BENZOPHENONE-SENSITIZED OXIDATION OF PHENOTHIAZINE

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Summary

Oxidation of phenothiazine sensitized by benzophenone gives 3-phenothiazone and phenothiazine-5-oxide as the primary products at low conversions in benzene. From the kinetic features a mechanism demonstrating energy transfer from triplet benzophenone to phenothiazine has been postulated. Triplet phenothiazine is shown to undergo oxidation essentially without any participation of $O_2({}^1\Sigma_g^+$ or ${}^1\Delta_g)$. No charge transfer complexation between the sensitizer and substrate is observed. The presence of hydroxylic solvents increases the net reaction and this effect has been discussed.

1. Introduction

The photosensitized oxidation of organic compounds in the presence of oxygen is reported to proceed through two mechanisms [1, 2]. Schenck and his coworkers [3 - 5] have postulated the interaction of the excited sensitizer with the substrate whereas Kautsky [6] has proposed a mechanism involving the interaction of the excited sensitizer with oxygen. In the latter case singlet oxygen is assumed to be the reactive intermediate which undergoes further reactions with the substrate.

It has been shown by previous workers that singlet oxygen is involved in the photooxidation of aliphatic amines sensitized by dyes [7] and carbonyl compounds [8]. However, Davidson and Bartholomew [9] have put forward the other pathway. Dye-sensitized oxidation of tertiary amines has also been shown to take place through the interaction of the sensitizer with the substrate [10].

Charge transfer complexation between triplet benzophenone (BP) and amines has been proposed by Cohen and coworkers [11, 12] and in nonpolar solvents an exciplex has also been postulated [13, 14]. The exciplex formation is rather like a polar transition state and triplet BP is known to react additively with diphenylamine to give a carbinol, 4-(N-phenylamine)-phenyl-diphenylmethanol, in t-butanol or acetonitrile apparently through an

ion pair [15]. In dye sensitization there is little likelihood of the energy transfer to yield triplet amines occurring and a report postulating this mechanism needs to be examined [16].

Phenothiazine (PTH), which according to the $4n + 2$ formula does not have π electrons, is expected to undergo photooxidation in which the reaction starts with an attack on nitrogen or sulphur giving rise to two separate mechanistic paths. A study of these two possible mechanisms can help in elucidating the details of the reaction. It is with this in mind that the hitherto unstudied BP-sensitized oxidation of PTH was undertaken and we report here the results of this study.

2. Experimental

All the reagents were obtained from standard suppliers and were purified either by fractional distillation or by crystallization before use. The photolyses were carried out in a Pyrex cell (24 mm in diameter $\times$ 170 mm long) fitted with a capillary and a small water condenser.

For identification of the products a mixture containing 5.0×10^{-3} M PTH and 2.0×10^{-1} M BP was photolysed (125 W Gallenkamp (U.K.) lamp with emission at 3660 Å) for 1 h. The excess solvent was evaporated under reduced pressure and the products were analysed by thin-layer chromatography (TLC) and UV and IR spectroscopy. The absorbances were measured on a precalibrated Hilger and Watts spectrophotometer.

3. Results and discussion

Separation on a silica gel G plate with benzene–methanol (19:1) gave two products which were identified as 3-phenothiazone (PTZ, I) and phenothiazine-5-oxide (II) from their UV spectra [17], and comparison of R_f values, melting points and IR spectra with those of standard samples
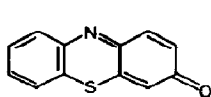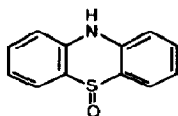
(I)   (II)

prepared by the method of Bodea and Raileanu [18] and by oxidation of PTH by H_2O_2 on a silica gel G plate [19] respectively.

The similarity in the visible spectra of the reaction mixture and of I showed it to be the only product absorbing in this region. Phenothiazine-5-oxide was monitored after TLC separation and Fig. 1 shows the results of a time study and the curves passing through the origin establish that both the products are primary products.
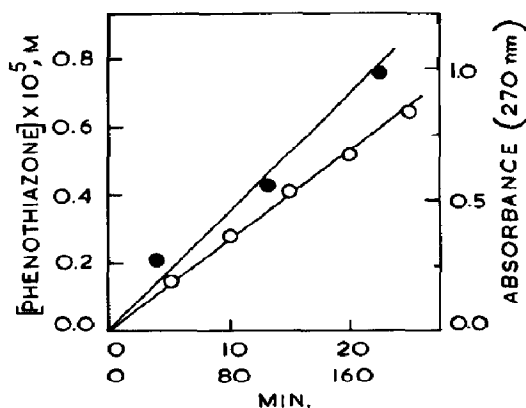
Fig. 1. Plot of 3-phenothiazone concentration (o) and phenothiazine-5-oxide absorbance (●) vs. time of irradiation. The upper and lower scales along the abscissa are for 3-phenothiazone and phenothiazine-5-oxide respectively.
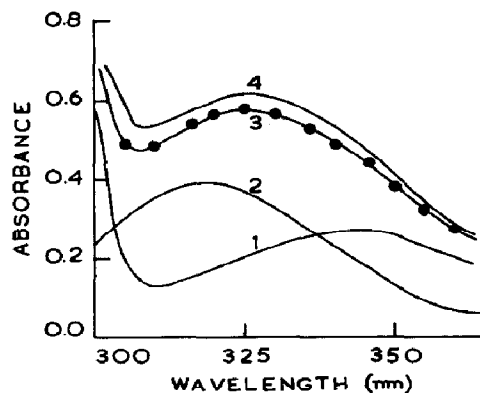
Fig. 2. Plot of absorbance vs. wavelength: [PTH] = 8.0 × 10^{-5} M; [BP] = 2.0 × 10^{-3} M. Curves 1 - 3 are for BP, PTH and BP–PTH respectively. Curve 4 was obtained in the presence of 8.3% t-butanol. ●, expected absorbance if there is no complexation. The solvent was benzene.
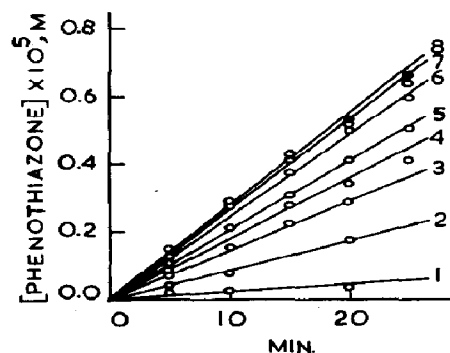

Fig. 3. Plot of 3-phenothiazone concentration vs. time of irradiation for different concentrations of BP: [PTH] = 2.0 × 10^{-3} M. Curves 1 - 8 are for [BP] values of 0.0 M, 1.6 × 10^{-3} M, 4.0 × 10^{-3} M, 8.0 × 10^{-3} M, 2.4 × 10^{-2} M, 1.6 × 10^{-1} M, 2.0 × 10^{-1} M and 3.6 × 10^{-1} M respectively. The solvent was benzene.

The energy transfer from triplet BP (E_T = 68.6 kcal [20]) to PTH (E_T = 55 kcal [21]) is expected to be diffusion controlled. BP can also abstract a hydrogen atom [22] and one would therefore expect some products arising from the diphenylhydroxymethyl radical including benzpinacol. A careful search revealed no such products; this is understandable since even in favourable conditions of hydrogen abstraction energy transfer is expected to be faster [23, 24].

The possibility of charge transfer complexation which is known to occur between amines and BP [15, 25 - 27] is ruled out by the results shown in Fig. 2, since in the event of complexation separation in the molecular orbitals is expected to decrease resulting in some red shift.

The effect of varying BP concentration was studied to examine the direct photolysis in the chosen conditions of sensitization and Fig. 3 shows the results. The rates are linear in the initial stages, and at the limit of maximum light absorption the reaction is 20 times greater than in the absence of BP. The direct photolysis can therefore be neglected, particularly in view of a further internal filter effect.
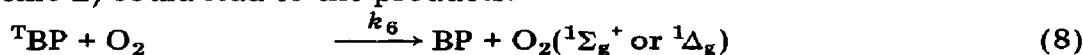
In view of the above observations and known features of BP sensitization the following mechanism (Scheme 1) can be considered:

$$BP + h\nu \xrightarrow{I_a} {}^S BP \tag{1}$$

$$^S BP \xrightarrow{k_1} {}^T BP \tag{2}$$

$$^T BP + PTH \xrightarrow{k_2} BP + {}^T PTH \tag{3}$$

$$^T BP \xrightarrow{k_3} BP \tag{4}$$

$$^T BP + O_2 \xrightarrow{k_4} BP + O_2 \tag{5}$$

$$^T PTH + O_2 \xrightarrow{k_5} products \tag{6}$$

This mechanism gives the rate expression

$$\frac{\alpha I_a}{rate} = 1 + (k_3 + k_4[O_2]) \frac{1}{k_2[PTH]} \tag{7}$$

where α is the intersystem crossing efficiency and has a value of 0.99 [28] and I_a is the absorbed intensity which is dependent upon BP concentration up to the region of complete absorption. If BP leads to the formation of singlet oxygen then in addition to steps (1), (2) and (4) the following steps (Scheme 2) could lead to the products:

$$^T BP + O_2 \xrightarrow{k_6} BP + O_2(^1\Sigma_g^+ \text{ or } {}^1\Delta_g) \tag{8}$$

$$O_2(^1\Sigma_g^+ \text{ or } {}^1\Delta_g) \xrightarrow{k_7} O_2 \tag{9}$$

$$PTH + O_2(^1\Sigma_g^+ \text{ or } {}^1\Delta_g) \xrightarrow{k_8} products \tag{10}$$

The rate of product formation derived from steps (1), (2), (4) and (8) - (10) is obtained from

$$\frac{\alpha I_a}{rate} = 1 + \frac{k_7}{k_8[PTH]} + \frac{k_3}{k_6[O_2]} \left(1 + \frac{k_7}{k_8[PTH]}\right) \tag{11}$$
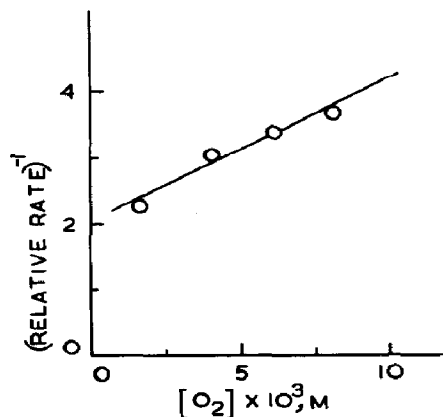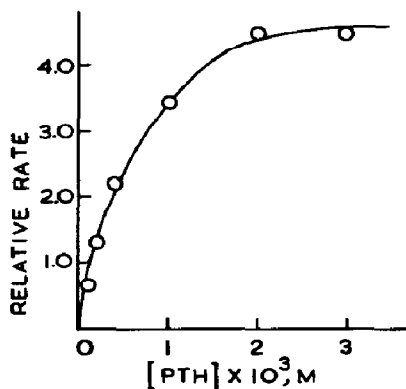
Fig. 4. Plot of relative reaction rate *vs.* [PTH] : [BP] = 2.0 × 10^{-1} M; solvent, benzene.

Fig. 5. Plot of (relative reaction rate)$^{-1}$ *vs.* [O$_2$] : [PTH] = 2.0 × 10^{-3} M; [BP] = 2.0 × 10^{-1} M; solvent, benzene.

However, it is quite likely that as in the case of some dye sensitizations [29] the reaction may be taking place through the interaction of BP with the substrate as well as the energy transfer to oxygen. The rate expression when both of these mechanisms are operative is

$$\frac{\alpha I_a}{\text{rate}} - 1 = \frac{k_6 k_7 [O_2]}{k_6 k_8 [O_2][PTH] + k_2 k_8 [PTH]^2 + k_2 k_7 [PTH]} \tag{12}$$

In eqn. (12) it is assumed that at the limit of maximum energy transfer deactivation by the solvent is negligible and singlet oxygen formation is very efficient compared with deactivation of triplet BP by oxygen.

Scheme 1 predicts a direct relation between rate and [PTH] at constant [O$_2$] and an inverse relation between rate and [O$_2$] at constant [PTH]. According to Scheme 2 the rate is expected to increase with increasing [O$_2$] at constant [PTH]. In eqn. (12) $k_2 \gg k_6$ because triplet–triplet energy transfer to amines is known to be diffusion controlled whereas singlet oxygen formation from triplet BP is an inefficient process [9]. Under the experimental conditions ([O$_2$] $\approx 10^{-2}$ M) the first term in the denominator of eqn. (12) can be neglected compared with the second term. At low [PTH] a plot of relative reaction rate *versus* substrate concentration at constant [O$_2$] is also expected to be a straight line. However, at higher [PTH] the rate should increase more rapidly. Figure 4 gives the results of varying [PTH]. The rate is linear before flattening which is in accordance with the mechanisms of Schemes 1 and 2. The flattening could occur because of complete quenching of either triplet BP or singlet oxygen.

The effect of varying [O$_2$] was studied and Fig. 5 shows the results. The rate decreases with increasing [O$_2$] which disagrees with Scheme 2 but is in accordance with Scheme 1. The increase in the reaction rate in the presence of 1,4-diazabicyclo[2,2,2]octane (DABCO), a singlet oxygen

TABLE 1

Effect of adding DABCO

[DABCO] $\times 10^3$ (M)	Relative reaction rate[a]
0.000	1.00
0.357	1.21
1.785	1.64
3.570	2.00
14.280	2.39

[PTH] = 2.0×10^{-3} M; [BP] = 2.0×10^{-1} M; solvent, benzene.
[a] Relative reaction rates have been calculated from the linear plots of [3-phenothiazone] *vs.* time of irradiation.

TABLE 2

Effect of the medium

Medium[a]	Dielectric	Relative reaction rate[b]
Benzene	2.284	1.0
Acetonitrile (1.362 M)	4.513	0.91
Acetone (1.362 M)	3.961	1.29
t-Butanol (0.21 M)	2.437	1.83
t-Butanol (0.42 M)	2.591	2.06
t-Butanol (0.63 M)	2.746	2.29
t-Butanol (1.05 M)	3.058	2.63
t-Butanol (2.10 M)	3.849	3.20

[PTH] = 2.0×10^{-3} M; [BP] = 2.0×10^{-1} M.
[a] Various solvents were added to benzene to obtain the given concentration.
[b] Relative reaction rates have been calculated from the linear plots of [3-phenothiazone] *vs.* time of irradiation.

quencher [10] (cf. Table 1) is further evidence against any participation of singlet oxygen. The reported participation of the BP–DABCO adduct [30] in the reaction should result in an induction time which was not observed. Furthermore, DABCO does not give any product absorbing in the monitor-

ing region and the increase can be attributed to efficient energy transfer from triplet BP to PTH via DABCO.

The role of any ionic intermediate was examined by studying the effect of changing the solvent and the results are given in Table 2. An increase in the dielectric constant of the medium does not favour the reaction and does not support the formation of ionic intermediates. There is a small enhancement in the absorption in the presence of alcohol (Fig. 2) but there is no change in the spectrum. However, increased absorption cannot be the reason for the increase in the reaction rate in the presence of alcohol since the addition of alcohol even at the maximum value of [BP] markedly increases the reaction rate. The postulate of enhanced energy transfer from BP in the presence of hydroxylic solvents [31] is also not valid because of other previous observations [32] and the observed enhancement in the reaction rate even in the region of complete energy transfer. Furthermore, an increase is observed even with acetone which cannot have any bonding with BP like that of alcohols. Triplet BP is reported to abstract hydrogen from methyl groups (*e.g.* in t-butanol [33]) but this reaction can be neglected compared with the energy transfer process. By analogy with some other similar photooxidation reactions it is likely that water is a product through HO_2^- radicals in the system, and greater stability of the intermediates and solvation of products like water in water-miscible solvents are the basis of the observed effects.

Acknowledgment

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