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The Reaction between *Iso*propoxy-methyl-phosphoryl Fluoride and Hydrogen Peroxide

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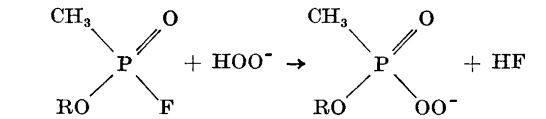
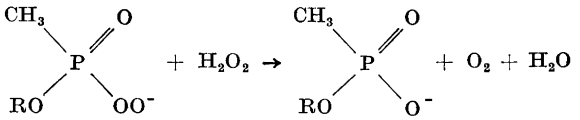
The reaction between *iso*propoxy-methyl-phosphoryl fluoride and hydrogen peroxide has been studied by measuring the amount of oxygen evolved during the reaction.
The mechanism of the decomposition reaction is discussed.

The bimolecular reaction between *iso*propoxy-methyl-phosphoryl fluoride and hydrogen peroxide has been studied by Larsson [1] by means of an automatic titration method. He concludes that the rate of the bimolecular reaction is proportional to the concentration of the anion of hydrogen peroxide. Gehauf *et al.*[2], Epstein *et al.*[3] and Larsson [1] suggest that the decomposition of the intermediately formed peroxyphosphorus acid is due to a bimolecular reaction of this acid with hydrogen peroxide. This last step is believed to be rate determining:



(1)



(2)

The kinetic of the second step of the above reactions has been the main interest of the present work. For this reason a volumetric method of measuring the oxygen evolution during the reaction has been developed.

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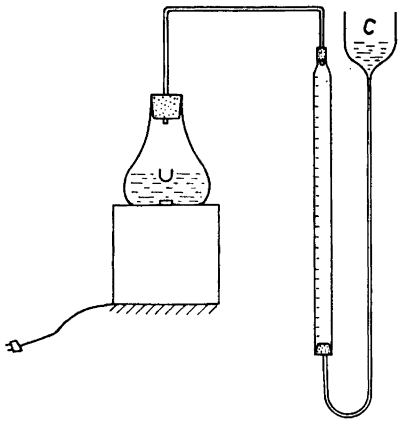


Fig. 1. Apparatus used for determination of the rate of oxygen evolution.

EXPERIMENTAL

*Materials. Iso*propoxy-methyl-phosphoryl fluoride was synthesized in this institute. Hydrogen peroxide was an E. Merck anal. reagent. The concentration of the hydrogen peroxide solutions was determined by titration with 0.1 N solution of potassium permanganate.

Kinetic measurements. The apparatus used for the study of the oxygen evolution is shown in Fig. 1. The oxygen is collected in a burette of 50 ml capacity connected by a glass tube to the reaction vessel. The reaction vessel consisted of a 100 ml Erlenmeyer flask. Fifty ml of hydrogen peroxide solution containing 0.2 M buffer was placed in the reaction vessel. The weighed sample of the fluorophosphorus compound was placed in a small conical glass vessel. The vessel was brought into the Erlenmeyer flask and placed on the surface of the hydrogen peroxide solution in floating position. The reaction is started by tipping the content of the conical flask into the solution. This is simply obtained by starting the magnetic stirrer whereupon the reaction vessel was placed. The amount of oxygen evolved is found by lowering of the level of the water in the container

Table 1. The reaction between *iso*propoxy-methyl-phosphoryl fluoride and hydrogen peroxide. Buffer: 0.2 M citrate — phosphate pH = 7.

0.000546 M fluorophosphorus compound +4.0 %H_2O_2 Temp. 18°C.	Time (min)	5	10	15	23	31	43	58	73	95	105	Calculated rate constant
	Oxygen evolved, cm^3(corr.)	(0.2)	(0.6)	1.8	2.9	3.2	4.4	5.0	6.0	6.1	6.2	0.026 min^{-1}
0.00160 M fluorophosphorus compound +4.0 %H_2O_2 Temp. 18°C.	Time (min)	9	19	26	32	44	54	65	73	100		Calculated rate constant
	Oxygen evolved cm^3(corr.)	(3.6)	7.5	9.5	10.0	13.3	14.8	16.3	16.9	17.8		0.026 min^{-1}

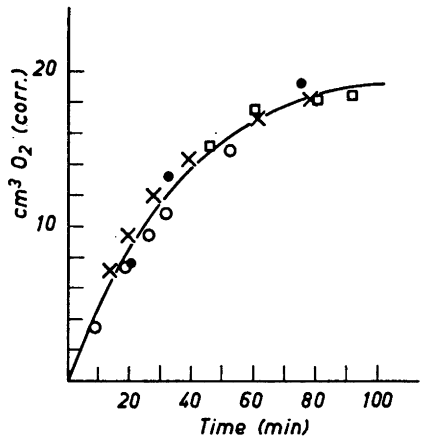


Fig. 2. The evolution of oxygen at different hydrogen peroxide concentration. Buffer 0.2 M citrate-phosphate, pH = 7.00. Temp. 18°C. Concentration of *iso*propoxy-methyl-phosphoryl fluoride: 0.0016 M. Hydrogen peroxide concentration: ×, 1.93 %; O, 2.98 %; ●, 3.94 %; □, 4.78 %.

C until the same level as the water in the burette. The water in the burette and the container is saturated with oxygen at room temperature. Correction was always made for the amount of oxygen evolved at the different pH studied due to the self-decomposition of the hydrogen peroxide solution. The self-decomposition was found to rise rapidly with increasing pH.

RESULTS

In Table 1 are recorded the experimental values of the oxygen evolution of two different concentrations of the fluorophosphorus compound when the hydrogen peroxide concentration is maintained constant. We find that the amount of oxygen evolved is proportional to the concentration of the fluorophosphorus compound.

In Fig. 2 are recorded the rates of oxygen evolution at four different concentrations of hydrogen peroxide. The concentration of the *iso*propoxy-methyl-

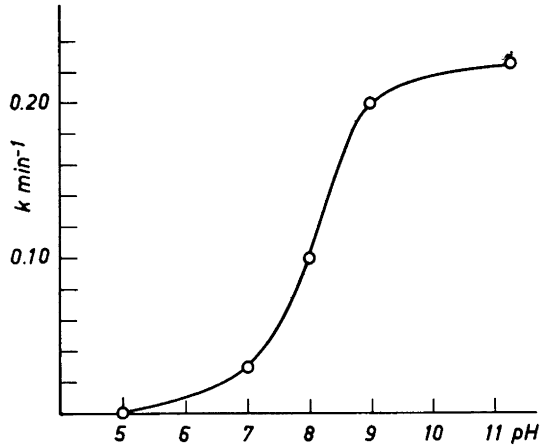


Fig. 3. The relation between the rate of oxygen evolution and pH of the solution. Buffers: 0.2 M citrate-phosphate (pH = 5, 7 and 8). 0.2 M boric acid-sodium hydroxide pH = 9. 0.2 M potassium dihydrogenphosphate-potassium hydroxide (pH = 11.3). Hydrogen peroxide concentration = 4 %.

phosphoryl fluoride is maintained constant. The full-drawn curve in Fig. 2 shows a first order reaction with a rate constant of 0.03 min^{-1}. The experimental points of the oxygen evolution at the four different hydrogen peroxide concentrations in Fig. 2 show average deviation of about 5 % from the first order reaction curve. This is within the limits of the experimental errors of the applied technique.

In Fig. 3 is plotted the rate constants of the oxygen evolution at five different pH (5, 7, 8, 9 and 11.3) as function of pH.

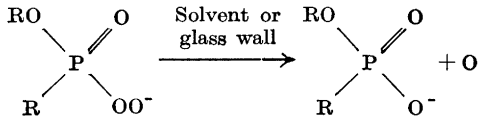
Some experiments were performed in order to determine the amount of hydrogen peroxide consumed when the decomposition reaction approached completion. When the initial concentration of hydrogen peroxide in the reaction solution varied between 0.010 M and 0.1 M the ratio between the hydrogen peroxide decomposed and the total concentration of fluorophosphorus compound varied between 1.5 and 1.9.

DISCUSSION

The first order rate of oxygen evolution which is observed under the conditions of the present experiments shows that the formation of the peroxyphosphorus acid according to eqn. (1) must be much more rapid than its decomposition, *i.e.* the decomposition of the peroxyphosphorus acid is the rate determining step. This observation is in agreement with the findings of Larsson [1]. From his calculated pseudo first order rate constant of the reaction between *iso*propoxy-methyl-phosphoryl fluoride and hydrogen peroxide at 25°C we may estimate that the pseudo first order reaction of the same step under the present conditions will be so rapid that the deviation of the second step from the first order reaction rate will not be observable.

The present results do not confirm the assumption of Gehauf *et al.*[2] and Epstein *et al.*[3] that the decomposition of the peroxyphosphorus acid is a true bimolecular reaction with hydrogen peroxide. If that had been so the ratio between the amount of hydrogen peroxide decomposed and the total concentration of fluorophosphorus compound should approach 2 at all concentrations of hydrogen peroxide. The present results and the observation of Larsson [1] are not in accordance with this reaction scheme. Another argument against this view is found in the results quoted in Fig. 2. The hydrogen peroxide in the four separate experiments is in sufficiently great excess as compared with the fluorophosphorus compound to give the postulated second order reaction between the peroxyphosphorus acid and hydrogen peroxide a pseudo first order character. The rate of oxygen evalution should therefore be expected to be proportional to the hydrogen peroxide concentration. On the contrary the results show nearly the same rate of oxygen evolution at the four different concentrations of hydrogen peroxide. It seems therefore reasonable to conclude that the hydrogen peroxide does not participate in the rate determining decomposition of the peroxyphosphorus acid. Larsson [1] has postulated a competing reaction between peroxyphosphorus acid and unreacted fluorophosphorus compound to explain the deviation of the second order kinetics of the decomposition of the peroxyphosphorus acid at low concentration of hydrogen peroxide. But it is difficult to explain the results quoted in Fig. 2

according to such a hypothesis. A more reasonable explanation seems therefore to be that the decomposition of the peroxyphosphorus acid is a rate-determining unimolecular reaction (perhaps influenced by the solvent or the glass wall) and that the oxidation of the hydrogen peroxide is a rapid process between "active oxygen" and hydrogen peroxide. The decreasing consumption of hydrogen peroxide with decreasing hydrogen peroxide concentration can then be explained to be due to a competing pairing formation of "active oxygen" to molecular oxygen:



(1)

$$O + H_2O_2 \rightarrow O_2 + H_2O \text{ and } O + O \rightarrow O_2 \quad (2)$$

A support for this view may be found from different sources concerning the decomposition of peroxide compounds [6].

The S-shaped relation between the decomposition of the peroxyphosphorus acid and the pH of the solution suggest that the decomposition proceeds *via* the anion of the peroxy acid and that the pK of this acid may have a value of approximately 8. Everett *et al.*[4] have found that the pK values of peroxy fatty acids lie in the range of pK 7.1—8.3. By analogy to the difference between the pK values of fatty acids and substitued phosphorus acids (the last-mentioned are 2—3 pH-units lower) Larsson [1] assumes that the difference between the pK of the corresponding peroxyacids is of the same order of magnitude. This need not necessary be so because the stabilization effect due to the perfect resonance of the anions of the oxyacids do not exist in the peroxyacids. It seems therefore doubtful that the inductive mechanism which must be assumed to be the chief electronic effect operating in the peroxyacids is able to maintain the same difference between pK-values of different peroxyacids as between corresponding oxyacids This argument is strengthened by the observation of Everett *et al.*[4] that the differences in the inductive effects between H, CH_3, C_2H_5, *iso*-C_3H_7 which are clearly reflected in the differences between the pK-values of water and alcohols are almost absent in the same serie of hydroperoxides. It is also some reason to question the accuracy of the titrimetric method used by Everett *et al.*[4] for determination of the pK-values of peroxyacids. This method may be encumbered with error due to the instability of the peroxyacids. This decomposition which produces the corresponding oxyacids increases rapidly with the rise of pH and will give as result that the observed pK-value of the peroxyacid will lie below the actual one. The error will increase with increasing rate of decomposition and increasing length of time used to obtain the titration curve. In Holleman-Richters' textbook of organic chemistry [5] the dissociation constant of peroxyacetic acid is quoted as 4×10^{-10} (pK = 9.4). Unfortunately the authors give no reference to the original work from which this value is taken. It seems also worth while to mention that the pK of the bisulphate ion and its corresponding peroxyacid are 1.7 and 9.4, respectively [7].

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