

## Studies on Singlet Oxygen in Aqueous Solution. Part 3.<sup>1</sup> The Decomposition of Peroxy-acids

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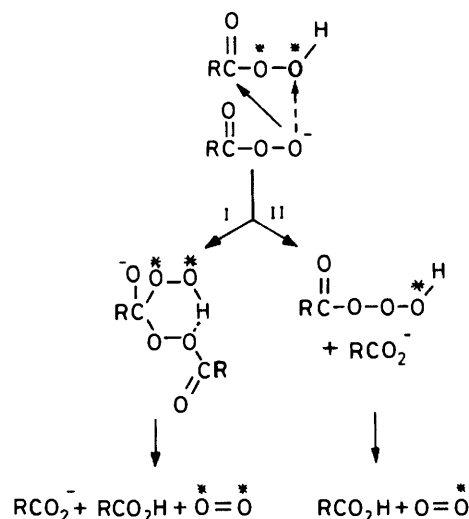
The decompositions of peroxyacetic acid, peroxymonosulphuric acid (Caro's acid), and monoperoxyphthalic acid have been studied in aqueous solution at pH values close to the  $pK_a$  of the acids. When precautions are taken to eliminate metal-ion catalysis, essentially quantitative yields of  $^1O_2$  are obtained, as determined using the caesium salt of anthracene-9,10-bis(ethanesulphonate) (aes) as a trap for  $^1O_2$ . With peroxyipivalic acid the maximum yield of  $^1O_2$  was only ca. 80%, but in this case non- $^1O_2$  attack on the aes also occurred. Negligible amounts of  $^1O_2$  are formed when  $H_2O_2$  reacts with monoperoxyphthalate or peroxyacetate anions at pH ca. 10.7 under normal 'clean' conditions. However, the presence of the chelating agent diethylenetriamine-*NNN'*N"-penta-(methylphosphonic acid) produces a dramatic decrease in the reaction rates. It is concluded that the reactions of  $H_2O_2$  with peroxy-acid anions are extremely sensitive to catalysis, probably by transition-metal ions.

Peroxy-carboxylic acids decompose spontaneously in aqueous solution to give the corresponding carboxylic acids and oxygen. The rate law is of the form  $v = k_2[RCO_3H][RCO_3^-]$ , and accordingly the reaction can be regarded as a nucleophilic attack of the anion upon the peroxy-acid.<sup>2,3</sup> Similar behaviour is shown by Caro's acid,  $H_2SO_5$ , and peroxyphosphoric acid.<sup>2,3</sup> The decompositions are susceptible to catalysis by transition-metal ions such as  $Co^{II}$ ,<sup>4</sup> but their effect was largely eliminated by adding a chelating agent such as ethylenediaminetetraacetate (edta). Competing reactions which can also occur in the absence of metal ions are, at low or very high pH, hydrolysis to give  $H_2O_2$ , and, for peroxy-carboxylic acids, the formation of small amounts of acyl peroxides.<sup>5</sup> Information concerning the detailed mechanism of the main reaction was obtained by Edwards and his co-workers,<sup>6-9</sup> who studied the reaction between a peroxy-acid doubly labelled at the peroxy-group with  $^{18}O$  and unlabelled peroxy-acid. It was concluded that two distinct routes were involved, with initial attack at either the central C (or S) atom (mechanism I), or at the outer peroxidic oxygen (mechanism II).

For the first route, the evolved oxygen gas should be a mixture of normal and doubly labelled molecules, while for the second, it should be scrambled. The results obtained are shown in Table 1, and indicate that for peroxyacetic acid the initial attack occurs mainly at the carbonyl carbon, but that for Caro's acid, monoperoxyphthalic and peroxyipivalic acid, oxygen attack predominates. The difference between peroxyacetic acid on the one hand, and monoperoxyphthalic and peroxyipivalic acids on the other, has been attributed to steric affects.<sup>3</sup>

On spin-conservation grounds, both mechanisms might be expected to give  $^1O_2$ , rather than ground-state  $^3O_2$ . Accordingly, in the present work the decomposition of these peroxy-acids has been studied in the presence of the caesium salt of anthracene-9,10-bis(ethanesulphonate) (aes) as a trap for  $^1O_2$ .<sup>10</sup> McKeown and Waters<sup>11</sup> showed that the decomposition of diperoxyisophthalic acid in ethanol at 'pH' 8-9 in the presence of 9-methyl-10-phenylanthracene gave the endoperoxide in 21% yield based on the hydrocarbon, and 10% yield based on available oxygen. However, they were unable to detect any endoperoxide with peroxyacetic acid under similar conditions.

We have also examined the related reaction which is reported to occur between  $H_2O_2$  and the anion of a peroxy-acid. This reaction is conveniently followed in the range pH 10-11, where the predominant species are the anion of the peroxy-acid and unionized  $H_2O_2$ .



**Table 1.** Isotopic composition of the oxygen evolved in the spontaneous decomposition of peroxy-acids

Peroxy-acid	Evolved oxygen (%)	
	O*=O* (Attack on C or S)	O=O* (Attack on outer peroxidic oxygen)
Peroxyacetic acid <sup>6</sup>	83	17
Caro's acid <sup>7</sup>	9	91
Monoperoxyphthalic acid <sup>8</sup>	26	74
Peroxyipivalic acid <sup>9</sup>	24	76

### Experimental

In following the decomposition of the peroxy-acids care was taken to eliminate, as far as possible, catalysis by transition-metal ions. The solvent was doubly distilled 'conductivity' water, or normal distilled water which had been passed through a mixed-bed ion-exchange resin. The buffer solutions, or the buffer solutions containing aes, were on occasion passed through a column containing Dowex chelating ion-exchange

resin. The reaction vessels were polypropylene tubes, which had been soaked in 5% Decon 90 followed by 10% HNO<sub>3</sub>, rinsed with pure water, and shaken dry.<sup>12</sup> One of three chelating agents was used, edta, cyclohexane-1,2-diamine-*NNN'*-tetraacetic acid (cdta), or Dequest 2060, *i.e.* diethylenetriamine-*NNN'*-*N''*-penta(methylphosphonic acid).

The peroxy-acids were analyzed iodometrically in an atmosphere of CO<sub>2</sub>, as was H<sub>2</sub>O<sub>2</sub>, after addition of ammonium molybdate. For solutions containing both H<sub>2</sub>O<sub>2</sub> and a peroxy-acid, two aliquots were taken. One was analyzed for H<sub>2</sub>O<sub>2</sub> by titration at 0 °C with cerium(IV) sulphate using [Fe(phen)<sub>3</sub>]<sup>2+</sup> (phen = 1,10-phenanthroline) as indicator, and the other iodometrically to give total peroxy-acid and H<sub>2</sub>O<sub>2</sub> content. The compound aes was determined spectrophotometrically at 398 nm, and the endoperoxide formed from reaction with <sup>1</sup>O<sub>2</sub> by h.p.l.c. as described previously.<sup>10</sup>

Peroxyacetic acid was obtained by fractional distillation of the commercial 40% acid in vacuum at room temperature. It was *ca.* 5 mol dm<sup>-3</sup> in peroxyacetic acid and 0.1 mol dm<sup>-3</sup> in H<sub>2</sub>O<sub>2</sub>, the remainder being water and acetic acid. Peroxypivalic acid was prepared as described by Koubek and Welsch,<sup>9</sup> except that the ether extract was shaken with an almost saturated sodium phosphate buffer at pH 6.8. It had a purity of *ca.* 78%, and contained less than 0.1% H<sub>2</sub>O<sub>2</sub>. Both acids were stored at -20 °C in Polythene containers. Monoperoxyphthalic acid was supplied by Interlox Chemicals Ltd., and had a purity of 83%, the remainder being phthalic acid. The source of the Carote ion was the triple salt, K<sub>2</sub>SO<sub>4</sub>·KHSO<sub>4</sub>·KHSO<sub>5</sub>, and the H<sub>2</sub>O<sub>2</sub> was a stabilizer-free 88% sample, both from Interlox Chemicals Ltd. In the H<sub>2</sub>O<sub>2</sub>-peroxy-acid reactions, the pH was adjusted using a 5 mol dm<sup>-3</sup> solution of AristaR NaOH which had been treated to remove iron.<sup>6,13</sup> To the vigorously stirred solution (50 cm<sup>3</sup>) was added 10% AnalaR Mg(ClO<sub>4</sub>)<sub>2</sub> solution (0.5 cm<sup>3</sup>), and the supernatant liquid used directly after centrifugation.

In the measurements of the yield of <sup>1</sup>O<sub>2</sub> the peroxy-acid was added to the buffer solution containing aes and the chelating agent, and samples removed immediately and analysed for aes and the peroxy-acid. After a suitable time interval the solution was analysed again for aes and the peroxy-acid, and also for endoperoxide. The high dilution involved in the spectrophotometric determinations effectively quenched the reaction. The total yield of oxygen gas was then given by the decrease in the peroxy-acid concentration. The calculated yields of <sup>1</sup>O<sub>2</sub> were based on the endoperoxide formed, rather than on the aes that had reacted.

## Results and Discussion

**Peroxy-acids.**—Since the decomposition of peroxy-acids in aqueous solution is very susceptible to catalysis by transition-metal ions,<sup>4</sup> the kinetics were first studied in the absence of aes. When the precautions detailed in the Experimental section were taken, consistent second-order plots were obtained for the initial 4/5 of the reaction. The values of *k*<sub>2</sub> are given in Table 2, together with the literature values. Measurements were carried out at a pH equal to the p*K*<sub>a</sub> for the peroxide proton of the acid, when *k*<sub>2</sub> = 2*k*, where *k* is the calculated second-order rate constant based on the total peroxy-acid concentration.

Except for one result for Caro's acid, the present values of *k*<sub>2</sub> are appreciably less than those in the literature. This may be partly due to salt effects, especially with Caro's acid, where attack of a 2- ion upon 1- ion is involved. The higher of the two literature values was obtained at high ionic strengths of 1.0–2.3 mol dm<sup>-3</sup>, while in the other work the ionic strength was *ca.* 0.2 mol dm<sup>-3</sup>.

The rates of decomposition of the peroxy-acids were not affected by the presence of aes, provided the aes solutions had previously been passed through the chelating ion-exchange

**Table 2.** Rate constants (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), *k*<sub>2</sub>, for the decomposition of peroxy-acids at 25 °C

Peroxy-acid	p <i>K</i> <sub>a</sub>	10 <sup>3</sup> <i>k</i> <sub>2</sub>	10 <sup>3</sup> <i>k</i> <sub>2</sub> (lit.)
Peroxyacetic acid	8.2	2.0	5.4 <sup>6</sup>
Caro's acid	9.3	47	41, <sup>15</sup> 210 <sup>14</sup>
Monoperoxyphthalic acid	8.2	7.2	11.2 <sup>8</sup>
Peroxypivalic acid	8.2	5.1	6.8 <sup>9</sup>

resin. With peroxyacetic acid, Caro's acid, and monoperoxyphthalic acid, and taking the usual precautions, the endoperoxide was the only detectable product. The amounts produced were, within experimental error, the same as the amounts of aes which had reacted. This criterion, in fact, seemed to be a more sensitive indication of metal-ion catalysis than the observed values of *k*<sub>2</sub>.

From the initial and final concentrations of aes and the peroxy-acid, and the amount of endoperoxide produced, it was possible to calculate the yields of <sup>1</sup>O<sub>2</sub> using the procedure described previously. These yields were ≥95% for all three peroxy-acids, *i.e.* essentially quantitative. One measurement for peroxyacetic acid in D<sub>2</sub>O gave a similar result. For peroxypivalic acid the maximum yield of <sup>1</sup>O<sub>2</sub> was only *ca.* 80%. However, in this case attack on the aes occurred to give unidentified products other than the endoperoxide, probably because the precautions taken did not completely inhibit the catalytic reaction. One run was carried out with monoperoxyphthalic acid in the presence of 1 × 10<sup>-5</sup> mol dm<sup>-3</sup> Co<sup>2+</sup>. A negligible amount of endoperoxide was obtained although other products were formed, presumably by attack on the aes by radicals involved in the catalysed reaction.

**Reaction between H<sub>2</sub>O<sub>2</sub> and Anions of Peroxy-acids.**—Several workers have reported reactions of the general type ROO<sup>-</sup> + H<sub>2</sub>O<sub>2</sub> → RO<sup>-</sup> + H<sub>2</sub>O + O<sub>2</sub>. Ball and Edwards<sup>14</sup> observed a rapid reaction between Caro's acid and H<sub>2</sub>O<sub>2</sub> above pH 10, even in the presence of edta. This reaction was also mentioned by Goodman and Robson.<sup>15</sup> McKeown and Waters<sup>11</sup> obtained an 18% yield of endoperoxide from the reaction of peroxy-*p*-toluic acid and H<sub>2</sub>O<sub>2</sub> at 'pH' 10 in ethanol in the presence of 9-methyl-10-phenylanthracene, and concluded that <sup>1</sup>O<sub>2</sub> was formed. Finally, Akiba and Simamura<sup>16</sup> studied the kinetics of the reaction between sodium peroxybenzoate and H<sub>2</sub>O<sub>2</sub> in 10<sup>-3</sup> mol dm<sup>-3</sup> NaOH, and derived a rate constant, *k*, of 19.4 × 10<sup>-3</sup> dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> at 0 °C. They also carried out the reaction with <sup>18</sup>O-labelled peroxybenzoate, and concluded that the evolved O<sub>2</sub> came almost entirely from the H<sub>2</sub>O<sub>2</sub>.<sup>17</sup>

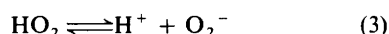
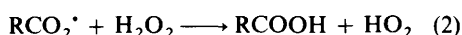
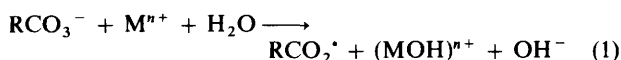
We have studied the reaction between the dianion of monoperoxyphthalic acid and H<sub>2</sub>O<sub>2</sub> at pH 10.7. At this pH, *ca.* 99.5% of the peroxy-acid is present as the dianion, but base-catalysed hydrolysis to give H<sub>2</sub>O<sub>2</sub> and phthalate is negligible. Under 'clean' conditions, but in the absence of a chelating agent, the reaction was stoichiometric, and the observed value of *k* is given in Table 3. In the presence of edta or cdta the reactions were still stoichiometric, but rather slower (Table 3). However, a dramatic effect was found when Dequest 2060 was used as the chelating agent. The reaction became very much slower and was no longer stoichiometric, with the amount of peroxy-acid which decomposed exceeding that of the H<sub>2</sub>O<sub>2</sub> (Table 4). This is clearly due to a significant contribution from the spontaneous decomposition of the monoperoxyphthalic acid, even though the pH is much higher than the second p*K*<sub>a</sub> of the acid (8.2).

The rate constant for the reaction of H<sub>2</sub>O<sub>2</sub> and monoperoxyphthalic acid cannot be obtained in the usual way from the data in Table 4. However, we have -d[H<sub>2</sub>O<sub>2</sub>]/dt = *k*-

**Table 3.** Rate constants,  $k$ , for the reaction of  $\text{H}_2\text{O}_2$  with monoperoxyphthalic acid and peroxyacetic acid under different conditions

Monoperoxyphthalic acid (25 °C, pH 10.7, 0.04 mol dm <sup>-3</sup> phosphate)	
No added chelating agent	10.3
1 × 10 <sup>-3</sup> mol dm <sup>-3</sup> edta	6.7
1 × 10 <sup>-3</sup> mol dm <sup>-3</sup> cdta	3.7
0.1 × 10 <sup>-3</sup> mol dm <sup>-3</sup> Dequest 2060	0.070
0.4 × 10 <sup>-3</sup> mol dm <sup>-3</sup> Dequest 2060	0.068
Peroxyacetic acid (25 °C, pH 10.8, 0.04 mol dm <sup>-3</sup> phosphate)	
3 × 10 <sup>-3</sup> mol dm <sup>-3</sup> cdta	0.2
0.2 × 10 <sup>-3</sup> mol dm <sup>-3</sup> Dequest 2060	0.01

$[\text{H}_2\text{O}_2][\text{monoperoxyphthalic acid}]$ . The concentrations of  $\text{H}_2\text{O}_2$  as a function of  $t$  were fitted to an expression of the type  $[\text{H}_2\text{O}_2]_t = a + bt + ct^2 + \dots$ . In practice, the simple expression  $[\text{H}_2\text{O}_2]_t = 0.1104 - 3.753 \times 10^{-7}t + 9.846 \times 10^{-13}t^2$  fitted the data to within better than 1%. By differentiating this expression, and substituting for  $t$ ,  $[\text{H}_2\text{O}_2]$ , and  $[\text{monoperoxyphthalic acid}]$ , it was possible to calculate values of  $k$  for each of the datum points and these are given in Table 4. A similar effect of the addition of Dequest 2060 was found with the  $\text{H}_2\text{O}_2$ -peroxyacetic acid reaction (Table 3). The rate constants given represent maximum values, since some spontaneous decomposition of the  $\text{H}_2\text{O}_2$  may have occurred. It seems that the reaction between  $\text{H}_2\text{O}_2$  and the anions of peroxyacids is extraordinarily sensitive to catalysis by metal ions, if, indeed, it occurs at all in their absence. It has been briefly reported by Unilever Ltd.<sup>18</sup> that the mutual decomposition of peroxyacetic acid and hydrogen peroxide is largely eliminated by the addition of certain phosphoric acid chelating agents. One possible mechanism for catalysis by a transition-metal ion of variable valence is as in equations (1)–(4).



Although it seems most likely that the function of the Dequest 2060 is to complex catalytic metal ions, it could conceivably be acting as an inhibitor of organic free radicals.

The uncatalysed reaction of the anion of a peroxy-acid with  $\text{H}_2\text{O}_2$  is analogous to the corresponding reaction with a peroxy-acid, and mechanism II, involving attack on one of the oxygens of  $\text{H}_2\text{O}_2$ , is still applicable. However, the reaction would be expected to be much slower with  $\text{H}_2\text{O}_2$  since the initial reaction involves the poor leaving group  $\text{OH}^-$ .

When the 'catalysed' reactions of monoperoxyphthalic or peroxyacetic acid with  $\text{H}_2\text{O}_2$  were carried out in the presence of aes, negligible amounts of endoperoxide were produced. This was initially very surprising, until the catalysed nature of the reactions was subsequently realized. For reactions involving radicals and transition-metal ions there will be no spin-conservation restrictions on the formation of ground-state  $^3\text{O}_2$ .

In the presence of Dequest 2060, some endoperoxide was

**Table 4.** The reaction between  $\text{H}_2\text{O}_2$  and monoperoxyphthalic acid in the presence of  $0.1 \times 10^{-3}$  mol dm<sup>-3</sup> Dequest 2060 at 25 °C, pH 10.7, in 0.04 mol dm<sup>-3</sup> phosphate

10 <sup>-3</sup> t/s	10 <sup>3</sup> [Monoperoxyphthalic acid] mol dm <sup>-3</sup>		10 <sup>5</sup> k/ dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
	10 <sup>3</sup> [H <sub>2</sub> O <sub>2</sub> ]	10 <sup>3</sup> [Monoperoxyphthalic acid]	
0	111	60.1	6.1
0	107	54.4	7.2
27.5	100	44.5	8.9
77.4	87.8	28.6	5.7
160	75.5	14.1	Av. 7.0

found, but the amounts obtained could be almost entirely accounted for by the spontaneous decomposition of the peroxyacids. This suggests that the very low rates observed in the presence of Dequest 2060 still do not represent the true uncatalysed reactions. In all cases, there was very little non- $^1\text{O}_2$  attack on the aes. Presumably, any organic radicals react preferentially with  $\text{H}_2\text{O}_2$  rather than with aes. This was supported by studies of the decomposition of monoperoxyphthalic acid in the presence of  $\text{Co}^{2+}$ . When a  $1 \times 10^{-2}$  mol dm<sup>-3</sup> solution of monoperoxyphthalic acid at pH 10.8 was allowed to decompose completely in the presence of  $3.54 \times 10^{-3}$  mol dm<sup>-3</sup> aes and  $2 \times 10^{-5}$  mol dm<sup>-3</sup>  $\text{Co}^{2+}$  the final concentration of aes was  $2.1 \times 10^{-3}$  mol dm<sup>-3</sup>. H.p.l.c. showed  $< 1 \times 10^{-4}$  mol dm<sup>-3</sup> endoperoxide, but appreciable amounts of other unidentified products. However, when the same reaction was carried out in the presence of  $2 \times 10^{-2}$  mol dm<sup>-3</sup>  $\text{H}_2\text{O}_2$  there was no detectable change in the concentration of the aes.

#### Acknowledgements

We thank Interlox Chemicals Ltd. for a maintenance grant (to M. W. U.) and the gift of chemicals.

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Received 8th August 1984; Paper 4/1405