A New Trap for Singlet Oxygen in Aqueous Solution

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Summary The sodium and caesium salts of anthracene-9,10-bisethanesulphonic acid are soluble in water, and readily react with singlet oxygen without appreciable quenching to give the stable endoperoxide; kinetic parameters are reported and it is shown that in the decomposition of peroxymonophthalic acid at pH 8·2, 69 ± 4% of the oxygen produced is in the singlet state.

THERE has been considerable interest in systems which may produce singlet ('Δg) oxygen in aqueous solution, including some of biological importance.[1,2] The common substrates or traps such as 1,3-diphenylisobenzofuran, tetraphenylcyclopentadienone, and 9,10-dimethylanthracene are virtually insoluble in water. 2,5-Dimethylfuran is soluble in water, and is very reactive towards singlet oxygen,[3] but has a number of disadvantages. It is volatile, the electronic absorption maximum lies at an inconveniently short wavelength (215 nm), and it is difficult to characterise the reaction products.[1] Accordingly, we propose the new compound AES (**1**), the sodium (or caesium) salt of anthracene-9,10-bisethanesulphonic acid. AES is readily soluble in water and in buffer solutions, is stable over a wide pH range, and, under normal conditions, is not affected by oxidants such as OCl^- and H_2O_2. Its concentration can be monitored from the strong absorption in the near u.v. region (ϵ_{399} 1·26 × 10^4). It reacts with $^1O_2$ (from Rose Bengal photosensitization or H_2O_2 and OCl^-) to give as sole detectable product the endoperoxide, which does not absorb above 320 nm and can be characterised by t.l.c. and polarography.

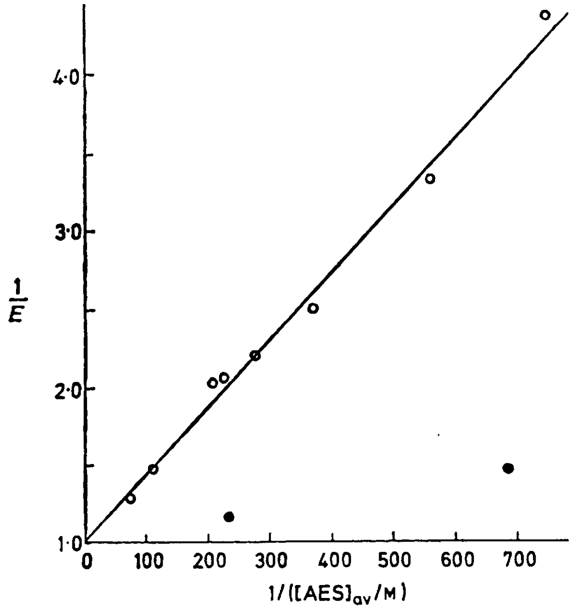


FIGURE. Plot of $1/E$ against $1/[AES]_{av.}$ for the reaction of H_2O_2 and OCl^- at pH *ca.* 10 in the presence of AES: H_2O (○), D_2O (●).

When $^1O_2$ is produced in the presence of substrate A, it may follow one of three main pathways: quenching by solvent (1), quenching by A (2), or reaction (3). Thus,

$$^1O_2 + S \xrightarrow{k_d} {}^3O_2 + S \qquad (1)$$

$$^1O_2 + A \xrightarrow{k_q} {}^3O_2 + A \qquad (2)$$

$$^1O_2 + A \xrightarrow{k_r} AO_2 \qquad (3)$$

equation (4) may be derived, where the efficiency E is the fraction of singlet oxygen which reacts to give AO_2. The lifetime of $^1O_2$ in D_2O is *ca.* 10 times that in H_2O.[4] Hence, under otherwise identical conditions, equations (5) and (6) may be derived, and equation (7) follows from these.

$$1/E = (k_r + k_q)/k_r + (k_d/k_r)(1/[A]) \qquad (4)$$

$$k_d(H_2O)/k_r[A] = 1/E(H_2O) - (k_r + k_q)/k_r \qquad (5)$$

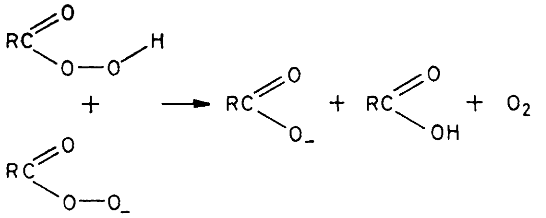
$$1/E(D_2O) = (k_r + k_q)/k_r + 0{\cdot}1\, k_d(H_2O)/(k_r[A]) \qquad (6)$$

$$E(D_2O) = E(H_2O)/[0{\cdot}1 + 0{\cdot}9E(H_2O)(1 + k_q/k_r)] \qquad (7)$$

The Figure shows a plot of $1/E$ (based on the total O_2 produced) against $1/[AES]_{av.}$ for the reaction of H_2O_2 and OCl^- in the presence of AES at various concentrations. In the measurement of E, a change in the [AES] term is necessarily involved. However, provided this change is ⩽20%, $[AES]_{av.}$ can be taken as the mean of the initial and final concentrations without serious error. The straight line has a slope β of 4·34 × 10^{-3} M, and an intercept of 1·02. The latter value shows that quenching of $^1O_2$ by AES is negligible, and also that the yield of $^1O_2$ from the H_2O_2–OCl^- reaction is very close to 100%, in agreement with the recent work of Held, Halker, and Hurst.[1] From the known value of k_d (5 × 10^5 s^{-1}),[4] k_r for the reaction of AES with $^1O_2$ is 1·15 × 10^8 dm^3 mol^{-1} s^{-1}.

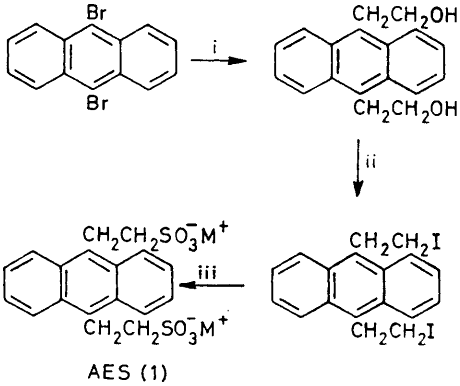
E was also measured at two AES concentration in D_2O. The observed values were considerably higher than in H_2O (Figure), and were in reasonable agreement with equation (7) [AES: 1·46 × 10^{-3} M, $E(D_2O)$ obs. 0·69$_1$, calc. 0·75$_9$; 4·3 × 10^{-3} M, $E(D_2O)$ obs. 0·87$_2$, calc. 0·89$_2$].

The utility of AES was tested in a study of the decomposition of peroxy acids in aqueous solution. The observed reaction[5] is shown in reaction (8).



(8)

McKeown and Waters[6] have presented qualitative evidence for the production of $^1O_2$ in the decomposition of di-isoperoxyphthalic acid in ethanol at 'pH' 8—9, using 9-methyl-10-phenylanthracene as the substrate.



AES (**1**)

M = Na or Cs

SCHEME. Reagents: i, Bu^{n}Li, oxiran; ii, $[(PhO)_3PMe]I$, dimethylformamide; iii, $(Et_4N)_2SO_3$, dioxan–water.

The rate of decomposition of peroxymonophthalic acid at pH 8·2 was not affected by the presence of AES, and the AES endoperoxide was the only product that could be detected. Analysis of the results, in both H_2O and D_2O, showed that 69 ± 4% of the oxygen produced by reaction (8) was in the singlet state.

AES was prepared as shown in the Scheme; ^1H n.m.r. δ (D_2O) 3·08 (4H, m), 3·61 (4H, m), 7·61 (4H, m), 8·12 (4H, m). The sodium and caesium salts were hygroscopic, but satisfactory microanalyses were obtained for the sparingly soluble tetraphenylphosphonium salt.

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