Studies on Singlet Oxygen in Aqueous Solution. Part 4.[1] The 'Spontaneous' and Catalysed Decomposition of Hydrogen Peroxide

Dennis F. Evans * **and Mark W. Upton**
Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY

The decomposition of H_2O_2 in alkaline solution has been studied in the presence of the chelating agent diethylenetriamine-*NNN'N''N''*-penta(methylphosphonic acid). A minimum rate constant of 4.7×10^{-7} dm^3 mol^{-1} s^{-1} at pH 11.6 and 35 °C was obtained. This is the slowest rate yet reported, but still probably represents a catalysed reaction. When the decomposition was carried out using the caesium salt of anthracene-9,10-bis(ethanesulphonate) (aes) as a trap for $^1O_2$ the production of small but significant amounts of $^1O_2$ was observed. If it is assumed that the 'spontaneous' reaction produces 100% $^1O_2$, then reasonably consistent corrected rate constants were obtained under different conditions, leading to a tentative 'true' value of 3.7×10^{-8} dm^3 mol^{-1} s^{-1} at 35 °C. The I^--catalysed decomposition of H_2O_2 produces 0.4% $^1O_2$, and an explanation of this low yield is given. In the Br^--catalysed decomposition (pH-independent region), the yields of $^1O_2$ varied from 11 to 80%, the upper value being consistent with that of 76% previously obtained for the direct reaction of HO_2^- and HOBr. The corrected rate constants are again in reasonable agreement. Catalysis by Cl^- in the pH-independent region is exceedingly slow. A yield of *ca.* 8.4% of $^1O_2$ was obtained in one run at 50 °C. The corrected rate constant (assuming 100% production of $^1O_2$ for the uncatalysed reaction) is approximately an order of magnitude less than the literature value. In the decompositions of H_2O_2 catalysed by Fe^{3+}, catalase, the Fe^{3+}–triethylenetetramine complex, and heterogeneously by Ag, Pt, or MnO_2, no $^1O_2$ could be detected, although with Fe^{3+} evidence is presented for the involvement of $^{\bullet}OH$ radicals.

The decomposition of hydrogen peroxide [equation (1)] is

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (1)$$

extremely sensitive to catalysis (both homogeneous and heterogeneous) by a wide variety of substances.[2,3] It is, in fact, still not clear whether, at temperatures close to ambient, the spontaneous decomposition occurs at any measurable rate, even in alkaline solutions where the so-called base-catalysed reaction (2)

$$H_2O_2 + HO_2^- \longrightarrow H_2O + OH^- + O_2 \qquad (2)$$

is favoured. It seems likely that there are two main types of mechanistic route for the catalysed decomposition. The first, exemplified by iron(III) catalysis,[2,4] involves one-electron steps, with the intermediate formation of the free radicals HO_2 (or O_2^-) and $^{\bullet}OH$, which are formed by alternate oxidation and reduction of the H_2O_2. The second route occurs by two-electron processes, for example:[5] reduced catalyst + H_2O_2 $\longrightarrow$ oxidized catalyst; oxidized catalyst + H_2O_2 $\longrightarrow$ reduced catalyst + O_2. For a two-electron process where both the reduced and oxidized forms of the catalyst are spin-paired, the production of $^1O_2$, rather than ground-state $^3O_2$, is a distinct possibility. A reaction of this type could provide a convenient source of $^1O_2$.

The present work is concerned with studies of both the catalysed and, as far as possible, the spontaneous decomposition of H_2O_2 in aqueous solution, using anthracene-9,10-bis(ethanesulphonate) (aes)[6] as a trap for $^1O_2$.

Results and Discussion

Action of $^{\bullet}$OH *and* HO_2 (O_2^-) *on aes.*—The reaction of $^1O_2$ with aes to give the 9,10-endoperoxide has been investigated in detail.[6] Since OH and HO_2 (O_2^-) are thought to be involved in certain catalysed decompositions of H_2O_2,[2,4] the reactivity of these species towards aes was first investigated.

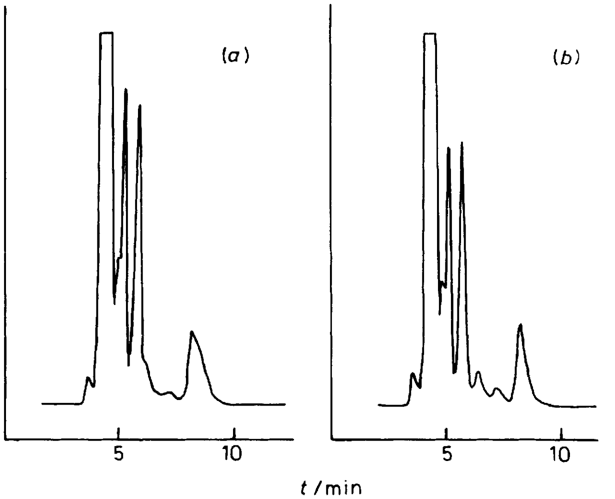

Figure. High-pressure liquid chromatograms (216 nm) of aes solutions in 0.1 mol dm^{-3} HNO_3: (*a*) after γ-irradiation (N_2O-saturated solution); (*b*) after treatment with Fe^{3+} and H_2O_2. The residual aes gave a peak at *ca.* 18 min. Conditions as in ref. 6

Hydroxyl radicals were generated by γ-irradiation of N_2O-saturated solutions of aes (*ca.* 4×10^{-3} mol dm^{-3}) using a ^{60}Co source. Irradiations were carried out in acidic solution (0.1 mol dm^{-3} HNO_3), and also at pH 10 and 12. Considerable attack on the aes occurred. H.p.l.c. showed that no endoperoxide was produced, but a variety of peaks was observed, which were different in the acidic and in the alkaline solutions. The chromatogram of an acidic solution of aes after irradiation is shown in the Figure (*a*).

A 0.15 mol dm^{-3} solution of KO_2 in dimethyl sulphoxide (dmso) containing 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was added very slowly[6] to an aqueous solution of aes (4×10^{-3} mol dm^{-3}, ratio of O_2^- added:aes *ca.* 3.5:1). The solutions were either at pH 3 (phosphate buffer) where HO_2 is the main species, or at pH 10 (phosphate buffer) where O_2^- predominates. In both cases, negligible attack on the aes was observed and no endoperoxide could be detected by h.p.l.c. The lack of reactivity of HO_2 or O_2^- is consistent with their known chemistry.[7] These experiments also provide additional confirmation that, in solution, reaction (3) produces $^3O_2$ rather than $^1O_2$,[8] and also that reaction (4) does not occur at any significant rate.[7]

$$HO_2 + O_2^- \longrightarrow HO_2^- + O_2 \quad (3)$$

$$O_2^- + H_2O_2 + H^+ \longrightarrow O_2 + H_2O + {}^{\bullet}OH \quad (4)$$

The Base-catalysed Decomposition of H_2O_2.—Early work on the decomposition of H_2O_2 in alkaline solution has been summarized by Schumb *et al.*[3] In 1961, Duke and Haas[9] reported a kinetic study using highly purified reagents. They observed a rate equation of the type $v = k_2[H_2O_2][HO_2^-]$ with $k_2 = 7.4 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} at 35 °C; k_2 is equal to $2k$ where k is the conventional second-order rate constant at the pK_a of H_2O_2 (11.5 at 35 °C).[10] A similar value for k_2 (7.0×10^{-4} dm^3 mol^{-1} s^{-1}) was subsequently obtained by Goodman *et al.*[11] In 1963 these results were shown to be incorrect by Edwards and his co-workers.[12] Using ethylenediaminetetra-acetate (edta) to complex catalytic impurities, and purified alkali, they observed an initial rate of decomposition of about one hundredth that reported by Duke and Haas and Goodman *et al.* Edwards and co-workers did not claim to have observed the spontaneous decomposition of H_2O_2. However, in a recent study, Galbacs and Csanyi,[13] again using edta, reported a value of 3×10^{-6} dm^3 mol^{-1} s^{-1} for the second-order rate constant k at 35 °C and pH 11.6, which they believed to be the true rate of alkali-induced decomposition.

The work described above was not concerned with the electronic state of the oxygen formed. Smith and Kulig[14] heated aqueous sodium stearate suspensions (pH 8.5—9.5) of cholesterol containing 4×10^{-3} mol dm^{-3} H_2O_2 at 50 °C for 6 h under N_2. From the steroids formed they concluded that the base-catalysed decomposition of H_2O_2 produced both $^1O_2$ and $^3O_2$ in a ratio of 1:3.

In the present work, experiments were initially carried out in the absence of aes, using solutions *ca.* 0.5 mol dm^{-3} in H_2O_2 at a pH of 11.6 ± 0.1. When edta or cyclohexanediamine-*NNN'N'*-tetra-acetate (cdta) was used to co-ordinate catalytic impurities, rates of decomposition were obtained which were similar to those reported by Edwards and co-workers and by Galbacs and Csanyi. However, in the presence of diethylenetriamine-*NNN'N''N''*-penta(methylphosphonic acid) (Dequest 2060) very marked reductions in the rate were observed. (Dequest 2060 has previously been shown[1] to be much more efficient than either edta or cdta in inhibiting catalysis of the reaction between H_2O_2 and the anions of peroxy-acids.) Thus, in one run with H_2O_2 at 35 °C in the presence of Dequest 2060, the experimental data over the first 71.5 h could be fitted by assuming a second-order rate constant k of 4.7×10^{-7} dm^3 mol^{-1} s^{-1}. Since in this period only 4.5% of the H_2O_2 had decomposed, an equally good fit could be obtained on the basis of first-order kinetics, with $t_{\frac{1}{2}} = 1\,030$ h. It is in fact difficult to apply normal kinetic criteria to a reaction so sensitive to adventitious catalysis. After the first 71.5 h a marked increase in the rate of decomposition was observed. Similar behaviour was also found by Edwards and co-workers[12] and by Galbacs and Csanyi,[13] and attributed to oxidation of the inhibitor by the H_2O_2.

It seems clear that the rate constant of 3×10^{-6} dm^3 mol^{-1} s^{-1} reported by Galbacs and Csanyi[13] represents a largely catalysed reaction. This is consistent with the observed formation of $^{\bullet}OH$ and O_2^- radicals. Very recently Csanyi *et al.*[15] have obtained a value for k of 5.6×10^{-7} dm^3 mol^{-1} s^{-1} at 30 °C by using diethylenetriaminepenta-acetic acid as the inhibitor. This is much closer to our value, although still effectively larger. Nevertheless, there seems to be no good reason for supposing that these values represent the true 'spontaneous' rate. In order to obtain further information, the decomposition was studied under similar conditions, but in the presence of aes (*ca.* 4×10^{-3} mol dm^{-3}) as a trap for $^1O_2$. It seems quite likely, on spin-conservation grounds, that the genuine base-catalysed decomposition would produce $^1O_2$ rather than ground-state $^3O_2$. One possible mechanism involves a nucleophilic attack of the HO_2^- ion on one of the oxygens of the H_2O_2, yielding HOOOH as an intermediate. Studies using ^{18}O-labelled peroxy-acids suggest a similar mechanism for the decomposition of peroxymonosulphuric acid[16] and monoperoxyphthalic acid[17] at their respective pK values. These reactions have been shown to produce $^1O_2$ in essentially quantitative yields.[1]

Table 1. Observed rate constants, k, $^1O_2$ yields, and corrected rate constants, k_{corr} for the decomposition of H_2O_2 under various conditions in the presence of aes

(*a*) 35 °C, pH 11.6

Chelating agent	10^6k/dm^3 mol^{-1} s^{-1}	% $^1O_2$	10^8k_{corr}/dm^3 mol^{-1} s^{-1}
None	20	0.18	3.7
edta	16	0.22	3.5
Dequest 2060	1.3	3.1	4.0

(*b*) 50 °C, pH 11.7

Chelating agent	10^6k/dm^3 mol^{-1} s^{-1}	% $^1O_2$	10^7k_{corr}/dm^3 mol^{-1} s^{-1}
cdta	25	1.1	2.8
Dequest 2060	5.0	5.3	2.6_5
Dequest 2060	5.0	4.4_5	2.2

It was found that the presence of aes increased the rate of decomposition of H_2O_2 several-fold. This is probably due to catalytic impurities in the aes. Small but significant amounts of endoperoxide were produced showing the formation of $^1O_2$ in yields up to 5.3%. Decreases in the aes concentration also occurred which were greater than the amounts of endoperoxide formed. Depending mainly on the inhibitor used, the rates of decomposition and the yields of $^1O_2$ varied widely. Nevertheless, the results were consistent with the presence of two concomitant reactions, a 'spontaneous' decomposition producing $^1O_2$ and a catalysed reaction producing ground-state $^3O_2$. Table 1 presents the observed rate constants, the yields of $^1O_2$, and the rate constants corrected on the assumption that the 'spontaneous' reaction gives 100% $^1O_2$. The corrected rate constants are in reasonably good agreement at both 35 and 50 °C. Evidence that the 'spontaneous' decomposition is second order in $[H_2O_2]$ was provided by two of the runs at 50 °C. Increasing the initial concentration of H_2O_2 by a factor of two (from 0.4 to 0.8 mol dm^{-3}) increased the initial rate of production of endoperoxide approximately four-fold. Accordingly we tentatively propose rate constants equal to 3.7×10^{-8} dm^3 mol^{-1} s^{-1} at 35 °C and *ca.* 2.5×10^{-7} dm^3 mol^{-1} s^{-1} at 50 °C for the 'spontaneous' decomposition of H_2O_2 at pH values close to its pK.

It is, of course, possible that the $^1O_2$ observed actually arose from a catalysed reaction. Such a route was initially suggested by the work of Navarro *et al.*[18] who found that the rate of decomposition of H_2O_2 in alkaline solution was considerably enhanced in the presence of CO_2, or air containing CO_2. This was explained by proposing the initial formation of peroxycarbonic acid H_2CO_4. The decomposition of this species could well yield $^1O_2$. Although in the present work the reaction vessels were securely stoppered, some exposure to atmosphere CO_2 would have taken place when aliquots were removed for analysis. However, very recently Csanyi and Galbacs[19] have shown that the CO_2 effect only occurs when appreciable amounts of catalytic impurities are present.

In the light of the above discussion, it seems extremely unlikely that the base-catalysed decomposition of dilute solutions of H_2O_2 in the range pH 8—9 could produce significant amounts of $^1O_2$ as reported by Smith and Kulig.[14] To test this, a solution 11.8×10^{-3} mol dm^{-3} in H_2O_2 and 2.1×10^{-3} mol dm^{-3} in aes at pH *ca.* 9 (0.2 mol dm^{-3} carbonate buffer) was heated in a glass tube for 6 h at 50 °C. The reagents were not specially purified and *ca.* 40% of the H_2O_2 decomposed. No endoperoxide could be detected although some attack on the aes occurred, probably caused by reactive free radicals such as $^{\bullet}OH$. In another similar system, where the buffer and aes solution had been passed through a chelating ion-exchange resin, a polypropylene vessel used and Dequest 2060 added, no change in the hydrogen peroxide concentration could be detected.

Halide-ion Catalysis.—It has been known for some considerable time that the decomposition of H_2O_2 is catalysed by Cl^-, Br^-, and (in particular) I^-. The general rate law[20] is (5). We

$$d[H_2O_2]/dt = k_1[H_2O_2][X^-] + k_2[H_2O_2][X^-][H^+] \quad (5)$$

have studied only the first, pH-independent, reaction, since in acidic solutions bromination or chlorination of the aes occurred. The generally accepted mechanism for this reaction is as in equation (6), which is rate-determining, followed by the

$$H_2O_2 + X^- \xrightarrow{k'} H_2O + XO^- \quad (6)$$

rapid reaction of XO^- with H_2O_2 (or of HOX with HO_2^-); k' is equal to $k_1/2$, where k_1 is the rate constant based on the disappearance of H_2O_2 as given in equation (5).

From previous studies[6] of the reaction of H_2O_2 with OCl^- and OBr^- we would expect a 100% yield of $^1O_2$ from the Cl^--catalysed reaction and a 76% yield with Br^-.

Iodide catalysis. The yields of $^1O_2$ obtained for the I^--catalysed decomposition of H_2O_2 at *ca.* 20 °C using *ca.* 4×10^{-3} mol dm^{-3} aes as a trap ($[H_2O_2]_0$ *ca.* 0.5 mol dm^{-3}, 0.2 mol dm^{-3} carbonate buffer, pH 10) were: 0.42 (14), 0.40 (43), 0.46 (48), 0.38% (70 mmol dm^{-3} I^-); average 0.42%. The values are virtually independent of $[I^-]$ which indicates that external quenching or chemical reaction of $^1O_2$ with I^- is not important. Like Br^-, I^- seems to quench $^1O_2$ only in aprotic solvents.[21] The chemical reaction of $^1O_2$ with I^- to give I_3^- is reported[22] to have a rate constant of 7×10^4 dm^3 mol^{-1} s^{-1} which is too low to be significant at the concentrations of I^- used here.

The catalytic decomposition was also studied with D_2O solutions. Although more endoperoxide was actually obtained, when the longer lifetime of $^1O_2$ in D_2O was taken into account, the calculated yield was slightly less, *ca.* 0.25%.

These low yields of $^1O_2$ are, at first sight, rather surprising. It might be thought that the yield would be similar to those found for the reactions of iodylbenzene and 4-iodosylbenzene-1-sulphonic acid with H_2O_2, *i.e.* 45—47%.[6] However from the relevant thermodynamic data,[23] it can be calculated that, in dilute aqueous solution, the reaction $HOI + HO_2^- \longrightarrow H_2O + I^- + {}^1O_2$ is *endothermic* to the extent of 9.5 kcal mol^{-1} (*ca.* 39.7 kJ mol^{-1}) (assuming that the heat of solution of $^1O_2$ in water is the same as that for $^3O_2$). The corresponding reactions with HOBr and HOCl are, as expected, exothermic.

Bromide catalysis. Bromide is a far less efficient catalyst than I^-. The yields of $^1O_2$ obtained varied from 50 to 80% at 35 °C and from 10 to 32% at 50 °C. The maximum yield of 80% is in reasonably good agreement with that of 76% obtained for the direct reaction of HO_2^- with HOBr.[6] Table 2 presents the observed values of k_1, the yields of $^1O_2$, and the corrected values of k_1 calculated assuming the true yield is 80%. The corrected rates are reasonably consistent, giving average values for k_1 of 1.1×10^{-6} dm^3 mol^{-1} s^{-1} at 35 °C and 5.5×10^{-6} dm^3 mol^{-1} s^{-1} at 50 °C. These rates are about half those in the literature[24] (2.3×10^{-6} and 11.7×10^{-6} dm^3 mol^{-1} s^{-1} respectively).

Table 2. Observed rate constants, k_1, $^1O_2$ yields, and corrected rate constants, k_1^{corr}, for the Br^--catalysed decomposition of H_2O_2 in 0.02 mol dm^{-3} phosphate buffer and 0.5 mmol dm^{-3} Dequest 2060

$[Br^-]$/mol dm^{-3}	10^6k_1/dm^3 mol^{-1} s^{-1}	% $^1O_2$	$10^6k_1^{corr}$/dm^3 mol^{-1} s^{-1}
(*a*) 35 °C, pH 6.7—9.0			
0.99	1.0_0	80	1.0_0
1.1	1.3_9	69	1.2_0
1.0[a]	1.5_9	51	1.0_1
			Av. 1.1
(*b*) 50 °C, pH 9—10			
0.10	$11._6$	$32._3$	4.7
1.05	$16._5$	$29._4$	6.1
0.09[b]	43	$10._5$	5.6
			Av. 5.5

[a] edta inhibitor. [b] AnalaR KBr.

Although the decomposition of H_2O_2 catalysed by Br^- does produce $^1O_2$, clearly the reaction is far too slow to have any practical importance. The reaction of H_2O_2 with Br^- to give HOBr is enormously catalysed by lactoperoxidase and chloroperoxidase. It has recently been shown by Kanofsky,[25,26] using the chemiluminescence at 1 268 nm, that these enzymes in the presence of H_2O_2 and Br^- give $^1O_2$ in good yield (essentially the same as in the direct reaction of HO_2^- and HOBr).

Chloride catalysis. Chloride is an even poorer catalyst than Br^-. The literature values of k_1 were not obtained directly, but by rather dubious extrapolations of the rates in acid solution to zero $[H^+]$. Only one run was carried out in the present work, at 50 °C with 0.438 mol dm^{-3} H_2O_2 at pH 6.4 (phosphate buffer) in the presence of Cl^- (1.3 mol dm^{-3}), aes (2.2×10^{-3} mol dm^{-3}), and Dequest 2060 (1×10^{-3} mol dm^{-3}). After 137 h, the concentration of H_2O_2 had dropped by only 3.4%, giving an uncorrected value of *ca.* 4.9×10^{-8} dm^3 mol^{-1} s^{-1} for k_1. A small amount of endoperoxide could be detected which corresponded to a *ca.* 8.4% yield of $^1O_2$. Since, for the Cl^--catalysed reaction, a yield of 100% would be expected, the corrected value of k_1 is *ca.* 4.1×10^{-9} dm^3 mol^{-1} s^{-1}. This probably represents an upper limit since some endoperoxide may have been formed by self sensitization of the aes. Nevertheless it is approximately an order of magnitude less than the literature values[24] (49.6 °C) of 3.3×10^{-8} (1 mol dm^{-3} Cl^-) and 7.8×10^{-8} dm^3 mol^{-1} s^{-1} (3 mol dm^{-3} Cl^-).

Chloroperoxidase catalyses the formation of HOCl from H_2O_2 and Cl^-. Kanofsky[26] has recently shown from the chemiluminescence at 1 268 nm that in the chloroperoxidase, H_2O_2, Cl^- system, $^1O_2$ is produced in almost stoicheiometric yield under optimum conditions.

Iron(III) *Catalysis.*—In the decomposition of H_2O_2 catalysed by Fe^{3+} in acidic solution, the involvement of species containing iron in oxidation states higher than 3, *e.g.* FeO^{3+}, has been suggested by several workers.[5] However, no species of this type has been definitely characterized and the main features of the reaction can be satisfactorily explained by a modified[4] Haber–Weiss[27] scheme [equations (7)—(13)]. When solutions

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad (7)$$

$$Fe^{3+} + H_2O_2 \rightleftharpoons Fe^{2+} + HO_2 + H^+ \qquad (8)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (9)$$

$${}^{\bullet}OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \qquad (10)$$

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (11)$$

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad (12)$$

$$O_2^- + Fe^{3+} \longrightarrow O_2 + Fe^{2+} \qquad (13)$$

of hydrogen peroxide (7×10^{-4} mol dm^{-3}) were allowed to decompose in the presence of $Fe(NO_3)_3$ (2×10^{-5} mol dm^{-3}) and aes (*ca.* 4×10^{-3} mol dm^{-3}) at pH 1 (0.1 mol dm^{-3} HNO_3) considerable attack on the aes occurred. The ratios mol aes consumed/mol H_2O_2 decomposed were *ca.* 1.8. Analysis of the products by h.p.l.c. showed that no endoperoxide was produced. However, the chromatograms were very similar to those obtained from acidic solutions of aes which had been subjected to γ-irradiation (Figure). This is consistent with the scheme above, which involves the formation of ${}^{\bullet}OH$ radicals. In this scheme, the O_2 is produced by reaction (13). On spin-conservation grounds, this reaction can give either ${}^1O_2$ or ground-state ${}^3O_2$ so it is not surprising that the latter is, in fact, produced.

Catalysis by Catalase and Iron(III)*–Triethylenetetramine* (*teta*).—When a 0.35 mol dm^{-3} solution of H_2O_2 (pH 7, 0.05 mol dm^{-3} phosphate buffer) containing aes (4×10^{-3} mol dm^{-3}) was allowed to decompose completely at 20 °C in the presence of catalase there was no measurable decrease in the aes concentration. A more sensitive criterion was provided by h.p.l.c. which showed no detectable endoperoxide ($\leqslant 5 \times 10^{-6}$ mol dm^{-3}), indicating that less than 0.01% of ${}^1O_2$ is produced. This is consistent with a previous trapping study[28] using 3,5-diphenylfuran which concluded that less than 0.5% of the oxygen formed was in the singlet state. Khan[29] reported an emission band at 1 640 nm in the H_2O_2–catalase system which he attributed to ${}^1O_2$. However, very recently Kanofsky[30] showed that this was actually thermal emission. No genuine ${}^1\Delta_g \longrightarrow {}^3\Sigma_g$ emission near 1 268 nm was observed, setting an upper limit of 0.02% on ${}^1O_2$ formation.

It has been shown by Wang[31] that the Fe^{3+}–triethylenetetramine (teta) complex is an efficient catalyst for the decomposition of H_2O_2. When a 0.168 mol dm^{-3} solution of H_2O_2 at pH 9 and 20 °C was allowed to decompose completely in the presence of Fe^{3+} (2×10^{-6} mol dm^{-3}), triethylenetetramine disulphate (6×10^{-3} mol dm^{-3}), and aes (4.02×10^{-3} mol dm^{-3}) the concentration of the aes dropped to 3.05×10^{-3} mol dm^{-3}. H.p.l.c. of the resulting solution showed a considerable number of peaks but the concentration of endoperoxide was $\leqslant 1 \times 10^{-5}$ mol dm^{-3}, indicating that $\leqslant$0.03% of the oxygen formed was in the singlet state. The comparatively small amount of attack on the aes was probably due to side reactions producing reactive free radicals. It is not certain that catalysis by the Fe^{3+}–teta system is really a homogeneous reaction. Beck and Gorog[32] from rates as a function of iron(III) concentration, have suggested that catalysis by a very active colloidal form of $Fe(OH)_3$ is also involved.

Heterogeneous Catalysis.—Hydrogen peroxide solutions (0.35 mol dm^{-3}) containing aes (*ca.* 4×10^{-3} mol dm^{-3}) at pH 7 (phosphate buffer) or pH 10 (carbonate buffer) were stirred with silver powder, platinum black, or MnO_2 until complete decomposition had occurred. In each case there was a negligible change in the aes concentration and no endoperoxide could be detected by h.p.l.c.

It has been shown unambiguously, using e.s.r. in a flow system, that O_2^- is formed in the aqueous phase when H_2O_2 decomposes in the presence of Ag[33] or metal oxides.[34] This is consistent with a Haber–Weiss type of mechanism. In view of this, it is perhaps surprising that there was no attack on the aes by the ${}^{\bullet}OH$ radical. Possibly this short-lived species remains adsorbed on the catalyst surface, which could affect its reactivity towards aes.

Experimental

For the very slow reactions the precautions described previously[1] were taken (*e.g.* polypropylene vessels, purified NaOH). Solutions were finally passed through a 0.22-μm polytetrafluoroethylene filter before addition of H_2O_2. Anthracene-9,10-bis(ethanesulphonate) was analysed by u.v. spectroscopy and the endoperoxide by h.p.l.c.[6] Hydrogen peroxide was determined iodometrically in an atmosphere of CO_2. In a number of cases it was necessary to follow quite small changes in concentration, and aliquots were taken using a constant-volume pipette with a reproducibility of better than 0.1%. In the base-catalysed runs the pH was adjusted by addition of NaOH. The pH accordingly changed as the reaction proceeded but this was not serious since in most cases only the initial part of the reaction was studied.

Purified NaBr solution was obtained in one of two ways. (*i*) A 5 mol dm^{-3} solution of commercial NaBr (20 cm^3) was rapidly stirred, and a pellet of AristaR NaOH added, followed by a few drops of 5% AnalaR $Mg(ClO_4)_2$ (aq). The solution was used after centrifugation. (*ii*) Hydrogen bromide was bubbled through doubly distilled water in a Polythene vessel. The solution was analysed by acid–base titration, and neutralized to pH 5—6 with AristaR Na_2CO_3. The H_2O_2 was an 88% unstabilized sample from Interox Chemicals Ltd. The salts NaCl and KI were of AnalaR grade, MnO_2 (precipitated) was from B.D.H., and catalase from Sigma. The Ag and Pt were prepared from $AgNO_3$ (aq) and $K_2[PtCl_4]$ (aq) by treatment with alkaline HCHO and $NaBH_4$ respectively.

Solutions of aes (*ca.* 4×10^{-3} mol dm^{-3}) saturated with N_2O were irradiated in stoppered glass tubes by a ${}^{60}Co$ source. A 40—50% reduction in the aes concentration occurred after 35—40 min with a dose of about 350 krad (3.5×10^3 J kg^{-1}).

Acknowledgements

We thank Interox Chemicals Ltd. for a maintenance grant (to M. W. U.) and Mr. B. Bennett of the Nuclear Engineering section, Imperial College for assistance with the ${}^{60}Co$ source.

References

1 Part 3, D. F. Evans and M. W. Upton, *J. Chem. Soc., Dalton Trans.*, 1985, 1151.
2 J. H. Baxendale, *Adv. Catal.*, 1952, **4**, 31.
3 W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, 'Hydrogen Peroxide,' Reinhold, New York, 1955.
4 W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, 1951, **47**, 591.
5 S. B. Brown, P. Jones, and A. Suggett, *Prog. Inorg. Chem.*, 1970, **13**, 159.
6 D. F. Evans and M. W. Upton, *J. Chem. Soc., Dalton Trans.*, 1985, 1141.
7 J. A. Fee, 'Oxygen and Life,' *Special Publ.*, The Royal Society of Chemistry, London, 1981, no. 39, p. 77.

8 C. S. Foote, F. C. Shook, and R. A. Aberkabl, *J. Am. Chem. Soc.*, 1980, **102**, 2503.

9 F. R. Duke and T. W. Haas, *J. Phys. Chem.*, 1961, **65**, 304.

10 M. G. Evans and N. Uri, *Trans. Faraday Soc.*, 1949, **45**, 224.

11 J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, 1962, **58**, 1846.

12 E. Koubek, M. L. Haggett, C. J. Bataglia, K. M. Ibne-Rasa, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, 1963, **85**, 2263.

13 Z. M. Galbacs and L. J. Csanyi, *J. Chem. Soc., Dalton Trans.*, 1983, 2353.

14 L. J. Smith and M. J. Kulig, *J. Am. Chem. Soc.*, 1976, **98**, 1027.

15 L. J. Csanyi, L. Nagy, Z. M. Galbacs, and I. Horvath, *Z. Phys. Chem. (Frankfurt am Main)*, 1983, **138**, 107.

16 E. Koubek, G. Levey, and J. O. Edwards, *Inorg. Chem.*, 1964, **3**, 1331.

17 R. F. Ball, J. O. Edwards, M. L. Haggett, and P. Jones, *J. Am. Chem. Soc.*, 1967, **89**, 2331.

18 J. Navarro, M. A. De La Rosa, M. Roncel, and F. F. De La Rosa, *J. Chem. Soc., Faraday Trans. 1*, 1977, 2323.

19 L. J. Csanyi and Z. M. Galbacs, *J. Chem. Soc., Faraday Trans. 1*, 1985, 113.

20 L. R. Wilson, in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 6, p. 406.

21 J. Rosenthal and A. Frimer, *Photochem. Photobiol.*, 1976, **23**, 209.

22 A. G. Kepka and L. I. Grossweiner, *Photochem. Photobiol.*, 1973, **18**, 49.

23 'Selected Values of Chemical Thermodynamic Properties,' Technical Note 270—3, National Bureau of Standards, Washington, 1968.

24 A. Mohammad and H. A. Liebhafsky, *J. Am. Chem. Soc.*, 1934, **56**, 1680.

25 J. R. Kanofsky, *J. Photochem.*, 1984, **25**, 105.

26 J. R. Kanofsky, *J. Biol. Chem.*, 1984, **259**, 5596.

27 F. Haber and J. Weiss, *Proc. R. Soc. London, Ser. A*, 1935, **147**, 332.

28 D. J. T. Porter and L. L. Ingraham, *Biochim. Biophys. Acta*, 1974, **334**, 97.

29 A. U. Khan, *J. Am. Chem. Soc.*, 1983, **105**, 7195.

30 J. R. Kanofsky, *J. Am. Chem. Soc.*, 1984, **106**, 4277.

31 J. H. Wang, *J. Am. Chem. Soc.*, 1955, **77**, 4715.

32 H. T. Beck and S. Gorog, *Acta Chim. Acad. Sci. Hung.*, 1959, **20**, 57.

33 Y. Ono, T. Matsumwa, N. Kitajima, and S. I. Fukuzumi, *J. Phys. Chem.*, 1977, **81**, 1307.

34 N. Kitajima, S. I. Fukuzumi, and Y. Ono, *J. Phys. Chem.*, 1978, **82**, 1505.

Received 19*th April* 1985; *Paper* 5/649