

was held at a temperature no higher than 26°. The effluent from the tube was passed through two traps, the first cooled in a Dry Ice-acetone bath, the second in liquid nitrogen. At the end of a pyrolytic run there was no residue in the flask from which the peroxide was sublimed, in the pyrolysis tube, or in areas of the apparatus which would experience intermediate temperatures, such as immediately preceding or following the pyrolysis tube. Thus there is no indication of the formation of any polyester analogous to **3** during vapor-phase pyrolysis.

Ketonic products were condensed in the Dry Ice-acetone bath. Acetone was identified by its retention time on glc, by coinjection with authentic acetone, and by conversion to its DNP derivative, mp 125–127° (lit.<sup>4</sup> mp 126°). The yield of acetone produced in the thermolysis was determined from the weight of DNP isolated. Cyclobutanone was identified by its retention time on glc, by coinjection with authentic cyclobutanone, and by conversion to its DNP derivative, mp 144–146° (lit.<sup>4</sup> mp 146°). Material collected in the Dry Ice-acetone trap exhibited no infrared absorption indicative of the presence of polyester analogous to **3**.

The yield of carbon dioxide was determined by venting the contents of the liquid nitrogen trap through a tube packed with Ascarite, and measuring the increase in weight.

Carbon monoxide was detected qualitatively by venting the contents of the liquid nitrogen trap through a solution of cuprous sulfate. An increase in weight signified the absorption of carbon monoxide.<sup>5</sup>

Cyclobutene was identified as a component of the contents of the liquid nitrogen trap by its retention time on glc, by coinjection with authentic cyclobutene, and by conversion to its Diels-Alder adduct with 1,3-diphenylisobenzofuran, mp 119–121°, identical with that of an authentic sample. The yield of cyclobutene was determined from the weight of the Diels-Alder adduct isolated.

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**Registry No.**—**4**, 40982-37-4; **5**, 34867-87-3; dimethylmalonic acid, 595-46-0; trimethylenemalonic acid, 5445-51-2; hydrogen peroxide, 7722-84-1.

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## Kinetics of the One-Electron Transfer Reaction of Trimethyl Phosphite with Quinones<sup>1</sup>

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The reaction of trialkyl phosphite with quinones is well known.<sup>3</sup> For example, the reaction of *o*-quinones such as phenanthrenequinone and *o*-benzoquinone gives 1:1 adducts at room temperature,<sup>4</sup> while acenaphthenequinone gives a 2:1 adduct, which was produced by a rapid reaction of the 1:1 adduct with the second

(1) Contribution No. 194.

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(3) (a) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, London, 1965, p 187; (b) F. Ramirez, *Accounts Chem. Res.*, **1**, 168 (1968).

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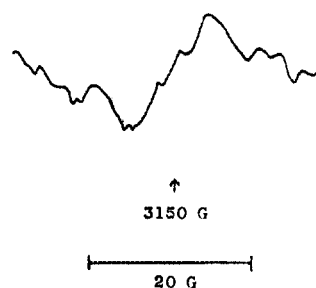


Figure 1.—Esr spectra obtained in the reaction of acenaphthenequinone with trimethyl phosphite in dioxane.

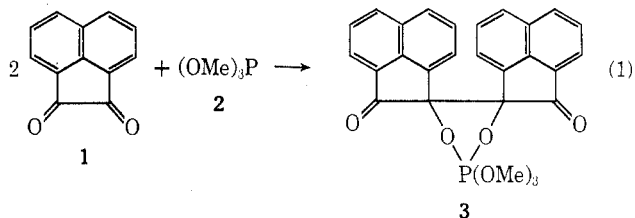
quinone molecule.<sup>5,6</sup> The reaction of *p*-quinones with trivalent phosphorus compounds yields reduction products of quinones, e.g., *p*-alkoxyphenols via quinone-donor adducts.<sup>7,8</sup> The electron paramagnetic resonance spectrum was observed during the reaction of triethyl phosphite with chloranil,<sup>9</sup> but little is known about the detail of this phenomenon.

We have reported that the reaction of acenaphthenequinone with trimethyl phosphite caused the color change, the initiation of autoxidation of trimethyl phosphite, and polymerization of styrene,<sup>10</sup> which suggest the occurrence of radicals in the reaction. However, nothing is known on the mechanism of this radical formation and the relative amount of the radical product to the ionic product (a 2:1 adduct).

The present paper will describe further evidence and kinetics of the radical formation via one-electron transfer from phosphite to quinones to clarify its mechanism and the ratio of the radical to ionic paths. The paper will also describe the relation between the rate and the reduction potentials of some quinones.

## Results and Discussion

As reported previously, the reaction of acenaphthenequinone (**1**) with excess trimethyl phosphite (**2**) at 25° under N<sub>2</sub> gave a 2:1 adduct of **1** and **2** [2,2,2-trimethoxy-4,5-biacenedionoxy-1,3,2-dioxaphospholane (**3**)] on the basis of its nmr and ir spectra.



The reaction mixture of acenaphthenequinone (**1**) and trimethyl phosphite (**2**) showed a red color shift. The color of DPPH vanished on addition of the reaction mixture, and the red color of the complex also disappeared. These observations suggest the presence of radicals.<sup>10</sup> On mixing **1** and **2** in dioxane, an esr signal was observed as shown in Figure 1. The rapid mea-

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TABLE I  
 RATE CONSTANTS FOR THE REACTION OF QUINONES WITH TRIMETHYL PHOSPHITE

Quinone	Initial concn, <i>M</i>		$10^2 k, M^{-1} \text{sec}^{-1}$	Solvent	Temp, °C
	[Quinone] <sub>0</sub>	[P(OMe) <sub>3</sub> ] <sub>0</sub>			
Acenaphthene-quinone	0.0170	0.329	1.99	Dioxane	30.0
	0.0170	0.165	1.96	Dioxane	30.0
	0.00850	0.329	1.90	Dioxane	30.0
	0.00425	0.165	2.01	Dioxane	30.0
	0.00697	0.152	6.78	Acetonitrile	21.0
5,6-Dinitro-acenaphthene-quinone	0.00544	0.394	$1.12 \times 10^{-2}$	Dioxane	30.0
	0.00544	0.197	$1.12 \times 10^{-2}$	Dioxane	30.0
	0.00272	0.394	$1.13 \times 10^{-2}$	Dioxane	30.0

surement of uv spectra of the reaction mixture in dioxane showed  $\lambda_{\text{max}}$  550 nm. The authentic acenaphthenequinone radical produced by the treatment of acenaphthenequinone with metallic sodium showed  $\lambda_{\text{max}}$  570 nm, which is similar to the results obtained by Evans, *et al.*<sup>11</sup> These results suggest the formation of acenaphthenequinone radical (4) and trimethyl phosphite radical cation (5).

The kinetic study of reaction of quinones with trimethyl phosphite was carried out spectrophotometrically in dioxane or acetonitrile at 20–30°. The rate law is first order in each of two substances (eq 2). The kinetic data are shown in Table I; the data fit eq 2.

$$v = -d[\text{quinone}]/dt = k[\text{quinone}][2] \quad (2)$$

The rate constant has a good constancy up to 90% conversion. The rate law and the data in Table I show that the first rearrangement step of phosphorus atom from carbonyl carbon atom to carbonyl oxygen atom may be rate determining.<sup>12</sup>

The rate of one-electron transfer reaction was followed by means of spectrophotometry of disappearing DPPH in dioxane under air or nitrogen atmosphere. No color change of DPPH was observed in the absence of either phosphite or quinone. The rate was independent of quinone and DPPH concentrations, as shown in Table II. The data in the table fit eq 3 except for the case in the absence of quinones.

$$v' = -d[\text{DPPH}]/dt = k'[2]^{0.4} \quad (3)$$

 TABLE II  
 RATE OF DISAPPEARANCE OF DPPH IN THE REACTION OF ACENAPHTHENEQUINONE WITH TRIMETHYL PHOSPHITE IN DIOXANE

Initial concn, <i>M</i>			Temp, °C	Atmosphere	Rate constant, <sup>a</sup> $10^3 k', 10^{0.6} \text{sec}^{-1}$
$10^3$ [Quinone] <sub>0</sub>	$10^2$ [P(OMe) <sub>3</sub> ] <sub>0</sub>	$10^3$ [DPPH] <sub>0</sub>			
7.87	7.50	2.54	30.0	Air	1.63
3.94	7.50	2.54	30.0	Air	1.63
7.87	3.75	2.54	30.0	Air	1.64
7.87	7.50	1.27	30.0	Air	1.64
7.87	15.4	2.54	30.0	Air	1.67
0	7.50	2.54	30.0	Air	0
7.90	8.77	0.149	25.0	Air	0.826
7.86	8.77	0.149	20.0	Air	0.415
8.04	8.67	0.149	30.0	N <sub>2</sub>	1.66

$$^a v = -d[\text{DPPH}]/dt = k'[2]^{0.4}$$

No appreciable effect of oxygen on the rate was observed. Temperature effect on the rate constant at

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20–30° afforded the values of energy and entropy of activation of 22 kcal/mol and –15 eu (at 25.0°), respectively. Electron-attracting substituents on quinones facilitate the electron transfer, as shown in Table III.

The reaction of chloranil with trimethyl phosphite with an induction period of *ca.* 2.5 min had a larger rate constant than that of acenaphthenequinone, which had no induction period. Virtually no decolorization of DPPH was observed with anthraquinone. DPPH is known to react in some cases with nonradical species, *e.g.*, a hydrogen atom is abstracted from anthracene,<sup>13</sup> but the observed no reaction of DPPH with phosphite or quinones implies that DPPH reacts with the radicals<sup>14</sup> produced by the reaction of phosphite with quinones.

The observed induction period for the decolorization of DPPH in the case of chloranil (8) and no decolorization in the absence of quinones seem to suggest the initial formation of a quinone–phosphite complex, *e.g.*, probably a charge-transfer complex, which is liable to give radical species and acts as a catalyst.

The order of 0.4 in phosphite is close to 0.5. The order of 0.5 seems to suggest that two radical species [Me· and ·P(O)(OMe)<sub>2</sub>] may be produced from 5 (Scheme I, path a), whose rate law is expressed as eq 4.

$$v = -d[\text{DPPH}]/dt = k_r[\text{radicals}][\text{DPPH}] = k_a'[2]^{0.5} \quad (4)$$

Alternatively, the order is explicable assuming that other radical species [MeO· and Me·] are produced from 5 (path b), whose rate law is represented by eq 5.

$$v = -d[\text{DPPH}]/dt = k_r'[\text{radicals}][\text{DPPH}] = k_b'[2]^{0.5} \quad (5)$$

However, there seems as yet to be no evidence to decide among paths a and b in view of the available literature.<sup>15</sup> Another mechanisms involving a simple one-electron transfer from phosphite to quinone followed by a chain reaction can be excluded from the observed rate law (eq 3).

The comparison of the consumption rate of 1 and DPPH in Tables I and II shows that the ionic reaction to produce an acenaphthenequinone–trimethyl phosphite (2:1) adduct (3) is much more important by a factor of 10<sup>2</sup>–10<sup>4</sup> than the one-electron transfer reaction to produce radical ions.

(13) J. S. Hogg, D. H. Lohmann, and K. E. Russell, *Can. J. Chem.*, **39**, 1394 (1961).

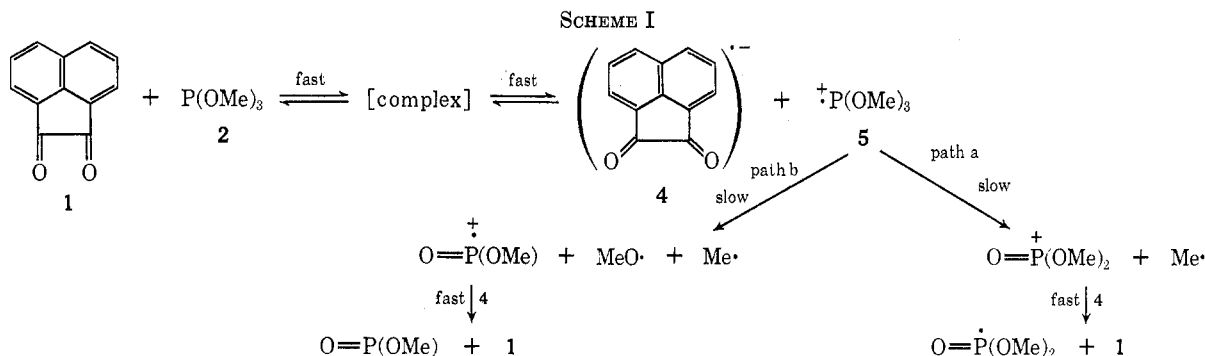
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TABLE III  
RATE OF DISAPPEARANCE OF DPPH IN THE REACTION OF VARIOUS QUINONES WITH TRIMETHYL PHOSPHITE IN DIOXANE AT 30.0°

Quinones	Initial concn, M			Rate constant $10^6 k'$ , $M^{0.6} \text{ sec}^{-1}$	Reduction potential, V
	$10^3[\text{Quinone}]_0$	$10^3[\text{P(OMe)}_3]_0$	$10^4[\text{DPPH}]_0$		
5,6-Dinitroacenaphthenequinone (6)	4.33	1.59	1.49	5.96	
5-Nitroacenaphthenequinone (7)	4.67	1.59	1.49	4.75	
Chloranil (8)	4.93	7.93	1.49	4.30 <sup>c</sup>	0.712 <sup>b</sup>
Acenaphthenequinone (1)	7.87	7.50	12.7	1.64	0.78
<i>p</i> -Benzoquinone (9)	4.67	507	1.49	0.312	0.698 <sup>c</sup>
Phenanthrenequinone (10)	6.07	507	1.49	$7.30 \times 10^{-4}$	0.458 <sup>d</sup>
Anthraquinone (11)	6.57	507	1.49	Too slow to measure	0.157 <sup>e</sup>

<sup>a</sup> Rate constant after induction period. <sup>b</sup> K. Wallenfels and W. Möhle, *Ber.*, **76**, 924 (1943). <sup>c</sup> J. B. Conant and L. F. Fieser, *J. Amer. Chem. Soc.*, **44**, 2480 (1922). <sup>d</sup> L. F. Fieser, *ibid.*, **51**, 3101 (1929). <sup>e</sup> J. B. Conant and L. F. Fieser, *ibid.*, **46**, 1855 (1924).



The rate of one-electron transfer reaction seems to correlate with the reduction potential of quinones; *i.e.*, a plot of  $\log k'$  vs. reduction potential fits well a straight line, whose slope is 12. This shows that the energy barrier for this reaction correlates with the reduction potential of this quinone (Table III). The substitution by a nitro group seems to afford a little higher reduction potential to acenaphthenequinone.<sup>16</sup>

#### Experimental Section

**Materials.**—Trimethyl phosphite [bp 58° (116 mm)], acenaphthenequinone (mp 261°), chloranil (mp 299°), phenanthrenequinone (mp 210°), *p*-benzoquinone [mp 115.5° (lit.<sup>17</sup> mp 115.7°)], anthraquinone [mp 286–287° (lit.<sup>18</sup> mp 286°)], 5-nitroacenaphthenequinone [mp 210° (lit.<sup>19</sup> mp 218°)], and 5,6-dinitroacenaphthenequinone [mp > 300° (lit.<sup>19</sup> mp > 300°)] were used.

**Product.**—The reaction of 1 with excess 2 was carried out at 25° under N<sub>2</sub>. After distillation of unreacted 2 *in vacuo*, the product was analyzed by nmr (CDCl<sub>3</sub>),  $\tau$  1.5–2.5 (multiplet, 12 H), 6.28 (doublet,  $J_{\text{PH}} = 10.6$  Hz, 9 H). The yield of 3 was almost quantitative.

**Kinetics.**—The disappearance of color of DPPH [ $\lambda_{\text{max}}^{\text{dioxane}}$  515 nm ( $\epsilon$  5310)] was followed by means of spectrophotometry. Each 1-ml portion of dioxane solution of 1, 2, and DPPH was introduced separately into a three-necked quartz uv cell. After air was substituted by N<sub>2</sub>, the three solutions were mixed and the cell was placed in a thermostated cell chamber of a Hitachi EPU-2A spectrophotometer. The consumption of DPPH was determined spectrophotometrically at appropriate intervals of time.

On the other hand, the disappearance of color of 1 [ $\lambda_{\text{max}}^{\text{dioxane}}$  473 nm ( $\epsilon$  17.9)] was followed by almost the same procedure as above.

**Esr Spectra.**—Esr spectra were observed by mixing a dioxane solution of trimethyl phosphite and acenaphthenequinone in an esr tube at the temperature of the melting point of dioxane. Field and modulation width were  $3150 \pm 100$  and 20 G, respectively.

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**Reduction Potential.**—The reduction potential of quinones was measured in 50% aqueous ethanol containing 0.1 N HCl as a  $10^{-4}$ – $10^{-3}$  M solution of substrate at 20° by a Yanagimoto P8-DPR polarograph potentiostated with a calomel electrode.

**Registry No.**—1, 82-86-0; 2, 121-45-9; 3, 40782-66-9; 6, 27471-02-9; 7, 24040-42-4; 8, 2435-53-2; 9, 106-51-4; 10, 84-11-7; 11, 84-65-1.

#### Conversion of *o*-Acylphenylacetic Acids to Naphthalene and Chrysene Derivatives<sup>1</sup>

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2-[(3,4-Dimethoxyphenyl)acetyl]-4,5-dimethoxyphenyl]acetic acid (1) has been used in a new total synthesis of 1-benzylisoquinoline alkaloids, and one of key intermediates in that work was 1-(3,4-dimethoxybenzylidene)-6,7-dimethoxy-3-isochromanone (2) obtained by thermal dehydration of 1.<sup>2</sup> The present work was undertaken in an effort to find a milder reaction to convert 1 to 2, and in the initial attempts the keto acid 1 was heated for 1 hr in a solution of acetic anhydride in pyridine. The purified product, obtained in about 52% yield, was identified as 1-acetyl-2,4-diacetoxy-3-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalene (3). The structure proof of 3 rested on the elemental analysis and on the uv, ir, nmr, and mass spectra (see Experimental Section) as well as on the chemical conversion to the known 1,4-naphthoquinone derivative 4.

(1) This study was supported in part by a grant from the National Science Foundation (GY 6169).

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