Mechanism of the oxidation of benzylic ethers photosensitized by a 2,4,6-triphenylpyrylium salt

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The photooxidation of various benzyl methyl ether derivatives ($XPhCH_2OMe$, with X = H, 4-MeO, 4-Me, 3-Cl, 4-CF_3 and 3-CF_3) sensitized by 2,4,6-triphenylpyrylium tetrafluoroborate in MeCN, in the presence of oxygen, was investigated by product analysis, fluorescence quenching and quantum yield determinations. The reaction is suggested to proceed through a benzylic radical cation intermediate, formed by electron transfer from the ether to the sensitizer. Besides the back electron transfer reaction, which gives the reactant again, the primarily formed radical cation is deprotonated and the resultant α-methoxybenzyl radical reacts through two different paths to yield benzaldehydes and methyl benzoates in a ratio that depends on the ring substituent. Fluorescence quenching and quantum yield studies have pointed out that (i) the singlet-excited state of the acceptor is mainly involved and (ii) the competition between deprotonation and back electron transfer reaction is regulated by the nature of the substituent. Hydrogen peroxide, detected together with the organic products, has been suggested to be formed in the TPP^+ regeneration process through the involvement of oxygen and the acidity of the medium.

Introduction

In recent years the chemistry of alkylaromatic radical cations has become more and more interesting because of their involvement in organic synthesis, in mechanistic studies and in many fields of application.[1] The most important reaction for this kind of radical cation is the side-chain fragmentation, where C–H, C–C and C–heteroatom bond breaking can compete.

In this area of research, alkyl benzyl and phenyl benzyl ether radical cations have been extensively investigated. In effect, the oxidation reaction, *via* radical cation intermediates, of this class of compounds is attracting growing attention because it provides useful information about the degradation of lignin, since phenyl ethers are simple model compounds for this biopolymer.[2] These intermediates have been generated mainly by a one-electron transfer oxidation of the corresponding ethers by metallic ions or quinones,[3] photochemically by sensitized electron transfer[4] and electrochemically.[5] On the basis of these studies, the breaking of the C–H benzylic bond is undoubtedly favoured, since the radical cations of alkylaromatic derivatives are generally very strong acids,[6] although the possibility of C–O bond cleavage has also been proposed.[5c]

In this paper we report the study of the photochemical behaviour of a series of benzyl methyl ethers ($XPhCH_2OMe$, with X = H, 4-MeO, 4-Me, 3-Cl, 4-CF_3 and 3-CF_3) in the oxidation reaction by photoinduced electron transfer promoted by the 2,4,6-triphenylpyrylium (TPP^+) sensitizer. TPP^+ has been used as a sensitizer in various photoinduced electron transfer reactions,[7] because it offers many advantages, such as not involving superoxide ion or singlet oxygen,[8,9] which could complicate the mechanistic investigation. Benzyl methyl ether derivatives were converted into the corresponding aldehydes and methyl benzoates in the presence of O_2 under visible irradiation of TPP^+ in MeCN. The aim of this study was mainly to evaluate how the nature of the substituent on the ring influences the product distribution and kinetic behaviour. In this context, the results obtained from the product analyses, fluorescence quenching and quantum yield determinations have shown that, in the TPP^+-sensitized oxidation of benzylic ethers, the kinetically important paths are the electron transfer from $XPhCH_2OMe$ to the sensitizer excited state and the following deprotonation of the radical cation formed. A possible mechanism for TPP^+ regeneration in the process has also been suggested.

Table 1 Product yields for TTP^+-sensitized photooxidation of $XPhCH_2OMe$ in O_2-saturated MeCN[a]

			Products (%)	
X	*t*/min	Reactant (%)	XPhCHO	XPhCOMe
4-OMe[b]	30	51	29	14
4-Me	45	45	22	33
H	45	51	16	33
3-Cl	510	53	12	35
4-CF_3	510	90	1.1	5.4

[a] Yields determined with respect to the initial moles of substrate; $[TTP^+] = 5.0 \times 10^{-4}$ M; $[XPhCH_2OMe] = 1.0 \times 10^{-2}$ M. [b] Traces of 4-$MeOPhCH_2OH$ and 4-$MeOPhCH_2NHCOMe$ were also detected.

Results

Product characterization

Irradiation at 410 nm (light absorbed exclusively by the sensitizer) of MeCN solutions containing catalytic amounts of TPP^+ (5.0×10^{-4} M) and benzylic methyl ethers (1.0×10^{-2} M), in the presence of bubbling O_2, gave benzaldehydes and methyl benzoates as shown in eqn. (1). Product yields are reported in Table 1.

$$XPhCH_2OMe \xrightarrow[\text{MeCN, } O_2]{TPP^+,\ h\nu} XPhCHO + XPhCOOMe \quad (1)$$

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Table 2 Reduction potentials (E_p) of $XPhCH_2OMe$, free energy changes (ΔG_{et}) for the electron transfer from the donors to the excited singlet, Stern–Volmer constants (K_{SV}) and fluorescence quenching rate constants (k_q)

X	$E_p{}^a$/V (*vs.* SCE)	$\Delta G_{et}{}^b$/kJ mol^{-1}	$K_{SV}{}^c$/M^{-1}	$10^9\,k_q{}^d$/M^{-1} s^{-1}
4-OMe	1.55	−85.8	102	24
4-Me	1.98	−44.3	65	15
H	2.23	−20.1	56	13
3-Cl	2.30	−13.4	37	8.8
3-CF_3	2.70	25.1	0.38	0.09
4-CF_3	2.80	34.7	0.17	0.04

[a] Measured by cyclic voltammetry in MeCN $LiClO_4$. [b] Calculated according to eqn. (3), see text. [c] Slopes of the plots ($I/I_o - 1$) *vs.* [$XPhCH_2OMe$] in MeCN. [d] Taking $\tau_s = 4.2$ ns.[10]

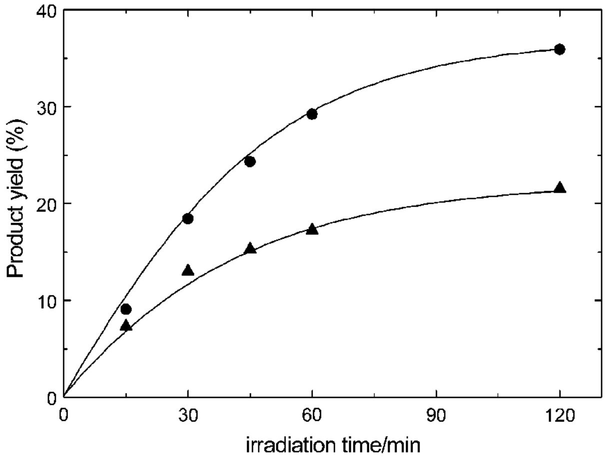


Fig. 1 Product yield *vs.* irradiation time for the photooxidation of $PhCH_2OMe$ (1.0×10^{-2} M) sensitized by TPP^+ (5.5×10^{-4} M) in O_2-saturated MeCN (●: methyl benzoate, ▲: benzaldehyde).

Analysis of these data suggests that for $PhCH_2OMe$ and ethers ring substituted by electron donating groups (X = 4-MeO, 4-Me), the conversions are high after just a short irradiation time, whereas with electron-withdrawing groups (X = 3-Cl and 4-CF_3), detectable yields are obtained only after some hours. Furthermore, the ratio between aldehyde and ester decreases on going from 4-MeO to 4-CF_3. In the experiments carried out at a different irradiation time for each substrate, this ratio remained constant, showing that the two compounds are formed through parallel reactions. For example, in the experiment performed with $PhCH_2OMe$ (Fig. 1), the value of the PhCHO : PhCOOMe ratio is *ca.* 1 : 2 at each irradiation time. Benzaldehyde (42% after 45 min) was the only product when the reactions were carried out without O_2 (by bubbling N_2 through solutions containing equimolar amounts of $PhCH_2OMe$ and TPP^+).

The catalytic efficiency of TPP^+ was evaluated by recording the absorption spectra before and after irradiation. For example, when a solution of 6.1×10^{-4} M TPP^+ and 1.1×10^{-2} M 4-$MeOPhCH_2OMe$ was irradiated for 30 min, the recovered amount of unreacted sensitizer was 50% (with respect to the starting material), while a 45% product conversion was obtained. This finding indicates that *ca.* 20 times less TPP^+ was consumed, if compared with the amount of product obtained. Furthermore, if the same reaction was performed without O_2, only traces of 4-MeOPhCHO were obtained and both substrate and sensitizer were largely recovered. Hence, TTP^+ acts as a catalyst in the photooxidation of ethers and O_2 must be present for it to be regenerated.

In addition to aldehydes and esters, hydrogen peroxide was also recovered. The amount of this product was determined, after work-up of the raw mixture, in the aqueous phase derived from the elaboration procedure (see Experimental). For example, in the photooxidation of 1.1×10^{-2} M $PhCH_2OMe$ with 5.0×10^{-4} M TPP^+ in MeCN, after 45 min of irradiation in the presence of O_2, 51% of the ether had not reacted. This was recovered along with 16% benzaldehyde, 33% methyl benzoate and 21% H_2O_2 (the percentages are based on the initial moles of ether). The H_2O_2 formation is very likely involved in the regeneration process of TTP^+ as discussed below.

Fluorescence quenching

The involvement of an excited singlet state of TPP^+ in the photooxidation process was established by a fluorescence quenching study. The fluorescence experiments were performed by recording the fluorescence emission intensity of TTP^+ alone (I_o) and in the presence of ether (I) at various ether concentrations ([Q]). All of the ethers efficiently quenched the TPP^+ fluorescence. The plots I_o/I *vs.* [Q] fitted the Stern–Volmer equation [eqn. (2)], giving the Stern–Volmer constants (K_{SV})

$$I_o/I = 1 + K_{SV}[Q] \qquad (2)$$

collected in Table 2, together with the quenching rate constants, $k_q = K_{SV}/\tau_s$, calculated[10] taking τ_s, the $^1TPP^{+*}$ lifetime, as 4.2 ns.

Quantum yield

In order to clarify whether the excited singlet is the only state responsible for the reaction and to obtain kinetic information about the steps following the primary photochemical process, the quantum yields (Φ) were determined.

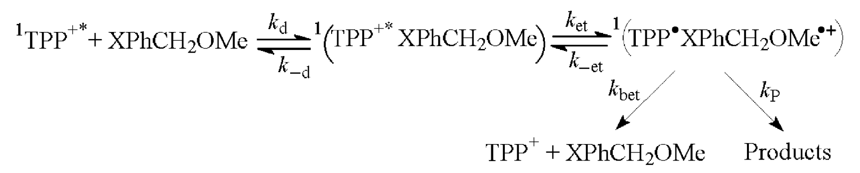
The quantum yields for the formation of the products (benzaldehydes and methyl benzoates) were determined in air-equilibrated MeCN solutions containing 5.0×10^{-4} M TPP^+ and $XPhCH_2OMe$ at different initial concentrations (0.003 to 0.10 M). With X = 4-Me, H and 3-Cl, the Φ values increased as the $XPhCH_2OMe$ concentration increased, approaching a limiting value at infinite concentration (Φ_{lim}). As an example, the dependence of Φ on the formation of PhCHO, PhCOOMe and the sum of both compounds as a function of [$PhCH_2OMe$] is shown in Fig. 2. Moreover, the plot of Φ^{-1} *vs.* [$XPhCH_2OMe$]$^{-1}$ is linear for all three substrates (Fig. 3).

It must be noted that the very low reactivity of 3- and 4-CF_3PhCH_2OMe did not allow the quantum yield to be determined as a function of the concentration, because the Φ value determined at high substrate concentration (5.0×10^{-2} M) was very low (≤0.004).

Discussion

The fluorescence quenching of TPP^+ by ethers very likely occurs *via* electron transfer from the substrate to the excited singlet state of TPP^+. Indeed, the photoinduced electron transfer is expected to be favoured according to the free energy changes (ΔG_{et}) estimated[11] by the Rehm–Weller expression [eqn. (3)]. The ΔG_{et} values, reported in Table 2, were negative for all the ethers investigated except 3-CF_3- and 4-CF_3PhCH_2OMe for which the process is slightly endergonic.

$$\Delta G_{et}/\text{kJ mol}^{-1} = 96.48[E(D^+/D) - E(TPP^+/TPP^\bullet)] - E_{0\text{-}0} \qquad (3)$$



Scheme 1

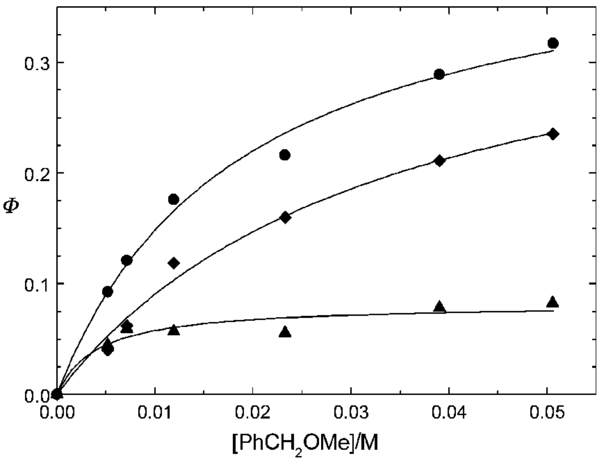


Fig. 2 Plot of Φ *vs.* [PhCH$_2$OMe] for the photooxidation of PhCH$_2$OMe by TTP$^+$ (5.0×10^{-4} M) in air-saturated MeCN (▲: quantum yield of PhCOOMe formation; ◆; quantum yield of PhCHO formation; ●: total quantum yield).

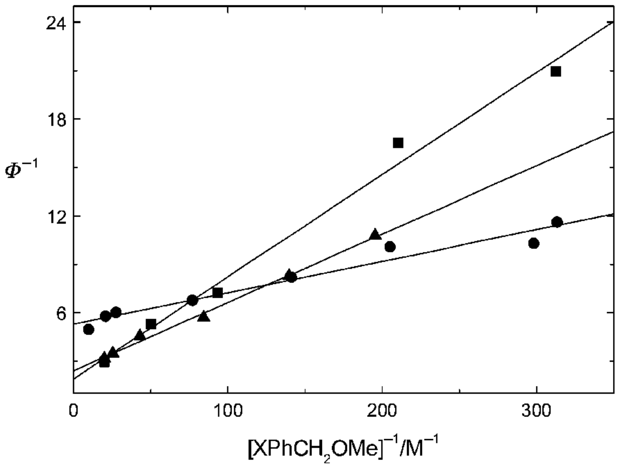


Fig. 3 Plot of Φ^{-1} *vs.* [XPhCH$_2$OMe]$^{-1}$ for the photooxidation of XPhCH$_2$OMe (■: X = 3-Cl; ▲: X = H; and ●: X = Me) by TPP$^+$ (5.0×10^{-4} M) in air-saturated MeCN.

In this equation, $E(D^+/D)$ is the reduction potential of the donor (the values are reported in Table 2), $E(TPP^+/TPP^•)$ is the reduction potential of TPP$^+$, taken as −0.29 V (*vs.* SCE)[12] and E_{0-0} is the singlet excitation energy of the sensitizer, taken[13] as 272 kJ mol^{-1}. The electrostatic term, $e^2/\varepsilon a$, which, in this case is the energy gained in bringing the neutral radical TPP$^•$ and the radical cation into an encounter distance a in a solvent of relative permittivity ε, was neglected, because TPP$^+$ is positively charged and, therefore, there is no charge change upon electron transfer. The general kinetic scheme for the fluorescence quenching by electron transfer in the present system is shown in Scheme 1, where ^{1}TPP^{+*} and the ether diffuse to reversibly form the precursor complex (k_d and k_{-d}) which, by reversible electron transfer reaction (k_{et} and k_{-et}), gives the successor complex. By back electron transfer (k_{bet}), this complex either forms the initial species or evolves to the products (k_P). By applying the steady-state treatment to the various intermediates of Scheme 1 and assuming $k_{bet} \gg k_{-et}$, the quenching rate constant (k_q) is obtained [eqn. (4)].

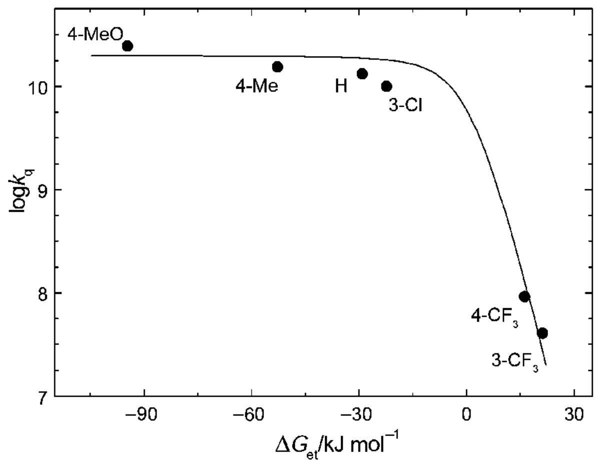


Fig. 4 Plot of log k_q *vs.* ΔG_{et} for electron transfer from XPhCH$_2$OMe to ^{1}TTP^{+*}. The curve was obtained using $\Delta G^‡$ from the Rehm–Weller relationship [eqn.(6).]

$$k_q = k_{et}/(1 + k_{-d}/k_{et}) \qquad (4)$$

By substituting k_{et} with $Z\exp(-\Delta G^‡/RT)$, where Z is the frequency factor and $\Delta G^‡$ is the activation Gibbs energy change for the electron transfer, eqn. (5) is derived.

$$k_q = k_d/[1 + k_{-d}/Z\exp(-\Delta G^‡/RT)] \qquad (5)$$

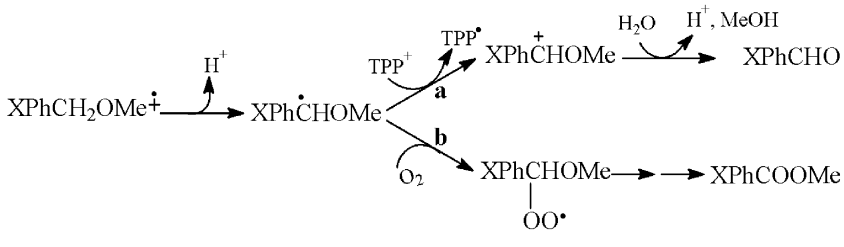
In Fig. 4 a plot of log k_q *vs.* ΔG_{et} is presented. As shown, the experimental points are fitted well by eqn. (5), in which $\Delta G^‡$ was substituted by the Rehm–Weller relationship [eqn. (6)],[11]

$$\Delta G^‡ = \Delta G_{et}/2 + \sqrt{(\Delta G_{et}/2)^2 + (\lambda/4)^2} \qquad (6)$$

confirming that the quenching occurs by electron transfer. In this equation, λ is the total reorganization energy (bonds and solvent) during the electron transfer process.

The best fit was obtained using the following parameters: $k_d = 2 \times 10^{10}$ M^{-1} s^{-1},[14] $k_{-d} = 2 \times 10^{10}$ s^{-1} and $Z = 5 \times 10^{12}$ s^{-1}. The λ parameter, optimized by the fitting, was 63 kJ mol^{-1}, a value higher than that (40 kJ mol^{-1}) obtained for the photooxidation of the same class of substrates sensitized by the excited singlet state of cyanoaromatics.[11] This is understandable because the positive charge is mainly localized on the oxygen atom of ^{1}TPP^{+*}, and therefore the electron transfer should likely require a reorganization energy that is larger than that required for cyanoaromatics, which have a structure with a more delocalized electronic density.

The products formed by the photooxidation of benzylic methyl ethers can be explained by the mechanism reported in Scheme 2. The radical cation of the ether, produced by electron transfer to the sensitizer, deprotonates to give the substituted α-methoxybenzyl radical, which may then react according to two paths: (i) oxidation to the corresponding carbonium ion (step a), which, through a hemiacetal intermediate, leads to the formation of benzaldehyde and methanol, as previously reported for the anodic[5d] and TiO$_2$-sensitized[4d] oxidation of benzyl ethers; (ii) capture of the α-methoxybenzyl radical by oxygen to produce the benzylic peroxide radical (step b), which,



Scheme 2

by further oxidation to carbonyl group, gives substituted methyl benzoates. Analogous mechanisms for the formation of methyl benzoates have already suggested in the photooxidation of benzyl ethers on irradiated TiO_2.[4a,d]

The increase of the benzaldehyde/benzoate value on going from ethers substituted by electron-donor groups to those with electron-withdrawing groups (Table 1) is well explained by Scheme 2. Indeed, the oxidation of the alkoxy radical to the carbocation (step a), probably by the ground state of TPP^+, should be more favourable if an electron donor on the ring stabilizes the positive charge.[15,16] Moreover, the oxidation of 4-$MeOPhCH_2OMe$, photosensitized by 9,10-dicyanoanthracene (DCA), gave an aldehyde/ester quotient of 0.17, compared with 2.1 obtained with TPP^+ (see Table 1), in agreement with the lower oxidant capacity of DCA ($E°_{DCA/DCA^{\cdot-}} = -0.89$ *vs.* SCE in MeCN[18]).

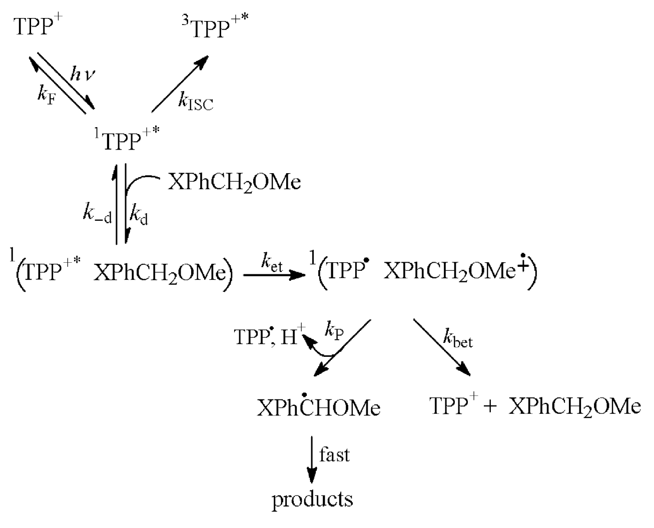
The presence of H_2O_2 among the products can be associated with the regeneration process of the sensitizer. It is already known that TPP^+ may be regenerated by the reaction of $TPP^\cdot$ in the presence of added acid and O_2,[10,19] yielding $HO_2^\cdot$ which disproportionates giving H_2O_2 and O_2 [eqn. (7) and (8)]. In this

$$TPP^\cdot \xrightarrow{O_2,\ H^+} TPP^+ + HO_2^\cdot \qquad (7)$$

$$2\,HO_2^\cdot \rightarrow H_2O_2 + O_2 \qquad (8)$$

case, even if no acid is added, the acidity of the medium could be sufficient so that reactions (7) and (8) may occur.

Concerning the dependence of quantum yields on the ether concentration in the presence of O_2, the results can be explained by the mechanism depicted in Scheme 3. The excitation of TPP^+ gives $^1TPP^{+*}$, which decays by a radiative pathway (k_F), which goes back to the ground state, and by an nonradiative pathway (k_{ISC}), which forms the triplet state $^3TPP^{+*}$. In the absence of quencher only these decay paths ($\Phi_F = 0.52$ and $\Phi_{ISC} = 0.48$)[7] are possible. In the presence of ether, the excited singlet state is quenched by electron transfer reaction (k_{et}), after the diffusion of the two reactants (k_d, k_{-d}). The triplet state $^3TPP^{+*}$ might also be quenched by electron transfer, but in a first approximation, it has been assumed that only the singlet excited state is involved in the process. The electron transfer process may be followed by the deprotonation step of the radical cation (k_P), which may compete with the back electron transfer process (k_{bet}). The steps following the proton transfer reaction, which give the final products, are supposed to be fast.



Scheme 3

Table 3 Quantum yield determinations for TTP^+-sensitized photooxidation of $XPhCH_2OMe$ in air-saturated MeCN[a]

X	$k_q\tau^a$/M	$\Phi_{lim}{}^b$	$k_P/k_{bet}{}^c$
4-Me	271	0.18	0.23
H	56	0.42	0.72
3-Cl	30	0.53	1.1

[a] Intercept/slope values from plots in Fig. 3. [b] Quantum yields of benzaldehyde and methyl benzoate formation at infinite ether concentration obtained from the intercepts of plots in Fig. 3. [c] Ratio calculated by eqn. (12).

By applying the steady-state approximation to the reactive species, the dependence of Φ can be derived [eqn. (9)]:

$$\Phi = \frac{k_P k_d k_{et}[XPhCH_2OMe]}{(k_{et}k_d[XPhCH_2OMe] + k_{-d}\tau_s^{-1} + k_{et}\tau_s^{-1})(k_P + k_{bet})} \qquad (9)$$

If eqn. (9) is rewritten as eqn. (10), a linear correlation

$$\frac{1}{\Phi} = \frac{k_P + k_{bet}}{k_P}\left(1 + \frac{k_{-d} + k_{et}}{k_d k_{et}\tau_s[XPhCH_2OMe]}\right) \qquad (10)$$

between 1/Φ *vs.* 1/[ether] is observed, in agreement with what was found experimentally (Fig. 3).

According to eqn. (10) the intercept to slope ratio (*i*/*s*) is given by eqn. (11).

$$i/s = k_d\tau_s/(1 + k_{-d}/k_{et}) = k_q\tau_s \qquad (11)$$

By comparing eqn. (11) with eqn. (4), this ratio coincides with the Stern–Volmer constant. From the plots shown in Fig. 3, the *i*/*s* quotients for 4-$MePhCH_2OMe$, $PhCH_2OMe$ and 3-$ClPhCH_2OMe$ are obtained (Table 3). The last two values agree very well with the K_{SV} (56 and 37 M^{-1}) derived from the fluorescence quenching of $PhCH_2OMe$ and 3-$ClPhCH_2OMe$, respectively (Table 2). Such an agreement strongly supports the pathway initiated by the excited singlet state of TPP^+ in Scheme 3.

The K_{SV} value of 4-$MePhCH_2OMe$, (65 M^{-1}, Table 2) is rather different from that obtained by quantum yield measurements, therefore the excited triplet state probably plays an important role in this process too. The free energy changes for the electron transfer from 4-$MePhCH_2OMe$ to the triplet state of $TPP^+$is −2.7 kJ mol^{-1}, taking into account that the triplet excitation energy is 222 kJ mol^{-1}. This slight exergonicity evidently makes this reaction possible (at least with a low concentration of 4-$MePhCH_2OMe$ where the $^3TPP^{+*}$ concentration is significant) and competitive[8] with the reaction of

^{3}TPP^{+}* with O_2. This reaction is much more endergonic with $PhCH_2OMe$ and 3-$ClPhCH_2OMe$ and, therefore, the only state involved in the photooxidation of these two substrates is the singlet state.

The Φ_{lim} values, determined from the intercept of the straight lines of Fig 3, are reported in Table 3; from these values k_p/k_{bet} ratios (see Table 3) can be calculated by eqn. (12) [obtained from eqn. (9) at infinite ether concentration].

$$\Phi_{\text{lim}} = k_p/(k_p + k_{\text{bet}}) \qquad (12)$$

The values of Φ_{lim} and k_P/k_{bet} reported for 4-$MePhCH_2OMe$ are obtained by using the same procedure and taking into account that no triplet state molecules of TPP$^+$ are present in the system at infinite concentration (where ^{1}TPP^{+}* is completely quenched). The k_P/k_{bet} values increase on going from 0.23 for 4-$MePhCH_2OMe$ to 1.1 for 3-$ClPhCH_2OMe$; it is also plausible to suppose that this value increases further with ethers substituted with more electron-withdrawing groups such as 3- and 4-CF_3 derivatives, even if Φ_{lim} data are not available due to their low reactivity. The observed behaviour may be explained by considering that strong electron-donating groups slow down the deprotonation of $XPhCH_2OMe^{+\bullet}$, because an increase in the electron-donor ability of the substituent leads to a worse acidity of the radical cation.[20] At the same time, assuming that the very exergonic back electron transfer occurs in the Marcus inverted region,[21] this reaction should proceed faster for the radical cations $XPhCH_2OMe^{+\bullet}$ with X as an electron donor (a more exergonic process). The opposite situation occurs for deactivated ethers: withdrawing substituents on the benzyl ether should disfavour the back electron transfer process and, at the same time, they should improve the acidity of the corresponding radical cations.

Conclusions

This paper reports the photooxidation of a series of substituted benzyl methyl ethers sensitized by TPP$^+$ in the presence of O_2 in MeCN. The process occurs *via* electron transfer from the ether to excited TPP$^+$. For all ethers only the excited singlet state of the sensitizer seems to be involved in the process, except for 4-$MePhCH_2OMe$, in which the involvement of the excited triplet state has also been suggested. According to the nature of the substituent, a significant balance is established between the electron and proton transfer capability of $XPhCH_2OMe$ and $XPhCH_2OMe^{+\bullet}$, respectively. Moreover, the deprotonation competes with the back electron transfer reactions. In particular, electron donors accelerate the back electron transfer and slow down the deprotonation; the opposite occurs with electron acceptors.

Finally, TPP$^+$, like other sensitizers,[22] can be efficiently regenerated by the acidity in the medium and oxygen.

Experimental

Materials

2,4,6-Triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$, Aldrich) was commercially available and was used without further purification. The benzylic ethers were prepared by reaction of the corresponding benzylic alcohol with CH_3I in dimethyl sulfoxide, according to a procedure reported in the literature.[23] Acetonitrile (Fluka, spectrophotometric grade) was used as received.

Instrumentation

UV–VIS spectra were recorded on a Diode Array HP 8451A spectrophotometer. Emission measurements were performed with a Spex Fluorolog F 112AF spectrofluorimeter. ^{1}H-NMR spectra were run on a Bruker AC 200 (200 MHz) spectrometer in $CDCl_3$. GC-MS analyses were performed on a HP 6890A gas chromatograph (HP-5-MS capillary columns, 30 m) coupled with a MSD-HP 5973 mass selective detector (70 eV). GC analyses were carried out on a HP 5890 gas chromatograph, using a HP-Innovax capillary column. E_p values were obtained with an AMEL 552 potentiostat controlled by a programmable AMEL 568 function generator (cyclic voltammetry at 100 mV s^{-1}, 1 mm diameter platinum disc anode) in CH_3CN–$LiClO_4$ (0.1 M).

Photooxidation reaction

A solution prepared by dissolving TPP$^+$ (0.05 mmol) and a benzylic ether (0.1 mmol) in 10 ml MeCN was irradiated in an Applied Photophysics multilamp apparatus with twelve phosphor-coated fluorescent lamps (15 W each) emitting at 355 nm ($\Delta\lambda_{\frac{1}{2}} = 20$ nm), at running water temperature (*ca.* 15 °C), with oxygen bubbling through the solution. After irradiation, the residual TPP$^+$ was evaluated by spectrophotometric determinations. The reaction mixture was worked up with water to remove the pyrylium salt and then extracted with diethyl ether. The solvent was evaporated and the residue analyzed. The products were identified by ^{1}H-NMR and GC-MS comparison with authentic samples. Product yields were determined by ^{1}H-NMR and GC analysis, using bibenzyl or durene as an internal standard.

The amount of H_2O_2 was quantitatively determined by titration with iodide ion; the aqueous solution, obtained from the work-up of the reaction mixture, was treated, after dilution, with an excess of NaI and the amount of I_3^- formed was determined from UV spectra ($\varepsilon = 2.50 \times 10^4$ M^{-1} cm^{-1} at $\lambda_{\text{max}} = 361$ nm).[24] The H_2O_2 determination could not be carried out directly on the MeCN solution, due to the interference of TPP$^+$ absorption in the spectrophotometric analysis of I_3^-. Blank experiments, performed by keeping a solution of TTP$^+$ and ether in the dark, showed no formation of H_2O_2.

Quantum yield determinations

A solution (3 ml) of TPP$^+$ (5.0×10^{-4}M) and benzylic ether at various concentrations (0.003 to 0.1 M) in MeCN was placed in a quartz cuvette and irradiated with two phosphor-coated fluorescent lamps emitting at $\lambda = 355$ nm. O_2 was bubbled through the solution before and during irradiation, under magnetic stirring. The final amount of TPP$^+$ was quantified by spectrophotometric measurements. The internal standard was then added (bibenzyl or durene) and product formation was determined by ^{1}H-NMR and/or GC analysis. Conversion to products never exceeded 10%. Light intensity was measured by potassium ferric oxalate actinometry (1.5×10^{-8} einstein s^{-1}).

Fluorescence quenching measurements

Fluorescence quenching experiments were carried out at room temperature (22 °C). The excitation wavelength of TPP$^+$ was $\lambda = 405$ nm, while the monitoring wavelength was $\lambda = 464$ nm, which corresponds to the maximum of the emission band. Relative emission intensities were measured for an air-equilibrated MeCN solution containing TPP$^+$ (6.0×10^{-6} M), with benzylic ether at various concentrations (0.004 to 0.1 M). Fluorescence quenching in the presence of the ether derivative always gave linear Stern–Volmer plots.

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