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# Investigation of non-Rehm–Weller kinetics in the electron transfer from trivalent phosphorus compounds to singlet excited sensitizers<sup>†</sup>

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Shinro Yasui<sup>a</sup>\* and Munekazu Tsujimoto<sup>a</sup>

Singlet excited states ( ${}^{1}S^{*}$  and  ${}^{1}S^{**}$ ) of neutral and monocationic sensitizers, S and S<sup>+</sup>, respectively, were quenched by electron transfer (ET) from a variety of trivalent phosphorus compounds (Z<sub>3</sub>P). The quenching rate constants  $k_{qr}$ , which are equal to the rate constants  $k_{ET}$  of the ET from Z<sub>3</sub>P to  ${}^{1}S^{*}$  or  ${}^{1}S^{**}$ , were determined by the Stern–Volmer method. The logarithm of  $k_{ET}$  was plotted against free-energy change  $\Delta G^{0}$  of the ET. The plot deviated upward from the line predicted by the Rehm–Weller (RW) theory in the endothermic region, the deviation being larger in the ET to a neutral acceptor  ${}^{1}S^{*}$  than in the ET to a cationic acceptor  ${}^{1}S^{+*}$ . Such a kinetic behavior is in sharp contrast to that observed in the ET from amines (R<sub>3</sub>N), where the ET to either neutral or cationic acceptor takes place according to the RW prediction. The ET from a donor, Z<sub>3</sub>P or R<sub>3</sub>N, to a neutral acceptor  ${}^{1}S^{*}$  is a charge-separation type, during which electrostatic attraction between the donor and the acceptor is generated, whereas the ET to a cationic acceptor  ${}^{1}S^{+*}$  is a charge-shift type, which results in neither electrostatic attraction nor repulsion. Difference in kinetics–energetics relationship by the type of ET, which is not recognized in the ET from R<sub>3</sub>N donor, becomes "visible" when Z<sub>3</sub>P is used as a donor. Copyright © 2013 John Wiley & Sons, Ltd. Supporting information may be found in the online version of this paper.

Keywords: trivalent phosphorus; electron transfer; Rehm–Weller theory; Stern–Volmer analysis; charge separation; charge shift

# INTRODUCTION

Electron transfer reactions (ET) are one of fundamental chemical reactions, which occur ubiquitously in inorganic and organic chemistry as well as in biological systems. Mechanistic aspects of ET have long been studied by both experimental and theoretical chemists to formulate dependency of ET rate constant ( $k_{\rm ET}$ ) on free-energy change ( $\Delta G^0$ ; opposite sign of driving force) of the ET. The Rehm–Weller (RW)<sup>[1]</sup> and the Marcus theory<sup>[2]</sup> are definitely successful examples.

Studies on ET kinetics have been developed mainly using compounds with second row elements such as amines ( $R_3N$ ) or alkoxybenzenes (ArOR) as a donor. Third row element counterparts of these donors, namely, phosphines and sulfides, respectively, also undergo ET under certain conditions. Nevertheless, kinetics of the ET from these compounds have been studied less often. There seems to be a naive belief that ET from compounds with third row elements occurs in a similar fashion as the ET from compounds with second row elements. Third row elements have *d*-orbitals so that the compounds with these elements might behave differently in the ET.

We have found that a variety of trivalent phosphorus compounds (Z<sub>3</sub>P; Z = alkyl, aryl, OR; R = aryl, alkyl) undergo ET to various types of electron-deficient compounds in the dark.<sup>[3-8]</sup> Analyzing the ET processes kinetically mainly based on UV-vis spectroscopy, we have found that ET from Z<sub>3</sub>P examined always give log $k_{\rm ET}$ - $\Delta G^0$  plots deviating upward from the line predicted by the RW theory in the endothermic region ( $\Delta G^0 > 0$ ). Plots deviating from the RW prediction are not events observed only

in ET from  $Z_3P$ , but there are in fact several reports on amine donors R<sub>3</sub>N giving deviating  $\log k_{\text{ET}} \Delta G^0$  plots.<sup>[9–17]</sup> Such a kinetic behavior has been interpreted to result from a highly exothermic reaction following the ET step. High exothermicity is supplied by follow-up reactions such as cleavage of a covalent bond,<sup>[12–15]</sup> formation of a covalent bond,<sup>[16]</sup> and second ET.<sup>[17]</sup> It should be emphasized that these follow-up reactions are carried out by reduced acceptors but not by amine radical cations R<sub>3</sub>N<sup>++</sup> resulting from the ET. As for our ET from  $Z_3P$ , the ET step generates trivalent phosphorus radical cation Z<sub>3</sub>P<sup>++</sup>, which subsequently undergoes an ionic reaction with a nucleophile such as water and alcohol in the solvent, to eventually afford the pentavalent oxo-compound  $Z_3P = O^{[3-5]}$  Use of <sup>18</sup>O labeled water has clearly shown ionic reaction occurring between  $\text{Ar}_3\text{P}^{*+}$  and water.  $^{[18]}$  The ionic reactions of  $Z_3P^{+}$  are exothermic enough to make the log $k_{ET} - \Delta G^0$  plots deviate upward.

This manuscript is dedicated to the memory of Professor Rory More O'Ferrall.

a S. Yasui, M. Tsujimoto

Institute of Human and Environmental Sciences, Tezukayama University, Gakuen-Minami, Nara, 631-8585, Japan

<sup>\*</sup> Correspondence to: Shinro Yasui, Institute of Human and Environmental Sciences, Tezukayama University, Gakuen-Minami, Nara, 631-8585, Japan. E-mail: yasui@tezukayama-u.ac.jp

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The Stern–Volmer (SV) method is widely used to collect kinetic data of ET processes. Quenching constant  $k_{qr}$ , which can be obtained from the slope of the SV plot together with the lifetime of the excited sensitizer, is identical to ET rate constant  $k_{ET}$  provided that the quenching occurs through ET mechanism. Previously, we performed the SV analysis on the ET quenching of rhodamine 6G (**Rho**<sup>+</sup>) in the singlet excited state, <sup>1</sup>**Rho**<sup>+\*</sup>, by  $Z_3P$  in aqueous acetonitrile.<sup>[19]</sup> To investigate dependency of  $k_{ET}$  on  $\Delta G^0$  over a wide range of  $\Delta G^0$ , we selected a variety of  $Z_3P$  (1) whose oxidation potentials spread in a range of more than 1.5 eV (145 kJmol<sup>-1</sup>). Then, we found that  $\log_{k_{ET}} \Delta G^0$  plot in the endothermic region deviates upward from the RW prediction.

Recently, we performed the SV analysis on the ET quenching of several neutral sensitizers, namely, 9,10-dicyanoanthracene (**DCA**) and 9-cyanoanthracene (**CA**), in the singlet excited states, <sup>1</sup>**DCA**\* and <sup>1</sup>**CA**\*, respectively, by Z<sub>3</sub>P in acetonitrile.<sup>[20,21]</sup> The ET to <sup>1</sup>**DCA**\* or <sup>1</sup>**CA**\* exhibited upward deviation in the log $k_{\text{ET}} \Delta G^0$ plot as well, but degree of the deviation was larger than the deviation observed in the ET to a cationic acceptor, <sup>1</sup>**Rho**<sup>+\*</sup>. That is, log $k_{\text{ET}} - \Delta G^0$  plots in the ET from Z<sub>3</sub>P separate depending on an acceptor. The upward deviation can be interpreted primarily by assuming that the resulting cation radical Z<sub>3</sub>P<sup>++</sup> reacts with water in the solvent highly exothermically. However, if the upward deviation of the plot results solely from the follow-up reaction of Z<sub>3</sub>P<sup>++</sup>, the degree of the deviation should be the same irrespective of an acceptor.

Charge distribution changes during the ET in different ways depending on whether the acceptor is cationic or neutral. ET from a neutral donor such as Z<sub>3</sub>P to a neutral acceptor, where a neutral-neutral pair becomes a cation-anion pair, generates electrostatic attraction between the donor and the acceptor. On the other hand, ET from a neutral donor to a cationic acceptor, where a cationic center moves from the acceptor to the neutral donor, results in neither electrostatic attraction nor repulsion. This difference in the type of ET may be responsible for the separate  $\log k_{\rm ET} \Delta G^0$  plots. In sharp contrast to the ET from  $Z_3P$ , we found that ET from a donor with second row element such as R<sub>3</sub>N or ArOR to both a cationic acceptor, <sup>1</sup>**Rho**<sup>+\*</sup><sup>[19]</sup> and a neutral acceptor, <sup>1</sup>**DCA**<sup>\*</sup> or <sup>1</sup>**CA**<sup>\*</sup>, gives a single  $\log k_{\rm ET} - \Delta G^0$  plot that traces well the RW prediction.<sup>[20]</sup> This fact shows that the separate plots appearing in the ET from Z<sub>3</sub>P originates from a property of phosphorus atom in Z<sub>3</sub>P.

We here discuss the origin of separate  $\log k_{\rm ET} - \Delta G^0$  plots observed in the ET from Z<sub>3</sub>P considering change of charge distribution within the redox pair during the ET. At some stage of the discussion, results from theoretical computations will be consulted. The quenchers examined in this study, trivalent phosphorus compounds Z<sub>3</sub>P (**1**), amines R<sub>3</sub>N (**2**), and alkoxybenzenes ArOR (**3**), are listed in Chart 1. Cationic sensitizer, 10-methylacridinium salt (**A**c<sup>+</sup>), and a neutral sensitizer, 10-methylacridon (**MA**), were also subjected to the examination in this study to obtain additional data. Sensitizers used in this work are given in Chart 2.

# **EXPERIMENTAL**

#### Instruments

UV–visible spectra were recorded on a Shimadzu UV-2200A spectrophotometer. Fluorescence from excited sensitizers was monitored on a Shimadzu RF-5000 spectrofluorophotometer. Rotating disk electrode (RDE) voltammetry was carried out with a BAS RDE-1 using an ALS electrochemical analyzer Model 620A.



Chart 1. Quenchers used in this work



Chart 2. Sensitizers used in this work

## Materials

Sensitizers (Tokyo Chemical Industry Co.) and trivalent phosphorus compounds **1** (Tokyo Chemical Industry Co. or Aldrich) were commercially available and purified before use if necessary. In the SV analyses, acetonitrile of fluorescence analysis grade (Nacalai Tesque) was used without purification.

#### **Electrochemical measurements**

The solution of a sample  $(5.0 \times 10^{-3} \text{M})$  and tetraethylammonium tetrafluoroborate (0.10 M) as a supporting electrolyte in acetonitrile was subjected to RDE measurement with a rotating disk platinum electrode (1000 rpm) as a working electrode and Ag/Ag<sup>+</sup> (in a solution of silver nitrate (0.01 M) and tetraethylammonium perchlorate (0.1 M) in acetonitrile) as a reference electrode. Values of half-wave potentials  $E_{1/2}$  were read on the voltammograms obtained.

#### SV analysis

The quenching rate constants  $k_{\rm q}$  were determined according to the procedure reported previously.^{[19]}

## Computation

Density functional theory (DFT) were performed with Gaussian 09 package at the B3LYP level of theory with a pertinent basis set such as 6-31G(d), 6-31+G(d), or 6-311+G(d).<sup>[22]</sup> Molecular structures were visualized using GaussView 5.0 (Gaussian, Inc.).

# RESULTS

#### **Electrochemical measurements**

Electrochemical measurements on trivalent phosphorus compounds **1a-r** were performed with a RDE in acetonitrile at 25 °C using Ag/Ag<sup>+</sup> as a reference electrode. The half-wave potentials  $E_{1/2}({}^{1}S^{()}*)$  of the sensitizers in the singlet photoexcited state  ${}^{1}S^{(-)}*$  (where () = 0 or +) were calculated according to Eqn (1).

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

where  $E_{1/2}(S_0^{()})$  is a half-wave potential of a sensitizer in the ground state, and  $\Delta E_{0,0}(S^{(\cdot)})$  is the zero–zero photoexcitation energy. The values of  $E_{1/2}(S_0^{(\cdot)})$  are available from literature.  $\Delta E_{0,0}(S^{(\cdot)})$  values were estimated by the absorption maximum of  $S^{(\cdot)}$  and the emission maximum of  ${}^{1}S^{(\cdot)*}$ . Electrochemical parameters are summarized in Table 1.

## SV analysis

When the solution of  $S^{(\)}$  in acetonitrile was excited at the wavelength of the absorption maximum of each sensitizer, the characteristic fluorescence was observed. The wavelengths of excitation and emission maxima of the fluorescence are given also in Table 1. The intensity of the fluorescence from each sensitizer decreased upon the addition of **1**, indicating that  ${}^{1}S^{()}*$  is quenched by **1**. Examples are shown in Fig. 1. Ratio  $I_0/I$ , where  $I_0$  and I are the intensity of the fluorescence from a sensitizer observed in the absence and presence of **1**, respectively, was plotted against the concentration of **1**. A linear line with the intercept being unity was obtained for each combination of **1** 

and  $S^{()}$ , showing that the SV equation (2) holds in quenching of  ${}^{1}S^{()}$  \* by **1**. Representative examples are given in Fig. 2.

$$I_0/I = 1 + k_q \tau_0[\mathbf{1}]$$
 (2)

The lifetime  $\tau_0$  of the fluorescence of each sensitizer is available from literature as given in Table 1, with which the quenching rate constant  $k_q$  was determined based on Eqn (2) for each combination of **1a–r** and S<sup>()</sup>. Table 2 reports the  $k_q$ values determined here under the term of ET rate constant  $k_{ET}$ , since  $k_q$  is equal to  $k_{ET}$  in this system (vide infra).

#### Mechanism of the fluorescence quenching

As has been shown previously,<sup>[19]</sup> steady-state photolysis of trivalent phosphorus compounds 1 with Rho<sup>+</sup> results in guantitative formation of the corresponding oxo-compound  $Z_3P = O$  (2). This observation shows the existence of trivalent phosphorus radical cation 1<sup>++</sup> along the reaction pathway. The radical cation 1<sup>++</sup> once formed undergoes easily the ionic reaction with a small amount of water contained in the solvent to eventually give 2. Thus, the singlet excited state of Rho<sup>+</sup>, <sup>1</sup>Rho<sup>+\*</sup>, is quenched through the ET from 1 to generate 1<sup>++</sup>. Meanwhile, considerations of the energy levels of Rho<sup>+</sup> exclude the possibility of singletsinglet energy transfer from <sup>1</sup>**Rho**<sup>+\*</sup> to **1** to quench <sup>1</sup>**Rho**<sup>+\*</sup>. We have also shown that the ET takes place from several types of phosphines (Z<sub>3</sub>P; Z = alkyl, aryl) to  $Ac^+$  under the photo-irradiation.<sup>[29–31]</sup> The ET from triarylphosphines ( $Z_3P$ ; Z = aryl) to the singlet photoexcite state of neutral acceptor <sup>1</sup>DCA<sup>\*</sup> is well known.<sup>[32]</sup> In fact, 355 nm-laser flash photolysis on the solution of triarylphosphines Ar<sub>3</sub>P in the presence of **DCA** and biphenyl gave a transient UV absorption of the corresponding radical cation  $Ar_3P^{+}$ . The close similarity in structure between **DCA** and **CA** predicts that <sup>1</sup>CA<sup>\*</sup> is also quenched by 1 through the ET mechanism. **MA** in the singlet excited state, <sup>1</sup>**MA**<sup>\*</sup>, is also a good one-electron acceptor.<sup>[27,33]</sup> In conclusion, singlet excited states of the sensitizers  ${}^1S^{(\,\dot{\,})\,*}$  examined here are quenched through the ET from **1**. That is, the quenching constants  $k_q$  obtained by the SV method represent the ET rate constants  $k_{\rm ET}$ .

Table 1. Photochemical and electrochemical properties of sensitizers									
Sensitizer	Absorption maximum/nm	Emission maximum of the fluorescence/nm	$\tau_0/{ m ns}$	$E_{1/2}(S_0^0)$ <sup>a</sup> /V vs Ag/Ag <sup>+</sup>	$E_{1/2}({}^{1}S^{0}*)$ <sup>b</sup> /V vs Ag/Ag <sup>+</sup>				
Rho <sup>+</sup>	525	545	3.0 <sup>c</sup>	– 1.10 <sup>d</sup>	1.22				
Ac <sup>+</sup>	358	482	32.9 <sup>e</sup>	– 0.73 <sup>e</sup>	2.22				
DCA	375	430	12.7 <sup>e</sup>	– 1.23 <sup>f</sup>	1.69				
CA	380	438	11.5 <sup>e</sup>	– 1.95 <sup>g</sup>	1.10				
МА	397 <sup>h</sup>	410	6.1 <sup>i</sup>	– 2.23 <sup>j</sup>	0.84				
<sup>a</sup> Half-wave potential of the sensitizer in the ground state (S <sub>0</sub> ). Adjusted to the values against Ag/Ag <sup>+</sup> . <sup>b</sup> Half-wave potential of the sensitizer in the singlet excited state. Calculated by Eqn (1). <sup>c</sup> Ref. 23. <sup>d</sup> Ref. 19.									

<sup>e</sup>Ref. 24.

<sup>f</sup>Ref. 18.

<sup>g</sup>Ref. 25.

<sup>h</sup>Ref. 26.

<sup>i</sup>Ref. 27. Values measured under deaerated conditions.

<sup>j</sup>Measured by RED in this work.



**Figure 1.** Decrease in intensity of the emission from a singlet excited sensitizer upon the addition of **1**. (**A**): [**DCA**] =  $1.6 \times 10^{-7}$ M, [**1q**] = 0,  $1.51 \times 10^{-3}$ ,  $4.53 \times 10^{-3}$ ,  $8.84 \times 10^{-3}$ M. (**B**): [**CA**] =  $3.4 \times 10^{-7}$ M. [**1f**] =  $1.99 \times 10^{-3}$ .  $3.98 \times 10^{-3}$ ,  $7.95 \times 10^{-3}$ ,  $1.19 \times 10^{-2}$ ,  $1.99 \times 10^{-2}$ . (**C**): [**MA**] =  $4.2 \times 10^{-7}$ M, [**1f**] = 0,  $5.36 \times 10^{-3}$ ,  $1.04 \times 10^{-2}$ ,  $1.44 \times 10^{-2}$ M. A sharp emission band with the short wavelength in each spectrum is an artificial one resulting from the excitation



Figure 2. Stern–Volmer plots for quenching of MA ( $\Box$ ), CA ( $\blacklozenge$ ), DCA ( $\Delta$ ), and Ac<sup>+</sup>I<sup>-</sup> ( $\blacklozenge$ ) by 1e

In addition, the UV-visible spectra of the sensitizers examined here did not change upon the addition of a large excess amount of **1** either in the dark or under the irradiation, suggesting that no chemical reaction takes place between **1** and the sensitizers.

# $k_{\rm ET} - \Delta G^0$ profile

The free-energy change  $\Delta G^0$  of ET step for each combination of donor (1) and acceptor ( ${}^{1}S^{()}$ \*) is given by Eqn (3).

$$\Delta G^{0} = E_{1/2}(\mathbf{1}) - E_{1/2}({}^{1}S^{()}^{*})$$
(3)

The logarithm of  $k_{\text{ET}}$  was plotted against  $\Delta G^0$  in Fig. 3. In an exothermic region ( $\Delta G^0 < 0$ ),  $\log k_{\text{ET}}$  is constant with  $k_{\text{ET}}$  being diffusion limited ( $\approx 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ). No Marcus' "inverted region" is observed even in a highly exothermic region (up to  $\Delta G^0 = -1.8 \text{ eV}$ ). In the endothermic region ( $\Delta G^0 > 0$ ),  $\log k_{\text{ET}}$  drops as  $\Delta G^0$  increases. Importantly, the plot for the ET from **1** to  ${}^{1}\text{S}^{()}$  \* in the endothermic region deviates upward from the prediction by the RW equation. On the other hand, the ET from R<sub>3</sub>N (**2**) and

ArOR (3) to the acceptors examined here gives  $\log k_{\rm ET} \Delta G^0$  plot that traces the RW prediction.

## **Theoretical computations**

To test a possibility of adduct formation between **1** and an acceptor during the ET, theoretical calculations were applied. Thus, gas-phase potential energy surface of an adduct **4a** formed between **1f** and **DCA** (Chart 3) was computed as a function of P–O length at the DFT B3LYP/6-311+G(d) level of theory. Similar computation was made on a model adduct **4b** between **MA** and PH<sub>3</sub> instead of **1f** for the sake of economy of computation at the DFT B3LYP/6-31+G(d). Energy profiles of **4a** and **4b** are given in Figs. 4a and 4b, respectively.

The optimized structures of  $Ph_3P^{++}$ ,  $Bu_3P^{++}$ , and  $(MeO)_3P^{++}$  at the B3LYP/6-31G(d) showed that a positive "hole" is located almost exclusively on the phosphorus atom in these radical cations (Figure S1).

## DISCUSSION

Logarithm of  $k_{\text{ET}}$  in the ET from Z<sub>3</sub>P (1) to <sup>1</sup>S<sup>0\*</sup> is plotted against  $\Delta G^0$  in Fig. 3. Various types of Z<sub>3</sub>P, namely, phosphines, phosphinites, phosphonites, and phosphites, construct a single line with respect to ET to each particular acceptor. This fact indicates that the ET from 1 takes place according to a common mechanism. In fact, theoretical calculations on radical cations from different types of Z<sub>3</sub>P, namely, triarylphosphines, trialkylphosphines, or trialkyl phosphites, show a positive charge located almost exclusively on the phosphorus atom. In other words, Z<sub>3</sub>P (**1a**-**r**) examined in this work can be taken as a series of compounds despite of divergent structures.

An important finding in Fig. 3 is that the plots deviate upward from the line predicted by the RW theory in the endothermic region ( $\Delta G^0 > 0$ ). The conventional Marcus equation also fails to reproduce the observed plot with any values of parameters. There have been several reports in which  $\log k_{\rm ET} - \Delta G^0$  plots deviate upward from the RW prediction. This behavior of kinetics is brought about when radical species generated during the ET step undergo highly exothermic follow-up reactions such as

Table 2. Quenching of the singlet excited sensitizers by 1							
Sensitizer	Z <sub>3</sub> P ( <b>1</b> )	$E_{1/2}(1)/V$ vs Ag/Ag <sup>+ a</sup>	$\Delta G^{0}/eV$	$k_{\rm ET}/10^9{ m M}^{-1}{ m s}^{-1}$ b			
Rho⁺	<i>o</i> -Tol <sub>3</sub> P ( <b>1c</b> )	0.88	- 0.37	5.39 <sup>c</sup>			
	<i>p</i> -Tol <sub>3</sub> P ( <b>1e</b> )	1.03	- 0.19	8.37 <sup>c</sup>			
	Ph <sub>3</sub> P ( <b>1f</b> )	1.19	- 0.03	7.78 <sup>c</sup>			
	Ph <sub>3</sub> P ( <b>1f</b> )	1.19	- 0.03	8.35			
	Bu <sub>3</sub> P ( <b>1k</b> )	1.10	- 0.12	7.65 <sup>c</sup>			
	Ph <sub>2</sub> POMe ( <b>1</b> )	1.21 <sup>e</sup>	- 0.01	5.12 <sup>c</sup>			
	Ph <sub>2</sub> POEt ( <b>1m</b> )	1.28	0.06	5.01 <sup>c</sup>			
	$PhP(OMe)_2$ ( <b>1n</b> )	1.49 <sup>e</sup>	0.27	1.26 <sup>c</sup>			
	$PhP(OEt)_2$ ( <b>10</b> )	1.49	0.27	2.39 <sup>c</sup>			
	(MeO) <sub>3</sub> P ( <b>1p</b> )	1.87	0.65	0.0762 <sup>c</sup>			
	(EtO) <sub>3</sub> P ( <b>1q</b> )	1.83	0.61	0.0456 <sup>c</sup>			
	(Pr <sup>i</sup> O)₃P ( <b>1r</b> )	1.71	0.49	0.159 <sup>c</sup>			
Ac <sup>+ f</sup>	Mes <sub>3</sub> P ( <b>1a</b> )	0.39	- 1.83	19.1			
	<i>o</i> -Tol <sub>3</sub> P ( <b>1c</b> )	0.88	- 1.34	19.4			
	Ph₃P ( <b>1f</b> )	1.19	- 1.03	21.0			
	<i>p</i> -Cl-Ph₃P ( <b>1j</b> )	1.32	- 0.90	13.2			
<b>Ac</b> <sup>+</sup> <sup>g</sup>	Mes <sub>3</sub> P ( <b>1a</b> )	0.39	- 1.83	18.6			
	<i>o</i> -Tol <sub>3</sub> P ( <b>1c</b> )	0.88	- 1.34	17.9			
	<i>p</i> -Cl-Ph₃P ( <b>1j</b> )	1.32	- 0.90	18.3			
DCA	Mes <sub>3</sub> P ( <b>1a</b> )	0.39	- 1.30	19.6			
	<i>p</i> -An <sub>3</sub> P ( <b>1b</b> )	0.65	- 1.04	16.2			
	o-Tol <sub>3</sub> P ( <b>1c</b> )	0.88	- 0.81	16.3			
	<i>p</i> -Tol <sub>3</sub> P ( <b>1e</b> )	1.03	- 0.66	16.5			
	Ph₃P ( <b>1f</b> )	1.19	- 0.50	15.3			
	<i>p</i> -Cl-Ph <sub>3</sub> P ( <b>1j</b> )	1.32	- 0.37	13.7			
	Ph <sub>2</sub> POEt ( <b>1m</b> )	1.28	- 0.41	13.7			
	PhP(OEt) <sub>2</sub> ( <b>10</b> )	1.49	- 0.20	8.26			
	(MeO) <sub>3</sub> P ( <b>1p</b> )	1.87	-0.18	6.08			
	(EtO) <sub>3</sub> P ( <b>1q</b> )	1.83	0.14	6.10			
CA	$Mes_3P(1a)$	0.39	- 0.71	20.0			
	<i>p</i> -An <sub>3</sub> P ( <b>1b</b> )	0.65	- 0.45	12.7			
	0-101 <sub>3</sub> P ( <b>1c</b> )	0.88	- 0.22	9.97			
	m-IOI <sub>3</sub> P (I <b>G</b> )	1.02	- 0.08	11.4			
	p-101 <sub>3</sub> P(1e)	1.03	- 0.07	10.1			
	$PII_3P(\mathbf{II})$ $Ph(\mathbf{a}, \mathbf{Tal})P(\mathbf{I}, \mathbf{r})$	1.19	0.09	10.2			
	Ph <sub>2</sub> (0-101)P ( <b>19</b> ) Ph (n-Tol)P ( <b>1h</b> )	1.14	0.04	10.4			
	$p_{-}E_{-}Dh_{-}Dh_{-}(11)$	1.11	0.01	10.5			
	p-r-r-rigr ( <b>11</b> ) p-Cl-Ph-P ( <b>1i</b> )	1.21	0.77	6.83			
	$p = C = T_3 (\mathbf{I}_{\mathbf{J}})$ Ph_POFt ( <b>1m</b> )	1.52	0.22	9.03			
	$PhP(OEt)_{2}$ ( <b>10</b> )	1.20	0.39	5.05			
	(MeO) <sub>2</sub> P ( <b>1p</b> )	1.87	0.77	0 180			
	(FtO) <sub>2</sub> P ( <b>1a</b> )	1.83	0.73	0.666			
	$(\Pr^{i}O)_{2}P(\mathbf{1r})$	1.71	0.61	1.45			
МА	<i>p</i> -An <sub>3</sub> P ( <b>1b</b> )	0.65	- 0.19	4.75			
	<i>p</i> -Tol₃P ( <b>1e</b> )	1.03	0.19	4.17			
	Ph₃P ( <b>1f</b> )	1.19	0.35	1.41			
	Ph <sub>3</sub> P ( <b>1f</b> )	1.19	0.35	1.54 <sup>d</sup>			
	Ph <sub>2</sub> (o-Tol)P ( <b>1g</b> )	1.14	0.30	1.49			
	Ph <sub>2</sub> POEt ( <b>1m</b> )	1.28	0.44	0.933			
	(EtO) <sub>3</sub> P ( <b>1q</b> )	1.83	0.99	0.0511			
	(Pr <sup>i</sup> O) <sub>3</sub> P ( <b>1r</b> )	1.71	0.87	0.247			
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<sup>a</sup>Half-wave potentials of **1**. Measured by RDE.

<sup>b</sup>Determined by the Stern–Volmer method in acetonitrile under the aerobic conditions unless otherwise noted. <sup>c</sup>Data from Ref. 24.

<sup>d</sup>Determined under an argon atmosphere. <sup>e</sup>Based on the peak oxidation potentials  $E_p^{\text{ox}}$  determined by cyclic voltammetry; calculated by assuming  $E_{1/2} = E_p^{\text{ox}} - 0.03$ .<sup>[28]</sup> <sup>f</sup>lodide salts.

<sup>g</sup>Tetrafluoroborate salts.



**Figure 3.** Dependency of  $\log k_{ET}$  on free-energy change  $\Delta G^{\circ}$  in the ET from a series of **1** to  ${}^{1}$ Rho<sup>+\*</sup> ( $\circ$ ),  ${}^{1}$ Ac<sup>+\*</sup> (idide salt) ( $\Box$ ),  ${}^{1}$ Ac<sup>+\*</sup> (tetrafluoroborate salt) (+),  ${}^{1}$ DCA<sup>\*</sup> ( $\nabla$ ),  ${}^{1}$ CA<sup>\*</sup> ( $\Delta$ ), and  ${}^{1}$ MA<sup>\*</sup> ( $\phi$ ). Symbols X denote the points for ET from **2** and **3** to  ${}^{1}$ Rho<sup>+\*</sup> and  ${}^{1}$ CA<sup>\*</sup> altogether. A solid line represents the prediction by the RW theory



Chart 3. Adducts between a sensitizer and Ph<sub>3</sub>P or PH<sub>3</sub>

cleavage<sup>[12–15]</sup> or formation<sup>[16]</sup> of a covalent bond or second ET.<sup>[17]</sup> To date, we have examined kinetically ET from various types of Z<sub>3</sub>P to various types of acceptors to find that any log $k_{\text{ET}}$ – $\Delta G^0$  plot for ET from Z<sub>3</sub>P deviates upward from the theory in the endothermic region.<sup>[6–8,19]</sup> Trivalent phosphorus radical cation Z<sub>3</sub>P<sup>++</sup> generated during the ET step reacts with a nucleophile such as water or alcohol such exothermically that the plot deviates upward. DFT calculations with B3LYP/6-31G(d) predict that the reaction Z<sub>3</sub>P<sup>++</sup> + OH<sup>-</sup>  $\rightarrow$  Z<sub>3</sub>P<sup>-</sup>OH is 818.9 kJ mol<sup>-1</sup> and 786.2 kJ mol<sup>-1</sup> exothermic when Z = Bu and Ph, respectively. Importantly, the lengths of P–O bonds in optimized structures of Z<sub>3</sub>P<sup>-</sup>OH are 1.81 Å and 1.70 Å, when Z = Bu and Ph, respectively, which are well within an expected value for a P–O single covalent bond.<sup>[34]</sup> We studied kinetics of the ET from tributylphosphine (**1k**) to "rigid" and "flexible" viologens in the dark in acetonitrile containing methanol.<sup>[35]</sup> We found in the ET that  $\log k_{\text{ET}} - \Delta G^0$  plots deviate upward from the RW prediction and the deviation is larger in the former than in the latter. To explain the deviating behavior in  $\log k_{\text{ET}} - \Delta G^0$  plots, we considered the reaction of  $Z_3 P^{++}$  with a nucleophile quantitatively. Thus, we proposed a modified Marcus equation (Eqn (4)) that includes free energy *B* gained by P–O bond formation between the resulting radical cation **1k**<sup>++</sup> and methanol. The value of *B* was calculated to be *ca*. 2 eV based on a thermochemical cycle, with which Eqn (4) well accommodated the deviating plots by taking 3.2–4.5 eV of reorganization energy  $\lambda$ .<sup>[36]</sup>

$$k_{\rm ET} = Z \exp\left[-\frac{\left(\Delta G^0 + \lambda + B\right)^2}{4k_{\rm B}T\lambda}\right] \tag{4}$$

However, this treatment cannot explain the separate plots in Fig. 3. While *B* value should be independent of charge on the acceptor in principle, whether the acceptor is neutral or cationic makes  $\log k_{\text{ET}} - \Delta G^0$  relationship in the endothermic region separate into two lines. The ET from **1** to a neutral acceptor,



**Figure 4.** Energies of adducts computed for **4a** at the DFT B3LYP/6-311 + G(d) (**A**) and for **4b** at the DFT B3LYP/6-31 + G(d) (**B**) as a function of the P–C distance designated in the structures in Chart 3

<sup>1</sup>**CA**<sup>\*</sup>, <sup>1</sup>**DCA**<sup>\*</sup>, or <sup>1</sup>**MA**<sup>\*</sup>, is charge-separation (CS) type, whereas the ET from **1** to a cationic acceptor, <sup>1</sup>**Rho**<sup>+\*</sup>, is charge-shift (CSh) type (Scheme 1). In the former ET, electrostatic attraction within the redox pair is being generated, which likely lowers the energy of the final stage in the ET step to contribute to the acceleration of the ET rate. In CSh type-ET, neither electrostatic attraction nor repulsion occurs during the ET, and this kind of acceleration is not operative.<sup>[37]</sup>

Multiple RW plots have been reported as to the ET quenching of **DCA**\* by *n*-donors such as aliphatic amines and by  $\pi$ -donors such as aromatic hydrocarbons.[38-42] The quenching by the former donors gives  $\log k_{\rm ET} \Delta G^0$  plot horizontally shifted to the positive direction relative to the plot for the quenching by the latter donors, which has been interpreted to result from a more efficient interaction of the former donors with <sup>1</sup>DCA\* than with the latter ones in the ground state.<sup>[41,42]</sup> Farid and Gould suggested more drastic interaction between a donor and an acceptor. They examined CS-type ET to neutral acceptors, singlet excited aromatic cyanides (including 'CA and 'DCA), and CSh-type ET to cationic acceptors, excited pyrylium salts, occurring in endothermic region.<sup>[43]</sup> In these ETs,  $\log k_{\rm ET} - \Delta G^0$ plots deviate upward from the RW prediction, with the degree of the deviation being larger in the former ET than in the latter ET. To explain their observation, they proposed "a bonded exciplex mechanism", which postulates the formation of a covalent bond during the exciplex stage. They claimed that pyridine donor effectively forms a "bonded exciplex" with aromatic cyanides and pyrylium salts, making the ET rate higher than the RW prediction. Their observation, based on which they have presented their model, is similar to ours in a sense that  $\log k_{\rm ET} \Delta G^0$  plots deviate upward in the endothermic region, and the deviation is larger in CS-type ET than in CSh-type ET. However, they interpreted the origin of the separate plots simply as a result of retardation of the ET to pyrilium cation by steric hindrance of this acceptor without taking into consideration difference in the change of charge distribution during ET.

We performed DFT B3LYP/6-311+G(d) computation to evaluate energy which would be generated by forming an adduct **4a** between **1f** and **DCA** as a function of the distance between the phosphorus atom in **1f** and the 9C carbon in **DCA**. Energy of a model adduct **4b** between PH<sub>3</sub> and **MA** was also computed as a function of P–9C distance. The results are shown in Figs. 4a and b, respectively. There is no energy gain by forming an adduct, and, furthermore, unlike in Gould's calculations on ET from pyridine, energy change of each adduct in our system, whether a real one or a model, hardly shows an appreciable inflection point. The results rule out a possibility that **DCA** or **MA** forms a covalent adduct with **1** in the ground state. In other words, interaction between **1** and the sensitizer is not the origin of the upward deviation of log $k_{\text{FT}}$ – $\Delta G^{0}$  plot.

In conclusion, here, the reaction of  $Z_3P^{++}$  with a nucleophile is a factor to make  $\log k_{\text{ET}^-} \Delta G^0$  plots deviate upward from the RW prediction. In addition to this factor, electrostatic interaction being generated with the ET proceeding contributes to acceleration of the ET rate. Interestingly, we have found that ET from  $Z_3P$  to iron(III) complexes occurring thermally also exhibits upward deviation of

$$Z_{3}P + {}^{1}S^{*} \xrightarrow{CS} Z_{3}P^{*+} + S^{*-}$$
$$Z_{3}P + {}^{1}S^{**} \xrightarrow{CSh} Z_{3}P^{*+} + S^{*}$$

Scheme 1. Charge separation ET (top) and charge shift ET (bottom).

$$Z_3P + {}^{1}S^{n+*} \xrightarrow{CSn} Z_3P^{\bullet+} + S^{(n-1)+} \quad (n > 2)$$

**Scheme 2.** Another type of charge shift ET, during which a neutral-cation pair becomes a cation-cation pair.

 $\log k_{\text{ET}} - \Delta G^0$  plots, even though electrostatic repulsion is generated during the ET (another CSh-type ET; Scheme 2).<sup>[6,7]</sup> The observation suggests that a reaction of  $Z_3P^{++}$  with a nucleophile contributes to upward deviation of  $\log k_{\text{ET}} - \Delta G^0$  plots more significantly than another factor, namely, electrostatic attraction within the resulting radical ion pair.

For the sake of comparison, we also performed the SV analysis on ET from  $R_3N$  (2) and ArOR (3) to  ${}^1CA^*$  and  ${}^1Rho^{+*}$  under the otherwise identical conditions to those for the ET from 1. The ET from 2 and 3 to either neutral or cationic acceptors takes place with approximately obeying the RW equation (Fig. 3)<sup>[19,20]</sup> For the RW equation to be held, the pair of the oxidized donor and the reduced acceptor must disappear rapidly.<sup>[1]</sup> Usually, back ET occurring from the latter to the former in the ground state contributes to the rapid disappearance of the pair. This is the case for the ET from 2 and 3. Back ET from the reduced acceptor to 2<sup>++</sup> or 3<sup>++</sup> is rapid enough to make the ET kinetics follows the RW prediction.<sup>[1,44]</sup> In turn, the consideration here highlights peculiar reactivity of the radical cation 1<sup>++</sup>. Radical cation 1<sup>•+</sup> may have slightly longer lifetime allowing it to interact with the reduced acceptor in the ground state. This is quite understandable because the radical cations resulting from 2 or **3**, namely,  $R_3N^{+}$  or ArOR<sup>++</sup>, respectively, cannot undergo an ionic reaction with a nucleophile which requires expansion of the covalency. No further reaction of the reduced acceptor such as **CA**<sup>--</sup> and **Rho**<sup>-</sup> faster than the back ET is possible, either.

Another issue in this study is to figure out why the Marcus inverted region is absent. The absence of the Marcus inverted region is often met when reorganization energy  $\lambda$  is large enough, namely, when ET occurs at a long distance because  $\lambda$  is a function of a distance between a donor and an acceptor. At this stage of our research, we cannot tell whether the distance between **1** and  ${}^{1}S^{0*}$  is long enough or not during the ET. We will discuss this point elsewhere in near future.

# CONCLUSION

We examined kinetics of ET from a variety of trivalent phosphorus compounds Z<sub>3</sub>P to neutral and monocationic sensitizers in the singlet excited states,  ${}^{1}S^{*}$  and  ${}^{1}S^{+}$ , respectively. The rate constant  $k_{ET}$ was determined based on the SV method, and logk<sub>ET</sub> was plotted against free-energy change  $\Delta G^0$  of the ET step. Log $k_{\rm ET}$ - $\Delta G^0$  plots in the endothermic region deviate upward from the prediction by the RW theory, which is interpreted to result from facile reaction of the resulting radical cation  $Z_3P^{*+}$  with a nucleophile such as water contained in the solvent. The degree of the deviation is larger in the ET from  $Z_3P$  to  ${}^{1}S^{*}$  than in the ET to  ${}^{1}S^{+}$ <sup>\*</sup>. In the former ET, the radical ion pair generated by the ET is stabilized through electrostatic attraction, which contributes to further acceleration of the ET rate. On the other hand, nitrogen counterparts of  $Z_3P$ , namely, amines R<sub>3</sub>N, as well as alkoxybenzenes ArOR, obey the RW theory in the ET to both  ${}^{1}S^{*}$  and  ${}^{1}S^{+}$ <sup>\*</sup>. Kinetic behavior of R<sub>3</sub>N and ArOR different from that of Z<sub>3</sub>P is understandable taking into account that the resulting radical cations R<sub>3</sub>N<sup>++</sup> and ArOR<sup>++</sup> cannot undergo nucleophilic reaction which requires expansion of covalency.

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