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Irreversibility of Single Electron Transfer Occurring from Trivalent Phosphorus Compounds to Iron(III) Complexes in the Presence of Ethanol

Shinro Yasui,*[ ] Kenji Itoh,† Munekazu Tsujimoto, and Atsuyoshi Ohno†,#

Laboratory of Biology and Chemistry, Tezukayama College, Gakuen-Minami, Nara 631-8585

†Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011

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Various types of trivalent phosphorus compounds (**1**; $Ph_{(3\text{-}n)}P(OR)_n$) underwent single electron transfer (SET) to unsubstituted (**2H**) and 5-chloro-substituted tris(1, 10-phenanthroline)iron(III) complexes (**2Cl**) in the presence of ethanol in acetonitrile, resulting in the reduction of **2** to the corresponding iron(II) complexes. The rate constants (k_p) for the overall SET process were determined spectrophotometrically to show that within each series of **1** with an identical alkoxy group OR, log k_p correlates linearly with the difference in the half-wave potentials ($\Delta E_{1/2}$) between **1** and **2**. The slope of each correlation line gave an α-value for each series of **1**. The α-values were significantly smaller than unity, indicating that the SET step is irreversible, even though this step is endothermic. The trivalent phosphorus radical cation $\mathbf{1}^{\bullet+}$ generated in the SET step undergoes a rapid ionic reaction with ethanol, which is certainly the origin of the irreversibility. Upon examining the α-values more closely, it was found that the transition state of the SET step becomes earlier with increasing bulkiness of the substituent OR. It is concluded that **1** and **2** form a tight encounter complex to undergo SET from the former to the latter.

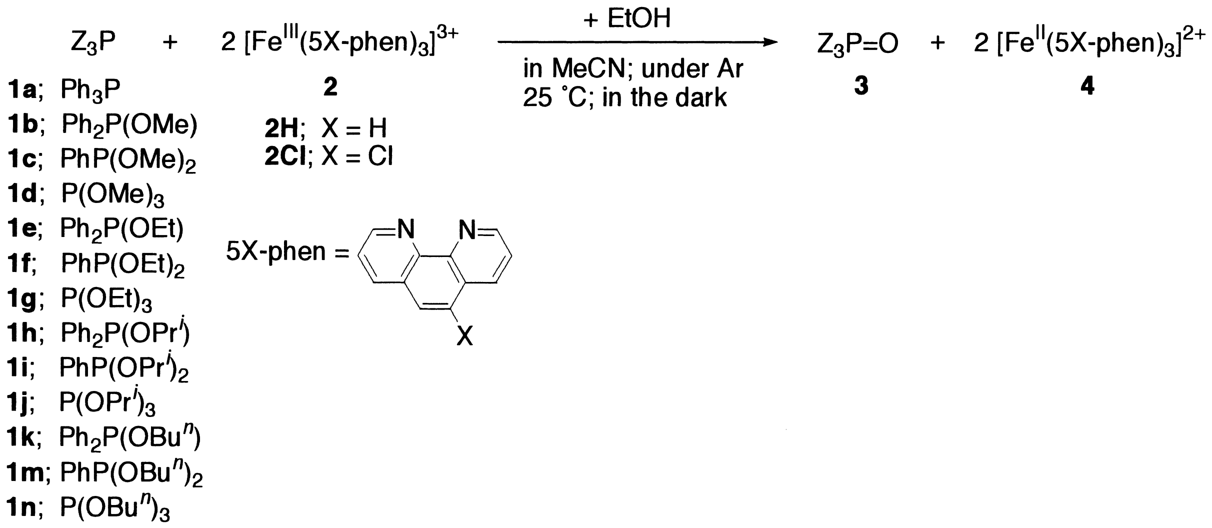
Single electron transfer (SET) is a fundamental process of chemical reactions. The energetics of the SET processes occurring in many types of redox pairs has been studied on both theoretical and experimental bases.[1,2] Nevertheless, concerning to energetics of SET from trivalent phosphorus compounds Z_3P, very few are known in spite of the fact that Z_3P is a good one-electron donor to several types of electron-deficient compounds.[3–10]

Recently, we found that Z_3P undergoes SET to a dye, rhodamine, in the photoexcited state, Rho^{+*}.[11] By analyzing this process kinetically, we showed that the SET step in the process remains irreversible, even when the SET step becomes endothermic. This finding is in sharp contrast to the fact that SET from amine counterparts usually takes place in a completely reversible way in the endothermic region.[1,12] Endothermic irreversible SET has been acknowledged to occur when a SET step is followed by a rapid chemical reaction.[13–23] In other words, in competition between the back SET and the "follow-up" reaction, the SET becomes irreversible if the latter overcomes the former. This idea was applied to our reaction of Z_3P with Rho^{+*}. Thus, we have concluded that in the SET occurring from Z_3P to Rho^{+*}, the trivalent phosphorus radical cation $Z_3P^{\bullet+}$, generated in the SET step, undergoes a rapid ionic reaction with water in the solvent; the ionic reaction competes effectively with the back SET to render the SET step irreversible.[11] Meanwhile, a kinetic model for endothermic irreversible SET presents an α-value, a parameter that is defined by the slope of a correlation line between the logarithm of the rate constant of the overall SET process and a free-energy change in the SET step.[13,15] This parameter is a measure of the position of the transition state in the SET step. Therefore, we can obtain more detailed information about a SET step, itself, by examining the α-values while varying the structure of the Z_3P, reaction conditions, and so on.

A family of iron(III) complexes is a typical one-electron acceptor, which has been used in a kinetic study of the SET processes.[24–26] These complexes have reduction potentials of around 0.8 V vs Ag/Ag^+, a value that is slightly lower than the oxidation potentials of most of trivalent phosphorus compounds, Z_3P. Therefore, SET from Z_3P to an iron(III) complex, if it takes place, would give an opportunity to examine the endothermic SET. In a preliminary report,[27] we showed that the endothermic SET takes place from various types of Z_3P to an iron(III) complex in the presence of ethanol. The SET step was irreversible despite its endothermicity, showing that the radical cation, $Z_3P^{\bullet+}$, generated in the SET step, undergoes a rapid ionic reaction with ethanol. More importantly, the α-value obtained in the kinetic analysis was dependent on the bulkiness of ligands Z on the phosphorus atom in Z_3P; as the ligands on the phosphorus become bulkier, the α-value becomes smaller, showing that the steric bulk of Z_3P determines the position of the transition state of SET from Z_3P.

In the present study, we elucidated the dependence of the α-value in SET from Z_3P to an iron(III) complex on steric bulk of Z_3P. For this purpose, we took trivalent phosphorus compounds **1a-n**, in which ligands Z on the phosphorus were changed systematically in the term of bulkiness, and allowed **1**

[#] Present address: Fukui University of Technology, Fukui 910-8505



Scheme 1.

to react with unsubstituted (**2H**) and 5-chloro-substituted tris(1, 10-phenanthroline)iron(III) complexes (**2Cl**) in the presence of ethanol. The reaction affords the corresponding redox products, oxo-pentavalent compound **3** and iron(II) complex **4**, providing the stoichiometry shown in Scheme 1. A conclusion can be made that the SET takes place from **1** to **2** within a tight encounter complex.

Results

Reaction of Trivalent Phosphorus Compounds (1) with Tris(1, 10-phenanthroline)iron(III) Complex (2). When **1** was reacted with **2** (PF_6^- salt) in acetonitrile in the presence of a large excess of ethanol under an argon atmosphere in the dark at 25 °C, the blue color from **2** changed rapidly to dark red. The resulting solution gave an UV-visible spectrum on a spectrophotometer that is the same as that of the authentic sample of tris(1, 10-phenanthroline)iron(II) complex (**4**) (λ_{max} = 508 nm), indicating that the color change results from the reduction of **2** to **4**.[24] Meanwhile, the reaction mixture of triphenylphosphine **1a** with **2H** was analyzed on a gas chromatograph (GC) and a gas chromatograph-mass spectrometer (GCMS) to show the formation of triphenylphosphine oxide **3a** in a theoretical amount (Scheme 1).

To determine the stoichiometry of the reaction, **2** at a constant concentration (1.00×10^{-2} M) (1 M = 1 mol dm^{-3}) was reacted with **1** at different concentrations. The yield of **4** from each reaction was determined based on the absorbance at 508 nm, which gave the stoichiometry $[\mathbf{1}]_0:[\mathbf{2}]_0 = 1:2$. As typical examples, the results obtained in the reactions of **1a** and **1b** with **2H** are shown in Fig. 1.

Kinetics. Kinetics was carried out under pseudo-first-order conditions where the concentrations of **1**, **2**, and ethanol were 2.00×10^{-3} M, 1.00×10^{-1} M, and 1.00×10^{-2} M, respectively. Rapid growth of the absorbance at 508 nm from **4** was monitored on a stopped-flow spectrophotometer to follow the progress of the reaction. For each reaction with **1a**-**n**, first-order kinetics was maintained at least up to 90% formation of **4**. Experiments were performed with **1** at different concentrations, and the observed pseudo-first-order rate constants k_{obs} (= d[**4**]/dt) were plotted against the concentration of **1**. Although the linearity of the plot was not so excellent (correlation coefficient $r > 0.99$), the slight scattering on the plot is highly likely attributable to uncertainties with respect to the concentration of **1** prepared in reservoir cells of a stopped-flow apparatus because the scattering was not systematic, but random. Thus, it is clear that the reaction obeys second-order kinetics with first-order with respect to the concentrations of **1** and **2**, respectively. Taking into account the observed stoichiometry, we obtain

$$k_{obs} = 2k_p[\mathbf{1}][\mathbf{2}]. \qquad (1)$$

Table 1 summarizes the second-order rate constants (k_p) determined based on Eq. 1, the errors in k_p resulting from the scattering in the k_{obs} − [**1**] plots (vide supra). The rate constant (k_p) was kept constant by increasing the concentration of ethanol up to 1.70×10^{-1} M. In addition, when ethanol was replaced by methanol, propanol, 1-butanol, 2-propanol, or *t*-butyl alcohol, k_p was identical within 5%, which was well within the range of the experimental errors.

Kinetics was carried out under identical conditions for the reactions of dibenzylamine **5a** and *t*-butylamine **5b** with **2**. The second-order rate constants (k_p) for these reactions are also listed in Table 1.

Peak Potentials. The peak oxidation potentials (E_p^{ox}) of **1a**-**n**[28] and **5** and the peak reduction potentials (E_p^{red}) of **2** were determined by cyclic voltammetry (CV). These values were independent of the scan rate over the range 50 – 400 mV s^{-1} within an instrumental error, indicating that the anodic oxidation of **1** and **5** and the cathodic reduction of **2** were nearly reversible. The reproducibility of each measurement was satisfactory. From these E_p^{ox} and E_p^{red} values, the half-wave potentials ($E_{1/2}$) of these compounds were estimated.[29] The $E_{1/2}$ values of **1** and **5** are listed in Table 1. The $E_{1/2}$ values of **2H** and **2Cl** are 0.76 V and 0.86 V vs Ag/Ag$^+$, respectively.

Discussion

Mechanism of the Reaction of 1 with 2. The iron(III)

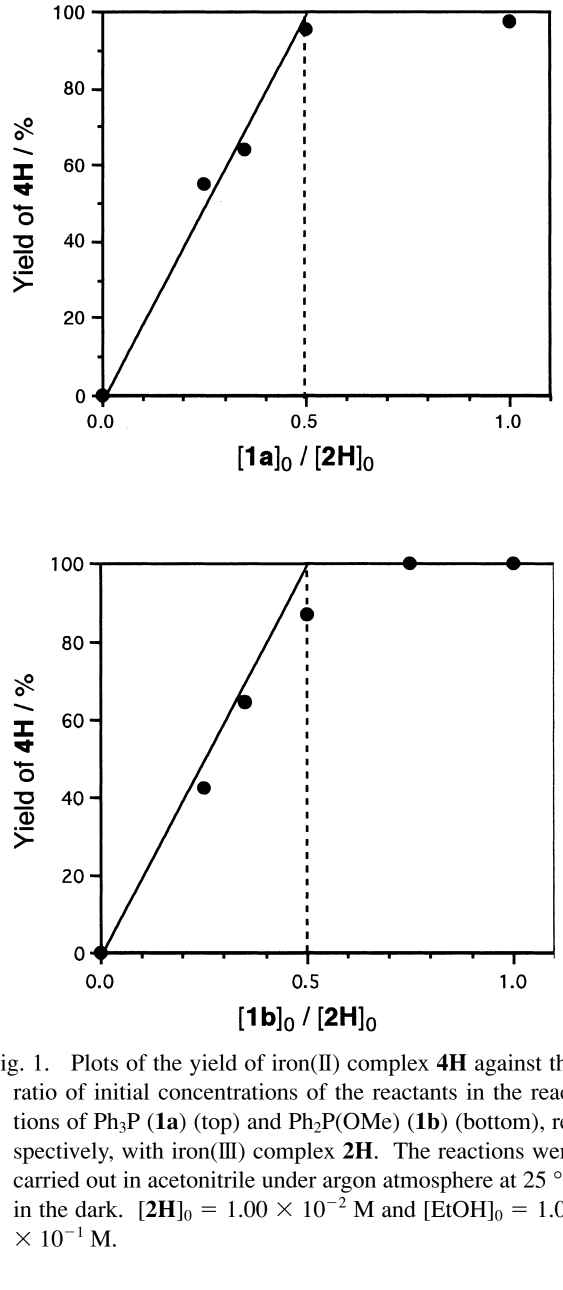


Fig. 1. Plots of the yield of iron(II) complex **4H** against the ratio of initial concentrations of the reactants in the reactions of Ph_3P (**1a**) (top) and $Ph_2P(OMe)$ (**1b**) (bottom), respectively, with iron(III) complex **2H**. The reactions were carried out in acetonitrile under argon atmosphere at 25 °C in the dark. $[\mathbf{2H}]_0 = 1.00 \times 10^{-2}$ M and $[EtOH]_0 = 1.00 \times 10^{-1}$ M.

complex **2** was reduced to the iron(II) complex **4** upon a reaction with a trivalent phosphorus compound **1**. Certainly, the reduction results from single electron transfer (SET) from **1** to **2**. Evidence for the SET occurring in the present reaction is a concomitant conversion of **1** to the corresponding oxo-pentavalent compound **3**; the SET generates the trivalent phosphorus radical cation $\mathbf{1}^{\bullet +}$, which collapses to **3** in the presence of alcohol according to the sequence shown in Scheme 2. In this sequence, a nucleophilic attack upon $\mathbf{1}^{\bullet +}$ by ethanol can easily take place; several types of trivalent phosphorus radical cations easily undergo a nucleophilic attack by a nucleophile, such as alcohol,[4] water,[4,10] thiol,[4] or pyridine.[5] Oxidation of the resulting phosphoranyl radical $\mathbf{1}^{\bullet}$**-OR** by a second molecule of **2** to the corresponding phosphonium cation $\mathbf{1}^{+}$**-OR** is energetically highly favorable, because $\mathbf{1}^{\bullet}$**-OR** has a much lower oxidation potential than the parent trivalent phosphorus compound **1**.[30,31] This mechanism predicts that each mole of **1** reduces two moles of **2** to **4**; that is, the stoichiometry of the reaction should be $[\mathbf{1}]_0:[\mathbf{2}]_0 = 1:2$, which has in fact been observed (Fig. 1). In further support of this mechanism, when the reaction of **1a** was carried out in the presence of benzyl alcohol in place of ethanol, benzyl ether was found on GC, although the yield was low.[32]

Endothermic SET. Let us assume a SET that takes place according to Scheme 3. Thus, an electron donor (D) and an acceptor (A) initially form an encounter complex at a diffusion-limited rate (k_{12}); then, SET takes place within the complex to give a pair of $D^{\bullet +}$ and $A^{\bullet -}$ (k_{23}), which is followed by a follow-up reaction (k_{30}). A steady-state approximation with respect to the encounter complex and the radical pair provides a rate expression,

$$k_p = \frac{k_{12}k_{23}k_{30}}{(k_{32} + k_{30})(k_{21} + k_{23}) - k_{32}k_{23}}. \tag{2}$$

When the SET step is endothermic, i. e., $\Delta G_{23} > 0$,[33] the rate expression depends on whether the SET step is reversible or irreversible.[11,13] If the SET step is reversible ($k_{32} >> k_{30}$), the rate is expressed by

$$k_p = K_{12}k_{30}\exp(-\Delta G_{23}/RT) \tag{3}$$

with $k_{12}/k_{21} = K_{12}$ and $k_{23}/k_{32} = K_{23} = \exp(-\Delta G_{23}/RT)$. On the other hand, if the SET step is irreversible ($k_{32} << k_{30}$), with the aid of the Horiuchi–Polanyi equation,[34] we obtain

$$k_p = K_{12}k_i\exp(-\alpha\Delta G_{23}/RT), \tag{4}$$

where k_i is the rate constant for a reaction when $\Delta G_{23} = 0$, and α is a proportionality constant that takes a value from 0 to 1. Here, ΔG_{23} is related to the difference in the half-wave potentials between **1** and **2** ($\Delta E_{1/2}$) by Eq. 5, where F is the Faraday constant.

$$\begin{aligned}\Delta G_{23} &= \Delta G_0 - (w_r + w_p)\\ &\approx F\Delta E_{1/2} - (w_r + w_p),\end{aligned} \tag{5}$$

where ΔG_0 is the free-energy change for the overall SET process, and w_r and w_p are work terms that stand for the work required to bring two components at certain distances in the encounter complex and the resulting pair, respectively. A reasonable assumption has been made that $\Delta E_{1/2}$ is nearly equal to the difference in the standard redox potentials (ΔE_0). Finally, Eqs. 3 and 4, respectively, are rewritten as

$$k_p = K_{12}k_{30}\exp[-F\{\Delta E_{1/2} - (w_r + w_p)\}/RT] \tag{6}$$

and

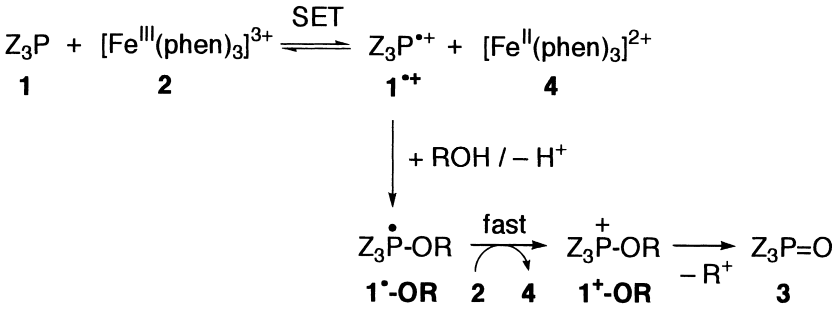
$$k_p = K_{12}k_i\exp[-\alpha F\{\Delta E_{1/2} - (w_r + w_p)\}/RT]. \tag{7}$$

Under the postulate that K_{12}, k_{30}, and k_i are constant irrespective of ΔG_{23}, Eq. 6 predicts that when the SET step is reversible, $\log k_p$ correlates linearly with $\Delta E_{1/2}$, with the slope being $-F/(2.3RT)$ ($= -16.8$ at 25 °C). Meanwhile, Eq. 7 states that a linear correlation between $\log k_p$ and $\Delta E_{1/2}$ also holds when

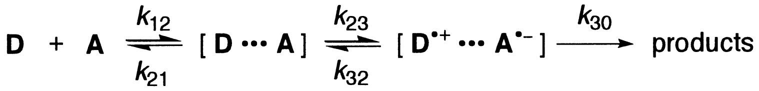
Table 1. Reaction of Trivalent Phosphorus Compound **1** with Fe^{III} Complex **2** in the Presence of EtOH[a)]

Z_3P(**1**)	**2**[b)]	$k_p/M^{-1}\ s^{-1}$	$E_{1/2}$/V[c)]	$\Delta E_{1/2}$/V[d)]
Ph_3P (**1a**)	**2H**	$(2.0 \pm 0.15) \times 10^5$	0.91	0.15
$Ph_2P(OMe)$ (**1b**)	**2H**	$(7.4 \pm 0.45) \times 10^3$	1.21	0.45
$PhP(OMe)_2$ (**1c**)	**2H**	$(9.4 \pm 0.49) \times 10$	1.49	0.73
$P\ (OMe)_3$ (**1d**)	**2H**	$(2.5 \pm 0.00) \times 10^{-1}$	1.81	1.05
	2Cl	1.8 ± 0.16		0.95
$Ph_2P(OEt)$ (**1e**)	**2H**	$(1.6 \pm 0.11) \times 10^4$	1.17	0.41
$PhP(OEt)_2$ (**1f**)	**2H**	$(4.6 \pm 0.16) \times 10^2$	1.47	0.71
	2Cl	$(1.2 \pm 0.028) \times 10^4$		0.61
$P(OEt)_3$ (**1g**)	**2H**	1.3 ± 0.14	1.87	1.11
	2Cl	$(1.4 \pm 0.09) \times 10$		1.01
$Ph_2P(OPr^i)$ (**1h**)	**2H**	$(2.8 \pm 0.08) \times 10^4$	1.16	0.40
$PhP(OPr^i)_2$ (**1i**)	**2H**	$(2.5 \pm 0.19) \times 10^3$	1.36	0.60
$P(OPr^i)_3$ (**1j**)	**2H**	7.4 ± 0.05	1.83	1.07
	2Cl	$(9.0 \pm 0.36) \times 10$		0.97
$Ph_2P(OBu)$ (**1k**)	**2H**	$(2.1 \pm 0.12) \times 10^4$	1.14	0.38
$PhP(OBu)_2$ (**1m**)	**2H**	$(7.4 \pm 0.36) \times 10^2$	1.38	0.62
$P(OBu)_3$ (**1n**)	**2H**	1.4 ± 0.07	1.85	1.09
$(PhCH_2)_2NH$ (**5a**)	**2H**	$(7.7 \pm 0.30) \times 10^3$	1.13	0.37
Bu^tNH_2 (**5b**)	**2H**	$(8.2 \pm 0.22) \times 10^2$	1.20[d)]	0.44

a) In MeCN under an argon atmosphere in the dark at 25 °C. $[\mathbf{1}]_0 = (2.00\text{–}8.00) \times 10^{-3}$ M, $[\mathbf{2}]_0 = 1.00 \times 10^{-4}$ M, $[EtOH]_0 = 1.00 \times 10^{-2}$ M. b) **2H**; $Fe^{III}\ (phen)_3\ PF_6^-$, **2Cl**; $Fe^{III}\ (5\text{-Cl-phen})_3\ PF_6^-$. c) vs Ag/Ag$^+$. Esitmated from the peak oxidation potential by using an equation, $E_{1/2} = E_p^{ox} - 0.03$. d) Difference in half-wave potentials between **1** and **2**, $E_{1/2}(\mathbf{1}) - E_{1/2}(\mathbf{2})$. d) Ref. 12.



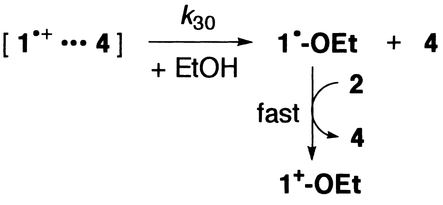
Scheme 2.



Scheme 3.

the SET step is irreversible, but the slope is $-\alpha F/(2.3RT)$ in this case. Since the α-value is less than unity, the slope is less negative in the latter case than in the former. In analogy with the Brönsted coefficient, the α-value is an index used to measure the position of the transition state of the SET under discussion; α becomes smaller with the transition state of the SET step going to the reactant side. Equations equivalent to Eq. 7 have been presented by us[11] and by other groups[13,15] to discuss the position of the transition state of the SET step.

Energetics of the SET from 1 to 2. The SET from **1** to **2** takes place according to Scheme 3. In this case, a follow-up reaction (k_{30}-step) is the separation of the ion pair into free-radicals, followed by an ionic reaction of $\mathbf{1}^{\bullet +}$ with ethanol (Scheme 4). Besides, the half-wave potentials ($E_{1/2}$) of trivalent phosphorus compounds **1a-n** as well as those of amines



Scheme 4.

5a-b are higher than those of **2H** and **2Cl**, thus showing the SET step (k_{23}-step) examined here to be endothermic ($\Delta G_{23} > 0$). That is, the SET from **1** as well as **5** to **2** is interpreted in terms of the endothermic SET formulated above.

In Fig. 2, are plotted the logarithms of the rate constants k_p (Table 1) against $\Delta E_{1/2}$. In this figure, the points for the reported values of the rate constants in the SET from alkylbenzenes to **2H** are also given. The SET from alkylbenezens is known to take place in a completely reversible way[24] and, as expected, these points make up a line whose slope is predicted by Eq. 6 (dotted line). Importantly, the points for SET from dibenzylamine **5a** and *t*-butylamine **5b** to **2** also fall on this line, showing that the SET from amines **5** to **2** is reversible. In contrast, the points for the SET from **1** are largely deviated from the dotted line. Apparently, although log k_p for the SET from **1** to **2** depends negatively on $\Delta E_{1/2}$, the dependence is weaker than predicted by Eq. 6. The kinetic behavior observed here is well described by Eq. 7.[35] Standing on a premise by which Eq. 7 was derived, the observation demonstrates that a follow-up chemical reaction of trivalent phosphorus cation radicals $\mathbf{1}^{\bullet+}$ (k_{30}) is rapid enough to overcome the back SET (k_{32}). The fact that k_p is independent of either concentration or kinds of alcohols strongly suggests that this is the case. In other words, the high reactivity of $\mathbf{1}^{\bullet+}$ toward ethanol results in an irreversible SET in an endothermic region. The indispensability of a rapid follow-up reaction for SET to occur is shown by the fact that SET from **5** is reversible; amine radical cations $\mathbf{5}^{\bullet+}$ act as a radical rather than a cation,[36,37] and no free-radical which can be coupled with the amine radical cations exists in the system.

Examining the points for **1** more closely, a linear correlation is found to hold within each series of **1** ($Ph_{(3-n)}P(OR)_n$) with an identical alkoxy group OR on the phosphorus atom (solid lines in Fig. 2). Although the k_p and $\Delta E_{1/2}$ values include experimental errors, these uncertainties are no larger than the range of the symbols in Fig. 2 (see Results section). Thus, these three lines are clearly distinguishable. From the slopes of these lines, the α-values for the reactions of **1** are calculated based on Eq. 7. As summarized in Table 2, the α-value becomes smaller in the order of R = Me > Et ≈ Bu > Pr^i in **1** ($Ph_{(3-n)}P(OR)_n$). That is, as the substituent OR on the phosphorus becomes bulkier, the transition state of the SET step becomes earlier.

This observation is interpreted in the term of SET occurring within the encounter complex [**1** ⋯ **2**] to give the complex [$\mathbf{1}^{\bullet+}$ ⋯ **4**]. Complexation is tighter in the former complex, "reactant" of the SET step, than in the latter, "product" of the SET step, because in the latter complex both components are positively charged. As a result, destabilization caused by a bulky ligand on the phosphorus is more significant in the former complex than in the latter. Thus, if we suppose two extreme cases here, namely, the reaction of a compound with a bulky ligand and that for a small ligand, then we can make up energy diagrams as illustrated in Fig. 3, which represent how the compound with a bulky ligand (solid curves) and the compound

Table 2. α-Values for the Reaction of **1** with **2**[a)]

R in $Ph_{(3-n)}P(OR)_n$	α-Value	r[b)]
Me	0.44 ± 0.02	0.998
Et	0.34 ± 0.02	0.998
Bu	0.35 ± 0.004	> 0.999
Pr^i	0.32 ± 0.002	> 0.999

a) At 25 °C. b) Correlation coefficient of the correlation between logk_p and $\Delta E_{1/2}$ in Fig. 2.

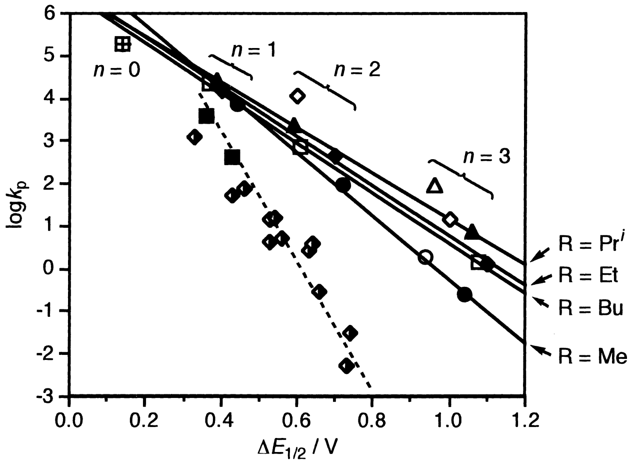


Fig. 2. Dependence of log k_p on $\Delta E_{1/2}$ in the reacrion of $Ph_{(3-n)}P(OR)_n$ (**1**) with iron(III) complexes (**2**). Each solid line is drawn for the reactions of a series of **1** with **2H**; R = Me (●), Et (◆), Pr^i (▲), and Bu (□). Symbols ○, ◇, and △ denote the reactions of **1d** (R = Me, n = 1), **1g** (R = Et, n = 1), and **1j** (R = Pr^i, n = 1) with **2Cl**, respectively. A symbol ⊞ denotes the reaction of **1a** with **2H**. Symbols ■ and ◆ denote the reactions of amines **5** and alkylbenzenes, respectively, with iron(III) complexes. A dashed line is drawn based on Eq. 6.

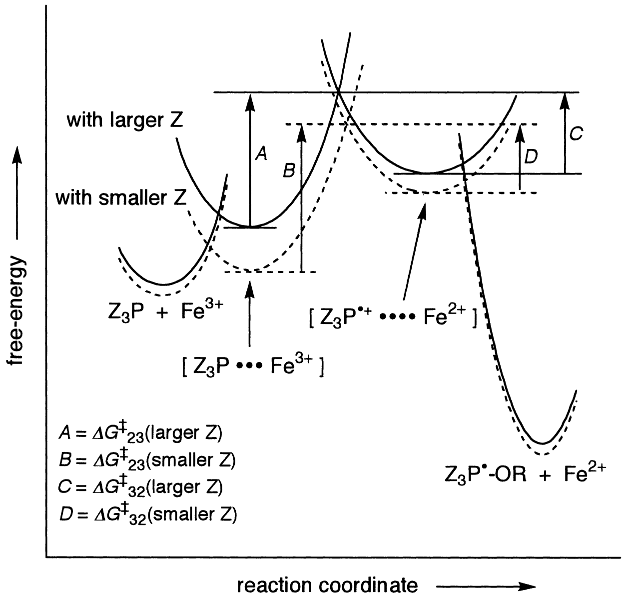


Fig. 3. Schematic presentation of energy diagrams of the SET reaction of **1** with **2**. The reactions of the phosphorus compounds with larger and smaller ligand(s) on the central phosphorus proceed according to solid curves and dashed curves, respectively.

with a small ligand (dashed curves) undergo reactions to afford products. Clearly, the SET from a compound with a bulkier ligand group has an earlier transition state.

The difference in the free-energy at the encounter complex stage corresponds to the difference in the work term (w_r) in Eq. 7. Such a situation, found in the present study, is in contrast to that in the typical outer-sphere SET, for which the work term (w_r) is often negligible. In other words, for the SET from **1** to **2** to undergo, the distance between the reactants within the encounter complex is required to be rather short. In this connection, an experimental fact is worth noting: an "ate" complex $[IrCl_6]^{2-}$, whose reduction potential is only about 0.1 V lower than that of **2**,[26a] did not give rise to the SET from **1**. If the difference in the half-wave potentials (which is sometimes termed "driving force") is the only factor to determine the reaction rate, the rate constant (k_p) of the reaction of **1a** with the iridate $[IrCl_6]^{2-}$ would be in the order of 10^5 M^{-1} s^{-1}. The observed inertness of the iridate to undergo SET is due to the intrinsically electron-rich character of the phosphorus compound **1**, which prevents the iridate from approaching **1** within an "effective" distance. It has been shown that SET from alkylmetals, such as R_4Sn to the iron(III) complex **2** and the iridate $[IrCl_6]^{2-}$, is subject to steric effects.[38] When the steric hindrance is significant between the reductant and the oxidant, SET takes place according to an outer-sphere mechanism. On the other hand, the alkylmetal undergoes an inner-sphere SET to a less-hindered reductant, namely, the iridate, via a tight encounter complex. An electrostatic force has been proposed to be a contributor to result in the tightness of the encounter complex. The consideration here thus demonstrates an inner-sphere character of the SET from **1** to **2**, where a tight encounter complex is formed prior to the SET.

The reaction of **1** with the chloro-substituted iron(III) complex **2Cl**, except for the reaction of methyl ester **1d**, has acquired acceleration in the rate compared with the reactions with the unsubstituted complex **2H**. As can be seen in Fig. 2, the points for the reactions with **2Cl** are deviated upward from the lines made up by the points for the corresponding reactions with **2H**. Since **2Cl** is bulkier than **2H**, a release of the steric congestion associated with the SET is more significant in the reaction with **2Cl** than in the reaction with **2H**, resulting in a rate acceleration for the reactions with **2Cl**. Such a steric effect has vanished in the reaction of **1d**. The methyl ester **1d** is too small to recognize the difference in size between **2H** and **2Cl**.

It is interesting to survey the α-values for an "irreversible SET" having appeared so far in the literature. In Table 3 are collected examples of such reactions together with the α-values. There is no simple tendency in magnitude of α depending on the rates of the follow-up reactions. For example, SET from ascorbic acid to an iron(III) complex (in the bottom row in Table 3) is followed by the second SET that must be very fast, but its α-value is the largest, that is, the transition state is the latest, among the reactions listed in this table. Reorganization of the reactants associated with SET could play an important role in determining the position of the transition state of the SET step.

Finally, we should examine our kinetic data in terms of the conventional theories. As we have seen before, the kinetics of the SET from **1** does not follow the prediction by Eq. 6. Since Eq. 6 (as well as Eq. 3) is an approximated version of the Rehm–Weller equation for SET occurring in an endothermic region, the observation shows that the SET from **1** is not in a category of the Rehm–Weller's model. On the other hand, it seems that such a kinetic behavior could be analyzed based on the Marcus equation.[2] However, any set of variables in the equation in fact failed to produce a quadratic curve that traces the experimental points. The "classical" Marcus theory has been evolving to afford several types of theories.[39–42] For example, the kinetics of nonadiabatic SET followed by dissociation of a covalent bond is well described in terms of an "evolved" Marcus theory, which has been developed while taking into account quantum mechanics as well as modified energetics brought about by a follow-up reaction.[42] Although the kinetic behavior observed in the present study may be explainable in terms of these theories, unfortunately our data set is too limited to allow such a discussion. In any case, it should be emphasized that a kinetic analysis according to Eq. 7 is not against the concept of the Marcus theory. The present study succeeded to abstract simplified aspects from intrinsically complicated kinetics of SET.

Summary

We studied kinetically SET from trivalent phosphorus compounds (**1**; $Ph_{(3-n)}P(OR)_n$) to iron(III) complexes **2** in acetonitrile containing ethanol. By examining the α-values obtained in a log $k_p - \Delta E_{1/2}$ plot, we found that (1) the SET step is irreversible, even though it is endothermic, and (2) the transition state of the SET step becomes earlier with increasing bulkiness of OR.

The latter finding leads to the conclusion that a tight encounter complex is formed between **1** and **2** prior to the SET.

Table 3. Irreversible SET Reactions and α-Values

Donor	Acceptor	Supposed follow-up reaction	α-Value	Ref.
2, 6-Di-*t*-butylphenol	Singlet oxygen	Formation of a C–O bond	0.20[a)]	17
Tetraalkyllead (R_4Pb)	$[Ir^{IV}Cl_6]^{2-}$	Cleavage of a C–Pb bond	0.37[a)]	18
Arene radical anion	Alkyl halide (RX)	Cleavage of a C–X bond	0.22–0.46[b)]	14,15
Fused aromatic compound	Peroxide	Cleavage of an O–O bond	0.30[b)]	13,20
Dihydroflavin	Nitroxide	H^+-transfer from oxidized flavin to reduced nitroxide	0.35[a)]	19
Ascorbic acid (HA^-)	$[Fe^{III}L_3]^{3+}$	SET from $HA^{\bullet}$ to Fe^{III}	0.50[a)]	26b
Ketene silyl acetal	Trityl cation	C–C bond formation	0.6[a)]	23

a) Calculated from the kinetic data reported. b) The values given in the referred papers.

Experimental

Instruments. GC and GCMS analyses were performed, respectively, with a Shimadzu GC-14B gas chromatograph and with a Shimadzu GCMS-QP2000A gas chromatograph-mass spectrometer equipped with a Shimadzu GC-MSPAC 200S data processor. UV/visible spectra were recorded on a Hitachi U-3212 spectrophotometer. Kinetics was carried out with a Union Giken RA-401 stopped-flow spectrophotometer. Cyclic voltammetry was carried out on a Cypress Systems OMNI90 potentiostat.

Materials. Triphenylphosphine (**1a**) was purchased (Nacalai Tesque). Trivalent phosphorus compounds **1b–g**, **j**, **n** were also commercially available (Tokyo Chemical Industry). These materials were purified by recrystallization or distillation, if necessary. Phosphinites **1h** and **1k** were obtained by the condensation of chlorodiphenylphosphine with 2-propanol and 1-butanol, respectively, in the presence of pyridine, followed by purification through distillation. Phosphonites **1i** and **1m** were obtained in a similar manner by the condensation of dichlorophenylphosphine with 2-propanol and 1-butanol, respectively. Tris(1, 10-phenanthroline)iron(III) hexafluorophosphate (**2H**) and tris(5-chloro-1, 10-phenanthroline)iron(III) hexafluorophosphate (**2Cl**) were synthesized according to literature procedure.[23]

Product Analysis. A solution of **1** ($(0.25 – 1.00) \times 10^{-4}$ M), **2** (1.00×10^{-4} M), and ethanol (1.00×10^{-2} M) in acetonitrile was allowed to react at 25 °C under an argon atmosphere for 5 min. The resulting solution was analyzed on a spectrophotometer to determine the yield of **4** based on the absorbance at 508 nm.[23] To determine the yield of **3a**, the reaction of **1a** (1.00×10^{-2} M) with **2** (1.00×10^{-2} M) in the presence of ethanol (1.00×10^{-1} M) was carried out under identical conditions. After 5 min, an aliquot of the reaction mixture was added to toluene containing dodecane as an internal standard, and the organic layer was analyzed by GC and GCMS.

Cyclic Voltammetry (CV). A solution of trivalent phosphorus compounds **1** or amines **5** (1.0×10^{-2} M) and a solution of iron(III) complexes (**2**) (5.0×10^{-2} M) were prepared in acetonitrile containing tetraethylammonium tetrafluoroborate (0.10 M) as the supporting electrolyte. The CV of these solutions was carried out at room temperature at a scan rate of 50 mV s^{-1}. The working electrode was platinum, and the reference electrode was Ag/Ag^+ (in a solution of silver nitrate (0.01 M) and tetraethylammonium perchlorate (0.1 M) in acetonitrile). The values of the peak potentials were read on the obtained cyclic voltammograms.

Kinetics. Stock solutions of **1** and **2** were prepared so that these concentrations became $(2.00 – 8.00) \times 10^{-3}$ M and 1.00×10^{-4} M, respectively, after mixing. The solutions were placed into separate reservoir cells of a stopped-flow spectrophotometer, which were maintained at 25 °C and charged with argon gas. After mixing, the increase in the absorbance at 508 nm was monitored.

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