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Oxidation of an electron-rich olefin induced by singlet oxygen: mechanism for tetraphenylethylene

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Abstract

The oxidation of an electron-rich olefin (tetraphenylethylene (TPE)) was studied using methylene blue as sensitizer. The Stern–Volmer correlation for methanolic solutions of TPE, using N_3^- as $^1O_2$ quencher, and the measurement of the pseudo-first- order constants for TPE disappearance (k^1) in reactions with air and oxygen saturation, confirm that oxidation occurs via a singlet-oxygen-based mechanism. The formation of an exciplex state, as a metastable intermediate involving TPE and $^1O_2$, was observed indirectly by studying the effect of solvent polarity on the reaction. The rate constant for oxidation in methanolic solutions ($k_r \cong 10^5$ M^{-1} s^{-1}) reveals that this mechanism involves a charge transfer intermediate. This intermediate can form a dioxetane oxidation product or be physically quenched. The observed second-order constant ($k_a = k_r + k_Q = 6.76 \times 10^7$ M^{-1} s^{-1}) shows that the physical quenching of $^1O_2$ due to TPE ($k_Q = 6.74 \times 10^7$ M^{-1} s^{-1}) is not diffusion limited, since it involves a charge transfer intermediate. The $^1O_2$ quenching promoted by the sensitizer is diffusion limited ($k_s = 3.0 \times 10^{10}$ M^{-1} s^{-1}). Theoretical calculations provide additional evidence for the formation of a charge transfer intermediate, the reversibility of this state and the competition of a similar process involving molecular oxygen in the ground state.

Keywords: Oxidation; Singlet oxygen; Exciplex intermediate

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1. Introduction

Oxidation by singlet oxygen has received considerable attention in recent years [1–4]. Its potential importance in photodynamic therapy has been discussed and many studies have been reported [5–8]. However, a competitive process based on a mechanism involving electron transfer from the substrate to the sensitizer has also been observed by rigorous studies [9–14]

$$^1S^* + A \longrightarrow S^{\cdot -} + A^{\cdot +}$$

$$S^{\cdot -} + {}^3O_2 \longrightarrow S + O_2^{\cdot -}$$

$$A^{\cdot +} + O_2^{\cdot -} \longrightarrow \text{Products}$$

In particular, cyanoaromatic sensitizers, e.g. 9,10-dicyanoanthracene, sensitize the photo-oxygenation of olefins by electron transfer or by the generation of singlet oxygen, depending on the solvent polarity [13,14]. Furthermore, under conditions of enhanced intersystem crossing, the route based on singlet oxygen becomes important [13,15]. In the case of aryl-substituted olefins, the preferential route is electron transfer, producing discrete radical ions [10–12]. However, the oxidation products obtained in these reactions are generally very different from those isolated in reactions induced by singlet oxygen [9].

The reactions of singlet oxygen ($^1\Delta_g$) seem to occur through a charge transfer mechanism [16–18]. However, Machado et al. [19] have presented evidence of the action of singlet oxygen based on electron transfer.

In this work, we study the mechanism of tetraphenylethylene (TPE) oxidation, promoted by singlet oxygen. This study was performed to verify the plausibility of the existence of an exciplex state involving charge transfer between TPE and $^1O_2$, before the formation of the dioxetane intermediate, and its influence on the oxidation efficiency. Some kinetic parameters related to this reaction are estimated. A parallel study of the exciplex formation pathway, involving quantum mechanical calculations, was performed.

2. Experimental details

Methylene blue (MB, Carlo Erba) was used as sensitizer. The role of MB as singlet oxygen quencher was investigated in methanolic solutions. Kinetic measurements were made at

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different concentrations of MB and TPE. The solvents were of analytical grade obtained from Merck.

The incident radiation was supplied by an incandescent lamp (125 W) at a distance of 3 cm from a reactor constructed of Pyrex glass. An aqueous solution of 2% $K_2Cr_2O_7$ was passed continuously around the reactor to keep it cool and to filter the incident radiation ($\lambda > 550$ nm).

The reaction medium was saturated with oxygen (Oxigênio do Brasil, 99.9%) continuously bubbled into the solution.

The reactions were monitored by gas–liquid chromatography (Shimadzu GC-14A), using a capillary column (phenylmethylsilane, 5%), for measurement of the TPE consumption. The consumption rate is given by

$$\ln C_t - \ln C_o = k^I t$$

where C_t is the concentration of TPE after t min of photolysis, C_o is the initial concentration of TPE and k^I is the pseudo-first-order rate constant related to the consumption of TPE

$$-\frac{d[\mathrm{TPE}]}{dt} = k^I[\mathrm{TPE}] = v_{ox}$$

with $k^I = k_r[{}^1O_2]$, where k_r is the second-order rate constant related to the oxidation of TPE.

The concentration of TPE in the chromatograms was estimated from the peak areas. A fluctuation of less than 5.5% was observed in these measurements.

To confirm whether the reaction is based on the action of singlet oxygen, a Stern–Volmer-like correlation for singlet oxygen quenching using sodium azide (Merck, 99.9%), a well-known singlet oxygen quencher [20], in methanolic solutions ($[\mathrm{TPE}] = 1.00 \times 10^{-4}$ M and $[\mathrm{MB}] = 1.00 \times 10^{-6}$ M) was constructed. A plot of k_0^I/k^I vs. $[N_3^-]$ gives K_{SV} and k_q, the Stern–Volmer constant and singlet oxygen quenching constant due to N_3^- respectively. In parallel, the pseudo-first-order rate constants for reactions performed separately under air and oxygen were compared, using a methodology proposed by Manring et al. [21]. In this case, $[\mathrm{MB}] = 9.93 \times 10^{-6}$ M and $[\mathrm{TPE}] = 0.01 \times 10^{-4}$ M in methanol.

Only benzophenone was isolated as reaction product in reactions with methanol as solvent. Thin layer chromatography (TLC) using silica gel plates and chloroform–cyclohexane (3:1) as eluent and Fourier transform IR (FT-IR) spectrometry (Shimadzu 8101) were used in the characterization. The product was isolated using a glass column (35 cm × 3 cm) packed with dry silica gel. The eluent was the same as used in TLC. The separation was monitored using TLC.

Actinometric measurements were carried out using previously recrystallized Reinecke's salt [22] in order to estimate the photonic flux and Φ_{ox}. From these data, it was possible to estimate k_r in methanol. In chloroform and other solvents, k_r could be estimated directly from k^I.

Theoretical studies were performed using MOPAC 5.0, provided with an AM1 hamiltonian, for quantum mechanical semi-empirical UHF-SCF calculations. Calculations were carried out for ${}^3\Sigma_g^-$ and ${}^1\Delta_g$ oxygen molecules and for TPE. Approach routes of O_2 to TPE were estimated using MOPAC 5.0. For the calculation involving a triplet complex formed between ${}^3O_2$ and TPE, a CI routine was employed. A 486-DX2 66 MHz personal computer was used to perform these calculations.

3. Results and discussion

The oxidation of TPE (Aldrich, 98%) by singlet oxygen was evaluated in different solvents with the aim to correlate the oxidation rate and the dielectric constant (ϵ).

3.1. Singlet oxygen quenching

Fig. 1 shows the Stern–Volmer correlation for singlet oxygen suppression. The plot in Fig. 1 shows a good linear correlation ($r = 0.990$) and demonstrates that sodium azide efficiently quenches the degradation of TPE. This is good evidence that the reaction is promoted by singlet oxygen. The quenching constant was evaluated from the slope ($K_{SV} = 10\,408$ M^{-1}). As $k_q = K_{SV}k_d$ [1,20] and k_d, the rate constant for singlet oxygen natural decay, is equal to 1.4×10^5 s^{-1} [23], k_q is equal to 1.5×10^9 M^{-1} s^{-1}. This value is higher than expected [24]. This discrepancy can be explained, in part, in terms of the ionic strength (I) of the solutions, as proposed by Rubío et al. [25]. On the other hand, the low concentration of the quencher (around 10^{-4} M) implies the complete ionization of this species in solution. The same occurs with MB, which in solution gives ${}^1MB^+$ and Cl^-. The presence of dissociated species in solution must increase the deactivation rate of singlet oxygen, as concluded by Miyoshi et al. [26] and Lindig and Rodgers [27]. These two effects are evidently associated. A deactivation mechanism for singlet oxygen based on the quenching caused by N_3^- has been proposed and is due to the charge transfer interactions between the species [26]. The presence of small amounts of water in the solvent must also have a positive

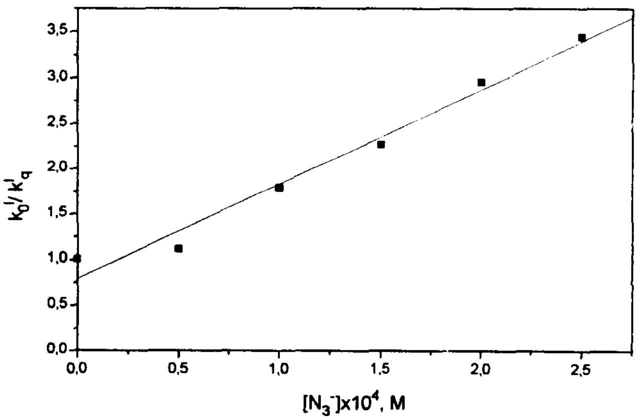


Fig. 1. Stern–Volmer correlation for singlet oxygen quenching induced by sodium azide.

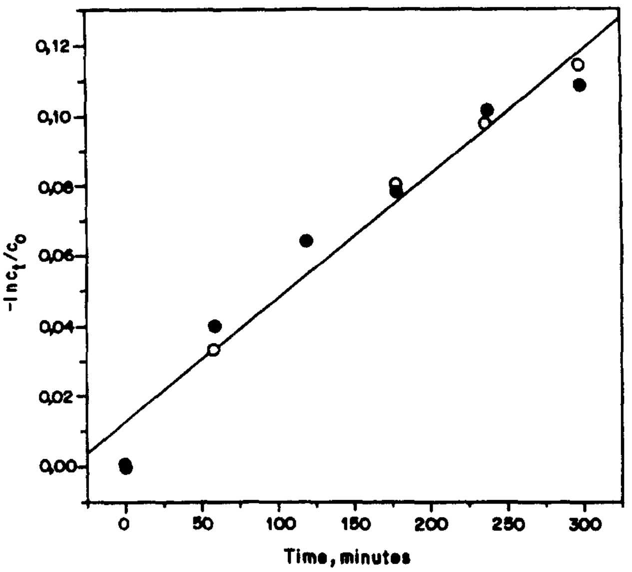


Fig. 2. Estimates of k^I for TPE oxidation under air (○) and oxygen (●) saturation.

influence on I [27] and does not need to be eliminated in these considerations. Although sodium azide is a good singlet oxygen quencher, its characteristics as an electron-rich quencher do not rule out the possibility of a direct electron transfer reaction. As shown in Fig. 2, when monitoring the oxidation under air and oxygen saturation, the pseudo-first-order rate constant due to the disappearance of TPE is the same in both cases. Since reactions induced by singlet oxygen do not depend on the oxygen concentration [21], as observed in the sensitized oxidation of *trans*-stilbene by direct electron transfer, where oxidation is faster in oxygen than in air, these results reinforce the proposed mechanism.

3.2. Proposed mechanism

Since the reaction is promoted by singlet oxygen, the mechanism below is proposed

$$^1MB^+ \xrightarrow{h\nu} {}^1MB^{+*} \xrightarrow{ISC} {}^3MB^{+*} \qquad v = I_a\Phi_T\gamma_\Delta$$

$$^3MB^{+*} + {}^3O_2 \xrightarrow{k_1} {}^1MB^+ + {}^1O_2$$

$$^1MB^+ + {}^1O_2 \xrightarrow{k_S} {}^1MB^+ + {}^3O_2$$

$$Q + {}^1O_2 \xrightarrow{k_q} Q + {}^3O_2$$

$$TPE + {}^1O_2 \xrightarrow{k_r} \text{Product}$$

$$TPE + {}^1O_2 \xrightarrow{k_Q} TPE + {}^3O_2$$

$$^1O_2 \xrightarrow{k_d} {}^3O_2$$

where ISC denotes intersystem crossing, I_a is the number of incident photons per unit time, Φ_T is the quantum yield for triplet state production from MB in the presence of oxygen, γ_Δ is the efficiency of singlet oxygen production and Q denotes the singlet oxygen quencher (sodium azide).

As the solutions were saturated with oxygen, we can suppose that $[^1O_2]$ is constant during the reaction. Then it can be assumed that the concentration of singlet oxygen reaches a steady state during the reaction

$$\frac{d[^1O_2]}{dt} = 0 \qquad (1)$$

The rate law for the consumption of TPE is

$$-\frac{d[TPE]}{dt} = k_r[TPE][^1O_2] = k^I[TPE] = v_{ox} \qquad (2)$$

Then, we can write, based on Eq. (1)

$$I_a\Phi_T\gamma_\Delta - k_d[^1O_2] + (k_r + k_Q)[^1O_2][TPE]$$
$$- k_S[^1O_2][MB] - k_q[^1O_2][Q] = 0$$

Then

$$[^1O_2] = \frac{U_z\Phi_T\gamma_\Delta}{k_d + (k_r + k_Q)[TPE] + k_S[MB] + k_q[Q]} \qquad (3)$$

Substituting in Eq. (2)

$$v_{ox} = \frac{k_r[TPE]I_a\Phi_T\gamma_\Delta}{k_d + (k_r + k_Q)[TPE] + k_S[MB] + k_q[Q]} \qquad (4)$$

Plotting v_{ox}^{-1} vs. $[TPE]^{-1}$, the reactivity parameter β can be obtained

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{k_d + k_S[MB] + k_q[Q]}{k_r + k_Q} = \beta \qquad (5)$$

β corresponds to the substrate concentration at which the rate of natural decay of singlet oxygen is equal to the rate of decay due to all other species present [24,28].

Fig. 3 shows the correlation $[TPE]^{-1}$ vs. v_{ox}^{-1} for $[MB] = 1.00 \times 10^{-6}$ M. This correlation is in good agreement with the proposed mechanism. This procedure was used to evaluate β as a function of [MB].

Considering $[MB] \rightarrow 0$ and $[Q] \rightarrow 0$, we can define β_0 as being related only to the substrate

$$\beta_0 = \frac{k_d}{k_a}$$

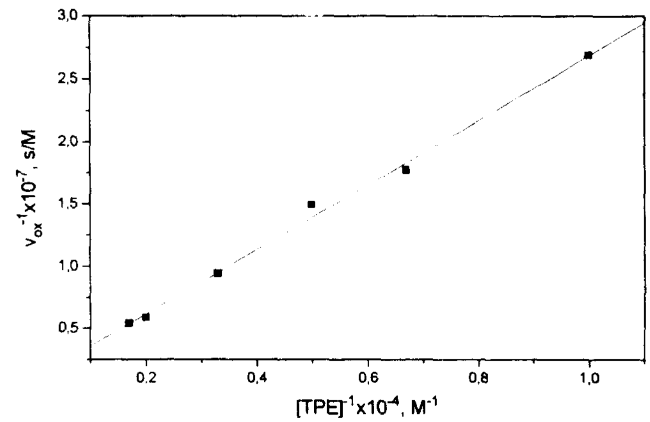


Fig. 3. Correlation between $[TPE]^{-1}$ and v_{ox}^{-1} for TPE oxidation induced by singlet oxygen.

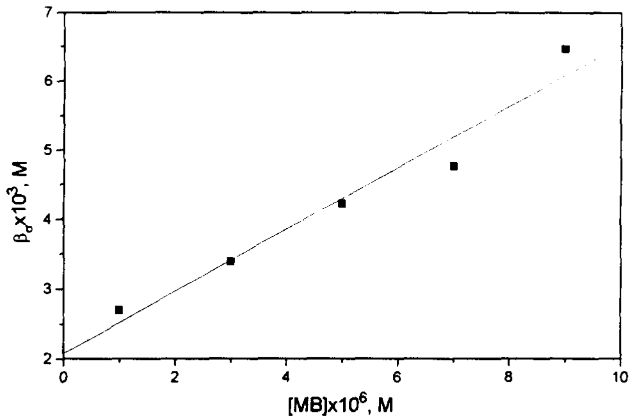


Fig. 4. Dependence of β_S on [MB].

where $k_a = k_r + k_Q$. Substituting this result in Eq. (5), we obtain

$$\beta = \beta_0(1 + k_S\tau_\Delta[\text{MB}] + k_q\tau_\Delta[\text{Q}]) \quad (6)$$

If $[\text{Q}] \rightarrow 0$, we define β_S, the reactivity index which is dependent on [MB], as

$$\beta_S = \beta_0(1 + k_S\tau_\Delta[\text{MB}]) \quad (7)$$

With this we can evaluate the quenching rate due to MB, k_S.

3.3. Singlet oxygen quenching due to MB

In order to determine the singlet oxygen quenching efficiency of MB, as proposed by Tanielian et al. [29], the reactivity index was estimated at different concentrations of MB in methanolic solution. Fig. 4 shows the linear correlation obtained from the plot of [MB] vs. β_S. From the slope of this plot, k_S could be estimated as 3.0×10^{10} M^{-1} s^{-1}.

The magnitude of this value shows that the quenching is essentially physical, and this is confirmed by the fact that the consumption of MB due to reactions with singlet oxygen was not verified. Tanielian et al. [30] observed the bleaching of the sensitizer MB due to consumption during polymer degradation involving singlet oxygen. Bleaching seems to be simultaneous with depolymerization.

MB may be involved in an electron transfer process due to its electron deficiency, although it is a poor electron transfer sensitizer [12]. Despite this, direct interaction between $^3\text{MB}^{+*}$ and TPE cannot be discarded, although it must make a minor contribution to the mechanism

$$^3\text{MB}^{+*} + \text{TPE} \longrightarrow {}^1\text{MB}^0 + \text{TPE}^{\bullet +} \longrightarrow {}^1\text{MB}^+ + \text{TPE}$$

This reaction could compete with the action of singlet oxygen, and could also inhibit the formation of singlet oxygen by quenching $^3\text{MB}^{+*}$. However, the above process should decrease in importance as ϵ is reduced.

Based on the k_S data, it is important in these reactions to avoid a high concentration of MB relative to that of TPE in order to minimize the competition between MB and TPE for singlet oxygen; this will lead to an increase in the action of singlet oxygen on TPE.

The value of β for the interaction of singlet oxygen with TPE was obtained from the intercept in Fig. 4 ($\beta_0 = 2.07 \times 10^{-3}$ M). In this value, the influence of MB on β was eliminated. Thus k_a, the observed rate constant which includes the sum of k_r and k_Q, can be estimated. The value obtained is $k_a = 6.76 \times 10^7$ M^{-1} s^{-1}. This rate constant is at least 10^3 times less than the diffusional limit. Therefore there must be many non-productive collisions between singlet oxygen and TPE which do not lead to oxidation. This also indicates that oxidation must occur with a very low rate because of the formation of a transition state between the reactants, involving a charge transfer interaction, which may or may not give oxidation products.

3.4. Separation of k_Q and k_r from k_a: considerations on the nature of the transition state

The proposed mechanism suggests that k_a is the singlet oxygen quenching constant due to TPE, and involves the sum of the two components mentioned above.

From the definition of the quantum yield, we have

$$\Phi_{\text{ox}} = \frac{([\text{TPE}]_0 - [\text{TPE}])V \times 10^{-3}}{P_0 t}$$

where $[\text{TPE}]_0$ is the molar concentration of TPE before photolysis, [TPE] is the molar concentration of TPE after t min of photolysis, V is the volume of solution submitted to photolysis (ml) and P_0 is the photon flux over the reaction medium (2.96×10^{-5} einsteins min^{-1}) estimated by actinometry.

Considering $[\text{TPE}]_0 = 1.0 \times 10^{-4}$ M and that, after 4 min, $[\text{TPE}] = 0.91 \times 10^{-4}$ M, then $\Phi_{\text{ox}} = 7.6 \times 10^{-4}$ calculated from the above equation. With the relation for Φ_{ox} [28,31]

$$\Phi_{\text{ox}} = \frac{k_r[\text{TPE}]\gamma_\Delta}{k_a([\text{TPE}] + \beta_0)}$$

it is possible to separate k_a into two rate constants: k_Q, related to physical quenching, and k_r, related to chemical quenching (oxidation).

The value of k_r is 2.2×10^5 M^{-1} s^{-1}. With this value we can state that k_a is almost essentially physical. This reinforces the consideration that the oxidation of TPE may involve the interaction of TPE and singlet oxygen, resulting in the formation of a state which has charge transfer character (Scheme 1). The magnitude of k_r varies between 10^5 and 10^7 for many other olefins [24].

Experimental evidence has been collected on the action of singlet oxygen over different substrates, showing that the interaction between the reagents involves the formation of a charge transfer complex [16–18]. With the aim to establish this, the interaction of singlet oxygen and TPE in solvents of different dielectric constant was evaluated.

A linear correlation is obtained when k^1 is related to ϵ (Fig. 5, Table 1).

Two small discrepancies can be observed: (a) when the solvent has a very low ϵ value (the dissolution of MB in chloroform is very difficult to accomplish and therefore the values obtained present a large fluctuation); (b) in the case of a viscous solvent where the value of k^1 is lower than expected. Considering that oxidation is dependent on the migration of the reactants, and that singlet oxygen has a small half-life in alcohols [24], the diffusion of the reagent species must be a limiting factor for oxidation.

The behaviour observed is compatible with that expected if an exciplex state involving charge transfer between singlet oxygen and TPE is formed during collision of the two species. The observed dependence on solvent polarity provides strong evidence for this assumption. The results observed, i.e. the oxidation of TPE is more efficient when the solvent has a small ϵ value, indicate that the formation of a dioxetane intermediate occurs during reorganization of this exciplex state; this process occurs more efficiently under low solvent polarity conditions.

The pseudo-first-order constants were considered to be representative of k_r, based on a study involving methanol and chloroform as solvents. Table 2 shows the constancy of the ratio between $k^1(CHCl_3)$ and $k^1(CH_3OH)$. The fluctuation of 14% can, in large part, be attributed to oscillations caused by the low solubility of MB in chloroform.

3.5. Characterization of the product

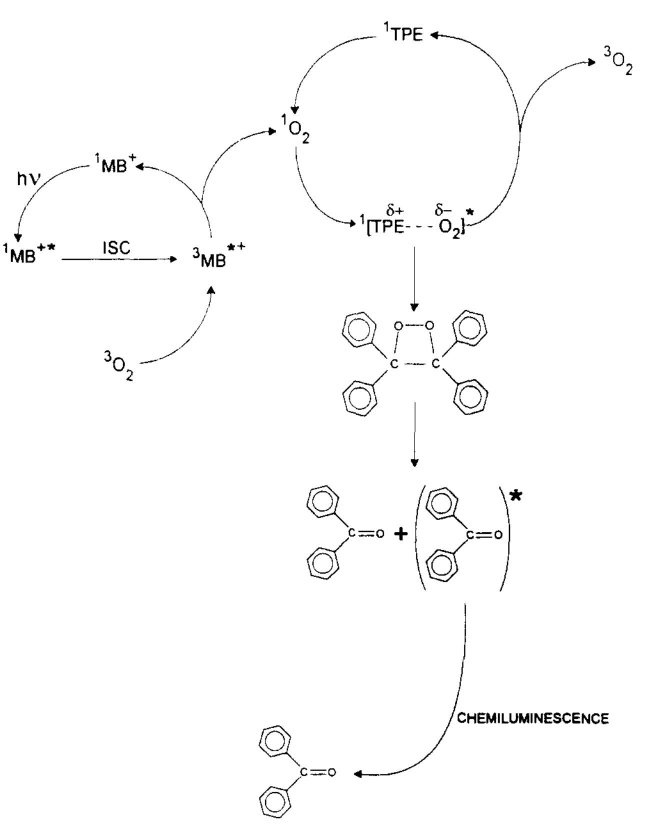
TLC shows that a unique product is obtained in the reaction, whose behaviour is very similar to benzophenone. The FT-IR spectrum of the isolated product is identical to that reported for benzophenone [32]. Despite this, Eriksen et al. [9] have reported that no products are formed during oxidation in acetonitrile induced by singlet oxygen using rose bengal or MB as photosensitizers. However, the same photooxygenation carried out using an electron transfer sensitizer resulted in a number of products [9]. Thus the reaction is dependent on the nature of the solvent used. It must be remembered that the quantum yield estimated for this reaction in methanol is very low ($\Phi_{ox} = 7.6 \times 10^{-4}$), increasing when the solvent polarity is decreased (in chloroform it was estimated to be 0.200).

3.6. Final considerations

AM1 calculations were performed to obtain a Z-matrix for TPE which possessed minimal energy relative to its structure.

Once the geometry was fixed, the physical approach of $^1O_2$ or $^3O_2$ to this molecule was simulated using MOPAC. Several approximations were evaluated. The best approximation occurred when the O–O axis was perpendicular to the C=C bond at the plane formed by atoms 1, 6 and 9, as shown in Fig. 6.

Fig. 7 shows the potential energy profiles for the formation of the exciplex and the triplet complex involving $^1O_2$ and TPE. The minimum on this plot corresponds to the equilibrium distance for the exciplex, and occurs when the nearest oxygen is about 0.42 nm from the C=C bond. The same



Scheme 1.

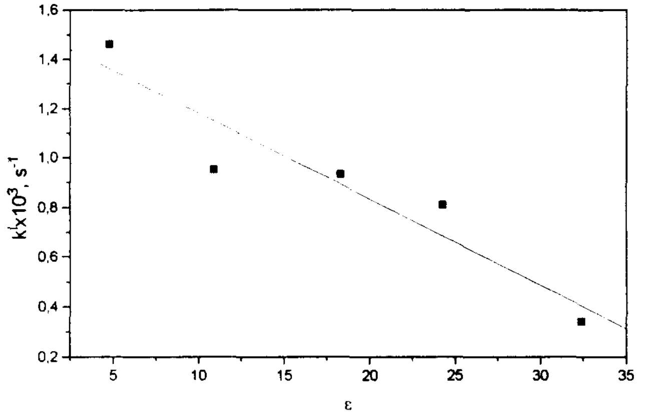


Fig. 5. Correlation between dielectric constant and k^1 for TPE oxidation induced by singlet oxygen.

Table 1
Correlation between ϵ and k^1

Dielectic constant (ϵ)	$k^1 \times 10^3$ (s^{-1})	Solvent
4.8	1.46	Chloroform
10.9	0.95	i-Butanol
18.3	0.93	i-Propanol
24.3	0.81	Ethanol
32.4	0.34	Methanol

$[TPE] = 2.00 \times 10^{-4}$ M. $[MB] = 1.00 \times 10^{-6}$ M.

Table 2
Ratio between $k^1(CHCl_3)$ and $k^1(CH_3OH)$

[TPE] × 10^4 (M)	$k^1(CHCl_3) \times 10^3$ (s^{-1})	$k^1(CH_3OH) \times 10^3$ (s^{-1})	$R = \frac{k^1(CHCl_3)}{k^1(CH_3OH)}$
1.00	1.63	0.372	4.38
1.50	1.45	0.376	3.86
2.00	1.46	0.335	4.36
3.00	1.07	0.356	3.01
4.00	1.38	0.339	4.07

[MB] = 1.00 × 10^{-6} M. $\bar{R} = 3.94 \pm 0.56$.

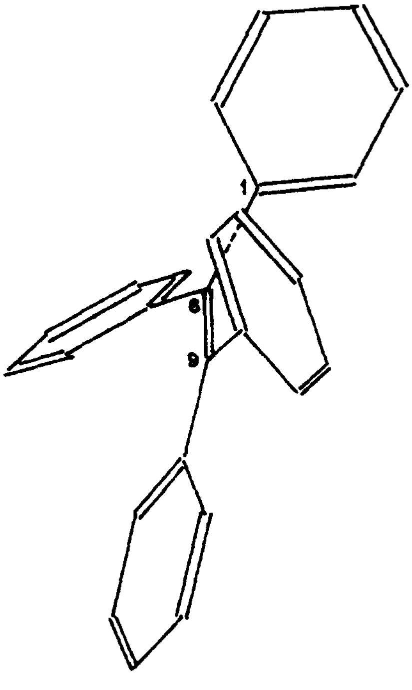


Fig. 6. Structure for TPE calculated from MOPAC using AM1 hamiltonian.

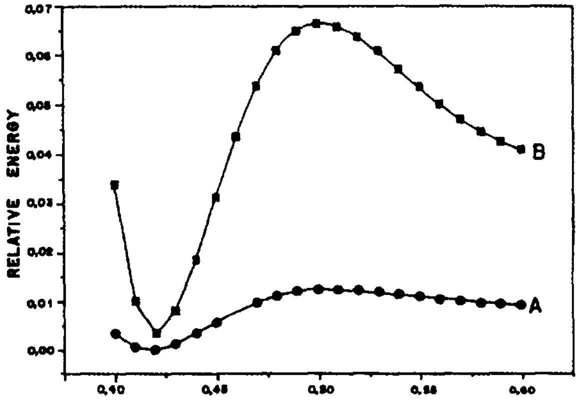


Fig. 7. Potential energy profiles for interaction between oxygen and TPE: (A) $^1O_2$/TPE; (B) $^3O_2$/TPE.

geometry and equilibrium distance were estimated for the approach of $^3O_2$ to TPE.

A structure for the exciplex state involving singlet oxygen and TPE, based on the data collected from semi-empirical quantum mechanical calculations, was obtained and is presented in Fig. 8.

Many computational investigations have been performed on the reaction coordinate for singlet oxygen and an olefin. Controversy still exists. Some calculations [33–35] have shown the possibility of the existence of a perepoxide intermediate; however, other studies have revealed that a biradical structure is more stable than a perepoxide [36,37]. From our calculations, the exciplex is a metastable intermediate possessing a perepoxide-like structure. A small energy barrier (0.126 kJ mol^{-1}), estimated from theoretical calculations, separates this state from the isolated molecules. This barrier shows that the exciplex can be formed easily from collisions of the two molecules, but the reversibility occurring between the exciplex and the separated molecules must also be considered. Nevertheless, the solvent molecules can supply this energy, promoting the separation of the species. The exciplex can undergo reorganization by a concerted reaction [1,38], probably involving a zwitterionic state, resulting in a dioxetane. Charge separation on the oxygen atoms is observed during the simulation of the approach of singlet oxygen to TPE. Increasing solvent polarity results in the deactivation of the exciplex due to better conditions of solvation, leading

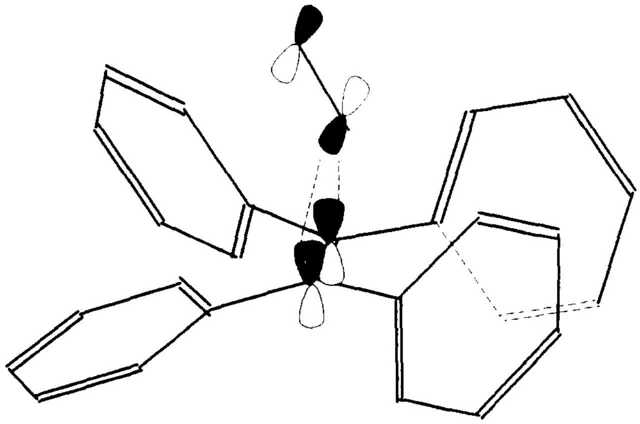
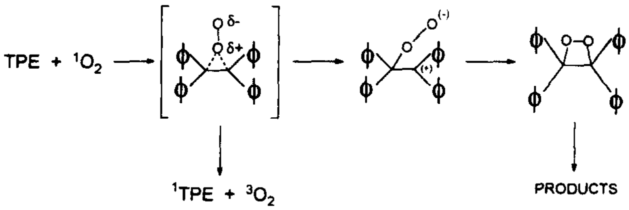


Fig. 8. Structure for the exciplex based on MOPAC calculations.



Scheme 2.

to charge separation between the species. In solvents of low polarity, this is more difficult, since the same charge separation results in poor solvation. Scheme 2 shows the processes involved.

The energy barrier related to the formation of the triplet complex is at least 9.3 times higher than the barrier involved in the formation of the exciplex. This is in agreement with the fact that oxidation occurs preferentially via singlet oxygen. Fig. 7 shows the high reversibility that must be expected after the formation of the exciplex state. The experimental data show that there must be a considerable reversibility associated with the exciplex, and that this reversibility can be reduced with a decrease in solvent polarity (represented by ϵ). This aids the rearrangement of the exciplex resulting in the dioxetane intermediate, which evolves to give benzophenone.

The proposed mechanism is consistent with a reaction based on singlet oxygen as active molecule. However, as TPE is an electron-rich olefin, a route involving electron transfer could be considered if an appropriate sensitizer was used to promote this pathway. It has been reported that MB is a poor sensitizer for electron transfer reactions [12]. Obviously, if TPE oxidation was induced by an electron transfer sensitizer in an appropriate solvent, the oxidation would be more rapid than that observed here. However, it has been demonstrated that certain electron transfer processes can involve competition by a route based on singlet oxygen which increases in importance when the solvent polarity is decreased [13,14].

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