Quenching of a Photosensitized Dye through Single-Electron Transfer from Trivalent Phosphorus Compounds

Shinro Yasui,*,† Munekazu Tsujimoto,† Kenji Itoh,‡ and Atsuyoshi Ohno‡,§

Tezukayama College, Gakuen-Minami, Nara, 631-8585, Japan, and Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011, Japan

yasui@tandai.tezukayama-u.ac.jp

Various types of trivalent phosphorus compounds **1** undergo single-electron transfer (SET) to the photoexcited state of rhodamine 6G (**Rho**$^{+*}$) in aqueous acetonitrile to quench the fluorescence from **Rho**$^{+*}$. The rate constants k_p for the overall SET process were determined by the Stern–Volmer method. The rate is nearly constant at a diffusion-controlled limit in the region of $E_{1/2}(\mathbf{1})$ < 1.3 V (vs Ag/Ag$^+$), whereas log k_p depends linearly on $E_{1/2}(\mathbf{1})$ in the region of $E_{1/2}(\mathbf{1})$ > 1.3 V, the slope of the correlation line being $-\alpha F/RT$ with $\alpha = 0.2$. The potential at which the change in dependence of log k_p on $E_{1/2}(\mathbf{1})$ occurs (1.3 V) is in accordance with the value of $E_{1/2}(\mathbf{Rho}^{+*})$ (1.22 V) that has been obtained experimentally. Thus, the SET step is exothermic when $E_{1/2}(\mathbf{1})$ < 1.3 V and endothermic when $E_{1/2}(\mathbf{1})$ > 1.3 V. The α-value (0.2) obtained in the endothermic region shows that the SET step from **1** to **Rho**$^{+*}$ is irreversible in this region. Trivalent phosphorus radical cation **1**$^{•+}$ generated in the SET step undergoes an ionic reaction with water in the solvent rapidly enough to make the SET step irreversible. In contrast, the SET from amines **2** and alkoxybenzenes **3** to **Rho**$^{+*}$ is reversible when the SET step is endothermic, meaning that the radical cations **2**$^{•+}$ and **3**$^{•+}$ generated in the SET step undergo rapid "back SET" in the ground state to regenerate **2** and **3**.

Introduction

Trivalent phosphorus compounds Z$_3$P readily undergo single-electron transfer (SET) to good electron acceptors, generating the corresponding trivalent phosphorus radical cations Z$_3$P$^{•+}$.[1,2] To elucidate energetics of SET processes from Z$_3$P is of great importance from a mechanistic point of view and also because Z$_3$P$^{•+}$ has synthetic potential.[3] However, there has been no report so far, except for the one from our group,[4] to discuss such SET processes quantitatively.

Rehm and Weller carried out kinetics on fluorescence quenching occurring through SET in a number of donor–acceptor pairs.[5] To explain a relationship found between SET rate and free-energy change, they presented a mechanistic model by postulating that a radical pair generated in the SET step disappears mainly through a rapid back SET; that is, SET takes place in a *reversible* way in this model. This model in fact explains well a kinetic behavior in many types of photoinduced SET reactions and has eventually been found applicable to SET reactions occurring in the dark.[6] Nevertheless, in some SET reactions, dependence of SET rate on free-energy change is weaker than predicted by the Rehm–Weller's model at the region where the SET step is endothermic.[7–12] Schuster showed that such a kinetic behavior is observed when the SET step is followed by a rapid chemical reaction of the resulting radical pair;[13] SET takes place in an *irreversible* way in this case.

A family of rhodamine dyes is a useful tool to study SET processes kinetically, because a dye of this family is intensely fluorescent on photoexcitation, and the fluorescence is quenched through SET from one-electron donors.[14,15] That is, a rate constant of SET to this dye in the photoexcited state is determined easily based on the Stern–Volmer (SV) method. We examined the photore-

---

* To whom correspondence should be addressed. Tel: +81-742-41-4764; Fax: +81-742-41-4762.
† Tezukayama College.
‡ Kyoto University.
§ Present address: Fukui University of Technology, Fukui, 910-8505, Japan.

(1) (a) Yasui, S. *Rev. Heteroatom Chem.* **1995**, *12*, 145–161 and references therein. (b) Yasui, S.; Shioji, K.; Tsujimoto, M.; Ohno, A. *Chem. Lett.* **1995**, 783–784. (c) Yasui, S.; Tsujimoto, M.; Shioji, K.; Ohno, A. *Chem. Ber./Recueil* **1997**, *130*, 1699–1707. (d) Yasui, S.; Shioji, K.; Tsujimoto, M.; Ohno, A. *J. Chem. Soc., Perkin Trans. 2* **1999**, 855–862.
(2) (a) Powell, R. D.; Hall, C. D. *J. Am. Chem. Soc.* **1969**, *91*, 5403–5404. (b) Pandey, G.; Hajra, S.; Ghorai, M. K. *Tetrahedron Lett.* **1994**, *35*, 7837–7840.
(3) (a) Ganapathy, S.; Dockery, K. P.; Sopchik, A. E.; Bentrude, W. G. *J. Am. Chem. Soc.* **1993**, *115*, 8863–8864. (b) Soma Sekhar, B. B. V.; Bentrude, W. G. *Tetrahedron Lett.* **1999**, *40*, 1087–1090.
(4) Yasui, S.; Itoh, K.; Tsujimoto, M.; Ohno, A. *Chem. Lett.* **1998**, 1019–1020.
(5) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259–271.

(6) (a) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3567–3577. (b) Patz, M.; Kuwahara, Y.; Suenobu, T.; Fukuzumi, S. *Chem. Lett.* **1997**, 567–568. (c) Baciocchi, E.; Lanzalunga, O.; Lapi, A.; Manduchi, L. *J. Am. Chem. Soc.* **1998**, *120*, 5783–5787.
(7) Grimshaw, J.; Langan, J. R.; Salmon, G. A. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 75–81.
(8) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455–461.
(9) Bank, S.; Juckett, D. A. *J. Am. Chem. Soc.* **1975**, *97*, 567–573.
(10) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 1855–1865.
(11) Chan, T. W.; Bruice, T. C.; *J. Am. Chem. Soc.* **1977**, *99*, 7287–7291.
(12) Thomas, M. J.; Foote, C. S. *Photochem. Photobiol.* **1978**, *27*, 683–693.
(13) Schuster, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 5851–5853.
(14) Nakashima, N.; Yoshihara, K.; Willig, F. *J. Chem. Phys.* **1980**, *73*, 3553–3559.
(15) Itoh, K.; Chiyokawa, Y.; Nakao, M.; Honda, K. *J. Am. Chem. Soc.* **1984**, *106*, 1620–1627.
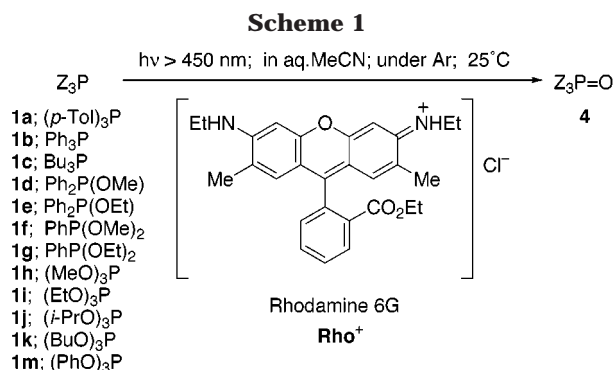
Scheme 1

hν > 450 nm; in aq.MeCN; under Ar; 25°C

Z₃P ——————————————————→ Z₃P=O

1a; (*p*-Tol)₃P
1b; Ph₃P
1c; Bu₃P
1d; Ph₂P(OMe)
1e; Ph₂P(OEt)
1f; PhP(OMe)₂
1g; PhP(OEt)₂
1h; (MeO)₃P
1i; (EtO)₃P
1j; (*i*-PrO)₃P
1k; (BuO)₃P
1m; (PhO)₃P

[EtHN—(xanthene ring system)—⁺NHEt] Cl⁻
Me ... Me
CO₂Et

Rhodamine 6G
Rho⁺

Table 1.   Photolysis of Trivalent Phosphorus Compounds Z₃P (1) with Rhodamine 6G (Rho⁺)[a]

Z₃P	time/h	yield, %[b]		MB[d]
		1[c]	**4**	
1b	5	75.6	23.3	98.9
1d	5	77.9	18.6	96.5
1h	7	92.6	6.5	99.1

[a] [**1**] = [**Rho⁺**] = 5.00 × 10⁻³ M in MeOH at 25 °C under an argon atmosphere. Irradiation at hν > 450 nm with a sharp-cut glass-filter. [b] Determined on GC. [c] Recovered. [d] Material balance.

action of trivalent phosphorus compounds **1a–m** (Z₃P; Z = aryl, alkyl, alkoxy) with rhodamine 6G (**Rho⁺**) in aqueous acetonitrile (aq MeCN) and found that each of these phosphorus compounds undergoes SET quenching of fluorescence from **Rho⁺** in the photoexcited state, **Rho⁺***. Then we determined rate constants of the SET reactions occurring from **1** to **Rho⁺*** based on the SV method. Meanwhile, we determined half-wave potentials of **1a–m** and **Rho⁺***; the values for **1** spread over more than 1 V, which is equivalent to more than 96.5 kJ mol⁻¹ in the free-energy scale.

With these values of the half-wave potentials as well as the rate constants of the SET process in hand, we examined energetics of the SET process from **1** to **Rho⁺***. Dependence of the rate of the overall SET process on the free-energy change in the SET step shows that the SET takes place in an irreversible way when the SET step is endothermic. The irreversibility in the SET results from a rapid reaction of trivalent phosphorus radical cation **1•⁺**, which is generated in the SET step, with water in the solvent. In contrast, the SET quenching of **Rho⁺*** by amines **2** and alkoxybenzenes **3** occurring when the SET step is endothermic was found to be completely reversible.

Results

Steady-State Photolysis of Trivalent Phosphorus Compounds with Rhodamine 6G. The solution of equimolar amounts (5.00 × 10⁻³ M) of **1** and rhodamine 6G (**Rho⁺**) in methanol was irradiated with the light of >450 nm for 5–7 h under an argon atmosphere at 25 °C. The resulting solution was analyzed on GC or GCMS, which showed formation of the corresponding pentavalent oxo-compound **4** (Scheme 1). The yield of **4** and the amount of the recovered starting material **1** are given in Table 1. The material balance shows that **1** is converted exclusively to **4** without side reactions taking place under the conditions. No reaction took place between **1** and **Rho⁺** in the dark. Without **Rho⁺**, no photoinduced decomposition of **1** was observed within the period examined.
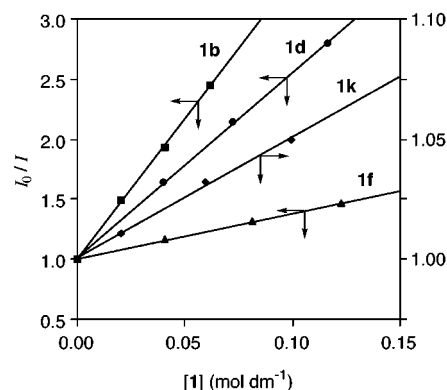

Figure 1. Stern–Volmer plots for SET quenching of **Rho⁺*** by **1**. For simplicity, only the plots for selected compounds are shown.

Stern–Volmer Analysis. When the solution of **Rho⁺** in aq MeCN (the concentration of water is about 5.6 × 10⁻² M) was irradiated at the wavelength of its absorption maximum (525 nm), intense fluorescence was observed at 545 nm. The fluorescence was quenched by **1**, and the quenching rate constant k_p (in M⁻¹ s⁻¹) was determined at 25 °C based on the Stern–Volmer equation, eq 1.

$$I_0/I = 1 + k_p\tau_0[\mathbf{1}] \tag{1}$$

where I_0 and I are fluorescence intensities observed in the absence and presence of **1**, respectively, and τ_0 is a lifetime of fluorescence from **Rho⁺***, the photoexcited state of **Rho⁺**, in aq MeCN. The ratio I_0/I was found to correlate linearly with the concentration of **1** with the intercept being unity for each compound as seen in Figure 1, showing validity of our analysis. The slope of each line gave the value of $k_p\tau_0$ as listed in Table 2. The fluorescence lifetime of **Rho⁺*** in ethanol has been reported to be 3.0 ns.[16] By assuming that the τ_0 value is unchanged with changing solvent from ethanol to aq MeCN, rate constants k_p are estimated from the $k_p\tau_0$ values, as listed in Table 2.[17] For some compounds, the reaction was carried out also in MeOH to determine k_p in this solvent.

The fluorescence from **Rho⁺*** was quenched also by amines **2** and alkoxybenzenes **3** in aq MeCN. The Stern–Volmer analysis gave the values of k_p for the quenching by these quenchers, as summarized in Table 3.

Electrochemical Measurements. Peak oxidation potentials E_p^{ox} of **1–3** were determined by cyclic voltammetry (CV) in aq MeCN at 25 °C using Ag/Ag⁺ as a reference electrode.[18,19] The E_p^{ox} value of each compound was hardly changed with changing scan rate, indicating that the anodic oxidation is nearly reversible. Obviously,

(16) Lessing, H. E.; von Jena, A.; Reichert, M. *Chem. Phys. Lett.* **1975**, *36*, 517–522.

(17) Uncertainty in the τ_0 value of **Rho⁺*** results only in movement of all points in Figure 2 in unison, providing little influence on the discussion here.

(18) The E_p^{ox} values of some trivalent phosphorus compounds have been reported in Yasui, S.; Tsujimoto, M.; Okamura, M.; Ohno, A. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 927–932.

(19) There is inconsistency in reported values of E_p^{ox} determined by CV for trivalent phosphorus compounds. For example, these values have been reported for **1b**: 0.83 V[20a] and 0.75 V[20b] in acetonitrile, and 1.15 V in butyronitrile[20c] (normalized as values vs Ag/Ag⁺). A value of E_p^{ox} could depend largely on purification methods of solvent. To avoid ambiguity in potentials, we measured the E_p^{ox} values of all compounds used in this work by ourselves using the same solvent as for the Stern–Volmer analysis.

Table 2. Fluorescence Quenching of Rhodamine 6G in the Photoexcited State (Rho^{+*}) by Trivalent Phosphorus Compounds Z$_3$P (1)^a

Z$_3$P (1)	$k_p\tau_0$, M^{-1}	$10^{-9}k_p$, M^{-1} s^{-1}	$E_{1/2}$, V^b
tri(*p*-tolyl)phosphine (**1a**)	25.1	8.37	0.79
triphenylphosphine (**1b**)	23.3 (24.0)^c	7.78 (8.00)^c	0.91
tributylphosphine (**1c**)	22.9	7.65	1.07
methyl diphenylphosphinite (**1d**)	15.4	5.12	1.21
ethyl diphenylphosphinite (**1e**)	15.0	5.01	1.17
dimethyl phenylphosphonite (**1f**)	3.79 (2.90)^c	1.26 (0.967)^c	1.49
diethyl phenylphosphonite (**1g**)	7.17 (5.61)^c	2.39 (1.87)^c	1.47
trimethyl phosphite (**1h**)	0.229	0.0762	1.81
triethyl phosphite (**1i**)	0.137	0.0456	1.87 [1.80]^d
triisopropyl phosphite (**1j**)	0.477	0.159	1.83
tributyl phosphite (**1k**)	0.504	0.168	1.85
triphenyl phosphite (**1m**)	0.136	0.0453	1.89

^{a} In aqueous acetonitrile under an argon atmosphere at 25 °C. ^{b} Half-wave potential vs Ag/Ag$^+$. ^{c} In parentheses are shown the values obtained in methanol. ^{d} Determined by rotating disk electrode.

Table 3. Fluorescence Quenching of Rhodamine 6G in the Photoexcited State (Rho^{+*}) by Several Quenchers^a

quencher	$k_p\tau_0$, M^{-1}	$10^{-9}k_p$, M^{-1} s^{-1}	$E_{1/2}$, V^b
N,N-dimethylaniline (**2a**)	78.0	26.0	0.51
triphenylamine (**2b**)	75.1	25.0	0.66
N-methylaniline (**2c**)	71.5	23.8	0.82
tributylamine (**2d**)	30.9	10.3	0.82
triethylamine (**2e**)	27.4	9.13	0.97
dicyclohexylamine (**2f**)	14.2	4.72	1.11
dipropylamine (**2g**)	10.1	3.36	1.11
dibutylamine (**2h**)	12.2	4.06	1.13
diethylamine (**2i**)	6.10	2.03	1.17
dibenzylamine (**2j**)	1.66	0.553	1.22
1,2,4-trimethoxybenzene (**3a**)	41.0	13.7	0.67
1,4-dipentoxybenzene (**3b**)	27.8	9.25	0.92 (0.96)^c
1,4-dimethoxybenzene (**3c**)	36.2	12.1	0.96
1,2-dimethoxybenzene (**3d**)	18.6	6.19	1.07
1,3-dimethoxybenzene (**3e**)	0.753	0.251	1.17
4-methylanisole (**3f**)	0.207	0.0690	1.23 (1.30)^c

^{a} In aqueous acetonitrile under an argon atmosphere at 25 °C. ^{b} Half-wave potential vs Ag/Ag$^+$. ^{c} Determined by rotating disk electrode.

one electron is transferred in the oxidation. Under these circumstances, E_p^{ox} is related to half-wave potential $E_{1/2}$ by eq 2 at 25 °C.[21]
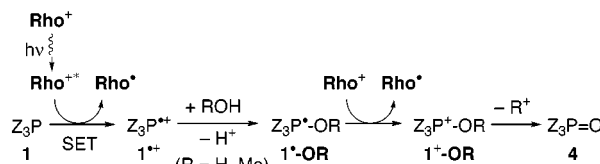
$$E_{1/2} = E_p^{ox} - 0.03 \quad (2)$$

The $E_{1/2}$ values of **1**−**3** were calculated based on eq 2, as listed in the last columns of Tables 2 and 3. For some compounds, the $E_{1/2}$ values were determined also by rotating disk electrode (RDE). The values obtained by both methods are in good agreement with each other.

The half-wave potential $E_{1/2}$ of **Rho^{+*}** was calculated from eq 3.[22]

$$E_{1/2}(\mathbf{Rho^+*}/\mathbf{Rho^{\bullet}}) = E_{1/2}(\mathbf{Rho^+}/\mathbf{Rho^{\bullet}}) + \Delta E_{0,0} \quad (3)$$

The value of $\Delta E_{0,0}$ in eq 3, the zero-zero excitation energy of **Rho$^+$** to **Rho^{+*}**, was estimated to be 2.32 eV from the absorption maximum of **Rho$^+$** and the wavelength of the emission from **Rho^{+*}**. Meanwhile, peak

(20) (a) Schiavon, G.; Zecchin, S.; Cogoni, G.; Bontempelli, G. *Electroanal. Chem. Interfacial Electrochem.* **1973**, *48*, 425−431. (b) Ohmori, H.; Nakai, S.; Masui, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1333−1335. (c) Culcasi, M.; Berchadsky, Y.; Gronchi, G.; Tordo, P. *J. Org. Chem.* **1991**, *56*, 3537−3542.

(21) See, for example, Oevering, H.; Paddon-Row: M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258−3269.
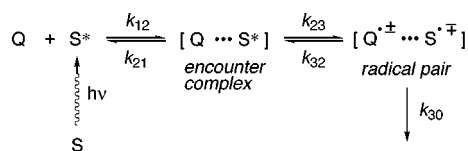
(22) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219−7223.

Scheme 2

reduction potential E_p^{red} of **Rho$^+$** in the ground state was determined by CV to be −1.13 V vs Ag/Ag$^+$ at 25 °C. Since the voltammogram showed reversible feature for the reduction of **Rho$^+$**, the half-wave potential of **Rho$^+$** is given by

$$E_{1/2}(\mathbf{Rho^+}/\mathbf{Rho^{\bullet}}) = E_p^{red}(\mathbf{Rho^+}/\mathbf{Rho^{\bullet}}) + 0.03 =$$
$$-1.10 \text{ V (vs Ag/Ag}^+) \quad (4)$$

With these values, $E_{1/2}(\mathbf{Rho^+*}/\mathbf{Rho^{\bullet}}) = 1.22$ V was obtained.

Discussion

Mechanism of Fluorescence Quenching. Photolysis of trivalent phosphorus compound **1** with **Rho$^+$** in methanol affords the corresponding pentavalent oxocompound **4**. The observation is evidence for single-electron transfer (SET) occurring from **1** to **Rho^{+*}**.[1,2] Thus, as shown in Scheme 2, the SET produces trivalent phosphorus radical cation **1$^{\bullet+}$**, which is attacked by methanol nucleophilically to afford phosphoranyl radical **1$^{\bullet}$-OMe**. Since **1$^{\bullet}$-OMe** has oxidation potential lower than that of **Rho$^+$** in the ground state,[23] its oxidation by **Rho$^+$** takes place easily to give the phosphonium cation **1$^+$-OMe**,[24] which subsequently collapses to **4**. In the quenching experiments performed in aq MeCN, water in the solvent acts as a nucleophile toward **1$^{\bullet+}$** to give **1$^{\bullet}$-OH**, which leads to **4** in a similar way.[25]

Singlet−singlet energy transfer from **Rho^{+*}** to **1** is impossible to occur judging from absorption maxima of **Rho$^+$** and **1**. Triplet−triplet energy transfer to quench **Rho^{+*}** is unlikely because the triplet excited state of **1** would be higher in energy than the triplet excited state

(23) Horner, L.; Röttger, F.; Fuchs, H. *Chem. Ber.* **1963**, *96*, 3141−3147.

(24) Phosphoranyl radicals are oxidized by diaryliodonium and triarylsulfonium salts to give the corresponding phosphonium cations. Kampmeier, J. A.; Nalli, T. W. *J. Org. Chem.* **1993**, *58*, 943−949.

(25) Yasui, S.; Shioji, K.; Ohno, A.; Yoshihara, M. *J. Org. Chem.* **1995**, *60*, 2099−2105.

Scheme 3

$$Q + S^* \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underbrace{[Q \cdots S^*]}_{\substack{\text{encounter}\\\text{complex}}} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underbrace{[Q^{\cdot\pm} \cdots S^{\cdot\mp}]}_{\text{radical pair}}$$

(with $h\nu$ upward arrow from S, and k_{30} downward arrow)

of **Rho**[+].[26] Besides, the quantum yield of intersystem crossing from **Rho**[+*] to its triplet excited state has been reported to be quite low (0.002).[27]

There is no evidence for formation of a covalent adduct between **1** and **Rho**[+]. No change in a UV−visible spectrum of **Rho**[+] is observed upon the addition of **1** either in the dark or under irradiation. In contrast, when tris(2,6-dimethoxyphenyl)phosphine (**5**), a trivalent phos-

(structure of compound 5: three 2,6-dimethoxyphenyl groups attached to P, with OMe and OMe labels, subscript 3)

5

phorus compound that is highly nucleophilic,[28] is added to the solution of **Rho**[+], the UV−visible spectrum of **Rho**[+] changes dramatically. The addition of **5** causes also significant decrease in the intensity of emission from **Rho**[+*]; if this decrease results only from the SET quenching by **5**, the quenching rate constant would be larger than 10^{12} M^{-1} s^{-1}, which is highly unlikely for reactions in solution. In addition, upon irradiation with **Rho**[+], **5** does not give the corresponding phosphine oxide, the product that would be produced if the SET from **5** takes place to give the radical cation **5**[•+]. Hence, **5** forms a covalent adduct with **Rho**[+],[29] preventing this phosphorus compound from undergoing SET, whereas **1a**−**m** do not form covalent adducts with **Rho**[+] and undergo SET to **Rho**[+*].
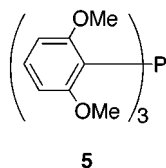
Certainly, the quenching of **Rho**[+*] by amines **2** and alkoxybenzenes **3** results from SET from these quenchers; **2** and **3** undergo SET to quench the photoexcited state of many types of substrates.[5,22,30] In conclusion, quenchers examined here, **1**, **2**, and **3**, undergo SET to **Rho**[+*] to quench the fluorescence from this dye.

Dependence of SET Rate on Free-Energy Change. Fluorescence quenching through SET is described by a sequence shown in Scheme 3.[5,13,22] Thus, an encounter complex is formed between a quencher (Q) and a photoexcited sensitizer (S*) (k_{12}),[31] and then SET takes place within the complex to give a radical pair (k_{23}), which disappears in some way (k_{30}). With a steady-state approximation with respect to concentrations of the encounter complex and the radical pair, the rate constant

k_p of the overall SET process is expressed by

$$k_p = \frac{k_{12}k_{23}k_{30}}{(k_{32} + k_{30})(k_{21} + k_{23}) - k_{32}k_{23}} \quad (5)$$

When the SET step (k_{23}-step) is exothermic, $k_{23} \gg k_{21}$ holds, and then eq 5 reduces to

$$k_p = k_{12} \quad (6)$$

which predicts a constant value of k_p at a diffusion-controlled limit, because k_{12} is a rate constant for encounter of a donor and an acceptor. Meanwhile, when the SET step is endothermic, $k_{23} \ll k_{21}$ holds. In this case, eq 5 becomes

$$k_p = K_{12}k_{23}k_{30}/(k_{32} + k_{30}) \quad (7)$$

with $K_{12} = k_{12}/k_{21}$. Let us assume that the SET step is irreversible, i.e., $k_{32} \ll k_{30}$. Then, eq 7 becomes

$$k_p = K_{12}k_{23} \quad (8)$$

Given the Horiuchi−Polanyi equation, increase in activation free-energy of the SET step ($\Delta G_{23}^{\ddagger}$) is proportional to increase in free-energy change of this step (ΔG_{23}) (eq 9).

$$\Delta G_{23}^{\ddagger} = \Delta G_{23}^{\ddagger}(0) + \alpha \Delta G_{23} \quad (9)$$

Accordingly,

$$k_{23} = k_i \exp(-\alpha \Delta G_{23}/RT) \quad (10)$$

In eqs 9 and 10, $\Delta G_{23}^{\ddagger}(0)$ and k_i are the activation free-energy and the rate constant, respectively, at $\Delta G_{23} = 0$, and α is a proportionality constant that takes a value from 0 to 1. Combination of eqs 8 and 10 leads to

$$k_p = K_{12}k_i \exp(-\alpha \Delta G_{23}/RT) \quad (11)$$

Free-energy change ΔG_{23} is related to difference in standard potentials of a donor (D) and an acceptor (A) by eq 12 with F as the Faraday constant (= 96.5 kJ mol^{-1} V^{-1}), which in turn is nearly equal to difference in half-wave potentials.

$$\Delta G_{23} = F\Delta E^{\circ} = F\{E^{\circ}(D) - E^{\circ}(A)\} \approx$$
$$F\{E_{1/2}(D) - E_{1/2}(A)\} = F\Delta E_{1/2} \quad (12)$$

Finally, eqs 11 is rewritten as

$$k_p = K_{12}k_i \exp(-\alpha F\Delta E_{1/2}/RT) \quad (13)$$

which predicts a linear correlation between log k_p and $\Delta E_{1/2}$ with the slope being $-\alpha F/(2.3RT)$ $(0 < \alpha < 1)$.

In Figure 2 is plotted log k_p for the SET from **1**−**3** against $E_{1/2}$ of **1**−**3**, in place of $\Delta E_{1/2}$, since an acceptor is the same (**Rho**[+*]) throughout the present study (i.e., $E_{1/2}(A)$ in eq 12 is constant). Clearly, the SET from **1** follows eq 6 in the region of $E_{1/2} < 1.3$ V; log k_p for **1** is constant at a diffusion-controlled limit. Meanwhile, in the

(26) *trans*-Stilbene, which has a higher E_T value (210 kJ mol^{-1}) than that of rhodamine 6G (201 kJ mol^{-1}),[27] has no influence on photodecomposition of triphenylphosphine (**1b**) occurring under the irradiation of light from a high-pressure mercury lamp. Yasui, S.; Itoh, K.; Ohno, A. Unpublished result.

(27) Korobov, V. E.; Shubin, V. V.; Chibisov, A. K. *Chem. Phys. Lett.* **1977**, *45*, 498−501.

(28) Wada, M.; Hayase, S.; Fujiwara, M.; Kawaguchi, T.; Iwasaki, T.; Uo, A.; Erabi, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 655−664.

(29) The reciprocal of difference in the absorbances of **Rho**[+] in the absence and presence of **5** depends linearly on the reciprocal of the square of a concentration of **5**, suggesting formation of a 1:2 adduct between **Rho**[+] and **5**. From the slope and the intercept of the plot, the stability constant is calculated to be $K = 1.62 \times 10^4$ M^{-2}.

(30) Kayser, R. H.; Young, R. H. *Photochem. Photobiol.* **1976**, *24*, 395−401.

(31) Throughout this paper, we use the term "encounter complex" to refer to a weakly bound complex that results from diffusional encounter between a donor and an acceptor, as in a pioneering report by Rehm and Weller.[5] Recently, Kochi and collaborators have given this term an alternative definition, according to which it designates a tightly bound complex such as an exciplex.[32]
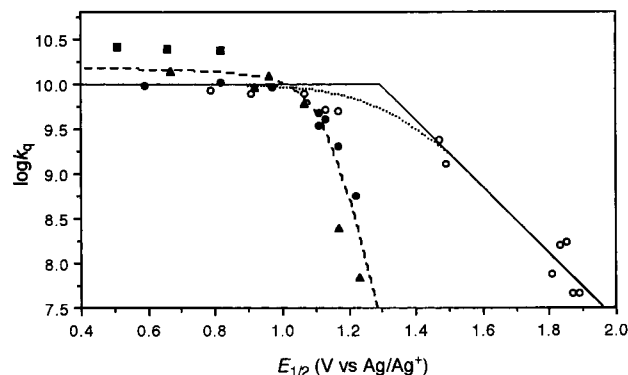
Figure 2. Plot of log k_q against $E_{1/2}$ of the quencher. $\bigcirc$, $\blacksquare$, $\bullet$, and $\blacktriangle$ represent the reactions with trivalent phosphorus compounds (**1**), aromatic amines (**2a**–**c**), aliphatic amines (**2d**–**j**), and alkoxybenzenes (**3**), respectively. The solid broken line obtained based on eqs 6 and 13, together with a dotted curve made by eq 15, traces the points for **1**. The dashed curve obtained based on eq 16 traces the points for **2** and **3**.

region of $E_{1/2} > 1.3$ V, log k_p for **1** shows negative linear dependence on $E_{1/2}$,[33] indicating that the SET in this region is endothermic. More importantly, the dependence is accommodated by eq 13, thus showing that the SET step from **1** to **Rho**$^{+*}$ is irreversible in this region. The slope of the correlation line is given as $-\alpha F/(2.3RT)$ with $\alpha = 0.2$. If one assumes that the SET step is reversible, i.e., $k_{32} \gg k_{30}$, then eq 7 finally affords

$$k_p = K_{12}k_{30}\exp(-F\Delta E_{1/2}/RT) \tag{14}$$

This equation requires the slope of a linear correlation between log k_p and $\Delta E_{1/2}$ be $-F/(2.3RT)$. This formula of the slope would be given also by eq 13 if $\alpha = 1$ (-17 at 25 °C), but this is not the case for the SET from **1**, confirming that the SET step from **1** to **Rho**$^{+*}$ is irreversible.

The potential at which the change in dependence of log k_p on $E_{1/2}$ occurs (1.3 V) is a boundary to determine whether the endothermic SET or the exothermic SET takes place. In other words, this value of the potential determines the value of $E_{1/2}$(**Rho**$^{+*}$/**Rho**$^{\bullet}$) to be 1.3 V.

Taking into consideration experimental uncertainties, this value of $E_{1/2}$ is in good agreement with the experimentally determined one (= 1.22 V, See the Results section).

Around $E_{1/2} = 1.3$ V (i.e., when $\Delta G_{23} \approx 0$), the rate constant experimentally observed k_{exp} is better reproduced with a correction according to eq 15.[7]

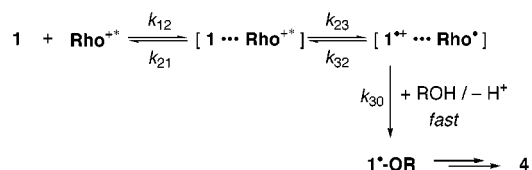$$1/k_{exp} = 1/k_p + 1/k_{12} \tag{15}$$

The curve made by eq 15 is shown by a dotted line in Figure 2, which in fact traces the experimental points better than the broken line made by eqs 6 and 13 does.

(32) (a) Rathore, R.; Hubig. S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 11468–11480. (b) Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 1688–1694.

(33) Since eq 1 has been derived by a series of approximations, sufficiently accurate quenching constants cannot be determined when $k_p\tau_0 < 0.1$ M^{-1}. In the present study, $k_p\tau_0$ values for the phosphites **1h**–**k,m** are very close to this border, making the points for these quenchers scattered. See ref 5.

(34) (a) Koo, J.-Y.; Schuster, G. B.; *J. Am. Chem. Soc.* **1977**, *99*, 6107–6109. (b) Koo, J.-Y.; Schuster, G. B.; *J. Am. Chem. Soc.* **1978**, *100*, 4496–4503.

Scheme 4

$$1 \; + \; \textbf{Rho}^{+*} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [\, 1 \cdots \textbf{Rho}^{+*} \,] \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} [\, 1^{\bullet+} \cdots \textbf{Rho}^{\bullet} \,]$$

$$k_{30} \downarrow \; {+ \text{ROH} / - \text{H}^+ \atop fast}$$

$$1^{\bullet}\text{-OR} \; \longrightarrow \; 4$$

Several SET processes have been claimed to include irreversible SET steps.[7–12,34,35] In these processes, SET steps are followed by chemical reactions such as cleavage[7–10,34] or formation[12] of a covalent bond as well as H$^+$-transfer.[11] That is, if the "back SET"[36] is overcome by a chemical reaction taking place followed by the SET step, the SET step is irreversible.[13] We have found, in the present study, that trivalent phosphorus radical cation **1**$^{\bullet+}$ generated in the SET step undergoes an ionic reaction with water in the solvent, which certainly results in irreversibility of the SET step. The radical cation **1**$^{\bullet+}$ undergoes the ionic reaction with water so rapidly that "back SET" from **Rho**$^{\bullet}$ to **1**$^{\bullet+}$ in the ground state is practically negligible (Scheme 4). In fact, when MeOH was used as a neat solvent in place of aq MeCN, no acceleration of the overall reaction was observed (Table 2),[37] showing that k_{30}-step (reaction of **1**$^{\bullet+}$ with MeOH in this case) is too rapid to be rate-determining.

In analogy with a transfer coefficient in electrolysis as well as the Brϕnsted coefficient, an α-value in eq 13 is thought to be a measure of the position of transition state in an SET step.[7] Thus, as the transition state moves to the reactant side, the α-value becomes smaller. On the other hand, with this movement of the transition state, the "back SET" becomes less favorable, and as a result, the SET step becomes less reversible. Consequently, an α-value can be taken also as an index of "reversibility" of SET step; the smaller the α-value, the less reversible the SET step and vice versa. Interestingly, the α-value observed here (0.2) is comparable to or smaller than values observed in dissociative SET reactions between arene radical anions and alkyl halides where the irreversibility in the SET step results from cleavage of a carbon-halide covalent bond in the intermediary radical anion RX$^{\bullet-}$.[7,9] This fact suggests that an ionic reaction of **1**$^{\bullet+}$ with water is as facile as cleavage of a carbon–halide covalent bond in RX$^{\bullet-}$.

SET from Amines and Alkoxybenzenes. In contrast to the SET from trivalent phosphorus compounds **1**, the SET from **2** and **3** to **Rho**$^{+*}$ follows the Rehm–Weller equation, eq 16, which is well-known to reproduce a kinetic behavior in SET occurring in many types of donor–acceptor pairs.[5]

$$k_p = \frac{k_{12}}{1 + (k_{21}/k_{30})\{\exp(\Delta G_{23}^{\ddagger}/RT) + \exp(\Delta G_{23}/RT)\}} \tag{16}$$

Thus, an iterative calculation based on eq 16 under a reasonable assumption[5] that $k_{12} = 2.0 \times 10^{10}$ M^{-1} s^{-1} eventually affords the best fit between theoretical and experimental values of the rate constants for amines **2**

(35) Pelizzetti, E.; Mentasti, E.; Pramauro, E.; *Inorg. Chem.* **1976**, *15*, 2898–2900.

(36) In photochemical processes such as fluorescence quenching, "back SET" takes place in the ground state to regenerate the starting materials. Thus, the term "back SET" used here does not mean the reverse reaction in terms of the principle of microscopic reversibility.

and alkoxybenzenes **3** with $\Delta G_{23}^{\ddagger}(0) = 7.0$ kJ mol^{-1} and $E_{1/2}(\textbf{Rho}^{+*}/\textbf{Rho}^{\bullet}) = 1.12$ V (vs Ag/Ag$^+$) (a dashed curve in Figure 2). Emphasized here is that the value of the half-wave potential of **Rho**$^{+*}$ "theoretically" predicted in this calculation is again in satisfactory agreement with the "experimentally" evaluated one (1.22 V). The points for aromatic amines **2a**–**c** appear above the "theoretical" curve. Such a discrepancy in SET rates between aromatic and aliphatic amines is not unusual; a similar kinetic behavior of amines has been observed in SET quenching of photoexcited states of transition metal complexes.[22] Equation 16 has been derived from eq 5 by assuming a highly exothermic "back SET" contributing predominantly to k_{30}-step.[5] So, the observation that the SET from **2** and **3** to **Rho**$^{+*}$ follows eq 16 indicates that cation radicals generated from **2** and **3** in the SET step undergo practically no reaction with a nucleophile such as water in the solvent. Neither is significant the reactivity of these radical cations as a free-radical in the present system, possibly because there is no powerful "free-radical trapping agent" available here.

Conclusion

In this study, we have shown that SET from trivalent phosphorus compounds Z$_3$P to a photoexcited dye takes place in an irreversible way even though the SET step is endothermic. The irreversibility results from high reactivity of radical cation Z$_3$P$^{\bullet+}$ as an electrophile toward a nucleophile. The finding here provides a further question; what endows Z$_3$P$^{\bullet+}$ with such high reactivity as an electrophile? It is our next target to find an answer to this question.

Experimental Section

Instruments. UV/visible spectra were recorded on a Shimadzu UV-2200A recording spectrophotometer. Fluorescence

---

(37) Instead, the values of k_p for the reactions of **1f** and **1g** obtained in MeOH were slightly smaller than those obtained in aq MeCN. This is attributable to small changes of the redox potentials of **1** and **Rho**$^+$ as well as $\Delta E_{0,0}$ of **Rho**$^+$, which could result from the change of the solvent.

(38) Yasui, S.; Shioji, K.; Ohno, A.; Yoshihara, M. *Chem. Lett.* **1993**, 1393–1396.

from **Rho**$^{+*}$ was monitored on a Shimadzu RF-5000 spectrofluorophotometer. GC analysis was done with a Shimadzu GC-14A gas chromatograph. Cyclic voltammetry (CV) was carried out on a Cypress Systems OMNI90 potentiostat using a platinum and Ag/Ag$^+$ as a working and a reference electrode, respectively, and with tetraethylammonium tetrafluoroborate (0.10 M) as the supporting electrolyte. Rotating disk electrode (RDE) was carried out with a BAS RDE−1 with the rotation rate being 1000 rpm using the same potentiostat and conditions as those for CV.

Materials. Trivalent phosphorus compounds **1** and **5**, amines **2**, and alkoxybenzenes **3** as well as rhodamine 6G (**Rho**$^+$) were commercially available (Tokyo Chemical Industry Co. or Aldrich). These materials were purified through recrystallization, column chromatography, or distillation, if necessary. Acetonitrile (Nacalai Tesque) was refluxed over calcium hydride for 5−6 h and distilled. The distillate (referred to as aq MeCN throughout the text) was used for the Stern−Volmer analysis and electrochemical measurements without further attempts for dehydration. The concentration of water in this solvent was estimated to be 5.6×10^{-2} M by the Karl Fischer method.[38]

Photoreaction of 1 with Rho$^+$. A solution of **1** in methanol (5.00×10^{-3} M) was irradiated with a light from an Ushio xenon arc short lamp UXL-500D-0 through a Toshiba sharp-cut filter Y-47 (irradiation at $h\nu > 450$ nm) in the presence of **Rho**$^+$ under an argon atmosphere for 5−7 h. The resulting solution was analyzed on GC to determine the recovered amount of **1** and the yield of **4**.

Stern−Volmer Analysis. In a quartz cell equipped with a septum and filled with an argon gas, was placed quencher **1**, **2**, or **3** in an appropriate amount. The solution of **Rho**$^+$ in aq MeCN (5.00×10^{-6} M) was added to the cell through a syringe to resolve the quencher. The solution was excited at 525 nm, and the intensity of the resulting emission was recorded at 545 nm on a spectrofluorophotometer.