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A New Mechanistic Channel for Photochemical Electron Transfer of Tris(2,2'-bipyridine)ruthenium(II) with Triethylamine. Possible Participation of a Nonemitting Excited State

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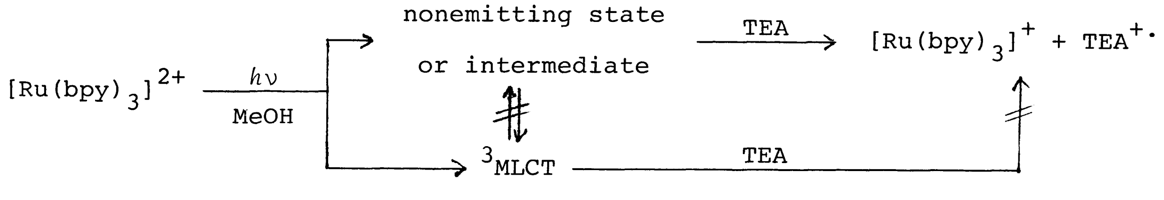
Laser-flash photolysis of $[Ru(bpy)_3]^{2+}$ (bpy=2,2'-bipyridine) and triethylamine in methanol gives $[Ru(bpy)_3]^{+}$ within 100 ns, even though the luminescence of $[Ru(bpy)_3]^{2+}$ is not quenched at all by triethylamine in this solvent. Possible participation of a non-emitting state in the redox reaction is suggested.

Electron-transfer photochemistry of $[Ru(bpy)_3]^{2+}$ and related Ru(II) complexes has been extensively investigated from mechanistic points of view as well as in applications to a variety of fields of redox chemistry. It is now generally accepted that photochemical electron transfer of $[Ru(bpy)_3]^{2+}$ with either an electron donor or an acceptor occurs in the luminescent metal-to-ligand charge-transfer triplet state (^{3}MLCT),[1,2] which is believed to be very rapidly populated with a unit efficiency upon photoexcitation.[2,3] In this paper, we wish to report that photochemical electron transfer of $[Ru(bpy)_3]^{2+}$ with triethylamine (TEA) in methanol proceeds through another mechanistic channel involving a nonemitting state or an intermediate independent of ^{3}MLCT.



A deaerated methanolic solution of $[Ru(bpy)_3]X_2$ (X=Cl, ClO_4, and PF_6) (5×10^{-5} mol dm^{-3}) in the presence or absence of TEA (1.0 mol dm^{-3}) was irradiated with 10-ns pulses at the second harmonic (532 nm) of a Nd:YAG laser.[4] Figure 1 shows the difference absorption spectra, in which the positive absorption at 370 nm and the negative one at 450 nm observed just after the laser pulse in either the presence or absence of TEA can be easily attributed to the ^{3}MLCT formation associated with the bleaching of ground-state $[Ru(bpy)_3]^{2+}$.[5,6] After ^{3}MLCT had completely disappeared within 8 μs, $[Ru(bpy)_3]^+$ (λ_{max} 510 nm[7]) was left as the only detectable transient in the presence of TEA.

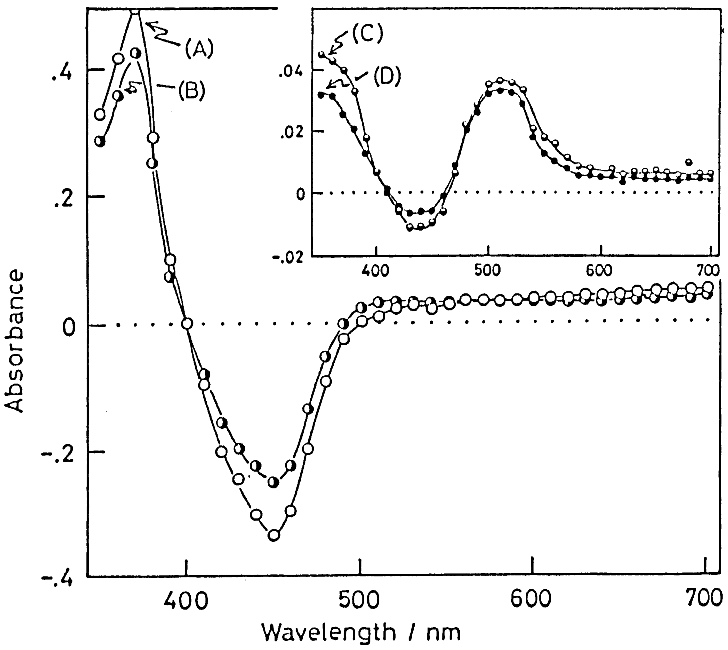


Fig. 1. Difference transient absorption spectra taken (A) immediately after the laser pulse and at the different delay times of (B) 200 ns, (C) 2.8 μs, and (D) 8.0 μs for a deaerated methanolic solution of 5×10^{-5} mol dm^{-3} $[Ru(bpy)_3]Cl_2\cdot6H_2O$ and 1.0 mol dm^{-3} TEA at room temperature.

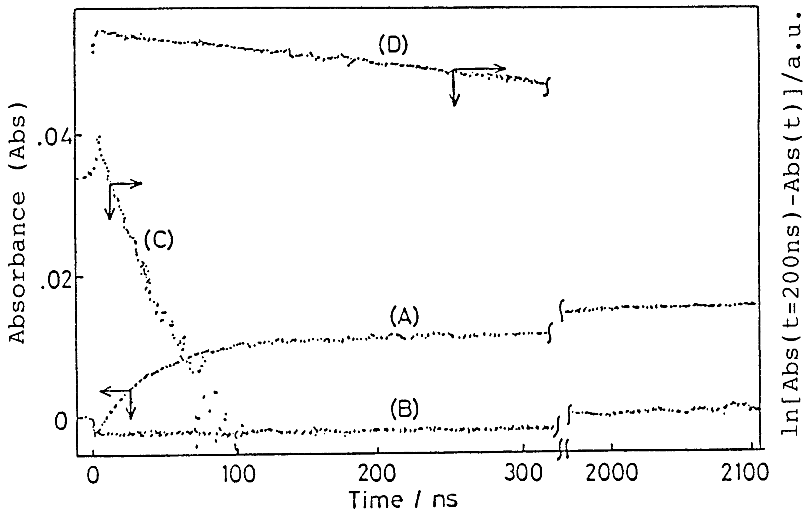


Fig. 2. The time-dependent behavior of the absorbance at 502 nm (A) in the presence of 1.0 mol dm^{-3} TEA and (B) in its absence. (C) A pseudo first-order kinetic plot of the rapid growth at 502 nm compared with (D) a first-order kinetic plot of the ^{3}MLCT luminescence at 610 nm. For a deaerated methanolic solution of 5×10^{-5} mol dm^{-3} $[Ru(bpy)_3](ClO_4)_2$ at room temperature.

The time dependence of the $[Ru(bpy)_3]$+ formation following the laser pulse was monitored at 502 nm where the positive absorption of ^{3}MLCT formed is virtually cancelled by the negative one of $[Ru(bpy)_3]^{2+}$ bleached.[5,6] Figure 2 reveals that TEA is essential for the formation of $[Ru(bpy)_3]^+$ and that the rise of the absorption at 502 nm has mostly completed within 100 ns after the laser pulse and then slowly grows up even at 6 μs. The slow growth can be attributed to the dark reduction of $[Ru(bpy)_3]^{2+}$ by 1-(diethylamino)ethyl radicals formed by the proton loss of TEA$^+$.[8] Surprisingly, however, neither the intensity nor the lifetime of the ^{3}MLCT luminescence is affected at all by 1.0 mol dm^{-3} TEA in methanol.[9] Nevertheless, the "rapid" formation of $[Ru(bpy)_3]^+$ is much faster than the decay rate of the luminescence, following a pseudo first-order kinetics which gives a rate constant of $\approx 2\times 10^7$ dm^3 $mol^{-1}s^{-1}$. Furthermore, yeild of $[Ru(bpy)_3]^+$ relative to ^{3}MLCT is ≈12% with X = Cl and ≈5% with X = ClO_4 and PF_6,[10] exceeding well over possible experimental errors in our intensity and lifetime measurements.

These observations clearly indicate that the observed electron transfer does not involve ^{3}MLCT nor its precursor nor excited states and intermediates following ^{3}MLCT.[11] Alternatively, a complex formed between TEA and $[Ru(bpy)_3]^{2+}$ in the ground state would participate in the photochemical electron transfer as reported for the $[Ru(bpy)_3]^{2+}$-photomediated reduction of methylviologen by ethylenediamine-tetraacetate dianion.[12] However, we obtained no indication for the complex formation in UV-visible, emission, IR, and ^{1}H NMR spectra of the TEA/$[Ru(bpy)_3]^{2+}$ system; there is expected no electrostatic binding force for the complex formation with TEA. These arguments strongly suggest that the "rapid" electron transfer occurs from TEA to a nonemitting state or an intermediate which should be independent of ^{3}MLCT. Although electron transfer in nonemitting states of nonemissive Ru(II) complexes was already reported,[13] the present work reveals a novel mechanistic aspect in electron-transfer photochemistry of emissive $[Ru(bpy)_3]^{2+}$ as well as in the excited-state dynamic behavior.[5,14,15]

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9) The luminescence is quenched by TEA in acetonitrile,[8a] N,N-dimethylformamide, and in acetone at (2-5)x10^5 $dm^3mol^{-1}s^{-1}$ but not at all in methanol. In these aprotic solvents, the "rapid" formation of $[Ru(bpy)_3]^+$ was accompanied by the slow electron transfer in the quenching of luminescence.

10) The relative yields were calculated by the use of the reported molar extinction coefficients of $[Ru(bpy)_3]^+$,[7a] ^{3}MLCT,[6b] and $[Ru(bpy)_3]^{2+}$.[6b]

11) The participation of a precursor of ^{3}MLCT should result in the luminescence quenching by TEA, whereas electron transfer to an excited state or an intermediate generated from ^{3}MLCT should be equal in rate to or slower than the luminescence decay. Another possibility that the "rapid" formation of $[Ru(bpy)_3]^+$ would be the consequence of electron transfer from X^- to ^{3}MLCT can be rigorously eliminated, since $[Ru(bpy)_3]^+$ is formed only in the presence of TEA and since the luminescence is not quenched at all by $[Et_4N]X$ even at 0.2 mol dm^{-3}.

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