

Photodynamic Oxidation of Iodide Ion by Anthracene Sulphonates*

K. K. ROHATGI-MUKHERJEE (*nee* ROHATGI) & A. K. GUPTA
Physical Chemistry Section, Jadavpur University, Calcutta 700032

Received 11 December 1975; accepted 9 February 1976

The water soluble anthracene sulphonates when exposed to 365 nm in the presence of KI are observed to photosensitize the oxidation of I⁻ ion. The reaction is detected spectrophotometrically by the formation of I₃⁻. No I₃⁻ is formed in the dark nor in the absence of anthracene sulphonates (ASO₃⁻). Observations show that ASO₃⁻ is not consumed in the reaction and acts as a photosensitizer only. The quantum yields (ϕI_3^-) of photosensitized oxidation of I⁻ follow asymptotic curves when plotted as a function of [I⁻], and [ASO₃⁻]. They also depend on the concentration of dissolved oxygen. Both O₂ and I⁻ are good quenchers of excited singlet and triplet states of ASO₃⁻. It appears that photosensitized oxidation of I⁻ is a kind of autocatalytic reaction. In aerobic conditions the reaction occurs by more than one photodynamic pathway through the intermediate formation of singlet oxygen ¹O₂ in an energy transfer step from the triplet state of the sensitizer. The sensitizer peroxide is also a likely oxidant. The reaction follows a type-II mechanism.

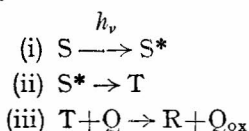
THE photodynamic oxidations^{1,2} in the presence of sensitizers are of immense photobiological interest^{3,4}. Carbohydrates, proteins, nucleic acids and other components of biological systems are transparent to solar radiation of wavelength greater than 300 nm. Therefore, there must be a built-in mechanism to initiate photobiological processes in these systems. The accessory pigments like chlorophyll and carotenoids are examples of such photosensitizers. The ubiquitous presence of molecular oxygen assigns it an important role in such oxidative processes where the sensitizer helps to activate the system⁵.

Photodynamic oxidation in general can be grouped under two headings⁶: dye-substrate mechanism (type-I) or D-D mechanism; and (ii) dye-oxygen mechanism (type-II) or D-O mechanism. The main difference between the two mechanisms is that in type-I mechanism the substrate is the first point of attack, whereas in type-II mechanism, the sensitizing-dye first reacts with molecular oxygen which then reacts with the substrate.

Steps involved in both types of reactions are shown below:

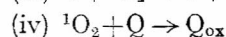
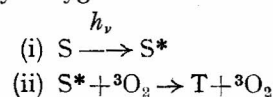
TYPE-I

Dye-substrate mechanism



TYPE-II

Dye-oxygen mechanism



where S is the ground state of sensitizer; T, the triplet state of sensitizer; Q, the substrate; R, the reduced form of sensitizer; and Q_{ox} is the oxidized form of the substrate.

Photodynamic oxidation of iodide ion was first observed by Straub where eosin, a dye, was used as a sensitizer. Later Grossweiner and Kepka⁷ studied the reaction and postulated type-II mechanism for the reaction. In the present paper our results on photodynamic oxidation of I⁻ with anthracene sulphonates (Na-salt) as sensitizer using 365 nm of mercury radiation are described. Iodide ion which absorbs strongly at 226 nm (assigned as charge-transfer-to-solvent spectra) is transparent to 365 nm and no photochemical changes occur in the absence of anthracene sulphonates (ASO₃⁻). The sulphonate was found not to be consumed in the reaction. So it can be said that ASO₃⁻ acts as a sensitizer only. The reaction was detected by formation of triiodide ion I₃⁻. The reaction does not occur in the dark.

Materials and Methods

Anthracene 1-, 2-mono and 1,5-di-sulphonates were prepared by reducing corresponding anthraquinones with Zn-dust and 20% NH₄OH for 4-6 hr. The products were treated with active animal charcoal to remove traces of anthraquinones and other impurities, crystallized three to four times from water and obtained as the sodium salt. Pro analysi grade potassium iodide was used.

Photochemical reactions were carried out in a specially designed cell in a dark room. Solution was stirred during exposure and oxygen or air, as required by the experiment, was bubbled through it. Temperature was maintained at 30° using a thermo-

*Presented at the Second Photobiology Symposium held in Nainital during April 28-30, 1975.

stat. The stabilized light source was a 300-watt Hanovia type 507/7 Hg discharge tube contained in a blackened box with a window towards the reaction vessel. A Wood's glass filter was used to isolate 365 nm radiation. 5 ml of solution were pipetted out at regular intervals and optical densities (OD) measured with a Beckman DU spectrophotometer model 4700.

Actinometry—The light source was standardized by ferrioxalate actinometer of Parker and Hatchard⁸.

Since I_3^- absorbs strongly at 350–380 nm, concentration of KI_3 formed during the sensitized photo-oxidation of I^- was obtained by measuring OD at two different wavelengths. The following expression (Eq. 1) was used to analyse the data:

$$C_{I_3^-} = \frac{\epsilon_{ASO_3^-}^{350} \cdot D^{380} - \epsilon_{ASO_3^-}^{380} \cdot D^{350}}{\epsilon_{ASO_3^-}^{350} \cdot \epsilon_{I_3^-}^{380} - \epsilon_{ASO_3^-}^{380} \cdot \epsilon_{I_3^-}^{350}} \quad \dots (1)$$

where D^{380} and D^{350} are optical densities at 380 nm and 350 nm respectively, $\epsilon_{I_3^-}^{380}$ and $\epsilon_{I_3^-}^{350}$ are molar extinction of KI_3 at 380 nm and 350 nm respectively and $\epsilon_{ASO_3^-}^{350}$, $\epsilon_{ASO_3^-}^{380}$ are molar extinction of anthracene sulphonate at 350 nm and 380 nm respectively.

To avoid inner-filter effect due to absorption by I_3^- , the kinetic runs were made in the presence of $10^{-4}M$ sodium thiosulphate solution. The iodine atom liberated is likely to be immediately reacted upon by thiosulphate. The amount of thio consumed was determined by adding known excess of iodine solution and I_3^- formed was estimated spectrophotometrically to get the iodine yield. Unless stated otherwise, all reactions were carried out at neutral pH.

Results

The water soluble anthracene sulphonates undergo photodimerization—a singlet state reaction, and photoperoxidation in the presence of oxygen subsequent to oxygen quenching—a triplet state reaction (Rohatgi *et al.*, unpublished data). For aromatic hydrocarbons, photoperoxidation has been shown by Stevens⁹ to proceed in general through singlet oxygen mechanism. When a solution of KI ($C = 0.1M$) was exposed to 365 nm in the presence of anthracene-1-sulphonate (1- ASO_3^-), optical density at 380 nm increased rapidly due to formation of I_3^- . From two component analysis of the OD data at two wavelengths, the concentration of 1- ASO_3^- was found to remain constant with exposure time. When anthracene sulphonate spectrum was subtracted from overall spectrum, the residual spectrum coincided with that for I_3^- (Fig. 1). The energy separation between the two peaks is equal to the energy difference between $2P_{1/2} - 2P_{3/2}$ levels of I atom.

The kinetics of the reaction was followed spectrophotometrically and initial rates were computed. The reaction yield was observed to be linearly proportional to light intensity (Fig. 2); hence the oxidation reaction is monophotonic. A dependence on $[H^+]$ was observed, the reaction was accelerated at pH below 3 but was completely inhibited at pH above 9. No dependence on viscosity was noted

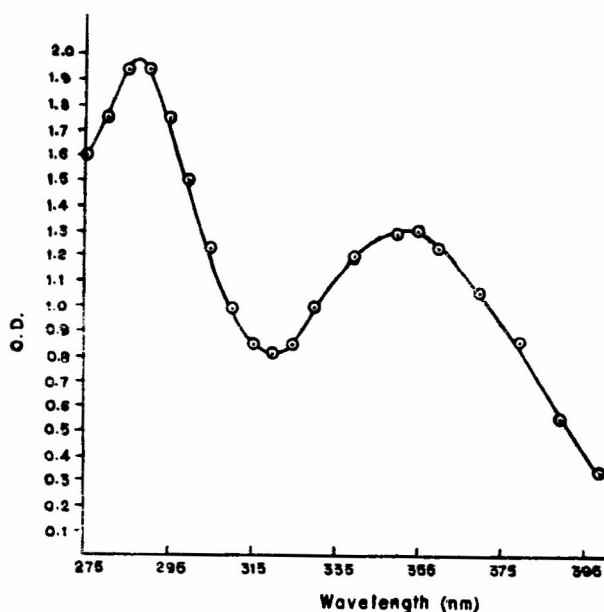


Fig. 1 — Absorption spectra of the product of photodynamic oxidation of I^-

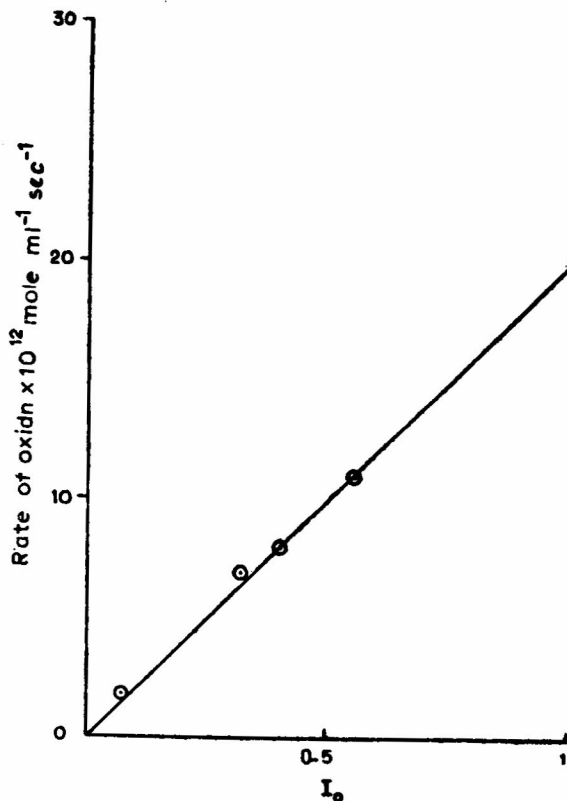
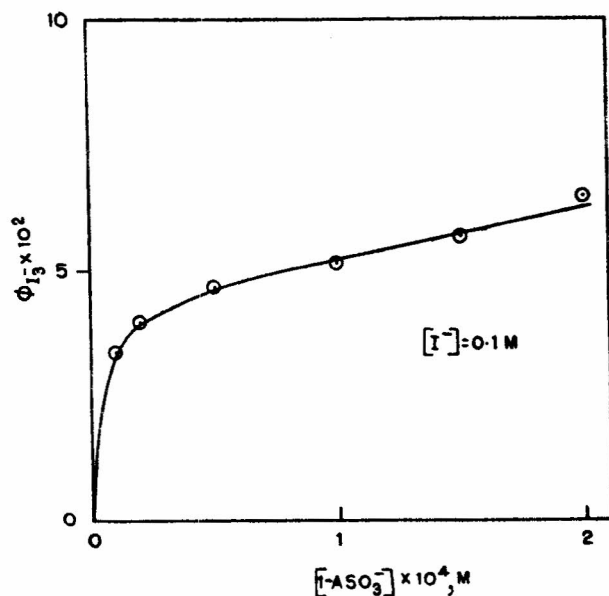


Fig. 2 — Dependence of rate of I^- oxidation on intensity of light (I_0)

when viscosity was changed by the addition of sucrose. Addition of ethylene glycol or methanol had erratic effect.

The reaction showed strong dependence on [sensitizer] and $[I^-]$ and small dependence on oxygen concentration. Sensitizer dependence of quantum yield $\phi_{I_3^-}$ as a function of $[ASO_3^-]$ for 1-substituted


 Fig. 3 — Dependence of quantum yield, $\phi_{I_3^-}$ on 1- ASO_3^- concentrations

sulphonate is given in Fig. 3. The reciprocal plots of $1/\phi_{I_3^-}$ vs $1/[ASO_3^-]$ at $[KI] = 0.1M$ is linear for concentration up to $1.5 \times 10^{-4}M$ but falls sharply at higher concentrations (Fig. 4). The extrapolated intercept from low concentration data is 18.3 with slope = 1.2×10^{-4} . Evidently another reaction responsible for oxidation of I^- takes over at higher [sensitizer]. The $\phi_{I_3^-}$ calculated from extrapolated linear plot when subtracted from observed $\phi_{I_3^-}$, gives the second mode of oxidation of I^- . The data are given in Table 1.

Therefore, the quantum yield of reaction can be expressed by the relation (2) as

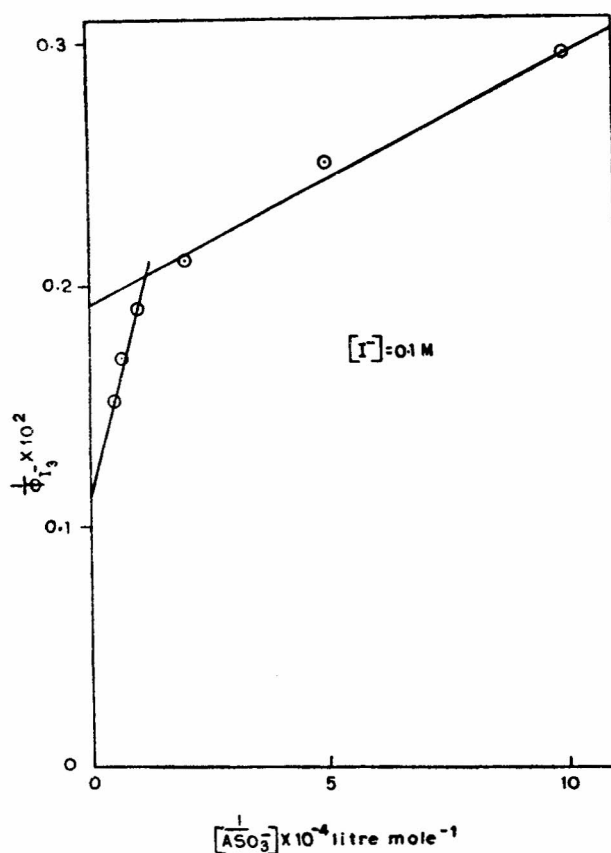
$$\phi_{I_3^-} = K \cdot \frac{k_r[A]}{k_d + k_r[A]} + f([A]) \quad \dots (2)$$

where k_r is the rate constant of reaction step and $[A]$ is the [sensitizer], viz. anthracene-1-sulphonate (1- ASO_3^-). The type of dependence necessarily-points to involvement of another molecule of sensitizer for subsequent oxidation of I^- ion. The ratio of slope/intercept = 6.6×10^{-6} from low concentration data. At higher concentrations a second term $f([A])$ which is a function of $[A]$ becomes important.

The iodide ion dependence of $\phi_{I_3^-}$ is more complex and is given in Fig. 5. An S-shaped curve is ob-

 TABLE 1 — DEPENDENCE OF $\phi_{I_3^-}$ ON 1- ASO_3^- CONCENTRATION
 $\{[KI]=0.1M$; intensity of light (I_0) = 4×10^{-7} ein. litre $^{-1}$ /sec $^{-1}$)

$C \times 10^5$ M	$\phi_{I_3^-} \times 10^{12}$ (exp.)	$\phi_{I_3^-} \times 10^{12}$ (calc.)	$\Delta\phi \times 10^2$
1.0	3.3	3.3	0
2.0	4.1	4.1	0
5.0	4.7	4.7	0
10.0	5.2	5.2	0
15.0	5.7	5.3	0.4
20.0	6.5	5.4	1.1
		Limit 5.5	


 Fig. 4 — Plot of $1/\phi_{I_3^-}$ against $\frac{1}{[1-ASO_3^-]}$

tained and again it indicates more than one competitive pathways for the oxidation of I^- . From a plot of ϕ vs $1/c$ which gives a fairly linear plot except for the dilute solution data, a limiting quantum yield for I^- oxidation is found to be 0.26. If $1/\phi$ vs $1/c$ is plotted, a break is observed at $[I^-] = 0.2M$ (Fig. 6). The type of dependence may be expressed by Eq. (3).

$$\phi_{I_3^-} = \frac{a + b[I^-]}{c + d[I^-]} \quad \dots (3)$$

The nature of dependence does not change when the [sensitizer] is changed but overall yields are increased.

The quantum yield of the reaction shows a small dependence on O_2 concentration. At $[O_2]$ of 3×10^{-3} and $0.6 \times 10^{-3}M$ the quantum yields $\phi_{I_3^-}$ are 0.052 and 0.047 respectively at $[1-ASO_3^-] = 1 \times 10^{-4}M$ and $[KI] = 0.1M$.

Discussion

The kinetics and mechanism of photodynamic oxidation of I^- by eosin has been studied by Grossweiner and Kepka⁷ using modulated light source and locked in illumination. A small yield of oxidized form of eosin was detected. It was concluded that the triplet state is the seat of action and quenching by O_2 is accompanied by electron transfer to oxygen besides simple deactivation to the ground state. The I^- reacts with the oxidized dye to form I atom

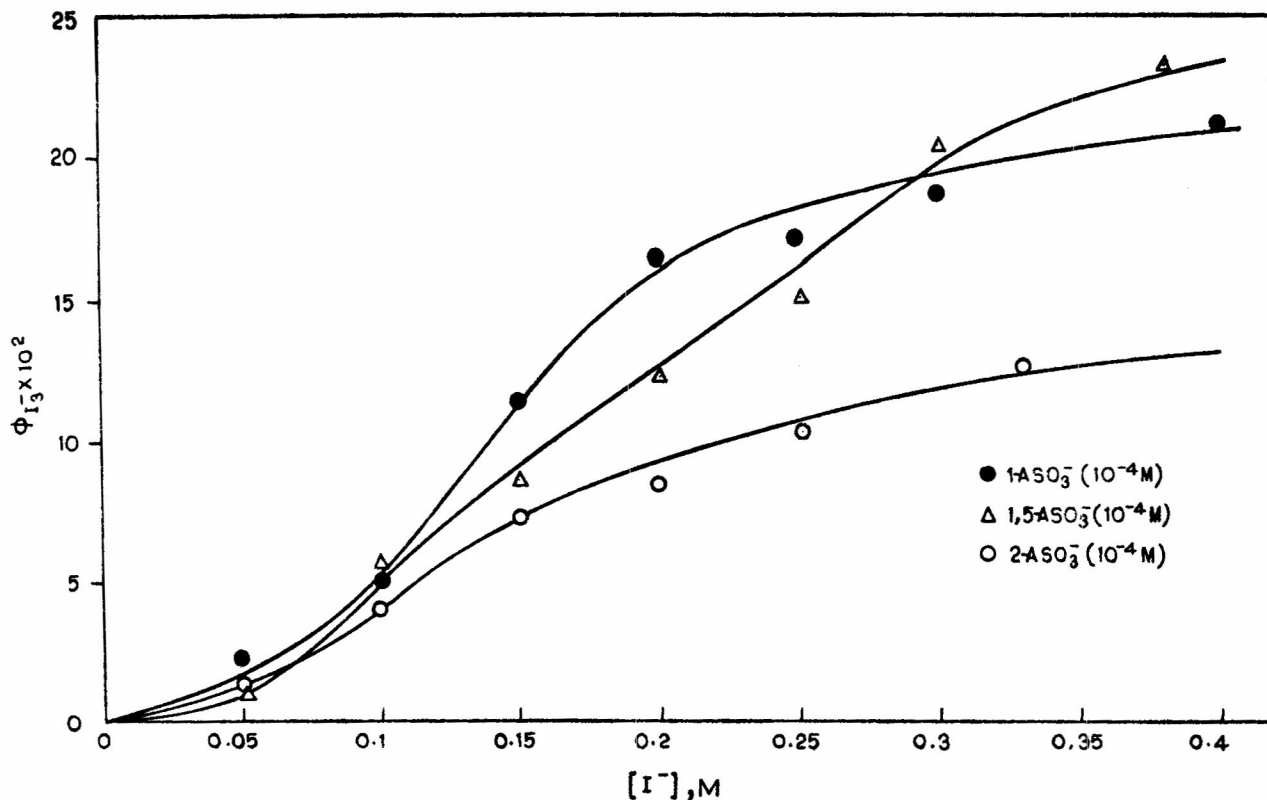


Fig. 5 — Dependence of $\phi_{I_3^-}$ on $[I^-]$ for 1- ASO_3^- , 2- ASO_3^- and 1,5- ASO_3^- as sensitizers

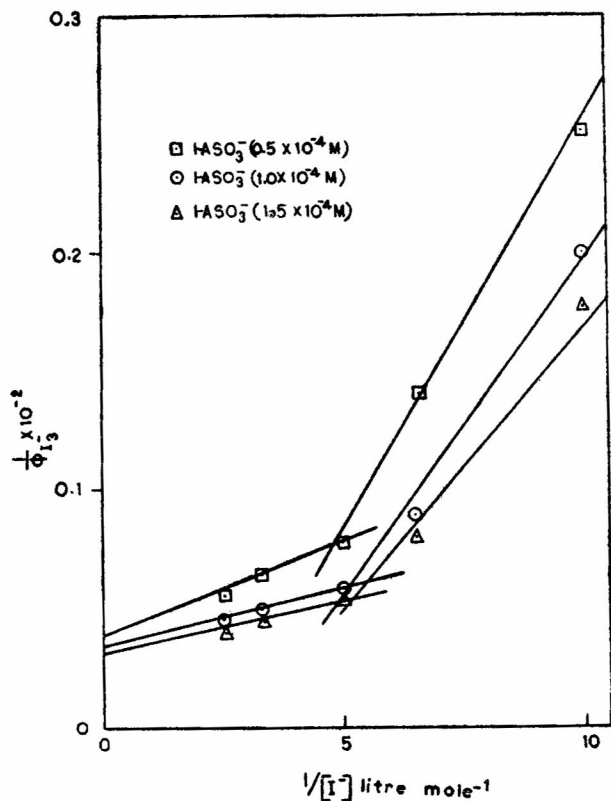
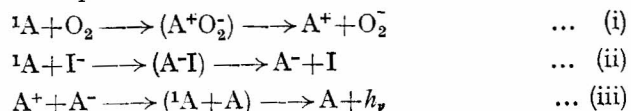


Fig. 6 — Plot for $1/\phi_{I_3^-}$ against $1/[I^-]$ at different 1- ASO_3^- concentrations

and the reaction follows type-II mechanism for photodynamic action. The direct involvement of singlet oxygen was not found to be feasible.

The type of dependence on $[ASO_3^-]$ suggests that a second molecule of sensitizer is necessary for the reaction. Since aromatic hydrocarbons are known to be quenched by O_2 and I^- by charge transfer mechanism, some similar plausible steps in the aqueous medium would be



The representation of ASO_3^- as A implies a negative charge on the sulphonate ion. Other charges are in addition to that. In (i), A^+ may be a zwitterion or a radical; in (ii) A^- is a doubly charged species assuming $-SO_3^-$ group to be non-interacting. The O_2 quenching is a faster process, but in presence of high $[I^-]$ concentration, the two rates (iii) and (iv) may become comparable. These steps require biphotonic dependence on light intensity which is not observed.

Such dependence on [sensitizer] is also observed in the photoperoxidation reaction of aromatic hydrocarbons via singlet oxygen intermediate^{10,11} and other¹² sensitized photooxygenation reactions. To check the involvement of singlet oxygen, 1O_2 , the reaction was carried out in the presence of sodium azide, a singlet oxygen quencher. The iodide oxidation was completely quenched confirm-

ing the participation of 1O_2 in the key reaction step. Hence the photodynamic oxidation of iodide ion follows type-II mechanism via singlet oxygen when aromatic hydrocarbon is used as the sensitizer. The singlet oxygen is likely to be generated by electronic energy transfer mechanism in the O_2 -quenching steps of an electronically excited singlet and triplet states. Stevens and Algar^{10,11} have shown that in aromatic hydrocarbons only the triplet quenching step leads to 1O_2 formation by diffusion-controlled exchange mechanism. Therefore, the spin-allowed exothermic step for the generation of 1O_2 is represented by step (iv)



Whereas the excited singlet state is quenched by O_2 leading to enhanced intersystem crossing as shown in (v).



The enhancement of intersystem crossing efficiency from triplet to ground state can also be visualized (step, vi) for quenching of triplet state by oxygen.



This step is likely to be less important than (v) by a factor of 100-1000 (ref. 12). Similar quenching steps (vii and viii) are expected for I^- quenching of both excited singlet and triplet states.



The intersystem crossing efficiency is enhanced due to heavy atom effect. The fluorescence quenching constant K_f for O_2 and I^- are 350 litre mole⁻¹ and 48 litre mole⁻¹ respectively for anthracene-1-sulphonate solutions. In aerated aqueous solution of 1- ASO_3^- , quantum yield for fluorescence emission is $\phi_f = 0.33$. Assuming no direct internal conversion to ground state, triplet yield $\phi_T = 1 - \phi_f = 0.67$. In the presence of 0.1M I^- ,

$$\phi_{T(I^-)} = 1 - \frac{\phi_f}{1 - K_f[I^-]} = 0.91, \text{ and for } [I^-] = 0.2M$$

$$\phi_{T(I^-)} = 0.97$$

The 1O_2 thus generated can decay by the pathways (ix-xi).



The formation of photoperoxide AO_2 by reaction (ix) is a well-established reaction^{8,9}. The peroxides are expected to be stronger oxidizing agents and it might be suggested that AO_2 further oxidizes the I^- in the dark by reaction (xii) leading to the observed effect,



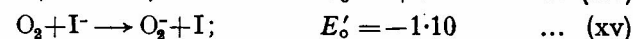
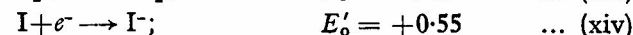
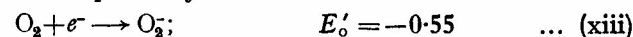
and the sensitizer is regenerated.

To check this possibility, a number of sealed test tubes containing 1- ASO_3^- was exposed to sunlight for one day. The amount of peroxide formed was estimated by measuring disappearance of 1- ASO_3^- spectrophotometrically (OD at 380 nm). KI was added in the dark to a final concentration of 0.1M. The amount of I^- formed in the thermal oxidation step was estimated spectrophotometrically. Only

partial oxidation of I^- was observed. Evidently this is one of the pathways for the photodynamic action and not necessarily the only one. Perhaps it occurs at the higher [sensitizer].

The other possibility is the direct oxidation of I^- by 1O_2 (reaction x). Kepka and Grossweiner⁷ had considered this possibility for eosin-sensitized reaction but from energetic considerations discarded it.

In acid solutions reduction potential E'_0 of the couple (O_2/HO_2) and E'_0 of the couple (I/I^-) at pH 7 are respectively

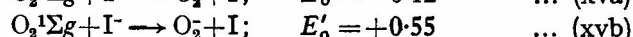
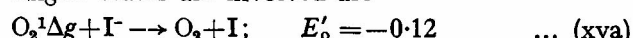


Thus oxidation of I^- to I by ground state oxygen is endothermic. But singlet oxygen state, $O_2^1\Sigma_g$ possessing 38 kcal/mole and $O_2^1\Delta_g$, 22.8 kcal/mole excess energy should be better oxidant^{12,13}.

$$E'_0(O_2^1\Delta_g/O_2^-) = -0.55 + 0.98 = 0.43 \text{ and}$$

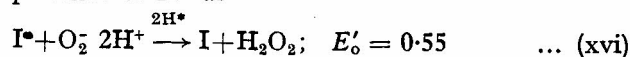
$$E'_0(O_2^1\Sigma_g/O_2^-) = -0.55 + 1.65 = 1.10 \text{ V}$$

The net e.m.f. for the reaction (xv) if excited singlet states are involved are

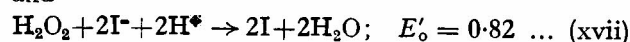


Although, $O_2^1\Delta_g$ is still not strong enough to oxidize I^- , $O_2^1\Sigma_g$ has enough potential to drive the reaction to right. In anthracene and its derivatives, a higher triplet T_2 is known to exist very close to the first excited singlet, $\Delta E_{ST} \simeq 800 \text{ cm}^{-1}$ ($E_{S_1} = 76 \text{ kcal/mole}$, $E_{T_2} = 74 \text{ kcal/mole}$) although T_1 is only 42 kcal/mole above the ground state. The fast intersystem crossing, populates the T_2 state and lives long enough ($\tau = 10^{-10} \text{ sec}$)¹⁴ to transfer its energy to a suitable acceptor molecule. With 3O_2 as an acceptor, $O_2^1\Sigma_g$ may be formed first although it is very short lived in aqueous solution. In order that $O_2^1\Sigma_g$ is able to oxidize I^- , the rate constant of reaction (xvb) must be faster than the rate constant for the decay of $O_2^1\Sigma_g$. In condensed system, $\tau O_2^1\Sigma_g$ is estimated to be 10^{-9} sec or less. An approximate value for rate constant may be put at about 10^{10} sec^{-1} or more.

The O_2^- produced may further oxidize I^- in the presence of H^+ as



and



In the presence of sodium thiosulphate, the iodine atom formed is immediately mopped up. But when no thio is added, triiodide ion is formed by the steps (xviii-xxi) in the presence of large excess of KI.

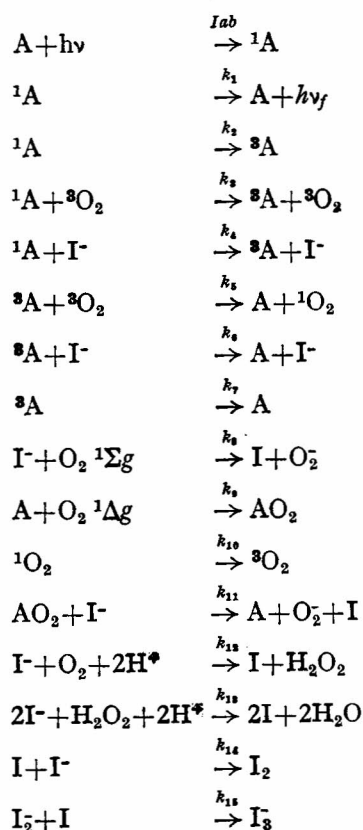


It is interesting to note that the nature of ϕ_{I^-} vs $[I^-]$ curve varies with the position of $-SO_3^-$ group in the anthracene ring. Whereas the curve is similar for different concentrations of 1-substituted sulphonates except for overall increase in the

quantum yield with concentration (Fig. 6), those for 2-substituted and 1,5-disubstituted sulphonates differ in details (Fig. 5).

A dependence on the position of $-\text{SO}_3^-$ in the sensitizer is also observed for photodimerization and direct photoperoxidation reaction, although the O_2 quenching constants are nearly the same within the experimental error: $K_{\text{O}_2} = 350 \pm 50$ litre mole $^{-1}$. The absorption spectra are not much affected but variations are observed in the emission spectra in aqueous solutions and only slightly in the quantum yield of fluorescence¹⁵. The structural variation is not likely to affect the energy transfer step for the formation of singlet oxygen but the steps leading to photoperoxidation and subsequent oxidation of I^- can be influenced. Structural variations can also become important if I^- forms a complex with the sensitizer. Therefore, the inclusion of the reactions (ix) and (xii) has further justification.

A tentative scheme for photodynamic oxidation of I^- is given in Scheme 1, where $\text{A} = \text{ASO}_3^-$.



Scheme 1

In the presence of thiosulphate, triiodide formation will not occur and inner filter effect is avoided. The rate of thio consumption will give the quantum yield for the formation of iodine atoms. From the considerations of photostationary states for the intermediates, the expression for quantum yield obtained is given by Eq. (4).

$$\phi_{\text{I}_2^-} = \frac{1}{I_{ab}} \frac{d[\text{I}^-]}{dt} = \frac{1}{2} \left(\frac{k_8[\text{I}^-] + k_9[\text{A}]}{k_8[\text{I}^-] + k_9[\text{A}] + k_{10}} \cdot \frac{k_5[\text{O}_2]}{k_5[\text{O}_2] + k_6[\text{I}^-] + k_7} \cdot \frac{k_2 + k_3[\text{O}_2] + k_4[\text{I}^-]}{k_1 + k_2 + k_3[\text{O}_2] + k_4[\text{I}^-]} \right) \dots (4)$$

which is of similar form as obtained experimentally.

Acknowledgement

Our thanks are due to Dr E. J. Bowen, F.R.S., Oxford University, for helpful suggestions. One of us (A.K.G.) thanks Jadavpur University for a research fellowship.

References

1. SPIKES, J. D. & LIVINGSTON, R., *Adv. rad. Biol.*, **3** (1969), 29.
2. GROSSWEINER, L. I., *Photochem. Photobiol.*, **10** (1969), 183.
3. GROSSWEINER, L. I. & KEPKA, A. G., *Photochem. Photobiol.*, **16** (1972), 305.
4. FAHRENHOLTZ, S. R., DOLEIDEN, F. H., TROZZOLO, A. M. & LAMOLA, A. A., *Photochem. Photobiol.*, **20** (1974), 505.
5. SPIKES, J. D. & GHIRON, C. A., *Physical processes in radiation biology* (Academic Press, New York), 1964, 309.
6. GOLLNICK, K., *Photooxygenation reaction in solution: Advances in photochemistry*, Vol. 6, edited by W. A. Noyes (Jr), G. S. Hammond & J. N. Pitts (Jr) (Interscience Publishers, New York), 1968, 27-34.
7. GROSSWEINER, L. I. & KEPKA, A. G., *Photochem. Photobiol.*, **14** (1971), 621.
8. PARKER, C. A. & HATCHARD, C. G., *Proc. R. Soc. London*, **A235** (1956), 518.
9. STEVENS, B., *Accounts Chem. Res.*, **6** (1973), 90.
10. STEVENS, B. & ALGAR, B. E., *J. phys. Chem.*, **72** (1968), 3458.
11. STEVENS, B. & ALGAR, B. E., *J. phys. Chem.*, **74** (1970), 3029.
12. KEARNS, D. R. & KHAN, A. U., *Photochem. Photobiol.*, **10** (1969), 193.
13. FOOTE, C. S., *Science*, **162** (1968), 963.
14. LIU, R. S. H. & EDMAN, J. R., *J. Am. chem. Soc.*, **90** (1968), 213.
15. ROHATGI, K. K. & SINGH, B. P., *J. phys. Chem.*, **75** (1971), 595.