ON THE INTERACTION OF ESTERS OF PHOSPHOROUS ACID WITH 1,1-DIPHENYLETHANE HYDROPEROXIDE

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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ON THE INTERACTION OF ESTERS OF PHOSPHOROUS ACID WITH 1,1-DIPHENYLETHANE HYDROPEROXIDE

Horner and Jürgeleit first reported on the reactions of hydroperoxides with derivatives of trivalent phosphorus—with trisubstituted phosphines ([1]). They found that the reaction proceeds with formation of a phosphine oxide and an alcohol formed from the hydroperoxide.

Fig. 1. Kinetic curves for the interaction of 1,1-diphenylethane hydroperoxide with triethyl phosphite (*I*), triisopropyl phosphite (*II*), tricresyl phosphite (*III*), tri-(tert-butyl)-phenyl phosphite (*IV*) (volume ratios of the concentrations of 1,1-diphenylethane hydroperoxide and phosphite 1 : 10, $t = 20^{\circ}$)

Fig. 2. Kinetic curves for the interaction of 1,1-diphenylethane hydroperoxide with the isobutyl ester of pyrocatechol phosphorous acid (*I*); the phenyl ester of pyrocatechol phosphorous acid (*II*); 4-tert-butylphenyl ester of pyrocatechol phosphorous acid (*III*); 4-methyl-2,6-di-(tert-butyl)-phenyl ester of pyrocatechol phosphorous acid (*IV*); 2,4,6-tri-(tert-butyl)-phenyl ester of pyrocatechol phosphorous acid (*V*) (volume ratios of the concentrations of 1,1-diphenylethane hydroperoxide and phosphite 1 : 10, $t = 20^{\circ}$)

In 1959 Walling and Rabinowitz ([2]) established that trialkyl phosphites also react with hydroperoxides, giving trialkyl phosphates and the corresponding alcohols. A number of subsequent works have been devoted to studying the interaction of various hydroperoxides with phosphines and to elucidating the possible mechanism of these reactions ([3]). Studies of the reactions of hydroper-

oxides with esters of phosphorous acid, however, are limited to very few works, concerning mainly its aliphatic esters, and are of a sporadic character ([4]).

As is known, phosphites and diphosphites currently attract considerable attention from researchers, owing to the possibility of using them as highly effective inhibitors of the thermooxidative destruction of polymers, which is probably due to their definite activity toward hydroperoxide compounds and free radicals.

Despite the undoubted theoretical and practical interest of these reactions, the literature contains almost no data showing changes in the reactivity of phosphites and diphosphites as a function of their structure.

The aim of our work was a kinetic study of the behavior of various esters of phosphorous acid (aliphatic and aromatic), mixed esters of pyrocatechol phosphorous acid, and diphosphites, and elucidation of the influence of the structure of the phosphites taken on the rate of interaction with 1,1-diphenylethane hydroperoxide.

For the investigation we used the polarographic method. The possibility of applying this method to the study of the reactions described above is based on the ability of hydroperoxides to be reduced at a mercury dropping electrode.

The investigations were carried out on a self-recording polarograph of the OH-101 type, with a galvanometer sensitivity of $4 \cdot 10^{-8}$ A/mm. The cathode was a dropping electrode with capillary constant $m^{2/3}\tau^{1/6} = 1.2$; the background was a solution composed of equal volumes of absolute methanol and benzene and containing 0.3 mole of lithium chloride per 1 liter. The anode was a saturated calomel electrode. Oxygen was removed from the solution by purging with nitrogen freed of oxygen by a copper–ammonia solution and dried over caustic potassium hydroxide and sulfuric acid.

To avoid evaporation of the solvent, a wash bottle containing the same mixture of solvents as in the electrolyzer was placed before the electrolyzer.

In carrying out the experiments, a definite volume of background was placed in the electrolyzer, through which dry nitrogen was passed for 20 min, after which its polarogram was recorded. Then a benzene

Table 1

Rate constants of reactions of phosphorous acid esters with 1,1-diphenylethane hydroperoxide

Figure 3: kinetic curves

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No.	$(RO)_3P$, R	$K \cdot 10^2$, L · mole^{-1} · sec^{-1}	No.	mixed pyrocatechol phosphite, R	$K \cdot 10^2$, L · mole^{-1} · sec^{-1}
1	C_2H_5	56.0	1	iso-C_4H_9	17.5
2	iso-C_3H_7	34.6	2	C_6H_5	15.8
3	p-$CH_3C_6H_4$	2.50	3	$(CH_3)_3C{-}C_6H_3{-}C(CH_3)_3$	4.00
4	p-$(CH_3)_3C{-}C_6H_4$	1.83	4	$CH_3{-}C_6H_2\{C(CH_3)_3\}_2$	0.36
			5	$(CH_3)_3C{-}C_6H_2\{C(CH_3)_3\}_2$	0.35

a solution of diphenylethane hydroperoxide of a specified concentration, whose polarogram was recorded after five minutes of purging with nitrogen. Finally, a benzene solution of the phosphorous acid ester under study was added to the hydroperoxide solution in the background electrolyte. The moment of addition was taken as the beginning of the reaction. Thereafter, at definite time intervals, polarograms of diphenylethane hydroperoxide were recorded; the change in the height of the polarographic wave corresponded to the change in its concentration in the reaction mixture during the reaction with the phosphites.

Fig. 3. Kinetic curves for the interaction of 1,1-diphenylethane hydroperoxide with dipyrocatechol ethyl glycol diphosphite *(I)*, dipyrocatechol diethylene glycol diphosphite *(II)*, tetraphenyl hydroquinone diphosphite *(III)*, and diisopropyl pirocatechin diphosphite *(IV)* (volume ratios of the concentrations of 1,1-diphenylethane hydroperoxide and diphosphite 1 : 10, $t = 20°$).

Using a previously constructed calibration line reflecting the relation between the height of the hydroperoxide wave and its concentration, kinetic curves were constructed for the interaction of the hydroperoxide with phosphorous acid esters.

From Fig. 1, which demonstrates the behavior of complete aliphatic and aromatic esters of phosphorous acid with 1,1-diphenylethane hydroperoxide, it is seen that aliphatic phosphites are more active than aromatic ones. Reactions with them proceed considerably faster, as is also indicated by the rate constants (Table 1), determined from the equation for bimolecular reactions of second order:

chemical structures

Figure 4: chemical structures

$$K = \frac{2.303}{t(a-b)} \lg \frac{b(a-x)}{a(b-x)},$$

where a is the concentration of phosphite, b is the concentration of hydroperoxide, x is the number of moles of HP that have reacted, and t is time.

A similar picture is also observed in the case of esters of pyrocatechol phosphorous and diphosphorous acids (Figs. 2, 3). Aliphatic esters of pyrocatechol phosphorous acid react at the highest rate, and aromatic ones at the lowest.

On the basis of the results obtained, all the phosphorous acid esters studied can be arranged according to the rate of their interaction with 1,1-diphenylethane hydroperoxide in the following series:

Complete esters of phosphorous acid:

$$(C_2H_5O)_3P > (\text{iso-}C_2H_7O)_3P > (n\text{-}CH_3C_6H_4O)_3P > [(CH_3)_3C{-}C_6H_4{-}O]_3\,P.$$

Esters of pyrocatechol phosphorous acid:

$$\text{AlkO}{-}P\left\langle \begin{matrix} O{-}C_6H_3 \\ O{-}C_6H_3 \end{matrix} > C_6H_5{-}O{-}P\left\langle \begin{matrix} O{-}C_6H_4 \\ O{-}C_6H_4 \end{matrix} > CH_3{-}C_6H_4{-}O{-}P\left\langle \begin{matrix} O{-}C_6H_4 \\ O{-}C_6H_4 \end{matrix} \right.\right.\right.$$

$$> CH_3{-}C_6H_2(C(CH_3)_3)_2{-}O{-}P\left\langle \begin{matrix} O{-}C_6H_4 \\ O{-}C_6H_4 \end{matrix} > (CH_3)_3C{-}C_6H_2(C(CH_3)_3)_2{-}O{-}P\left\langle \begin{matrix} O{-}C_6H_4 \\ O{-}C_6H_4 \end{matrix} \right.\right.;$$

Diphosphites:

We also investigated the effect of concentration and temperature on the rate of the reaction between phosphorous acid esters and hydroperoxide. Increasing the concentration of one of the reacting substances (the ratio of hydroperoxide to phosphite in the experiments was 1:10, 1:3.1, 1:2, 1:1.5) and raising the temperature (20°, 25°, 30°) promote an increase in its rate.

It is of interest that the regularities found for the interaction of 1,1-diphenylethane hydroperoxide with phosphorous acid esters show a definite dependence on the inhibiting properties of the latter with respect to the thermooxidative destruction of polymers.

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Note: Figure translations are in progress. See original paper for figures.