534. *Decomposition of Inorganic Peroxyacids in Aqueous Alkali.*

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A study has been made of the uncatalysed decomposition of peroxymonosulphuric acid in aqueous alkali. Second-order kinetics were observed, with maximum rates at 50% dissociation of the peroxyacid. This is analogous to the decomposition of substituted aromatic peroxyacids under identical conditions. A general mechanism for peroxyacid decomposition is proposed; it can be applied also to the decomposition of hydrogen peroxide at high pH and the interaction and mutual decomposition of peroxy-compounds.

In a previous study[1] it was shown that uncatalysed decomposition of aromatic peroxyacids in aqueous alkali occurs by a second-order process, the rate of which is a maximum at 50% dissociation of the peroxyacid. It was proposed that the rate-determining step was nucleophilic attack of the peroxyacid anion on the carbonyl-carbon atom of the un-ionised peroxyacid. The second step was rapid decomposition of this intermediate to the carboxylic acid and oxygen as the main products. It was suggested that this mechanism could be extended to inorganic peroxy-compounds, in particular hydrogen peroxide[2] and peroxymonosulphuric acid.[3] This paper describes a study of the decomposition of these inorganic peroxyacids in aqueous solution at various pH's and temperatures, by a technique similar to that employed for the aromatic peroxyacids.[1]

EXPERIMENTAL

Materials.—Samples of peroxymonosulphuric acid were prepared by the action of 80% hydrogen peroxide on freshly distilled chlorosulphuric acid.[3,4] The peroxyacid obtained was contaminated with free hydrogen peroxide. As it was found that a pH-dependent reaction took place between hydrogen peroxide and peroxymonosulphuric acid, the former was eliminated by neutralising the peroxymonosulphuric acid with potassium carbonate; the peroxyacid was then precipitated as the monopotassium salt, $KHSO_5$, in admixture with K_2SO_4 and $KHSO_4$. Samples containing ~45% of the peroxyacid salt were generally obtained. Industrial potassium peroxymonosulphate was found to be identical with the product produced in laboratory experiments, and samples from the two sources gave identical results in the decomposition experiments.

For the study on hydrogen peroxide the commercial product (B.D.H.; 100-vol.) was used without purification.

Dissociation Constants.—The dissociation constant of the hydrogen peroxymonosulphate ion, HSO_5^{1-}, was determined at different temperatures by potentiometric titration under nitrogen. Owing to the rapid decomposition of the peroxyacid, the accuracy of the values obtained for the pK was low ($\pm 0{\cdot}2$ unit). The value for the dissociation constant of hydrogen peroxide was taken from the literature.[5]

Rate Measurements.—Ball and Edwards[3] studied the decomposition of peroxymonosulphuric acid in phosphate and carbonate buffers, but the influence of these anions on the rate of reaction is unknown. We have established that borate ions accelerate peroxyacid decompositions and to avoid such complication the reaction has been studied in dilute sodium hydroxide solution. The catalytic effect of heavy-metal impurities has been markedly diminished, if not completely removed, by addition of disodium dihydrogen ethylenediaminetetra-acetate (EDTA) to the reaction system. Thus preliminary experiments showed that addition of increasing quantities of EDTA caused the rate of reaction to approach a minimum value, but that an excess over that required to chelate the metal impurities reacted slowly with the peroxyacid.

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[1] Goodman, Robson, and Wilson, *Trans. Faraday Soc.*, 1962, **58**, 1846.
[2] Duke and Haas, *J. Phys. Chem.*, 1961, **65**, 304.
[3] Ball and Edwards, *J. Amer. Chem. Soc.*, 1956, **78**, 1125.
[4] D'Ans and Friederich, *Ber.*, 1910, **43**, 1880.
[5] Evans and Uri, *Trans. Faraday Soc.*, 1949, **45**, 224.

The rate of decomposition of peroxymonosulphuric acid in aqueous alkali was followed in carefully cleaned glass flasks, immersed in a constant-temperature bath ($\pm 0{\cdot}1°$). A solution of potassium peroxymonosulphate in redistilled water containing EDTA was transferred to the reaction flask and allowed to reach temperature equilibrium. The pH of the reaction mixture was adjusted to the required value by addition of sodium hydroxide solution and monitored throughout the experiment with a glass electrode, the pH being kept constant at $\pm 0{\cdot}03$ unit by slow addition of alkali. Aliquot parts of the reaction mixture were pipetted at specific time intervals into 10% sulphuric acid containing a known amount of standard sodium arsenite solution. The concentration of peroxymonosulphuric acid was determined by titrating the excess of arsenite with ceric sulphate in the presence of osmic acid, with ferroin as an indicator.[6] The reaction was also followed by determining the rate of addition of standard alkali required to maintain the pH constant over fixed time intervals. In addition to the main products, small quantities of peroxydisulphate ion were formed. The concentration of this species was determined [6] by adding a further volume of standard arsenite solution to the titration flask after estimation of peroxymonosulphate. A small piece of solid carbon dioxide was then added to maintain an inert atmosphere, and the solution was heated to the b. p. to hydrolyse the peroxydisulphuric to peroxymonosulphuric acid. After cooling, the excess of arsenite was titrated with ceric sulphate as before.

The technique described above could not be used to establish the exact variation of the rate of decomposition of hydrogen peroxide with pH. Thus the uncatalysed decomposition occurs at a measurable rate only at high temperatures and high pH. Evaporation at elevated temperatures was shown to cause a serious error. Moreover, the uncatalysed reaction had to be followed in Polythene beakers, and the glass electrode could be placed in the solution only momentarily to monitor the pH. The high temperature and high alkalinity had a marked effect on the performance of the electrode: however, measurements were reliable in the region of the pK of hydrogen peroxide at 35°. Hydrogen peroxide was estimated directly by titration with ceric sulphate, with ferroin as indicator.

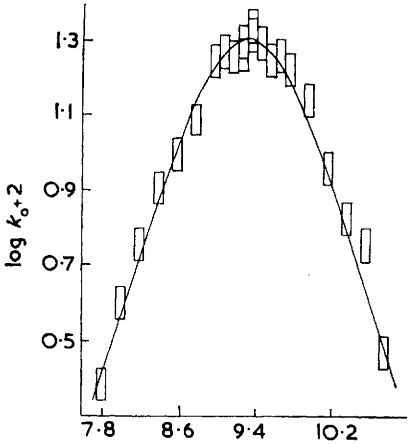

FIG. 1. Variation of log k_0 with pH for peroxymonosulphuric acid at 25°.

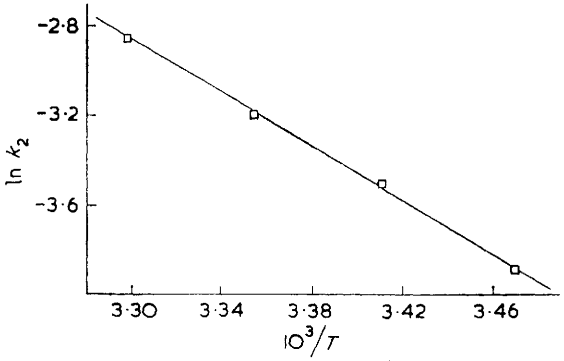

FIG. 2. Plot of ln k_2 against $10^3/T$ for peroxymonosulphuric acid.

RESULTS

At a fixed temperature and pH, the decomposition of peroxymonosulphuric acid occurred by a second-order process. The observed rate constant k_0 was given by the slope of the line obtained by plotting the reciprocal of the peroxymonosulphuric acid concentration against time. It was shown that the rate of the reaction was independent of the nature of the vessel (Polythene or glass) but exhibited a salt effect. To ensure that experiments were carried out at constant ionic strength identical weights of material were taken for each run. The reaction proceeded with a maximum rate at pH's in the region of the pK of the peroxyacid,

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[6] Csanyi and Solymosi, *Acta Chim. Acad. Sci. Hung.*, 1957, **13**, 257; *Chem. Abs.*, 1958, **52**, 19,687.

which was shown to be 9·3 ± 0·2 at 25°. Fig. 1 shows the variation of log k_0 with pH at 25°, the rectangles representing experimental errors. Experiments were conducted at several temperatures in the region of 50% dissociation and an activation energy of 11·9 kcal./mole was calculated from the plot shown in Fig. 2. It was shown that the rate of formation of acid, presumably bisulphate ion, was half the rate of disappearance of the available oxygen. Small quantities of peroxydisulphate ion were also formed, but the quantity was always less than 10% of the total products.

DISCUSSION

Kinetics of Decomposition.—Peroxymonosulphuric acid decomposed by a second-order mechanism, the rate of which rose to a maximum at 50% ionisation of the system:

$$HSO_5^{1-} + H_2O \overset{K}{\rightleftharpoons} SO_5^{2-} + H_3O^+ \qquad (1)$$

where K is the dissociation constant for the acid anion.

Both the hydrogen peroxymonosulphate ion and the peroxymonosulphate ion must, therefore, be concerned in the rate-determining step as follows:

$$HSO_5^{1-} + SO_5^{2-} \xrightarrow{k_2} \text{Intermediate} \longrightarrow HSO_4^{1-} + SO_4^{2-} + O_2 \qquad (2)$$

where
$$\text{Rate of reaction} = k_2[HSO_5^{1-}][SO_5^{2-}] \qquad (3)$$

We have shown previously[1] that the observed second-order rate constant k_0 for such a system should vary with pH in the following manner:

$$k_0 = 2Ak_2/(1 + A)^2 \qquad (4)$$

where $A = [H^+]/K$.

At 50% dissociation of the peroxyacid, $A = 1$ and $k_2 = 2k_0$. As $\partial k_0/\partial[H^+] = 0$ at this point the most accurate value of k_2 is obtained. By substituting this value for k_2 into equation (4) the variation of k_0 with pH may now be constructed (solid line in Fig. 1). Satisfactory agreement is obtained, confirming equation (3) for the kinetic form of the reaction. Also in agreement with these kinetics is the observation that the rate of reaction, as measured by the rate of evolution of acid, was half that calculated from the rate of disappearance of available oxygen.

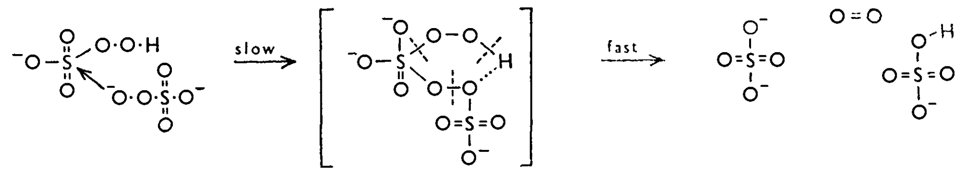
Ball and Edwards's results[3] for the decomposition of peroxymonosulphuric acid in carbonate and phosphate buffers fit equation (4), with a value of $k_2 = 2{\cdot}10 \times 10^{-1}$ l. mole^{-1} sec.$^{-1}$ at 25°, compared with our value of $4{\cdot}08 \times 10^{-2}$ for the reaction in sodium hydroxide solution. The ionic strengths of the reaction mixtures in the two series of experiments were different. Ball and Edwards used ionic strengths of 1·0—2·3; in the present work the ionic strength was maintained approximately constant at 0·2. The difference in observed rate constants may be due to a primary salt effect. However, we found that on raising the ionic strength to 2·0 by addition of sodium sulphate, the values of k_2 in sodium hydroxide solution were greater than those we obtained in phosphate solutions at the same pH. Thus, the influence of inorganic anions in aqueous solutions of peroxyacids appears complex. We also observed that increasing amounts of borax gradually change the kinetics from second- to first-order. It appears preferable to work with peroxyacids in aqueous systems in the absence of inorganic buffers.

We should expect the kinetic equation for the uncatalysed decomposition of hydrogen peroxide to be analogous to equation (3) such that,

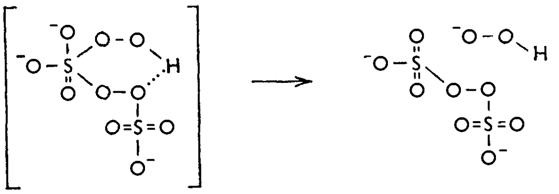
$$-\partial[H_2O_2]_t/\partial t = k_2'[HO_2^-][H_2O_2], \qquad (5)$$

where $[H_2O_2]_t = [HO_2^-]$ plus $[H_2O_2]$ at time t. This is identical with the equation proposed by Duke and Haas.[2] Our experimental errors were too great to permit full correlation with equation (4), such as has just been described for peroxymonosulphuric acid. However, we were able to show that decomposition occurred by a second-order process and that the rate passed through a maximum in the region of the pK of the hydrogen peroxide. The maximum value obtained for k_0 at 35°, $3{\cdot}5 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ agrees well with the figure of $3{\cdot}7 \pm 0{\cdot}6 \times 10^{-4}$ l. mole^{-1} sec.$^{-1}$ obtained by Duke and Haas. There are strong indications, therefore, that equation (5) correctly represents the kinetic form of the decomposition of hydrogen peroxide.

Mechanism of Decomposition.—It has been shown that the kinetics of the uncatalysed decomposition of peroxy-aromatic acids and peroxymonosulphuric acid are identical. It is reasonable, therefore, that the decompositions should occur by similar mechanisms. Extending the mechanism proposed[1] for the decomposition of aromatic peroxyacids to peroxymonosulphuric acid we obtain:

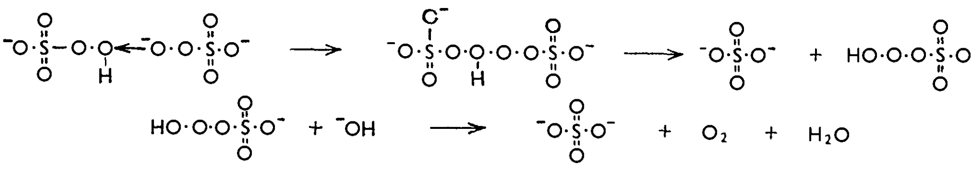


The intermediate is presumed to decompose through an intramolecularly hydrogen-bonded form. This mechanism is supported by formation of peroxydisulphate as a by-product, indicating the formation of an S–O·O·S bond. This peroxide can be produced by an alternative breakdown of the intermediate:



Peroxydisulphate might have arisen by the combination of sulphate ion-radicals in solution. The presence of free radicals in the system, however, could not be detected for neither acrylonitrile nor methyl methacrylate was polymerised when added to the system, although both monomers were oxidised slowly.

This mechanism is different from that suggested by Ball and Edwards.[3] They postulated the formation of the transition state by attack of the nucleophilic SO_5^{2-} ion on the oxygen of the HSO_5^{1-} ion with ensuing formation of an HSO_6^{1-} entity. The last ion then gives the products by alkaline hydrolysis.



Although we cannot unequivocally distinguish between the two mechanisms, we consider it unlikely that the reaction should proceed by nucleophilic attack of an oxygen anion upon oxygen.[7]

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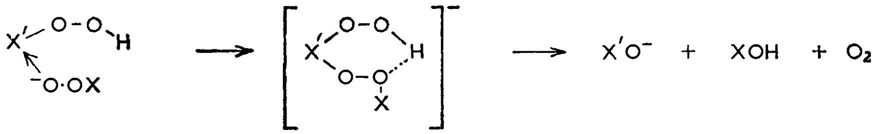
[7] Davies, " Organic Peroxides," Butterworths Scientific Publns., London, 1961, p. 132.

The mechanism proposed in this paper for peroxy-compound decomposition may be written in the general form:



For the aromatic peroxyacids $X = X' = Ar{\cdot}CO$, for peroxymonosulphuric acid $X = X' = SO_3^-$, and for hydrogen peroxide $X = X' = H$, thereby giving the mechanism for the decomposition of hydrogen peroxide proposed by Duke and Haas.[2] Reactions involving the interaction and mutual decomposition of different peroxy-compounds can also proceed by this general mechanism. One example, the decomposition of mixtures of aromatic peroxyacids ($X' = NO_2{\cdot}C_6H_4{\cdot}CO$, $X = Me{\cdot}C_6H_4{\cdot}CO$) has been described previously.[1] Another example, the pH-dependent reaction between hydrogen peroxide and peroxymonosulphuric acid ($X' = H$, $X = SO_3^-$) mentioned in this paper can proceed in an analogous manner.

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