

## Studies on singlet oxygen in aqueous solution<sup>†</sup>

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The caesium and sodium salts of anthracene-9,10-bis(ethane sulphonate) (AES) are readily soluble in water over a wide range of pH and react with  $^1\text{O}_2$  to give the endoperoxide as the sole detectable product. The reaction can be followed both from the UV absorption of AES and by high pressure liquid chromatography (HPLC) of the endoperoxide. The trapping efficiency of AES for  $^1\text{O}_2$  has been measured as a function of concentration. AES does not react with  $\text{O}_2^-$  or  $\text{HO}_2$ , but acts as a trap for radicals such as  $\cdot\text{OH}$ . The products, however, can readily be distinguished from the endoperoxide by HPLC.

AES has been used to study quantitatively the production of  $^1\text{O}_2$  in a variety of reactions occurring in aqueous solution.

1. *Two-electron oxidation of  $\text{H}_2\text{O}_2$ .* The reaction of  $\text{H}_2\text{O}_2$  with *N*-chlorosuccinimide and chloramine T produces  $^1\text{O}_2$  with about 100% efficiency. With chloramine T, the reactive species is dichloramine T produced by disproportionation.

Both iodoxybenzene and iodosobenzene sulphonic acid react with  $\text{H}_2\text{O}_2$  to give oxygen, of which about 45% only is in the singlet state. This may be due to spin-orbit coupling involving the heavy iodine atom. With  $\text{IO}_4^-$  and  $\text{H}_2\text{O}_2$ , the yields of  $^1\text{O}_2$  are irreproducible and slightly lower, indicating a concomitant free-radical reaction.

2. *Decomposition of peroxyacids at their pK.* When sufficient precautions to avoid catalysis by transition metal ions are taken, the decomposition of peroxyimonophthalic, peroxyacetic and peroxymonosulphuric acids give  $^1\text{O}_2$  in essentially quantitative yields. The reported reaction of  $\text{H}_2\text{O}_2$  with peroxyacid anions does not produce  $^1\text{O}_2$ , and in the absence of metal catalysis is very slow indeed, if it occurs at all.

3. *Catalysed decomposition of  $\text{H}_2\text{O}_2$ .*

## Optical determination of the rates of formation and decay of $\text{O}_2(^1\Delta_g)$ in $\text{H}_2\text{O}$ , $\text{D}_2\text{O}$ and other solvents<sup>†</sup>

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Recent experimental investigation, using dissolved photosensitizers subjected to pulsed laser radiation, has permitted accurate determination of the quenching rates of  $\text{O}_2(^1\Delta_g)$  in a wide variety of solvents. Of particular importance in this application is the use of remote optical sensing to monitor the temporal behavior of the resultant  $\text{O}_2(^1\Delta_g)$  concentration produced [1 - 3]. Such optical sensing involves detection of the relatively weak emission accompanying the collisionally induced radiative transition to the  $^3\Sigma_g^-$

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