

Studies on Singlet Oxygen in Aqueous Solution. Part 1. Formation of Singlet Oxygen from Hydrogen Peroxide with Two-electron Oxidants

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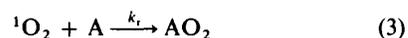
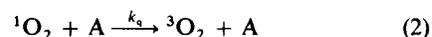
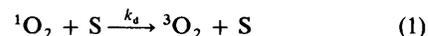
Kinetic parameters are reported for the trapping of singlet oxygen by anthracene-9,10-bis(ethanesulphonate) (aes) in water and deuterium oxide solutions. The kinetics of the reactions of *N*-chlorosuccinimide, chloramine T (*N*-chlorotoluene-*p*-sulphonamide), *N*-chloromethanesulphonamide, and *N,N*-dichloromethanesulphonamide with hydrogen peroxide have been studied. For chloramine T and *N*-chloromethanesulphonamide the rate-determining step is formation of the corresponding dichloro-compounds, which are the reactive species. Using aes as a trap, it is shown that both chloramine T and *N*-chlorosuccinimide with H₂O₂ produce singlet oxygen in essentially quantitative yield. Iodylbenzene reacts with H₂O₂ to give, in the rate-determining step, iodosylbenzene and oxygen and then iodobenzene and oxygen; 47% of the oxygen produced is in the singlet state. For the corresponding reaction with 4-iodosylbenzene-1-sulphonic acid, the yield of singlet oxygen is 45%, *i.e.* indistinguishable within experimental error. Periodate and H₂O₂ give lower yields of singlet oxygen, and it is considered that two concomitant processes are involved. With hypobromite and H₂O₂ the yield of singlet oxygen is 76%. These variations in yield are briefly discussed.

The present work is concerned with two aspects of singlet oxygen. First, the characterization of anthracene-9,10-bis(ethanesulphonate) (aes)¹ as a trap for ¹O₂ in aqueous solution. Secondly, its use to determine quantitatively the yields of ¹O₂ when hydrogen peroxide reacts with a variety of two-electron oxidizing agents. It has been known for some time that oxidation of H₂O₂ by hypochlorite^{2,3} and hypobromite⁴ produces ¹O₂. In a detailed study, Held *et al.*,⁵ using 2,5-dimethylfuran as a trap, showed that in the alkaline region the reaction of H₂O₂ and OCl⁻ (or more probably the nucleophilic attack of HO₂⁻ on HOCl) gives essentially 100% yields of ¹O₂, as would be expected on spin-conservation grounds. More recently, Hurst *et al.*⁶ have studied the kinetics of oxidation of H₂O₂ by *N*-chlorosuccinimide and *t*-butyl hypochlorite, and shown qualitatively that ¹O₂ is produced.

Results

Reaction of aes with ¹O₂.—The caesium and sodium salts of aes are readily soluble in water, even at low pH, unlike related carboxylic acids such as 5,6,11,12-tetraphenylanthracene-2,3,8,9-tetracarboxylic acid,⁷ 9,10-diphenylanthracene-2,3-dicarboxylic acid,⁸ 9,10-diphenylanthracene-2,3,6,7-tetracarboxylic acid,⁹ and anthracene-9,10-dipropionic acid.¹⁰ Solutions should, however, be less than 0.1 mol dm⁻³ in K⁺, since the potassium salt of aes is sparingly soluble in water. The compound aes reacts with ¹O₂ (from photosensitization with Rose Bengal, or from the reaction of OCl⁻ with H₂O₂) to give the 9,10-endoperoxide (an -O-O- bridge at 9,10 positions) as the sole detectable product. The endoperoxide was characterized in solution by its proton resonance and u.v. spectra, and by t.l.c. with development by Fe²⁺-NCS⁻. The production of endoperoxide can be followed quantitatively, either from the disappearance of the strong u.v. absorption of aes, or by direct analysis of the endoperoxide using h.p.l.c. For the study of ¹O₂ in aqueous solution, it is desirable to use both techniques, since aes will react with species other than ¹O₂, for example reactive free radicals such as [•]OH.¹¹ These reactions also normally result in the disappearance of the anthracene-type u.v. absorption, but the products formed can readily be distinguished from the endoperoxide by h.p.l.c.

When ¹O₂ is produced in the presence of a trap A, such as aes, it may follow one of three pathways: quenching by solvent (1), quenching by A (2), or reaction (3).



The efficiency *E* can be defined as the fraction of ¹O₂ which reacts to give AO₂ and is given by the expression (4) where

$$\frac{1}{E} = \frac{k_r + k_a}{k_r} + \frac{k_d}{k_r} \cdot \frac{1}{[\text{A}]_{\text{av}}} \quad (4)$$

[A]_{av} = (A₀ - A_∞)/log_e(A₀/A_∞); A₀ is the initial concentration of A and A_∞ is that remaining after the reaction. A plot of 1/*E* versus log_e(A₀/A_∞)/(A₀ - A_∞) should be a straight line, with a slope equal to k_d/k_r and an intercept of 1 + (k_a/k_r). The results obtained for aes in H₂O and D₂O solutions are shown in the Figure. The ¹O₂ was generated by the reaction of OCl⁻ and H₂O₂, which was assumed to occur with 100% efficiency. Quite good straight lines are obtained, although there is a tendency for the points to lie above the line at the highest concentrations where the measurements were most accurate. This is almost certainly due to aggregation of the aes ions, since marked deviations from Beer's law in the u.v. spectrum and upfield shifts of the proton resonances were observed at these concentrations. The intercepts of the straight lines are 1.37 in H₂O and 1.33 in D₂O, indicating that k_d/k_r is *ca.* 0.35. Even if the efficiency of ¹O₂ production is not exactly 100%, it can hardly be low enough to give intercepts of 1, corresponding to no quenching. It is not surprising that aes quenches ¹O₂, since for the very similar molecule 9,10-dimethylanthracene in 1,2,2-trichlorotrifluoroethane k_d/k_r is 0.6, based on direct laser excitation of ¹O₂.¹² Previous results for aes, reported in a preliminary note,¹ gave an intercept of almost exactly 1. However, in these experiments only the disappearance of aes was studied and it is thought likely that attack of OCl⁻ on the

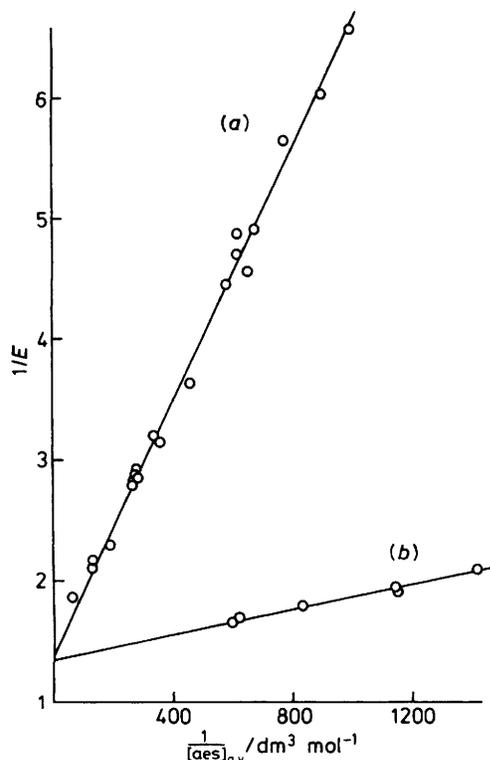


Figure. A plot of $1/E$ against $1/[\text{aes}]_{\text{av}}$ for the reaction of $^1\text{O}_2$ with aes in (a) H_2O and (b) D_2O solutions

aes occurred, since the H_2O_2 was added to aes containing OCl^- rather than in the reverse way.

The slopes of the lines in H_2O and D_2O are 5.32×10^{-3} and $5.27 \times 10^{-4} \text{ mol dm}^{-3}$ respectively. The ratio of the two slopes (10.1) should represent the ratio of the lifetimes of $^1\text{O}_2$ in D_2O and in H_2O . Other determinations of this range from 10 to 17,^{10,13-15} with the higher, directly determined, values probably being more accurate. The presence of small amounts of H_2O in the D_2O solutions (derived from the reagents) may partly account for the rather low value obtained in this work. If the lifetime of $^1\text{O}_2$ in H_2O is taken to be $4 \mu\text{s}$,¹³ then k_t for the reaction of $^1\text{O}_2$ with aes is $4.7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In a reaction producing oxygen the fraction x of the oxygen which is present in the singlet state can be calculated from equation (5),

$$x = \frac{\text{moles of endoperoxide produced}}{\text{moles of oxygen formed}} \cdot \frac{1}{E_{\text{av}}} \quad (5)$$

where E_{av} is the trapping efficiency at $[\text{A}]_{\text{av}}$ and is obtained from A_0 , A_∞ , and the equation of the appropriate straight line. For aqueous solutions the concentration of aes was normally ca. $4 \times 10^{-3} \text{ mol dm}^{-3}$, when ca. 37% of the $^1\text{O}_2$ is trapped.

N-Chlorosuccinimide (ncs).—Over the range pH 4.0–5.7 the reaction between ncs and H_2O_2 is first order in the concentration of both reactants and, to a reasonable approximation, the rate is inversely proportional to the hydrogen-ion concentration as previously found by Hurst *et al.*⁶ in the range pH 5.8–8.4. Values of k are given in Table 1.

These simple kinetics, together with the fact that the rates were unaffected by the addition of succinimide, indicate that direct reaction of HOCl formed by hydrolysis does not play a significant part. The rate constant k for the reaction of HO_2^- and ncs of $1.26 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25°C is in reasonable

Table 1. Rate constants ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for the reaction of ncs with H_2O_2 , k , and for the reaction of ncs with HO_2^- , k' [assuming K (acid dissociation constant) $\text{H}_2\text{O}_2 = 2.24 \times 10^{-12} \text{ dm}^3 \text{ mol}^{-1}$ at 25°C],* at 25°C and in 0.2 mol dm^{-3} acetate buffer

| pH | k | $10^{-5} k'$ |
|------|--------|--------------|
| 4.03 | 0.0034 | 1.42 |
| 4.70 | 0.0145 | 1.29 |
| 5.45 | 0.0672 | 1.07 |
| 5.67 | 0.134 | 1.28 |

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

Table 2. Production of $^1\text{O}_2$ from the reaction of H_2O_2 with ncs*

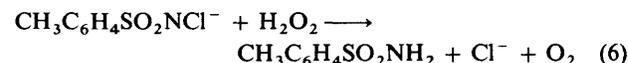
| $[\text{aes}]_0$ | $[\text{aes}]_\infty$ | $\Delta(\text{aes})$ | Total O_2 produced | $[\text{aes}]_{\text{av}}^{-1}$ | $E(^1\text{O}_2)$ | % $^1\text{O}_2$ |
|-----------------------|-----------------------|----------------------|-----------------------------|---------------------------------|-------------------|------------------|
| mmol dm^{-3} | mmol dm^{-3} | μmol | μmol | $\text{dm}^3 \text{ mol}^{-1}$ | | |
| 4.228 | 3.053 | 3.219 | 9.30 | 277 | 0.351 | 99 |
| 4.081 | 3.352 | 2.080 | 5.70 | 270 | 0.356 | 102 |
| 4.103 | 3.002 | 3.003 | 8.94 | 312 | 0.331 | 102 |

* Solutions of aes and ncs in pH 5.7 acetate buffer were analysed for aes and ncs. Excess of H_2O_2 was slowly added to well stirred aliquots using a micrometer syringe. After 40 min the mixtures were analyzed by u.v. spectroscopy and h.p.l.c., left for another 40 min, and reanalyzed. The total O_2 produced was calculated from the amount of ncs taken and the known stoichiometry of the reaction.

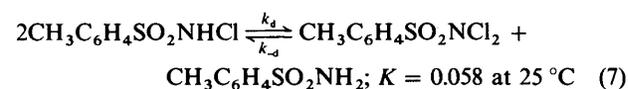
agreement with that of $0.91 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ found by Hurst *et al.*⁶ in a different buffer system.

Details of the trapping experiments are given in Table 2. It can be seen that, within experimental error, all the oxygen produced is in the singlet state (or, more strictly, the yield of $^1\text{O}_2$ is the same as that in the reaction of OCl^- and H_2O_2).

Chloramine T (cat).—Chloramine T reacts with H_2O_2 according to equation (6). Although solutions of cat contain



small amounts of HOCl or OCl^- formed by hydrolysis,¹⁶ the detailed work of Higuchi and Hussain^{17,18} has shown that in the chlorination of *p*-cresol the rate-determining step is the disproportionation to give dichloramine T, which is the reactive species [equation (7)]. The forward rate of disproportionation



k_d is pH dependent and reaches a maximum at the pK of cat (4.55 at 25°C).¹⁷ A similar mechanism seems to be involved in the reaction of cat with H_2O_2 . When the initial molar ratio of H_2O_2 to cat was 5:1, the reaction showed a reasonable second-order dependence on the concentration of cat. There was an initial fast reaction, which can be attributed to the small concentration of dichloramine T present at equilibrium. The rate constants are given in Table 3, together with values of k_d calculated from the equation given by Higuchi *et al.*¹⁷ The agreement between the two sets of values is quite satisfactory.

Yields of $^1\text{O}_2$ for the cat- H_2O_2 reaction were 97, 102, and 103% in separate experiments, *i.e.* essentially quantitative. The reaction between NaOCl and H_2O_2 in aqueous methanol has been used for organic preparations by Foote *et al.*¹⁹ One disadvantage is that aqueous methanol is not a particularly

Table 3. Rate constants ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for the reaction of cat with H_2O_2 , k , and for disproportionation of cat, k_d ,¹⁷ at 25 °C, in 0.2 mol dm^{-3} phosphate buffer for k

| pH | k | k_d |
|------|------|-------|
| 2.50 | 0.71 | 0.78 |
| 3.17 | 3.2 | 3.5 |
| 5.80 | 5.2 | 4.5 |
| 6.87 | 0.40 | 0.43 |

Table 4. Rate constants, k (second order in concentration of $\text{CH}_3\text{SO}_2\text{NHCl}$) for the reaction of $\text{CH}_3\text{SO}_2\text{NHCl}$ with excess of H_2O_2 at 0 °C in 0.2 mol dm^{-3} acetate buffer

| pH | $k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ |
|------|---|
| 3.10 | 0.51 |
| 3.98 | 2.63 |
| 4.60 | 6.61 |
| 4.96 | 5.01 |
| 5.22 | 3.98 |

good solvent for many organic compounds, and replacing it by solvents such as dioxane considerably reduces the yield of $^1\text{O}_2$. Both H_2O_2 and cat are soluble in chloroform-methanol (1:1, v/v) and a reasonable yield of *cis*-dibenzoylstilbene from tetraphenylcyclopentadienone was obtained (see Experimental section). A disadvantage of this method of producing $^1\text{O}_2$ is that both H_2O_2 and cat are strong oxidizing agents.

N-Chloromethanesulphonamide and N-Dichloromethanesulphonamide.—Dichloramine T is only very sparingly soluble in water, and hence it is difficult to follow its reaction with H_2O_2 . Accordingly, the system $\text{CH}_3\text{SO}_2\text{NHCl}-\text{CH}_3\text{SO}_2\text{NCl}_2$ was studied, since both compounds are readily soluble in water. The reaction of H_2O_2 with $\text{CH}_3\text{SO}_2\text{NHCl}$ showed similar kinetics to that with cat, and values of k are given in Table 4. The maximum at pH ca. 4.6 is consistent with the value of 4.69 at 25 °C found for the p*K* of $\text{CH}_3\text{SO}_2\text{NHCl}$ (pH of half-neutralized solution).

Solutions of $\text{CH}_3\text{SO}_2\text{NCl}_2$ were stable only under acidic conditions. There was a rapid initial reaction with H_2O_2 to give $\text{CH}_3\text{SO}_2\text{NHCl}$ and O_2 . The rate was first order in the concentration of both reactants, and the rate constants are given in Table 5. As with ncs, they are inversely proportional to $[\text{H}^+]$, and the calculated rate constant for the (assumed) attack of HO_2^- on $\text{CH}_3\text{SO}_2\text{NCl}_2$ is $3.6 \times 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$, which approaches that for a diffusion-controlled reaction. One run carried out at 25 °C gave $k' = 4.1 \times 10^9 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$. It should be noted that to calculate k' from k requires a knowledge of the p*K* for H_2O_2 at the appropriate temperature, and the value taken at 0 °C is an extrapolated one.

Trapping experiments with aes gave slightly variable results, but the maximum yield of endoperoxide obtained for $\text{CH}_3\text{SO}_2\text{NHCl}$ indicated production of ca. 83% $^1\text{O}_2$, and for $\text{CH}_3\text{SO}_2\text{NCl}_2$ only ca. 60%. However, some attack on aes occurred to give products other than the endoperoxide, and it seems likely that the lower yields compared to ncs and cat are an artefact of the trapping procedure.

Iodylbenzene, 4-Iodosylbenzene-1-sulphonic acid, and Periodate.—It was reported in 1893²⁰ that iodylbenzene in glacial acetic acid reacts with H_2O_2 to give iodobenzene and O_2 . The reaction was studied here in aqueous solution, and found to be quantitative, and also first order in the concentration of both reactants. It occurs in two steps [equations (8) and (9)]. The

Table 5. Rate constants ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for the reaction of $\text{CH}_3\text{SO}_2\text{NCl}_2$ with H_2O_2 , k , and for the reaction of $\text{CH}_3\text{SO}_2\text{NCl}_2$ with HO_2^- , k' (assuming $K \text{H}_2\text{O}_2 = 7 \times 10^{-13} \text{ dm}^3 \text{mol}^{-1}$ at 0 °C, see Table 1), at 0 °C in 0.2 mol dm^{-3} chloroacetate and acetate buffers

| pH | k | $10^{-9} k'$ |
|------|------|------------------|
| 2.48 | 0.72 | 3.3 ₉ |
| 2.93 | 2.34 | 3.9 ₄ |
| 4.03 | 24.5 | 3.2 ₆ |
| 4.51 | 83.2 | 3.6 ₈ |
| 5.02 | 25.7 | 3.5 ₂ |



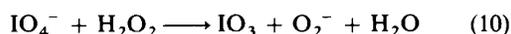
overall rate is determined by the first step. Values of k_1 are given in Table 6. The reasons for the variation of k_1 with pH are not clear. Iodylbenzene is reported to be slightly amphoteric²¹ and this, together with the possible reaction of HO_2^- at high pH, may account for some of the variation. Salt effects may also play a part although the presence of 0.5 mol dm^{-3} NaClO_4 did not affect the observed rate. The yields of $^1\text{O}_2$ were found to be 45, 47, 49, 48, and 46%, average 47%. In view of the low yield, the trapping experiments were studied in some detail. Iodylbenzene does not attack aes over the pH range studied, and the yields of endoperoxide were, within experimental error, the same as the amounts of aes which reacted. The reaction rate was not affected by the presence of aes, and readings taken as a single reaction proceeded showed no variation in the observed yields, showing that the iodobenzene formed does not quench $^1\text{O}_2$. Finally, one experiment in D_2O gave a very similar result.

Iodosylbenzene is only very sparingly soluble in water, and although qualitative experiments showed that it reacted very rapidly with H_2O_2 , further measurements were made with 4-iodosylbenzene-1-sulphonic acid, which is readily soluble in water. 4-Iodosylbenzene-1-sulphonic acid reacted very rapidly with H_2O_2 over the range pH 3–10. Like iodosylbenzene,²² 4-iodosylbenzene-1-sulphonic acid slowly disproportionates in aqueous solution to the corresponding iodyl and iodo-compounds. However, it was possible to determine the yields of $^1\text{O}_2$ using a modified procedure (see Experimental section). 4-Iodosylbenzene-1-sulphonic acid also attacks aes (to give products other than the endoperoxide), but because of its very rapid reaction with H_2O_2 no problems were encountered when a solution of 4-iodosylbenzene-1-sulphonic acid was added to aes containing excess of H_2O_2 . The yields of $^1\text{O}_2$ were 44, 45, and 46%, *i.e.* indistinguishable within experimental error from that obtained with iodylbenzene.

The IO_4^- ion is known to react rapidly and quantitatively with H_2O_2 in acid, neutral, and alkaline solutions to give IO_3^- and O_2 .²³ Periodate slowly attacks aes, but in view of its very rapid reaction with H_2O_2 no complications would be expected from this. Nevertheless the yields of $^1\text{O}_2$ were rather variable. At pH 7 the endoperoxide produced corresponded to a 34% yield of $^1\text{O}_2$, but the amount of aes consumed was more than the amount of endoperoxide produced, and an appreciable number of additional h.p.l.c. peaks appeared. At pH 10.5 the yields of $^1\text{O}_2$ increased to 38–40%, and the extent of non- $^1\text{O}_2$ attack on the aes decreased. It seems likely that two concomitant reactions are occurring. One reaction is a two-electron oxidation of H_2O_2 similar to that with iodylbenzene and 4-iodosylbenzene-1-sulphonic acid, and the other is a radical process, presumably involving an iodine(vi) species such as IO_3 , *e.g.* as in equation (10). The free radicals are then trapped by the

Table 6. Rate constants $k (= k_1)$ for the reaction $C_6H_5IO_2 + 2H_2O_2 \longrightarrow C_6H_5I + 2H_2O + 2O_2$ in 0.1 mol dm^{-3} phosphate buffer at 25 °C

| pH | $10^2 k / dm^3 mol^{-1} s^{-1}$ | pH | $10^2 k / dm^3 mol^{-1} s^{-1}$ |
|------|---------------------------------|-------|---------------------------------|
| 2.74 | 0.49 | 7.30 | 0.77 |
| 3.36 | 0.34 | 8.25 | 0.82 |
| 4.32 | 0.27 | 9.20 | 1.29 |
| 5.51 | 0.31 | 9.45 | 1.74 |
| 6.19 | 0.40 | 9.90 | 2.72 |
| 6.60 | 0.48 | 10.50 | 7.95, 7.70 |
| 7.08 | 0.63 | | |



aes with quite high efficiency. It is known that iodine(vi) species are formed by photolysis and radiolysis of aqueous iodate and periodate solutions.²⁴

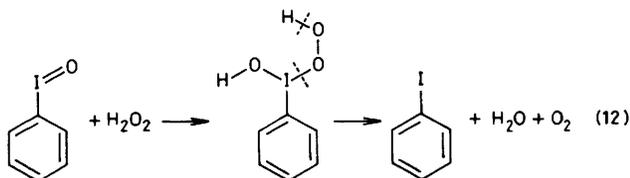
Hypobromite.—In view of the low yields obtained with iodylbenzene and 4-iodosylbenzene-1-sulphonic acid, it was thought of interest to study the reaction of HOBr with HO_2^- . The HOBr–OBr⁻ system is formed rapidly and quantitatively from OCl⁻ and excess of Br⁻ in sufficiently alkaline solution.²⁵ Solutions prepared in this way (pH 11–12) were found, from reaction with excess of H₂O₂ and analysis of the remaining H₂O₂, to be stable for about 1 h at room temperature in the dark. The reaction with H₂O₂ was very rapid, and the yields of ¹O₂ using freshly prepared solutions were 79, 78, 74, 76, 74, and 73%, average 76%. The yields were independent of the excess of Br⁻ (up to 0.5 mol dm^{-3}), showing the absence of external quenching by Br⁻; Br⁻ seems to quench ¹O₂ only in aprotic solvents.²⁶

Discussion

It is not surprising that the reactions of H₂O₂ with ncs and cat produce the same yield of ¹O₂ as that with OCl⁻ (essentially quantitative). A plausible first step with the chloroamines is as in equation (11). The species HOCl has been postulated as an



intermediate in the reaction of Cl₂ and H₂O₂.²⁷ At first sight, the low yields of ¹O₂ obtained with iodylbenzene and 4-iodosylbenzene-1-sulphonic acid seem surprising, since reasonable concerted reactions can be written which should, in principle, give 100% ¹O₂; e.g. with C₆H₅IO [equation (12)].



A possible explanation is spin-orbit coupling involving the heavy iodine atom, which can mix singlet and triplet states. The 76% yield with OBr⁻ (relative to 100% for OCl⁻) is consistent with this hypothesis.

Experimental

Preparation of aes.—*Anthracene-9,10-diethanol.* 9,10-Dibromoanthracene (49 g, 0.146 mol) and anhydrous diethyl ether

(350 cm^3) were stirred under N₂ or Ar, cooled to 5 °C, and 1.6 mol dm^{-3} n-butyl-lithium in hexane (200 cm^3 , 0.32 mol) was added over a period of 10 min. Stirring was continued for a further 20 min. An excess of ethylene oxide (30 cm^3 , 0.6 mol) in cold diethyl ether (70 cm^3) was added over 10 min and the mixture was allowed to warm up to room temperature. It was then poured over crushed ice (100 g), the dialcohol filtered off, washed with a little ether, and then well with water. Yield of crude material 33.4 g. Recrystallization from ethanol gave 14.7 g (38%) of the product, m.p. 221–225 °C (lit.,²⁸ 223.5–224.5 °C). ¹H N.m.r. in (CD₃)₂SO: δ 3.79 (8 H, s, CH₂CH₂OH coincident), 4.90 (2 H, s, OH), 7.52 (4 H, m, H², H³, H⁶, H⁷), and 8.35 (4 H, m, H¹, H⁴, H⁵, H⁸).

9,10-Bis(2-iodoethyl)anthracene. The dialcohol (14.7 g, 0.055 mol) was dissolved in dry dimethylformamide (dmf) (150 cm^3), the solution was cooled to 15 °C, and methyltriphenoxylphosphonium iodide²⁹ (90 g, 0.2 mol) was added with stirring. After 1 h, methanol (150 cm^3), followed by water (150 cm^3), were added, and the mixture cooled to 0 °C. The yellow product was filtered off, washed with methanol, air-dried, and recrystallized from benzene. Yield 17.0 g (63%), m.p. ca. 180 °C (decomp.) (Found: C, 45.7; H, 3.35; I, 52.95. C₁₈H₁₆I₂ requires C, 44.45; H, 3.30; I, 52.2%).

Anthracene-9,10-bis(ethanesulphonate), caesium salt, dihydrate. The di-iodide (14.7 g, 0.030 mol) was stirred under reflux with 0.75 mol dm^{-3} [NEt₄]₂SO₃ (110 cm^3 , 0.083 mol) and dioxane (110 cm^3) for 6 h when an almost clear solution was obtained. This solution was evaporated to dryness (rotary evaporator), and the residue dissolved in water (100 cm^3). After filtration, the filtrate was heated to boiling, and CsCl (50 g) added in portions. After cooling to 0 °C, the yellow solid was filtered off, washed with aqueous CsCl (50%, w/v), a little methanol, and then well with ethanol. When dried in air it was obtained as the dihydrate. Yield 17.1 g (81%) (Found: C, 31.4; H, 2.60%; weight loss *in vacuo* at 100 °C, 5.0%. C₁₈H₁₆Cs₂O₆S₂·2H₂O requires C, 31.15; H, 2.90%; weight loss, 5.2%). H.p.l.c. gave a single peak only. ¹H N.m.r. (D₂O, 0.015 mol dm^{-3}): δ 3.29 (4 H, m, CH₂S), 4.08 (4 H, m, CH₂CH₂S), 7.70 (4 H, m, H², H³, H⁶, H⁷), and 8.43 (4 H, m, H¹, H⁴, H⁵, H⁸). U.v. in water: 398 (12 300), 377 (12 600), 358 (7 450), and 341 nm (ϵ 3 370 $dm^3 mol^{-1} cm^{-1}$).

The corresponding sodium salt was obtained by substituting AnalaR NaCl (20 g) for the CsCl, washing the solid with aqueous NaCl (20%, w/v), aqueous NaClO₄ (50%, w/v) to remove the NaCl, and finally well with ethanol (Found: C, 44.9; H, 3.35%; weight loss 9.2%. C₁₈H₁₆Na₂O₆S₂·2H₂O requires C, 45.55; H, 4.25%; weight loss 7.6%). In view of the uncertain hydration, it is advisable to determine the concentration of this salt in aqueous solution by u.v. spectroscopy.

0.75 mol dm^{-3} Tetraethylammonium sulphite was obtained by passing SO₂ through a 25% aqueous solution of NEt₄OH (BDH Ltd.) until the pH was 10.0 \pm 0.1. One of the advantages of [NEt₄]₂SO₃ over Na₂SO₃³⁰ for preparing organic sulphonates is that a homogeneous solution is quickly produced during the reaction with the organic halide.

Sodium Hypochlorite Solution.—Chlorine was bubbled through a stirred Aristar NaOH solution (100 cm^3 , 3 mol dm^{-3}) kept below 0 °C in an ice-salt bath until in excess (pH ca. 8). Sodium hydroxide solution was immediately added until the pH was 11–11.5. The final solution contained no detectable ClO₂⁻ or ClO₃⁻, and was stored in the dark at 4 °C in plastic bottles which had previously contained household bleach.

Dichloromethanesulphonamide.—This was prepared as described by Newcombe,³¹ m.p. 84–86 °C (lit., 84–86 °C). Purity (iodometric) 99.7%.

Iodylbenzene.—Iodosylbenzene was added to vigorously boiling water until a saturated solution of iodylbenzene was obtained and the iodobenzene had volatilized. After cooling, the iodylbenzene was filtered off and washed with a little water. Purity (iodometric) 99.7%.

4-Iodosylbenzene-1-sulphonic acid.³²—40% Peracetic acid (4.5 cm³) was added to 4-iodobenzene-1-sulphonic acid (7.5 g) suspended in glacial acetic acid (15 cm³) and stirred in a bath at 20 °C. After 1.5 h the product was filtered off, washed with glacial acetic acid followed by a little water, and dried *in vacuo*. Yield 1.6 g. Purity (iodometric) 98.8%.

Preparation of cis-Dibenzoylstilbene from Chloramine T, H₂O₂, and Tetraphenylcyclopentadienone.—To a stirred solution of tetraphenylcyclopentadienone (0.83 g) in a mixture of CH₂Cl₂ (10 cm³) and CH₃OH (10 cm³) was added chloramine T (4.0 g) followed after 30 s by 30% H₂O₂ (2.0 cm³). The violet colour disappeared after about 5 min. The mixture was poured into water (60 cm³), the CH₂Cl₂ layer shaken with 1 mol dm⁻³ KOH to remove toluene-*p*-sulphonamide, evaporated to dryness, and the residue recrystallized from ethanol. Yield 0.42 g (52%), m.p. 216 °C (lit.,¹⁹ 215.9–216.3 °C). The product was further characterized from its i.r. spectrum.³³

Chloramine T (BDH Ltd.) had an iodometric purity of ca. 99%, and was used directly. *N*-Chlorosuccinimide was recrystallized from warm water, and had an iodometric purity of 99.3%. The H₂O₂ was an 88% unstabilized sample from Laporte Industries. Sodium hypobromite solution was prepared by adding an excess of solid NaBr to NaOCl solution. After 5–10 min it was appropriately diluted with 0.1 mol dm⁻³ phosphate buffer of pH ca. 12, and used directly. *N*-Chloromethanesulphonamide was prepared by mixing equimolar amounts of CH₃SO₂NCl₂ and CH₃SO₂NH₂ in the buffer.

Analyses.—Hydrogen peroxide and the oxidants were analyzed iodometrically under an atmosphere of CO₂. The concentration of aes was monitored at 398 nm, using a Perkin-Elmer 551UV/Vis spectrophotometer which had been calibrated against a dichromate absorption standard (BDH Ltd.). In addition, at least two h.p.l.c. determinations of endoperoxide concentration were made for each reaction. Routine analyses used an Ultrasphere CN 5μ column, with a mobile phase of methanol–water (65:35) containing 0.3% NBu₄HSO₄ adjusted to pH ca. 4 with 5 mmol dm⁻³ phosphate buffer. The monitoring wavelength was 216 nm. As a check, an Ultrasphere ODS 5μ column was occasionally used, with a mobile phase of methanol–water (77:23) containing 0.5% NMe₄Cl. Concentrations of endoperoxide down to at least 10⁻⁵ mol dm⁻³ could be quantitatively determined. Standard endoperoxide solutions were prepared by irradiating oxygen-saturated aes solutions containing a trace of Rose Bengal with visible light (Kodak K2 filter) from an A231 cine projector lamp. The irradiation was continued until >99% of the aes had reacted. Such solutions were stable almost indefinitely when stored at 4 °C.

General Experimental Procedure.—In reactions producing oxygen, it was usually found necessary to mix the reactants quite slowly to avoid ¹O₂ being lost in the bubbles formed. Accordingly, one of the reactants was contained in a Burroughs Welcome micrometer syringe (0.5 cm³), driven by a slow-speed electric motor. The delivery rate was 5 μl min⁻¹, and the receiving solution was kept vigorously stirred. Except for ncs and iodylbenzene, the oxidant was added in this way to an aes solution containing excess of H₂O₂. The reaction of OCl⁻ and H₂O₂ was carried out at pH ca. 10 (carbonate or phosphate buffers).

The reaction with iodylbenzene is slow, and the reagents were

mixed in a conventional manner. Aliquots were periodically withdrawn and analyzed for aes, endoperoxide, and oxidizing capacity.

Since 4-iodosylbenzene-1-sulphonic acid disproportionates in solution, a modified procedure was used. The H₂O₂ was present in only ca. 10% excess, the reaction was carried out at pH ca. 4.5 where the iodylbenzene–H₂O₂ reaction is slowest, and the reaction solution was analysed for oxidizing capacity very soon after the addition of the 4-iodosylbenzene-1-sulphonic acid. It was then assumed that the reduction in oxidizing capacity was solely due to the reaction of 4-iodosylbenzene-1-sulphonic acid with H₂O₂. Air-saturated solutions of aes when exposed to light slowly produce endoperoxide by a self-sensitized reaction. Extreme precautions were not necessary, but reaction vessels were normally covered with foil, or coated with Kodak Linagraph stabilizing lacquer.

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