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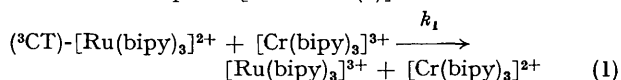
## Bimolecular Electron Transfer Reactions of Electronically Excited States of Co-ordination Compounds

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**Summary** The quenching of  $(^3\text{CT})\text{-}[\text{Ru}(\text{bipy})_3]^{2+}$  by  $[\text{Cr}(\text{bipy})_3]^{3+}$  and of  $(^2\text{MC})\text{-}[\text{Cr}(\text{bipy})_3]^{3+}$  by  $[\text{Ru}(\text{bipy})_3]^{2+}$  takes place by an electron transfer mechanism.

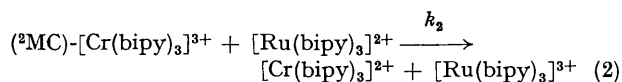
RECENT developments in the photochemistry of co-ordination compounds<sup>1,2</sup> have neglected bimolecular reactions of electronically excited states. A notable exception is the electron transfer from excited tris(bipyridyl)ruthenium(II),  $[\text{Ru}(\text{bipy})_3]^{2+}$ , to several electron acceptors.<sup>3-5</sup> We are investigating the bimolecular redox properties of electronically excited co-ordination compounds, and, in addition to another example of electron transfer from excited  $[\text{Ru}(\text{bipy})_3]^{2+}$ , we have observed what appears to be the first example of electron transfer to an excited state of a transition-metal complex.

Luminescence emission at 610 nm (aqueous, air-equilibrated solution, 23 °C,  $\mu = 0.2$ ) of the so-called<sup>6</sup> triplet charge-transfer excited state of the tris(bipyridyl)ruthenium(II) complex,  $(^3\text{CT})\text{-}[\text{Ru}(\text{bipy})_3]^{2+}$ , is quenched by  $[\text{Cr}(\text{bipy})_3]^{3+}$ ; the bimolecular quenching constant,  $k_1$ , calculated from a Stern-Volmer plot is  $3.3 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ . In view of the reported phosphorescence emission of  $[\text{Cr}(\text{bipy})_3]^{3+}$  at 727 nm in aqueous solution and at room temperature,<sup>7</sup> it is reasonable to expect that, if quenching occurs *via* energy transfer, a sensitized emission of  $[\text{Cr}(\text{bipy})_3]^{3+}$  should be observed. From quantitative luminescence measurements, we have found that the energy transfer efficiency<sup>2</sup> must be  $< 5\%$ . The only quenching mechanism which is efficient enough<sup>2</sup> to explain the high value of  $k_1$  is that of electron transfer from the excited  $\text{Ru}^{\text{II}}$  to the ground state  $\text{Cr}^{\text{III}}$  complex [reaction (1)]. If the reduction



potential of  $[\text{Ru}(\text{bipy})_3]^{3+}/(^3\text{CT})\text{-}[\text{Ru}(\text{bipy})_3]^{2+}$  is  $-0.88 \text{ V}$ ,<sup>4,5</sup> reaction (1) involves a free-energy change of  $-14.5 \text{ kcal/mol}$ . No permanent chemical change could be observed in continuous irradiation experiments, indicating that the products of reaction (1) undergo a rapid back electron transfer reaction which leads to ground state  $[\text{Ru}(\text{bipy})_3]^{2+}$  and  $[\text{Cr}(\text{bipy})_3]^{3+}$  (see below).

Under the same experimental conditions, we have also observed that the emission at 727 nm of the doublet metal-centred excited state of tris(bipyridyl)chromium(III),  $(^2\text{MC})\text{-}[\text{Cr}(\text{bipy})_3]^{3+}$ , is quenched by  $[\text{Ru}(\text{bipy})_3]^{2+}$ ; the bimolecular quenching constant,  $k_2$ , as calculated from a Stern-Volmer plot is  $4.0 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ . As the energy of the lowest excited state of  $[\text{Ru}(\text{bipy})_3]^{2+}$  is  $17,100 \text{ cm}^{-1}$ ,<sup>8</sup> and that of the  $^2\text{MC}$  excited state of  $[\text{Cr}(\text{bipy})_3]^{3+}$  is  $13,800 \text{ cm}^{-1}$ ,<sup>7</sup> the energy transfer process from  $(^2\text{MC})\text{-}[\text{Cr}(\text{bipy})_3]^{3+}$  to  $[\text{Ru}(\text{bipy})_3]^{2+}$  would necessitate an activation energy as high as  $9.5 \text{ kcal/mol}$ . This is incompatible with the high value obtained for the quenching constant  $k_2$ , even though the lifetime for the  $^2\text{MC}$  excited state is rather long ( $35.8 \mu\text{s}$ ). Thus, quenching *via* energy transfer is not possible and the only plausible quenching mechanism<sup>2</sup> is, again, one of electron transfer [reaction (2)]. If the free energy difference



between the  $^2\text{MC}$  and the ground state of  $[\text{Cr}(\text{bipy})_3]^{3+}$  is taken to be the spectroscopic excitation energy ( $13,800 \text{ cm}^{-1}$ ) the reduction potential for the  $(^2\text{MC})\text{-}[\text{Cr}(\text{bipy})_3]^{3+}/[\text{Cr}(\text{bipy})_3]^{2+}$  couple is  $+1.47 \text{ V}$  and the free energy change in reaction (2) is  $-5.3 \text{ kcal/mol}$ . It should also be noted that since  $k_2 < k_1$ , the deactivation of  $(^3\text{CT})\text{-}[\text{Ru}(\text{bipy})_3]^{2+}$  *via*

energy transfer to ( $^2\text{MC}$ )- $[\text{Cr}(\text{bipy})_3]^{3+}$  followed by reaction (2) can be ruled out.

Thus, in a solution containing  $[\text{Ru}(\text{bipy})_3]^{2+}$  and  $[\text{Cr}(\text{bipy})_3]^{3+}$  light absorption leads to the same products,  $[\text{Ru}(\text{bipy})_3]^{3+}$  and  $[\text{Cr}(\text{bipy})_3]^{2+}$ , irrespective of the absorbing species. Such products, however, cannot accumulate under continuous irradiation conditions as their back electron transfer reaction, leading to ground state  $[\text{Ru}(\text{bipy})_3]^{2+}$  and  $[\text{Cr}(\text{bipy})_3]^{3+}$ , is thermodynamically favoured  $\{E^\circ$  for  $[\text{Ru}(\text{bipy})_3]^{3+}/[\text{Ru}(\text{bipy})_3]^{2+} = 1.24 \text{ V}$ ;<sup>9</sup>  $E^\circ$  for  $[\text{Cr}(\text{bipy})_3]^{3+}/[\text{Cr}(\text{bipy})_3]^{2+} = -0.25 \text{ V}^{10}\}$  and, presumably, it does not require a large reorganization energy.<sup>4,11</sup> We are now attempting to show the formation of  $[\text{Ru}(\text{bipy})_3]^{3+}$  and  $[\text{Cr}(\text{bipy})_3]^{2+}$  in reactions (1) and (2) by flash photolysis.

The results reported here show that in addition to charge-

transfer excited states, metal-centred excited states of co-ordination compounds may also be involved in bimolecular redox processes. The extension of these investigations is promising. Theoretically, it will be interesting to see whether electron-transfer outer-sphere reactions involving electronically excited states can be interpreted by the Marcus-Hush theory.<sup>11</sup> Practically, such reactions should prove useful in the conversion of light energy into chemical energy, a problem which has received much attention lately.<sup>12</sup>

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