

Role of Dielectric Constant of Medium in Dye-sensitized Photooxidations

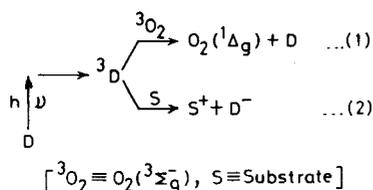
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Received 23 December 1985; revised and accepted 23 January 1986

A change in the dielectric of the medium does not observably affect either the nature or proportion of the reaction products in the methylene blue, rose bengal and eosin yellow sensitized photooxidations of phenothiazine, phenoxazine and diphenylamine in the presence of oxygen. The fit of the experimental data into a linear relationship between $\log(R)$ and $1/\epsilon_0$ (where R = rate and ϵ_0 = dielectric constant of the medium), as predicted by the electrostatic theory for a reaction involving ions, is shown to be a fortuitous result and thus it cannot be taken as an evidence for the participation of $O_2(^1\Delta_g)$. The results, on the other hand, are in agreement with a polar transition state arising from two neutral molecules in which $\log(R)$ is proportional to $(\epsilon_0 - 1)/(2\epsilon_0 + 1)$. The quantitative dielectric effect depends upon the course of the reaction and it can be used as diagnostic probe in such systems to ascertain the reaction pathways.

Solvents play an important role in all the processes – beginning with the initial photon-molecular interaction and ending with formation of stable products – in a photochemical reaction. They operate through (i) dispersion interaction; (ii) reaction field and Stark effects; and (iii) specific interactions¹. Although the influence of various individual properties of the solvent is not yet fully understood, the effect of some of the bulk properties, for example dielectric constant of the reaction medium^{2,3} is well recognized and even used as a diagnostic tool for elucidation of mechanism⁴. In the dye (D)-sensitized photooxidations the key and discriminating primary processes are (1) and (2).



In process (1) energy transfer occurs whereas in process (2) electron transfer takes place^{5,6}. Many workers have investigated these processes and some have reported on the effects of dielectric constant of the medium on these reactions^{4,7}. A perusal of these reports has revealed that there are gaps in the interpretation of the reported effects of the dielectric constant on the reaction rates and that a further study in this direction is called for. Hence the need for title investigation. For the purpose of this investigation we have selected phenothiazine, phenoxazine and diphenylamine as the substrates and 3,9-bis(dimethyl-amino)phenoazathionium chloride (methylene blue or MB), 2,4,5,7-tetrabromofluorescein sodium salt (eosin

yellow or EY) and tetraiodotetrachlorofluorescein sodium salt (rose bengal or RB) as the dyes for dye-sensitized photooxidation of these substrates. The effect of dielectric constant of the medium has been reinterpreted in terms of the electrostatic theory⁸.

Materials and Methods

Solvents used were of high purity and were distilled before use. MB and EY (E Merck, Germany) and RB (BDH, India) were crystallised from *n*-butanol. Phenoxazine (K&K Labs, USA) was purified by sublimation *in vacuo*. Phenothiazine (Fluka, Switzerland) was crystallised from benzene-pet. ether to a sharp melting point. Diphenylamine (Riedel, Germany) was purified by repeated crystallisation from aqueous ethanol. 1,4-Diazabicyclo[2.2.2]octane and β -carotene (K&K Labs, USA) were used as such.

Photolysis was carried out in flat pyrex cells ($2 \times 2 \times 8$ cm³) using either a mercury lamp (125 watt) or a halogen lamp (1000 watt) (both from Philips, India). The light was filtered through water and/or appropriate cut-off glass filters (Ealing, U K). The details of the set-up have been described elsewhere⁹.

The products were identified as reported previously⁹⁻¹¹. The reaction was monitored spectrophotometrically at or near the maxima of the products in the visible region employing one or two wavelengths. Dielectric constants of binary mixtures (ϵ_0) were calculated from the relationship (3)

$$\epsilon_0 = \epsilon'_0 + w(\epsilon''_0 - \epsilon'_0) \quad \dots (3)$$

where ϵ'_0 is the dielectric constant of the solvent to which the solvent of the dielectric constant ϵ''_0 has been added and w is the weight of the solvent added per gram of the total solvent.

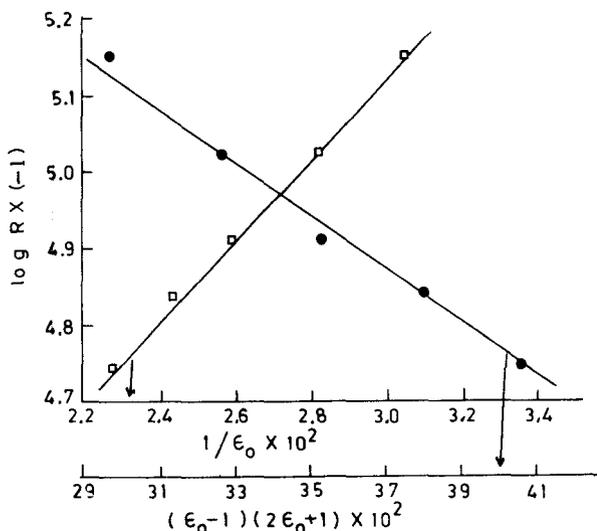


Fig. 1—Effect of dielectric constant of medium on MB-sensitized oxidation of phenothiazine in air saturated methanol-water mixtures ($[\text{Phenothiazine}] = 2.0 \times 10^{-3} M$; $[\text{MB}] = 1.3 \times 10^{-4} M$).

Results and Discussion

The dielectric constant of the medium was varied by adding water to solvent methanol, ethylene glycol or acetonitrile. Except for ethylene glycol essentially no change in viscosity was expected as a result of the addition of water¹². In the experiments with a given substrate and a dye the total UV/visible absorption spectrum of the product mixture remained unaltered with change in composition of the solvent. This shows that the product(s) or their proportion does not change with change in the medium which is an unusual result because the products have been shown to be medium-dependent in many investigations¹³⁻¹⁶. A plot of $\log(\text{rate})$ of the reaction (R) at a fixed absorbed light intensity for phenothiazine versus $1/\epsilon_0$ is shown in Fig. 1. The oxidation takes place via $\text{O}_2(^1\Delta_g)^{10}$ and the plot can be taken to support the singlet oxygen mechanism since such linear plots have been observed in some similar photooxidations^{4,17}. This, however, appears odd since one would not expect any effect of the dielectric constant of the medium on a reaction where ions are not involved. In terms of the electrostatic theory, the dependence of the rate constant on the dielectric constant is given by the relation (4),

$$\ln k = \ln k_0 - NZ_A Z_B e^2 / \epsilon_0 RT r_{\ddagger}^{\ddagger} \quad \dots (4)$$

where k is the rate constant; k_0 is the rate constant in a medium of infinite dielectric constant; Z_A , Z_B are the charges on two reacting ions A and B; and r_{\ddagger}^{\ddagger} is the equilibrium distance in the activated complex. When concentration terms are included, the rate (R) is given by the expression (5),

$$\ln R = \ln k_0 + \alpha \ln C - NZ_A Z_B e^2 / \epsilon_0 RT r_{\ddagger}^{\ddagger} \quad \dots (5)$$

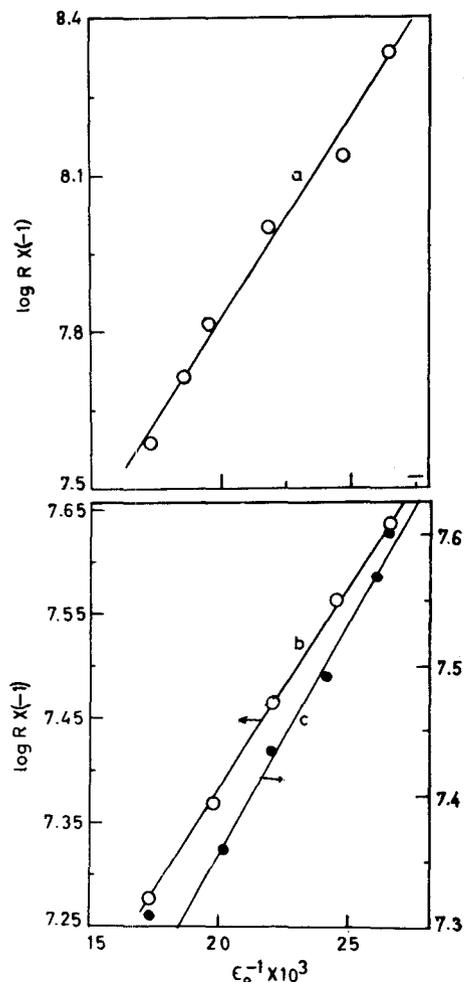


Fig. 2—Plots of $\log R$ versus $1/\epsilon_0$ for photooxidation of phenoxazine in ethylene glycol-water $\{[\text{MB}] = 1.66 \times 10^{-4} M$; $[\text{phenoxazine}] = 7.28 \times 10^{-4} M$ (a); $[\text{RB}] = 3.14 \times 10^{-5} M$; $[\text{phenoxazine}] = 5.24 \times 10^{-4} M$ (b); and $[\text{EY}] = 5.59 \times 10^{-5} M$; $[\text{phenoxazine}] = 3.48 \times 10^{-4} M$, (c).

where α and C are the combined concentration coefficient and concentration respectively. It is obvious that the plot of $\log R$ versus $1/\epsilon_0$ should be linear for a reaction between ions. For the reaction through $\text{O}_2(^1\Delta_g)$ one is compelled to postulate a step represented by Eq.(6),



However, this again does not appear correct since the observed slope is negative (Fig. 1a) which is predicted only for reactions between like ions. One is, therefore, compelled to believe that the agreement is a fortuitous result.

The plots of $\log R$ versus $1/\epsilon_0$ for the photooxidation of phenoxazine in the presence of dyes MB, RB and EY in ethylene glycol-water medium are given in Figs. 2 and 2a. The plots are linear although it has been shown that this oxidation does not involve $\text{O}_2(^1\Delta_g)$ (ref. 9). It is thus clear that the linearity of these plots

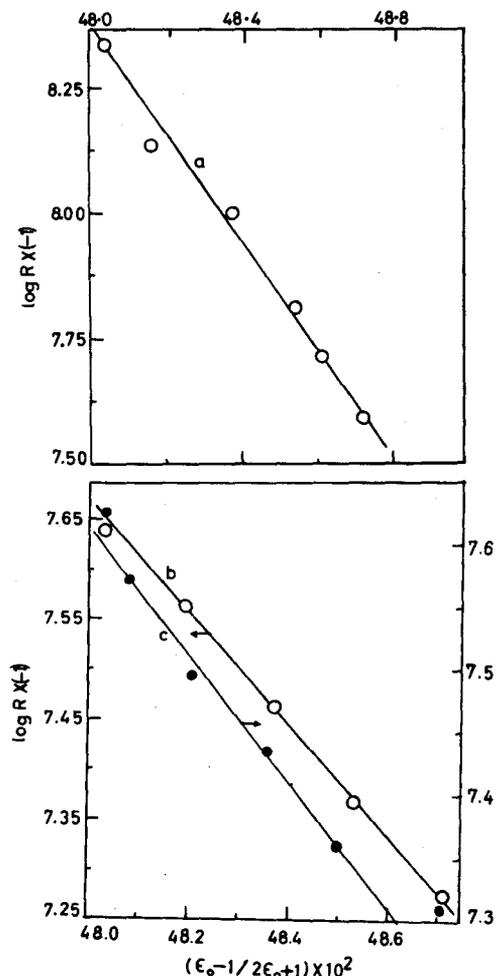


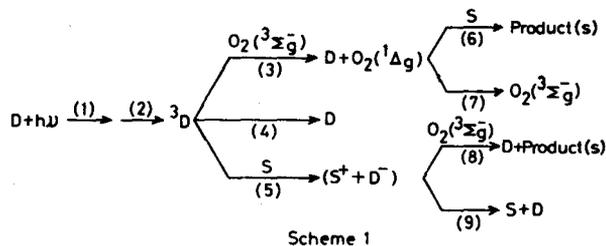
Fig. 3—Plots of $\log R$ versus $(\epsilon_0 - 1)/(2\epsilon_0 + 1)$ for photooxidation of phenoxazine in ethylene glycol-water $\{[MB] = 1.66 \times 10^{-4} M$; $[\text{phenoxazine}] = 7.28 \times 10^{-4} M$ (a); $[RB] = 3.14 \times 10^{-5} M$; $[\text{phenoxazine}] = 5.24 \times 10^{-4} M$ (b) and $[EY] = 5.59 \times 10^{-5} M$; $[\text{phenoxazine}] = 3.48 \times 10^{-4} M$, (c).

cannot be taken as a support for $O_2(^1\Delta_g)$ participation. In fact it appears to be a manifestation of a more basic feature of the reaction. The observed effect is no doubt in agreement with the prediction where the transition state complex is more polar than the reactants and in this case a linear relationship is expected between $\log R$ versus $(\epsilon_0 - 1)/(2\epsilon_0 + 1)$ (ref. 18). These plots are given in Figs. 3 and 3a. Though the fit of the data in linear plots is not very good, the most significant feature is that this explanation agrees with the nature of the slope (positive or negative) and clearly points to an ionization type process from two neutral reactants. A specific solvent effect is possible⁴ but does not appear to be supported by the results. It appears that in these oxidations the transition state is polar irrespective of the fact whether $O_2(^1\Delta_g)$ participates or not.

In ethylene glycol-water system the viscosity markedly decreases with increase in the proportion of water. The observed change in rate is at least not

entirely due to decrease in viscosity because of the similarity of the phenomenon with the system where there is little change in viscosity (cf. methanol-water and acetonitrile-water media). Moreover, one expects a viscosity effect only if the rate is diffusion-controlled. It is to be noted that Foote has observed no viscosity effect in similar systems^{7b}.

With diphenylamine the effect of the dielectric has been examined at two concentrations of the amine (Fig. 4). The results at low concentration of the amine and at low value of the dielectric constant are markedly different. The explanation of the difference lies in the mechanism of the oxidation presented in Scheme 1.



The filtered light is absorbed by the dye only and the basic absorption process is the electronic excitation through a spin-allowed $\pi^* \leftarrow \pi$ transition³. Earlier studies have shown unequivocally that in xanthen dye-sensitized oxygenation reactions, only triplet sensitizers take part in the energy transfer process¹⁹ and this is also true for MB²⁰. Furthermore, in the present study any interaction of the substrate with the excited singlet dye is unlikely because of the short lifetime of the singlet state and the low concentration of the substrates. Processes (3) and (5) in Scheme 1 are well-documented in a number of reports on the competitive quenching of the sensitizers through energy transfer to $O_2(^3\Sigma_g^-)$, and chemical interaction with appropriate substrates⁵—particularly amines⁶. A steady state treatment gives:

$$\text{Rate} = \frac{\alpha I_a k_2}{\left\{ k_3 [O_2] + k_5 [S] + k_4 \right\}} \left\{ \frac{k_3 k_6}{(k_6 [S] + k_7)} + \frac{k_5 k_8}{k_8 [O_2] + k_9} \right\} [S] [O_2] \quad \dots (7)$$

In Eq. (7) α is an efficiency factor. In the complete quenching region of the triplet dye $k_4 \sim 0$. The curves in Fig. 4 consist of two parts, the processes (3) and (5) of Scheme 1 predominate in the upper and lower parts respectively. For these regions Eq. (7) splits into two equations (7a) and (7b) corresponding to upper and lower regions.

$$\text{Rate}(u) = \alpha I_a k_2 k_6 / (k_6 [S] + k_7) \times [S] \quad \dots (7a)$$

$$\text{Rate}(l) = \alpha I_a k_2 k_8 / (k_8 [O_2] + k_9) \times [O_2] \quad \dots (7b)$$

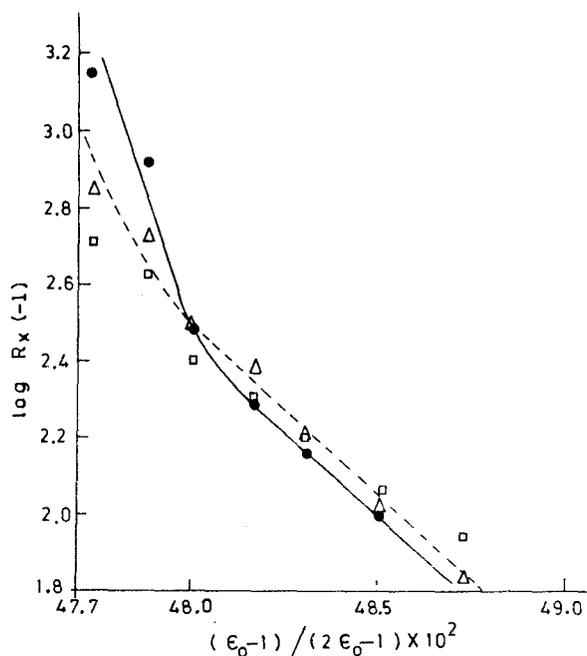


Fig. 4—Effect of dielectric constant of medium on MB-sensitized oxidation of diphenylamine in air saturated methanol-water mixtures ($[MB] = 1.0 \times 10^{-5} M$; $[diphenylamine] = 8.0 \times 10^{-4} M$ in \bullet — \bullet ; $4.0 \times 10^{-3} M$ in Δ — Δ and $8.0 \times 10^{-3} M$ in \square).

A change in the dielectric constant brought about by a change in the composition of the solvent also brings about a change in $[O_2(^3\Sigma_g^-)]$ in the medium because of its widely different solubilities ($2.12 \times 10^{-3} M$ in methanol and $0.26 \times 10^{-3} M$ in water). However, Eq. (7a) shows that the observed effect is a result of a change in k_6 and/or k_7 . The reported values for pseudo-unimolecular k_7 are $20.0 \times 10^4 s^{-1}$ in methanol²² and $50.0 \times 10^4 s^{-1}$ in water²³ and predict an opposite effect. Bellus²¹ has also observed that polarity, viscosity, polarizability, ionization potential and oxygen solubility as well as presence of a heavy atom in solvent molecule appear to be unimportant factors for k_7 . There is thus no doubt that the dielectric constant affects k_6 and the transition state involved in the process is polar.

Equation (7b) does not give a simple dependence of rate on $[O_2]$. The linearity of the curve in itself is a proof of the effect of the dielectric on k_9 . There is also no doubt that $k_5 > k_3$ in polar media.

In summary the dielectric constant effect is consistent with a polar transition state and it operates through the interaction of substrate with $O_2(^1\Delta_g)$ and excited dye—substrate complex with $O_2(^3\Sigma_g^-)$ and can be used to differentiate between the operating mechanisms in appropriate sensitized photo-oxidations.

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