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Kinetics of the Autoxidation of Dialkyl Phenylphosphonites*

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The kinetics and mechanism for the autoxidation of trialkylphosphine and trialkyl phosphite have been reported,[1,2] but little is known about the autoxidation of phosphonite and phosphinite. The present note reports our kinetic study on the radical-initiated autoxidation of dialkyl phenylphosphonite in *o*-dichlorobenzene to discuss the mechanism.

Results and Discussion

The autoxidation of dimethyl phenylphosphonite (I) at 60—80°C with 2,2′-azobisisobutyronitrile (AIBN) gave quantitatively dimethyl phenylphosphonate. The observed stoichiometry is shown in Table 1, and expressed as Eq. (1). No reaction of I with AIBN or *o*-dichlorobenzene was observed.

$$PhP(OR)_2 + \frac{1}{2}O_2 \longrightarrow PhP(O)(OR)_2 \qquad (1)$$

(I) $R=Me$
(II) $R=Et$
(III) $R=i\text{-}Pr$

Table 1. The stoichiometry in autoxidation of dimethyl phenylphosphonite in *o*-dichlorobenzene at 60°C[a)]

$PhP(OMe)_2$ (10^{-4} mol)	O_2 absorption (10^{-4} mol)	$O/PhP(OMe)_2$[b)]
5.55	2.68	0.97
6.61	3.24	0.98

a) 5×10^{-6} mol of AIBN was used.
b) The ratio of consumed amount of atomic oxygen to phosphonite.

The autoxidation of dimethyl phenylphosphonite (I) in *o*-dichlorobenzene with AIBN at 60°C was followed by measuring the consumption of O_2 in the apparatus previously reported by us.[4)] The effects of concentration of I, partial pressure of O_2 (p) and concentration of AIBN are shown in Table 2, which shows that the rate law of autoxidation of dimethyl phenylphosphonite (I) in *o*-dichlorobenzene is expressed as Eq. (2) up to 70—85% conversion.

Table 2. Autoxidation of dimethyl phenylphosphonite in *o*-dichlorobenzene at 60.0°C

Partial pressure of O_2 (mmHg)	$[PhP(OMe)_2]_0$[a)] (10^{-2} M)	$[AIBN]_0$[a)] (10^{-3} M)	10^4k_a[b)] (sec^{-1})
200	1.31	5.39	5.00
200	3.92	5.39	4.02
200	6.54	5.39	4.84
200	5.94	9.25	10.4
200	5.94	4.62	4.50
200	5.94	2.31	3.22
200	5.94	0.00	0.0
420	5.55	4.42	6.17
200	5.55	4.42	6.17
100	5.55	4.42	6.15

a) [ ]$_0$ means initial concentration.
b) Pseudo-first-order rate constant.

$$v = -\frac{d[O_2]}{dt} = k[PhP(OMe)_2][AIBN] \qquad (2)$$

The value of k was calculated to be $0.105\,\text{M}^{-1}\text{sec}^{-1}$ at 60.0°C.

The autoxidation of dialkyl phenylphosphonite was found to involve radical intermediates, since no autoxidation occurs without AIBN. The zero-order dependence of rate on oxygen pressure (p) was observed. The same phenomenon has been observed in the autoxidation of tributyl phosphite.[1b)] This suggests a mechanistic similarity of the autoxidation of phosphonite to that of phosphite. The first-order dependence on AIBN concentration suggests that the autoxidation may involve a unimolecular termination.[5)] The autoxidation product of dialkyl phenylphosphonites was the corresponding phosphonates. These results suggest the following mechanism.

$$AIBN \xrightarrow{k_i} 2R'\cdot + N_2 \qquad (3)$$

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* Contribution No. 178.

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$$\text{R}'\cdot + \text{O}_2 \xrightarrow{k_1} \text{R}'\text{O}_2\cdot \tag{4}$$

$$\text{R}'\text{O}_2\cdot + \text{PhP(OR)}_2 \xrightarrow{k_2} \text{PhP(O)(OR)}_2 + \text{R}'\text{O}\cdot \tag{5}$$

$$\text{R}'\text{O}\cdot + \text{PhP(OR)}_2 \xrightarrow{k_3} \text{PhP(O)(OR)}_2 + \text{R}'\cdot \tag{6}$$

$$\text{R}'\text{O}_2\cdot \xrightarrow{k_t} \text{inactive product} \tag{7a}$$

$$\text{R}'\text{O}\cdot \xrightarrow{k'_t} \text{inactive product} \tag{7b}$$

Here, R is Me, Et, and *i*-Pr, and R'· is Me$_2\dot{\text{C}}$CN. Even if O_2 may be produced from steps 7a and 7b, the amount of formed O_2 is negligible when the radical chain length is long enough. Thus the rate of absorption of O_2 is expressed as:

$$v = -\text{d}[\text{O}_2]/\text{d}t = k_1[\text{R}'\cdot][\text{O}_2] \tag{8}$$

If the termination occurs *via* step 7a alone, the application of steady state method assuming approximate constant concentrations of R'O_2·, R'O·, and R'· as probable carriers leads to Eq. (9).

$$v = 2k_i[\text{AIBN}] + \frac{2k_ik_2}{k_t}[\text{AIBN}][\text{PhP(OR)}_2] \tag{9}$$

Since $k_t \ll k_2$, Eq. (9) is reduced to Eq. (10).

$$v = k[\text{AIBN}][\text{PhP(OR)}_2] \tag{10}$$

Here, $k=2k_ik_2/k_t$

If the termination is effected by step 7b alone, the analogous derivation gives Eq. (11).

$$v = k'[\text{AIBN}][\text{PhP(OR)}_2] \tag{11}$$

Here, $k'=2k_ik_3/k'_t$

In general, R'O· seems to be more reactive than R'O_2· with dialkyl phenylphosphonites.[6] Therefore, the unimolecular termination of R'O_2· is more probable than that of R'O·. The other termination mechanisms (*e.g.*, R'· → inactive product or simultaneous reactions of Eqs. (7a) and (7b)) lead rate equations conflicted with the observed rate law.

The effect of substituent R of PhP(OR)$_2$ on the autoxidation rate was estimated in *o*-dichlorobenzene at 60.0°C. The rate law for PhP(OR)$_2$ [R=Et (II) and R=*i*-Pr (III)] was the same as that of PhP(OMe)$_2$. The second-order rate constants (k) for R at 60.0°C were Me, 0.105; Et, 0.110; *i*-Pr, 0.112$\text{M}^{-1}\text{sec}^{-1}$. The Taft plot for PhP(OR)$_2$ gives a ρ^* value of -0.058 (correlation coefficient, r, -0.95). Hence, the substituents in dialkyl phenylphosphonites affects the autoxidation rate much more than that of the radical intermediate.

The radical chain length (*CL*) was calculated to be 200—2000 by means of Eq. (12), using values of $a=0.6$ and $k_i=3.2\times10^{-6}\ \text{sec}^{-1}$.[1b]

$$\begin{aligned} CL &= (k_2[\text{R}'\text{O}_2\cdot] + k_3[\text{R}'\text{O}\cdot])[\text{PhP(OR)}_2]_0/2ak_i[\text{AIBN}]_0 \\ &= k_a[\text{PhP(OR)}_2]_0/2ak_i[\text{AIBN}]_0 \end{aligned} \tag{12}$$

Here, a is the efficiency of initiation and k_i is the decomposition rate of radical initiator (AIBN), and k_a is an apparent first-order rate constant.[1b]

Experimental

Materials. Phenylphosphonous dichloride was prepared by the Friedel-Crafts reaction of benzene with PCl_3,[8] bp 101—104°C/17 mmHg (lit,[8] bp 68—70°C/1 mmHg), yield 68%. Dimethyl phenylphsophonite was prepared by the esterification of phenylphosphonous dichloride,[9] bp 101—102°C/23 mmHg (lit,[9] bp 98°C/17 mmHg), yield 30%. Diethyl and diisopropyl phenylphosphonites were also prepared by the similar procedure; bp and yield were 78—79°C/8 mmHg (lit,[10] bp 110—111°C/10—13 mmHg), 27% and 82—85°C/8 mmHg (lit,[11] bp 121—122°C/10 mmHg), 11%, respectively. Dimethyl phenylphosphonate was prepared by the Ullmann reaction of trimethyl phosphite with iodobenzene,[12] bp 122—125°C/7 mmHg (lit,[12] bp 115°C/0.9 mmHg), yield 35%. Diisopropyl phenylphosphonate was prepared by the esterification of phenylphosphonic dichloride, bp 116—117°C/3 mmHg (lit,[12] bp 94°C/0.1 mmHg), yield 33%. All phosphonates were identified by IR (a Perkin-Elmer Model 337 spectrophotometer) and NMR (a JNM-C-60HL spectrometer). Commercial solvents, AIBN, O_2, and N_2 were purified by ordinary methods and used.

Product Analysis. The autoxidation product of dialkyl phenylphosphonite was confirmed to be the corresponding phosphonate alone by means of glc (a Yanagimoto GCG 550F gas chromatograph with a flame ion detector) with 3% Apiezone Grease L on Cellite 545 using programming attachment.

Kinetic Procedure. The autoxidation apparatus has been reported previously.[4] A typical kinetic run was as follows: O_2 gas at 200 mmHg and N_2 gas at 350 mmHg were mixed in the apparatus and introduced into the reaction vessel at 60.0°C containing $6.54\times10^{-2}\text{M}$ dimethyl phenylphosphonite in *o*-dichlorobenzene (10 m*l*), then $5.39\times10^{-3}\text{M}$ AIBN in *o*-dichlorobenzene (1 m*l*) was added into it. The reaction was started with vigorous stirring. The partial pressure difference between the reaction mixture and the reference solution was measured at appropriate intervals of time. The observed pseudo-first-order rate constant was calculated by means of Eq. (13).

$$\log(a-2x) = -\frac{2}{2.303}k_at + \log a \tag{13}$$

Here, a and a-$2x$ are the concentrations of substrate at the start and at time t, respectively.

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