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PHENAZINE-SENSITIZED PHOTOBLEACHING OF METHYLENE BLUE

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Summary

It is observed through selective excitation that, whereas the ground state of phenazine quenches the excited $^3(n, \pi^*)$ state of methylene blue through charge transfer exciplexation and thus prevents its photostationary-state-limited bleaching to leuco methylene blue in alcohols, excited $^1(n, \pi^*)$ phenazine bleaches ground state methylene blue in a straight reaction through a non-energy transfer process in which the phenazine concentration does not change. The latter is an example of chemical sensitization which is first order with respect to the dye with zero induction period and, unlike a similar sensitization through initial hydrogen abstraction in $^3(n, \pi^*)$ carbonyl compounds, it takes place via a charge transfer phenazine–alcohol exciplex. A comparison of quantum yields reveals photobleaching to be more efficient than the photoreduction of phenazine. The effects of changing the dielectric constant and viscosity of the medium and the density of the intermediates have been shown to be consistent with the proposed mechanism.

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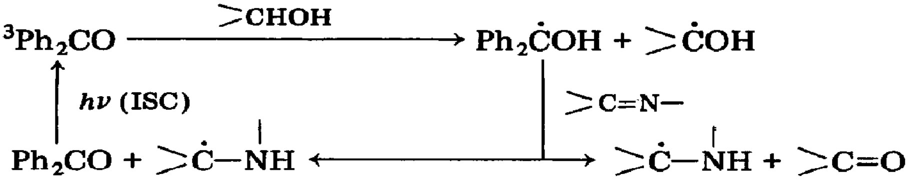
1. Introduction

Numerous examples of photosensitization through energy transfer from both the singlet and triplet excited states of the donors are known [1 - 3]. A few cases of chemical sensitization, where the physical exchange of electronic energy does not take place, have also been reported [4, 5]. In the latter category, for example, it has been shown that aryl imines undergo reduction via hydrogen atom transfer from ketyl radicals arising from an abstraction process undergone by the excited triplet of the carbonyl compound [5]:



$$\begin{tikzcd}
{}^3\mathrm{Ph_2CO} \arrow[r, "{>}\mathrm{CHOH}"] & \mathrm{Ph_2\dot{C}OH} + {>}\mathrm{\dot{C}OH} \arrow[d, "{>}\mathrm{C{=}N{-}}"] & \\
\mathrm{Ph_2CO} + {>}\mathrm{\dot{C}{-}\overset{|}{N}H} \arrow[u, "h\nu\ (\mathrm{ISC})"] & {} \arrow[l] \arrow[r] & {>}\mathrm{\dot{C}{-}\overset{|}{N}H} + {>}\mathrm{C{=}O}
\end{tikzcd}$$

Paraquat salts are very efficiently reduced in aqueous propan-2-ol through a similar mechanism [6]. The reactive (n, π^*) electronic states of carbonyls and imines are rather similar. Six-membered monoaza aromatics, acridines [7] and phenazine [8] undergo hydrogen abstraction. It was thus considered desirable to examine the photochemistry of phenazine (P) from the viewpoint of its acting as a non-energy transfer sensitizer.

Methylene blue (MB^+) was chosen as a probe because its photochemistry, particularly sensitization through its excited triplet state, has been the subject of many investigations and the elementary processes involved in its reduction are almost completely understood [9 - 11].

We report here results showing that P acts as a chemical sensitizer and that the one-electron reduction of ground state MB^+ is an efficient process.

2. Experimental details

Phenazine and methylene blue were guaranteed reagents (E. Merck) and were used as received. All other reagents and solvents were purified using known methods.

The radiation source was a high pressure mercury lamp (HPL Philips 125W) which was fed from a stabilized power supply. The light was filtered to achieve selective absorption by either MB^+ or P. A filter with a cut-off at 470 nm was used to excite MB^+ and another filter with maximum emission at 366 nm (bandwidth at half-height, 50 nm) was employed to excite P. The radiation beam was collimated by passage through a blackened tube 50 mm long and 15 mm in diameter placed between the lamp and the filter. The photolyses were carried out in a 10 mm square Pyrex cell with a B_{10} joint fitted at the top.

The system was flushed with pure nitrogen for deoxygenation. Oxygen was removed from the commercial nitrogen (purity, 99%) by passing it over freshly reduced finely divided copper deposited over kieselguhr (60 - 80 mesh) and kept at 200 °C. Traces of water were removed by passing the nitrogen through a column of activated silica gel. In order to prevent evaporation of the solvent from the solution in the photolysis cell the gas was presaturated with the desired solvent. As a further precaution the solutions were deaerated using freeze–pump–thaw cycles. The freezing was carried out using liquid nitrogen and the pumping was performed with an all-glass pumping system capable of attaining a pressure of 10^{-6} Torr.

A Hilger and Watts H-700 spectrophotometer was used for the UV–visible region and an Erma LS-7 spectrometer was employed for the visible region. The two instruments were carefully calibrated and checked for mutual consistency.

A potassium ferrioxalate actinometer [12] was employed for measuring the absorbed light intensities when the light was fully absorbed. When absorption is incomplete the absorbed intensity I_a is a complex function of the geometry of the cell. However, because the beam was almost parallel it was assumed that

$$I_a = I_0(1 - 10^{-\mathrm{OD(total)}})$$

It was assumed further that a species absorbed light in proportion to its optical density at the wavelength of interest.

In the final experiment an oxygenated solution containing 6.31×10^{-5} M P and 5.61×10^{-6} M MB^+ in methanol was photolysed at 366 nm for 1 h. The solvent from the photolysed mixture was evaporated off under vacuum and the solid residue was dissolved in benzene and analysed using thin-layer chromatography (TLC) (eluent, 95:5 $CHCl_3$–CH_3OH mixture; adsorbent, silica gel G).

3. Results and discussion

The light filtered through the 470 nm cut-off filter is absorbed only by MB^+ which undergoes an (n, π^*) transition. The results of the photolysis of deaerated solutions of MB^+ in the presence and absence of P in this system are given in Fig. 1. It is apparent that (a) MB^+ disappears and (b) this disappearance is quenched in the presence of P. The total UV–visible absorption spectrum of the photolysed mixture with $[MB^+] = 5.05 \times 10^{-6}$ M and $[P] = 3.45 \times 10^{-5}$ M also remained unchanged. The solutions in which the dye had partially disappeared developed a maximum at 340 nm concomitant with the decrease in MB^+ concentration. The maximum corresponds to λ_{max} of leuco methylene blue (LMB) [13]. Furthermore, the dye fully recovered on aeration which shows that the disappearance is due to the reduction of MB^+. The cycle of reduction and recovery could be repeated several times without any loss of dye.

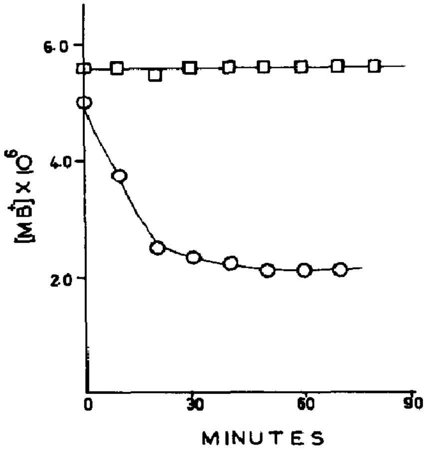


Fig. 1. Plot of the disappearance of MB^+ in methanol *vs.* photolysis time (470 nm cut-off filter): ○, $[MB^+]_0 = 4.80 \times 10^{-6}$ M; □, $[MB^+]_0 = 5.61 \times 10^{-6}$ M + $[P] = 3.45 \times 10^{-5}$ M.

The three excited states observed for P are located at 645.1 nm, 434.9 nm and 361.0 nm corresponding to the $^3(\pi, \pi^*)$, $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ excitations respectively [14]. The first excited singlet and triplet levels of MB^+ [15] are below the lowest excited state of P, and a spin-allowed energy transfer (there is no evidence for a large spin–orbit coupling) from excited MB^+ to P which yields the reactive excited states of P ($^3(\pi, \pi^*)$ is a chemically inert state [16]) is not possible.

The UV–visible absorption spectrum of a mixture of MB^+ (4.80×10^{-6} M) and P (4.15×10^{-5} M) in methanol was found to be additive. This eliminates any significant ground state complexation and any interference by P in the basic excitation process undergone by MB^+. In Fig. 1 the photostationary state is reached at an LMB concentration of 2.92×10^{-6} M and complete quenching takes place at $[P] \geqslant 3.45 \times 10^{-5}$ M. The photostationary state is apparently reached in the bleaching of MB^+ in alcohols because of the deactivation of $^3MB^+$ by LMB [17]. Since the quantum yield for fluorescence of MB^+ is 0.017 and $\Phi_{ISC} = 0.52$ [11], the primary bleaching process is

$$^3MB^+ + MeOH \longrightarrow M\dot{B} + Me\overset{\bullet +}{OH} \qquad (1)$$

where $^3MB^+$ is formed from $^1MB^+$ by intersystem crossing (ISC) and $M\dot{B}$ is a semiquinone radical. It should be noted that semiquinone radicals have been directly observed in flash photolysis of MB^+ and a rapid dismutation rate has been reported for their disappearance [18]. P must interfere with process (1) in order to prevent the bleaching because it does not interact with LMB (see below), and the reaction

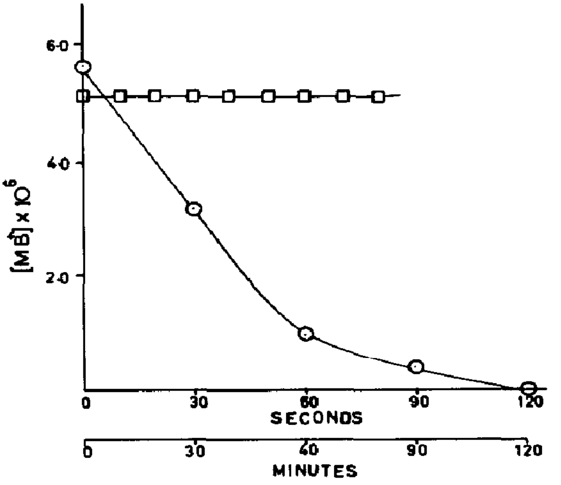
$$M\dot{B} + P \longrightarrow MB^+ + P^- \qquad (2)$$

does not take place because the dihydrophenazine which would be expected to be formed from P^- was not observed. Exciplexes have been reported with triplet benzophenones and anilines [19]. Electron transfer from electron donor substrates through triplet excimers to thionine has been postulated [20]. By analogy with these systems deactivation could take place through the process

$$^3MB^+ + P \longrightarrow {}^3[MB^{\delta -}\ldots P^{\delta +}] \qquad (3)$$

It is difficult to estimate the extent of charge separation in the exciplex but it is expected to be far from complete in methanol. Furthermore, in the event of the separation of the two entities, the observed results require 100% efficient back-electron transfer which is unlikely even within a solvent cage because of the low viscosity of the alcohols used here. The two interacting molecules have fundamentally similar geometry and heteroatom configuration, and the charge transfer interaction may have a strong resonance character rendering some extra stability to the complex. The exciplex is expected to split after spin inversion, resulting in non-radiative deactivation. It should be noted that the rate constants for the reduction of excited MB^+ by a series of amines have been measured, and a partial charge transfer complex has been postulated on the basis of the correlation between the rate constants and the ionization potentials of the substrates [10].

The results of selective excitation of P at 366 nm ($\epsilon(P)/\epsilon(MB^+)$ is greater than 10 at 366 nm [21, 22]) are given in Fig. 2. In contrast with the results shown in Fig. 1, there is a reaction in the presence of P and no reduction takes place since absorption by MB^+ results in its $\pi^* \leftarrow \pi$ excitation. At the same time, unlike previous results, the reduction goes to completion. The dye was completely recovered on aeration as shown by comparison of the absorption spectra. P can undergo both the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transitions in the system and although energy transfer to MB^+ is exothermic and feasible, particularly in view of the diffusion-controlled quenching of acridine by eosine [7], it does not lead to the observed reaction. The first-order plots for MB^+ at three initial concentrations are given in Fig. 3. The rate is proportional to $[MB^+]$ and no induction period is observed. However, the results given in Table 1 show that the quantum yield of disappearance of MB^+ saturates at higher concentrations as expected. The products and mechanism of the photoreduction of P show substantial differences in the presence and absence of acids [14, 23], and despite an



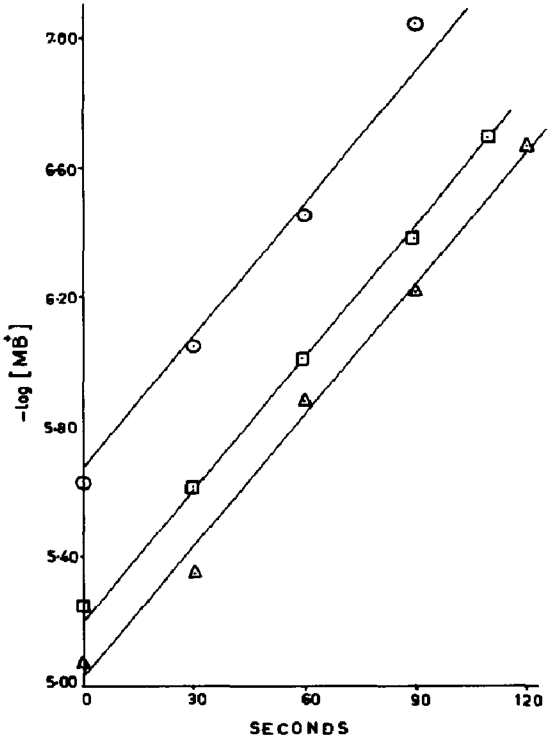


Fig. 2. Plot of the disappearance of MB^+ in methanol *vs.* photolysis time (irradiation at 366 nm): ⊙, $[MB^+]_0 = 5.61 \times 10^{-6}$ M + $[P] = 6.31 \times 10^{-5}$ M (scale in seconds); □, $[MB^+]_0 = 4.80 \times 10^{-6}$ M (scale in minutes).

Fig. 3. Plot of $-\log[MB^+]$ *vs.* photolysis time at various initial concentrations of MB^+ and $[P] = 6.31 \times 10^{-5}$ M (solvent, methanol; $I_0 = 2.61 \times 10^{-6}$ einsteins l^{-1} s^{-1}; ⊙, $[MB^+]_0 = 2.25 \times 10^{-6}$ M; □, $[MB^+]_0 = 5.61 \times 10^{-5}$ M; △, $[MB^+]_0 = 8.42 \times 10^{-6}$ M.

TABLE 1

Effect of the initial concentration of methylene blue

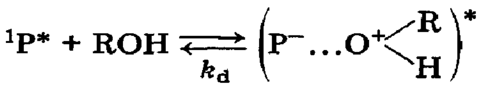
Number	$[MB^+]_0 \times 10^6$ (M)	$I_a \times 10^6$ (einsteins l^{-1} s^{-1})		*Decay time* τ *for* MB^+ (s)	Φ_0 $(-MB^+)$
		Total	*By P*		
1	2.25	2.25	2.34	31.5	0.030
2	5.61	2.36	2.32	32.0	0.076
3	8.42	2.37	2.30	38.5 (31.0)[a]	0.095 (0.118)[a]

$[P] = 6.31 \times 10^{-5}$ M; $I_0 = 2.61 \times 10^{-6}$ einsteins l^{-1} s^{-1}; solvent, methanol.

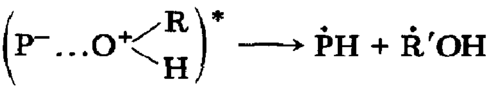
[a] Values computed from the same experiment but taking a concentration of 6.00×10^{-6} M from within the bleaching run as the initial concentration.

initial uncertainty as to the identity of the excited reactive state [8] it is now established that it is the first (n, π*) singlet state which initiates the reaction in all these systems [24]. Alcohols are even weaker acids than water ($pK_a \approx 16$) and very little protonation is expected in the present system (the ground state pK_a of P in CH_3OH is 4.5 [25]). The excited state of P may be much more basic and there is strong evidence for this [26]. It is also known that aza compounds are a factor of 10^6 more basic in the excited state than in the ground state. However, no products arising from the protonated species have been observed in alcohols [26] and it is safe to conclude that protonated P has no role in such a solvent. The following processes deserve consideration:

$$P + h\nu(366\text{ nm}) \xrightarrow{\alpha I_a} {}^1P^*(n,\pi^*) \qquad (4)$$



$$ {}^1P^* + ROH \underset{k_d}{\rightleftharpoons} \left(P^-\ldots O^+\begin{smallmatrix} R \\ H \end{smallmatrix}\right)^* \qquad (5)$$



$$\left(P^-\ldots O^+\begin{smallmatrix} R \\ H \end{smallmatrix}\right)^* \longrightarrow \dot{P}H + \dot{R}'OH \qquad (6)$$

$$\dot{P}H + MB^+ \longrightarrow P + M\dot{B} + H^+ \qquad (7)$$

$$M\dot{B} + M\dot{B} \longrightarrow \dot{M}\dot{B}^- + MB^+ \qquad (8)$$

$$M\dot{B} + \dot{R}'OH \longrightarrow \dot{M}\dot{B}^- + R'CO + H^+ \qquad (9)$$

$$\dot{P}H + ROH \longrightarrow PH_2 + \dot{R}'OH \qquad (10)$$

The ^{1}(n, π*) state is reached directly and via the ^{1}(π, π*) state because both states are initially excited owing to their overlapping absorption bands.

α represents the fraction that deactivates to the ground state either directly or via the $^3(\pi, \pi^*)$ state, which has been shown to be unreactive even towards tri-*n*-butylstannane possibly because of a lack of (n, π^*) character as a result of poor mixing of the (n, π^*) and (π, π^*) states owing to the large energy gap between them [24].

Alcohols can hydrogen bond at the hetero nitrogen atom of P, although very weakly compared with the bonding with the oxygen of a carbonyl group, and through the π electron system of the molecule. The former bonding will be lost in the (n, π^*) state but the latter is expected to keep an alcohol molecule close to $^1P^*$ in a non-random orientation. There have been many reports of hydrogen atom abstraction by the electron-deficient oxygen of the excited carbonyl group [27, 28]. It has also been reported for other systems, *e.g.* imines, six-membered monoaza aromatics and acridines [29]. Table 2 gives the results for bleaching in various alcohols. Recent relevant hydrogen atom abstraction data are included for comparison. A rather high rate is observed in *t*-butanol and this rules out direct hydrogen abstraction by the electrophilic nitrogen in $^1P^*$, at least as the only process. It is for this reason that a charge transfer exciplex has been proposed in step (5). The relative stability of the moiety from alcohols in the complex within the solvent cage or separate from the other part is in accordance with the observed relative rates and the reported quantum yields for the photoreduction of phenazine in various alcohols (see Table 2). Such complexes have been reported in similar systems [19], and a particular example is the initial electron transfer from acetic acids to $^1P^*$ in an overall decarboxylation process [32]. The complete electron transfer to $^1P^*$ is expected to be in the π^* molecular orbital because transfer to an orbital localized on nitrogen is likely to give an extremely strained hetero ring owing to a change in the geometry of nitrogen to the tetragonal shape. It

TABLE 2

Relative photoreduction rates in alcohols

Number	*Solvent*	*Viscosity* η (cP)	*Dielectric constant* ϵ'	*Relative rate*	$k_r \times 10^5$ ($l\ mol^{-1}\ s^{-1}$)	$\Phi(PH_2)$
1	Methanol	0.551	32.70	1.00	—	0.023
2	Ethanol	1.078	26.22	1.12	—	0.037
3	*n*-Propanol	2.256	30.25	1.36	21	—
4	Propan-2-ol	2.858	22.83	2.52	41	0.050
5	*t*-Butanol	3.316	16.58	1.20	0.53	—

$[MB^+]_0 = 5.61 \times 10^{-6}$ M; $[P] = 6.31 \times 10^{-5}$ M; $I_a = 2.32 \times 10^{-6}$ einsteins $l^{-1}\ s^{-1}$.
The values for methanol and the literature values in the sixth column are for 100% solvent; the others are for solvent containing 20 vol.% methanol.
k_r is the rate constant for reduction of triplet benzophenone [30].
$\Phi(PH_2)$ is the quantum yield of 5,10-dihydrophenazine in the photoreduction of phenazine [31].

is of course well known that excited states are better electron donors as well as better electron acceptors. A comparison of the optimum quantum yields in the reduction of MB^+ in the present system (see Table 1) and P in the reported system shows that there are more energy-wasting processes in the latter system.

The observed quantum yields (see Table 1) together with the reported minimum rate of hydrogen abstraction by $^1P^*$ in propan-2-ol (about 10^6 l mol^{-1} s^{-1} [24]) rule out the possibility of any interaction between $^1P^*$ and MB^+ since such an interaction would have to be a factor of 10^2 - 10^3 faster than the diffusion step in order to compete with the reduction step (6) which may have separated radical ions as intermediates. Despite a report to the contrary it is believed that PH_2 and the phenazinium cation radical are effective electron transfer agents [33], but MB^+ is not reduced by PH_2 in the present system as shown by the zero induction period and the first-order nature of the reaction with respect to MB^+ throughout the entire bleaching process. The latter aspect also indicates that PH_2, which is formed during the incomplete quenching by MB^+ through process (10), has no filter effect. The semiquinone radicals $MB^{\cdot}$ are known to disproportionate at a diffusion-controlled rate, whereas the corresponding rate constant for the $\dot{P}H$ radicals is about 3×10^7 l mol^{-1} s^{-1} [8]. The latter reaction may be important towards the end of photobleaching but the data in that region are unreliable because of the analytical uncertainty and no conclusions can be drawn regarding this aspect.

The effect of the dielectric constant ϵ' of the medium was examined by varying the proportion of water in methanol. A linear relationship is expected between the logarithm of the rate constant for the disappearance of MB^+ and $1/\epsilon'$ for a polar transition state [34] and this is confirmed by Fig. 4. The point corresponding to pure methanol does not lie on the straight line and provides evidence for the role of some specific effect in addition to the pure polarity effect of the medium. It is likely that in pure alcohol there is very little separation of the proton from LMB in step (9).

In order to examine the effect of the density of radical intermediates the density of the absorbed light was changed by varying [P] over a wide range; the results are shown in Table 3. At the lower concentrations of P a deactivating effect predominates as has been reported previously [8]. In the upper concentration range the quantum yield for the disappearance of MB^+ tends to increase. Radical–radical reactions, which compete to some extent with the geminate back recombination, appear to predominate here. This is supported by the results shown in Fig. 5 where the viscosity of the medium has been increased by 30% by adding ethylene glycol to the methanol solvent (a larger increase was limited by solubility considerations). The increase in viscosity resulted in a 40% increase in the rate of photobleaching. The results in Table 2 support the conclusion that this increase is due to viscosity-limited diffusion.

A steady state treatment of the mechanism (processes (4) - (10)) gives

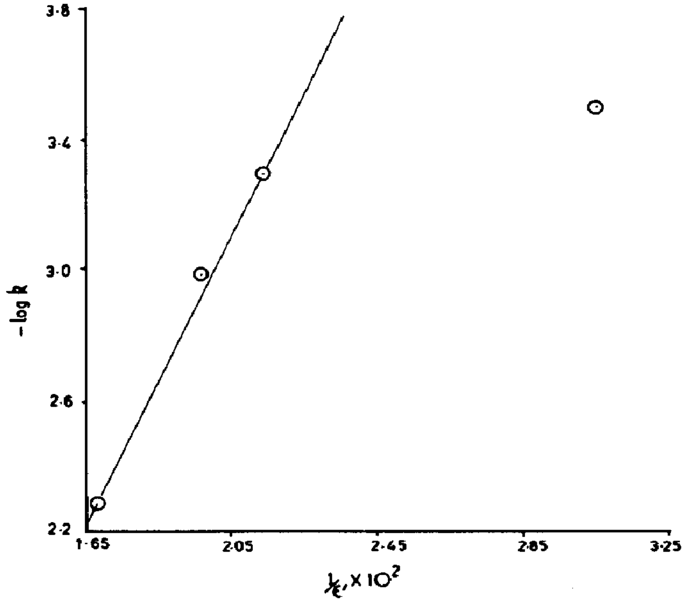


Fig. 4. Plot of $-\log k$ (for the disappearance of MB^+) *vs.* $1/\epsilon'$: $[P] = 6.31 \times 10^{-5}$ M; $[MB^+]_0 = 5.61 \times 10^{-6}$ M; $I_a = 2.36 \times 10^{-6}$ einsteins l^{-1} s^{-1}.

TABLE 3

Effect of the phenazine concentration (methanol solvent)

Number	$[P] \times 10^4$ (M)	$I_a \times 10^6$ (einsteins l^{-1} s^{-1}) *Total*	$I_a \times 10^6$ (einsteins l^{-1} s^{-1}) *By P*	*Decay time* τ *for* MB^+ (s)	$\Phi_0(-MB^+)$
1	0.139	1.10	1.02	45.0	0.120
2	0.631	2.36	2.32	32.0	0.076
3	5.55	2.61	2.61	25.5	0.084
4	55.5	2.61	2.61	21.0	0.100

$[MB^+]_0 = 5.61 \times 10^{-6}$ M; $I_a = 2.36 \times 10^{-6}$ einsteins l^{-1} s^{-1}.

$$-\frac{d[MB^+]}{dt} = \frac{\alpha I_a k_6 k_7 [MB^+]}{(k_d + k_6)(k_7[MB^+] + k_{10}[ROH])}$$

which for $k_{10}[ROH] \gg k_7[MB^+]$ correctly predicts the first-order dependence with respect to $[MB^+]$. In terms of quantum yield

$$\frac{1}{\Phi(-MB^+)} = \frac{(k_d + k_6)k_{10}[ROH]}{\alpha k_6 k_7 [MB^+]}$$

The least-squares linear plot of this equation for methanol given in Fig. 6 supports the proposed mechanism.

An oxidized product (possibly phenazine oxide) has been reported in the photolysis of P in methanol in the presence of oxygen [24]. When

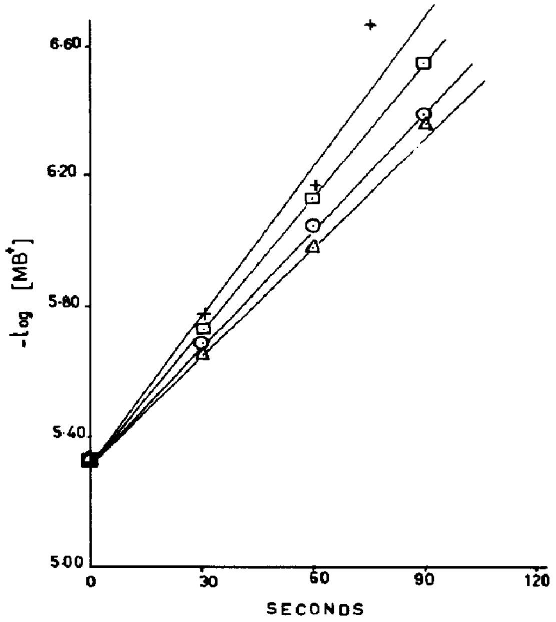


Fig. 5. Plot of $-\log[MB^+]$ *vs.* photolysis time in methanol containing ethylene glycol ($[MB^+]_0 = 4.77 \times 10^{-6}$ M; $[P] = 6.31 \times 10^{-5}$ M): △, zero glycol; ⊙, 3 vol.% glycol; ⊡, 5 vol.% glycol; +, 7 vol.% glycol.

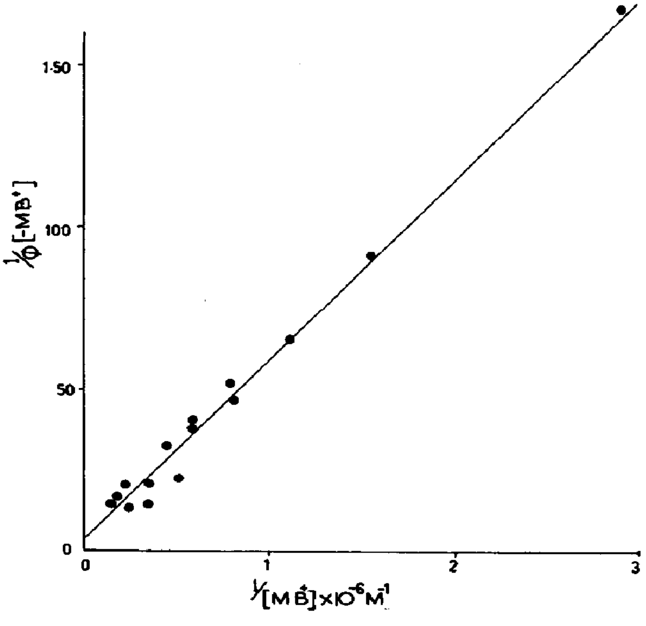


Fig. 6. A least-squares plot of the reciprocal of the quantum yield of disappearance of MB^+ *vs.* the inverse of its concentration: $[P] = 6.31 \times 10^{-5}$ M; $I_0 = 2.61 \times 10^{-6}$ einsteins l^{-1} s^{-1}.

photolysis at 366 nm was performed in the present system in the presence of oxygen six products which were separable by TLC were obtained. The major product showed a pink colouration. This suggests a different reaction path and not just the oxidation of PH_2 and LMB. An investigation of this reaction, particularly from the point of view of participation of $O_2(^1\Delta_g)$, would be mechanistically very important and we have initiated some work in this direction.

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