

## 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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ground electronic state. One distinct advantage inherent in this method, in addition to the fact that it obviates problems associated with alternatives such as chemical acceptors, is that a positive identification of the emitting species as  $O_2(^1\Delta_g)$  is possible through determination of the emission spectrum.

Another important advantage of remote optical monitoring is that  $O_2(^1\Delta_g)$  concentrations may be determined in a heterogeneous medium [4], one of the most important applications in this regard being the interface separating a lipid and aqueous phase. It is clear that rather significant  $O_2(^1\Delta_g)$  concentration gradients at this interface must occur as a result of the fact that in general lifetimes in  $H_2O$  are approximately an order of magnitude shorter than in a hydrocarbon environment. Recent studies [5] have shown that the quenching rate for a given solvent depends strongly on the presence of bound hydrogen atoms and in particular on the exact nature of the binding, *i.e.* C—H or O—H type.

The relatively long decay times in hydrocarbon solvents provide a particularly favorable case for optical monitoring. Thus, for example, the lifetime of  $O_2(^1\Delta_g)$  in benzene has been established as lying in the range 30 - 35  $\mu s$ . Addition of OH groups causes a systematic lowering of lifetimes, *e.g.* 15  $\mu s$  for ethanol and 4.8  $\mu s$  for ethylene glycol [4]. Earlier measurements of the lifetimes in  $H_2O$  have ranged from 2 to 7  $\mu s$ . The factors tending to complicate lifetime measurements in this important case are twofold: (1) relatively long (2 - 3  $\mu s$ ) times required for transfer of energy from the sensitizer triplet and (2) interference due to the presence of an IR component of the sensitizer fluorescence. Separation of the latter from the  $O_2(^1\Delta_g)$  emission places a premium on fast detector response time. Earlier measurements indicated that germanium photodiodes used as detectors were inadequate in this regard. Recent measurements, however, using an InGaAs device have yielded much more satisfactory results [4].

The problem of determination of the lifetime of  $O_2(^1\Delta_g)$  in  $H_2O$  in addition to requiring detectors capable of rapid response also requires use of a sensitizer capable of providing a high  $O_2(^1\Delta_g)$  yield and exhibiting high resistance to subsequent oxidation. Evaluation of a series of water-soluble synthetic porphyrins led to the selection of tetra-(4-*N*-methylpyridil)porphin (T4MPP) as being the optimum sensitizer. This sensitizer, soluble in  $H_2O$  over a wide range of pH, proved extremely resistant to degradation even when incident laser pulse energies of 100 mJ were used, ten times the level used normally. Possibly this inertness is due to an absence of photoionization processes [6].

A detailed series of measurements was carried out in  $H_2O$  using a T4MPP sensitizer for air-saturated oxygen-enriched and oxygen-depleted samples, for low, medium and high pulse energies. No systematic dependence of decay time on laser pulse energy was observed; however, a definite shortening of the formation time in air-saturated solutions was observed with increasing laser power. Because the triplet transfer times and  $O_2(^1\Delta_g)$  decay times were very close to the same value for the case of air saturation, it was impossible to carry out an accurate determination of the respective time constants. Thus, determination of  $O_2(^1\Delta_g)$  decay times necessitated the use of oxygen-enriched samples with correspondingly reduced triplet energy transfer times. Statistical averaging of the decay times for 14 independent runs gave the value  $\tau_D = 3.21 \pm 0.12 \mu s$ . In all these runs the sensitizer concentration was fixed at  $1 \times 10^{-4}$  M. Similar runs with the concentration reduced to  $5 \times 10^{-5}$  M produced results in agreement with this value. Using this value for the  $O_2(^1\Delta_g)$  decay time, triplet transfer times were extracted from the formation times characterizing the air saturation cases. Analysis of the data gives  $\tau_T = 2.43 \pm 0.18 \mu s$ .

Similar runs were carried out using the same sensitizer in  $D_2O$ . In this case the  $O_2(^1\Delta_g)$  decay time is greatly lengthened while the triplet transfer time is essentially unchanged, thus permitting the use of air-saturated solutions. Analysis of the data yielded  $\tau_D = 68 \mu s$  and  $\tau_T = 2.1 \mu s$ . Thus solvent deuteration gives rise to an increase in the  $O_2(^1\Delta_g)$  decay time of more than an order of magnitude. It is interesting to point out that earlier measurements using another water-soluble synthetic porphyrin tetra(4-sulfonatophenyl)porphine gave for  $D_2O$  an initial value of 55  $\mu s$ ; however, this value steadily decreased with increasing length of exposure to the laser radiation. This sensitizer

degradation is possibly due to its known ability to photoionize [6] coupled with the relatively long  $O_2(^1\Delta_g)$  lifetime. No such effects were observed using the T4MPP sensitizer.

Other solvents investigated were ethylene glycol, characterized by increased viscosity and correspondingly lengthened triplet transfer times, 1-octanol, with similar behavior but with a significantly longer  $O_2(^1\Delta_g)$  decay time, glacial acetic acid and formamide.

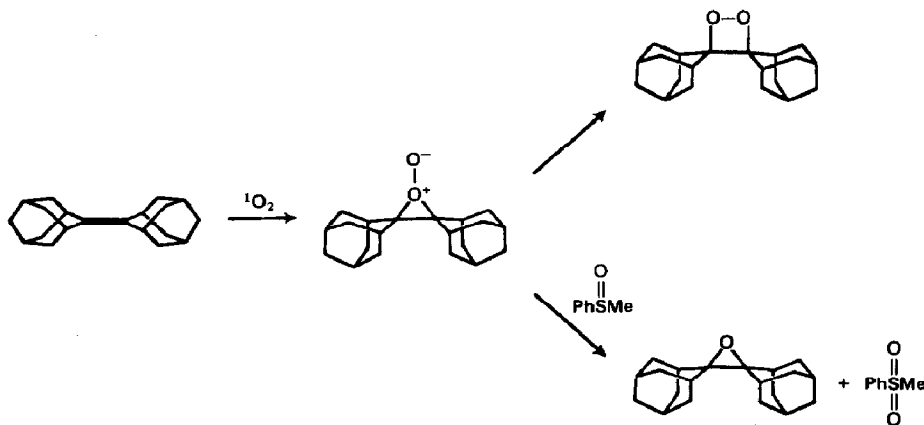
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### Nucleophilic oxygen atom transfer from a perepoxyde intermediate to sulfoxides<sup>†</sup>

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$^1O_2$  reacts with adamantylideneadamantane to form an unusually stable 1,2-dioxetane. We have recently obtained evidence for a trappable intermediate in this 1,2-cycloaddition reaction of  $^1O_2$ . This species, which we propose is the perepoxyde, can be quantitatively trapped by nucleophilic oxygen atom transfer to sulfoxides to yield sulfones and the epoxide:



The ratio of epoxide to dioxetane is found to be a function of the concentration of the sulfoxide.

Additional evidence for the proposed mechanism is provided by a study of substituent effects on the trapping reaction. A series of competition experiments with substituted

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