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STUDIES ON PHOTOACTIVATED ELCTRON-TRANSPORT SYSTEMS. II. ELECTRON-TRANSFER QUENCHING OF PHOTOEXCITED RUTHENIUM(II) COMPLEXES BY VARIOUS BIPYRIDINIUM IONS[1)]

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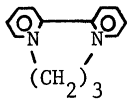
Rate constants for quenching emission from photoexcited tris-(2,2'-bipyridine)- and tris(1,10-phenanthroline)Ru(II) complexes by bipyridinium ion vary with the redox potential of the quencher. Annihilation of the geminate ion pairs at the quenching step can be reduced by the addition of EDTA. The effect of EDTA increases with the concentration but quickly reaches asymptotic values as expected in the presence of an extremely fast geminate recombination of ion pairs in a cage.

Tris(2,2'-bipyridine)ruthenium(II) complexes have been suggested to be one of the most promising catalysts for the photodecomposition of water into hydrogen and oxygen.[2)] Various studies have been carried out by the use of flash photolysis techniques, which proved that an electron-transfer from the photoexcited ruthenium(II) complex to an electron-acceptor is generally followed by an energy-wasting, back-electron-transfer process.[3)] The back-electron-transfer is effectively suppressed, however, if bipyridinium ions are used as the electron-acceptor together with EDTA as a reducing agent in the redox system.[4)] In order to find out some means of minimizing the back-electron-transfer, the mechanistic details of the reactions were investigated by the use of a series of bipyridinium ions and EDTA under various conditions.

The investigated Ru(II) complexes are tris(2,2'-bipyridine)Ru(II) dichloride ($Ru(bpy)_3Cl_2$) and tris(1,10-phenanthroline)Ru(II) perchlorate ($Ru(phen)_3(ClO_4)_2$). An aqueous solution containing the Ru(II) complexes (5×10^{-6} M) and appropriate amounts of bipyridinium ions (2×10^{-4} M $\sim$ 1×10^{-3} M) was deaerated by flushing with purified argon gas and emission from the Ru(II) complex was measured with a Shimadzu Model RF-500 spectrofluorophotometer. The quenching rate constant (k_q) was evaluated by Stern-Volmer plots, where the following value was adopted as the life time of each photoexcited Ru(II) complex: 0.6 μs for $Ru(bpy)_3Cl_2$ and 0.9 μs for $Ru(phen)_3(ClO_4)_2$. Relative rate (k_r) for reduction of Hemin mediated by the same combination of Ru(II) complex and bipyridinium ion was measured by the use of the method described in a previous paper.[4)] Both k_q- and k_r-values are summaried in Table 1, where the redox potential for each bipyridinium ion is included for comparison.

Among the investigated combinations, the largest k_q-value was obtained with

Table 1. Rate constant (k_q) for quenching emission and relative rate (k_r) of reducing Hemin by the use of bipyridinium ions and Ru(II) complexes

Bipyridinium Salt	$E_{pH,5.2}$(V)	$k_q/10^9\ M^{-1}s^{-1}$		k_r	
		$Ru(bpy)_3^{2+}$	$Ru(phen)_3^{2+}$	$Ru(bpy)_3^{2+}$	$Ru(phen)_3^{2+}$
Ph-CH_2-N$\bigcirc$-$\bigcirc$N-CH_2-Ph · Cl_2	-0.24	2.4	3.1	100	135
$HO(CH_2)_2$-N$\bigcirc$-$\bigcirc$N-$(CH_2)_2OH$ · Br_2	-0.30	2.1	2.7	82	110
CH_3-N$\bigcirc$-$\bigcirc$N-CH_3 · Cl_2	-0.34	1.7	2.4	65	94
 · Br_2	-0.44	1.3	2.1	45	69

benzylviologen-$Ru(phen)_3^{2+}$ system. The k_q-value ($3.1 \times 10^9\ M^{-1}s^{-1}$) is a diffusion-controlled limit as it is commonly observed with electron-transfer quenching of the photoexcited Ru(II) complexes.[5] Scince triplet energies of all the investigated bipyridinium ions (ca. 70 kcal/mole) are much higher than those of the Ru(II) complexes (ca. 50 kcal/mole), electron-transfer must be responsible for the quenching in all cases.[6] In agreement with this expectation, k_q-value is found to decrease by as much as $10^9\ M^{-1}s^{-1}$ when $E_{pH,5.2}$-value changes by 0.2 V (Fig. 1). Quenching constants of the emission from Ru(II) complexes have also been reported to depend on the reduction potential of nitro compound (quencher), and the result has been taken to be one of the evidences for electron-transfer quenching mechanism.[7]

In this regard, it is rather surprising that k_q-value for $Ru(bpy)_3^{2+}$ is always less than that for $Ru(phen)_3^{2+}$ by approximately $10^9\ M^{-1}s^{-1}$. The luminescence

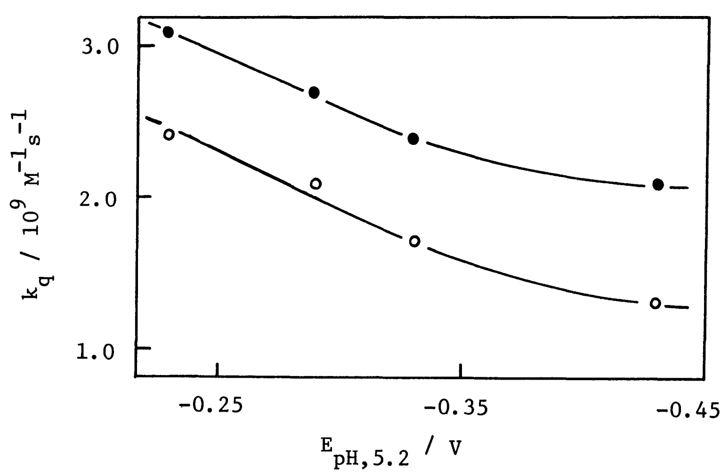


Fig. 1. Relationship between quenching constant (k_q) and redox potential ($E_{pH,5.2}$) of bipyridinium ion: $Ru(bpy)_3^{2+}$ (-o-) and $Ru(phen)_3^{2+}$ (-●-).

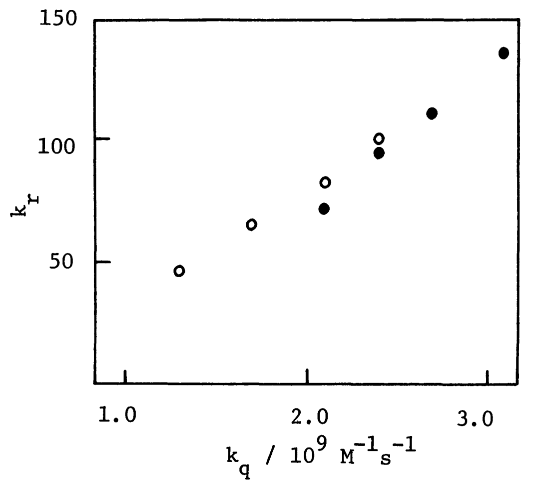


Fig. 2. Correlation between k_q-value and relative reduction rate (k_r) of Hemin. Notations are the same as those in Fig. 1.

spectra of the two ruthenium(II) complexes indicate that the photoexcited species of $Ru(phen)_3^{2+}$ ($E_{pH,5.2}$ = -1.18 V) is a somewhat better reducing agent than that of $Ru(bpy)_3^{2+}$ ($E_{pH,5.2}$ = -1.15 V).[5] The variation in $E_{pH,5.2}$ (0.03 V), however, is too small to account for the difference in k_q-value.

The k_r-values are nicely correlated to k_q-values as shown in Fig. 2. At first, it might be suggested that all of the electron transferred from the ruthenium(II) complexes in the quenching process are transported to Hemin. Quantitative examination, however, clarified that the true situation is fairly different from this suggestion. An aqueous solution containing $Ru(bpy)_3Cl_2$ (5 x 10^{-5} M), MV (5 x 10^{-4} M) and EDTA (1 x 10^{-3} M) was irradiated at the wavelength above 375 nm. Under these conditions, the Stern-Volmer plot indicates that 13 % of the emission from $Ru(bpy)_3^{2+}$ is quenched. In other words, the electron-transfer efficiency from the photoexcited $Ru(bpy)_3^{2+}$ to MV^{2+} at the quenching step must be 13 %. Under steady irradiation of the light, however, the quantum yield for the formation of methylviologen cation radical ($MV^{\dot{+}}$) was 0.02, which means that only 15 % of the electrons transferred at the quenching step survive. The remaining 85 % of the electrons must be lost by back-electron-transfer process. In the absence of EDTA, on the other hand, the efficiency of back-electron-transfer reaches 100 %, as it has been found by laser photolysis techniques.[3] Apparently, the back-electron-transfer and reduction of Ru(III) complex by EDTA are competing with each other. In agreement with this observation, the quantum yield for the formation of $MV^{\dot{+}}$ increases with the concentration of EDTA at first, but the curve quickly reaches a plateau region (Fig. 3).

The most plausible explanation may be that EDTA reduces only free Ru(III) complex which escaped from Coulomb field of the bipyridinium ion radical, the counterpart of the geminate ion-pairs as produced by the photo-induced redox reaction. Formation of free, solvated ions from photoinduced geminate ion pairs has frequently been observed, and the dissociation yield has been noted to vary considerably depending on the situation.[9] In the case of photoexcited charge-transfer complexes, Thomas and his co-workers reported that an extremely fast, geminate recombination of ion pairs proceeds via back-electron-transfer in certain type of cage.[10] A suggestion has been made that electron-transfer quenching of photoexcited Ru(II) complex also takes place in a cage.[11] The effect of EDTA concentration (Fig. 3) is in good agreement with this suggestion.

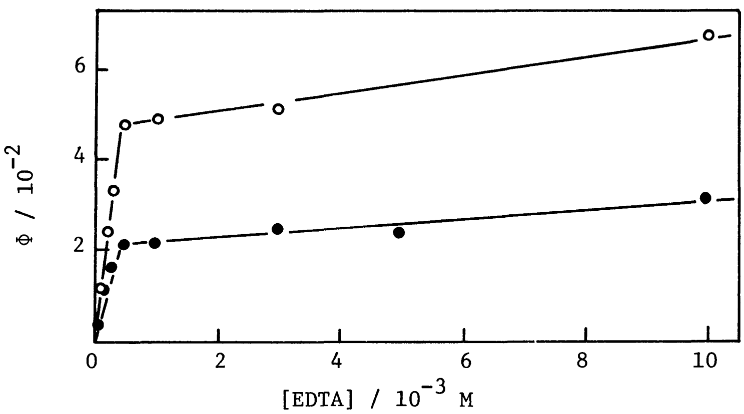


Fig. 3. Effect of EDTA concentration on the quantum yield for formation of bipyridinium ion radicals: $\Phi_{BV^{\dot{+}}}$ (-o-) and $\Phi_{MV^{\dot{+}}}$ (-●-).[8] The reaction was sensitized by $Ru(bpy)_3Cl_2$.

In order to use photoexcited Ru(II) complex for energy-conversion purpose, it is very important to separate the ion-pairs before the geminate recombination takes place. The data in Table 1 indicate that the charge-separation efficiency may be controlled up to some extent by the choice of an electron-acceptor with appropriate redox potential. More pronounced effects are observed with the cases where the electronic charge of an electron-acceptor is varied. One of the examples is Ru(II) complex-sensitized reduction of sodium-1-sulfonate (AQαS) as reported in a previous paper.[4] In the present experiment, the emission from photoexcited $Ru(bpy)_3^{2+}$ was found to be quenched by AQαS with a rate constant ($1 \times 10^{10}\ M^{-1}s^{-1}$), which is somewhat larger than the diffusion-controlled value. Some static quenching might also be involved in this case. The triplet energy of AQαS (ca. 62 kcal/mole) is much higher than that of $Ru(bpy)_3Cl_2$, while the $E_{pH,5.2}$-value (-0.11 V) is located at more positive side than that of BV^{2+}. Then, the quenching must proceed via electron-transfer process.[12] In spite of that, the rate of the photosensitized reduction of AQαS is less by a factor of 14 than the case where the electron transport is mediated via BV^{2+} as reported before.[4] It is quite likely that the geminate recombination of the ion-pairs is a very efficient process in the excited Ru(II) complex-AQαS system, where AQαS bears two negative charges after recieving an electron and finds difficulties in leaving positively charged Ru(III) complex. In the case of BV^{2+}, on the other hand, both components of the ion pair retain positive charges and Coulombic repulsion will facilitate the charge separation of the ion pair. Remarkable effects of Coulombic electric field on the geminate recombination process have also been reported of the photoactivated charge-transfer complex,[10] and Zn-tetraphenylporphyrin-anthraquinonesulfonate at the micellar interfaces.[13] Efficient energy-conversion systems might be obtained by the combination of photo-excited Ru(II) complex and interfaces with electrical field gradient.

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