Kinetics of the Autoxidation of Trimethyl Phosphite, Methyl Diphenylphosphinite, and Triphenylphosphine

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Auotoxidation of trimethyl phosphite, methyl diphenylphosphinite, and triphenylphosphine has been studied kinetically in *o*-dichlorobenzene at 60·0 °C with 2,2′-azobisisobutyronitrile (AIBN) as a radical initiator. The autoxidation proceeded after a short induction period to give predominantly the corresponding quinquecovalent phosphorus compounds. The rates are always independent of oxygen pressure and the rate law for the first two compounds is $-d[O_2]/dt = k_2'[\text{AIBN}][\text{substrate}]$, which was analogous to that for dimethyl phenylphosphonite. The rate law for triphenylphosphine was $-d[O_2]/dt = k_1'[\text{AIBN}](1 + k_2'[\text{substrate}])$. The autoxidation may have a radical chain mechanism involving chain carriers R·, RO·, and RO_2·. The different kinetic behaviour of triphenylphosphine is attributable to the stability of a radical carrier, $Ph_3\dot{P}O_2R$, and resulting lower reactivity of RO_2· with Ph_3P. The rate constants decrease in the order: methyl diphenylphosphinite > trimethyl phosphite > triphenylphosphine. The application of Taft equation, $\log (k/k_0) = \rho^*\Sigma\sigma^*$, to trimethyl phosphite, methyl diphenylphosphinite, and dimethyl phenylphosphonite gives a ρ^* value of $-0{\cdot}380$, which implies a mechanism involving a nucleophilic attack of phosphorus atom.

TERVALENT phosphorus compounds such as trialkylphosphines and trialkyl phosphites are autoxidised photochemically or in the presence of a radical initiator.[1,2] The main products are quinquecovalent phosphorus

$$P(OEt)_3 \xrightarrow[\text{peroxide}]{O_2} P(O)(OEt)_3 \qquad (1)$$

$$PBu_3 \xrightarrow[\text{radical source}]{O_2} \underbrace{P(O)Bu_3 + P(O)(OBu)Bu_2}_{\text{major product}} + \underbrace{P(O)(OBu)_2Bu + P(O)(OBu)_3}_{\text{minor product}} \qquad (2)$$

compounds. A few workers have reported kinetic studies of their autoxidation, where the rate laws were $v = k[\text{AIBN}][Bu_3P]/p_{O_2}$ and $v = k[\text{AIBN}][(RO)_3P]$.[3] The autoxidation of phosphinites and phosphonites is scarcely known.[4,5] Our kinetic study on the autoxidation of dialkyl phenylphosphonites revealed the rate law $v = k[\text{AIBN}][PhP(OR)_2]$, and relatively long chain processes involving alkyl, alkoxy-, and alkylperoxy-radicals.[6] The rate of autoxidation was reported to be in the order $(BuO)_3P < Bu_3P$, but there was little systematic study and no convincing explanation of the order was presented.

We now report a kinetic study of the autoxidation of trimethyl phosphite, methyl diphenylphosphinite, and triphenylphosphine in *o*-dichlorobenzene initiated by 2,2′-azobisisobutyronitrile, and discuss the effect of their structure, including dimethyl phosphonite.

RESULTS

The autoxidation of trimethyl phosphite (I), methyl diphenylphosphinite (II), and triphenylphosphine (III) initiated by azobisisobutyronitrile was conducted in *o*-dichlorobenzene at 60·0 °C at oxygen pressures of 50—550 mmHg. The products were analysed by g.l.c., t.l.c., and i.r., and it was confirmed that compound (I) gave predominantly trimethyl phosphate, (II) gave methyl diphenylphosphinate, and (III) gave triphenylphosphine oxide. The rate of autoxidation was measured by a manometric method [6,7] at the total pressure of 550 mmHg.

Stoicheiometry.—The observed stoicheiometry is shown in Table 1. The autoxidation of tervalent phosphorus compounds needs 1 g-atom of oxygen [see equation (3)]. Therefore, the observed pseudo-first-order rate constants

TABLE 1

Stoicheiometric relationship for the autoxidations in *o*-dichlorobenzene at 60 °C

Compound	$10^4 \times$ Quantity (mol)	$10^5 \times$ AIBN (mol)	Partial pressure of O_2 (mmHg)	$10^4 \times O_2$ consumed (mol)	O : P [a]
(I) $(MeO)_3P$	6·50	1·64	400	2·64	0·93
	5·00	2·26	200	2·28	0·89
(II) $Ph_2P(OMe)$	2·16	1·19	200	2·18	1·01
	2·16	1·19	100	2·25	0·98
	2·16	1·19	100	2·12	1·04
(III) Ph_3P	4·78	1·24	200	2·37	0·99
	4·78	1·24	200	2·46	1·03
	4·78	1·24	400	2·29	0·96

[a] The ratio of consumed atomic oxygen to used tervalent phosphorus compound.

$$R^1R^2R^3P + \tfrac{1}{2}O_2 \xrightarrow[60^\circ]{\text{AIBN}} R^1R^2R^3PO \qquad (3)$$

(I) $R^1 = R^2 = R^3 = MeO$
(II) $R^1 = R^2 = Ph,\ R^3 = MeO$
(III) $R^1 = R^2 = R^3 = Ph$

(k_{1a}) were calculated by means of equation (4) where

$$\log (a - 2x) = -\frac{2}{2{\cdot}303}\,k_{1a}t + \log a \qquad (4)$$

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

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Autoxidation of $(MeO)_3P$ *and* $Ph_2P(OMe)$.—The conditions, results, and rate constants are shown in Tables 2 and 3, and are in accordance with equations (5) and (6).

TABLE 2

Autoxidation of trimethyl phosphite in *o*-dichlorobenzene at 60·0 °C

Partial pressure of O_2 (mmHg)	Initial concn. (M) $10^2[(I)]_0$	10^3 [AIBN]$_0$	10^4k_{1a}/s^{-1}	$10^2k_2'$/l mol^{-1} s^{-1}
50	10·8	2·78	2·18	7·99
100	10·8	2·78	2·02	
200	10·8	2·78	2·37	
400	10·8	2·78	2·29	
200	8·33	3·77	3·05	8·18
200	4·17	3·77	3·48	
200	2·08	3·77	2·94	
200	1·04	3·77	2·88	
200	8·33	1·89	1·73	8·81
200	8·33	0·943	0·821	8·72
200	8·33	0·471	0·451	9·58
200	8·33	0	0	
			Mean second-order rate constant	8·34

The rate is independent of the pressure of oxygen. The autoxidation of $Ph_2P(OMe)$ is faster than that of $PhP(OMe)_2$ for which k_2' is $1{\cdot}05 \times 10^{-1}$ l mol^{-1} s^{-1}.[6]

$$v = -d[O_2]/dt = k_{1a}[(I)] = k_2'[(I)][AIBN] \qquad (5)$$

$$v = k_{1a}[(II)] = k_2'[(II)][AIBN] \qquad (6)$$

Autoxidation of Ph_3P.—Table 4 shows that the rate is independent of oxygen pressure and has a first-order dependence on azobisisobutyronitrile concentration. The effect of the initial concentration of triphenylphosphine (III) is shown in Table 5. The plot of zero-order rate constant (k_0) against initial concentration of (III) gave an intercept at $2{\cdot}88 \times 10^{-7}$ mol l^{-1} s^{-1} (see Figure), the rate being expressed as equation (7). From the intercept

$$v = k_1'[AIBN](1 + k_2'[(III)]) \qquad (7)$$

and slope ($2{\cdot}22 \times 10^{-6}$ s^{-1}) in the Figure, the first-order rate constant (k_1') and the second-order rate constant (k_2') were calculated to be $1{\cdot}25 \times 10^{-4}$ s^{-1} and $1{\cdot}78 \times 10^{-2}$ l mol^{-1} s^{-1}, respectively.

TABLE 3

Autoxidation of methyl diphenylphosphinite in *o*-dichlorobenzene at 60·0 °C

Partial pressure of O_2 (mmHg)	Initial concn. (M) $10^2[(II)]_0$	10^3[AIBN]$_0$	10^4k_{1a}/s^{-1}	$10k_2'$/l mol^{-1} s^{-1}
100	4·12	1·98	7·48	3·94
200	4·12	1·98	7·91	
400	4·12	1·98	7·99	
550	4·12	1·98	7·77	
200	2·06	2·13	8·25	3·90
200	1·03	2·13	8·25	
200	0·515	2·13	8·47	
200	4·12	4·51	16·9	3·75
200	4·12	2·26	8·17	3·61
200	4·12	1·07	3·00	2·81
200	0·515	0	0	
			Mean second-order rate constant	3·76

TABLE 4

Autoxidation of triphenylphosphine in *o*-dichlorobenzene at 60·0 °C

Partial pressure of O_2 (mmHg)	Initial concn. (M) 10^2 [(III)]$_0$	10^3 [AIBN]$_0$	10^5k_{1a} [a]/ s^{-1}	$10^3k_1''$ [b]/ s^{-1}
100	7·29	2·25	4·77	1·55
200	7·29	2·25	4·87	1·58
400	7·29	2·25	5·04	1·63
550	7·29	2·25	6·00	1·94
200	7·97	1·83	5·70	2·48
200	7·97	0·915	3·19	2·78
200	7·97	0·458	1·41	2·45
200	7·97	0	0	

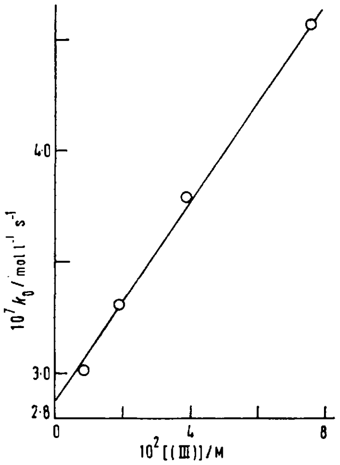
[a] Initial pseudo-first-order rate constant. [b] The value of k_1'' was calculated from $k_{1a}[(III)]_0 = k_1''$ [AIBN]$_0$.

TABLE 5

Dependence of rate on initial concentration of substrate in autoxidation of triphenylphosphine at 60·0 °C

Partial pressure of O_2 (mmHg)	Initial concn. (M) 10^2 [(III)]$_0$	10^3[AIBN]$_0$	10^5k_{1a} [a]/ s^{-1}	10^7k_0 [b]/ s^{-1}
200	7·61	2·30	6·00	4·57
200	3·81	2·30	10·0	3·81
200	1·90	2·30	17·4	3·30
200	0·95	2·30	31·5	3·00

[a] Initial pseudo-first-order rate constant. [b] The value of k_0 was calculated from $k_{1a}[(III)]_0 = k_0$.



Plot of zero-order rate constant (k_0) *vs.* initial concentration of (III). The intercept is $2{\cdot}88 \times 10^{-7}$ mol l^{-1} s^{-1} and the slope is $2{\cdot}22 \times 10^{-6}$ s^{-1}.

DISCUSSION

Tables 2—4 show that the autoxidations need a radical initiator, which suggests a radical mechanism for the reaction, as with trialkylphosphines and trialkyl phosphites.[1]

Autoxidation of Compounds (I) *and* (II).—The observed independence of rate on oxygen pressure (p),[3] the first-order dependence on initiator, as well as the formed products, show that the autoxidation of (I) and (II) may have a mechanism shown in reactions (8)—(12) involving a unimolecular termination of $RO_2\cdot$ or less probably $RO\cdot$,[8] which is similar to that of autoxidation

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[8] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 418.

of dialkyl phenylphosphonite.[6] Here, R^1, R^2, and R^3

$$\mathrm{AIBN} \xrightarrow{k_i} 2\mathrm{R}\cdot + \mathrm{N_2} \tag{8}$$

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{k_1} \mathrm{RO_2}\cdot \tag{9}$$

$$\mathrm{RO_2}\cdot + \mathrm{R^1R^2R^3P} \xrightarrow{k_2} \mathrm{R^1R^2R^3PO} + \mathrm{RO}\cdot \tag{10}$$

$$\mathrm{RO}\cdot + \mathrm{R^1R^2R^3P} \xrightarrow{k_3} \mathrm{R^1R^2R^3PO} + \mathrm{R}\cdot \tag{11}$$

$$\mathrm{RO_2}\cdot \xrightarrow{k_t} \text{inactive product} \tag{12a}$$

$$\mathrm{RO}\cdot \xrightarrow{k_t'} \text{inactive product} \tag{12b}$$

represent phenyl or methoxy-groups, and R is a radical species such as Me_2CCN.

Even if O_2 can be produced from steps (12a) and (12b), the amount of oxygen formed is negligible if the chain length is long. Thus the rate of absorption of oxygen is expressed as equation (13). The application

$$v = -\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_1[\mathrm{R}\cdot][\mathrm{O_2}] \tag{13}$$

of the steady-state method, on the assumption of the approximately constant concentrations of $R\cdot$, $RO\cdot$, and $RO_2\cdot$, leads to equation (14) as obtained previously.[6]

$$v = 2k_i[\mathrm{AIBN}] + 2k_ik_2k_t^{-1}[\mathrm{AIBN}][\mathrm{R^1R^2R^3P}] \tag{14}$$

When the chain is long, *i.e.*, $k_t \ll k_2$, equation (14) leads to equation (15) where $k = 2k_ik_2k_t^{-1}$. Therefore, the

$$v = k[\mathrm{AIBN}][\mathrm{R^1R^2R^3P}] \tag{15}$$

mechanism can be expressed by equations (8)—(12). Since $RO\cdot$ is a more reactive species than $RO_2\cdot$, equation (12a) may be the predominant termination step.

Autoxidation of Compound (III).—Because of the observed rate law for (III) [equation (7)] the first term on the right of equation (14) cannot here be neglected. Equation (14) coincides with the observed rate law. This shows that equations (8)—(12) are operating in the mechanism for (III) and that k_2/k_t for compound (III) is smaller than that for (I) or (II) and $(k_2/k_t)[R^1R^2R^3P]$ is comparable with unity. This may be attributable to the stability of the carrier radical, $R^1R^2R^3\dot{P}O_2R$ ($R^1 = R^2 = R^3 = Ph$) by resonance with phenyl groups.

Since the $RO\cdot$ radical is very reactive, the rate constant k_3 may be larger than k_2.

Substituent Effect in Tervalent Phosphorus Compounds.—The autoxidation rates which have the same rate-law increase in the order: $P(OMe)_3 < PhP(OMe)_2 < Ph_2P(OMe)$. Application of the Taft equation to their reaction rates gives equation (16) (Table 6). Here, $\Sigma\sigma^*$

$$\log(k/k_0) = -0{\cdot}380\Sigma\sigma^* \tag{16}$$

represents a sum of σ^* values for substituents in tervalent phosphorus compounds. The correlation coefficient (r) is $-0{\cdot}928$. The negative ρ^* value implies that a radical attack of phosphorus atom in equations (10) and (11) is nucleophilic, *i.e.*, $RO_2\cdot$ and $RO\cdot$ are electrophilic radicals toward the tervalent phosphorus compounds, although the trend is poor.

TABLE 6

Substituent effect in tervalent phosphorus compounds on the autoxidation rate in *o*-dichlorobenzene at 60·0 °C

	$10^2k_2'$/l mol^{-1} s^{-1}	$\log [k_2'/(k_2')_0]$	$\Sigma\sigma^*$ [b]
$P(OMe)_3$	8·34	0·000	4·38
$PhP(OMe)_2$ [a]	10·5	0·100	3·52
$Ph_2P(OMe)$	37·6	0·654	2·66

[a] Ref. 6. [b] The sum of σ^* (σ^* values for Ph and OMe groups are $+0{\cdot}600$ and $+1{\cdot}46$, respectively).

The Taft equation (17) was also applicable to the substituent effect in dialkyl phenylphosphonites, $PhP(OR)_2$ ($R = Me$, Et, and Pr^i).[6] The value of r was

$$\log(k/k_0) = -0{\cdot}058\sigma^* \tag{17}$$

$-0{\cdot}95$. The smaller negative ρ^* value, compared with that obtained in the present study, may be attributable to the β-position of the substituents for the reaction site.

It has been reported[3] that the autoxidation of Bu_3P was *ca.* 1·5 times faster than that of $(BuO)_3P$. This may be explained by the above substituent effect in tervalent phosphorus compounds.

Radical Chain Length.—The radical chain length (C. L.) can be calculated by means of equation (18),[6] by use of values of the efficiency of initiation (a) of 0·6 and the decomposition rate of radical initiator (k_i) of $3{\cdot}2 \times 10^{-6}$

$$\mathrm{C.\ L.} = k_a[\mathrm{R^1R^2R^3P}]_0/2ak_i[\mathrm{AIBN}]_0 \tag{18}$$

s^{-1},[3] and where k_a is an observed first-order rate constant. The calculated C. L. values were 500—5000, 1000—10,000, and *ca.* 860 for compounds (I), (II), and (III), respectively.

EXPERIMENTAL

Materials.—Trimethyl phosphite (I) was purified, b.p. 51° at 83 mmHg (lit.,[9] b.p. 111—112°). Methyl diphenylphosphinite (II) was prepared by disproportionation of phenylphosphonous dichloride $PhPCl_2$ [10] followed by esterification; overall yield 40%, b.p. 123—124° at 3 mmHg (lit.,[11] 151—152° at 10 mmHg). Trimethyl phosphate was synthesised from $POCl_3$ and MeONa [12] in 60% yield, b.p. 92° at 21 mmHg (lit.,[12] 73° at 10 mmHg). Methyl diphenylphosphinate was prepared by the reaction of the phosphinite (II) with benzoyl peroxide, the crude product being used for g.l.c. analysis and i.r. spectra as an authentic sample. Triphenylphosphine oxide was synthesised from triphenylphosphine (III) and benzoyl peroxide.[13] Recrystallisation from ligroin gave a yield of 91%, m.p. 156° (lit.,[13] 153·5°). Commercial G.R. triphenylphosphine and azobisisobutyronitrile were used. *o*-Dichlorobenzene was purified, b.p. 86—88° at 41—43 mmHg.

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Autoxidation of Tervalent Phosphorus Compounds.—Autoxidations were carried out with addition of *ca.* 0·1 mol. equiv. of initiator and at 200 mmHg of oxygen pressure in *o*-dichlorobenzene and/or neat at 60 °C for 1—3 days. They consumed 0·5 mol. equiv. of oxygen and dominantly gave the corresponding quinquecovalent phosphorus compounds, *i.e.*, trimethyl phosphate, methyl diphenylphosphinate, and triphenylphosphine oxide, respectively. Trimethyl phosphate was identified by g.l.c. (Chromosorb W, acid washed, coated with 8% silicone SE 30; column temperature 90 °C) by comparison with an authentic sample. Methyl diphenylphosphinate was identified by g.l.c. (same column at 160 °C), t.l.c. (silica gel; eluant, ethyl acetate–light petroleum 3 : 8), and i.r. spectra [1442 and 1017 (P–Ph),[14,15] and 1228 cm^{-1} (P=O) [16,17] in *o*-dichlorobenzene] by comparison with the authentic sample. Triphenylphosphine oxide was identified by t.l.c. (silica gel; ethyl acetate–light petroleum 3 : 7).

Kinetic Procedure.—The apparatus has been reported.[7] A typical run was as follows: $4{\cdot}12 \times 10^{-2}$M-methyl diphenylphosphinite in *o*-dichlorobenzene (5 ml) and $1{\cdot}98 \times 10^{-3}$M-initiator in *o*-dichlorobenzene (1 ml) were mixed in a reaction vessel of 96 ml, then oxygen (200 mmHg) and nitrogen (350 mmHg) were mixed and introduced into the apparatus. The apparatus was thermostated at 60·0 °C and the autoxidation was started with vigorous magnetic stiring. The partial pressure difference between the mixture and the reference solution was measured at intervals. The partial pressure of oxygen was allowed for at the temperature, and used for calculation. The observed pseudo-first-order rate constants (k_{1a}) were were calculated by equation (4).

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