

Hydrolysis and First Ionization Constant of Monoperoxyphthalic Acid

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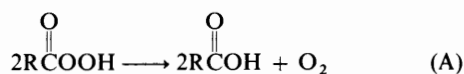
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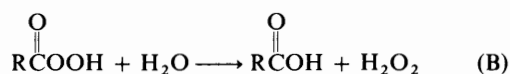
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The ionization constant for the carboxy proton of monoperoxyphthalic acid (MPPA) has been determined as 1.1×10^{-3} , based on pK_{a1} 2.96 ± 0.05 at 21 °C and ionic strength 0.024 mol dm⁻³ obtained by a distribution method. In the pH range 1–4 the observed rate constant for hydrolysis of MPPA increases by a factor of >2 presumably as a result of intramolecular catalysis by the carboxylate function in the peroxy acid monoanion. At pH > 4, trace-impurity-induced decompositions of both MPPA and hydrogen peroxide prevented satisfactory studies of the hydrolysis reaction. At pH < 1 the hydrolysis rate constant at first decreases, as a result of an activity coefficient effect, to reach a minimum value at $\log_{10}[H^+] \text{ ca. } 0.7$, and then increases rapidly with the onset of an acid-catalysed reaction at higher acidity.

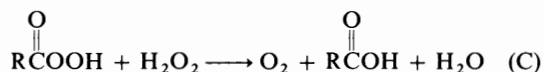
Aqueous solutions of peroxy acids are finding industrial and commercial applications as oxidation and bleaching systems.† The stabilities of peroxy acid solutions are influenced by a number of processes: (i) uncatalysed decomposition (A) of peroxydicarboxylic acid into parent acid and oxygen; (ii)



hydrolysis (B) of peroxyacid to form parent acid and hydrogen



peroxide; and (iii) transition metal-catalysed decompositions with the same stoichiometry as process (A). In solutions where both peroxy acid and hydrogen peroxide are present (as in the present study), a coupled decomposition (iv) (C) also must be



considered although it may not have a simple stoichiometry. The catalysed decomposition is not well understood and may involve both the peroxy acid and its hydrolysis product, hydrogen peroxide. The transition metals may be active even at the trace level (10^{-5} – 10^{-8} mol dm⁻³). The study of processes (A) and (B) can be severely complicated by adventitious metals present in solution.

The uncatalysed decompositions of peroxyacids, including monoperoxyphthalic acid (MPPA),¹ have been extensively studied by both kinetic and isotopic tracer methods.² The reactions are second order in peroxy acid and the observed rate constant has a maximum value at pH = pK_a for ionization of the peroxide proton. The results are consistent with a mechanism involving nucleophilic attack of peroxyanion on the peroxy acid molecule. However, the tracer results imply that the reactions are more complex in that, in all cases, the overall reaction is the sum of two processes which involve 'isomeric'

transition states, distinguishable by double-¹⁸O-labelling techniques.² Recently, Evans and Upton³ found that the decomposition of MPPA at pH = pK_a in the presence of chelating agents gave 95% singlet oxygen suggesting that both the isomer transition states yield predominantly singlet oxygen.

The hydrolysis of MPPA was first recognized by Baeyer and Villiger.⁴ Bunton *et al.*⁵ showed by tracer experiments using ¹⁸O-labelled water, that the carbon–oxygen bond is cleaved and the oxygen–oxygen bond of peroxide remains intact in the reaction and this result has been confirmed¹ using ¹⁸O-labelled MPPA. The reaction is related to the hydrolysis of other phthalic acid derivatives, which have been extensively studied⁶ with a view to establishing the relative importance of intra- and inter-molecular catalytic contributions to the total reaction. The studies suggest the likelihood of intramolecular influence by an *ortho*-carboxylate group in the hydrolysis of MPPA and it was therefore important in the present work to determine the pK_a for the carboxy proton. This is not a straightforward matter since samples of MPPA prepared by the standard method contained only 50–80% MPPA with phthalic acid as the additional constituent. Several recrystallizations from ether raised the purity to 85% at best. The dissociation constants of phthalic acid at 25 °C are well established as pK_{a1} 2.98 and pK_{a2} 5.41. Thus the presence of phthalic acid impurity does not complicate the determination of the dissociation constant of the peroxide proton of MPPA (pK_{a2} 8.2 ± 0.1 at 25 °C),¹ but presents a problem for the determination of pK_{a1} , which was estimated on the basis of free energy relationships to be *ca.* 3.3. The results of two independent methods for determination of pK_{a1} for MPPA are reported here.

Hydrolysis of MPPA is sufficiently slow as not to intrude in studies of the uncatalysed decomposition reaction at pH > 5.5. Conversely, the occurrence of uncatalysed decomposition limits studies of the hydrolysis reaction to pH < 5.5. In the decomposition studies near pH 8 trace-impurity-catalysed decomposition was suppressible by addition of EDTA.^{1–3} In the present studies of the hydrolysis reaction, trace-impurity-catalysed decomposition which is not completely EDTA suppressible has been observed at pH > 4; indeed, addition of EDTA further complicates the system. Thus, interpretable data for the hydrolysis reaction must be obtained under carefully controlled conditions. A word on significant figures is appropriate. The rate constants are given with the three figures

† Magnesium monoperoxyphthalate is a novel reagent of this type; for a technical review see: V. I. Routledge, 'Speciality Chemicals,' 1986, p. 25.

Table 1. Determination of pK_{a1} for MPPA^a.

pH	K_d	F_{ion} obs	F_{ion} calc ^d	pK_{a1} ^e
1.49	(8.20) ^b			
2.30	6.66	0.19	0.18	2.93
2.81	4.94	0.40	0.42	2.98
3.09	3.26	0.61	0.58	2.90
3.15	3.69	0.56	0.61	3.05
3.38	2.61	0.69	0.72	3.00
3.65	1.43	0.84	0.83	2.93
3.99	0.857	0.91	0.92	2.99
4.15	0.603	0.94	0.94	2.96
4.37	0.391	0.96	0.96	2.93
5.33	(0.099) ^c			
5.82	(0.113)			

^a Data based on distribution experiments carried out at 21.5 °C with I 0.024 mol dm⁻³ in the aqueous phase. ^b This value used for $K_{d,HA}$. ^c The average value (0.106) used for K_{d,A^-} . ^d F_{ion} calculated from assumed pK_{a1} 2.96. ^e Values calculated from individual experiments.

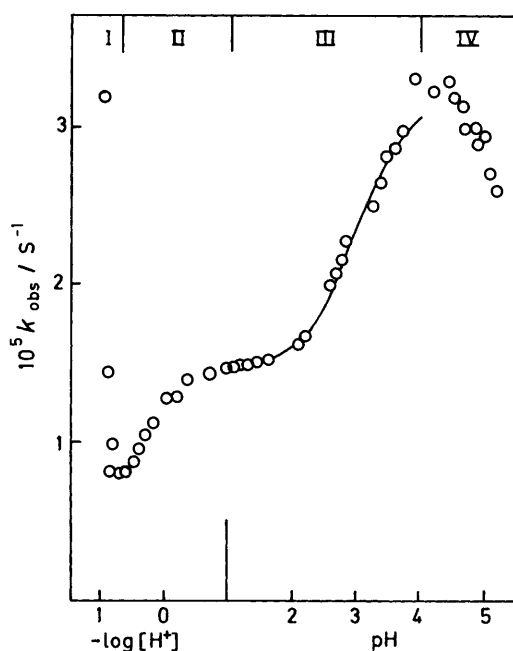


Figure 1. Variation of the experimental first-order hydrolysis rate constant (k_{obs}) with solution acidity at 25 °C, as determined from the kinetics of formation of hydrogen peroxide using a single sample of MPPA. EDTA present.

to which they were measured, but only two of these are considered significant.

Results and Discussion

Determination of pK_{a1} for MPPA.—Method 1. If the potentiometric titration curve for a weak acid HA' (ionization constant $K_{HA'}$) is compared with that obtained for a solution containing HA' at the same concentration together with a second weak acid HA'' , then the difference in added titrant concentration (ΔC) at constant pH is related to the ionization constant of HA'' ($K_{HA''}$) according to equation (1), so, when $\Delta C = 1/2[HA'']$, $pH = pK_{HA''}$.

$$K_{HA''} = \frac{[H^+]\Delta C}{[HA''] - \Delta C} \quad (1)$$

Potentiometric titration curves for a pure phthalic acid solution and a series of solutions containing the same concentration of phthalic acid and various concentrations of MPPA were compared. Solutions containing 5, 10, 20, 40, and 60% MPPA were employed although it was not possible to make up these solutions exactly and the experimental titration curves were normalized to the phthalic acid concentration used in the reference solutions. Potentiometric titration curves for MPPA at $pH < 7$ were then constructed as graphs of pH versus ΔC . The value of pK_{a1} for MPPA obtained was 3.05 ± 0.2 at room temperature (ca. 20 °C).

Method 2. MPPA can be distributed between n-octanol and water. When $pH \ll pK_{a1}$ the observed distribution coefficient ($K_{d,HA}$) is that for the un-ionized acid. When $pH \gg pK_{a1}$ (but $pH \ll pK_{a2}$) the distribution coefficient (K_{d,A^-}) is that for the monoperoxophthalate monoanion. Since the analyses are for peroxide in the two phases, the distribution of phthalic acid does not interfere in any way with this technique.

At intermediate pH values the experimental distribution coefficient K_d varies with pH depending on the degree of ionization of MPPA. The data may be calculated using form (2)

$$K_{a1} = \left\{ \frac{K_{d,HA} - K_d}{K_d - K_{d,A^-}} \right\} [H^+] \quad (2)$$

where the K_d constant is the distribution coefficient observed at a particular pH. The data may also be used in a titration type curve based on equation (3) with plots of F_{ion} and pH values for

$$F_{ion} = \left\{ \frac{K_{d,HA} - K_d}{K_{d,HA} - K_{d,A^-}} \right\} \quad (3)$$

a number of experiments as those in Table 1 giving the titration curve. The symbol F_{ion} , which represents the fraction ionized in the aqueous phase, is defined as $F_{ion} = [A^-]_w / ([HA^-]_w + [A^-]_w)$. Drawing a smooth curve through the points and locating the point of F_{ion} 0.50, one can then have $pH = pK_a$.

Solutions of MPPA were adjusted to the required pH (KOH-HCl) and ionic strength (KCl; 10.042 mol dm⁻³). Distribution experiments were carried out at 21.5 °C and the pH of the aqueous phase was measured after attainment of distribution equilibrium. The results are shown in Table 1.

The results obtained by the two methods are in agreement within experimental error. The value obtained by Method 2 (pK_{a1} 2.96 \pm 0.05, at 21.5 °C and I 0.042 mol dm⁻³) is the more reliable. This value is rather low for a substituted benzoic acid and is close to pK_{a1} of phthalic acid itself, suggesting the occurrence of an unusually large ortho-effect in MPPA. This is consistent with X-ray crystallographic studies of the magnesium salt of MPPA where the plane of the carboxylate ion is almost at right angles to the plane of the benzene ring.⁷

Hydrolysis of MPPA.—The variation with solution acidity of the observed first-order rate constant, determined from the kinetics of formation of hydrogen peroxide at 25 °C, using a single sample of MPPA, is shown in Figure 1. Changing the hydrogen ion concentration of the solution by more than six orders of magnitude produced, at maximum, only a four-fold change in the rate constant. The profile is, however, quite complex and is conveniently divided into four ranges: I, $-\log [H^+] < -0.7$; II, $-0.7 < -\log [H^+] < 1.0$; III, $1.0 < pH < 4.0$; IV, $pH > 4.0$, each discussed separately below.

Range III.—The results in range III are straightforward to interpret. The form of the curve suggests the importance of the ionization of the carboxy proton of MPPA (pK_{a1} 2.96) as an influence upon the kinetics of the reaction. The results are well described by the mechanism (4)–(6).

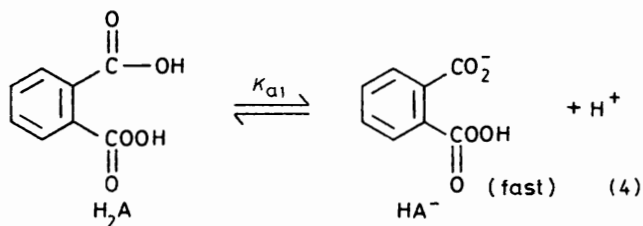


Table 2. Variation of k_{obs} with ionic strength I (adjusted with NaClO_4) at $[\text{HClO}_4]$ equals 0.29 mol dm^{-3} , temperature 21.8°C .

$I/\text{mol dm}^{-3}$	$10^5 k_{\text{obs}}/\text{s}^{-1}$
0.29	1.08
0.79	0.85
1.24	0.70
2.05	0.57
3.0	0.49
4.0	0.38

The solid line in range III in Figure 1, is made by fitting equation (7) to reactions (4)–(6) using the assumed values k_1

$$k_{\text{obs}} = \frac{k_1 + k_2 K_{a1}/[\text{H}^+]}{1 + K_{a1}/[\text{H}^+]} \quad (7)$$

$1.45 \times 10^{-5} \text{ s}^{-1}$ and $k_2 3.26 \times 10^{-5} \text{ s}^{-1}$, gives an excellent fit. The increase in rate of hydrolysis as the MPPA is converted into the mono-anion is not unexpected since the carboxylate ion function can perform an intramolecular catalysis of the reaction, either as a nucleophile or as a general base. Activation parameters were determined from the temperature coefficients of k_{obs} at pH 1.47 ($\Delta H^\ddagger 90 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger -38 \text{ J mol}^{-1} \text{ K}^{-1}$) and at pH 3.97 ($\Delta H^\ddagger 100 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger +21 \text{ J mol}^{-1} \text{ K}^{-1}$). The activation values at pH 3.97 must be accepted with caution because of the possible complication of induced peroxy acid decomposition.

In range III values of k_{obs} were unaffected by using different samples of MPPA, by addition of phthalic acid or potassium acid phthalate, or by addition of EDTA. It is also important to note that, in this range, studies of the hydrolysis reaction by measurement both of $-\text{d}[\text{MPPA}]/\text{d}t$ and $+\text{d}[\text{H}_2\text{O}_2]/\text{d}t$ gave identical rates.

Range II.—Although the variation of k_{obs} with $-\log[\text{H}^+]$ at pH < 1.0 at first suggested the intrusion of an additional protonation process, such is not likely. The data presented in Table 2 suggest a probable alternative. Addition of sodium perchlorate to solutions of MPPA in $0.29 \text{ mol dm}^{-3} \text{ HClO}_4$ brings about decreases in hydrolysis rate constant that closely parallel the effect of increasing HClO_4 (without ionic strength compensation) in this range. The decrease in rate constant seen in range II as acid concentration increases is therefore ascribed to an activity coefficient effect on the aqueous hydrolysis. A considerable number of effects of this type have been described for hydrolysis reaction in this acidity range.^{8,9}

Range I.—Increase in acidity at acid concentrations $> 5 \text{ mol dm}^{-3}$ produces a marked increase in k_{obs} . This increase is

ascribed to an acid-catalysed hydrolysis. It is possible to estimate a rate constant for the acid-catalysed path (range I) from the rate at highest acidity; the value so obtained, assuming

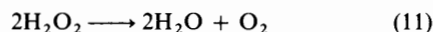
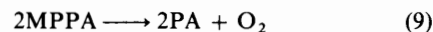
$$-\text{d}[\text{MPPA}]/\text{d}t = k_{\text{H}}[\text{MPPA}][\text{H}^+] \quad (8)$$

the rate law term (8) is $3 \times 10^{-6} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. In a separate study,¹⁰ the hydrolysis of *p*-sulphonatoperoxybenzoic acid in acid was followed; the rate constant obtained is $4.1 \times 10^{-6} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The good agreement between the constants for the two substituted peroxybenzoic acids is expected since acid-catalysed hydrolyses of esters have rate constants independent of substituent nature.¹¹

Range IV.—The downward curve for the rate constant above pH 4 is seen in Figure 1. This was cause for concern because no reasonable mechanistic basis involving hydrolysis alone could be visualized. However, the combination of a decomposition process intrusion (along with hydrolysis), and an analytical procedure based on product concentration could bring about a result which is an artifact. It became important to explore this possibility, because it bears on the whole question of peroxide stability near pH 5.

We consider the analytical aspect of the problem first. In the hydrolysis solution, there are two peroxides MPPA and H_2O_2 which are reactant and product, respectively. It was decided to analyse for both during the hydrolysis by obtaining titres for hydrogen peroxide and for total peroxide as a function of time. From these, since MPPA concentration is equal to total peroxide less H_2O_2 concentration, one obtains two measures of reaction rate, namely $+\text{d}[\text{H}_2\text{O}_2]/\text{d}t$ and $-\text{d}[\text{MPPA}]/\text{d}t$. If no decomposition occurs the two rates will be identical and the total peroxide concentration will be constant. On the other hand, if some decomposition takes place in the hydrolysis solution, then the two rate values will not be equal and total peroxide concentration will decrease. The latter situation was found to be the case above pH 4.

The steps that result in loss of peroxide by decomposition must now be considered. There are three conceivable simple stoichiometries (9)–(11) for loss of peroxide. Decompositions



(10) and (11) would lower the $+\text{d}[\text{H}_2\text{O}_2]/\text{d}t$ rate directly; decomposition (9) would lower this value indirectly and probably only to a minor extent if initial rates are followed. Decompositions (9) and (10) would increase $-\text{d}[\text{MPPA}]/\text{d}t$, and decomposition (11) would have no effect on this rate.

Some of the results we have obtained in the absence of a chelating agent for rate runs in the pH range 3.9–6.2 are presented in Table 3 and Figure 2. It is immediately apparent that the two rates are divergent; that is to say, when the value of $k_{\text{H}}(\text{H}_2\text{O}_2)$ is significantly low (compared with $3.3 \times 10^{-5} \text{ s}^{-1}$) the rate of MPPA loss is high. It is concluded, from the observation that the total peroxide concentration is decreasing with time, that decomposition accompanies hydrolysis.

Some further conclusions may be drawn from these data and from a number of similar experiments carried out. Levelling off of the rate constant plot against pH at *k ca.* $3.3 \times 10^{-5} \text{ s}^{-1}$ is expected above pH 4 up to the point that the second-order decomposition becomes a factor (near pH 5.5). The values of $-\text{d}[\text{MPPA}]/\text{d}t$ and $-\text{d}[\text{H}_2\text{O}_2]/\text{d}t$ deviate from the expected value in ways that indicate both peroxides are decomposing when EDTA is not present. This excludes decomposition (11) as the sole contributor.

Table 3. Comparative initial rate constants.^a

$10^3[\text{MPPA}]_0$	pH	$10^5k_h(\text{MPPA})$	$10^5k_h(\text{H}_2\text{O}_2)$
1.25	3.90	4.69	3.94
1.25	4.00	3.26	3.26
2.50	4.00	3.31	3.26
1.25	4.20	3.26	3.04
2.24	4.20	3.22	3.22
2.50	4.70	3.00	3.00
1.25	4.80	3.98	2.67
1.25	4.80	3.45	3.45
2.50	5.08	3.58	2.67
2.50	5.08	3.56	2.69
1.25	5.12	2.86	2.66
1.25	5.18	2.67	2.67
2.50	5.20	2.95	2.19
1.25	5.35	3.65	2.42

^a Concentration of MPPA in mol dm^{-3} . Rate constants have units of s^{-1} . Data taken at 21 °C. No chelating agent present.

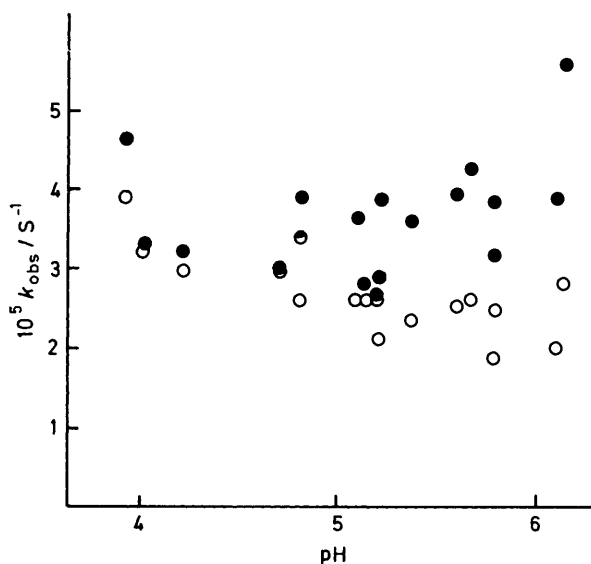


Figure 2. Comparison of k_{obs} values determined from formation of H_2O_2 (○) and loss of MPPA (●) at $\text{pH} \geq 4$ and 21 °C. There are four coincident values (⊙) obtained with a single sample of MPPA. No EDTA present.

As seen in Figure 2 and Table 3, the two measures of rate show comparable deviations which might suggest a close coupling of the peroxide losses as in decomposition (10). This is not the case as addition of EDTA decreased the rate of loss of MPPA while making hydrogen peroxide less stable. Therefore, the decomposition data indicate that no one of the three simple stoichiometries provides an adequate explanation. The difference in results when EDTA is absent and when present can be understood in terms of the known chemistry of this ligand and metal ions.

Mixtures of the two peroxides [H_2O_2] $1\text{--}6 \times 10^{-3}$; [MPPA] $4\text{--}6 \times 10^{-3} \text{ mol dm}^{-3}$) at $\text{pH} 5.2$ and 21 °C showed loss of both with time; 4–15% of the total peroxide decomposed in 3 h. If small amounts of cobalt(II), say $1 \times 10^{-7} \text{ mol dm}^{-3}$, were added, MPPA decomposed significantly without much loss of H_2O_2 . This is very consistent with the observations that cobalt is an effective catalyst for peroxyacid decomposition and that EDTA can tie up the cobalt in an inactive form.^{1–3,12} By way of comparison, H_2O_2 is decomposed primarily by trace amounts of iron(III) ion¹³ and surprisingly the iron(III) ion–EDTA complex is also a catalyst for hydrogen peroxide

decomposition.^{13c} We found that in the experiments near $\text{pH} 5$ the rate of hydrogen peroxide loss was greater when EDTA was present than when it was absent.

MacKirdy¹⁴ has found in his experiments on MPPA hydrolysis carried out independently that the rate of loss of MPPA was equal to the rate of formation of H_2O_2 within an experimental error of $\pm 5\%$ near $\text{pH} 4$. No EDTA or other chelating agent was employed.

Previous observations^{3,15} of the reaction between hydrogen peroxide and peroxyacids have been carried out at high pH where the peroxyanion is the predominant species. At these high pH values (*ca.* 10.8), the reaction is certainly trace metal catalysed. No evidence was found³ for a direct redox interaction between the peroxyanion and hydrogen peroxide.

EDTA is truly a mixed blessing in controlling trace metal catalysis of peroxide decomposition. For monosubstituted peroxides ROOH which are very susceptible to cobalt-catalysed decomposition, the chelating agent is remarkably effective.² On the other hand, it can enhance the decomposition of hydrogen peroxide when traces of iron species are present. In our system where we had both MPPA and H_2O_2 it was not possible to prevent the mutual decomposition since neither the presence nor the absence of EDTA allowed control of the trace metal catalysis. The recent work of Evans and Upton^{3,13e} indicates that Dequest 2060 (diethylenetriamine–*NNN'N'N'*-penta-methylenephosphonic acid) is preferable to EDTA as a ligand to control trace metal catalysis.

Experimental

Analytical grade materials were used whenever possible. Hydrogen peroxide was 85–90% w/w unstabilized material; distilled water was employed throughout. MPPA was prepared by reaction of finely ground phthalic anhydride with alkaline H_2O_2 at -5°C using standard procedures.¹⁶ Following acidification with *ca.* 3 mol dm^{-3} cold sulphuric acid, extraction with ether, drying of extracts, and removal of ether the solid MPPA product was stored at 0 °C. A number of variations in the procedure were tried in an attempt to improve the purity of the product without significant success. The best preparations contained *ca.* 85% MPPA with the remaining constituent being phthalic acid and these were obtained after several recrystallizations of the initial material from ether.

For studies of the distribution of MPPA between water and *n*-octanol the pH and ionic strength *I* of aqueous solutions of peroxy acid were adjusted using KOH, KCl, and HCl solutions. An equal volume of *n*-octanol was added to the aqueous solution in a separator funnel. When distribution equilibrium was attained the pH of the aqueous phase was again measured and this value employed in the calculations. Analysis for peroxy acid was by iodometry in each phase after separation.

For hydrolysis experiments solutions of varying pH were prepared by the addition, to aqueous solutions of peroxy acid, of appropriate amounts of NaOH or HClO_4 solution. In some experiments NaClO_4 was used for adjustment of ionic strength. Initial concentrations of peroxy acid were in the range of 10^{-2} – $10^{-3} \text{ mol dm}^{-3}$. For solutions with $\text{pH} > 1$, the pH was measured (Beckman glass electrodes) initially and at several times during the reaction. For more acidic solutions, $-\log[\text{H}^+]$ was calculated from the stoichiometric concentration of added HClO_4 . Progress of the reaction was studied by quenching samples of the solutions with ice-cold, $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. Hydrogen peroxide concentration was determined cerimetrically and then KI was added and the residual peroxy acid determined iodometrically. The reaction was found to be first order with respect to peroxy acid for at least 50% reaction. Near $\text{pH} \text{ ca. } 2.5$ the pH of the essentially unbuffered reaction solutions changed by up to 0.2 pH units during the course of the

reaction. At lower pH this effect was unimportant and the kinetic form was satisfactory first order for a greater extent of the reaction. Complications from the simultaneous occurrence of decomposition reactions were only evident at $\text{pH} \geq 4$ and $\log [\text{H}^+] > 0.7$.

Acknowledgements

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