^{-2} *M*) and Ox (1–5 × 10^{-4} *M*) in H_2SO_4 0.5 *M* were mixed in the cell of a Durrum stop-flow equipment. When Ox was $S_2O_8^{2-}$ or Tl^{3+}, a transient light emission was obtained and recorded on the oscilloscope. A tipical oscilloscope trace for the Cr(bpy)$_3^{2+}$–$S_2O_8^{2-}$ system is reported in Fig. 1. By insertion of suitable cutt-off or interference filters between the mixing cell and the photomultiplier it was possible to show that the emission was in the 700–750 nm range, as expected for (^2E_g)Cr(bpy)$_3^{3+}$ emission. Check experiments showed that no emission was obtained upon mixing free bpy and $S_2O_8^{2-}$ solutions.

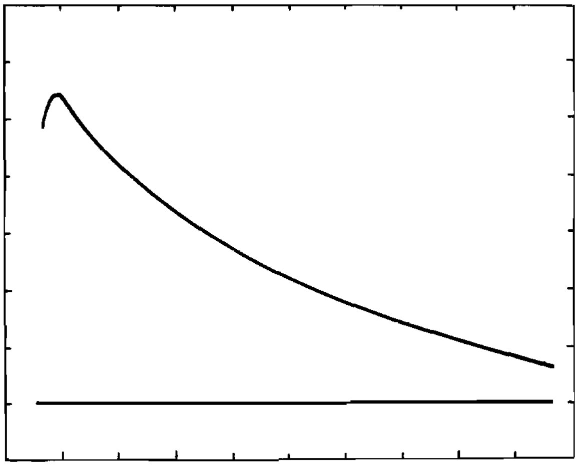


Fig. 1. Transient chemiluminescence emission at 727 nm of Cr(bpy)$_3^{2+}$ 3.5 × 10^{-3} *M* oxidized by $S_2O_8^{2-}$ 1 × 10^{-4} *M*, 20 mV, 10 ms/div.

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*Author to whom correspondence should be addressed.

[a] Istituto Chimico 'Ciamician'.

[b] Istituto FRAE del CNR.

[†] When light emission occurs from the reaction of ions generated at an electrode surface, the phenomenon is referred as electrogenerated chemiluminescence (ELC).

The most probable reaction scheme for the chemical formation of $(^2E_g)Cr(bpy)_3^{3+}$ is:

$$Cr(bpy)_3^{2+} + S_2O_8^{2-} \text{ (or } Tl^{3+}\text{)} \longrightarrow Cr(bpy)_3^{3+} + SO_4^{-} + SO_4^{2-} \text{ (or } Tl^{2+}\text{)} \quad (4)$$

$$Cr(bpy)_3^{2+} + SO_4^{-} \text{ (or } Tl^{2+}\text{)} \longrightarrow (^2E_g)Cr(bpy)_3^{3+} + SO_4^{2-} \text{ (or } Tl^{+}\text{)} \quad (5)$$

No chemiluminescence was obtained when $Cr(bpy)_3^{2+}$ solutions were reacted with H_2O_2. Presumably, OH radicals give an addition reaction to the coordinated bpy ligands [17] rather than an outer-sphere electron transfer reaction with $Cr(bpy)_3^{2+}$. For the $Cr(bpy)_3^{2+}$–$S_2O_8^{2-}$ or Tl^{3+} systems, the formation* of $(^2E_g)Cr(bpy)_3^{3+}$ in our experimental conditions follows a (pseudo) first-order kinetics. A detailed study of these systems will be reported elsewhere.

Acknowledgements

Financial support from Assoreni and from European Communities (Contract 360-77-11ESI) is appreciated.

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*Due to the big difference between the lifetime of $(^2E_g)Cr(bpy)_3^{3+}$ (~50 μs) [15] and the decay time of the observed chemiluminescence, the intensity decay is a probe of the rate of formation of $(^2E_g)Cr(bpy)_3^{3+}$ in the chemical reaction.

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