Reactivity of Triarylphosphine Peroxyl Radical Cations Generated through the Reaction of Triarylphosphine Radical Cations with Oxygen

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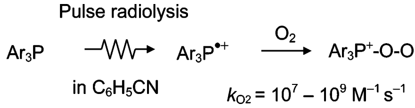

One-electron oxidation of triarylphosphines (Ar_3P, Ar = phenyl and substituted phenyl) in benzonitrile (PhCN) has been studied using pulse radiolysis technique. One-electron oxidation of Ar_3P occurred to yield the radical cation ($Ar_3P^{•+}$) which showed an intense absorption with a peak at 360−370 nm together with a broad band at 500−600 nm. The addition of molecular oxygen (O_2) to the phosphorus atom of $Ar_3P^{•+}$ took place at the second-order rate constant of 10^7−10^9 dm^3 mol^{-1} s^{-1} to yield the peroxyl triarylphosphinyl radical cation ($Ar_3P^+OO^•$). It is found that the electron-releasing substituents on the *para* position of the phenyl ring of Ar_3P influence the rate constants of the reaction of $Ar_3P^{•+}$ with O_2 and that *o*-methyl substituents on the phenyl ring influence the reactivity of $Ar_3P^+OO^•$.

Introduction

Oxidations of trivalent phosphorus compounds such as phosphines and phosphites (L_3P) giving the L_3P oxides ($L_3P{=}O$) as the stable product have been widely investigated from both mechanistic and synthetic points. One-electron oxidation of L_3P occurs initially to give the corresponding L_3P radical cations, $L_3P^{•+}$, as the intermediate in various chemical and electrochemical reactions.[1] Because of the presence of an unpaired electron and a positive charge of $L_3P^{•+}$, it is expected that $L_3P^{•+}$ exhibits dual reactivities as an electrophile and free radical. In fact, it is established from the product analysis that $L_3P^{•+}$ reacts with various nucleophiles such as water, methanol, halide anions, and hydroxide anions and bases such as pyridine.[2] We have recently reported that nucleophilic attack of H_2O toward the phosphorus atom of $Ar_3P^{•+}$ occurs to give the adduct ($Ar_3POH_2^{•+}$), from which deprotonation and further bond dissociation subsequently occur to give the triarylphosphine oxide ($Ar_3P{=}O$) as the final stable product.[3] Although the reactivities of $L_3P^{•+}$ against various nucleophiles have been widely investigated with the product analyses and electrochemical measurements, the kinetic study has been rarely performed.

The reactivity of $L_3P^{•+}$ as a radical is still unclear, although suggested by several groups. Zagumennov et al. have recently suggested that the higher reactivity of trimesitylphosphine radical cation with mercaptans rather than with water and alcohols corresponds to the radical character,[2a] showing an example of the radical reactivity of $L_3P^{•+}$. The reactivity of $Ar_3P^{•+}$ with O_2 has been investigated by Neta et al. and us. Neta et al. proposed the mechanism in which triphenylphosphine radical cation reacts with O_2 to give the peroxyl radical cation during the radiolytic reaction.[4] We have recently found that triarylphosphine radical cations ($Ar_3P^{•+}$) undergo radical coupling with O_2 during the laser flash photolysis of Ar_3P in the presence of

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Ar$_3$P
1a, $(C_6H_5)_3P$
1b, $(C_6H_5)_2(2\text{-}CH_3C_6H_4)P$
1c, $(C_6H_5)_2(4\text{-}CH_3C_6H_4)P$
1d, $(2\text{-}CH_3C_6H_4)_3P$
1e, $(3\text{-}CH_3C_6H_4)_3P$
1f, $(4\text{-}CH_3C_6H_4)_3P$
1g, $(4\text{-}CH_3OC_6H_4)_3P$
1h, $(2,5\text{-}(CH_3)_2C_6H_3)_3P$
1i, $(3,5\text{-}(CH_3)_2C_6H_3)_3P$
1j, $(2,4,6\text{-}(CH_3)_3C_6H_2)_3P$
1k, $(4\text{-}FC_6H_4)_3P$
1l, $(4\text{-}ClC_6H_4)_3P$

9,10-dicyanoanthracene as a photosensitizer and BP as a cosensitizer in "dry" acetonitrile under aerobic conditions. Certainly, this reaction gives the peroxyl radical cation Ar$_3$P$^+$OO$^\bullet$, which in fact explains the formation of the observed product Ar$_3$P═O. However, the intermediate Ar$_3$P$^+$OO$^\bullet$ has not been directly observed.[5] Herein, we investigated the kinetics of the reaction of Ar$_3$P$^{\bullet+}$ with O$_2$ during the pulse radiolysis of Ar$_3$P in aerobic PhCN. We succeeded in observing the formation of peroxyl radical cation Ar$_3$P$^+$OO$^\bullet$ and elucidated its reaction with the transient absorption measurement.

Results and Discussion

Formation and Decay of Ar$_3$P$^{\bullet+}$. It is established that radiolysis of various molecules (M) in PhCN causes one electron oxidation of M via hole trapping to give M radical cation (M$^{\bullet+}$).[6] Although electron is generated initially together with hole during the pulse radiolysis of a PhCN solution, electron can be stably trapped by PhCN and does not affect the formation of M$^{\bullet+}$. Ar$_3$P$^{\bullet+}$ can be generated during the pulse radiolysis of Ar$_3$P in argon-saturated PhCN (eqs 1−3).

$$\text{PhCN} \rightsquigarrow \text{hole} + e^- \tag{1}$$

$$\text{hole} + \text{Ar}_3\text{P} \rightarrow \text{Ar}_3\text{P}^{\bullet+} \tag{2}$$

$$\text{PhCN} + e^- \rightarrow \text{PhCN}^{\bullet-} \tag{3}$$

Figure 1 shows the transient absorption spectra observed after an electron pulse during the pulse radiolysis of tris(*p*-tolyl)phosphine **1f** with the concentrations of 1.0×10^{-2} M (M ≡ mol dm^{-3}). The transient absorption spectra exhibited two absorption bands with the maxima at 380 and 550 nm, respectively, immediately after an electron pulse. This spectrum is essentially same as that observed during the γ-radiolysis of **1f** in rigid glass of *n*-butyl chloride at 77 K[3] and is similar to that observed during the pulse radiolysis of triphenylphosphine **1a** in chlorocyclohexane.[7] The absorption spectrum observed immediately after the electron pulse is assigned to **1f** radical cation (**1f**$^{\bullet+}$). The decay profile of the transient aborptions of **1f**$^{\bullet+}$ at 550 nm was analyzed according to the first-order rate equation, giving the apparent decay rate constant of $k_{\text{decay}} = 3.9 \times 10^5$ s^{-1}.

Pulse radiolyses of other Ar$_3$P were also examined in PhCN. The observed transient absorption spectra of Ar$_3$P$^{\bullet+}$ with two peaks at 380 nm and around 500−600 nm were similar to that of **1f**$^{\bullet+}$, although the visible absorption band shifted to longer wavelength side with an increase of the electron-donating character of *ortho* and *para* substituents (Supporting Information, S1). The longer wavelength shift of the absorption bands of Ar$_3$P$^{\bullet+}$ may result from the delocalization of the positive charge of Ar$_3$P$^{\bullet+}$. The transient absorption of Ar$_3$P$^{\bullet+}$ disappeared in the time scale of μs to a few tens μs except for **1j**$^{\bullet+}$. The k_{decay} values for Ar$_3$P$^{\bullet+}$ were estimated from the single-exponential fitting of the kinetic traces to be the pseudo-first-order rate constants of $k_{\text{decay}} = (4-7) \times 10^5$ s^{-1} (Table 1), while $k_{\text{decay}} = 1 \times 10^5$ s^{-1} for **1j**$^{\bullet+}$ was much smaller (Figure 2). The pseudo-first-order decay of Ar$_3$P$^{\bullet+}$ corresponds to the dimerization of Ar$_3$P$^{\bullet+}$ with Ar$_3$P to form phosphine dimer radical cation(Ar$_3$P−PAr$_3$)$^{\bullet+}$.[8] The dimerization of **1j**$^{\bullet+}$ with **1j** seems to be suppressed by the steric effects of two *o*-methyl substituents on the phenyl ring of **1j**.

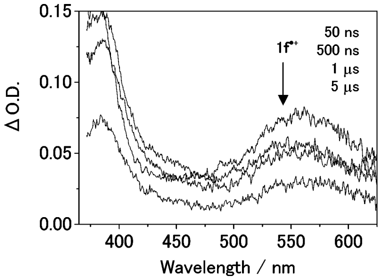

FIGURE 1. Transient absorption spectra observed at 50 ns, 500 ns, 1 μs, and 5 μs after an electron pulse during the pulse radiolysis of **1f** (10 mM) in argon-saturated PhCN.

TABLE 1. Absorption Peak (λ_{max}), Reactivities of 1$^{\bullet+}$ (k_{decay} (Ar) and k_{O_2}), and the Summation of the Hammett's Substituent Constant ($\Sigma\sigma^\bullet$)

radical cation (**1**$^{\bullet+}$)	$\lambda_{\max}$[a] (nm)	k_{decay} (Ar)[b] (10^5 s^{-1})	k_{O_2}[c] (10^8 M^{-1} s^{-1})	$\Sigma\sigma^{\bullet}$[e]
1a$^{\bullet+}$	380, 530	4.2	0.65	0
1b$^{\bullet+}$	380, 550	6.0	0.46	0.39
1c$^{\bullet+}$	380, 550	3.6	0.74	0.39
1d$^{\bullet+}$	380, 550	6.6	2.4	1.17
1e$^{\bullet+}$	380, 540	3.9	9.3	*d*
1f$^{\bullet+}$	380, 550	3.9	17	1.17
1g$^{\bullet+}$	380, 600	4.9	19	1.26
1h$^{\bullet+}$	380, 550	7.4	2.6	*d*
1i$^{\bullet+}$	380, 550	4.9	16	*d*
1j$^{\bullet+}$	−, 600	1.4	13	3.51
1k$^{\bullet+}$	380, 540	6.7	1.9	0.36
1l$^{\bullet+}$	380, 560	5.2	2.2	0.36

[a] Wavelength of the **1**$^{\bullet+}$ transient absorption peaks. "−" denotes "not detected". [b] Apparent decay rate constant according to the first-order rate equation under Ar atmosphere. Experimental error of ±10%. [c] Bimolecular rate constant obtained from the plot of the pseudo-first-order rate constant vs concentration of O$_2$. The concentration of O$_2$ for the O$_2$-saturated PhCN has been reported to be 8.5×10^{-3} M in ref 9. [d] Not available. [e] The $\sigma^\bullet$ values are taken from ref 10.

The pulse radiolysis of **1f** was examined also in 1,2-dichloroethane and benzene. The transient absorption observed in these solvents, although the absorbance was smaller than in PhCN, showed the maxima at 380 and 550 nm and was assigned to **1f**$^{\bullet+}$. Nevertheless, the decay of **1f**$^{\bullet+}$ was much faster in these solvents than in PhCN and could not be followed precisely. Therefore, we used PhCN as the solvent to study the formation and reaction of Ar$_3$P$^{\bullet+}$.

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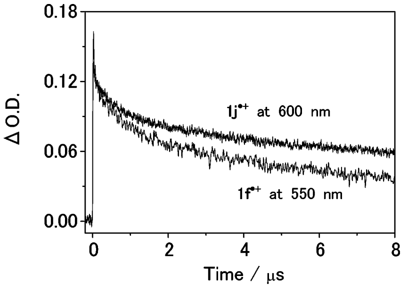

FIGURE 2. Time profiles of ΔOD obtained at 550 and 600 nm, assigned to $\mathbf{1f}^{\bullet+}$ and $\mathbf{1j}^{\bullet+}$, respectively, observed after an electron pulse during the pulse radiolysis of **1f** and **1j** (10 mM) in argon-saturated PhCN.

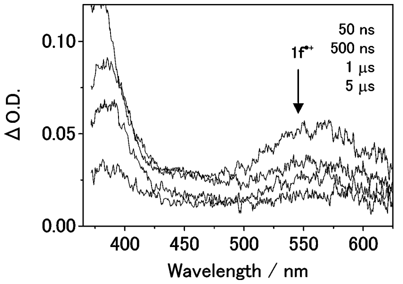

FIGURE 3. Transient absorption spectra observed at 50 ns, 500 ns, 1 μs, and 5 μs after an electron pulse during the pulse radiolysis of **1f** (10 mM) in O_2-saturated PhCN.

Since no transient absorption of $Ar_3P^{\bullet-}$ and $^3Ar_3P^{*11}$ was observed in the region of 500−700 nm, the formation of $Ar_3P^{\bullet-}$ and $^3Ar_3P^*$ is neglected during the pulse radiolysis of Ar_3P in PhCN.

Reactions of $Ar_3P^{\bullet+}$ with O_2. Figure 3 shows the transient absorption spectra observed after an electron pulse during the pulse radiolysis of **1f** in O_2-saturated PhCN, which were similar to that in argon-saturated PhCN. The time profile of the transient absorption at 550 nm (Figure 4) shows that the decay of $\mathbf{1f}^{\bullet+}$ was accelerated to be $k_{decay} = 2.3 \times 10^7$ s^{-1}. The k_{decay} value depended on the concentration of O_2 (8.5×10^{-3} M for the O_2-saturated PhCN[9]), suggesting that $\mathbf{1f}^{\bullet+}$ reacts with O_2 bimolecularly. The second-order rate constant (k_{O2}) for the reaction of $\mathbf{1f}^{\bullet+}$ with O_2 (eq 4) was calculated to be 1.7×10^9 M^{-1} s^{-1} in PhCN.

$$\mathbf{1f}^{\bullet+} + O_2 \rightarrow (\mathbf{1f}\text{-}O_2)^{\bullet+} \tag{4}$$

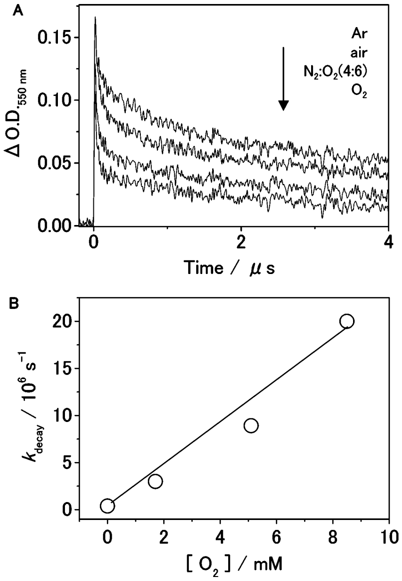

FIGURE 4. (A) Time profiles ΔOD obtained at 550 nm, assigned to $\mathbf{1f}^{\bullet+}$, observed after an electron pulse during the pulse radiolysis of **1f** (10 mM) in argon, air, N_2/O_2 (4:6), and O_2-saturated PhCN. (B) Plot of pseudo-first-order rate constant (k_{decay}) vs concentration of O_2.

Pulse radiolyses of other Ar_3P in O_2-saturated PhCN were examined. The results are summarized in Table 1. The reaction of tris(*p*-anisyl)phosphine radical cation ($\mathbf{1g}^{\bullet+}$) with O_2 was found to occur at $k_{O2} = 1.9 \times 10^9$ M^{-1} s^{-1}. The k_{O2} values were similar to those for the reactions of carbon-centered radicals such as para-substituted benzyl radicals with O_2.[12] The finding that $\mathbf{1}^{\bullet+}$ reacts with O_2 at the rate constant of $k_{O2} = 10^8$−10^9 M^{-1} s^{-1} is surprising because radical cations generally do not react with O_2 or react slowly with O_2. Nelsen reported the radical cation catalyzed chain oxygenation of alkylated olefins and dienes, although the peroxy intermediate was not spectroscopically detected.[13] As only one example of a kinetic study on the reactivity of radical cations toward O_2, we have reported that *p*-methoxy-substituted stilbene radical cations react with O_2 at $k_{O2} = (1.2$−$4.5) \times 10^7$ M^{-1} s^{-1} during pulse radiolysis and laser flash photolysis.[14] The high reactivity of the radical cation toward O_2 corresponds to the localization of unpaired electron and positive charge on the α- and β-olefinic carbons, respectively, induced specifically by the *p*-methoxyl substituent on the phenyl ring of stilbene radical cations. On the basis of the product analysis, there are several reports on the reactivity of radical cations toward O_2. Addition reactions of radical cations of aromatic compounds, such as aryl-substituted cyclopropanes and cyclobutanes, and aromatic alkenes, with O_2 have been reported to yield the corresponding peroxyl radical cations by several groups with assumption of 1,ω-distonic radical cations.[15−18] Mizuno et al. investigated the formation of 1,4-radical cations of 1,ω-bis(diarylethenyl)alkanes and its trapping by molecular oxygen.[15] Fukuzumi et al. reported that 1,4-dimer radical cation of aromatic alkene reacts with O_2 to produce the 1,6-peroxyl radical cation[16] and that O_2 adds to α-methylstyrene radical cation to give the peroxyl radical cation, which may transform to the more stable dioxetane radical cation.[17] Tokumaru et al.

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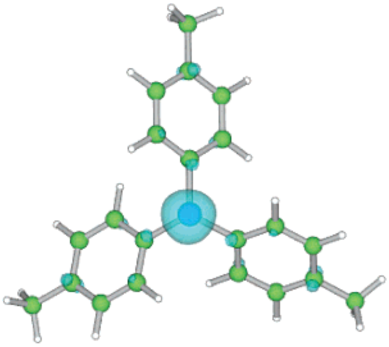

FIGURE 5. Optimized structure and spin distribution of **1f**$^{\bullet+}$ obtained by the density functional theory at UB3LYP/6-31G* level.

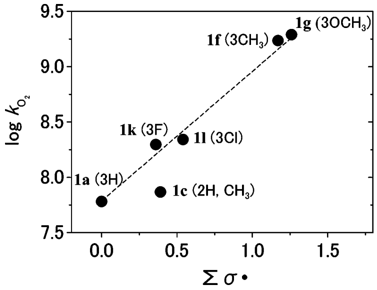

FIGURE 6. Plot of log k_{O2} vs $\Sigma\sigma^{\bullet}$ for various *para*-substituted $Ar_3P^{\bullet+}$ in O_2-saturated PhCN.

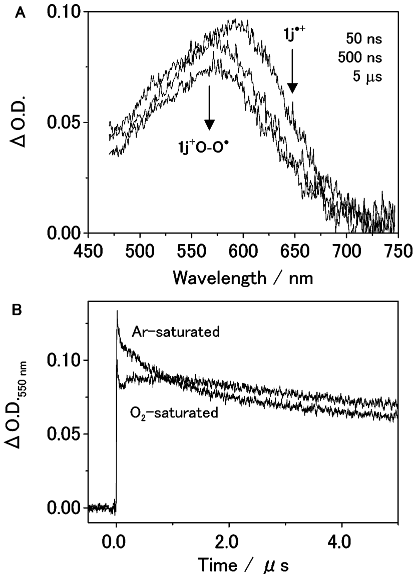

FIGURE 7. (A) Transient absorption spectra observed at 50 ns, 500 ns, and 5 μs after an electron pulse during the pulse radiolysis of **1j** (10 mM) in O_2-saturated PhCN. (B) Time profiles of ΔOD obtained at 550 nm during the pulse radiolysis of **1j** in argon- or O_2-saturated PhCN.

reported the interaction between stilbene radical cations with O_2.[18] However, factors controlling the reactivities of radical cations toward O_2 are not clear. The k_{O2} values of free benzyl radical and **1f**$^{\bullet+}$ are found to be two orders larger than those for stilbene radical cation, suggesting that an unpaired electron is completely localized on the phosphorus atom in $Ar_3P^{\bullet+}$. It has been reported that the unpaired electron should be localized on the phosphorus atom of **1f**$^{\bullet+}$.[19] The optimized structure of **1f**$^{\bullet+}$ calculated using the density functional theory is shown in Figure 5, indicating that the unpaired electron of **1f**$^{\bullet+}$ is localized on the phosphorus atom. The localization of the unpaired electron on the phosphorus atom was confirmed for all $Ar_3P^{\bullet+}$ by the theoretical calculation.

For the bimolecular reaction of free benzyl radical with O_2, the electronic effect of *para* substituents on the phenyl ring has been observed on k_{O2}.[12] The similar remarkable *para* substituent effect on the k_{O2} value for **1a**$^{\bullet+}$–**1e**$^{\bullet+}$ was found, while almost the same k_{O2} value, $(1.7 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, was obtained for **1f**$^{\bullet+}$, **1g**$^{\bullet+}$, and **1j**$^{\bullet+}$. As shown in Figure 6, a linear correlation was found for the plot of k_{O2} against $\Sigma\sigma^{\bullet}$, which is the summation of the Hammett's substituent constant $\sigma^{\bullet}$,[10] for the *para* substituents on the phenyl rings of Ar_3P. The $\sigma^{\bullet}$ scale has been defined for the homolytic cleavage of dibenzylmercury as a measure of the spin density developing on the benzyl carbon atom at the transition state. The k_{O2} value for **1c**$^{\bullet+}$ was slightly smaller than that expected from $\Sigma\sigma^{\bullet}$. It is suggested that the structural and electronic properties may change slightly between **1c**$^{\bullet+}$ and other **1**$^{\bullet+}$ (**1a**$^{\bullet+}$, **1f**$^{\bullet+}$, **1g**$^{\bullet+}$, **1k**$^{\bullet+}$, and **1l**$^{\bullet+}$) which have one and three *para*-substituted phenyl groups on the phosphorus atom of **1**$^{\bullet+}$, respectively.

The HOMO of Ar_3P is the nonbonding orbital (n-orbital) of the phosphorus atom.[20] Therefore, an electron is removed from the n-orbital of the phosphorus. Since the positive charge of the phosphorus atom is more delocalized in **1f**$^{\bullet+}$ and **1g**$^{\bullet+}$ than in other $Ar_3P^{\bullet+}$ because of the π-electron conjugation including the phenyl rings, the k_{O2} values of **1f**$^{\bullet+}$ and **1g**$^{\bullet+}$ are larger than that of **1a**$^{\bullet+}$.

Alternatively, $Ar_3P^{\bullet+}$ could undergo radical coupling with the superoxide radical anion ($O_2^{\bullet-}$) generated by the electron transfer from $PhCN^{\bullet-}$ to O_2. In this case, the decay of $Ar_3P^{\bullet+}$ would follow the second-order kinetics. However, the decay of $Ar_3P^{\bullet+}$ was analyzed by the pseudo-first-order kinetics. Thus, taking into account the fact that the concentration of $O_2^{\bullet-}$ is lower than that of $PhCN^{\bullet-}$ (approximately 1×10^{-5} M) generated initially during pulse radiolysis, the pseudo-first-order rate constant is predicted to be smaller than 10^5 s^{-1}, assuming that the second-order rate constant is diffusion-limited. This value is not consistent with the observed k_{O2} of 10^6–10^7 s^{-1}, indicating that the radical coupling between $Ar_3P^{\bullet+}$ and $O_2^{\bullet-}$ can be eliminated from the $Ar_3P^{\bullet+}$ decay mechanism.

The present work is the first example to clarify that the reactivity of $Ar_3P^{\bullet+}$ toward O_2 is controlled predominantly by the electron density of the phosphorus atom.

Figure 7A shows the transient absorption spectra observed after an electron pulse during the pulse radiolysis of trimesitylphosphine **1j** in O_2-saturated PhCN. The transient absorption of **1j**$^{\bullet+}$ observed at 50 ns after an electron pulse was similar to that in argon-saturated PhCN. The transient absorption of **1j**$^{\bullet+}$ with a peak at 600 nm decayed in the time scale of a few hundreds nanoseconds and shifted to the shorter wavelength side to have a peak at 570 nm. The similar spectral change has been also observed for the reaction of 1,1-dianisylethylene dimer radical cation with O_2, where the dimer radical cation having a peak at 490 nm reacts with O_2 to give the peroxyl radical cation with a peak at 500 nm.[16] In the presence of oxygen, the transient absorption at 550 nm decayed within 100 ns, accompanied by the formation of new absorption as shown in Figure 7B.

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Therefore, the observed absorption spectrum with a peak at 570 nm can be reasonably assigned to the peroxyl radical cation of **1j** ((2,4,6-$(CH_3)_3C_6H_2)_3P^+OO^\bullet$) (eq 5)

$$\mathbf{1j}^{\bullet+} + O_2 \rightarrow (2,4,6\text{-}(CH_3)_3C_6H_2)_3P^+OO^\bullet \qquad (5)$$

and (2,4,6-$(CH_3)_3C_6H_2)_3P^+OO^\bullet$ was found to be very stable species with a lifetime of longer than 10 μs estimated from the decay profile of the transient absorption. The transient absorption spectral changes for $\mathbf{1d}^{\bullet+}$ and $\mathbf{1h}^{\bullet+}$ with an *o*-methyl substituent were similar to those observed for $\mathbf{1j}^{\bullet+}$ (Supporting Information, S2). For example, the absorption spectrum with a peak at 560 nm, assigned to the corresponding peroxy radical cation, was observed at 100 ns after an electron pulse during the pulse radiolysis of **1d** in PhCN under O_2 atmosphere.

Reaction of $Ar_3P^+OO^\bullet$. A transient absorption of Ar_3P^+-$OO^\bullet$ was not observed during the bimolecular reaction of $Ar_3P^{\bullet+}$ having no *o*-methyl substituent with O_2, suggesting that a lifetime of these peroxy radical cations is very short. The reaction of $Ar_3P^{\bullet+}$ with O_2 gives the corresponding phosphine oxide ($Ar_3P{=}O$) as the final product in nearly quantitative yield through the formation and decomposition of $Ar_3P^+OO^\bullet$. Neta et al. proposed that $Ph_3P^+OO^\bullet$ has no significant absorbance at λ >300 nm and that a chain reaction occurs involving the electron transfer from Ar_3P to $Ar_3P^+OO^\bullet$(eq 6) during the γ-radiolysis of Ar_3P in CH_2Cl_2.[4]

$$Ar_3P^+OO^\bullet + Ar_3P \rightarrow Ar_3P^+OO^- + Ar_3P^{\bullet+} \qquad (6)$$

Peroxyl radicals oxidize organic compounds by a mechanism involving either electron transfer or hydrogen atom and oxygen atom transfer. The electron transfer from organic compounds to peroxy radical can occur in a halogenated peroxyl radical in polar solvent such as water and alcohol.[21] On the other hand, *tert*-butylperoxy radicals reacts rapidly with **1a** to give *t*-$BuOOP^\bullet$-Ph_3.[22] Similarly, $Ar_3P^+OO^\bullet$ may not only act as a one-electron oxidant. Thus, another possible mechanism is oxidation of Ar_3P involving oxygen atom transfer from $Ar_3P^+OO^\bullet$ to Ar_3P to give $Ar_3P^+O^\bullet$ and $Ar_3P{=}O$ (eq 7) followed by electron transfer from Ar_3P to $Ar_3P^+O^\bullet$ to give $Ar_3P^{\bullet+}$ and $Ar_3P{=}O$ (eq 8) [4a]

$$Ar_3P^+OO^\bullet + Ar_3P \rightarrow [Ar_3P^+OOP^\bullet Ar_3] \rightarrow Ar_3P^+O^\bullet + Ar_3P{=}O \qquad (7)$$

$$Ar_3P^+O^\bullet + Ar_3P \rightarrow Ar_3P{=}O + Ar_3P^{\bullet+} \qquad (8)$$

Equation 7 is similar to that suggested for the reaction of *tert*-butylperoxyl radical ($ROO^\bullet$) with a trivalent phosphorus atom through the four-coordinate phosphoranyl radical ($Ar_3P^\bullet$-$OOPAr_3$), which undergoes the β scission to give the oxidation products, $Ar_3P{=}O$ and $Ar_3P^+O^\bullet$. Generally, the oxyl radicals ($RO^\bullet$) are stronger oxidants than the corresponding peroxyl radicals ($ROO^\bullet$).[23] The oxyl radical cations ($Ar_3P^+O^\bullet$) are also stronger oxidants than the corresponding peroxyl radical cations ($Ar_3P^+OO^\bullet$).[24] Therefore, the oxyl radical cations should readily oxidize Ar_3P via eq 8 to produce $Ar_3P^{+\bullet}$. Fukuzumi et al. reported that the oxygen atom transfer occurs from cumylperoxy radical to Ar_3P to give cumyl oxy radical and $Ar_3P{=}O$ rather than the electron transfer from Ar_3P to cumylperoxy radical.[25]

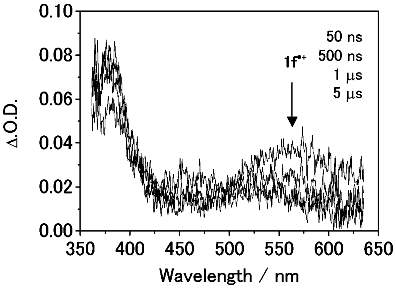

FIGURE 8. Transient absorption spectra observed at 50 ns, 500 ns, 1 μs, and 5 μs after an electron pulse during the pulse radiolysis of **1f** (10 mM) and MeOH (200 mM) in argon-saturated PhCN.

In the case of Ar_3P having no *o*-methyl, the absorption spectrum of $Ar_3P^{\bullet+}$ was observed even at 10 μs after an electron pulse during the pulse radiolysis of Ar_3P at high concentrations in O_2-saturated PhCN. This absorption corresponds to $Ar_3P^{\bullet+}$ regenerated via eq 8.

Since no absorption spectrum of reproduced $Ar_3P^{\bullet+}$ was observed for the reactions of $\mathbf{1d}^{\bullet+}$, $\mathbf{1h}^{\bullet+}$, and $\mathbf{1j}^{\bullet+}$, the *o*-methyl substituents prevent the formation of dimeric radical cation $Ar_3P^+OOP^\bullet Ar_3$. Consequently, the corresponding $Ar_3P^+OO^\bullet$ with *o*-methyl substituents have long enough lifetimes for the spectroscopic detection. This result shows the steric inhibition by *o*-methyl substituents on the radical attack. In fact, the yield of $Ar_3P{=}O$ from the reaction of *o*-methyl-substituted $Ar_3P^{\bullet+}$ with O_2 was considerably low.[5b]

It is found that $Ar_3P^{\bullet+}$ reacts with O_2 much faster than with methanol, which is explained by considerable localization of the lone-pair electron on the phosphorus atom but not much localization of the positive charge on the phosphorus atom of $Ar_3P^{\bullet+}$. Such properties of $Ar_3P^{\bullet+}$ are different from those of other various radical cations which react with methanol at the diffusion-controlled rate. Figure 8 shows the transient absorption spectra observed after an electron pulse during the pulse radiolysis of **1f** in the presence of methanol with the concentrations of 2.0×10^{-1} M. This spectrum was in good agreement with those of $\mathbf{1f}^{\bullet+}$ in the absence of methanol. The yield of $\mathbf{1f}^{\bullet+}$ in PhCN decreased with the addition of methanol, although the decay rate of $\mathbf{1f}^{\bullet+}$ in the presence of methanol was similar to that of $\mathbf{1f}^{\bullet+}$ in the absence of methanol. Therefore, the rate constant for the addition reaction of $\mathbf{1f}^{\bullet+}$ with methanol is suggested to be slower than 1×10^7 M^{-1} s^{-1} in PhCN.

Conclusions

The $Ar_3P^{\bullet+}$ exhibited two absorption bands in the 350−400 and 500−600 nm regions immediately after an electron pulse in PhCN. In the presence of O_2, the addition of O_2 to the phosphorus atom of $Ar_3P^{\bullet+}$ takes place at the rate constant of 10^7−10^9 M^{-1} s^{-1} to yield the triarylphosphine peroxyl radical cation ($Ar_3P^+OO^\bullet$). Electron-releasing substituents on the para position of the phenyl ring affected the rate constants of the reaction of $Ar_3P^{\bullet+}$ with O_2. The positive charge of the phosphorus atom is delocalized in $Ar_3P^{\bullet+}$ because of the

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π-electrons conjugation of the aromatic ring, while an unpaired electron is localized on the phosphorus atom of $Ar_3P^{\bullet+}$. Therefore, the rate constants of $Ar_3P^{\bullet+}$ with O_2 are larger than that of $Ar_3P^{\bullet+}$ with methanol. The present study has shown that $Ar_3P^{\bullet+}$ exhibits a free-radical character rather than a cationic character for the phosphorus atom. $Ar_3P^+OO^\bullet$ undergoes the radical attack to Ar_3P, producing a dimeric radical cation Ar_3P^+-$OOP^\bullet Ar_3$ as the key intermediate in which one phosphorus atom has an unpaired electron and other one has positive charge. *o*-Methyl substituents on the phenyl ring of Ar_3P lowers the reactivity toward peroxyl radical cation $Ar_3P^+OO^\bullet$ to form the dimeric radical cation $Ar_3P^+OOP^\bullet Ar_3$.

Experimental Section

Materials. Ar_3P compounds **1a**−**1l** were used after recrystallization from ethanol. HPLC-grade PhCN was used as solvent without further purification.

Pulse Radiolysis. Pulse radiolysis experiments were performed using an electron pulse (28 MeV, 8 ns, 0.87 kGy per pulse) from a linear accelerator at Osaka University. All experiments were performed in PhCN saturated with argon or O_2 gas for 20 min through a capillary. A 1-mL solution was placed in a quartz cell (10 × 5 × 40 mm) and sealed with a silicon rubber stopper. The kinetic measurements were performed using a nanosecond photoreaction analyzer system. The monitor light was obtained from a pulsed 450-W Xe arc lamp, which was operated by a large current pulsed-power supply synchronized with the electron pulse. The monitor light was passed through an iris with a diameter of 0.2 cm and sent into the sample solution at a perpendicular intersection to the electron pulse. The monitor light passing through the sample was focused on the entrance slit of a monochromator and detected with a photomultiplier tube. The transient absorption spectra were measured using a photodiode array with a gated image intensifier as a detector.

Theoretical Calculations. Optimized structures of $Ar_3P^{\bullet+}$ were estimated by density functional theory at the UB3LYP/6-31G* level, as the most stable one with the absence of the imaginary frequencies among various equilibrated structures.

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Supporting Information Available: Transient absorption spectra observed during the pulse radiolysis of **1a**−**l** in PhCN. This material is available free of charge via the Internet at http://pubs.acs.org.

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