Kinetic Deuterium Isotope Effect in Single-Electron Transfer Occurring from Tributylphosphine to Viologens

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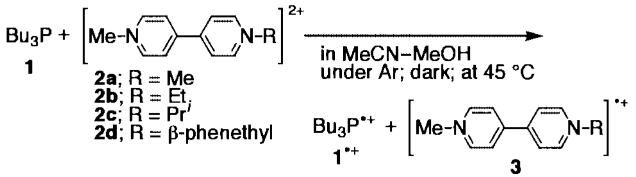
Single electron transfer (SET) takes place from tributylphosphine (**1**) to 1-methyl-1'-alkyl-4,4'-bipyridinium salts (viologens; **2**) in acetonitrile–methanol. Significant kinetic deuterium isotope effect has been observed with respect to hydrogens of a methyl (or an ethyl) substituent in **2**. The results are interpreted in terms of SET occurring within a tight encounter complex formed between **1** and **2**.

Single electron transfer (SET) processes have been studied intensively, affording classical models to predict dependence of SET rate on free-energy change of the SET step.[1–3] Meanwhile, kinetics observed in some SET processes has been interpreted in terms of quantum effects.[4,5] These studies have usually been done by using typical one-electron donors such as transition metal complexes, amines, or alkyl-substituted benzenes, which undergo outer-sphere SET. In contrast, trivalent phosphorus compounds Z_3P form a tight encounter complex with an acceptor to undergo SET.[6–9] Such behavior of Z_3P is worth examining in terms of either classical or quantum formalism; the examination would provide complementary information in understanding energetics of SET processes.

Tributylphosphine (**1**) has been found to undergo SET to methylviologen (**2a**) in the presence of alcohol.[10] If the SET takes place through formation of a tight encounter complex between **1** and **2a**, displacement of a methyl substituent in **2a** by other alkyl substituents would bring about some effect on its kinetics. Then, we examined kinetically the reaction of **1** with viologens with various alkyl substituents on the nitrogens **2a–d** as well as their deuterated derivatives.



Scheme 1.

Although the SET from **1** to **2a** is highly endothermic, the step is driven by nucleophilic attack by alcohol on the radical cation $1^{\bullet+}$ generated in the SET step.[10] So, in the present study, we carried out kinetics in acetonitrile containing large excess of methanol (MeCN:MeOH = 1:1 (v/v)) under an argon atmosphere at 45 °C. Phosphine **1** was also in large excess to attain pseudo-first-order conditions. Under these conditions, **2a–d** gave the corresponding radical cations **3a–d** (indicated by their characteristic UV–vis spectra)[11–13] (Scheme 1). Increase in the absorbance at 600 nm (λ_{max} of **3**) was then followed spectrophotometrically. In the early stage of the reaction, was found a linear correlation between logarithm of the absorbance and time, but it persisted only for a period of two or three half-lives, and after that increased in the absorbance dwindling. This shows that contribution of a "backward" reaction of $1^{\bullet+}$ (back SET from **3** to $1^{\bullet+}$) to the kinetics is not yet negligible under these conditions.[14] Nevertheless, linearity in the correlation in the early stage of the reaction was reliable enough to determine pseudo-first-order rate constants. Experiments with different concentrations of **1** confirmed second-order kinetics with first-order with respect to **1** and **2**, respectively, and second-order rate constants k^2 were calculated as given in Table 1.

Table 1. Reaction of tributylphosphine **1** with viologens **2**[a]

2	Me	R	10^3k^2 / $M^{-1}s^{-1}$ [b]	$k^2(H)/k^2(D)$
2a	CH_3	CH_3	3.9±0.2	
2a-d_3	CH_3	CD_3	1.1±0.1	4.1±0.7
2a-d_6	CD_3	CD_3	0.87±0.07	4.5±0.6
2b	CH_3	CH_3CH_2	2.7±0.3	
2b-d_3	CD_3	CH_3CH_2	0.65±0.04	4.1±0.8
2b-d_5	CH_3	CD_3CD_2	0.73±0.07	3.6±0.8
2c	CH_3	$(CH_3)_2CH$	2.5±0.3	
2c-d_3	CD_3	$(CH_3)_2CH$	0.56±0.02	4.5±0.8
2d	CH_3	$PhCH_2CH_2$	2.5±0.3	

[a] $[\mathbf{1}]_0 = 1.5 \times 10^{-1}$ M, $[\mathbf{2}]_0 = 2.0 \times 10^{-4}$ M. In MeCN–MeOH (1:1 (v/v)) under argon atmosphere at 45 °C in the dark. [b] Errors are standard deviations.

As expected from the fact that there is little difference among reduction potentials of **2a–d**, k^2 values are different only within experimental errors except for a slightly higher value for the dimethyl derivative **2a**. The result suggests that **1** approaches **2** from its methyl side with avoiding the larger alkyl group. The higher value for **2a** is attributable to statistical reason. More importantly, analyzing the reactions of **2a–d** bearing a methyl-d_3 or an ethyl-d_5 substituent on its nitrogen, deuterium isotope effect was found to be about 4.3 for each set of viologens.

The reaction of **1** with methylviologen **2a** (R = Me) proceeds according to an SET mechanism involving an encounter complex formed between **1** and **2a** prior to the SET step (eq 1).[10,15] Clearly, the same mechanism is operative in the reaction of **1** with other viologens **2b–d** as well as the deuterated derivatives.

$$\mathbf{1} + \mathbf{2} \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} [\mathbf{1} \cdots \mathbf{2}] \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} [\mathbf{1}^{\bullet+} \cdots \mathbf{3}] \xrightarrow[+\ \mathrm{MeOH}]{k_{30}} \text{products} \qquad (1)$$

With steady-state approximation with respect to concentrations of the encounter complex and the radical pair in eq 1, we obtain

$$d[\mathbf{3}]/dt = \frac{2k_{12}k_{23}k_{30}[\mathbf{1}][\mathbf{2}][\mathrm{MeOH}]}{(k_{32} + k_{30}[\mathrm{MeOH}])(k_{21} + k_{23}) - k_{32}k_{23}} \quad . \qquad (2)$$

Redox potentials of **1** and **2a–d** are $E_{1/2}$ = 1.07 V and –0.78 to

–0.76 V vs Ag/Ag$^+$, respectively. Comparison of these values indicates that the SET from **1** to **2** is endothermic, that is, $k_{21} >> k_{23}$. Then,

$$d[\mathbf{3}]/dt = 2K_{12}k_{23}k_{30}[\mathbf{1}][\mathbf{2}][\mathrm{MeOH}]/(k_{32} + k_{30}[\mathrm{MeOH}]), \qquad (3)$$

where $K_{12} = k_{12}/k_{21}$. If MeOH exists in such large excess that $k_{32} << k_{30}$[MeOH], eq 3 further reduces to

$$d[\mathbf{3}]/dt = 2K_{12}k_{23}[\mathbf{1}][\mathbf{2}]. \qquad (4)$$

Linearity seen in the semi-logarithmic plot between [**3**] and time confirms validity of the assumptions we have taken here.

Now, we remind that no hydrogen transfer takes place in this reaction. Nevertheless, a considerable value for deuterium isotope effect is observed. Reduction potential of **2** is little affected by deuteration of CH_3 or C_2H_5 substituent in **2**, showing that the observed isotope effect results from dynamics of the process, that is, a kinetic isotope effect (KIE). Since rate constants listed in Table 1 are products of two constants, i.e., $k^2 = K_{12}k_{23}$, either k_{12} or k_{23} step could contribute to the observed KIE. Hydrogen bonding between a hydrogen atom on a methyl (or an ethyl) group in **2** and the phosphorus atom in **1** at the encounter complex stage is a possibility to cause the isotope effect in k_{12} step. However, this is unlikely because the hydrogen bond, if formed, would reduce ability of **1** as an electron donor significantly. Therefore, the observed KIE results from effects occurring in the SET (k_{23}) step.

To explain the KIE in SET, we invoke quantum effects that have been taken to elucidate the origin of KIE found in SET between metal complexes.[16] Thus, deuteration of ligands such as NH_3 or H_2O of a metal complex results in a modest value of KIE at room temperature. It has been concluded that change of the metal-ligand configuration at the high frequency N–H (or O–H) vibrational mode is responsible for the KIE. In fact, a theory predicts that KIE for a self-exchange reaction could be about 30 at low temperature. The conclusion tells us qualitatively that the shorter the distance between a donor and an acceptor in the encounter complex, the larger the value of the KIE; thus, configurational change (reorganization of solvent, as well) for the redox pair with N–H (or O–H) bonds differs from that for the pair with N–D (O–D) bonds, and the difference would be more significant when the pair is tighter.

Such argument may be valid for the present SET if we are allowed to assume that displacement of C–H bonds on a methyl (or an ethyl) group in **2** by C–D bonds is analogous to deuteration of ligands in metal complexes. That is, depending on whether **2** has C–H bonds or C–D bonds, configurational change as well as reorganization of solvent caused by the SET is different, and if **1** forms a tight encounter complex with **2**, the difference could be large enough to give a practical value for the KIE. That trivalent phosphorus compounds Z_3P are apt to form a tight encounter complex with an acceptor has been shown in a kinetic study on SET from Z_3P to an iron(III) complex.[8] Importantly, when we used hydrosulfite $S_2O_4^{2-}$ in place of **1** to reduce **2**, no deuterium KIE was observed. It has been shown that rates of SET from $S_2O_4^{2-}$ to viologens and their analogs depend on reduction potentials of these acceptors such that the dependence is predictable from an outer-sphere SET mechanism.[17] This in turn suggests importance of formation of a tight encounter complex for deuterium KIE to be exerted in SET to viologen. Meanwhile, it should be noted that viologen **2**, a dicationic species, becomes a monocation upon the SET, which results in significant loss of the solvation. In other words, contribution of the reorganization of solvent to the SET is rather large.

As a more direct cause of the observed KIE, we may suppose an interaction between an alkyl substituent in **2** and the solvent molecule, although it is not clear at the present what kind of an interaction is possible here. If such an interaction is operative, difference in solvent reorganization energy would reflect directly the difference in the type of a bond in the alkyl group (C–H or C–D), which eventually results in KIE. A viologen bearing deuterium on an ethyl group but no deuterium on a methyl group (**2b**-d_5) exhibited a similar value of the KIE (Table 1), suggesting importance of contribution of an interaction of the alkyl group in **2** with the solvent molecule to SET rate.

In conclusion, we have observed a large value of KIE in the SET reaction between the phosphine **1** and the viologen **2**, which we have interpreted in terms of quantum effects to result from formation of a tight encounter complex between **1** and **2** prior to the SET. The discussion developed here is still very immature and several questions are open; for example, we have to elucidate the structure of a supposed encounter complex. It is also unclear why **2a**-d_3 and **2a**-d_6 as well as **2b**-d_5 exhibit an identical value of KIE although **1** is able to approach these viologens from the CH_3 sides. Nevertheless, the present study demonstrates importance of considering quantum effects even for KIE in organic reactions occurring at room temperature.

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14 In a previous kinetic study on SET from **1** to **2a**, we adjusted the concentrations of **1** and alcohol in large excess such that **1**$^{\bullet+}$ undergoes a “forward” reaction with alcohol and a “backward” reaction in comparable efficiency. Under these pseudo-first-order conditions, increase in the amount of **3a** obeyed “bent kinetics”, which enabled us to evaluate rate constant for nucleophilic reaction of **1**$^{\bullet+}$ with alcohol. See ref 10.

15 In eq 1, k_{30} step is composed of several elemental steps; **1**$^{\bullet+}$ and **3** in the radical pair are separated into free-radicals, **1**$^{\bullet+}$ undergoes nucleophilic attack by methanol, and the resulting phosphoranyl radical $Z_3P^{\bullet}$–OR is oxidized by the second molecule of **2**. This sequence predicts stoichiometry of the reaction to be [**1**]:[**2**] = 1:2, which has in fact been observed.

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