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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}CT)-$[Ru(bipy_3)]^{2+}$ by $[Cr(bipy)_3]^{3+}$ and of (^{2}MC)-$[Cr(bipy)_3]^{3+}$ by $[Ru(bipy)_3]^{2+}$ takes place by an electron transfer mechanism.

RECENT developments in the photochemistry of co-ordination compounds[1,2] have neglected bimolecular reactions of electronically excited states. A notable exception is the electron transfer from excited tris(bipyridyl)ruthenium(II), $[Ru(bipy)_3]^{2+}$, to several electron acceptors.[3-5] We are investigating the bimolecular redox properties of electronically excited co-ordination compounds, and, in addition to another example of electron transfer from excited $[Ru(bipy)_3]^{2+}$, 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, $\mu = 0{\cdot}2$) of the so-called[6] triplet charge-transfer excited state of the tris(bipyridyl)ruthenium(II) complex, (^{3}CT)-$[Ru(bipy)_3]^{2+}$, is quenched by $[Cr(bipy)_3]^{3+}$; the bimolecular quenching constant, k_1, calculated from a Stern–Volmer plot is $3{\cdot}3 \times 10^9$ l mol^{-1} s^{-1}. In view of the reported phosphorescence emission of $[Cr(bipy)_3]^{3+}$ at 727 nm in aqueous solution and at room temperature,[7] it is reasonable to expect that, if quenching occurs *via* energy transfer, a sensitized emission of $[Cr(bipy)_3]^{3+}$ should be observed. From quantitative luminescence measurements, we have found that the energy transfer efficiency[2] must be $<5\%$. The only quenching mechanism which is efficient enough[2] to explain the high value of k_1 is that of electron transfer from the excited Ru^{II} to the ground state Cr^{III} complex [reaction (1)]. If the reduction

$$(^3\mathrm{CT})\text{-}[Ru(bipy)_3]^{2+} + [Cr(bipy)_3]^{3+} \xrightarrow{k_1} [Ru(bipy)_3]^{3+} + [Cr(bipy)_3]^{2+} \quad (1)$$

potential of $[Ru(bipy)_3]^{3+}$/(^{3}CT)-$[Ru(bipy)_3]^{2+}$ is $-0{\cdot}88$ V,[4,5] reaction (1) involves a free-energy change of $-14{\cdot}5$ 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 $[Ru(bipy)_3]^{2+}$ and $[Cr(bipy)_3]^{3+}$ (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}MC)-$[Cr(bipy)_3]^{3+}$, is quenched by $[Ru(bipy)_3]^{2+}$; the bimolecular quenching constant, k_2, as calculated from a Stern–Volmer plot is $4{\cdot}0 \times 10^8$ l mol^{-1} s^{-1}. As the energy of the lowest excited state of $[Ru(bipy)_3]^{2+}$ is 17,100 cm^{-1},[8] and that of the ^{2}MC excited state of $[Cr(bipy)_3]^{3+}$ is 13,800 cm^{-1},[7] the energy transfer process from (^{2}MC)-$[Cr(bipy)_3]^{3+}$ to $[Ru(bipy)_3]^{2+}$ would necessitate an activation energy as high as 9·5 kcal/mol. This is incompatible with the high value obtained for the quenching constant k_2, even though the lifetime for the ^{2}MC excited state is rather long (35·8 μs). Thus, quenching *via* energy transfer is not possible and the only plausible quenching mechanism[2] is, again, one of electron transfer [reaction (2)]. If the free energy difference

$$(^2\mathrm{MC})\text{-}[Cr(bipy)_3]^{3+} + [Ru(bipy)_3]^{2+} \xrightarrow{k_2} [Cr(bipy)_3]^{2+} + [Ru(bipy)_3]^{3+} \quad (2)$$

between the ^{2}MC and the ground state of $[Cr(bipy)_3]^{3+}$ is taken to be the spectroscopic excitation energy (13,800 cm^{-1}) the reduction potential for the (^{2}MC)-$[Cr(bipy)_3]^{3+}$/$[Cr(bipy)_3]^{2+}$ couple is $+1{\cdot}47$ V and the free energy change in reaction (2) is $-5{\cdot}3$ kcal/mol. It should also be noted that since $k_2 < k_1$, the deactivation of (^{3}CT)-$[Ru(bipy)_3]^{2+}$ *via* energy transfer to (^{2}MC)-[Cr(bipy)$_3$]$^{3+}$ followed by reaction (2) can be ruled out.

Thus, in a solution containing [Ru(bipy)$_3$]$^{2+}$ and [Cr(bipy)$_3$]$^{3+}$ light absorption leads to the same products, [Ru(bipy)$_3$]$^{3+}$ and [Cr(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 [Ru(bipy)$_3$]$^{2+}$ and [Cr(bipy)$_3$]$^{3+}$, is thermodynamically favoured {$E°$ for [Ru(bipy)$_3$]$^{3+}$/[Ru(bipy)$_3$]$^{2+}$ = 1·24 V;[9] $E°$ for [Cr(bipy)$_3$]$^{3+}$/[Cr(bipy)$_3$]$^{2+}$ = − 0·25 V[10]} and, presumably, it does not require a large reorganization energy.[4,11] We are now attempting to show the formation of [Ru(bipy)$_3$]$^{3+}$ and [Cr(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.[11] Practically, such reactions should prove useful in the conversion of light energy into chemical energy, a problem which has received much attention lately.[12]

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