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Dramatic effect of *N*-substituents in viologens on single electron transfer from tributylphosphine

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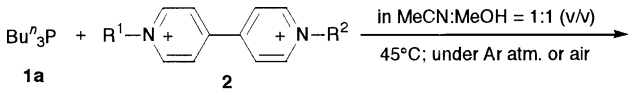
Received 8th September 2005, Accepted 12th October 2005
First published as an Advance Article on the web 2nd November 2005

A single electron transfer (SET) takes place from tributylphosphine (**1a**) to 1-alkyl-1'-methylviologens in acetonitrile containing a large amount of methanol under an argon atmosphere. In contrast, no SET takes place from **1a** to viologens whose alkyl groups on the nitrogens are larger than the methyl group under the same conditions, **1a** instead nucleophilically attacking the viologen to form a covalent adduct. This dramatic substituent effect is discussed in terms of SET occurring within a tight encounter complex formed between the phosphine and the viologen.

Introduction

Trivalent phosphorus compounds Z_3P act as an electron donor toward electron-deficient compounds.[1] We have examined the mechanism of single electron transfer (SET) from Z_3P to many types of acceptors based on their kinetics and product analysis.[2–6] During these studies, we have obtained evidence that SET from Z_3P to an acceptor takes place *via* a tight encounter complex formed between the former and the latter.[7] This mechanism is in contrast to that for SET from amine counterparts, which takes place in an outer-sphere manner.[8,9] To confirm our proposed mechanism, it is essential to detect the encounter complex. Indeed, an encounter complex has been spectrophotometrically observed during the electron self-exchange between TCNQ or TCNE and its anion radical[10a] or between phenothiazine and its cation radical;[10b] the encounter complexes absorb light in the near-infrared region.[10] In SET from Z_3P, unfortunately, no spectroscopic evidence for the formation of the encounter complex has been obtained, but the complex should be able to be "seen" if it is so tight that a steric effect by either the Z_3P or an acceptor is operative and affects the reaction pathway.

1,1′-Dialkyl-4,4′-bipyridinium dications (viologens) undergo a one-electron reduction with various types of electron donors to bring about a large spectral change; the resulting viologen radical cations exhibit characteristic UV-visible absorption spectra with λ_{max} *ca.* 600 nm.[11–13] This feature in the spectral change of viologens upon their reduction makes this family of compounds a useful tool for kinetic studies.[14–17] We previously carried out the reaction of tributylphosphine (**1a**) with 1,1′-dimethyl-4,4′-bipyridinium tetrafluoroborate (methylviologen) (**2a**) in acetonitrile containing a large amount of methanol to find that the SET from **1a** to **2a** easily takes place.[18] A kinetic study of this reaction in the presence of various nucleophiles such as alcohols or thiols made it possible to evaluate the reactivity of the tributylphosphine radical cation generated through the SET toward nucleophiles. This reaction system might also be useful to examine the steric effect on the SET from Z_3P, because steric congestion during the reaction can be tuned by varying the alkyl groups on the nitrogens in viologen **2**. We then examined the reaction of **1a** with viologens having various alkyl groups on the nitrogens (Scheme 1). When **1a** was reacted with 1-alkyl-1′-methyl-4,4′-bipyridinium tetrafluoroborate (alkylmethylviologen) (**2b**–**e**), in which one methyl group in **2a** is substituted by another alkyl group, under an argon atmosphere, the SET from the former to the latter took place as with **2a** (Scheme 2).[19] Substitution of both methyl groups in **2a** by other alkyl groups caused a dramatic change in the reaction pathway. Thus, when **1a** was reacted with viologens **2f**–**k** that bear *N*-alkyl substituents



	R^1	R^2
2a	Me	Me
b	Me	Et
c	Me	Pr^i
d	Me	$PhCH_2$
e	Me	$PhCH_2CH_2$
f	Et	Et
g	Et	Pr^i
h	Et	$PhCH_2$
i	Et	$PhCH_2CH_2$
j	*n*-Heptyl	*n*-Heptyl
k	$PhCH_2CH_2$	$PhCH_2CH_2$

Scheme 1

larger than a methyl group, no SET but another reaction took place. NMR and MS spectral analyses of the product strongly suggest that **1a** nucleophilically attacks **2f**–**k** to form a covalent adduct in these cases (Scheme 2).

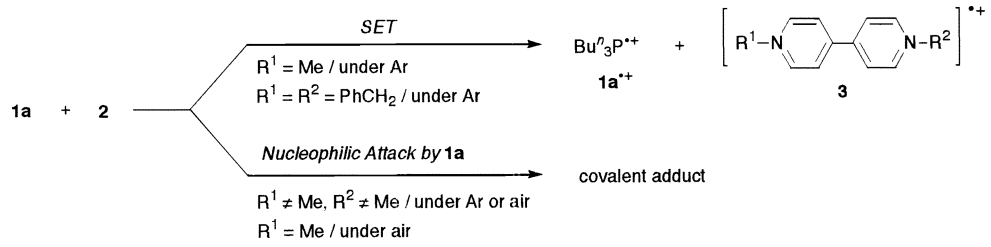
This dramatic effect by the *N*-alkyl groups in **2** in determining the reaction pathway is interpreted in the term of the tight encounter complex formed between **1a** and **2** prior to SET.

Results and discussion

Reaction of tributylphosphine (1a) with viologen 2a-e under an argon atmosphere

Tributylphosphine (**1a**) was reacted with alkylmethylviologen **2a**–**e** (R^1 = Me, R^2 = alkyl) in acetonitrile containing a large excess of methanol (MeCN : MeOH = 1 : 1 (*v*/*v*)) under an argon atmosphere at 45 °C. The reaction resulted in the gradual appearance of the absorption around λ_{max} *ca.* 600 nm (Fig. 1), which is characteristic of the radical cation of **2** (**3**).[12–14,18,19] Clearly, upon the reaction of **1a** with **2a**–**e**, a single electron transfer (SET) takes place from the former to the latter, which also gives the tributylphosphine radical cation $\mathbf{1a}^{\bullet+}$ from **1a**. In fact, our previous study based on ^1H and ^{31}P NMR and GC–MS spectroscopies has shown that the reaction of **1a** with **2a** under these conditions produces tributylphosphine oxide (**4a**); the formation of **4a** is evidence for the generation of $\mathbf{1a}^{\bullet+}$.[18] Although a comparison of the half-wave potentials of **1a** and **2** predicts a high endothermicity for the SET from **1a** to **2**,

DOI:10.1039/b512678a



Scheme 2

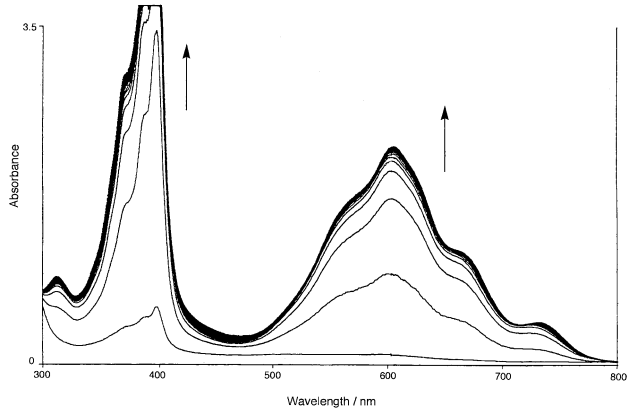
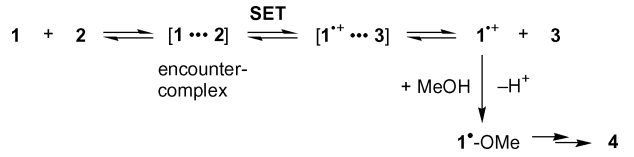


Fig. 1 Spectral change in the reaction of **1a** (0.15 ml dm^{-3}) with **2a** (2.0 × 10^{-4} ml dm^{-3}) in MeCN : MeOH (1 : 1 (*v*/*v*)) under an argon atmosphere at 45 °C. Time interval: 8 min.



Scheme 3

the process is driven by a follow-up reaction of the resulting phosphine radical cation **1a**$^{\bullet+}$ with methanol (Scheme 3).

Reaction of 1a with 2a–e in the air

The aerobic conditions dramatically altered the reaction pathway. When the reaction of **1a** with **2a**–**e** was carried out in air under otherwise identical conditions, the absorption spectrum at λ_{max} *ca.* 400 nm appeared without giving the absorption of the radical cation **3** (Fig. 2), indicating that a reaction other than the SET takes place in this case.

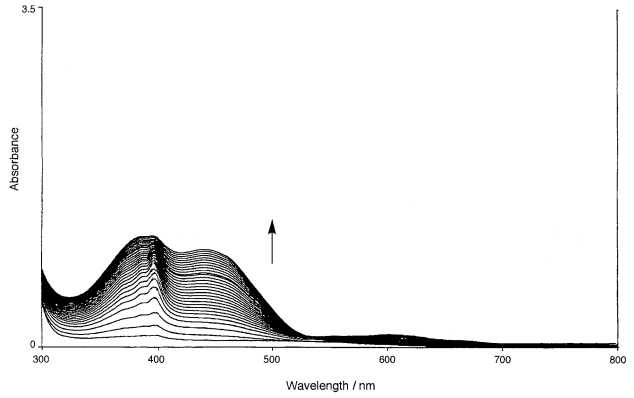


Fig. 2 Spectral change in the reaction of **1a** (0.15 ml dm^{-3}) with **2a** (2.0 × 10^{-4} ml dm^{-3}) in MeCN : MeOH (1 : 1(*v*/*v*)) in the air at 45 °C. Time interval: 8 min.

The kinetics for the reactions of **1a** with **2a**–**c** was carried out in acetonitrile containing a large excess of methanol (MeCN : MeOH = 1 : 1 (*v*/*v*)) under pseudo-first-order conditions with **1a** being in large excess in air. The growth of the absorbance around 400 nm was monitored on a UV-vis spectrophotometer to follow the reaction. A linear correlation between the logarithm of the absorbance and time persisted up to nearly two half-lives, from which the pseudo-first-order rate constants k_{obs} were determined.[20] Experiments that varied the concentration of **1a** (7.5 × 10^{-2}–1.5 × 10^{-1} ml dm^{-3}) gave a linear correlation between k_{obs} and the initial concentration of **1a**, showing second-order kinetics with first-order with respect to each of the concentrations of **1a** and **2**, respectively. Table 1 summarizes the second-order rate constants k_2.

Table 1 Second-order rate constants k_2 for the reaction of tributylphosphine (**1a**) with viologens (**2**)[a]

Run	Viologen (**2**)	Atmosphere	k_2/dm^3 mol^{-1}s^{-1}
1	**2a**	Air	3.3 × 10^{-3}
2	**2b**	Air	1.4 × 10^{-3}
3	**2c**	Air	1.5 × 10^{-3}
4	**2c**	O_2	1.7 × 10^{-3}
5	**2f**	Ar	1.1 × 10^{-3}
6	**2f**	O_2	1.8 × 10^{-3}
7	**2f**[b]	Ar	1.2 × 10^{-3}
8	**2i**	Ar	0.95 × 10^{-3}
9	**2j**	Ar	0.81 × 10^{-3}
10	**2j**	O_2	1.3 × 10^{-3}
11	**2k**	Ar	1.0 × 10^{-3}

[a] In MeCN : MeOH = 1 : 1 (*v*/*v*) at 45 °C. [**1a**]$_0$ = 7.5 × 10^{-2}–1.5 × 10^{-1} mol dm^{-3}, [**2**]$_0$ = 2.0 × 10^{-4} mol dm^{-3}. [b] Br$^-$ salt.

Reaction of 1a with viologen 2f–k

Tributylphosphine **1a** was reacted with viologens that have no methyl substituent on the nitrogens, **2f**–**k** (R^1 ≠ Me, R^2 ≠ Me), under an argon atmosphere. Interestingly, no absorption around 600 nm was observed even under an argon atmosphere, showing that no SET takes place from **1a** to **2f**–**k**. Instead, the absorption was observed around 400 nm that is similar to those observed in the reactions of **1a** with **2a**–**e** under the aerobic conditions. As an example, the spectral change in the reaction with **2f** under an argon atmosphere is shown in Fig. 3.

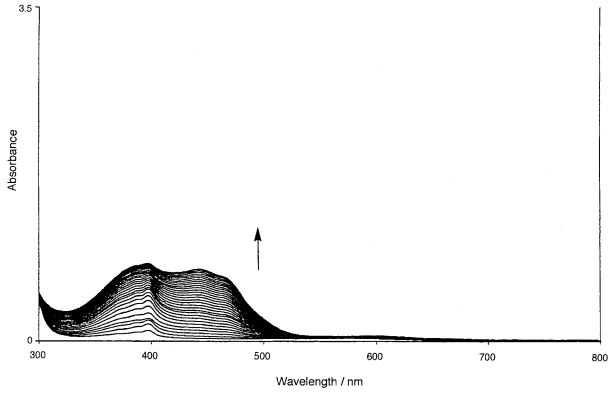


Fig. 3 Spectral change in the reaction of **1a** (0.15 ml dm^{-3}) with **2f** (2.0 × 10^{-4} ml dm^{-3}) in MeCN : MeOH (1 : 1(*v*/*v*)) under an argon atmosphere at 45 °C. Time interval: 8 min.

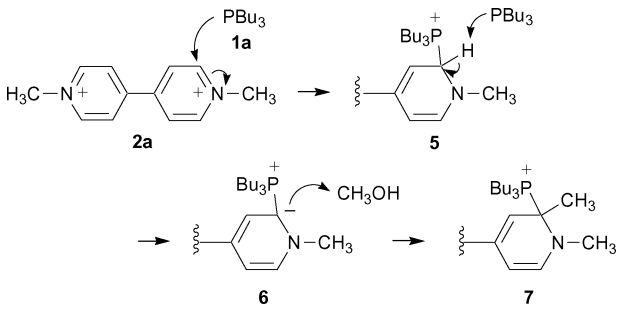
The kinetics for the reactions of **1a** with **2f**,**i**,**j**,**k** were carried out under an argon atmosphere. The conditions as well as the measurement procedure were the same as those for the reactions with **2a** in air (*vide supra*). The results are summarized in Table 1, which shows that the substituents of the nitrogens have little effect on the reaction rate.

Identification of the products that have λ_{max} around 400 nm

The similarity in the UV-vis spectra shown in Fig. 2 and 3 guarantees that the products from the reaction with **2a**–**e** in the air and from the reaction with **2f**–**k** under an argon atmosphere results from the same type of reaction. To find what type of reaction took place, we carried out the reaction of **1a** with **2a** under the aerobic conditions on a larger scale. The oily material resulting from the reaction gave almost the same UV-vis spectrum as that observed for the small-scale reaction mentioned above. This material was then analyzed by FAB-MS. A fragment appeared at m/z 400 with a high intensity, which certainly results from the product of the reaction under discussion because the reaction of **1a** with methylviologen having perdeuterated methyl groups **2a**-d_6 gave a major fragment at m/z 406.[21] The exact mass number was determined by high-resolution FAB-MS to be m/z 400.2994, representing the composition of $C_{25}H_{41}N_2P$.[22]

The oily material resulting from the reaction of **1a** with **2a** under aerobic conditions was further analyzed by NMR spectroscopy. On the ^{1}H NMR spectrum, two doublets were observed at low field (7.80 and 8.82 ppm, J = *ca.* 6 Hz), indicating that one of the rings of **2a** is intact. The ^{31}P NMR signal appeared at 31.9 ppm,[23] suggesting that the product has a phosphonium center.[24] The products from the reaction of **1a** with **2f** were also analyzed by NMR spectroscopy in a similar way, giving analogous results.

The NMR analyses of the product strongly suggest the nucleophilic attack by **1a** on the pyridine ring of **2a**. Thus, the attack would occur on C-2 in **2a** to afford the phosphonium **5**, which is easily converted to the ylide **6** under the conditions where **1a** can act as a base.[25] The ylide **6** attacks methanol existing in a large amount, which could explain the formation of the "C_{25}" product that has been predicted by high-resolution FAB-MS (Scheme 4).[26] Further attempts to isolate the product failed, either due to many by-products formed during the prolonged reaction period or due to instability of the product, preventing complete identification of the product. Nevertheless, we are convinced that the initial event of the reaction under consideration is the nucleophilic attack by **1a** on one of pyridinium rings of **2a**.



Scheme 4

An argument may be made that the reaction we observed is the Hoffmann degradation, which can, in principle, take place for the viologens that have *N*-alkyl substituents with β-hydrogen(s), namely the viologens **2f**–**k**. However, in all reactions with **2f**–**k**, the resulting UV-vis spectra are not the same as what is expected for the Hoffmann degradation products (*e.g.*, 4,4′-dipyridine). Especially, styrene, which would be formed in the Hoffmann degradation of **2k**, was not detected on the GC for the reaction with **2k**. In addition, while the Hoffmann degradation requires only one *N*-alkyl group with β-hydrogen(s), the alkylmethylviologens **2b**–**e** prefer the SET under an argon atmosphere. Most importantly, methylviologen **2a** ($R^1 = R^2$ = Me), which cannot be subjected to the Hoffmann degradation, undergoes this type of reaction with **1a** under the aerobic conditions.

Dichotomy in the reactivity of 1a toward 2

A prominent finding in this study is the dramatic effect of the *N*-alkyl substituents in **2** on the reaction pathway. Phosphine **1a** undergoes either SET or nucleophilic attack upon the reaction with the viologens **2** depending on the alkyl substituents in **2**. Table 2 summarizes the reaction types occurring between **1** and **2** under the given conditions. Viologen with at least one methyl substituent on the nitrogen undergoes the SET from **1a** under an argon atmosphere, whereas viologen with two substituents larger than a methyl group undergoes the nucleophilic attack by **1a** irrespective of the atmosphere. Under the aerobic conditions, the nucleophilic reaction is always observed.

A closer examination of Fig. 2 and 3 shows a slight increase in the absorption around 600 nm, indicating that the SET from **1a** to **2** could always competitively take place, even though in a small portion. That is, the rate constants k_2 reported in Table 1 are upper limits of the rate constants for the nucleophilic reaction. Although it is highly difficult to independently evaluate the constants for the nucleophilic reaction, the rate of the nucleophilic attack may be compared with that of the SET. The second-order rate constants for the SET from **1a** to **2a**–**e** have been reported to be on the order of 10^{-2} dm^3 mol^{-1} s^{-1}, which are one-order higher than the rate constants for the nucleophilic reaction listed in Table 1. For example, **2a** undergoes the nucleophilic reaction under aerobic conditions with $k_2 = 3.3 \times 10^{-3}$ dm^3 mol^{-1}s^{-1} (run 1 in Table 1), which is ten times slower than the reported rate constant of the SET occurring under an argon atmosphere.[19] In other words, if the conditions allow **2** to undergo SET, the SET would be significantly preferable to the nucleophilic reaction.

We have proposed that SET from trivalent phosphorus compound Z_3P to an acceptor takes place within an encounter complex (Scheme 3).[7] The fact that the SET in the present reaction is completely inhibited by alkyl groups larger than the methyl group confirms the indispensability of a tight encounter complex for the SET from **1a** to **2** to occur. When the viologen **2** bears two substituents larger than the methyl group on the nitrogens, **1a** cannot approach **2** within an effective distance for SET, resulting in the nucleophilic reaction. Kochi and co-workers have acknowledged the importance of the steric hindrance between a donor and an acceptor to determine the mechanism of SET.[27,28] They showed that SET from arenes to quinones takes place *via* an inner-sphere mechanism when the arenes have methyl substituents, and, on the other hand, *via* an outer-sphere mechanism when the arenes have larger alkyl substituents such as ethyl or *t*-butyl substituents.[27]

The steric effect by alkyl groups observed in the present study further suggests that the horizontal approach of **1a** toward the pyridinium ring of **2** is preferable. The approach in this way may be favored by the p_π–d_π overlap as in the reaction of chlorophosphates with pyridines.[29] Simon and co-workers have pointed out that kinetics of SET between chlorine oxide and benzenes is affected by a direction in which a donor approaches an acceptor.[30] It has also been argued that the orientation between a donor and an acceptor is important for determining which reaction, SET or the nucleophilic reaction, is preferred for the reaction between the ketyl radical anion and alkyl halide.[31–33] Experimental evidence for such an orientational effect has been obtained by examining the product distribution in the intramolecular reactions of the radical anions [Ar–CO–$(CH_2)_n$–X]$^{\bullet-}$ (n = 2–4).[34,35]

Table 2 Reaction type occurring between **1** and **2**[a]

Run	Z_3P (**1**)	Viologen (**2**)	R^1 in **2**	R^2 in **2**	Atmosphere[b]	Reaction type[c]
1	Bu_3P (**1a**)	**2a**	Me	Me	Ar	SET
2		**2a**	Me	Me	air	Nu
3		**2b**	Me	Et	Ar	SET
4		**2b**	Me	Et	air	Nu
5		**2c**	Me	Pr^i	Ar	SET
6		**2c**	Me	Pr^i	air	Nu
7		**2c**	Me	Pr^i	O_2	Nu
8		**2d**	Me	$PhCH_2$	Ar	SET
9		**2e**	Me	$PhCH_2CH_2$	Ar	SET
10		**2f**	Et	Et	Ar	Nu
11		**2f**[d]	Et	Et	Ar	Nu
12		**2g**	Et	Pr^i	Ar	Nu
13		**2h**	Et	$PhCH_2$	Ar	Nu
14		**2i**	Et	$PhCH_2CH_2$	Ar	Nu
15		**2j**	Heptyl	Heptyl	Ar	Nu
16		**2k**	$PhCH_2CH_2$	$PhCH_2CH_2$	Ar	Nu
17	$Bu^i{}_3P$ (**1b**)	**2a**	Me	Me	Ar	Nu
18		**2a**	Me	Me	air	Nu
19		**2f**	Et	Et	Ar	No reaction

[a] In MeCN : MeOH = 1 : 1 (*v*/*v*) at 45 °C. $[\mathbf{1}]_0 = 1.5 \times 10^{-1}$ mol dm^{-3}, $[\mathbf{2}]_0 = 2.0 \times 10^{-4}$ mol dm^{-3}. Viologens are BF_4^- salts unless otherwise indicated. [b] Ar denotes argon. [c] SET and Nu denote single electron transfer from **1** to **2** and nucleophilic attack by **1** on **2**, respectively. [d] Br^- salt.

Triisobutylphosphine (**1b**), which has bulkier ligands than **1a** on the phosphorus, affords another support for the important role of the steric bulk in the present study. As seen in runs 17 and 18 in Table 2, no SET from **1b** to **2a** takes place, instead **1b** undergoing the nucleophilic reaction, even though the driving force ΔG for the SET from **1b** to **2a** is only 1.9 kJ unfavorable relative to ΔG for the SET from **1a**. Meanwhile, when reacted with **2f**, the steric bulk of **1b** works to suppress the nucleophilic reaction (Table 2, run 19). The steric effect on the nucleophilic attack is very subtle. It has been shown that the rate of nucleophilic attack by alkyl diphenylphosphinites (Ph_2POR) on C-10 of the 1-methylacridinium cation is governed by the bulkiness of the alkyl group R.[36]

Experimental

Materials

Tributylphosphine **1a** (Tokyo Chemical Industry Ltd.) and triisobutylphosphine **1b** (Aldrich) were purchased. The viologens **2** were synthesized by the reaction of the alkyl halide with 4,4′-bipyridine.[37] The resulting materials were treated with $AgBF_4$ solution in methanol to exchange the counter anion. The obtained tetrafluoroborate salts were recrystallized from methanol.

Instruments

UV-vis spectra were recorded using a Hitachi U-3210 spectrophotometer. The ^{1}H NMR (300 MHz) and ^{31}P NMR (121 MHz) spectra were measured in $CDCl_3$ using a JEOL JNM AL-300 spectrometer at room temperature. The mass spectra were obtained using a JEOL JMS-700 spectrometer.

Product Analysis

Phosphine **1** (0.15 ml dm^{-3}) was mixed with viologen **2** (2.0×10^{-4} ml dm^{-3}) in a UV cell and then allowed to react in acetonitrile containing a large excess of methanol (MeCN : MeOH = 1 : 1 (*v*/*v*)) at 45 °C either under an argon atmosphere or in air. The progress of the reaction was followed by periodically monitoring the absorption spectrum using a spectrophotometer. For the NMR and FAB-MS spectroscopies, the reaction was carried out on a larger scale as described below: Into 300 ml of acetonitrile-methanol (1 : 1 (*v*/*v*)) was dissolved 1.5 mmol (0.54 g) of **2a** and then 4.5 mmol (1.1 ml) of **1a** was added. The mixture was stirred for 2 d in air at room temperature and concentrated *in vacuo*. The residue was washed with hexane to give a brown solid, which was extracted with dichloromethane and concentrated *in vacuo* to give a brown oil (0.21 g). This oily product was analyzed by UV-vis spectrophotometry as well as by ^{1}H NMR, ^{31}P NMR, and FAB-MS spectroscopies.

Kinetics

Viologen **2** was dissolved in acetonitrile containing a large excess of methanol (MeCN : MeOH = 1 : 1 (*v*/*v*)) in order that the concentration was 2.0×10^{-4} ml dm^{-3}. A 3-ml portion of the solution of **2** was put in a quartz cell. The cell was kept in a compartment of the UV-vis spectrophotometer maintained at 45 °C. An appropriate amount of **1a** was added to the cell as a neat material. The increase in the absorption at the appropriate wavelength was monitored by the spectrophotometer.

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20 After two or three half-lives, the increase in the absorption around 400 nm dwindled, which could result from the reversible feature of the reaction. This is the case for the SET from **1a** to **2a**. See ref. 18*b*.
21 We have also observed major fragments at *m*/*z* 487 and 493 in the reactions with **2a**-h_6 and with **2a**-d_6, respectively. The difference between the mass numbers of these fragments and those we have mentioned corresponds, respectively, to the mass of BF_4^- (= 87).
22 The high-resolution mass for the fragment at *m*/*z* 487 was 487.3041, which represents the composition of $C_{25}H_{41}N_2PBF_4$.
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