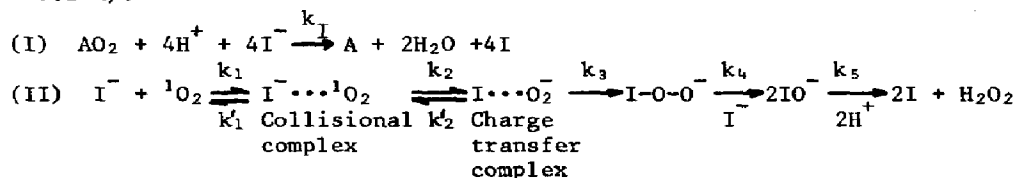


FLASH PHOTOLYSIS STUDY OF PHOTSENSITIZED OXIDATION OF IODIDE ION

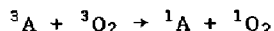
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Steady state studies at 365 nm from 300 W medium pressure Hg-discharge lamp indicated that photosensitized oxidation of I^- by variously substituted anthracene sulphonate proceeds via two pathways: (I) through sensitizer peroxide (AO_2) (important step at low concentration of I^-) and (II) by direct attack of singlet oxygen (1O_2) on I^- (important step at higher concentration of I^- , i.e. > 0.2 M).



The 1O_2 is generated by the energy transfer reaction between the triplet sensitizer 3A and the ground state oxygen 3O_2 according to exchange mechanism



A further insight into the mechanism was obtained from flash photolysis studies. These preliminary studies were carried out at the Royal Institution (Gt. Britain). From the densitometer tracings of the spectrum obtained after photolysis flash at different delay times (ranging from 1 μ s to 0.1 s), transient changes were observed in two regions: (a) between 400 and 500 nm and (b) between 330 and 380 nm. In the long wavelength region two peaks were observed, the main peak at 452 nm and a smaller one at 425 nm. The peak at 452 nm decayed at a faster rate than the one at 425 nm. The decay rate for the peak at 378 nm was much slower than those in the visible region and had a structured spectrum.

The decay kinetics for transients at 452 nm and 378 nm were studied by kinetic flash spectroscopy and oscillogram traces photographed with a Polaroid camera. The decay constants obtained from the slopes of the semilog plots are collectively presented in Table I:

	τ 380 (ms)	τ 450 (μ s)
1 - ASO_3^-	16	140
2 - ASO_3^-	43	150
1,8 - $A(SO_3^-)_2$	250	140
1,5 - $A(SO_3^-)_2$	21	110

The 380 nm peaks for the three sensitizers decayed with good unimolecular kinetics. The decay constants are in the millisecond range and vary with the nature of the sensitizer. Because of the sensitizer dependence of λ 380 and the structured nature of the spectra, the likely candidate appears to be a radical of the type AOO^{\cdot} , which could be an intermediate in the reaction of AO_2 with I^- . The low intensity 425 nm peak appears to be due to triplet-triplet absorption of anthracene sulphonates! The 450 nm peak initially decays with unimolecular kinetics (τ 450 = 140 ± 20 us) which on longer observation is found to change over to bimolecular decay. The decay constant is the same for all the sensitizers hence is not likely to belong to sensitizer moiety. Therefore 450 nm peak may be assigned to IO_2 which then reacts further with I^- .

According to scheme II over-all rate constant of 1O_2 quenching by I^- can be expressed as

$$k_{II} = k_I \left\{ 1 + \frac{k'_1}{k_2} + \frac{k'_1 k'_2}{k_3 k_2} \right\}^{-1}$$

where k_1 = diffusion controlled rate constant = $7.4 \times 10^9 M^{-1} s^{-1}$; k_3 = frequency factor = $10^{11} s^{-1}$; $k_2/k'_2 = \exp(-\Delta G_2/RT)$ and $k_2 = k_3 \exp(-\Delta G_2^{\ddagger}/RT)$. ΔG_2 and ΔG_2^{\ddagger} are the free energy change and the activation free energy change for the charge transfer step. ΔG_2 can be calculated as follows:

$$\Delta G_2 = 23.06 \{ E(I^-/I) - E(O_2^-/O_2) \} - \Delta E^1O_2$$

where $E(I^-/I)$ and $E(O_2^-/O_2)$ are redox potentials³ of I^-/I and O_2^-/O_2 couple and ΔE^1O_2 energy of $O_2^1\Delta_g$. Calculating ΔG_2^{\ddagger} as suggested by Rehm and Weller⁴ it is possible to calculate $k_1 = (6 \times 10^6 M^{-1} s^{-1})$ which is in good agreement with experimental value ($8 \times 10^6 M^{-1} s^{-1}$) obtained from azide ion quenching experiment⁵.

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References

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