

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

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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: $v = k[I][II]^{0.7-1.0}$. 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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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 $\text{C}_{24}\text{H}_{12}\text{O}_3$: 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 ($\log \epsilon$ 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, $J_{\text{PH}}=11$ Hz) and IR ($\text{P}=\text{O}$; 1267 cm^{-1} , $\text{P}-\text{O}-\text{C}$; 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, $J_{\text{PH}}=10.6$ Hz, 9H).

Kinetics. A dioxane solution of trimethyl phosphite (2 ml) and a dioxane 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

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 ($\text{C}_{24}\text{H}_{12}\text{O}_3$) [J. H. Beynon, "Mass Spectrometry and its Application to Organic Chemistry," Elsevier, Amsterdam (1960), p. 305].

intensity and then gradually vanished.

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.