Reaction of Trivalent Phosphorus Compounds with an Fe(III) Complex in the Presence of Alcohol. Single Electron Transfer Accompanied by a P-O Bond Formation

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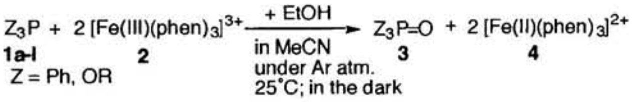
Reactions of various types of trivalent phosphorus compounds with iron(III) complex in the presence of ethanol have been examined kinetically, showing that the single electron transfer from the former compounds to the latter is followed by rapid reaction of the resulting trivalent phosphorus radical cations with ethanol.

Energetics of single electron transfer (SET) occurring from many types of compounds has been studied on both a theoretical and an experimental bases to find relationship between the rate and the free-energy change of the process.[1,2] However, SET from trivalent phosphorus compounds Z_3P has never been a subject of a kinetic study, in spite of the fact that Z_3P is easily oxidized to the radical cation $Z_3P^{\bullet +}$ upon treatment with an electron-deficient compound.[3,4] We determined rate constants of SET from Z_3P, for the first time, by examining the reaction of various types of trivalent phosphorus compounds (**1**) with tris(1,10-phenanthroline)iron(III) complex (**2**) in the presence of ethanol in acetonitrile. The kinetic data obtained are well interpreted in terms of the model presented by Schuster,[5] which is a modified version of the Rehm-Weller model.[1]

When a solution of **2** (PF_6^- salt) in acetonitrile (1.00×10^{-2} M) was mixed with an acetonitrile solution of **1** in various concentrations in the presence of a large excess of ethanol (1.00×10^{-1} M) under an argon atmosphere in the dark at 25 °C, **2** was reduced rapidly to the corresponding Fe(II) complex (**4**). Spectrophotometric analysis based on absorbance at 510 nm (λ_{max} of **4**) gave the stoichiometry $[\mathbf{1}]_0:[\mathbf{2}]_0 = 1:2$, **4** being formed in a quantitative yield when $[\mathbf{1}]_0/[\mathbf{2}]_0 > 0.5$. Analysis with ^1H and ^{31}P NMR showed that **1** is oxidized to afford the corresponding pentavalent oxo-compound **3** (Scheme 1).[6]



$$\underset{\substack{\mathbf{1a\text{-}l}\\ Z = Ph,\ OR}}{Z_3P} + \underset{\mathbf{2}}{2\,[Fe(III)(phen)_3]^{3+}} \xrightarrow[\substack{\text{in MeCN}\\ \text{under Ar atm.}\\ \text{25°C; in the dark}}]{+\ EtOH} \underset{\mathbf{3}}{Z_3P{=}O} + \underset{\mathbf{4}}{2\,[Fe(II)(phen)_3]^{2+}}$$

Scheme 1.

Kinetics was carried out at 25 °C under pseudo-first-order conditions, where **1** and ethanol were in a large excess (see footnote of Table 1). Increase in the concentration of **4** was followed on a stopped-flow spectrophotometer. For each reaction with **1a-l**, first-order kinetics was maintained up to more than 90% formation of **4**, and the pseudo-first-order rate constant obtained showed linear dependence on the concentration of **1**. The observation show clearly that the present reaction proceeds according to a second-order kinetics with first-order with respect to concentrations of **1** and **2**, respectively. Taking into account the observed stoichiometry, we obtain

$$d[\mathbf{4}]/dt = 2k_p[\mathbf{1}][\mathbf{2}]. \qquad (1)$$

Table 1. Rate constants of the reaction of **1** with **2**[a]

1		k_p / $s^{-1}M^{-1}$ [b]	E_p^{ox} / V[c]
$Ph_2P(OMe)$	(**1a**)	7.37×10^3	1.24
$PhP(OMe)_2$	(**1b**)	9.42×10	1.52
$P(OMe)_3$	(**1c**)	2.50×10^{-1}	1.84
$Ph_2P(OEt)$	(**1d**)	1.57×10^4	1.20
$PhP(OEt)_2$	(**1e**)	4.63×10^2	1.50
$P(OEt)_3$	(**1f**)	1.34	1.90
$Ph_2P(OPr^i)$	(**1g**)	2.77×10^4	1.19
$PhP(OPr^i)_2$	(**1h**)	2.48×10^3	1.39
$P(OPr^i)_3$	(**1i**)	7.42	1.86
$Ph_2P(OBu^n)$	(**1j**)	2.14×10^4	1.17
$PhP(OBu^n)_2$	(**1k**)	7.38×10^2	1.41
$P(OBu^n)_3$	(**1l**)	1.40	1.88

[a] $[\mathbf{1}]_0 = (2.00 \sim 8.00) \times 10^{-3}$ M, $[\mathbf{2}]_0 = 1.00 \times 10^{-4}$ M, $[EtOH]_0 = 1.00 \times 10^{-2}$ M. [b] Errors are within 7%. [c] vs Ag/Ag$^+$.

Table 1 summarizes the second-order rate constant k_p thus obtained, along with peak oxidation potential E_p^{ox} of **1**.[7] Oxidation peak of the iron complex **2** appeared at 0.80 V vs Ag/Ag$^+$ on a cyclic voltammogram obtained in acetonitrile.[8]

A key observation in the present reaction is irreversible formation of **4**, which results certainly from SET from **1** to **2**. To analyze kinetics of an SET reaction that results in irreversible formation of the product, Schuster has presented a reaction scheme shown in Eq.2.[5] That is, an electron donor D and an electron acceptor A form an encounter complex at a diffusion-limited rate (k_{12}), SET takes place within the complex (k_{23}), and the product P is produced irreversibly (k_{30}).

$$D + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} [D \cdots A] \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} [D^{\bullet +} \cdots A^{\bullet -}] \xrightarrow{k_{30}} P \qquad (2)$$

With steady-state approximation with respect to concentrations of an encounter complex and a radical ion pair, rate constant k_p for increase in [P] is expressed as

$$k_p = \frac{k_{12}k_{23}k_{30}}{(k_{32} + k_{30})(k_{21} + k_{23}) - k_{32}k_{23}} \qquad (3)$$

which predicts different kinetic behaviors in the following three cases.[9]

Case I: SET-step (k_{23}) is exothermic ($\Delta G_{23} < 0$) and irreversible ($k_{32} << k_{30}$). In this case, $k_{23} >> k_{21}$, then

$$k_p = k_{12}. \qquad (4)$$

Case II: SET-step (k_{23}) is endothermic ($\Delta G_{23} > 0$) and reversible ($k_{32} >> k_{30}$). In this case, $k_{23} << k_{21}$, then taking $k_{23}/k_{32} = \exp(-\Delta G_{23}/RT)$ and $\Delta G_{23} = F(E_0^{ox} - E_0^{red}) = F\Delta E^0$,

$$k_p = k_{30}K_{12}\exp(-F\Delta E^0/RT) \qquad (5)$$

where $K_{12} = k_{12}/k_{21}$.

Case III: SET-step (k_{23}) is endothermic ($\Delta G_{23} > 0$) and irreversible ($k_{32} << k_{30}$). As in Case II, $k_{23} << k_{21}$, then

$$k_p = K_{12}k_{23}. \qquad (6)$$

In this case, the Horiuchi-Polanyi equation, which assumes that increase in activation free energy ($\Delta G^{\ddagger}_{23}$) is proportional to increase in free-energy change (ΔG_{23}) as expressed in Eq.7, is applied.[5,10] Eq.7 leads to Eq.8.

$$\Delta G^{\ddagger}_{23} = \Delta G^{\ddagger}_{0} + \alpha \Delta G_{23}. \qquad (7)$$

$$k_{23} = k_i \exp(-\alpha \Delta G_{23}/RT). \qquad (8)$$

Here, $\Delta G^{\ddagger}_0$ and k_i are the activation free energy and the rate constant, respectively, when $\Delta G_{23} = 0$. From Eqs.6 and 8,

$$k_p = K_{12} k_i \exp(-\alpha \Delta G_{23}/RT) = K_{12} k_i \exp(-\alpha F \Delta E^0/RT). \qquad (9)$$

From Eqs. 4, 5, and 9, we see that in the plot of $\log k_p$ vs ΔE^0, the slopes are 0, $-F/(2.3RT)$ (= −16.8 at 25 °C), and $-\alpha F/(2.3RT)$ for the Cases I, II, and III, respectively. Thus, if a linear correlation with a negative slope is found between $\log k_p$ and ΔE^0 in a given reaction, the reaction follows the reaction sequence of Eq.2 with $\Delta G_{23} > 0$, and, furthermore, the slope of the correlation determines whether SET-step is reversible or irreversible. In other words, we can find it out if k_{30}-step takes place rapidly enough to overcome the reverse SET (k_{32}).

Peak potentials E_p of **1** and **2** were found to be invariable with changing scan rate in cyclic voltammetry, indicating reversible feature for anodic oxidation of **1** and cathodic reduction of **2**. Therefore, an approximation, ΔE_p (= $E_p(\mathbf{1}) - E_p(\mathbf{2})$) ≈ ΔE^0 (= $E_0(\mathbf{1}) - E_0(\mathbf{2})$), can be taken here.[11] Then, $\log k_p$ was plotted against ΔE_p in place of ΔE^0 in Figure 1. In accordance with ΔE_p > 0 in the present reaction, a linear correlation with a negative slope was given for each series of **1** with an identical alkoxy group on the phosphorus (correlation coefficient $r > 0.998$). Importantly, the values of the slopes listed in Table 2 are smaller than that predicted in Case II and meet prediction in Case III. That is, k_{30}-step in the present reaction is rapid enough to make k_{23}-step irreversible. Trivalent phosphorus radical cations are known to react easily with nucleophiles such as alcohols.[3,4a] So, a conclusion here is obvious; radical cation $\mathbf{1}^{\bullet+}$ generated in the SET undergoes ionic reaction with ethanol very rapidly (Eq.10). The reaction is followed by a sequence shown in Eq.11; the resulting phosphoranyl radical $Z_3P^{\bullet}$-OR undergoes SET to **2** to give phosphonium cation, from which ethyl cation equivalent is eliminated to yield the final product **3**. The process is highly exothermic.[3] In support for this mechanism, the rate constant k_p was unchanged by increasing the concentration of ethanol to 1.70 × 10^{-1} M. The observed stoichiometry, $[\mathbf{1}]_0:[\mathbf{2}]_0 = 1:2$, also verifies this mechanism.

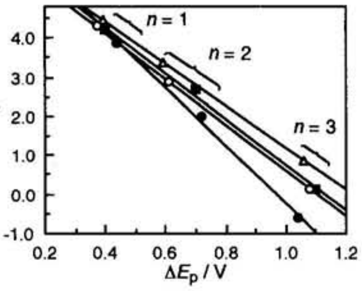


Figure 1. Dependence of $\log k_p$ on ΔE_p in the reaction of $Ph_{3-n}P(OR)_n$ (**1**) with **2**. ● ; R = Me, ■ ; R= Et, △ ; R = Pr^i, ○ ; R = Bu^n.

Table 2. Slopes in the plot of $\log k_p$ vs ΔE_p^{ox}

R in $Ph_{3-n}P(OR)_n$ (**1**)	Slope
Me	−7.46±0.37
Et	−5.84±0.35
Bu^n	−5.88±0.07
Pr^i	−5.34±0.03

$$[\,Z_3P^{\bullet+} \cdots Fe^{2+}\,] \xrightarrow[+\,EtOH\,/\,-\,H^+]{k_{30}} Z_3P^{\bullet}\text{-OEt} + Fe^{2+} \qquad (10)$$

$$Z_3P^{\bullet}\text{-OEt} \xrightarrow{\mathbf{2}\ \curvearrowright\ \mathbf{4}} Z_3P^{+}\text{-OEt} \xrightarrow{-\,Et^+} \mathbf{3} \qquad (11)$$

A similar kinetic behavior is seen when an SET is followed by a rapid and irreversible chemical reaction.[5,10,12-16] For example, SET from various types of electron donors to alkyl halides is followed by rapid cleavage of the carbon-halogen bond in the resulting radical anion.[10,12,13] Also, SET from substituted phenols to singlet oxygen is likely to be associated with formation of a carbon-oxygen bond.[14] In contrast, amines undergo endothermic SET to photoexcited acceptors but with following kinetics predicted in Case II;[1,2,17] there is no evidence for further reaction of the resulting amine radical cations.

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