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Counter Ion Effect on Photoinduced Electron Transfer Reaction between Ruthenium Complexes

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Abstract : Quenching experiments by photoinduced electron transfer between a charged donor and a neutral acceptor were carried out in acetonitrile, dichloromethane and mixed solvents of acetonitrile and dichloromethane. Tris(2,2'-bipyridine) ruthenium(II) ($[Ru(bpy)_3]^{2+}$) which has 2+ charge and dicyanobis (2,2'-bipyridine) ruthenium(II) ($Ru(bpy)_2(CN)_2$) which has no charge were used as electron donors, and a series of tris(ß-diketonato)ruthenium (III) was used as acceptor . In dichloromethane, $[Ru(bpy)_3]^{2+}$ and its counter ions (ClO_4^-) form ion pair. In the estimate of ΔG of electron transfer, the electrostatic potential between counter ions and product ion pair produced by electron transfer must be taken into account. A similar effect of counter ions was found in mixed solvents of 10, 30, 50, 70 and 90% acetonitrile ratio in volume. The effect of counter ion on ΔG became smaller with the increase in acetonitrile ratio. The result in mixed solvents suggests that $[Ru(bpy)_3]^{2+}$ and its counter ions form ion pair even in 90% acetonitrile solution.

Keywords : Photoinduced electron transfer, Ion pair formation, Electrostatic interaction, ionization in mixed solvent

1. Introduction

Tris(2,2'-bipyridine)ruthenium(II) complex ($[Ru(bpy)_3]^{2+}$) has been used as electron donor or electron acceptor [1-8], because its oxidation and reduction potential in the excited state are appropriate for electron donor and acceptor. Most of these experiments were carried out in water or polar organic solvent such as acetonitrile and $[Ru(bpy)_3]^{2+}$ has been treated as a dissociated ion in these works. In low-polar solvent, $[Ru(bpy)_3]^{2+}$ would form ion pair with counter ions. [9] Counter ions which exist in the immediate neighborhood of $[Ru(bpy)_3]^{2+}$ should influence electron transfer. In this paper, quenching

experiments of $[Ru(bpy)_3](ClO_4)_2$ via photoinduced electron transfer by a series of tris(ß-diketonato)ruthenium(III) ($Ru(ß\text{-diketonato})_3$) were carried out in dichloromethane (low polar solvent), acetonitrile (polar solvent) and acetonitrile-dichloromethane mixed solvents. The result was compared with dicyanobis(2,2'-bipyridine)ruthenium(II) complex ($Ru(bpy)_2(CN)_2$) system which has no charge, therefore the effect of counter ions does not arise. In the relationship between k_q and ΔG estimated on the assumption that $[Ru(bpy)_3]^{2+}$ is dissociated ion, $[Ru(bpy)_3]^{2+}$ system was different from $Ru(bpy)_2(CN)_2$ system in dichloromethane, greatly. However, such a difference was not found in acetonitrile. These results are attributable to the effect of the electrostatic potential between counter ions and product-ion pair by electron transfer on ΔG.

ΔG of oxidative photoinduced electron transfer is expressed as a following equation [10],

$$\Delta G = -E(A) + E(D) - E_{0-0}(^*D) + Z_a Z_d e^2/\varepsilon a \quad (1)$$

where $E(A)$ is the reduction potential of electron acceptor, $E(D)$ is the oxidation potential of electron donor, $E_{0\text{-}0}(^*D)$ is the energy of the excited state of electron donor, Z_d and Z_a are the charge of electron donor and acceptor after electron transfer, e is the relative dielectric constant of solvent, and a is the distance between nucleus of electron donor and acceptor, respectively.

The last term of eq(1) is the electrostatic energy of the product-ion pair which arises after electron transfer. In the case that $[Ru(bpy)_3]^{2+}$ and its counter ions form the ion pair, the electrostatic energy between the counter ions around $[Ru(bpy)_3]^{2+}$ and the product-ion pair produced by electron transfer should be taken into consideration in the estimate of ΔG of electron transfer. In this paper, ΔG of electron transfer will be discussed considering the electrostatic energy of the counter ions of $[Ru(bpy)_3]^{2+}$.

2.Experimental

2-1 Materials. $Ru(bpy)_2(CN)_2$ and a series of $Ru(ß\text{-diketonato})_3$ complexes were prepared according to the method reported earlier [11] except $Ru(acac)_2(dbm)$ and $Ru(dpm)_2(acp)$. $[Ru(bpy)_3](ClO_4)_2$ was prepared according to Palmer's method.[12] $Ru(acac)_2(dbm)$ and $Ru(dpm)_2(acp)$ were prepared by the substitution reaction of $[Ru(acac)_2(CH_3CN)_2]ClO_4$ and $[Ru(dpm)_2(CH_3CN)_2]ClO_4$, respectively. [13] All the complexes used in this work were identified by elemental analysis.

2-2 Measurements Absorption, emission, emission lifetime and electrochemical measurements were described earlier. [11] Sample solutions were parged by bubbling argon gas before lifetime measurements. All the quenching experiments were carried out at 298 K.

3. Results and Discussion

3-1 Quenching mechanism The quenching rate constants (k_q) were determined by Stern-Volmer plot of emission life time. All the plots gave straight lines whose intercepts were unity. With the decrease in the reduction potential of the quenchers, k_q became smaller . This result indicates that the quenching takes place in the oxidative quenching mechanism. The quenching of luminescence of $[Ru(bpy)_3](ClO_4)_2$ and $Ru(bpy)_2(CN)_2$ is ascribed to electron transfer from ruthenium(II) complexes to ruthenium(III) complexes.

3-2 The relationship between ΔG and k_q In the oxidative quenching mechanism, ΔG is expressed as eq(1). [10] $E_{0\text{-}0}(^*D)$ is estimated from the energy of the emission peak which is calibrated by Lippert's method [14]. In this work, a is estimated to be 10Å. [15, 16] The values of ΔG were estimated by eq(1) on the assumption that Z_d is 3+ for $[Ru(bpy)_3]^{2+}$

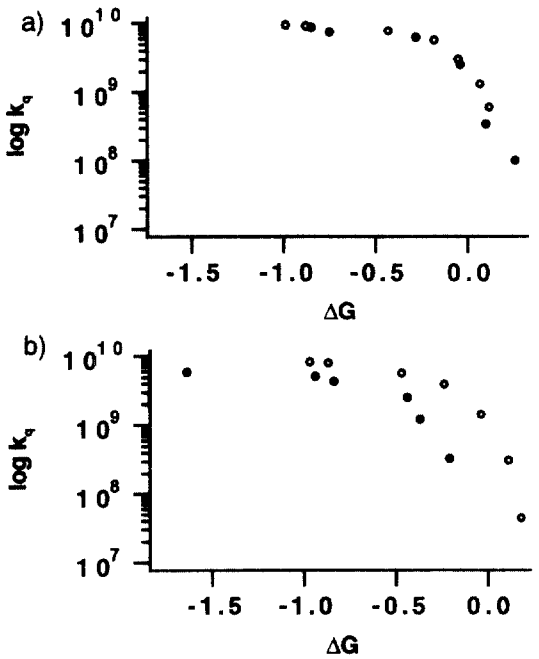

Fig.1 Relationship between ΔG and log k_q of $[Ru(bpy)_3](ClO_4)_2$ (●) and $Ru(bpy)_2(CN)_2$ (○) a) in acetonitrile b) in dichloromethane

system. Fig. 1 shows the relationship between ΔG and k_q. In acetonitrile (fig.1(a)), there was no remarkable difference between $Ru(bpy)_2(CN)_2$ system and $[Ru(bpy)_3]^{2+}$ system. However, in dichloromethane, an obvious difference was found between those systems. $[Ru(bpy)_3]^{2+}$ system was shifted about 0.3 eV to the exothermic region.

Vining *et al.* indicated that $[Os(phen)_3]^{2+}$ forms ion pair with its counter ions in dichloromethane. [9] Therefore, $[Ru(bpy)_3]^{2+}$ would form ion pair with ClO_4^- ions in dichloromethane. In low polar solvent, counter ions exist in the immediate neighborhood of electron donor, therefore counter ions may affect on electron transfer. The main effects of counter ions on electron transfer reaction are as follows.

(i) Reorientation energy.

In Marcus' treatment [17-19], the activation energy of outer sphere electron transfer is expressed as eqs(2)-(4),

$$\Delta G^{\ddagger} = \frac{(-\Delta G - \lambda)^2}{4\lambda} \tag{2}$$

$$\lambda = \lambda_{in} + \lambda_{out} \tag{3}$$

$$\lambda_0 = (\Delta e)^2 \left[\frac{1}{2r_1} + \frac{1}{2r_2} - \frac{1}{a}\right]\left[\frac{1}{D_{op}} - \frac{1}{D_s}\right] \tag{4}$$

where λ is the reorientation energy which consists the inner sphere reorientation energy (λ_{in}) and the outer sphere reorientation energy (λ_{out}), λ_0 is the solvent reorientation energy which mainly constitutes λ_{out}, r_1 and r_2 are radii of reactants, a is the distance between nucleus of electron donor and acceptor, and D_s and D_{op} are the static and optical dielectric constants of solvent, respectively. The electric structure of electron donor and acceptor in this study is low spin d^6-d^5 before electron transfer and low spin d^5-d^6 after electron transfer. In such a redox system, the structural change of complexes is very small over electron transfer. Thus, λ_{in} is negligibly small compared with λ_{out}. According to eq(4), the redox systems, in which radii of reactants of each system are the same, have the same solvent reorientation energy. In the redox systems, the radii of $Ru(bpy)_2(CN)_2$ and $[Ru(bpy)_3]^{2+}$ are almost the same. Therefore, the solvent reorientation energies of both redox systems are almost the same. Actually, ΔG dependence of k_q in acetonitrile is the same, as shown in fig. 1(a). In dichloromethane, $[Ru(bpy)_3]^{2+}$ forms ion pair with ClO_4^- and the radius of reactant seems to increase. However, counter ions do not participate in electron transfer reaction, *i.e.*, counter ions do not contribute to λ_0, because Δe in eq(4) is zero for the counter ions.

(ii) The electrostatic effect on ΔG.

The last term of eq(1) is the electrostatic potential of ion pair which is produced by electron transfer. In the situation that $[Ru(bpy)_3]^{2+}$ and ClO_4^- form ion pair, the counter ions which exist in the immediate neighborhood of $[Ru(bpy)_3]^{2+}$ should interact electrostatically with the product-ion pair produced by electron transfer. This electrostatic potential must be taken into consideration in the estimate of ΔG. However, ΔG was estimated using eq(1) under the assumption that the electron donor was a dissociated ion (in eq(1), Z_d=3+) and the interaction of counter ions was neglected. Neglect of

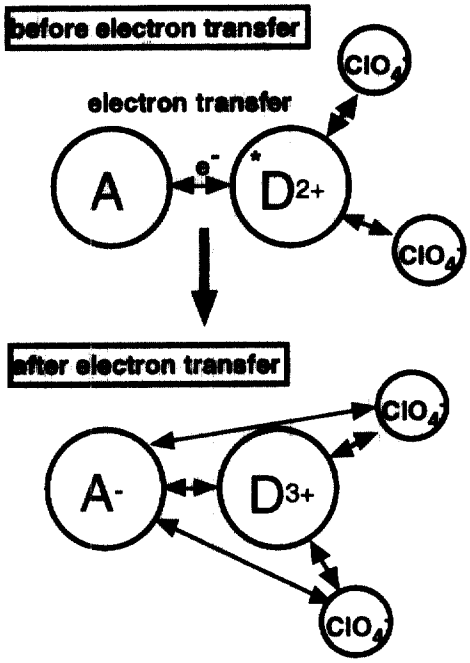

Fig. 2 The electrostatic interaction before and after electron transfer

this effect seems to be the main reason of the obvious difference between $[Ru(bpy)_3](ClO_4)_2$ system and $Ru(bpy)_2(CN)_2$ system in dichloromethane, because the effect of the electrostatic potential is large in low polar solvent.

3-3 The electrostatic interaction by counter ions before and after electron transfer In the situation mentioned above, the estimate of ΔG should be reconsidered. Fig. 2 indicates the electrostatic interactions before and after electron transfer schematically, where D^{2+} is electron donor ($[Ru(bpy)_3]^{2+}$), A is electron acceptor (Ru(ß-diketonato)$_3$), and ClO_4^- is the counter ion of electron donor.

Before electron transfer, the electrostatic interaction serves only between D^{2+} and ClO_4^-.

The electrostatic potentials, which are produced after electron transfer, are those between D^{3+} and A^-, between D^{3+} and ClO_4^-, and between A^- and ClO_4^-. The first potential is contained in eq(1). The electrostatic interaction between electron donor and its counter ions both before and after electron transfer

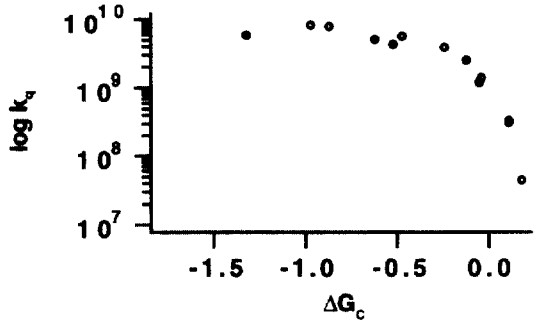

Fig.3 Relationship between ΔG_C and log k_q of $[Ru(bpy)_3](ClO_4)_2$ (●) and $Ru(bpy)_2(CN)_2$ (○) in dichloromethane

seems to be included in E(D) and $E_{0\text{-}0}(^*D)$ obtained experimentally, because E(D) and $E_{0\text{-}0}(^*D)$ were determined in the condition that $[Ru(bpy)_3]^{2+}$ and ClO_4^- form ion pair in low polar solvent. Therefore, the potential which should be taken into consideration is that between A^- and ClO_4^-.

ΔG which contains this electrostatic potential is expressed as in eq(5),

$$\Delta G_C = -E(A) + E(D) - E_{0-0}(^*D) + Z_a Z_d e^2/\varepsilon a + C Z_c Z_c e^2/\varepsilon b \quad (5)$$

where C is the number of counter ion, Z_c is the charge of a counter ion and b is the distance between [Ru(ß-diketonato)$_3$]$^-$ and ClO_4^-.

3-4 ΔG in $[Ru(bpy)_3](ClO_4)_2$ system in low polar solvent The ΔG dependence of k_q in $[Ru(bpy)_3](ClO_4)_2$ system can be superposed to that of $Ru(bpy)_2(CN)_2$ system by changing the value of b. These two systems fitted very well at b=10Å. The result of fitting is shown in fig. 3. The estimated value of b(10 Å) may be felt too short, because the estimated value of the nuclear distance between complexes (a) is 10 Å, too. This result suggests that $[Ru(bpy)_3](ClO_4)_2$ behaves as 1+ charged complex after electron transfer between $[Ru(bpy)_3](ClO_4)_2$ and Ru(ß-diketonato)$_3$ in low polar solvent.

3-5 The relationship between ΔG and k_q in the mixed solvents The electrostatic effect on ΔG by the counter ions of $[Ru(bpy)_3]^{2+}$ which form ion pair in

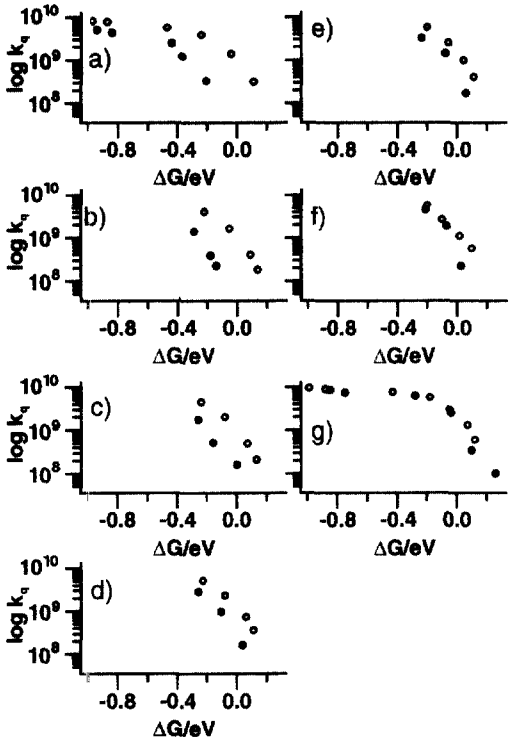

Fig.4 Relationship between ΔG and log k_q of $[Ru(bpy)_3](ClO_4)_2$ (●) and $Ru(bpy)_2(CN)_2$ (○) in mixed solvents
The ratio of acetonitrile is a) 0% b) 10% c) 30% d) 50% e) 70% f) 90% g) 100%.

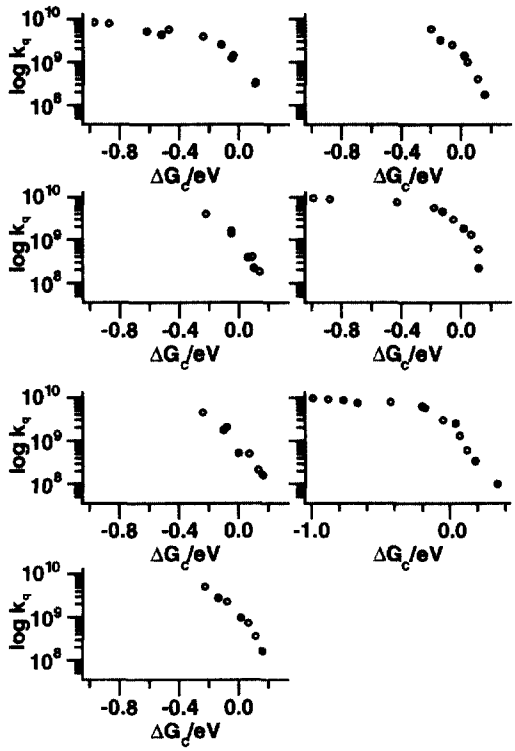

Fig.5 Relationship between ΔG_C and log k_q of $[Ru(bpy)_3](ClO_4)_2$ (●) and $Ru(bpy)_2(CN)_2$ (○) in mixed solvents
The ratio of acetonitrile is a) 0% b) 10% c) 30% d) 50% e) 70% f) 90% g) 100%.

low polar solvent was found in dichloromethane, however not in acetonitrile. This effect of counter ions seems to be applicable to the study of the dissociation of $[Ru(bpy)_3](ClO_4)_2$ in mixed solvents. The quenching experiments of $[Ru(bpy)_3](ClO_4)_2$ and $Ru(bpy)_2(CN)_2$ by Ru(ß-diketone)$_3$ were carried out in dichloromethane-acetonitrile mixed solvents (10, 30, 50, 70, 90% acetonitrile in the volume ratio).

In the estimate of ΔG, we used the experimental values for E(A), E(D) and $E_{0\text{-}0}$(*D). Dielectric constants of mixed solvents were assumed to be proportional to the ratio of solvent.

The relationships between ΔG and k_q in 0-100% acetonitrile solvent were shown in fig. 4. In 0-90% acetonitrile solutions, the relationship in $[Ru(bpy)_3](ClO_4)_2$ system was shifted to the exothermic region compared with $Ru(bpy)_2(CN)_2$ system. This shift became smaller with the increase in the ratio of acetonitrile. The relationships between ΔG_C (the energy gap estimated by eq(5)) and k_q in 0-100% acetonitrile solvent were also shown in fig. 5. In the estimation of ΔG_C in mixed solvents, the value of *b* was adopted the same value in dichloromethane (10Å). The relationships of both systems agree with each other in 0-100% acetonitrile solutions. The decrease in the difference in the relationship between k_q and ΔG with the increase in acetonitrile content is attributed to the decrease in the electrostatic interaction by the increase in the dielectric constant of solvent but not to the dissociation of $[Ru(bpy)_3](ClO_4)_2$. In other words, perchlorate ions exist in the immediate neighborhood of $[Ru(bpy)_3]^{2+}$, and the dissociation by the selective solvation of ion

pair does not occur even in 90% acetonitrile mixed solvent.

In 100% acetonitrile solution, the relationship of ΔG and k_q in $[Ru(bpy)_3](ClO_4)_2$ system almost agreed with that in $Ru(bpy)_2(CN)_2$ system, and the relationship between ΔG_C and k_q in $[Ru(bpy)_3](ClO_4)_2$ system agreed with that in $Ru(bpy)_2(CN)_2$ system, too. Considering the result in 90% acetonitrile solution, this result seems to indicate that $[Ru(bpy)_3]^{2+}$ and ClO_4^- form ion pair even in 100% acetonitrile solution and also shows that the difference in ΔG dependence of k_q between $[Ru(bpy)_3](ClO_4)_2$ system and $Ru(bpy)_2(CN)_2$ system was not observed in acetonitrile because the electrostatic interaction by counter ions is small owing to the high dielectric constant of acetonitrile.

Conclusion

In this paper, the counter ion effect on photoinduced electron transfer reaction is demonstrated using ruthenium (II)-ruthenium (III) complexes redox system. In dichloromethane (low polar solvent), charged complex formed ion pair with its counter ions. Counter ions in ion pair affected on ΔG of electron transfer. In the re-estimation process of ΔG, it was ascertained that whole of ion pair behaved as 1+ charged complex after electron transfer. In dichloromethane-acetonitrile mixed solvent, charged complex formed ion pair with its counter ions even in 90% acetonitrile solution.

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