Autoxidation of Trimethyl Phosphite Initiated by One-Electron Transfer from Phosphite to Quinones*

Yoshiro OGATA and Mitsuji YAMASHITA
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

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The reaction of trimethyl phosphite (I) with acenaphthenequinone (II) under air affords quantitatively trimethyl phosphate (III) and 1:2 adduct (IV), which was converted into δ-lactone (V) and III by addition of water, while only IV was obtained quantitatively under N_2 atmosphere. ESR and UV spectra, decolorization of 1,1-diphenyl-2-picrylhydrazyl (DPPH), and initiation of styrene polymerization suggest the transient formation of radical ions VI and VII. The rate law for the autoxidation of I is expressed as: $v=k[\mathrm{I}][\mathrm{II}]^{0.7-1.0}$. The reaction in chloroform proceeds faster than that in dioxane. The reaction of I with chloranil is much slower, and no reaction occurs with phenanthrenequinone and anthraquinone which have low reduction potentials. A mechanism which involves one-electron transfer from phosphite to acenaphthenequinone followed by autoxidation was proposed for the reaction under air.

The reaction of trimethyl phosphite with acenaphthenequinone was reported to give a 1:2 adduct under nitrogen atmosphere.[1] Trimethyl phosphite is stable toward molecular oxygen in the absence of a radical source or light.[2] The peculiar behavior in the reaction of phosphite with acenaphthenequinone, *i.e.*, the rapid red-shift of color of the reaction mixture followed by a slow blue-shift,[3] prompted us to study the reaction in detail.

Some reactions of trivalent phosphorus compounds with carbonyl compounds are of radical character, but little evidence is available.[4] The present paper is a summary of our study on the products and mechanism of the autoxidation of trimethyl phosphite initiated by one-electron transfer reaction from phosphite to acenaphthenequinone.

Results and Discussion

The reaction of trimethyl phosphite (I) with acenaphthenequinone (II) proceeds exothermally at room temperature. The color of II fades rapidly,[3] producing trimethyl phosphate (III) in the air as the only liquid product together with a white solid. The former was confirmed by glc, tlc, IR and NMR spectra, and latter was identified by means of NMR to be an adduct of I to II in a molar ratio of 1:2. The adduct after treatment with water and recrystallization gave 8-[hydroxy(2-oxo-acenaphthenylidene)methyl]-1-naphthoic acid δ-lactone (V) [see Experimental].

The reaction of acenaphthenequinone with a large excess of trimethyl phosphite under oxygen atmosphere gives an excess equivalent of trimethyl phosphate, while under nitrogen atmosphere the yield is lower, most of trimethyl phosphite being recovered as shown in Table 1. This shows that the autoxidation of I occurs under O_2 atmosphere. The 1:2 adduct (IV) does not initiate the autoxidation. An increase of ratio of trimethyl phosphite to acenaphthenequinone under O_2 atmosphere results in a higher yield of phosphate (based on the used quinone), indicating a long length of radical chain (Table 2).

Stoichiometry. Stoichiometry of the autoxidation of trimethyl phosphite in the presence of acenaphthenequinone was determined in dioxane at 25.0 °C by use of an apparatus for kinetic study.[3] The reaction produced a quantitative amount of trimethyl phosphite with consumption of a half equivalent of molecular oxygen (Table 3). As reported by Ramirez and Ramanathan,[1] acenaphthenequinone is converted into a 1:2 adduct (IV) with trimethyl phosphite [(1a), (1b)]. We found that the adduct gives δ-lactone (V) and trimethyl phosphate (III) by treatment with water. Both reaction (1a) and (1b) take place in the air, but only (1b) under N_2.

Detection of Radicals. When trimethyl phosphite was added to a dioxane solution of acenaphthenequinone, the yellow color of the solution deepened (red-shift) and then faded away gradually. Immeasurably fast change of color was observed in chloroform. ESR spectra in dioxane showed a broad signal.[5] On addition of DPPH to the reaction mixture, the color

TABLE 1. EFFECT OF OXYGEN ON THE YIELD OF TRIMETHYL PHOSPHATE AT ROOM TEMPERATURE[a)]

Acenaphthenequinone (mmol)	Trimethyl phosphite (mmol)	Atmosphere	Yield of trimethyl phosphate[b)] [mmol (%)]
0.53	25	Air	5.6 (1100)
0.62	11	N_2	0.75 (120)

a) Neat.
b) Based on acenaphthenequinone.

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* Contribution No. 191.

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3) Y. Ogata and M. Yamashita, *ibid.*, **1972**, 730.

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Table 2. Effect of molar ratio of trimethyl phosphite (I) *vs.* acenaphthenequinone (II) on the yield of trimethyl phosphate in $CHCl_3$ at room temperaturee for 10 hr

Concentration		Ratio of I to II	Yield of trimethyl phosphate[a] (%)
[I], (10^{-1}M)	[II], (10^{-2}M)		
29	8.1	28	590
15	8.1	14	380
7.3	8.1	6.9	230
29	4.1	56	830
29	2.0	100	1400

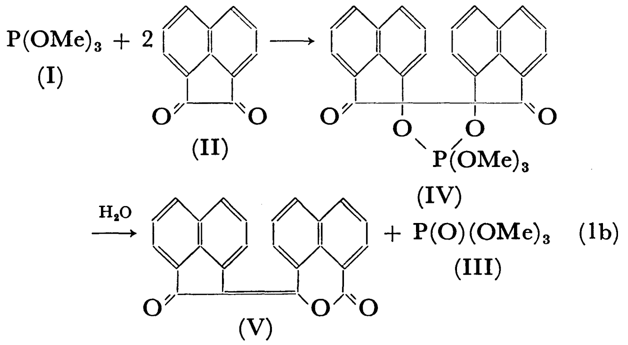
a) Based on II.

Table 3. The stoichiometry of autoxidation of trimethyl phosphite in dioxane at 25 °C[a]

$P(OMe)_3$ (10^{-4} mol)	Consumed oxygen (10^{-4} mol)	$2\ O_2/P(OMe)_3$[b]
2.58	1.19	0.92
6.49	3.08	0.95
11.4	9.90	0.89

a) Acenaphthenequinone used was 9.0×10^{-6} —3.4×10^{-5} mol.
b) Molar ratio of oxygen to trimethyl phosphite.

$$P(OMe)_3 + \frac{1}{2}O_2 \xrightarrow{\text{acenaphthenequinone (II)}} P(O)(OMe)_3 \qquad (1a)$$



of DPPH vanished rapidly, but it did not vanish by the action of IV, I, or II. The decolorization rate of DPPH was much faster in chloroform than in dioxane. A similar decolorization was observed for the reaction with chloranil (though slow in the initial period), but not with phenanthrenequinone.[3] These facts suggest that the reaction of trimethyl phosphite with acenaphthenequinone produces radical species by one-electron transfer as in the case of chloranil and that the autoxidation is initiated by these radicals. The formation of a charge-transfer complex of I with II is less probable, since no autoxidation of I would occur in the stage of charge-transfer complex.

Triphenylphosphonium radical cation ($Ph_3P^{\dot{+}}$) may be an intermediate in the reaction of triphenylphosphine with some quinones.[6] The ESR spectra of some semiquinone radicals are well-known,[7] while those of phosphoranyl radicals[8] and phosphoranylperoxy radicals,[9] prepared by the photolysis of di-*t*-butyl peroxide in the presence of trivalent phosphorus compounds, have been reported recently. The observed broad signal may be either an anion radical of ketyl or a cation radical of phosphorus, or both.

Kinetics. The kinetics of the autoxidation was studied by the manometric method.[3] As shown in

Table 4. Rate constants for the autoxidation of trimethyl phosphite (I) with acenaphthenequinone (II) in dioxane at total pressure of 760 mmHg

Concentration		Partial pressure of O_2 (mmHg)	Temp. (°C)	Rate and rate constant	
$[I]_0$ (10^{-1} M)	$[II]_0$ (10^{-3} M)			$10^5\ v$[a] (M sec^{-1})	$10^2\ k_2$[b] ($M^{-1}\ sec^{-1}$)
1.90	4.27	159	25.0	2.54	1.57
3.25	9.20	760	25.0	8.33	1.39
3.25	9.20	159	25.0	8.11	1.36
4.86	4.60	159	25.0	6.96	1.64
2.03	6.00	159	25.0	4.32	1.78
0.508	6.00	159	25.0	1.08	1.78
2.11	8.50	159	35.0	3.06	1.71
1.99	8.45	159	45.0	3.51	2.09
1.99	8.45	159	60.0	4.08	2.43

a) $v=d[O_2]/dt$.
b) $v=k_2[I][II]$.

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7) a) M. Adams, M. S. Blois, Jr., and R. H. Sands, *J. Chem. Phys.*, **28**, 774 (1958). b) E. Warhust and A. M. Wilds, *Trans. Faraday Soc.*, **65**, 1413 (1969). c) A. G. Evans, J. E. Evans, and E. H. Godden, *J. Chem. Soc., B*, **1969**, 546. d) G. A. Russell, "Radical Ions," ed. by K. T. Kaiser and L. Kevan, Interscience Publishers, New York (1968), Chapter 3.

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9) G. B. Watts and K. U. Ingold, *ibid.*, **94**, 2528 (1972).

Table 4, the rate is independent of partial pressure of oxygen as expressed by

$$v = k[\mathrm{I}][\mathrm{II}]^{0.7-1.0} \qquad (2)$$

It is also shown that the temperature effect is small, which reflects a small activation energy for the initiation. Chloranil initiates the autoxidation very slowly,[10] while rapid autoxidation is observed with AIBN (Table 5).

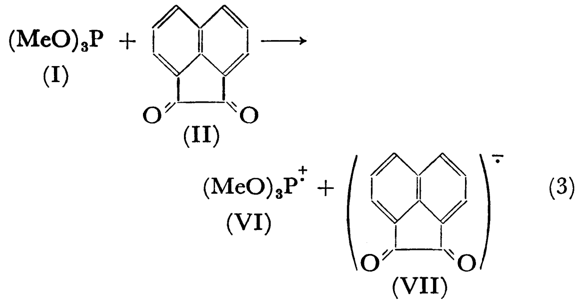
TABLE 5. SECOND-ORDER RATE CONSTANTS FOR AUTOXIDATION OF TRIMETHYL PHOSPHITE IN DIOXANE AT 60.0 °C

$[(\mathrm{MeO})_3\mathrm{P}]_0$ (10^{-1} M)	Added compound (concentration) (10^{-3} M)	k_2 [a] ($\mathrm{M^{-1}\,sec^{-1}}$)
1.99	Acenaphthenequinone (8.45)	2.43×10^{-2}
1.99	AIBN (9.40)	4.84×10^{-2}
1.99	Chloranil (7.95)	1.61×10^{-7}

a) $v=k_2[(\mathrm{MeO})_3\mathrm{P}][\text{Added compound}]$.

Mechanism. The above fact suggest that the one-electron transfer occurs at the initiation step, and the radicals formed initiate the autoxidation of trimethyl phosphite. Thus a probable initiation reaction is expressed as follows.

Initiation:



Radicals VI and/or VII, represented by R·, may initiate the autoxidation.

The propagation reaction can be expressed by the mechanism involving alkyl, alkoxy, and alkylperoxy radicals as chain carriers,[3] *e.g.*,

$$(\mathrm{MeO})_3\mathrm{P} + \mathrm{RO_2}\cdot \longrightarrow (\mathrm{MeO})_3\mathrm{PO} + \mathrm{RO}\cdot$$

$$\text{or } (\mathrm{MeO})_3\mathrm{P} + \mathrm{RO}\cdot \longrightarrow (\mathrm{MeO})_3\mathrm{PO} + \mathrm{R}\cdot.$$

The termination reaction can be expressed as follows.

$$2\mathrm{RO_2}\cdot \longrightarrow \mathrm{RO_4R} \text{ or other inactive products} \qquad (4)$$

$$\mathrm{RO_2}\cdot \longrightarrow \text{inactive products} \qquad (5)$$

$$\mathrm{RO_2}\cdot + \mathrm{R'}\cdot \longrightarrow \text{inactive products} \qquad (6)$$

where R'· represents radicals other than $\mathrm{RO_2}\cdot$.

If step (4) is favorable for termination, the order with respect to II in the rate law should be 0.5, while if steps (5) and/or (6) occur, the order should be 1,[3] on applying the steady state approximation to this mechanism. Actually, the order in II Eq. (2) is 0.7—1.0. This might be explained by assuming the occurrence of bimolecular termination [step (4)] along with unimolecular termination [steps (5) and (6)]. The radical chain may need small energy of activation, thus the temperature dependence of the autoxidation rate is small (E_a=5.9 kcal/mol and $\Delta S^{\neq}=-54$ e.u. at 25.0 °C).

Formation of trimethyl phosphate is due to the autoxidation of I but not to the hydrolysis of phosphorus intermediate reported in the reaction of phosphite with chloranil.[11] One-electron transfer occurred in the reaction of trimethyl phosphite with acenaphthenequinone or chloranil, but none in that with phenanthrenequinone or anthraquinone. The different behaviors in these quinones can be attributed to the difference of reduction potentials of quinones,[12] *i.e.*, reduction potentials of quinones: chloranil (0.712 V),[12b] phenanthrenequinone (0.458 V),[12c] anthraquinone (0.157 V),[12d] and acenaphthenequinone (0.78 V). The last has not been reported.

Polymerization. Copolymerization of added styrene-divinylbenzene was initiated during the reaction of trimethyl phosphite with acenaphthenequinone at 60 °C under O_2 or N_2, while formed IV did not initiate the polymerization. This indicates the presence of a free radical in the reaction mixture of trimethyl phosphite with acenaphthenequinone and the fact that the radical has a life long enough to initiate polymerization.

Experimental

Apparatus. The NMR spectra were measured with a JNM-C60-HL model of Japan Electron Optics Laboratory Co., Ltd; IR spectra with a Perkin-Elmer 337 grating infrared spectrophotometer; ESR spectra with a JES-ME1X model of Japan Electron Optics Laboratory Co., Ltd; UV spectra with a Hitachi 124 spectrophotometer; and mass spectra with a Hitachi RMS-4 model. A Yanagimoto GCG 550F gas chromatograph was used for glc analysis, and a Yanagimoto P8-DPR polarograph for the measurement of reduction potentials.

Materials. Trimethyl phosphite (bp 58 °C/116 mmHg; lit,[13] bp 111—112 °C), acenaphthenequinone (mp 261 °C; lit,[14] mp 259—260 °C), chloranil (mp 299 °C; lit,[15] mp 291—293 °C), styrene (bp 49—50 °C/25 mmHg; lit,[16] bp 54 °C/30 mmHg), phenanthrenequinone (mp 210 °C; lit,[17] mp 208.5—210 °C), and solvents were purified before use.

Reaction of Trimethyl Phosphite (I) with Acenaphthenequinone (II). The reaction of I with II was carried out at room temperature in neat or in a dioxane or chloroform solution. The tlc analysis (silica gel/acetone) of the reaction mixture gave two spots, one (R_f=0.59) being detected by $\mathrm{CoCl_2}$, and the other (R_f=0.80) by I_2. After separation of formed precipitate by filtration (reaction in neat), the solid

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product was washed with water, then extracted by $CHCl_3$. The extract gave a solid which was identified to be 8-[hydroxy(2-oxo-1-acenaphthenylidene)methyl]-1-naphthoic acid δ-lactone (V) mp 274 °C.

Found: C, 82.1; H, 3.52%. Calcd for $C_{24}H_{12}O_3$: C, 82.8; H, 3.47%.

The NMR spectra gave only aromatic protons (in $CDCl_3$). The mass spectra are shown in Table 6. The UV spectra in CH_3CN are as follows: λ_{max} 249 nm (log ε 4.92), 285 nm (4.64), 301 nm (4.61), 316 nm (4.60), and 342 nm (4.53). The crude yield of V was quantitative. The filtrate gave only one peak in glc (Apiezon Grease L 3% on Celite 545), whose structure was confirmed to be trimethyl phosphate (III) by NMR (6.26 τ, doublet, $J_{PH}=11$ Hz) and IR (P=O; 1267 cm^{-1}, P-O-C; 1035 cm^{-1}). The reaction in dioxane or in $CHCl_3$ gave the same results as described above. The structure of 1:2 adduct (IV) was determined by NMR spectra without purification (1.5—2.5 τ, multiplet, 12H; 6.28 τ doublet, $J_{PH}=10.6$ Hz, 9H).

Kinetics. A dioxane solution of trimethyl phosphite (2 ml) and a doixane solution of acenaphthenequinone (2 ml) was mixed under 159 mmHg partial pressure of oxygen. The autoxidation rate was measured manometrically.[3] The stoichiometry was determined by the consumed amount of oxygen after being kept standing for a long time.

ESR Spectra. A dioxane solution of acenaphthenequinone was introduced into an ESR tube and frozen out at liquid nitrogen temperature under N_2 flow. A dioxane solution of trimethyl phosphite was then introduced into the tube and also frozen out. Two separate layers were gradually mixed by raising the temperature. The observed broad ESR signal having center at 3150 G soon reached a maximum intensity and then gradually vanished.

TABLE 6. MASS SPECTRA OF δ-LACTONE (V)

m/e	Relative intensity
126	100
154	85
182	38
320	12
348 (M^+)	30 (100) [a]
349 (M^++1)	(25)
350 (M^++2)	(3.7)

a) Numerals in parenthesis denote relative intensity based on M^+. The calculated intensity of M^++1 and M^++2 is 26.1 and 1.3, respectively ($C_{24}H_{12}O_3$) [J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier, Amsterdam (1960), p. 305)].

Polymerization of Styrene. Acenaphthenequinone (0.007 g) was dissolved in a mixture of 4 ml styrene and 0.1 ml divinylbenzene. Bubbling nitrogen gas, 1 ml trimethyl phosphite was added to the mixture at 60 °C and then the tube was sealed. The homo and popcorn polymerization was almost complete after two days, but no such polymerization was observed without trimethyl phosphite and acenaphthenequinone.

Reduction Potential. The reduction potential of quinones was measured in 50% aqueous ethanol containing 0.1M HCl as a saturated solution of substrate at 20 °C by means of a Yanagimoto P8-DPR polarograph potentiostated with a calomel electrode.