Reinvestigation of the Peculiar Dependency of the Rate on the Free-Energy Change in the Electron Transfer from Trivalent Phosphorus Compounds Based on the Extended Marcus Equation

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Introduction

Electron transfer (ET) takes place from trivalent phosphorus compounds Z_3P to a variety of acceptors. The ET from Z_3P exhibits a peculiar behavior in kinetics-dynamics relationship. That is, neither the Rehm-Weller theory nor the conventional Marcus theory predicts dependency of the ET rate k_{ET} on the free-energy change ΔG^0. Such a kinetic behavior is in sharp contract with that for the ET from "typical" electron donors such as amines and alkoxyl benzenes. The kinetic behavior of the ET from Z_3P can be interpreted in terms of "irreversible ET"; the trivalent phosphorus radical cation resulting from the ET undergoes rapid ionic reaction with a nucleophile such as water or alcohol in the solvent, making the ET step irreversible. Here, the author attempts to reinvestigate the dependency of k_{ET} on ΔG^0 in ET from Z_3P based on the extended Marcus equation, for which the free-energy gained in the follow-up reaction and the Coulomb term that results from the ET are taken into account.

Background

Electron transfer reactions (ET) are one of fundamental chemical reactions. These reactions occur ubiquitously in inorganic and organic chemistry as well as in biological systems. The mechanism of ET has been subjected to many studies by both experimental and theoretical chemists. First, the author surveys briefly theories developed so far to describe the relationship between the ET rate and free-energy change (driving force).

Conventional Marcus equation

Let us draw the potential curves of the initial and final states, then ET occurs when the energy of the initial state is elevated to the point where these two potential curves intersect. When the efficiency of transmission at the intersection is 100%, namely, transmission coefficient $\kappa = 1$, the ET is called "adiabatic". Connecting this concept with the transition state theory,

Marcus presented a simple quadratic equation (1), which describes rate constants k_{ET} of ET reactions as a function of free-energy change ΔG^0.[1)]

$$k_{ET} = Z \exp[-\frac{(\Delta G^0 + \lambda)^2}{4k_B T\lambda}] \ ,$$ (1)

where Z is the collision frequency that takes a value of $\sim 10^{11}$ $M^{-1}s^{-1}$ for homogeneous reaction, k_B is the Boltzmann constant, and T is the absolute temperature. The parameter λ is called reorganization energy, which represents the movements of the reactants and the solvent during the ET. When $\Delta G^0 = 0$, $\lambda/4$ equals to the activation energy of the ET step.

The transmission from the initial state to the final state at the intersection of the potential curves does not necessarily take place with $\kappa = 1$. When the $\kappa < 1$, the ET processes are called "non-adiabatic". The rates of non-adiabatic ET processes are described by Eq.(2) that includes the electronic coupling matrix element H_{DA}, the parameter that represents adiabaticity of ET.

$$k_{ET} = (2\pi/h)|H_{DA}|^2 (4\pi k_B T\lambda)^{-1/2} \exp[-\frac{(\Delta G^0 + \lambda)^2}{4k_B T\lambda}]$$ (2)

Importantly, the Marcus equation (Eq.(1)) as well as its modified version (Eq.(2)) predicts decrease in the ET rate in the exothermic region ($-\Delta G^0 < \lambda$) (so-called "inverted region"). Although such a phenomenon may be against instinct of chemists, the existence of inverted region was proved later experimentally.[2)]

Rehm-Weller equation

Rehm and Weller carried out kinetics of ET reactions occurring within a large number of the donor-acceptor pairs under the photochemical conditions, and examined the relationship between rate constant k_{ET} and free-energy change ΔG^0. Against the Marcus' prediction, there was no "inverted region" observed. Based on the reaction sequence shown in Scheme 1, they derived Eq.(3).[3)]
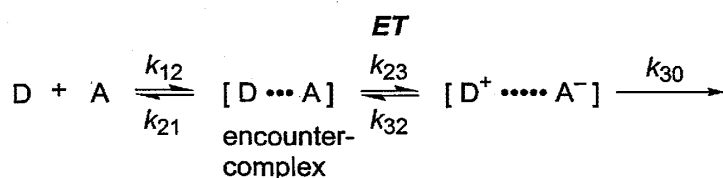
Scheme 1. A common reaction sequence of ET.

$$k_{ET} = \frac{k_{12}}{1 + \dfrac{k_{12}}{\Delta V k_{30}}\left[\exp\left(\dfrac{\Delta G_{23}^{\ddagger}}{RT}\right) + \exp\left(\dfrac{\Delta G_{23}}{RT}\right)\right]} \quad , \tag{3}$$

$$\Delta V = k_{12}/k_{21}$$

where ΔG_{23} and $\Delta G_{23}^{\ddagger}$ are free-energy change (corresponding to ΔG^{0} in the previous sections) and activation free-energy of the ET step, respectively. k_{30} is the rate constant for all possible modes of disappearance of the resulting radical pair. According to Eq.(3), the ET occurs at the rate of diffusion-controlled limit throughout the exothermic region; that is, $k_{ET} = k_{12}$ when $\Delta G_{23} < 0$. In the endothermic region ($\Delta G_{23} > 0$), Eq.(3) is approximated to Eq.(4). This approximation manifests that the slope in the plot of $\log k_{ET}$ vs ΔG_{23} (in eV) in this region is -17.2 at $20°C$.

$$k_{ET} = (\Delta V/2)\{\exp(-\Delta G_{23}/RT)\} \tag{4}$$

To elucidate the reason why the "inverted region" is not observed, several theoretical studies have been presented.[4]

ET accompanied by a follow-up reaction

Species generated in the ET step sometimes undergoes a follow-up reaction such as cleavage of a covalent bond, formation of a covalent bond, or the second ET. If the follow-up reaction is such fast that $k_{32} \ll k_{30}$, the ET step affords the product(s) irreversibly even when the ET is endothermic ($\Delta G_{23} > 0$). The rate of "irreversible ET" in the endothermic region is expressed by Eq.(5).[5]

$$k_{ET} = K_{12}k_{i}\{\exp(-\alpha\Delta G_{23}/RT)\} \tag{5}$$

where $K_{12} = k_{12}/k_{21}$ and k_{i} is the rate constant when $\Delta G_{23} = 0$. The α-value, which takes a value between 0 and 1, represents the position of the transition state of the ET step. The smaller the α-value, the earlier the transition state. Comparing Eqs.(4) and (5), it is apparent that the dependency of k_{ET} on ΔG_{23} in the irreversible ET is weaker than in the conventional Rehm-Weller prediction that assumes "reversible ET".

As a typical irreversible ET, dissociative ET has been studied extensively. One electron reductions of aryl halides in homogeneous and heterogeneous reactions are followed by the cleavage of the carbon-halide bond.[6-8]

Results and Discussion

ET from trivalent phosphorus compounds

Many types of trivalent phosphorus compounds Z_3P undergo ET to electron deficient compounds under the photochemical conditions[9-12] or in the dark.[13-15] The kinetic investigation has been made on some of these reactions, which always shows that the dependency of $\log k_{ET}$ on ΔG^0 is weaker than that predicted from the Rehm-Weller equation (4), that is, the slope of the plot $(-\log k_{ET}/\Delta G^0)$ is less negative than -17.2 at $20°C$. This suggests strongly that the ET from Z_3P is accompanied by a follow-up reaction. Indeed, the product analyses have shown that trivalent phosphorus cation radicals $Z_3P^{•+}$ resulting from the ET undergo rapid ionic reaction with a nucleophile such as water or alcohol in the solvent (Scheme 2). That is, the ET from Z_3P belongs to the category of "irreversible ET" and is interpreted based on Eq.(5).

$$Z_3P^{•+} \ + \ ROH \ \longrightarrow \ Z_3\overset{•}{P}\text{-}OR \ + \ H^+$$
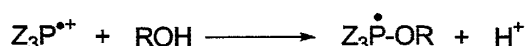
Scheme 2. Follow-up reaction in the ET from Z_3P.

The ET from $Ph_{3-n}P(OR)_n$ ($n = 1\sim3$; $R = Me$, Et, Pr^i, Bu^n) to Fe(III) complexes was examined kinetically (Scheme 3).[15] It was found that the bulkier the OR ligand on the phosphorus atom, the smaller the α value is, meaning that the transition state of the ET step becomes earlier with increasing bulkiness of OR. This study was successful within the framework of the Rehm-Weller theory. Nevertheless, it should be tested if the results in this study can be adapted to the Marcus equation (1).
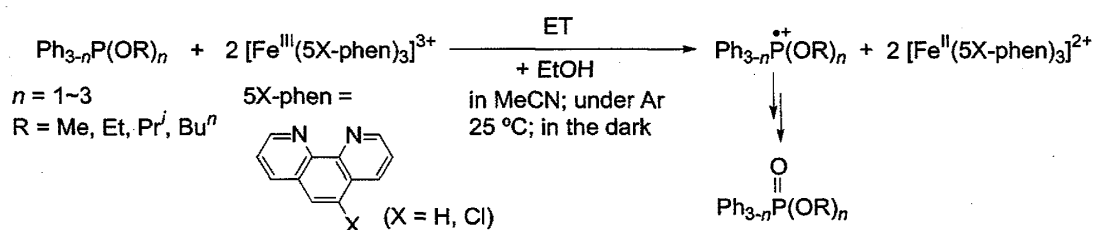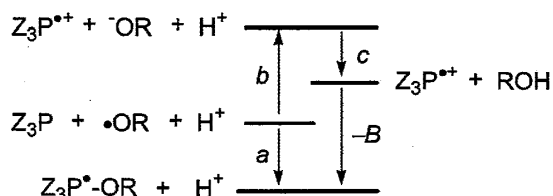

Scheme 3. ET from Z_3P to Fe(III) complexes.

Marcus equation modified using energy gained in the follow-up reaction

When the follow-up reaction is concerted with the ET step, the Marcus equation is modified to Eq.(6) by taking into account the free-energy $-B$ gained in the follow-up reaction.[6f,j]
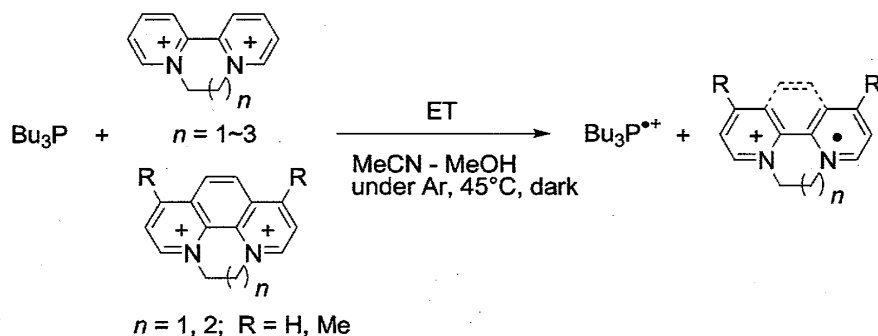
$$k_{ET} = Z\exp[-\frac{(\Delta G^0 + \lambda + B)^2}{4k_BT\lambda}] \tag{6}$$

Since the P-O covalent bond is formed in the follow-up reaction in the ET from Z_3P, $-B$ can be calculated based on a thermochemical cycle shown in Scheme 4. With the calculated value of $-B$ in hand, one can analyze the rate data based on Eq.(6).
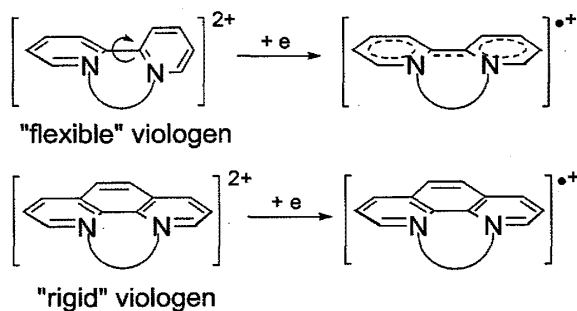
$$Z_3P^{\bullet+} + {}^-OR + H^+$$

$$Z_3P + \bullet OR + H^+$$

$$Z_3P^{\bullet}\text{-}OR + H^+$$

$$Z_3P^{\bullet+} + ROH$$

(with labels b, c, a, $-B$)

Scheme 4. Thermochemical cycle to calculate $-B$.

Before reinvestigating the ET from Z_3P to Fe(III) complexes based on Eq.(6), the author will discuss the ET reaction from tributylphosphine Bu_3P to "flexible" and "rigid" cyclic viologens (diquarternary salts of 2,2'-bipyridine and 1,10-phenanthroline, respectively) (Scheme 5).[14c] The ET reactions with these cyclic viologens were kinetically examined to find that the points in the $\log k_{ET}$ – ΔG^0 plot were again largely deviated from the line predicted by the conventional Marcus equation (1) and the Rehm-Weller equation (3), the deviation being much larger in the ET to "rigid" viologens than in the ET to "flexible" ones. In an attempt to analyze the data based on Eq.(6), the $-B$ value was estimated to be < 256 kJ mol^{-1} (< 2.65 eV) using the value of a from the literature[16] and the value of b obtained by electrochemical measurements.[17] The validity of this value is supported, although indirectly, by the result of the calculation for a similar compound. Thus, the bond energy of the P-O(C) (ax) of a phosphorane has been calculated to be about 300 kJmol^{-1};[18] the model phosphorane takes the same geometry as that of the phosphoranyl radical, except that the former has the alkoxyl ligand instead of an unpaired electron in the phosphoranyl radical. Eventually, the value of $-B$ estimated here well reproduces the experimental data through the modified Marcus equation (6) with certain λ values. Best fit of the data to Eq.(6) is shown in Figure 1. Quite interestingly, "flexible" viologens, whose structural change during the ET is more significant (Scheme 6), undergo the ET with the higher reorganization energy λ than "rigid" ones.

$$Bu_3P \ + \quad n = 1\sim3 \quad \xrightarrow[\text{under Ar, 45°C, dark}]{\text{MeCN - MeOH}} \quad Bu_3P^{\bullet+} \ +$$

$$n = 1, 2; \ R = H, Me$$

Scheme 5. ET from Bu_3P to cyclic viologens.

"flexible" viologen

"rigid" viologen

Scheme 6. Structural change of "flexible" and "rigid" viologens during ET.
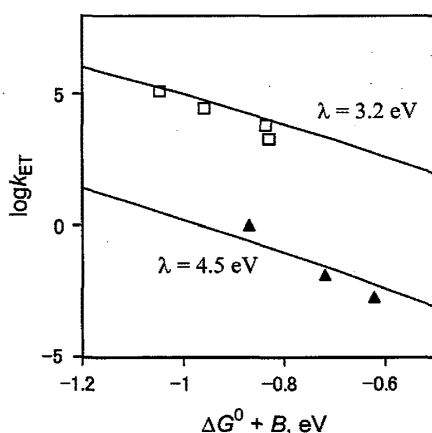
Figure 1. Best fits of the plots to the modified Marcus equation (6). ▲ and ☐ denote the points for the ET from Bu_3P to "flexible" and "rigid" viologens, respectively. Data from Ref.14c.

Now, the author returns to the point where the ET from Z_3P to Fe(III) is reinvestigated based on Eq.(6), for which dependency of $\log k_{ET}$ on free-energy change ΔG^0 once has been interpreted in terms of "irreversible ET" (Eq.(5)).[15] Thus, reinvestigation of this ET reaction taking into account $-B$ eventually gave the best fit of the data points to Eq.(6) with $-B = 2.4$ eV and $\lambda = 5.0$ eV. The $-B$ value obtained here is very close to that in the ET from Bu_3P to cyclic viologens (2.65 eV), revealing the validity of this treatment. Since $-B$ is the net free-energy gained in the reaction of $Z_3P^{\bullet+}$ with a nucleophile, it should be independent of the acceptor, and approximately the same value of $-B$ is applied to any ET occurring from Z_3P.
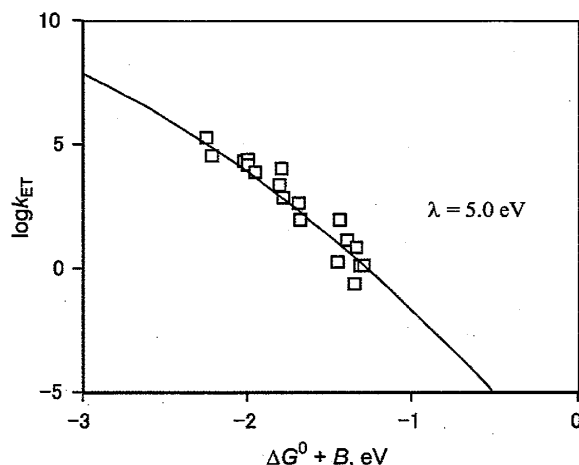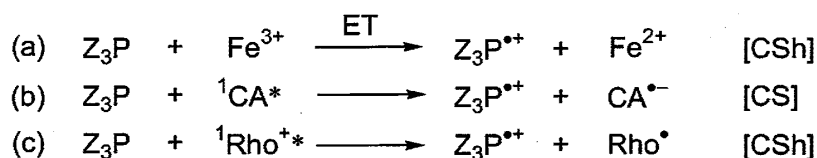
Figure 2. Best fits of the plots to the modified Marcus equation (6) in the ET from Z_3P to $Fe(III)$ complexes. Data from Ref.15.

The Marcus equation modified using energy gained in the follow-up reaction (Eq.(6)) seems successful in predicting the rate of the ET from trivalent phosphorus compounds. The experimental data from the ET reactions with different acceptors are well accommodated to Eq.(6) with a similar value of $-B$, the energy of the formation of the P-O bond from $Z_3P^{\bullet+}$ and ROH. Yet, it should be mentioned that the λ value (0.5 eV) assumed above is too large to be convinced as a true value, suggesting that another parameter is required to describe $\log k_{ET} - \Delta G_0$ profile in the ET reactions more precisely.

Modified Marcus equation with the Coulomb term

The ET from Z_3P to $Fe(III)$ complexes, the energetics of which has been discussed in the previous sections, gives the radical cation $Z_3P^{\bullet+}$ and $Fe(II)$ complexes from the former and the latter, respectively. In other words, the ET produces the electrostatic repulsion. Such a type of ET is categorized as "charge-shift (CSh)", ((a) in Scheme 7). Since this change in the electrostatic interaction certainly affects the ET rate, it cannot be neglected for precise description of the dependency of k_{ET} on ΔG^0.

(a) Z_3P + Fe^{3+} $\xrightarrow{\text{ET}}$ $Z_3P^{\bullet+}$ + Fe^{2+} [CSh]

(b) Z_3P + $^1CA*$ $\longrightarrow$ $Z_3P^{\bullet+}$ + $CA^{\bullet-}$ [CS]

(c) Z_3P + $^1Rho^{+}*$ $\longrightarrow$ $Z_3P^{\bullet+}$ + $Rho^{\bullet}$ [CSh]

Scheme 7. Different types of ET. (a) Charge shift (CSh) generating electrostatic repulsion. (b) Charge separation (CS) generating electrostatic attraction. (c) Charge shift (CSh) resulting in no change in electrostatic interaction.

Here, the author proposes the further modified Marcus equation (7) taking into account the electrostatic (Coulomb) term C, where the sign of C is defined plus and minus for the ET reactions which generates the electrostatic attraction and repulsion, respectively. According to this definition, the C value in the ET from Z_3P to Fe(III) is negative. Although the absolute value of C in this ET cannot be estimated at this moment, the correction by C makes the simulation curve in Figure 2 shift to the positive direction. A preliminary simulation was performed with the fixed value of $-B$ (2.4 eV) with varying C from -2 to -1 arbitrarily, then the best fit of the rate data to Eq.(7) was obtained when the value of λ is between 2 and 3. This value of λ seems reasonable for the ET from Z_3P to Fe(III).

$$k_{ET} = Z \exp[-\frac{(\Delta G^0 + \lambda + B - C)^2}{4k_B T \lambda}] \tag{7}$$

Recently, interesting results were obtained from the ET quenching by Z_3P of 9-cyanoanthracene (CA) and rhodamine (Rho^+) in the singlet-photoexcited states ($^1CA^*$ and $^1Rho^{+*}$, respectively). The logarithms of the ET rate constants, which were determined by the Stern-Volmer method, were plotted against free-energy change ΔG^0. The dependency of $\log k_{SET}$ on ΔG^0 in the endothermic region was weaker than that expected by the conventional Marcus equation (1) and the Rehm-Weller equation (4), as in the other ET reactions occurring from Z_3P. Interestingly, the plot for the ET to $^1CA^*$ was more deviated from the theoretical curves than that for the ET to $^1Rho^{+*}$. The former ET gives an ion pair of $Z_3P^{\bullet+}$ and $CA^{\bullet-}$, generating electrostatic attraction ((b) in Scheme 7). This type of ET is categorized as charge-separation (CS). Meanwhile, the latter ET is categorized as charge-shift (CSh) but results in neither electrostatic attraction nor repulsion ((c) in Scheme 7). As a result, for the former and the latter, a positive value and null are taken as C, respectively. According to the Eq.(7), the difference in the change of the charge distribution during the ET, namely, the difference in the C value, explains, although qualitatively at the present, the origin of the different $\log k_{SET} - \Delta G^0$ plots for the ET to $^1CA^*$ and to $^1Rho^{+*}$.

Several reports have been presented with respect to "multiple Rehm-Weller plots", where the dependency of k_{ET} on ΔG^0 follows two different lines depending on difference in the property of a donor and/or an acceptor within a series of ET reactions.[19,20] For example, in the ET from aromatic and aliphatic donors to the singlet photoexcited state of a neutral aromatic sensitizer such as 9,10-dicyanoanthracene, the $\log k_{SET} - \Delta G^0$ plot for the aliphatic donor in the region of $\Delta G^0 > 0$ is shifted to the positive direction. An explanation for the observations comes from difference in the electrostatic interaction between the donor and the acceptor.[19] Electrostatic interaction of the aliphatic donor (n-donor) with the neutral aromatic acceptor is more favorable than that of the aromatic donor (π-donor). This explanation is in line with the

concept revealed in Eq.(7).

Acknowledgment

References and Notes

1) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966-978. (b) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 979-989. (c) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853-857. (d) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891-899.

2) (a) Miller, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 3047-3049. (b) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057-5068. (c) Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1990**, *117*, 5353-5354.

3) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259-271.

4) (a) Kakitani, T.; Mataga, N. *J. Phys. Chem.* **1987**, *91*, 6277-6283. (b) Tachiya, M.; Murata, S. *J. Phys. Chem.* **1992**, *96*, 8441-8444. (c) Murata, S.; Nishimura, M.; Matsuzaki, S. Y.; Tachiya, M. *Chem. Phys. lett.* **1994**, *219*, 200-206.

5) (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. (c) Dixon, B. G.; Schuster, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 3116-3118. (d) Schuster, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 5851-5853. (e) Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519-2523. (f) Wölfle, I.; Lodaya, J.; Sauerwein, B.; Schuster, G. B. *J. Am. Chem. Soc.* **1992**, *114*, 9304-9309.

6) (a) Workenitn, M. S.; Maran, F.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 2120-2121. (b) Antonello, S.; Musumeci, M.; Wayner, D. D. M.; Maran, F. *J. Am. Chem. Soc.* **1997**, *119*, 9541-9549. (c) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1997**, *119*, 12595-12600. (d) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1998**, *120*, 5713-5722. (e) Donkers, R. L.; Maran, F.; Wayner, D. D. M.; Workentin, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 7239-7248. (f) Antonello, S.; Maran, F. *J. Am. Chem. Soc.* **1999**, 121, 9668-9676. (g) Antonello, S.; Formaggio, F.; Moretto, A. Toniolo, C.; Maran, F. *J. Am. Chem. Soc.* **2001**, *123*, 9577-9584. (h) Antonello, S.; Benassi, R.; Gavioli, G.; Taddei, F.; Maran, F. *J. Am. Chem. Soc.* **2002**, *124*, 7529-7538. (i) Antonello, S.; Crisma, M.; Formaggio, F.; Moretto, A.; Taddei, F.; Toniolo, C.; Maran, F. *J. Am. Chem. Soc.* **2002**, *124*, 11503-11513. (j) Antonello, S.; Daasbjerg, K.; Jensen, H.; Taddei, F.; Maran, F. *J. Am. Chem. Soc.* **2003**, *125*, 14905-14916.

7) (a) Savéant, J.-M. *Acc. Chem. Res.* **1993**, *26*, 455-461. (b) Cardinale, A.; Isse, A. A.; Gennaro, A.: Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2002**, *124*, 13533-13539. (c) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 105-112. (d) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 16051-16057. (e) Costentin, C.; Robert, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **2005**, *126*, 16834-16840.

8) Grimshaw, J.; Langan, J. R.; Salmon, G. A. *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 75-81.

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

10) Yasui, S.; Tsujimoto, M.; Shioji, K.; Ohno, A. *Chem. Ber./Recueil* **1997**, *130*, 1699-1707.

11) Yasui, S.; Tsujimoto, M.; Itoh, K.; Ohno, A. *J. Org. Chem.* **2000**, *65*, 4715-4720.

12) (a) Yasui, S.; Tojo, S.; Majima, T. *J. Org. Chem.* **2005**, *70*, 1276-1280. (b) Yasui, S.; Tojo, S.; Majima, T. *Org. Biomol. Chem.* **2006**, *4*, 2969-2973.

13) Yasui, S.; Fujii, M.; Kawano, C.; Nishimura, Y.; Shioji, K.; Ohno, A. *J. Chem. Soc., Perkin Trans. 2.* **1994**, 177- 83.

14) (a) Yasui, S.; Shioji, K.; Tsujimoto, M.; Ohno, A. *J. Chem. Soc., Perkin Trans. 2* **1999**, 855-862. (b) Yasui, S.; Itoh, K.; Ohno, A.; Tokitoh, N. *Org. Biomol. Chem.* **2005**, *3*, 4188-4192. (c) Yasui, S.; Itoh, K.; Ohno, A.; Tokitoh, N. *Org. Biomol. Chem.* **2006**, *4*, 2928-2931.

15) Yasui, S.; Itoh, K.; Tsujimoto, M.; Ohno, A. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1311-1318.

16) Bentrude, W. G. in *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Wiley, West Sussex, England, **1990**, Vol. 1, Ch. 14, pp. 531-566.

17) Since the energy c required for the deprotonation of the alcohol is not available, the upper limit of $-B$ is obtained.

18) Range, K.; McGrath, M. J.; Lopez, X.; York, D. M. *J. Am. Chem. Soc.* **2004**, *126*, 1654-1665.

19) (a) Jacques, P.; Haselbach, E.; Henseler, A.; Suppen, P. *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 3811-3813. (b) Jacques, P.; Burget, D. *J. Photochem. Photobiol. A: Chem.* **1992**, *68*, 165-168. (c) Jacques, P.; Allonas, X. *J. Photochem. Photobiol. A: Chem.* **1994**, *78*, 1-5.

20) (a) Inada, T. N.; Kikuchi, K.; Takahashi, Y.; Ikeda, H.; Miyashi, T. *J. Photochem. Photobiol. A: Chem.* **2000**, *37*, 93-97. (b) Burshtein, A. I.; Ivanov, K. L. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4115-4125.