

Kinetics and Mechanism of the Reaction of Tripropyl Phosphite with Water in Acetonitrile

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The reaction of tripropyl phosphite with water and with deuterium oxide in acetonitrile has been studied. In the concentration range 0.1–0.5 M of reactants, the reaction is found to obey a third order rate law, first order in phosphite and second order in water. Experiments with 86 atom % ^{18}O -enriched water have shown that it is a phosphorus-oxygen bond in the trialkyl phosphite which is broken during the hydrolysis. The rate constant for the reaction of tripropyl phosphite with deuterium oxide is eight times smaller than the rate constant for the reaction with water at the same temperature.

A transition state including one phosphite molecule and two water molecules is proposed. The deuterium isotope effect suggests that ionization of a water molecule occurs in the rate determining step.

Trialkyl phosphites have long been known to be easily hydrolysed by water in the presence of acids.¹ Against pure water they have been reported to be stable up to 100°C, with the exception of trimethyl phosphite which on boiling with water was found to give dimethyl phosphite and methanol.¹ Arbuzov and Imajev² showed that in the presence of dialkyl phosphites the trialkyl phosphites are readily hydrolysed by water, to dialkyl phosphites and the corresponding alcohols. The rate of hydrolysis of trialkyl phosphites, as studied by Imajev³ by a dilatometric method, decreases in the series: trimethyl > triethyl > tripropyl > tributyl. Dialkyl phosphites were found to have an autocatalytic effect on the reaction. Since trialkyl phosphites are only sparingly soluble in water, stirring of the trialkyl phosphite-water mixture was employed. Due to the heterogeneity of the reaction mixture, the method is unsuitable for reaction kinetic studies, and calculations of rate constants were not attempted.

During studies of Michaelis-Arbuzov rearrangements of trialkyl phosphites with alkyl iodide in acetonitrile, the present authors discovered that trialkyl phosphites are rapidly hydrolysed by small amounts of water in the acetonitrile.⁴ This paper reports the results of kinetic studies of the reaction between tripropyl phosphite and water respectively deuterium oxide in acetonitrile.

EXPERIMENTAL

Materials. Tripropyl phosphite was made from phosphorus trichloride and propyl alcohol in the presence of dimethylaniline.⁵ The reaction was performed in absolute ether as solvent. 68.7 g freshly distilled phosphorus trichloride was dissolved in 400 ml absolute ether. 90 g dry propyl alcohol and 181.5 g dimethylaniline were diluted with 300 ml absolute ether and the mixture added dropwise to the phosphorus trichloride solution under rapid stirring. When the addition was complete, the precipitated salt was filtered off, the ether removed at normal pressure and the tripropyl phosphite fractionated *in vacuo*. In order to remove the small amount of dipropyl phosphite formed, the fractionated reaction product was dissolved in 100 ml absolute ether and 5 g of sodium wire added. After 24 h the precipitated sodium salt of dipropyl phosphite was filtered off and the product fractionated *in vacuo* until the tripropyl phosphite was pure by gas chromatographic analysis. Tripropyl phosphite, b.p.₁₀ = 82°C, n_D^{20} = 1.4245. (Imajev:³ b.p.₁₀ 84.5 – 85°, n_D^{20} = 1.4245). It is especially important that the tripropyl phosphite is absolutely free of the tertiary base used in the synthesis, since the rate of hydrolysis with water is strongly dependent on the pH of the solvent.

Acetonitrile (Fluka puriss, b.p. 80–81°) was boiled with phosphorus pentoxide for one hour. The dry acetonitrile was then fractionated on a 70 cm Vigreux column, b.p. 81°C. The dryness of the acetonitrile was checked by showing that the infrared spectrum of a 0.2 M solution of tripropyl phosphite in the acetonitrile at 52°C remained unchanged after 12 h.

Deuterium oxide, 99.79 % by weight, $d = 1.10515$, produced by Norsk Hydro-Elektrisk Kvalstofaktieselskab, was used.

¹⁸O-Enriched water, produced by Yeda Research and Development Co., Ltd., Rehovoth, Israel, had the following specifications: ¹⁸O: 86.36 atom %; ¹⁷O: 0.14 atom %.

Water. Ordinary distilled water was used.

Rate measurements. The reaction was started by mixing temperature-equilibrated acetonitrile solutions of tripropyl phosphite with water. The initial concentrations in the reaction solution varied from 0.1 to 0.5 M. The formation of dipropyl phosphite with time was followed by measuring the infrared absorption of the reaction solution in the region of the phosphoryl absorption band of dipropyl phosphite (1258 cm⁻¹). Calibration spectra were obtained as previously described⁶ and the concentration of dipropyl phosphite was calculated from

$$E_{\text{total}} = K_d x d + K_t (a - x) d$$

where E_{total} = extinction of the reaction solution, K_d and K_t = extinction coefficients of dipropyl phosphite and tripropyl phosphite at 1258 cm⁻¹ (the peak of the phosphoryl band), d = cell length and x = concentration of dipropyl phosphite.

The spectra were recorded on an Unicam spectrophotometer, S.P. 100, Mk. 2.

Calculation of rate constants. The rate constants were calculated according to the equation:

$$\frac{dx}{dt} = k(a - x)(b - x)^2 \quad (I)$$

where x = concentration of dipropyl phosphite at time t , a and b are initial concentrations of tripropyl phosphite and of water respectively, k = third order rate constant (l³/mole²hour). Two solutions of eqn. (1) are needed:

Case I: $a \neq b$

$$F(x) = \frac{1}{a - b} \left(\frac{1}{b - x} - \frac{1}{b} \right) + \frac{1}{(a - b)^2} \ln \frac{a}{b} \frac{b - x}{a - x} = k \cdot t \quad (I)$$

Case II: $a = b$

$$F(x) = \frac{1}{2} \left(\frac{1}{(a - x)^2} - \frac{1}{a^2} \right) = k \cdot t \quad (II)$$

RESULTS AND DISCUSSION

The reaction between tripropyl phosphite and water in acetonitrile is extremely sensitive towards impurities in the reagents. In order to get reproducible values in various runs, chromatographically pure reagents are necessary. As already mentioned by Imajev,³ the method of synthesis of the trialkyl phosphites strongly influences the rate of reaction with water. He reported that the method of Milobendzki⁵ using pyridine as tertiary base for the synthesis of trialkyl phosphites gave products which reacted with water at a rate twelve times lower than products made with dimethylaniline as base. Our studies have shown that the difficulties arise from the presence in the product of a small amount of the tertiary base which retards the reaction very strongly. The presence of as little as 10^{-4} M of pyridine had a marked retarding influence on the rate. On the other hand, acids and metal cations as Cu^{2+} , Ag^+ , and Fe^{3+} were found to accelerate the reaction in concentrations above 10^{-5} M.

The autocatalytic effect of dialkyl phosphite observed by Imajev³ on the reaction between trialkyl phosphite and water is absent when the reaction is performed in acetonitrile solution. The autocatalysis is clearly a solubilizing effect: Since trialkyl phosphite and water give a two-phase system due to the low solubility of water in trialkyl phosphite and *vice versa*, the formed dialkyl phosphite which is unlimitedly soluble in water as well as trialkyl phosphite, will act as solubilizer. The effective concentrations of reagents in homogeneous phase will therefore increase, producing an acceleration of the rate of hydrolysis with time.

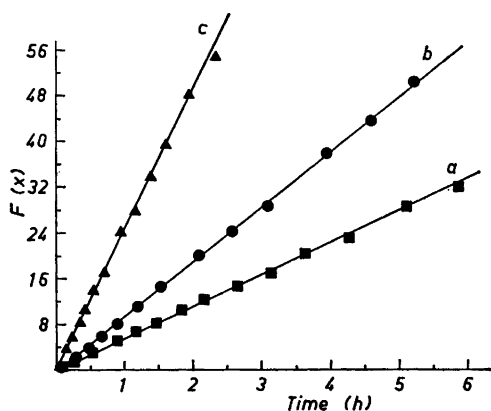


Fig. 1. Experimental data for the reaction between tripropyl phosphite and water plotted according to a third order rate law (eqn. II). Start concentrations of tripropyl phosphite and of water: a) 0.198 M, b) 0.188 M, c) 0.160 M. Temp. 45.2, 52.1, 65.0°C, respectively.

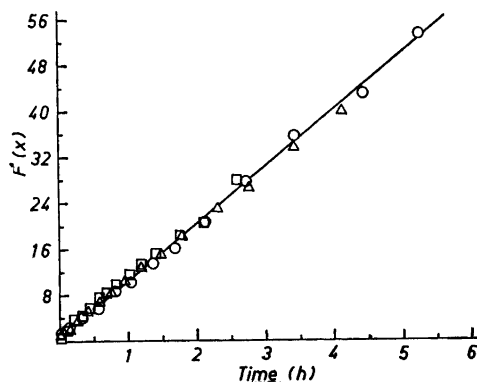
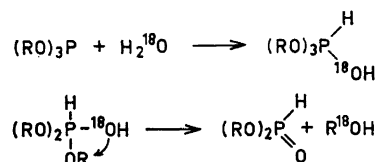


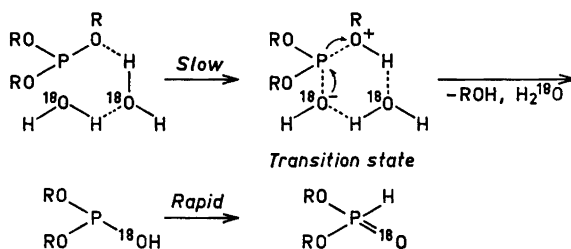
Fig. 2. Experimental data for the reaction between tripropyl phosphite and water with equimolecular as well as different start concentrations of substrate and reagent, plotted according to eqns. (I) and (II). Start concentrations of tripropyl phosphite and water: a) \square , 0.120 and 0.252 M, (b) \circ , 0.199 and 0.131 M, c) \triangle 0.180 and 0.180 M, respectively. Temp. 60°C.

In the concentrations range studied, 0.1–0.5 M of tripropyl phosphite and water in acetonitrile, the reaction is very nearly of first order in phosphite and second order in water. Fig. 1 shows third order plots for three separate runs at different temperatures. Equivalent concentrations of reagents have been used in each run. In Fig. 2 the initial concentrations of reagents are different in two of the runs shown (a and b), whereas in the third run (c) equimolecular concentrations are used. Runs (a) and (b) are plotted according to rate eqn. (I), and (c) according to eqn. (II). Since the three runs are performed at the same temperature (60°C), a plot of $F(x)$ against time shall result in a single straight line with slope k . The experimental values plotted in Fig. 2 show this to be the case.

Arbuzov^{1,2} assumed that the mechanism of the reaction between trialkyl phosphite and water is similar to an ordinary Michaelis-Arbuzov reaction of trialkyl phosphite and alkyl halogenide:



The first step in this scheme is an electrophilic attack of the water hydrogen on phosphorus. However, the very strong acid catalysis observed for the hydrolysis (the reaction is then too fast to be studied accurately by the present method), suggests that the hydrogen atom of the water molecule attacks the most basic center, *i.e.* one of the oxygen atoms. The third order rate dependence observed for the overall reaction, first order in phosphite and second order in water, points to a concerted reaction mechanism:



According to the mechanism of Arbuzov the oxygen atom of the alcohol formed should come from the water, whereas according to the proposed concerted mechanism the water oxygen will be found in the phosphoryl group of the dialkyl phosphite produced. In the latter case, when ^{18}O -enriched water is used, an infrared phosphoryl band containing ^{18}O will appear. The greater mass of ^{18}O will displace the stretching vibration band of the phosphoryl group towards lower frequencies. Ignoring the substituents linked to phos-

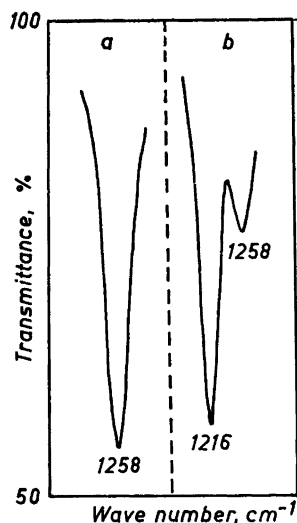


Fig. 3. The stretching vibration bands of a) $P=^{16}O$, b) $P=^{16}O$ and $P=^{18}O$ in dipropyl phosphite.

phorus, calculations according to Hooke's law ⁷ predict a displacement of 45 cm^{-1} . In triphenylphosphine oxide Halmann and Pinchas ⁷ found a difference of 30 cm^{-1} between the peaks of $P=^{16}O$ and $P=^{18}O$.

In Fig. 3 are shown the phosphoryl bands of dipropyl phosphite obtained (a) from the reaction of tripropyl phosphite in acetonitrile with ordinary water and (b) with 86 atom % ^{18}O -enriched water. Ordinary water gives rise to a single absorption band at 1258 cm^{-1} . In the experiment with ^{18}O only a small peak corresponding to the 14 atom % ^{16}O is observed at 1258 cm^{-1} . The major peak which must be due to the $P=^{18}O$ band is found at 1216 cm^{-1} . The experiment proves that in the reaction between trialkyl phosphite and water it is the phosphorus-oxygen bond which is broken, and strongly argues for a concerted reaction mechanism.

Table 1. Data for the reaction of tripropyl phosphite with water and with deuterium oxide in acetonitrile.

Reagent	Temp. °C	Start conc. mole/l		Rate constant $l^2 \text{ mole}^{-2} \text{ h}^{-1}$
		tripropyl phosphite	H_2O resp. D_2O	
H_2O	45.2	0.198	0.198	5.57
»	52.1	0.188	0.188	9.58
»	65.0	0.160	0.160	24.40
D_2O	52.0	0.126	0.320	1.15
»	»	0.163	0.163	1.15
»	»	0.164	0.164	1.17

Further support for a concerted reaction mechanism comes from correlating studies of the reactions of tripropyl phosphite with water and with deuterium oxide. In Table 1 are recorded data for the water and deuterium oxide reaction in the temperature region 45–65°. The decrease in rate constant from the reaction with water to deuterium oxide is approximately 8 times at 52°C, which is also the order of magnitude of the ratio between the ionization constant of water in water and deuterium oxide in deuterium oxide ($K_{\text{H}}/K_{\text{D}} = 6.5$).⁸ The deuterium isotope effect indicates that ionization of a water molecule is involved in the rate determining step.

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