Kinetics–energetics relationship during the electron transfer from trivalent phosphorus compounds to the singlet photoexcited sensitizers

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The rate constants k_{ET} for the electron transfer (ET) from trivalent phosphorus compounds Z_3P to the singlet photoexcited states $^1S^*$ of neutral sensitizers, i.e., 9,10-dicyanoanthracene (DCN) and 9-cyanoanthracene (CA), were determined based on the Stern–Volmer (SV) method. As previously found in the ET from Z_3P to the singlet photoexcited states $^1S^{+*}$ of a monocationic sensitizer, i.e., rhodamine 6G (Rho^+), the plot of $\log k_{ET}$ *versus* the free-energy change of the ET step, ΔG_0, in the endothermic region deviated upward from the line predicted by the Rehm–Weller theory. The deviation was slightly greater during the ET to $^1S^*$ than during the ET to $^1S^{+*}$. Copyright © 2008 John Wiley & Sons, Ltd.

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Various types of trivalent phosphorus compounds Z_3P quench the singlet photoexcited states of sensitizers through an ET mechanism.[1–4] This quenching system is a convenient tool to evaluate the dependence of the rate of the ET from Z_3P on the free-energy change of the ET step, ΔG_0, because the rate constant k_{ET} is easily determined using the Stern–Volmer (SV) method and also because ΔG_0 can be tuned by combination of a sensitizer with Z_3P having various oxidation potentials. Previously, we examined the mechanism of the ET quenching of a monocationic acceptor, the singlet photoexcited state of Rho^+ ($^1Rho^{+*}$), using a series of Z_3Ps based on the SV method.[1] This type of the ET is accompanied by the shift of the cationic charge from the acceptor to the donor. In the present study, we performed the SV analysis of the ET quenching of a neutral counterpart, the singlet photoexcited states of **DCA** and **CA** ($^1DCA^*$ and $^1CA^*$, respectively), which is accompanied by the charge separation to afford the geminate radical ion pair. Comparing the results of these studies, the dependence of the ET rate on ΔG_0 was found to depend on whether the acceptor is neutral ($^1CA^*$) or monocationic ($^1Rho^{+*}$). The quenching of the singlet photoexcited state of 10-methylacridinium cation Ac^+ ($^1Ac^{+*}$) was also examined in the present study to obtain additional data for the ET from Z_3P to a monocationic acceptor (Scheme 1).

The intensities of the fluorescence from a sensitizer S^0 (() = 0 or +) in the singlet photoexcited state $^1S^{0*}$ in the absence and presence of Z_3P, I_0 and I respectively, were recorded on a Shimadzu spectrofluorophotometer RF-5000 at room temperature in acetonitrile.[5] For each combination of Z_3P and S^0, the relationship between the ratio I_0/I and the concentration of added Z_3P, $[Z_3P]$, obeyed the SV equation (Eqn (1)). The quenching constant k_q was obtained dividing the slope of the plot by the life time of the fluorescence τ:

$$I_0/I = 1 + k_q \tau [Z_3P] \tag{1}$$

The half-wave potential of Z_3P, $E_{1/2}(Z_3P)$, was measured by a rotating disk electrode (RDE) using a BAS RDE-1 equipped with an ALS electrochemical analyzer Model 620A in acetonitrile at room temperature (Table 1). The half-wave potential of $^1S^{0*}$, $E_{1/2}(^1S^{0*})$, was calculated according to

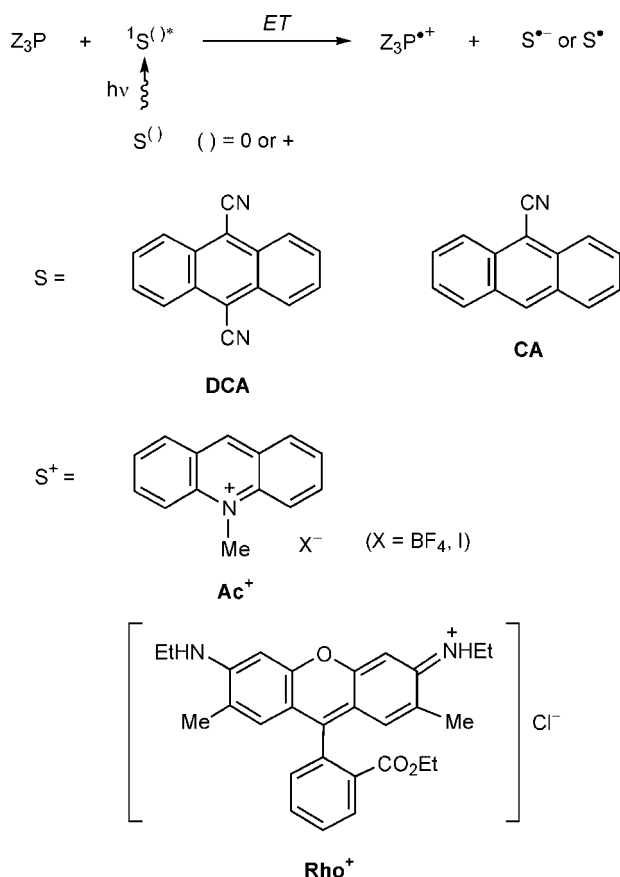$$E_{1/2}(^1S^{()*}) = E_{1/2}(S^{()}) + \Delta E_{0,0}(S^{()}) \tag{2}$$

where $E_{1/2}(S^0)$ is the half-wave potential of the sensitizer in the ground state S^0, and $\Delta E_{0,0}(S^0)$ is the photoexcitation energy from S^0 to $^1S^{0*}$. Finally, the free-energy change of the ET step ΔG_0 (in eV) is given by Eqn (3). Table 2 lists the $E_{1/2}(S^0)$ and $E_{1/2}(^1S^{0*})$ values along with the τ values:

$$\Delta G_0 = E_{1/2}(Z_3P) - E_{1/2}(^1S^{()*}) \tag{3}$$

Since the quenching of $^1S^{0*}$ occurs through the ET mechanism, the quenching constant k_q is equivalent to the ET rate constant k_{ET}. Indeed, the UV-visible spectra of the evaluated sensitizers did not change upon the addition of Z_3P either in the dark or under the irradiation. The logarithm of k_{ET} ($=k_q$) is plotted *versus* ΔG_0 in Fig. 1, which shows that the rate of the ET occurring in the exothermic region ($\Delta G_0 < 0$) is diffusion limited ($\approx 2 \times 10^{10}\,M^{-1}s^{-1}$). In the endothermic region ($\Delta G_0 > 0$), the rate drops as ΔG_0 becomes more positive. The decrease in the ET rate with increasing ΔG_0 is predictable by the Rehm–Weller (RW) theory,[10] but the plots in Fig. 1 deviate upward from the prediction by the

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$$Z_3P \quad + \quad {}^1S^{()*} \quad \xrightarrow{ET} \quad Z_3P^{\bullet+} \quad + \quad S^{\bullet-} \text{ or } S^\bullet$$

$$h\nu \Bigg\updownarrow$$

$$S^{()} \quad (\,) = 0 \text{ or } +$$

S =

DCA

CA

$S^+ =$

Ac$^+$ X^- (X = BF$_4$, I)

Rho$^+$

Scheme 1.

Table 2. Photochemical and electrochemical properties of sensitizers

Sensitizer	τ/ns[a]		$E_{1/2}(S^0)$	$E_{1/2}({}^1S^{0*})$
	in MeCN	in CH$_2$Cl$_2$	/V versus Ag/Ag$^+$	/V versus Ag/Ag$^+$
Rho$^+$	3.0[b]	—	−1.10[c]	1.22
Ac$^+$	32.9[d]	—	−0.73[d]	2.22
DCA	12.7[d]	12.2[e]	−1.23[f]	1.69
CA	11.5[d]	12.5[e]	−1.95[e]	1.10

[a] Fluorescence lifetime in aerated solution.
[b] Reference [6] in EtOH.
[c] Measured by RDE in this study. This value is in good agreement with the value previously estimated on the basis of the peak reduction potential E_p^{red}. As given in Reference [1].
[d] Reference [7].
[e] Reference [8].
[f] Reference [9].

within the category of the RW theory.[8] Thus, the peculiar kinetics observed here results from the intrinsic character of the phosphorus compounds. The trivalent phosphorus radical cation $Z_3P^{\bullet+}$ resulting from the ET from Z_3P undergoes a rapid reaction with a nucleophile such as water or alcohol in the solvent,[1,9,12–14] which makes the ET step irreversible and causes the $\log k_{ET}$–ΔG_0 plot to deviate upward. The similar deviated plot has been observed in several "irreversible ET" reactions, where the ET step is driven by a rapid follow-up reaction such as bond-breaking.[15,16] Such a reactivity of $Z_3P^{\bullet+}$ is in sharp contrast to that of amine or carbon radical cations.

Interestingly, Fig. 1 shows two separate lines, one for the ET to monocationic acceptors, ${}^1Rho^{+*}$ and ${}^1Ac^{+*}$, and another for the ET to neutral acceptors, ${}^1DCA^*$ and ${}^1CA^*$. Our previous study has shown that when the plot is approximated by a linear line, the slope that represents the degree of the deviation from the theory is an index of the position of the transition state (TS) in the ET
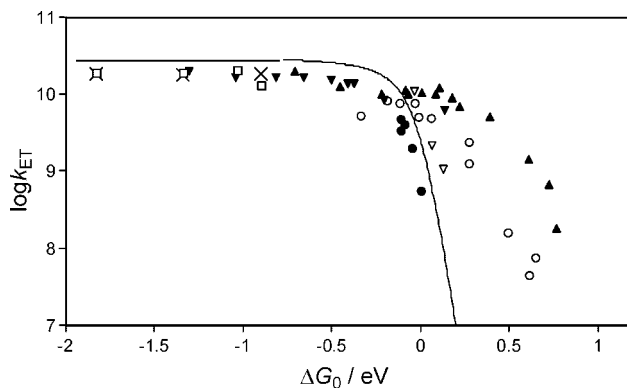
theory. Meanwhile, we found in the present study that amines or alkoxylbenzenes also quench ${}^1Rho^{+*}$ and ${}^1CA^*$ through the ET mechanism, the $\log k_{ET}$–ΔG_0 plots for both cases giving the points that fall on a single line following the RW theory.[11] It has also been shown that the dependence of k_{ET} on ΔG_0 during the ET quenching of ${}^1Ac^{+*}$ and ${}^1DCA^*$ by alkyl- or alkoxybenzenes is

Table 1. Half-wave potential of Z_3P

Z_3P	$E_{1/2}$/V versus Ag/Ag^{+a}	Z_3P	$E_{1/2}$/V versus Ag/Ag^{+a}
Mes$_3$P	0.39	p-Cl-Ph$_3$P	1.32
p-An$_3$P	0.65	Bu$_3$P	1.10
o-Tol$_3$P	0.88	Ph$_2$POMe	1.21[b]
m-Tol$_3$P	1.02	Ph$_2$POEt	1.28
p-Tol$_3$P	1.03	PhP(OMe)$_2$	1.49[b]
Ph$_3$P	1.19	PhP(OEt)$_2$	1.49
Ph$_2$(o-Tol)P	1.14	(MeO)$_3$P	1.87
Ph$_2$(p-Tol)P	1.11	(EtO)$_3$P	1.83
p-F-Ph$_3$P	1.21	(Pr^{i}O)$_3$P	1.71

[a] Half-wave potential measured by RDE in MeCN.
[b] Based on the peak oxidation potentials E_p^{ox} determined by cyclic voltammetry; calculated by assuming $E_{1/2} = E_p^{ox} − 0.03$. As given in Reference [1].

Figure 1. Plot of $\log k_{ET}$ versus ΔG_0 for the ET from Z_3P to ${}^1S^{0*}$ in MeCN. S^0 = ▲; **CA**, ▼; **DCA**, ○; **Rho$^+$**, □; **Ac$^+$** (iodide salt), × ; **Ac$^+$** (tetrafluoroborate salt). ● and ▽ denote the plots for the ET from amines to ${}^1Rho^{+*}$ and from alkoxybenzenes to ${}^1CA^*$, respectively. The line represents the prediction by the RW theory

step; the less negative the slope, the earlier the TS becomes.[13] According to this hypothesis, the product of the ET to ^{1}**DCA*** and ^{1}**CA*** should be more stable than that of the ET to ^{1}**Rho**$^{+*}$ and ^{1}**Ac**$^{+*}$ to make the TS earlier. Indeed, the former ET results in the geminate radical ion pair that may be stabilized by the Coulombic interaction. Anticipating that the Coulombic stabilization must be more important in the ET in less polar solvent, we measured the rates of the ET from Ph$_3$P, *p*-Cl-Ph$_3$P, and (EtO)$_3$P to ^{1}**CA*** using dichloromethane as solvent instead of acetonitrile. However, the obtained rates were almost identical to those of the corresponding ET occurring in acetonitrile (not plotted in Fig. 1), showing that the contribution of the Coulombic stabilization of the radical ion pair generated during the ET to the neutral acceptor is small, if any. Alternatively, the present finding could be accounted for on the basis of the brand new mechanism proposed by Farid and Gould, a bonded exciplex mechanism, which states that an ET rate higher than the RW prediction in the endothermic region results from the formation of a covalent bond during the exciplex stage.[17] This mechanism is an extension to the previously reported "multiple RW plots,"[18–22] where the ET quenching of ^{1}**DCA*** by *n*-donors such as aliphatic amines gives the $\log k_{ET}$–ΔG_0 plot horizontally shifted in the positive direction relative to the plot for the quenching by π-donors such as aromatic hydrocarbons. This finding has been interpreted to result from a more efficient interaction of the former donors with ^{1}**DCA*** than with the latter ones.[21,22] If this mechanism is operative in our ET, the "dual RW plots" in Fig. 1 imply the difference in the affinity of the phosphorus atom in Z$_3$P toward **CA** and **Rho**$^+$.

Acknowledgements

REFERENCES

[1] S. Yasui, M. Tsujimoto, K. Itoh, A. Ohno, *J. Org. Chem.* **2000**, *65*, 4715–4720.

[2] S. Yasui, K. Shioji, A. Ohno, M. Yoshihara, *J. Org. Chem.* **1995**, *60*, 2099–2105.

[3] S. Fukuzumi, K. Ohkubo, T. Suenobu, K. Kato, M. Fujitsuka, O. Ito, *J. Am. Chem. Soc.* **2001**, *123*, 8459–8467.

[4] S. Yasui, S. Tojo, T. Majima, *J. Org. Chem.* **2005**, *70*, 1276–1280.

[5] There was no appreciable difference in k_{ET} whether the solvent was deaerated or aerated.

[6] H. E. Lessing, A. Von Jena, M. Reichert, *Chem. Phys. Lett.* **1975**, *36*, 517–522.

[7] K. Kikuchi, C. Sato, M. Watabe, H. Ikeda, Y. Takahashi, T. Miyashi, *J. Am. Chem. Soc.* **1993**, *115*, 5180–5184.

[8] T. Niwa, K. Kikuchi, N. Matsusita, M. Hayashi, T. Katagiri, Y. Takahashi, T. Miyashi, *J. Phys. Chem.* **1993**, *97*, 11960–11964.

[9] M. Nakamura, M. Miki, T. Majima, *J. Chem. Soc. Perkin Trans. 2* **2000**, 1447–1452.

[10] D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259–271.

[11] For simplicity, only the selected points for the ET from amines and alkoxylbenzenes to ^{1}**Rho**$^{+*}$ and ^{1}**CA***, respectively, are given in Fig. 1.

[12] S. Yasui, K. Shioji, M. Tsujimoto, A. Ohno, *J. Chem. Soc. Perkin Trans. 2* **1999**, 855–862.

[13] S. Yasui, K. Itoh, M. Tsujimoto, A. Ohno, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1311–1318.

[14] S. Yasui, K. Itoh, A. Ohno, N. Tokitoh, *Org. Biomol. Chem.* **2006**, *4*, 2928–2931.

[15] G. B. Schuster, *J. Am. Chem. Soc.* **1979**, *101*, 5851–5853.

[16] J. M. Savéant, *Acc. Chem. Res.* **1993**, *26*, 455–461.

[17] R. S. Farid, I. R. Gould, *J. Org. Chem.* **2007**, *72*, 6970–6981.

[18] P. Jacques, E. Haselbach, A. Henseler, D. Pilloud, P. Suppan, *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 3811–3813.

[19] P. Jacques, D. Burget, *J. Photochem. Photobiol. A: Chem.* **1992**, *68*, 165–168.

[20] P. Jacques, X. Allonas, *J. Photochem. Photobiol. A: Chem.* **1994**, *78*, 1–5.

[21] T. N. Inada, K. Kikuchi, Y. Takahashi, H. Ikeda, T. Miyashi, *J. Photochem. Photobiol. A: Chem.* **2000**, *37*, 93–97.

[22] A. I. Burshtein, K. L. Ivanov, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4115–4125.

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