Kinetic study on the reaction of tributylphosphine with methylviologen. Reactivity of the phosphine radical cation intermediate towards nucleophiles

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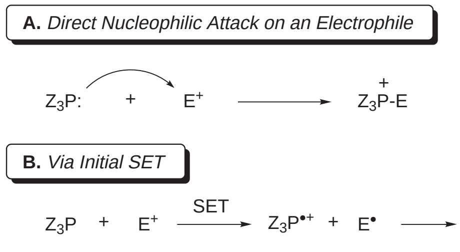
Tributylphosphine, $\mathrm{Bu^n{}_3P}$ (**BP**), was reacted with 1,1′-dimethyl-4,4′-bipyridinium (methylviologen; $\mathbf{MV}^{2+}$) in the presence of an alcohol or thiol (RXH; X = O, S) in acetonitrile under an argon atmosphere at 50 °C, which resulted in the gradual formation of the one-electron reduced form of the $\mathbf{MV}^{2+}$, $\mathbf{MV}^{+}$. Meanwhile, **BP** was oxidized to tributylphosphine oxide (**BP-O**). The increase in the amount of $\mathbf{MV}^{+}$, which was followed spectrophotometrically with **BP** and RXH being in large excess, did not obey first-order kinetics. The observation, along with the results from product analysis, shows that single-electron transfer (SET) takes place from **BP** to $\mathbf{MV}^{2+}$ to generate tributylphosphine radical cation $\mathbf{BP}^{\cdot+}$, as well as $\mathbf{MV}^{+}$, and the resulting $\mathbf{BP}^{\cdot+}$ undergoes ionic reaction with RXH and back electron transfer from $\mathbf{MV}^{+}$ in comparable efficiency. A regression analysis of the kinetic data gave the relative value of the second-order rate constant, $k_{\mathrm{Nu}}{}^{\mathrm{rel}}$, for the ionic reaction of $\mathbf{BP}^{\cdot+}$ with RXH. Comparison of the $k_{\mathrm{Nu}}{}^{\mathrm{rel}}$ values thus obtained for reactions with various RXH's shows that the reaction of $\mathbf{BP}^{\cdot+}$ with nucleophile RXH is governed by both steric and electronic factors of RXH. The activation energy E_{a} of the reaction was found to be significantly large, which is in contrast to previous observations that ionic reactions of carbon radical cations with nucleophiles usually have very small values of E_{a}.

Anodic oxidation of trivalent phosphorus compounds[1–4] or irradiation of these compounds with γ-rays[5–7] generates the corresponding trivalent phosphorus radical cations. Such radical cations are generated also as intermediates of thermal[8,9] and photochemical[10–12] reactions of precursor trivalent phosphorus compounds with electron-deficient compounds. Meanwhile, it has been accepted that trivalent phosphorus compounds ($\mathrm{Z_3P}$) act as nucleophiles when reacted with electrophiles; that is, the proposed mechanism includes single-step nucleophilic attack by the phosphorus atom in $\mathrm{Z_3P}$ on the electrophilic center of electrophile E^+ (mechanism A in Scheme 1). However, that trivalent phosphorus radical cations are produced readily under certain circumstances suggests that this "nucleophilic" mechanism should be reconsidered; the reaction could take place through initial single-electron transfer (SET) from $\mathrm{Z_3P}$ to E^+ followed by coupling of the resulting radical species (mechanism B in Scheme 1). In fact, an SET process has been proposed in a Mitsunobu reaction on the basis of results of EPR, giving another mechanism for this conventional reaction.[13] To inspect the possibility of mechanism B in "nucleophilic" reactions of trivalent phosphorus compounds, it is essential to understand the reactivity of the putative intermediate, trivalent phosphorus radical cation ($\mathrm{Z_3P}^{\cdot+}$). In addition, such radical cations have potential uses in organic syntheses; for example, the reaction of such radicals can be used in the synthesis of a cyclic adenosine monophosphate (AMP) analogue.[14] Elucidation of the reactivity of trivalent phosphorus radical cations is of importance for this reason, as well.



Scheme 1 Possible mechanisms for nucleophilic attack by a trivalent phosphorus compound $\mathrm{Z_3P}$ on an electrophile E^+.

While trivalent phosphorus radical cations have in principle both cationic and radical characteristics, many reports have shown that these radicals readily undergo ionic reaction with various kinds of nucleophiles.[9,11,12,15] So, in the evaluation of the reactivity of trivalent phosphorus radical cations, investigation of the ionic reaction of these radical cations with nucleophiles is a first step. However, such investigations have been qualitative so far, and in particular, no kinetic study has been reported. Measurement of the amount of such a short-lived radical generated during the reaction may be the main difficulty.

1,1′-Dimethyl-4,4′-bipyridinium dication (methylviologen; $\mathbf{MV}^{2+}$) is a good one-electron acceptor.[16–22] We found that $\mathbf{MV}^{2+}$ is gradually reduced to its one-electron reduced form, $\mathbf{MV}^{+}$, when treated with tributylphosphine (**BP**) in the presence of an alcohol or thiol.[23] Product analysis as well as other evidence showed that the accumulation of $\mathbf{MV}^{+}$ results from the initial SET from **BP** to $\mathbf{MV}^{2+}$ followed by an ionic reaction of the resulting radical cation $\mathbf{BP}^{\cdot+}$ with the alcohol or thiol. In this reaction system, quantitative evaluation of the reactivity of trivalent phosphorus radical cations toward nucleophiles is possible without measurement of the amount of $\mathbf{BP}^{\cdot+}$. Thus, the increase in the amount of $\mathbf{MV}^{+}$ can be monitored spectrophotometrically, and analysis of the kinetic data based on the proposed reaction mechanism gives the relative value of the second-order rate constant, $k_{\mathrm{Nu}}{}^{\mathrm{rel}}$, for the reactions of $\mathbf{BP}^{\cdot+}$ with nucleophiles.

In this article, we describe the mechanism of the reaction of **BP** with $\mathbf{MV}^{2+}$ in the presence of an alcohol or thiol. We hereafter present the relative second-order rate constants for

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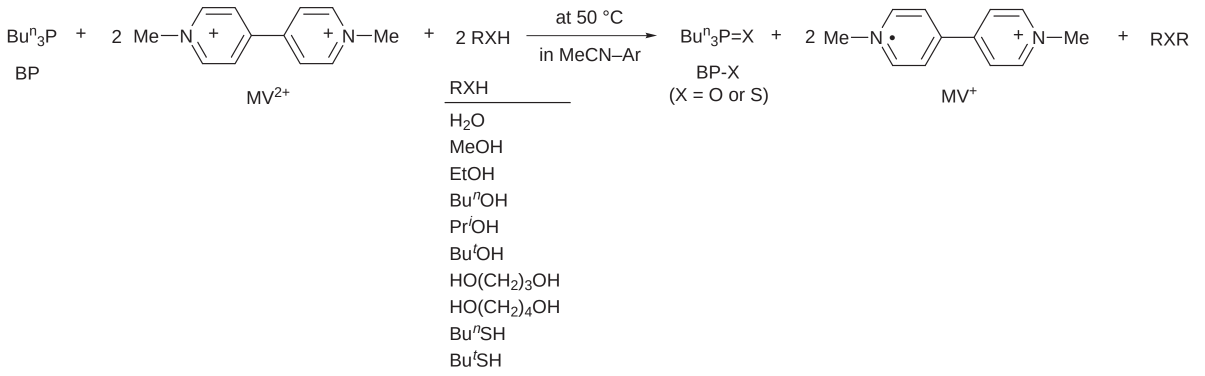

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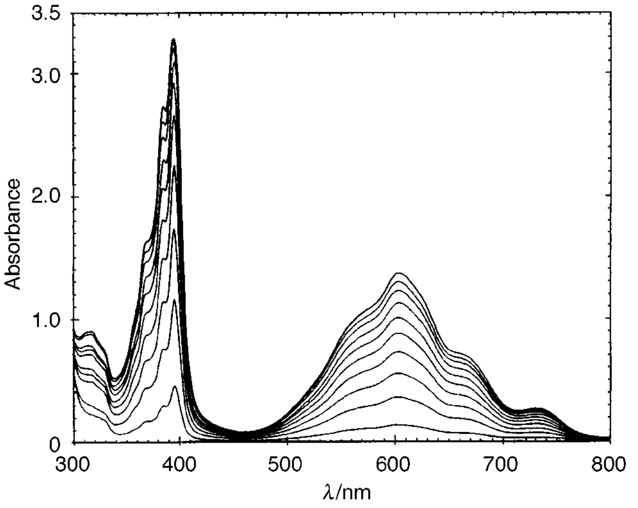


Fig. 1 Changes in the UV–visible spectrum during the reaction of **BP** with **MV**^{2} in the presence of MeOH in acetonitrile at 50 °C under an argon atmosphere in the dark. $[\mathbf{BP}]_0 = 1.50 \times 10^{-1}$ mol dm^{-3}, $[\mathbf{MV}^{2+}]_0 = 1.00 \times 10^{-4}$ mol dm^{-3}, and $[\text{MeOH}]_0 = 12.5$ mol dm^{-3}. Spectra recorded at 15, 30, 60, 120, 180, 240, 300, 360, 420, and 480 minutes are shown.

Table 1 Reaction of tributylphosphine **BP** with methylviologen **MV**$^{2+}$ in the presence of EtOH[a]

	Yield (%)[b]		Conversion (%)[c]			
t/min	**MV**$^+$	[eq.][d]	**BP**	[eq.][d]	EtOH	[eq.][d]
15	4.5	[2.0]	2.2	[1]	4.2	[1.9]
35	5.5	[2.0]	2.8	[1]	5.6	[2.0]

[a] $[\mathbf{BP}]_0 = [\mathbf{MV}^{2+}]_0 = 1.00 \times 10^{-5}$ mol dm^{-3}, $[\text{EtOH}]_0 = 2.00 \times 10^{-5}$ mol dm^{-3}. In acetonitrile at 50 °C under an argon atmosphere in the dark. [b] Determined on a spectrophotometer. [c] Determined on an NMR spectrometer. [d] Numbers in square brackets denote equivalence of the yield or the conversion against the conversion of **BP**.

the reactions of **BP**$^{\bullet+}$ with nucleophiles, $k_{\text{Nu}}^{\text{rel}}$, to discuss the reactivity of **BP**$^{\bullet+}$ towards nucleophiles.

Results and discussion

Reaction of BP with MV^{2+} in the presence of nucleophile

Tributylphosphine (**BP**) was reacted with **MV**$^{2+}$ (tetrafluoroborate salt) in acetonitrile at 50 °C under an argon atmosphere in the dark in the presence of a large excess of alcohol (ROH). Spectrophotometric measurements showed gradual increases in the absorption at 398 and 605 nm, wavelengths characteristic of the one-electron reduced form of **MV**$^{2+}$, **MV**$^{+}$.[16–18] The formation of **MV**$^+$ was found to be nearly theoretical based on its extinction coefficient at 605 nm.[16,24] Fig. 1 shows changes in the UV–visible spectrum during the reaction in the presence of MeOH.[25] The changes show that **MV**$^{2+}$ undergoes one-electron reduction to **MV**$^+$ without further reduction to its two-electron reduced form, **MV**^{0}. The reaction mixture in acetonitrile-d_3 was analyzed with ^{1}H and ^{31}P NMR spectroscopy, which showed the formation of tributylphosphine oxide (**BP-O**) together with ether ROR. The formation of **BP-O** was also monitored by GC-MS. The yield of **MV**$^+$ and the conversions of **BP** and ROH were determined by spectrophotometric and ^{1}H NMR spectroscopic analyses after an appropriate reaction time. Table 1 lists the results along with the initial concentrations of the starting materials. Clearly, each mole of **BP** reduces 2 equivalents of **MV**$^{2+}$ to **MV**$^+$ with consumption of 2 equivalents of ROH [eqn. (1)].

When **BP** was reacted with **MV**$^{2+}$ in the presence of a large excess of thiol (RSH) instead of alcohol under otherwise identical conditions, **MV**$^{2+}$ was gradually reduced to **MV**$^+$. Results of GC-MS showed that tributylphosphine sulfide (**BP-S**) was formed together with a small amount of **BP-O**. The oxygen in **BP-O** resulted from water contaminating the solvent.[26] Thiol itself did not reduce **MV**$^{2+}$ to **MV**$^+$.

Reaction mechanism

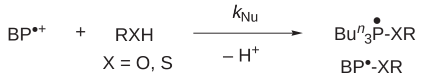
A key observation in the present reaction is one-electron reduction of **MV**$^{2+}$ to **MV**$^+$, which certainly results from the transfer of an electron from **BP** to **MV**$^{2+}$. This process is composed of three successive steps;[27] formation of an encounter complex between **MV**$^{2+}$ and **BP**, single-electron transfer (SET) within the complex, and dissociation of the pair of the resulting radical species [eqn. (2)]. Results of cyclic voltammetry showed that

$$\text{BP} + \text{MV}^{2+} \rightleftharpoons \text{BP}\bullet\bullet\bullet\text{MV}^{2+} \overset{\text{SET}}{\rightleftharpoons} \text{BP}^{\bullet+}\bullet\bullet\bullet\text{MV}^{+} \rightleftharpoons \text{BP}^{\bullet+} + \text{MV}^{+} \qquad (2)$$

peak potentials E_p for **BP** and **MV**$^{2+}$ are 1.45 and −0.43 V, respectively, *vs.* Ag/AgCl in acetonitrile. This large difference in E_p (1.88 V) predicts that the SET is highly endothermic.

Such a highly endothermic SET could take place when the process is associated with an exothermic chemical reaction of the resulting radical species. For example, an endothermic SET from a one-electron donor to an alkyl halide is accomplished by virtue of energy-gaining cleavage of the carbon–halogen bond in the resulting alkyl halide radical anion.[28–31] Schuster has shown,[32] by presenting several examples,[33–36] that SET processes, which are energetically unfavorable and would otherwise be unlikely to occur, in fact take place easily when the resulting radical species undergo follow-up chemical reactions rapidly. As for reactions with trivalent phosphorus compounds Z_3P, we have found that a highly endothermic SET from Z_3P to an iron(III) complex takes place in association with a rapid reaction of the resulting trivalent phosphorus radical cations with alcohol.[37] We therefore conclude that the accumulation of **MV**$^+$ observed in the present reaction results from a follow-up reaction of **BP**$^{\bullet+}$.

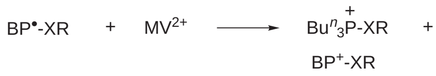
The present reaction gives **BP-O** as a final product from **BP** in the presence of ROH, which shows the fate of **BP**$^{\bullet+}$; a P–O bond is formed through nucleophilic attack by ROH on **BP**$^{\bullet+}$, yielding phosphoranyl radical **BP$^{\bullet}$-OR** [eqn. (3)].[9,11,12,15] In analogy with alcohol, thiol RSH undergoes an ionic reaction



$$\mathrm{BP^{\bullet+}} + \underset{\mathrm{X = O,\,S}}{\mathrm{RXH}} \xrightarrow[-\mathrm{H^+}]{k_{\mathrm{Nu}}} \underset{\mathrm{BP^{\bullet}\text{-}XR}}{\mathrm{Bu}^n{}_3\overset{\bullet}{\mathrm{P}}\text{-XR}} \qquad (3)$$

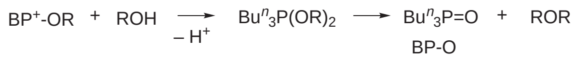
with **BP$^{\bullet+}$** giving the corresponding phosphoranyl radical **BP$^{\bullet}$-SR**. More evidence that nucleophilic attack by RXH (X = O, S) on **BP$^{\bullet+}$** is needed if **MV$^+$** is to accumulate was provided by the reaction with mesityldiphenylphosphine ($MesPh_2P$) used in place of **BP**. The concentration of **MV$^+$** did not increase in the reaction of $MesPh_2P$ with **MV^{2+}** in the presence of MeOH, despite the prediction that $MesPh_2P$ would give more **MV$^+$** than **BP** did because the oxidation peak potential E_p^{ox} (1.14 V *vs.* Ag/AgCl)[4] is lower than that of **BP**. Radical cation $MesPh_2P^{\bullet+}$ is generated, but, as suggested by examination of Corey–Pauling–Koltun (CPK) molecular models, its cationic center is protected sterically by the mesityl ligand from nucleophilic attack by MeOH.

Phosphoranyl radicals are known to preferentially cleave the O–C bond to give alkyl radicals when the radical is stable enough.[38,39] However, we saw no evidence for the products derived from the *tert*-butyl radical in the reaction in the presence of Bu^{t}OH. In the present system, therefore, **MV^{2+}** is likely to very rapidly oxidize the phosphoranyl radical **BP$^{\bullet}$-XR** (X = O, S) to the phosphonium ion **BP$^+$-XR** [eqn. (4)]; the half-wave potential $E_{1/2}$ of a related compound, tetraphenylphosphoranyl radical, is −1.73 V *vs.* Ag/Ag$^+$ (=−1.51 V *vs.* Ag/AgCl).[40] In addition, the oxidation of **BP$^{\bullet}$-XR** is so rapid that a possible α-scission of a P–C bond in this phosphoranyl radical to liberate *n*-butyl radical would be negligible, if present at all.

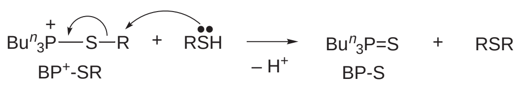


$$\mathrm{BP^{\bullet}\text{-}XR} + \mathrm{MV^{2+}} \longrightarrow \underset{\mathrm{BP^{+}\text{-}XR}}{\mathrm{Bu}^n{}_3\overset{+}{\mathrm{P}}\text{-XR}} + \mathrm{MV^{+}} \qquad (4)$$

An alkyl cation equivalent is eliminated from **BP$^+$-XR** by attack by alcohol ROH or thiol RSH. In reactions with ROH, ROH, which is classified as a hard base,[41] attacks the phosphorus atom, a harder electrophilic center in **BP$^+$-OR**, to form a phosphorane intermediate,[42] which collapses to yield **BP-O** as well as ether ROR [eqn. (5)].[9d] In reactions with RSH, on the other hand, RSH is a soft base[41] and attacks in S_N2 fashion the carbon atom in the alkylthio ligand, a softer electrophilic center in **BP$^+$-SR**, to give **BP-S** as well as sulfide RSR in a single step [eqn. (6)]. It should be emphasized that the decomposition occurs in any case *after* a rapid and practically irreversible reaction, reaction (4). As a result, the rate of increase in the concentration of **MV$^+$**, monitored for calculation of rate constants, is completely independent of the fate of **BP$^+$-XR**.



$$\mathrm{BP^{+}\text{-}OR} + \mathrm{ROH} \xrightarrow[-\mathrm{H^+}]{} \mathrm{Bu}^n{}_3\mathrm{P(OR)_2} \longrightarrow \underset{\mathrm{BP\text{-}O}}{\mathrm{Bu}^n{}_3\mathrm{P{=}O}} + \mathrm{ROR} \qquad (5)$$



$$\underset{\mathrm{BP^{+}\text{-}SR}}{\mathrm{Bu}^n{}_3\overset{+}{\mathrm{P}}\text{—S—R}} + \mathrm{R\ddot{S}H} \xrightarrow[-\mathrm{H^+}]{} \underset{\mathrm{BP\text{-}S}}{\mathrm{Bu}^n{}_3\mathrm{P{=}S}} + \mathrm{RSR} \qquad (6)$$

The phosphine **BP** acting as the nucleophile to trap **BP$^{\bullet+}$** is in principle possible.[1,2a,5,6] However, reaction in acetonitrile without added nucleophile resulted in very sluggish formation of **MV$^+$** (less than 4% after 3.5 h, resulting probably from the reaction of **BP$^{\bullet+}$** with a small amount of water in the solvent). So, this pathway clearly does not contribute significantly to the reaction observed.

Control experiments with added sulfide eliminated the possibility that this reaction product reduces **MV^{2+}** under our conditions.[43] When the reaction was carried out with dibutyl sulfide ($Bu^n{}_2S$) instead of **BP** and in the presence of MeOH ($[Bu^n{}_2S]_0$ = 1.50×10^{-1} mol dm^{-3}, $[\mathbf{MV}^{2+}]_0 = 2.00 \times 10^{-4}$ mol dm^{-3}, and $[MeOH]_0 = 12.0$ mol dm^{-3}), no **MV$^+$** was detected. Furthermore, kinetic parameters of the reaction of **BP** and **MV^{2+}** in the presence of MeOH were unchanged when $Bu^n{}_2S$ (2.00×10^{-3} mol dm^{-3}) was added to the reaction mixture.

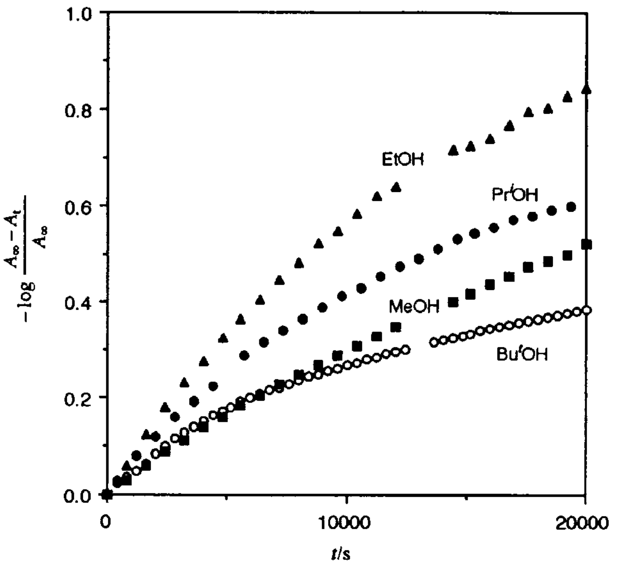
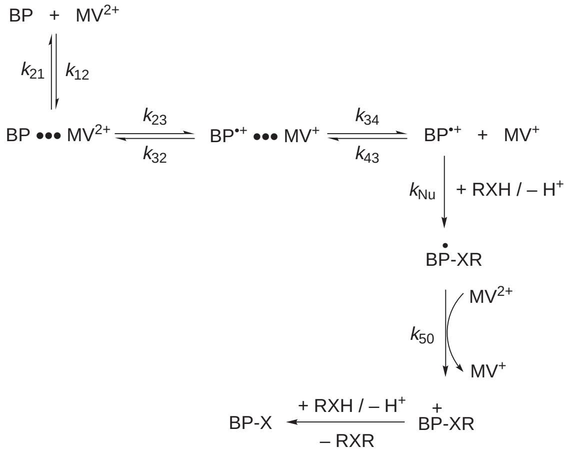


Fig. 2 Logarithmic plot of increase in the absorption of **MV$^+$** at 605 nm against time. ■, ▲, ●, and ○ denote the points for the reactions with MeOH, EtOH, Pr^{i}OH, and Bu^{t}OH, respectively.

In conclusion, the present reaction proceeds according to the mechanism represented by eqns. (2)–(6), which is summarized in Scheme 2. This mechanism represents the stoichiometry observed (see Table 1).



Scheme 2 The mechanism of the reaction of tributylphosphine (**BP**) with methylviologen (**MV^{2+}**) in the presence of alcohol or thiol (RXH).

Kinetics

The reaction of **BP** with **MV^{2+}** was carried out in the presence of a nucleophile RXH under pseudo-first-order conditions, with the concentrations of **BP** and RXH being 750 and 7500 times higher, respectively, than the concentration of **MV^{2+}**. The increase in the absorption at 605 nm from **MV$^+$** was monitored spectrophotometrically. Fig. 2 shows the plots of $-\log\{(A_\infty - A_t)/A_\infty\}$ against time for the selected reactions, where A_∞ is the final absorption at 605 nm (= 2.78 under our experimental conditions) and A_t is the absorption at a given time t. If the reaction obeys first-order kinetics, this type of a logarithmic plot should give a linear line for each reaction. However, each plot shows downward deviation.

Table 2 Kinetic parameters in the reaction of tributylphosphine **BP** with methylviologen $\mathbf{MV}^{2+}$ [a]

entry	RXH	$(k^+/a)/10^{-4}$ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ [b]	$10^{-3}\,(k^-/a)/k_{\mathrm{Nu}}$ [b]	$k_{\mathrm{Nu}}^{\mathrm{rel}}$ [c]
1	H_2O	8.9	3.3	0.61
2	MeOH	3.3	4.0	0.50
3[d]	MeOH	3.2	3.8	0.53
4	EtOH	7.0	2.0	1
5[e]	EtOH	7.4	2.1	0.95
6	EtOD[f]	7.1	2.1	0.95
7	$\mathrm{Bu^nOH}$	7.2	1.2	1.7
8	$\mathrm{Pr^iOH}$	6.8	3.7	0.54
9	$\mathrm{Bu^tOH}$	7.5	26	0.077
10	$\mathrm{Bu^nSH}$	85	3.6	0.56
11	$\mathrm{Bu^tSH}$	68	3.5	0.57

[a] $[\mathbf{BP}]_0 = 1.50 \times 10^{-1}$ mol dm^{-3}, $[\mathbf{MV}^{2+}]_0 = 2.00 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{RXH}]_0 = 1.50$ mol dm^{-3}. In acetonitrile at 50 °C under an argon atmosphere in the dark. [b] Errors are within 3%. [c] Relative value of rate constant k_{Nu}. [d] In the presence of dibutyl sulfide (2.00×10^{-3} mol dm^{-3}). [e] $[\mathrm{EtOH}]_0 = 1.18$ mol dm^{-3}. [f] Ethanol-*O*-d_1 was used.

Such kinetic behavior is interpreted in terms of the mechanism shown in Scheme 2. Taking the steady-state approximation with respect to concentrations of $\mathbf{BP}\cdots\mathbf{MV}^{2+}$, $\mathbf{BP}^{\cdot+}\cdots\mathbf{MV}^{+}$, $\mathbf{BP}^{\cdot+}$, and $\mathbf{BP}^{\cdot}\text{-}\mathbf{OR}$, the increase in the concentration of $\mathbf{MV}^+$ is expressed by eqn. (7), where $k^+ = k_{12}k_{23}k_{34}$, $k^- = k_{21}k_{32}k_{43}$,

$$\mathrm{d}[\mathbf{MV}^+]/\mathrm{d}t = \frac{2(k^+/a)k_{\mathrm{Nu}}[\mathbf{BP}][\mathbf{MV}^{2+}][\mathrm{ROH}]}{(k^-/a)[\mathbf{MV}^+] + k_{\mathrm{Nu}}[\mathrm{ROH}]} \qquad (7)$$

and $a = (k_{21} + k_{23})(k_{32} + k_{34}) - k_{23}k_{32}$. This equation predicts downward deviation in the logarithmic plot when two terms in the denominator, $(k^-/a)[\mathbf{MV}^+]$ and $k_{\mathrm{Nu}}[\mathrm{ROH}]$, are of similar importance.[44] That is, the observed "bent" kinetics show that $\mathbf{BP}^{\cdot+}$ undergoes the forward reaction leading to the products and the backward reaction giving back the starting materials with comparable efficiency. Similar "bent" kinetics have been observed for the oxidation of toluene derivatives with metal complexes.[45–47] The kinetics have been analyzed quantitatively by multiple nonlinear regression; the reaction scheme in that analysis, as well as the rate expression derived, is essentially the same as ours. Then, our kinetic data were analyzed by this method, affording the parameters k^+/a and $(k^-/a)/k_{\mathrm{Nu}}$ as summarized in Table 2. Curve-fitting of the regression was satisfactory for each reaction (correlation coefficient, $r > 0.9990$). Examples are shown in Fig. 3 for the reactions with EtOH and $\mathrm{Pr^iOH}$. These kinetic parameters were cross-checked by experiments with different initial concentrations of **BP** [entries 4 and 5 in Table 2]. Table 2 lists also the relative values of k_{Nu}, $k_{\mathrm{Nu}}^{\mathrm{rel}}$ $(= k_{\mathrm{Nu}}^{\mathrm{RXH}}/k_{\mathrm{Nu}}^{\mathrm{EtOH}})$, which were estimated taking into account that k^-/a is the same for all of the reactions. Apparently, $k_{\mathrm{Nu}}^{\mathrm{rel}}$ represents relative reactivity of $\mathbf{BP}^{\cdot+}$ towards a nucleophile RXH. For the reaction with EtOH, activation parameters for the k_{Nu} step were determined as shown in Table 3, from the Arrhenius plot shown in Fig. 4.

As expected from the premise that the process from $\mathbf{BP} + \mathbf{MV}^{2+}$ to $\mathbf{BP}^{\cdot+} + \mathbf{MV}^{+}$ is independent of any nucleophile being added, there is little variation in k^+/a depending on the nucleophile within a series of the reactions with alcohols, which verifies our kinetic treatment. An exception is seen for the reaction with MeOH, in which the k^+/a value is slightly smaller than expected. A possible explanation is that the complexation between $\mathbf{MV}^{2+}$ and MeOH, which has been proposed previously,[48–50] makes k_{12} smaller, resulting in the smaller value of k^+/a. The reactions with thiols gave larger k^+/a values than the reactions with alcohols, which results at least partly from participation of the nucleophile as a solvent in k_{23} step (the SET step). Table 4 lists the peak potentials of **BP** and $\mathbf{MV}^{2+}$ measured by cyclic voltammetry in the presence or absence of a nucleophile. The peak potentials of **BP** and $\mathbf{MV}^{2+}$ changed little if at all when ethanol was added to the acetonitrile solution at the same concentration as that for kinetics, but the addition of the same concentration of butane-1-thiol lowered the peak potential of **BP** and raised that of $\mathbf{MV}^{2+}$ to a significant extent. This trend in the changes of the peak potentials is in the expected direction.

Table 3 Activation energy of the reaction of tributylphosphine radical cation $\mathbf{BP}^{\cdot+}$ with EtOH [a]

T/°C	$k_{\mathrm{Nu}}^{\mathrm{rel}}$ [b]
30	0.074
40	0.23
50	1
E_a/kJ mol^{-1}	107 ± 15

[a] $[\mathbf{BP}]_0 = 1.50 \times 10^{-1}$ mol dm^{-3}, $[\mathbf{MV}^{2+}]_0 = 2.00 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{EtOH}]_0 = 12.3$ mol dm^{-3}. In acetonitrile under an argon atmosphere in the dark. [b] Relative rate constant with $k_{\mathrm{Nu}}^{\mathrm{EtOH}}$ (50 °C) = 1. Errors are within 3%.

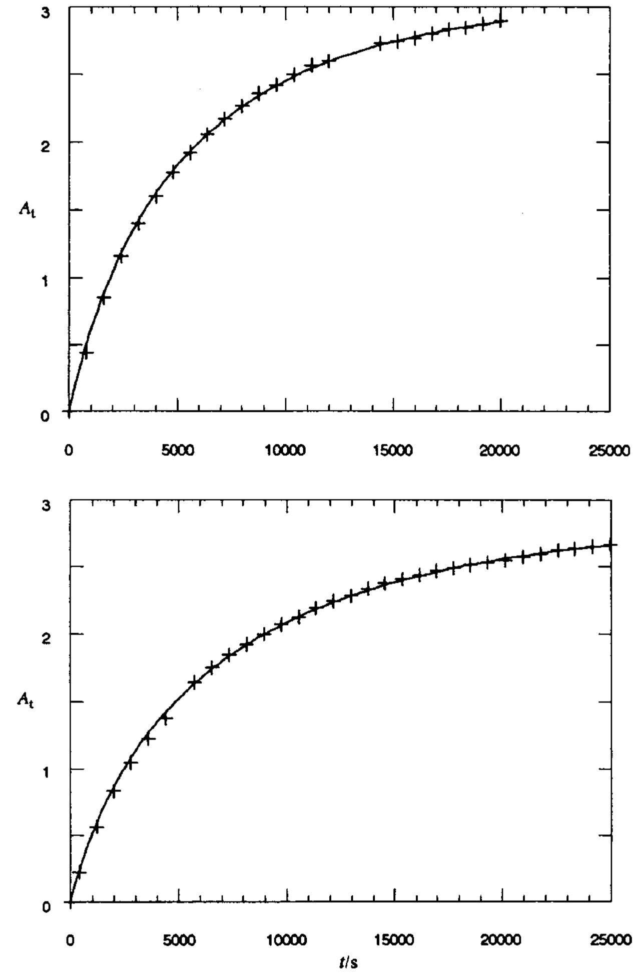


Fig. 3 Time-course of increase in the absorption of $\mathbf{MV}^+$ at 605 nm for the reactions with EtOH (top) and $\mathrm{Pr^iOH}$ (bottom). The crosses (+) represent the experimental points. The lines represent the best fit curve based on eqn. (7).

Reactivity of $\mathbf{BP}^{\cdot+}$ towards nucleophiles

Table 2 shows that the reaction of $\mathbf{BP}^{\cdot+}$ with alcohol becomes slower as the alcohol goes from the primary to the secondary and to the tertiary [entries 7, 8, and 9]. Meanwhile, as seen in a series of reactions with primary alcohols, $k_{\mathrm{Nu}}^{\mathrm{rel}}$ increases with increasing electron-releasing ability of the alcohol [entries 2, 4, and 7]. These observations simply provide a conclusion that the

Table 4 Peak potentials of tributylphosphine **BP** and methylviologen $\mathbf{MV}^{2+}$ [a]

RXH[b]	*E*p/V[c]		ΔE_p[d]
	BP	$\mathbf{MV}^{2+}$	
None[e]	1.45	−0.43	1.88
EtOH	1.45	−0.43	1.88
Bu*ⁿ*SH	1.34 ± 0.04	−0.39	1.73 ± 0.04

[a] Measured by cyclic voltammetry in acetonitrile using tetraethylammonium tetrafluoroborate as a supporting electrolyte. [b] $[\mathrm{RXH}]_0 = 1.50$ mol dm^{-3}. [c] *vs.* Ag/AgCl. [d] $E_p(\mathbf{BP}) - E_p(\mathbf{MV}^{2+})$. [e] No RXH added.

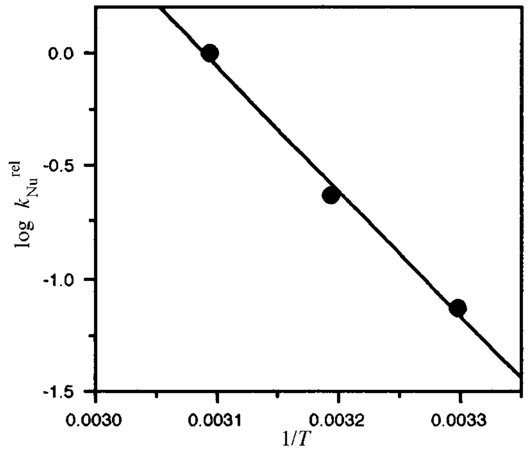


Fig. 4 The Arrhenius plot for the ionic reaction of radical cation $\mathbf{BP}^{\cdot+}$ with EtOH.

reaction is governed by both steric and electronic factors of ROH. In fact, attempts to correlate k_{Nu}^{rel} with a single steric or electronic parameter of R in ROH failed. Fig. 5a and b, for example, show scattered plots of log k_{Nu}^{rel} against the electronic and steric substituent constants σ^* and E_s, respectively. The data set of k_{Nu}^{rel} fits Taft's equation [eqn. (8)] better; in this equation, the constants σ^* and E_s are used simultaneously.[51]

$$\log(k_{Nu}^{ROH}/k_{Nu}^{MeOH}) = \rho^*\sigma^* + \delta E_s \quad (8)$$

Thus, the correlation improves as shown in Fig. 6, when $\rho^* = -3.08$ and $\delta = 1.03$.[52] Yet, the correlation is not significant (correlation coefficient, $r > 0.87$ with all points; $r > 0.97$ when the point for Bu*ⁿ*OH is ignored). This lack of significance is partly because the parameters used for this analysis have been defined in carbon-centered reactions. In addition, only a few datum points are available in this study. So, our discussion must be qualified, but the regression coefficients obtained here allow us, at least in a qualitative way, to depict the structure of the transition state of the reaction of $\mathbf{BP}^{\cdot+}$ with ROH. The large negative value of ρ^* suggests that a positive charge develops largely on the oxygen at the transition state. Meanwhile, the value of δ is close to unity, which indicates proximity of both reactants at the transition state. The value $\delta = 1.482$ has been obtained for the Menschutkin reaction between dimethyl(*ortho*-substituted phenyl)amine and methyl iodide,[53] the transition state of which must be crowded.

Correlation analysis therefore predicts the structure of the transition state for the reaction of $\mathbf{BP}^{\cdot+}$ with ROH; at the transition state, formation of the P–C bond is almost completed without a great extent of O–H bond cleavage, and as a result, the positive charge resides mostly on the oxygen atom (Scheme 3). Compatible with this structure of the transition state is the observation that the reaction of $\mathbf{BP}^{\cdot+}$ with ethanol exhibits no appreciable kinetic isotope effect k_{Nu}^{H}/k_{Nu}^{D} (entries 4 and 6 in Table 2).

The nucleophilic attack by alcohol on $\mathbf{BP}^{\cdot+}$ is governed by general acid-catalysis. When the reaction of **BP** with $\mathbf{MV}^{2+}$ was carried out in the presence of propane-1,3-diol, the rate of the k_{Nu} step was higher than predicted from electronic and steric contributions of the propanediol (Table 5). This increase in the

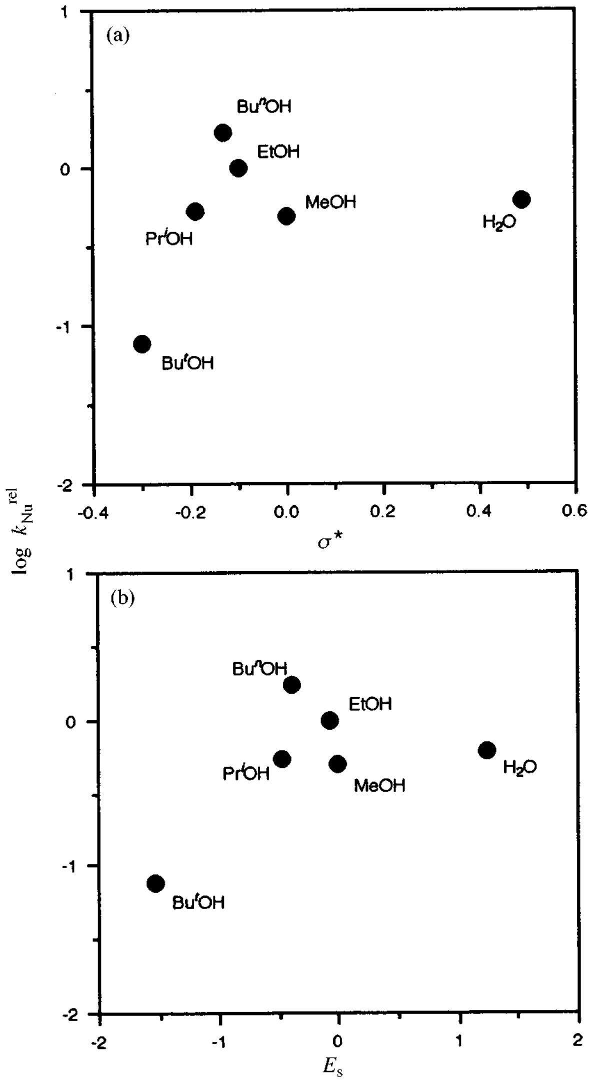


Fig. 5 Dependence of log k_{Nu}^{rel} on the Taft's electronic parameter σ^* (a) and on the steric parameter E_s (b) of R in ROH.

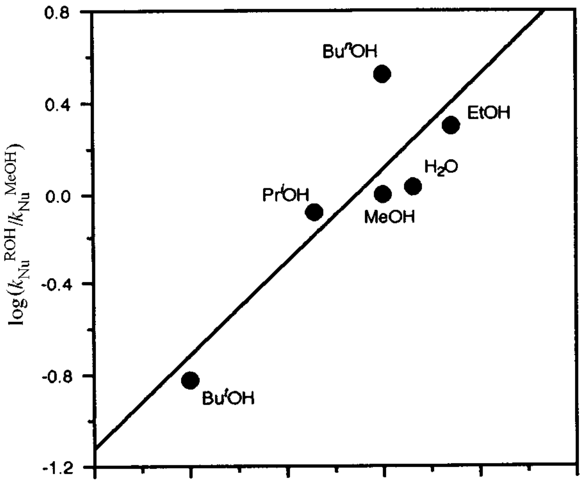
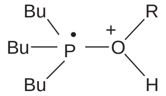


Fig. 6 Correlation of log ($k_{Nu}^{ROH}/k_{Nu}^{MeOH}$) with $\rho^*\sigma^* + \delta E_s$ in Taft's dual-parameter equation.

Table 5 Reaction of tributylphosphine **BP** with methylviologen $\mathbf{MV}^{2+}$ in the presence of diols[a]

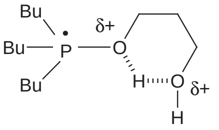
ROH	$(k^+/a)/10^{-4}$ dm^3 mol^{-1} s^{-1} [b]	$10^{-3}\,(k^-/a)/k_{\mathrm{Nu}}$ [b]	$k_{\mathrm{Nu}}{}^{\mathrm{rel}}$ [c]
EtOH	7.0	2.0	1
HO–(CH$_2$)$_3$–OH	10	0.32	6.3
HO–(CH$_2$)$_4$–OH	6.5	2.0	1.0

[a] $[\mathbf{BP}]_0 = 1.50 \times 10^{-1}$ mol dm^{-3}, $[\mathbf{MV}^{2+}]_0 = 2.00 \times 10^{-4}$ mol dm^{-3}, $[\mathrm{ROH}]_0 = 12.3$ mol dm^{-3}. In acetonitrile at 50 °C under an argon atmosphere in the dark. [b] Errors are within 3%. [c] Relative rate constant, $k_{\mathrm{Nu}}{}^{\mathrm{ROH}}/k_{\mathrm{Nu}}{}^{\mathrm{EtOH}}$.



Scheme 3 Transition state of the reaction of radical cation $\mathbf{BP}^{\bullet+}$ with ROH.

rate results from intramolecular general acid-catalysis; the transition state of the reaction of $\mathbf{BP}^{\bullet+}$ with the propanediol is stabilized by the formation of a six-membered ring as shown in Scheme 4. On the other hand, the terminal hydroxy hydrogen in butane-1,4-diol has no effect on the rate. Certainly, there is an entropic or configurational disadvantage (or both) in the formation of a ring structure at the transition state for the reaction of $\mathbf{BP}^{\bullet+}$ with the butanediol.[54] The nucleophilicity of water toward $\mathbf{BP}^{\bullet+}$ is smaller than expected from its basicity (entry 1 in Table 2). The magnitude is almost the same as that of propan-2-ol, as has been observed before in reactions of carbocations with nucleophiles.[55–57] Hydrogen bonding among water molecules is so strong that water cannot act as a general acid-catalyst, and instead the hydrogen bonding contributes to cluster formation lowering the nucleophilicity.



Scheme 4 Transition state of the reaction of radical cation $\mathbf{BP}^{\bullet+}$ with propane-1,3-diol.

The steric bulk of the thiol has little effect on the rate constants k_{Nu} in reactions with $\mathbf{BP}^{\bullet+}$ unlike with alcohol (entries 10 and 11). It would appear that the results are accounted for by a sulfur atom being larger than an oxygen atom; the distance between the phosphorus atom in $\mathbf{BP}^{\bullet+}$ and the R group in a nucleophile at the transition state may be longer in the reaction with thiol RSH than in the reaction with alcohol ROH. Alternatively, the lack of a steric effect in the k_{Nu} step with RSH may mean that the reaction between $\mathbf{BP}^{\bullet+}$ and RSH proceeds through single-electron transfer (SET) from RSH to $\mathbf{BP}^{\bullet+}$, giving neutral phosphine **BP** and radical cation $\mathrm{RSH}^{\bullet+}$.[43] Nevertheless, that phosphine sulfide **BP-S** is the final product of this reaction shows that, if the SET occurs, radical attack by $\mathrm{RSH}^{\bullet+}$ on **BP** takes place rapidly, eventually giving the phosphoranyl radical intermediate $\mathbf{BP}^{\bullet}$**-SR**.

The value of activation energy E_a for the nucleophilic attack on phosphine radical cation $\mathbf{BP}^{\bullet+}$ is worth comparing with values reported for reactions of carbon radical cations (see Table 3). The reactions of anthracene radical cations with amine nucleophiles take place rapidly with extremely small or sometimes negative activation energy.[58] It has also been reported that styrene radical cations react with nucleophiles such as azide,[59a,b] halides,[59b] alcohols,[59b] and alkenes[59c] as rapidly as the related carbocations do. These findings have been taken as evidence against the configuration mixing (CM) model developed by Pross;[60] according to this model, nucleophilic attack on a certain radical cation is a high-energy pathway and hence a forbidden process, whereas the corresponding attack on cation species is allowed. The present study has revealed that $\mathbf{BP}^{\bullet+}$ undergoes nucleophilic attack by an alcohol with a quite large activation energy. This fact thus suggests that the reaction of phosphine radical cations with nucleophiles is forbidden as predicted by the CM model.

Experimental

Instruments

UV–visible spectra were recorded on a Shimadzu UV-2200A UV–vis recording spectrophotometer. GC analysis was done with a Shimadzu GC-14A gas chromatograph. Mass spectra were obtained on a Shimadzu GCMS-QP2000A gas chromatograph-mass spectrometer equipped with a Shimadzu GC-MSPAC 200S data processor. ^{1}H and ^{31}P NMR spectra were obtained on a Varian XL 200 NMR spectrometer operating at 200 and 81 MHz, respectively. Cyclic voltammetry was done on a Cypress Systems OMNI 90 potentiostat in acetonitrile with platinum and Ag/AgCl electrodes as the working and the reference electrodes, respectively, and with tetraethylammonium tetrafluoroborate (0.10 mol dm^{-3}) as the supporting electrolyte.

Materials

Tributylphosphine (**BP**) was commercially available (Tokyo Chemical Industry) and distilled before use. Mesityldiphenylphosphine was prepared according to the literature procedure.[4] 1,1′-Dimethyl-4,4′-bipyridinium (methylviologen; $\mathbf{MV}^{2+}$) tetrafluoroborate was obtained from the corresponding chloride salt (Tokyo Chemical Industry) as follows. The chloride salt was treated with silver tetrafluoroborate in methanol, and after filtration of the resulting precipitate, the filtrate was concentrated under reduced pressure. Extraction of the residue with acetonitrile and evaporation of the solvent gave the tetrafluoroborate salt of $\mathbf{MV}^{2+}$ as a crude solid, which was purified by recrystallization from acetonitrile–diethyl ether. Alcohols, thiols, and acetonitrile were purchased (Tokyo Chemical Industry) and distilled before use.

General procedures

To a UV-cell equipped with a septum and filled with argon gas were added successively solutions of $\mathbf{MV}^{2+}$ and of RXH (X = O, S) in acetonitrile, and then tributylphosphine (**BP**) (as a neat material). The initial concentrations of **BP**, $\mathbf{MV}^{2+}$, and RXH were 1.50×10^{-1}, 2.00×10^{-4}, and 1.50 mol dm^{-3}, respectively. The UV-cell was kept in a cell holder of a spectrophotometer maintained at 50 °C, and the UV–visible spectrum was taken every 18 seconds. The reaction was carried out also in an NMR tube with acetonitrile-d_3 at $[\mathbf{BP}]_0 = [\mathbf{MV}^{2+}]_0 = 1.00 \times 10^{-5}$ mol dm^{-3} and $[\mathrm{RXH}]_0 = 2.00 \times 10^{-5}$ mol dm^{-3}, and the ^{1}H NMR spectrum was recorded after an appropriate reaction period.

Kinetics

The reaction was carried out in a UV-cell, and the growth of the absorbance at 605 nm was monitored on a spectrophotometer every 18 seconds. Kinetic data obtained were analyzed as described in the literature.[45–47]

Eqn. (7) is derived as follows, from eqns. (9)–(13), when

$$\mathrm{d}[\mathbf{BP}\cdots\mathbf{MV}^{2+}]/\mathrm{d}t = k_{12}[\mathbf{BP}][\mathbf{MV}^{2+}] + k_{32}[\mathbf{BP}^{\bullet+}\cdots\mathbf{MV}^{+}] - (k_{21} + k_{23})[\mathbf{BP}\cdots\mathbf{MV}^{2+}] = 0 \quad (9)$$

$$\mathrm{d}[\mathbf{BP}^{\cdot+}\cdots\mathbf{MV}^{+}]/\mathrm{d}t = k_{23}[\mathbf{BP}\cdots\mathbf{MV}^{2+}] + k_{43}[\mathbf{BP}^{\cdot+}][\mathbf{MV}^{+}] - (k_{32} + k_{34})[\mathbf{BP}^{\cdot+}\cdots\mathbf{MV}^{+}] = 0 \quad (10)$$

$$\mathrm{d}[\mathbf{BP}^{\cdot+}]/\mathrm{d}t = k_{34}[\mathbf{BP}^{\cdot+}\cdots\mathbf{MV}^{+}] - (k_{43}[\mathbf{MV}^{+}] + k_{\mathrm{Nu}}[\mathrm{RXH}])[\mathbf{BP}^{\cdot+}] = 0 \quad (11)$$

$$\mathrm{d}[\mathbf{BP}^{\bullet}\text{-}\mathbf{XR}]/\mathrm{d}t = k_{\mathrm{Nu}}[\mathrm{RXH}][\mathbf{BP}^{\cdot+}] - k_{50}[\mathbf{BP}^{\bullet}\text{-}\mathbf{XR}][\mathbf{MV}^{2+}] = 0 \quad (12)$$

$$\mathrm{d}[\mathbf{MV}^{+}]/\mathrm{d}t = k_{34}[\mathbf{BP}^{\cdot+}\cdots\mathbf{MV}^{+}] + k_{50}[\mathbf{BP}^{\bullet}\text{-}\mathbf{XR}][\mathbf{MV}^{2+}] - k_{43}[\mathbf{BP}^{\cdot+}][\mathbf{MV}^{+}] \quad (13)$$

$[\mathbf{BP}\cdots\mathbf{MV}^{2+}]$, $[\mathbf{BP}^{\cdot+}\cdots\mathbf{MV}^{+}]$, $[\mathbf{BP}^{\cdot+}]$, and $[\mathbf{BP}^{\bullet}\text{-}\mathbf{XR}]$ in Scheme 2, respectively, are in the steady-state concentrations. The rate expression is given in eqn. (13). Eliminating $[\mathbf{BP}^{\cdot+}\cdots\mathbf{MV}^{+}]$, $[\mathbf{BP}^{\bullet}\text{-}\mathbf{XR}]$, and $[\mathbf{BP}^{\cdot+}]$ in eqn. (13) through eqns. (9)–(12) and taking $k^{+} = k_{12}k_{23}k_{34}$, $k^{-} = k_{21}k_{32}k_{43}$, and $a = (k_{21} + k_{23})(k_{32} + k_{34}) - k_{23}k_{32}$, we obtain eqn. (7).

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