Reactivity of Cation Radicals Generated from Trivalent-Phosphorus Compounds in the Reaction with Methylviologen: Kinetic Analysis

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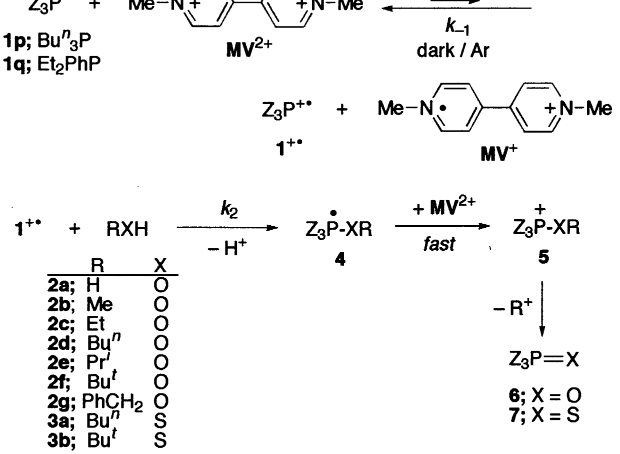
Cation radicals generated from trivalent-phosphorus compounds through single-electron transfer to methylviologen undergo ionic reactions with alcohols or thiols. A kinetic analysis of the reactions has suggested that the reaction of the trivalent-phosphorus cation radicals with alcohols possesses a tighter transition state than that with thiols.

Trivalent-phosphorus cation radicals, which are readily generated through single-electron transfer (SET) from parent trivalent-phosphorus compounds to good electron acceptors,[1,2] have potential utility in organic syntheses.[3] To obtain a wider scope in such use, it is important to elucidate the reactivity of these cation radicals. A principal reaction of trivalent-phosphorus cation radicals is an ionic reaction with a nucleophile. However, the reaction has never been analyzed kinetically. We examined the reaction of phosphines **1** with 1,1'-dimethyl-4,4'-bipyridinium dication (methylviologen; $\mathbf{MV}^{2+}$) in the dark in the presence of nucleophiles such as alcohols or thiols. The results of kinetics as well as product analysis were reasonably interpreted assuming a mechanism in which cation radicals $\mathbf{1}^{+\bullet}$ generated through SET from **1** to $\mathbf{MV}^{2+}$ react with the nucleophile to give the products. We herein present the rate constants for the ionic reaction of $\mathbf{1}^{+\bullet}$ evaluated according to this mechanism, and discuss the reactivity of $\mathbf{1}^{+\bullet}$ toward nucleophiles based on these constants.

A large excess of tributylphosphine (**1p**) or diethylphenylphosphine (**1q**) was reacted with $\mathbf{MV}^{2+}$ (fluoroborate salt) in acetonitrile at 50 °C in the dark in the presence of water (**2a**) or alcohol (**2b-f**). Spectrophotometric measurement indicated that the reduced form of $\mathbf{MV}^{2+}$, $\mathbf{MV}^{+}$, is produced gradually.[4] The final amount of $\mathbf{MV}^{+}$ was nearly quantitative and no further reduction to $\mathbf{MV}^{0}$ was observed. ^{1}H and ^{31}P NMR, IR, and GCMS spectroscopy showed the formation of the corresponding phosphine oxide **6**. The observations are compatible with the mechanism depicted in Scheme 1; thus, **1** transfers an electron to $\mathbf{MV}^{2+}$ with simultaneous formation of $\mathbf{1}^{+\bullet}$, which subsequently reacts with **2** to afford a phosphoranyl radical **4**.[2,5] Oxidation of **4** by $\mathbf{MV}^{2+}$ followed by elimination of an alkyl cation equivalent from the resulting phosphonium ion **5** affords **6**.[6] Judging from a half-wave potential of tetraphenylphosphonium ion (–1.68 V vs. SCE),[7] the oxidation potential of **4** is estimated to be much lower than the reduction potential of $\mathbf{MV}^{2+}$ (–0.43 V vs. SCE).[4] Thus, oxidation of **4** by $\mathbf{MV}^{2+}$ is very fast and practically irreversible. In the reaction of **1p** with $\mathbf{MV}^{2+}$ in the presence of benzyl alcohol (**2g**) (molar ratio; 2:1:4), benzyl ether was detected on a GCMS (4% yield based on the amount of **1p** used at 6% conversion of **1p**) besides **6p**. This finding may support the proposed mechanism because benzyl ether should be a product when **5** (R = benzyl) decomposes to **6p**.[8] When the reaction of **1p** with $\mathbf{MV}^{2+}$ was carried out in the presence of a thiol (**3a-b**) in place of an alcohol under otherwise identical conditions, the corresponding phosphine sulfide (**7p**) was formed as well as $\mathbf{MV}^{+}$. Control experiments have shown that no SET takes place from **3** to $\mathbf{MV}^{2+}$ under our experimental conditions, so it seems highly likely that $\mathbf{1}^{+\bullet}$ reacts with **3** as does with an alcohol **2**.



Scheme 1.

Progress of the reaction was followed under these conditions by monitoring increase in the absorbance at 602 nm from $\mathbf{MV}^{+}$. It was found that the reaction does not follow simple first-order kinetics, which suggests that the back-electron transfer from $\mathbf{MV}^{+}$ to $\mathbf{1}^{+\bullet}$ (k_{-1}) and the reaction of $\mathbf{1}^{+\bullet}$ with a nucleophile (k_2) take place with comparable efficiency. The same kinetics have been observed for the oxidation of toluene derivatives by metal complexes, and the mathematical method has been provided to analyze such kinetics.[9,10] Based on this method, we performed a regression analysis to fit the present kinetic data to theoretical time-absorbance curves, which afforded k_1 and k_{-1}/k_2 as summarized in Table 1. In this analysis, the curve fits were satisfactory, which verifies the proposed mechanism. Relative values of k_2, $k_{2\mathrm{rel}}$ (= $k_2^{\mathrm{RXH}}/k_2^{\mathrm{MeOH}}$), in Table 1 were estimated by assuming k_{-1} to be the same for all reactions;[9,11] as will be mentioned later, a redox potential of a $\mathbf{1}^{+\bullet}/\mathbf{1}$ couple was found to be about 2V higher than that of a $\mathbf{MV}^{2+}/\mathbf{MV}^{+}$ couple, so k_{-1} can be estimated to be very close to the diffusion-controlled limit.

Use of the nucleophile **2** in a slightly smaller amount had little effect on the rate constants (Table 1, entry 4). On the other hand, the addition of 50% (v/v) of **2** into acetonitrile resulted in appreciable differences in the rate constants (data not shown). Clearly, the added nucleophile in this large amount participates as a major part of the solvent in each step of the reaction (*vide infra*).

In a series of the reactions with primary alcohols (**2b-d**), $\mathbf{1p}^{+\bullet}$ reacts more readily with more electron-rich alcohols (Table 1, entries 2, 3, 5), suggesting that the positive charge has been transferred considerably to the oxygen at the transition state. Meanwhile, $k_{2\mathrm{rel}}$ decreases with increasing steric bulk at the α-carbon in the alcohol (entries 5-7). Thus, the stability of the transition state of this reaction is determined by both the steric

Table 1. Reaction of Phosphine **1** with Methylviologen[a]

entry	Z_3P	RXH	10^3k_1, $sec^{-1}M^{-1}$[b]	$10^{-3}k_{-1}/k_2$[b]	k_{2rel}[c]
1	**1p**	**2a**	0.89	3.3	1.2
2		**2b**	0.33	4.0	1
3		**2c**	0.70	2.0	2.0
4[d]		**2c**	0.74	2.1	1.9
5		**2d**	0.72	1.2	3.3
6		**2e**	0.68	3.7	1.1
7		**2f**	0.75	26	0.15
8		**3a**	8.5	3.6	0.95
9		**3b**	6.8	3.5	0.97
10	**1q**	**2b**	0.77	5.6	0.72
11		**2c**	1.7	34	0.12

[a] $[\mathbf{1}]_0 = 1.50 \times 10^{-1}$ M, $[\mathbf{MV}^{2+}]_0 = 2.00 \times 10^{-4}$ M, $[RXH]_0 = 1.50$ M. In acetonitrile at 50 °C in the dark under an argon atmosphere. [b] Errors are within 3%. [c] Relative value of the rate constant k_2 estimated by assuming that k_{-1} is the same for all runs. See the text. [d] $[\mathbf{2c}]_0 = 1.18 \times 10^{-1}$ M.

bulk and the electron-releasing ability of the alkyl group in the alcohol. In contrast, the reactions of the cation radicals derived from styrene derivatives with alcohols are governed solely by steric bulk of the alcohol.[12] The trend of reactivity of these carbon cation radicals is the same as those observed for several types of carbocations.[13] The difference in reactivity may indicate that the reactions of $\mathbf{1p}^{+\bullet}$ with alcohols have later transition states than those of the styrene cation radicals.

Cation radical $\mathbf{1q}^{+\bullet}$ is stabilized by delocalization of its unpaired electron into the phenyl ligand on the phosphorus. In fact, higher stability of $\mathbf{1q}^{+\bullet}$ than $\mathbf{1p}^{+\bullet}$ is implied by larger value of k_1 for the reaction of **1q** than that for **1p**. Such stabilization of $\mathbf{1q}^{+\bullet}$ not only lowers the rate of the reaction of $\mathbf{1q}^{+\bullet}$ with alcohol but also shifts its transition state to the product side, which would make the steric effect predominant in this reaction. The results show that this is the case; k_{2rel} is larger with methanol than with ethanol (entries 10 and 11).

The reaction rates of $\mathbf{1p}^{+\bullet}$ with thiols are hardly affected by steric bulk of the nucleophile (entries 8 and 9) indicating a looser transition state for the reaction with thiols than that with alcohols. Apparently, a larger size of a sulfur atom than an oxygen atom accounts for such a transition state.

Inconstancy of k_1 values with different nucleophiles added is attributable at least partly to solvent effects exerted by the nucleophile. Cyclic voltammetry has shown that peak potentials of **1p** and $\mathbf{MV}^{2+}$ are 1.45V and –0.43V vs. Ag^+/Ag, respectively, in the presence of **2c** at the same concentration as that for kinetics, and 1.34±0.04V and –0.39V vs. Ag^+/Ag, respectively, in the presence of **3a** at the same concentration. Thus, difference between the peak potentials (ΔE_p) of the oxidant $\mathbf{MV}^{2+}$ and of the reductant **1p** is 1.88V in the presence of **2c**, while ΔE_p in the presence of **3a** is 1.73±0.04V. Comparison of these ΔE_p values accounts for a one-order larger value of k_1 in the reaction with a thiol than with an alcohol. In fact, solvent effects on intermolecular SET have been reported.[14] Different solvation at the transition state of k_1-step may also be responsible for the inconstancy of k_1 values. Preliminary experiments have suggested that activation parameters for this step exhibit significant values (*e.g.*, $\Delta S^\ddagger$ is largely negative), indicating that this step is a composite of plural steps involving an SET step. Thus, k_1-step is subjected to solvent effects both in thermodynamic and kinetic terms.

There is an alternative mechanism for the present reaction; thus, cation radical $\mathbf{1}^{+\bullet}$ reacts with **1** giving the dimeric cation radical $Z_3P^\bullet\text{-}P^+Z_3$.[15] The resulting cation radical is oxidized by $\mathbf{MV}^{2+}$ to the dication $Z_3P^+\text{-}P^+Z_3$, which undergoes an ionic reaction with **2** to eventually give **6**. Although this mechanism cannot be ruled out at the present, we emphasize that the mechanism depicted in Scheme 1 is consistent with kinetic behaviors and product distributions observed in this study. The work is now in progress to find which mechanism is valid.

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