PERKIN 2

Photoionization of α-alkoxybenzyl radicals to yield α-alkoxybenzyl cations. Photochemistry of ω,ω-dimethoxy-ω-phenylacetophenone in polar solvents at high light intensities

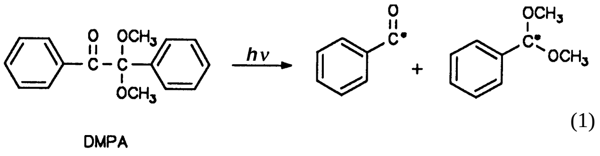
Joaquim Luís Faria[1] **and Steen Steenken**

Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim, Germany

On photolysis of the photopolymerization initiator $PhC(O)C(OMe)_2Ph$ in aqueous or alcoholic solution with 248 nm laser pulses or with 248 nm followed by 308 nm pulses (two-laser–two-colour technique), the short-lived species $PhC^{\bullet}(OMe)_2$, $PhC^{+}(OMe)_2$ and e^{-}_{solv} were detected by their optical absorptions. The carbocation $PhC^{+}(OMe)_2$ and e^{-}_{solv} are the products of the monophotonic ionization of the radical $PhC^{\bullet}(OMe)_2$ [φ(308 nm) = 0.2 in aqueous solution] generated from the parent, $PhC(O)C(OMe)_2Ph$, by α-cleavage [φ(248 nm) *ca.* 0.5]. $PhC^{+}(OMe)_2$ reacts with water to produce the hemi-orthoester $PhC(OMe)_2OH$ and H^{+} which was identified by time-resolved conductance. $PhC(OMe)_2OH$ decomposes to yield $PhC(O)OMe$ and MeOH (identified by GC). The α-alkoxybenzyl radicals $PhCH^{\bullet}OR$, produced by 248 nm photoinduced α-cleavage of the benzoin ethers $PhC(O)CH(OR)Ph$ (R = Me, Et, Pr^i, Bu^t), also undergo ionization upon 248 or 308 nm photolysis. The rate constants for reaction of $PhCH^{\bullet}OR$ with the oxidants $Fe(CN)_6^{3-}$, $Ir(Cl)_6^{2-}$, O_2 and PhI^{2+} are on average 5.9×10^9, 4.2×10^9, 2.8×10^9 and 1.7×10^8 dm^3 mol^{-1} s^{-1}, respectively. From the facile photoionization of the α-alkoxybenzyl radicals it is concluded that this process may also take place under the typical high-intensity light conditions used in industrial photocuring, *i.e.* that the latter may involve cationic polymerization.

Introduction

ω,ω-Dimethoxy-ω-phenylacetophenone [$PhC(O)C(OMe)_2Ph$, DMPA] is a photopolymerization initiator and photocuring agent of great industrial importance. For this reason, its photochemistry[2–7] and that of related compounds[8–12] have received considerable and continuing attention. From these studies it has been concluded that upon electronic excitation the DMPA molecule undergoes, probably from a triplet state,[2,13] a very rapid ($k \geqslant 10^{10}$ s^{-1}) and efficient ($\varphi = 0.15$–0.5)[14] α-cleavage (Norrish type I)[15] of the central C–C bond to yield the benzoyl radical, $PhC^{\bullet}O$ and the α,α-dimethoxybenzyl radical, $PhC^{\bullet}(OMe)_2$, eqn. (1).



(1)

DMPA

The α,α-dimethoxybenzyl radical is thermally and, as shown recently,[5,6,13] also photochemically labile, cleaving (in benzene or acetonitrile solution) to yield methyl benzoate and methyl radical, eqn. (2). This reaction is an example for a more general

$$PhC^{\bullet}(OMe)_2 \xrightarrow{h\nu \text{ or heat}} PhC(O)OMe + Me^{\bullet} \qquad (2)$$

fragmentation reaction characteristic of α-alkoxy-alkyl or -benzyl radicals in which oxo compounds and alkyl radicals are formed.[16–18]

The photochemical decomposition of $PhC^{\bullet}(OMe)_2$ has been studied using product analysis, CIDNP, ESR,[5,13] and optical techniques.[5,6,13] A quantum yield of 0.5 or 0.8 was reported[5,6] for destruction of the radical and it was assumed that this reaction proceeds only by O–Me homolysis, eqn. (2). However, it has recently been shown that benzyl-type radicals tend to undergo photoionization in polar environments,[19–23] and this reaction mode is expected to be particularly favourable for α-(di)alkoxybenzyl radicals, due to their low ionization potentials.[24] On photoionization of radicals, carbenium ions (carbocations) are produced, and these species can initiate cationic polymerization. In fact, many industrial applications of DMPA as photocuring agent in the hardening of surface coatings and inks are based on the conversion of the radicals produced in the cleavage of DMPA *via* a bimolecular reaction with suitable oxidants (typically onium salts) to yield cations.[25–29] It is these cations, in other words, the one-electron oxidized radicals, which initiate the chain reaction leading to polymerization, *e.g.* of epoxides, cyclic ethers and vinyl ethers.[28] Compounds such as DMPA have been termed ‘promoters’ of cationic polymerization.

If radicals are photoionized, cations are directly formed, *i.e.* without oxidants and much more rapidly than under conditions of their bimolecular production by oxidation of the precursor radicals. In the following, we will present evidence for photoionization of α-alkoxybenzyl radicals and compare this method with that of chemical oxidation.

Experimental

ω,ω-Dimethoxy-ω-phenylacetophenone [$PhC(O)C(OMe)_2Ph$, DMPA] and $PhC(O)CH(OR)Ph$ (R = Me, Et, Pr^i, Bu^t) were obtained from Ciba-Geigy in a purity ⩾ 97% and used as received. Benzaldehyde dimethyl acetal (from Aldrich) was distilled prior to use to a purity ⩾ 99.8%. $K_3Fe(CN)_6$ and CH_3CN (‘Uvasol’) were from Merck, Na_2IrCl_6 from Ventron, and $[CF_3C(O)O]_2$ IPh from Aldrich. In order to speed up dissolution of the organic solutes in water (purified with a Millipore Milli-Q system), they were predissolved in isopropyl alcohol (Merck; purity ⩾ 99.7%), followed by addition of water (⩾ 95% v/v total solvent content) containing 1 mM Na_2HPO_4 to prevent the solutions from becoming acidic. The concentrations of DMPA or the benzoin ethers were typically 0.1 mM, which corresponds to an absorbance (A) at 248 nm of *ca.* 1 and 0.05 cm^{-1} at 308 nm, respectively.

The deoxygenated aqueous solutions were flowed through the 2 mm (in the direction of the laser beam) by 4 mm (direction of the analysing light) Suprasil quartz cell with flow rates of 2.5 ml min^{-1}, in order to minimize accumulation of photolysis products (secondary photolysis). To minimize photolysis by the analysing light, it was passed through cut-off filters (280, 320, 360 or 400 nm) placed in front of the photolysis flow cell. Conductance experiments were performed (with solutions containing no phosphate) with a 10–20 V, 10 MHz AC bridge (time resolution 1–2 μs) or a 200 V DC system (resolution *ca.* 20 ns), using *ca.* 0.1 mol dm^{-3} $HOCH_2CH_2Cl$ to scavenge e^-_{aq}.

For product analysis, solutions (0.2 mM, 5% isopropyl alcohol, 1 mM Na_2HPO_4) were irradiated with 2–20 pulses (20 ns, 50–60 mJ $pulse^{-1}$) of 248 nm light from a KrF* excimer laser (Lambda Physik EMG103MSC), using a 1 × 1 cm Suprasil quartz cell with integrated double-pass stopcock for degassing or flushing. The products CH_4 (3 m Porapak T column), MeOH and $PhC(OMe)_2C(OMe)_2Ph$ (15 m CW-20M pre-column, 50 m SE-54 column) were determined by GC(MS); PhC(O)OMe, PhCHO, PhC(O)Me and PhC(O)C(O)Ph by both GC (15 m CW-20M pre-column, 50 m SE-54 column) and HPLC [125 × 4.6 mm column Nucleosil-3-C_{18}, mobile phase: (A) 10^{-2} mol dm^{-3} KH_2PO_4, pH 6.6; (B) 20% (A)/80% MeOH (v/v), detection at 254 nm]; and PhC(O)OH by HPLC (conditions as above), using the authentic compounds for identification and calibration. At conversions below 20%, the yield–dose dependences were linear.

The one-colour and two-laser–two-colour laser flash photolysis experiments were performed as previously described.[30] For the determination of the photonities and quantum yields, for excitation with 248 nm light, solutions in water or MeCN with $A = 0.5$ cm^{-1} were used. Actinometry was performed with an aqueous solution of $K_2S_2O_8$ of the same A at 248 nm, monitoring the absorption at 445 nm due to $SO_4^{\bullet-}$, and taking $\varepsilon(SO_4^{\bullet-})_{445}$ nm = 1450 dm^3 mol^{-1} cm^{-1} and $\varphi(SO_4^{\bullet-}) = 1.91$.[31] With 308 nm excitation, the solutions had $A = 0.15$ cm^{-1}. For actinometry, solutions of acetophenone (AP) in MeCN were used, monitoring the A at 320 nm, the λ_{max} of the AP triplet whose ε is 1.25 × 10^4 dm^3 mol^{-1} cm^{-1} and which is formed with $\varphi = 1.0$.[32] In order to minimize decomposition of primarily formed species [$PhC^{\bullet}(OMe)_2$], pulses with very low power (I) were used (< 7 mJ). Under these conditions, the yield of $PhC^{\bullet}(OMe)_2$ increased linearly with I.

Table 1 Spectroscopic data concerning the α,α-dimethoxybenzyl radical

λ_{max}/ nm	ε(apparent)[a]/ dm^3 mol^{-1} cm^{-1}	ε[b]/ dm^3 mol^{-1} cm^{-1}	ε(apparent) ε(from ref. 5)	ε/dm^3 mol^{-1} cm^{-1}
232				10 400[d]
275	10 630			19 800[c]
304[e]	3 400	6 300	0.540	6 300[b]
318[e]	2 300	4 200	0.548	4 200[b]
418	430	800	0.538	800[b]

[a] These values were obtained by pulse radiolysis of an N_2O-saturated 0.1 mM solution of $PhCH(OMe)_2$ containing 0.5 mol dm^{-3} KOH and they are based on KSCN dosimetry using $G(SCN)_2^{\bullet-} = 6.0$ and $\varepsilon[(SCN)_2^{\bullet-}]$ at 480 nm to be 7600 dm^3 mol^{-1} cm^{-1}, and assuming that $G[PhC^{\bullet}(OMe)_2] = G(O^{\bullet-}) = 6.6$, *i.e.* that $O^{\bullet-}$ abstracts H only at the α-position. [b] From ref. 5. [c] This value was obtained by dividing the value from pulse radiolysis (10 630 dm^3 mol^{-1} cm^{-1}) by the average (0.542) of the ratio ε(apparent):ε(from ref. 5) for 304, 318 and 418 nm and correcting[38] for the depletion of the parent. [d] Radical produced from DMPA (see Fig. 1); ε corrected for depletion of parent at 232 nm using the 275 nm band for calibration. [e] Shoulder.

Results and discussion

Products formed by 248 nm photolysis

Deoxygenated (by bubbling with Ar) or O_2-saturated (1 mM) 3 ml samples of aqueous solutions (pH *ca.* 8.4) containing 5% isopropyl alcohol as a solubilizing agent and H-atom donor, 1 mM Na_2HPO_4 (to fix the pH at *ca.* 8) and 0.2 mM ω,ω-dimethoxy-ω-phenylacetophenone (DMPA) were photolysed with 1–20 pulses (20 ns, 50–60 mJ $pulse^{-1}$) of 248 nm laser light (KrF*). Under these conditions, the light is absorbed only by DMPA. Samples (10 μl) of the irradiated solutions were analysed for photochemical decomposition products using GC with FID and HPLC with optical detection ($\lambda = 254$ nm). As products were found PhC(O)OMe (major product), PhCHO, $PhC(OMe)_2C(OMe)_2Ph$, PhC(O)C(O)Ph, PhC(O)Me, $PhCO_2H$, MeOH (major product), and CH_4. Except for MeOH and $PhCO_2H$, these products have previously been found[5] on photolysis of DMPA in acetonitrile solution. The formation of PhC(O)OMe and PhC(O)Me has been explained[5] in terms of thermal and photo-fragmentation [eqn. (2)] of the primarily formed [eqn. (1)] radical, $PhC^{\bullet}(OMe)_2$, followed by combination of the appropriate radicals produced in eqns. (1) and (2). PhC(O)C(O)Ph and $PhC(OMe)_2C(OMe)_2Ph$ are the combination products of $PhC^{\bullet}O$ and $PhC^{\bullet}(OMe)_2$, respectively, and PhCHO and CH_4 the products of H-abstraction of $PhC^{\bullet}O$ and $CH_3^{\bullet}$, probably from the added isopropyl alcohol.[33]

The photochemical products previously not reported are MeOH and $PhCO_2H$. In addition to PhC(O)OMe, MeOH is the major product. On the basis of the results obtained by time-resolved laser photolysis (see the following sections), it is suggested to be formed by photoionization of $PhC^{\bullet}(OMe)_2$ [eqn. (3)], followed by reaction of the resulting carbocation with

$$PhC^{\bullet}(OMe)_2 \xrightarrow[\text{248 or 308 nm}]{h\nu} PhC^+(OMe)_2 + e^-_{aq} \qquad (3)$$

water [eqn. (4)] and subsequent decomposition[34] of the hemiorthoester [eqn. (5)].

$$PhC^+(OMe)_2 + H_2O \longrightarrow PhC(OMe)_2OH + H^+ \qquad (4)$$

$$PhC(OMe)_2OH \longrightarrow PhC(O)OMe + MeOH \qquad (5)$$

The benzoic acid formed could be the consequence of photoionization of $PhC^{\bullet}O$ to give the benzoyl cation, PhC^+O, followed by its rapid reaction with water [eqn. (6)]. However,

$$PhC^{\bullet}O \xrightarrow{h\nu,\ -e^-} PhC^+O \xrightarrow{H_2O,\ -H^+} PhCO_2H \qquad (6)$$

benzoic acid is also produced on reaction of the benzoyl radical with O_2, which may be present in the solutions as an impurity. In agreement with this is the observation that on saturating the solution with O_2 (1 mM), the yield of benzoic acid increased (by a factor of 5). There was also an increase in the yield of PhC(O)OMe (factor 2) and of MeOH (factor 2). This is probably due to formation of $PhC^+(OMe)_2$ by oxidation of O_2 [analogous to eqn. (9), see below] followed by hydrolysis [eqns. (4) and (5)]. The yields of all the other products decreased, mostly to levels below the detection limits. This is as expected on the basis of the radical combination mechanism[5] described above.

Product studies were also performed on the photolysis of DMPA with the low-intensity light (254 nm) of a medium pressure Hg lamp (Phillips HPK 125 W/L): the same products were seen as with the high-intensity laser pulses (248 nm). However, at equal conversion (20%), the yield of MeOH was lower by a factor of 2.6 whereas that of CH_4 was larger by a factor of 2.9. This result is in agreement with the photoionization reaction, eqn. (3), whose likelihood should decrease with decreasing light intensity.

Time-resolved studies after photolysis with one pulse (248 nm)

In Fig. 1 (circles) is shown the spectrum observed at 400 ns after the pulse on 248 nm photolysis of a deoxygenated aqueous solution of DMPA (0.1 mM) with (the low) pulse-power of *ca.* 7

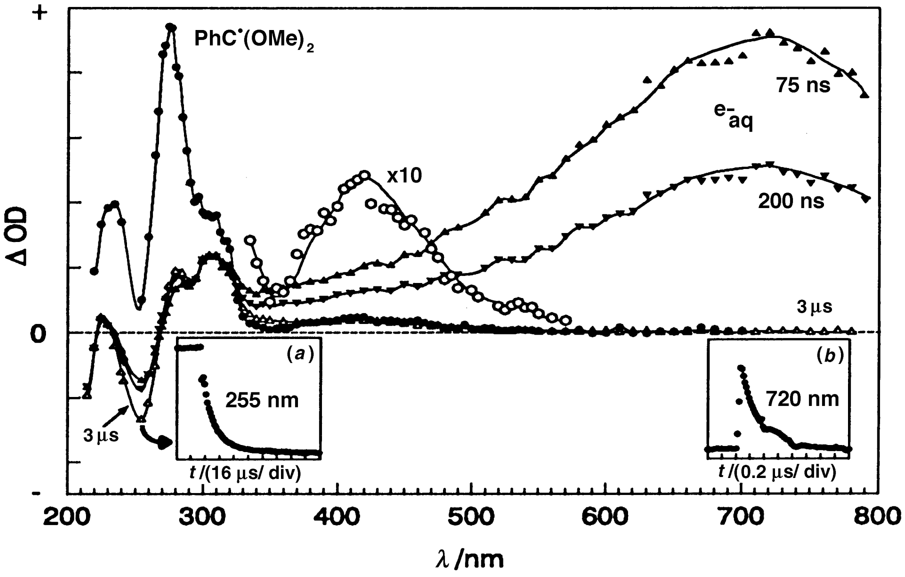


Fig. 1 Full circles: absorption spectrum recorded at 400 ns after photolysing (248 nm) with a pulse of *ca.* 7 mJ an aqueous 0.1 mM DMPA solution containing 5% isopropyl alcohol and 1 mM Na_2HPO_4 and purged with Ar. Open circles: 420 nm band magnified ten times. Triangles: spectra recorded at 75 ns, 200 ns and 3 µs after a *ca.* 65 mJ pulse. Insets: kinetic traces obtained under high intensity conditions (as with the spectrum characterized by the triangles) monitored at 255 nm (*a*), which reflects the decay of $PhC^+(OMe)_2$, and (*b*), at 720 nm (decay of e^-_{aq}).

mJ. There are strong peaks at 232 and at 275 nm, shoulders in the region 295–330 nm, and another, considerably weaker peak at *ca.* 420 nm. The decay of the absorptions (by second-order kinetics) was found to be independent of wavelength at 250–500 nm. The wavelength-independence of the decay was also observed when O_2 was admitted to the solutions, in which case the decay was dramatically accelerated (see below). The conclusion is thus that the peaks belong to only one species. The 420 nm peak and the 295 to 330 nm shoulder have previously been identified as due to the α,α-dimethoxybenzyl radical, $PhC^•(OMe)_2$, produced in acetonitrile by photohomolysis of the central C–C bond of DMPA.[5,6] However, the 232 and 275 nm peaks were not seen, probably due to the intensity of the analysing light being too low. In order to substantiate the assignment to $PhC^•(OMe)_2$ of the spectrum with the dominant peak at 275 nm observed by us, we produced this radical from a different precursor, *i.e.* from $PhCH(OMe)_2$, by H-abstraction[35] with the radical $O^{•-}$, the conjugate base of $OH^•$ ($pK_a = 11.8$), which can easily be generated by radiolysis of aqueous solutions.[36] In Fig. 3 (circles) is displayed the spectrum obtained on pulse radiolysis of an N_2O-saturated (in order to convert the radiation-chemically produced e^-_{aq} into $OH^•$) aqueous solution of $PhCH(OMe)_2$ (1 mM) containing 0.5 mol dm^{-3} KOH (to convert $OH^•$ into $O^{•-}$). It is evident that this spectrum is the same[37] as that in Fig. 1 (circles). For calibration of the spectra in terms of ε (see Figs. 1 and 3, circles) it was assumed that the absorptions in water (measured by us) have the same ε values as in acetonitrile, which were determined by Fischer *et al.*[5] This way, the ε value for the main peak of $PhC^•(OMe)_2$ at 275 nm is calculated[38] to be 19 800 $dm^3\ mol^{-1}\ cm^{-1}$ (see Table 1). This order of magnitude agrees with that for the benzyl radical, $PhCH_2^•$ ($\varepsilon = 14\ 000\ dm^3\ mol^{-1}\ cm^{-1}$ at 258 nm[39]).

Taking 19 800 $dm^3\ mol^{-1}\ cm^{-1}$ for $\varepsilon[PhC^•(OMe)_2]$ at 275 nm, the percentage of H-abstraction at C_α of $PhCH(OMe)_2$ by $O^{•-}$ can be calculated from the measured amplitude of the pulse radiolysis signal at 275 nm (see Table 1) to be 54%. This number documents a selectivity of $O^{•-}$ of 6:1 in favour of H-abstraction from the acetalic (and benzylic) C–H, compared to the six methoxy hydrogens.[40]

It was found that the shape of the absorption spectrum recorded after the pulse changes as the pulse power is increased. This is shown in Fig. 1, triangles, which symbolize the time-dependent spectra measured on 248 nm photolysis with pulses of *ca.* 65 mJ of the same solution as that recorded using *ca.* 7 mJ pulses (Fig. 1, circles). It is evident that the 275 nm band is much weaker than in the case of the *ca.* 7 mJ pulse and that there is a very strong and broad band with a maximum at *ca.* 720 nm which decays relatively rapidly [*ca.* 500 ns, see inset (*b*)]. This band is due to the hydrated electron, e^-_{aq}, as shown by its characteristic[41] reactivity with O_2, N_2O or halogenated hydrocarbons such as CH_2Cl_2 or $HOCH_2CH_2Cl$.

The presence of e^-_{aq} proves that ionization has occurred. If this is the case, there must also be a cationic species and this was found to be the case by measuring the conductance change resulting from the 248 nm photolysis of 0.1 mM DMPA solutions.[42] In acidic solutions (pH *ca.* 4), there was an increase in conductance developing exponentially with a rate of 1×10^5 s^{-1}. In contrast, in basic solutions there was a conductance decrease, again with a rate of $1 \times 10^5\ s^{-1}$, but with a lower amplitude. The inversion of the conductance polarity by going from acidic to basic conditions can be explained by assuming that the change is caused by production of H^+, which is neutralized by OH^- in basic solution leading to a decrease in its concentration and thus to a conductance decrease in this circumstance. If this is so, the amount of conductance change in base should be the same as that in acidic conditions if corrected for the mobilities of H^+ and OH^-. This was found to be the case (within 10%) and it can thus be concluded that (high-intensity) photolysis of DMPA produces a cationic species that decays in aqueous solution with a rate of *ca.* 1×10^5 s^{-1} to give rise to H^+. This rate has previously been shown to be characteristic for the reaction of the α,α-dimethoxybenzyl cation, $PhC^+(OMe)_2$, with water,[34,43] eqn. 4. On this basis, the cationic species formed in the photolysis of DMPA is identified as $PhC^+(OMe)_2$

$PhC^+(OMe)_2$ has been reported[34,44] to be characterized in aqueous solution by λ_{max} *ca.* 260 nm with an ε of the order 10^4 $dm^3\ mol^{-1}\ cm^{-1}$. This wavelength is very close to $\lambda_{max} = 255$ nm of the parent, DMPA, whose depletion by the laser light causes a negative signal (see Fig. 1). On this basis, it is difficult to distinguish spectroscopically the expected cation from the other contributions to the overall *A* changes in this wavelength range. However, in the region *ca.* 255 nm is visible, after the initial rapid bleaching, a further (‘slow’) decrease of *A* with exponential kinetics [see Fig. 1 and inset (*a*)] with a rate of *ca.* 1×10^5 s^{-1} which is not influenced by O_2, but can be accelerated by the nucleophile N_3^- ($k = ca.\ 2.9 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$).[45] The species responsible is identified as $PhC^+(OMe)_2$ which decays accord-

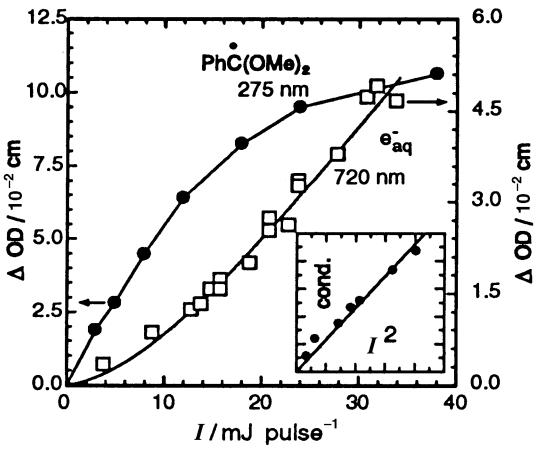


Fig. 2 Dependence of the yield of $PhC^{\bullet}(OMe)_2$, measured at 275 nm (circles), and of e^-_{aq}, monitored at 720 nm (squares), as a function of the laser pulse power (I mJ^{-1}) at 248 nm. Inset: amplitude of the conductance signal *vs.* I^2. Deoxygenated aqueous solution of DMPA (0.1 mM) at pH 3.7.

ing to eqn. (4). Thus, this optical observation is support for the conclusions drawn from the conductance data.

In order to obtain more information on the formation mechanism of the transient photolysis products from DMPA, the dependence of the yield of $PhC^{\bullet}(OMe)_2$ (measured at 275 nm) and of e^-_{aq} (monitored at 720 nm) on the intensity of the 248 nm laser light was determined by attenuating the light with neutral density filters. In addition, the yield of $PhC^+(OMe)_2$ was measured by conductance at pH *ca.* 4 or 11 (see above). The results are shown in Fig. 2. Concerning $PhC^{\bullet}(OMe)_2$, it is clear that its initial linear yield levels off above *ca.* 10 mJ pulse^{-1}. It is above this value that the formation of e^-_{aq} becomes very noticeable. The e^-_{aq} *vs.* mJ dependence is 'curved up', and it is thus evident that e^-_{aq} is produced at the expense of $PhC^{\bullet}(OMe)_2$. Concerning $PhC^+(OMe)_2$, its yield (measured *via* conductance, see inset in Fig. 2) increases quadratically with laser power, like that of e^-_{aq}, and this means that the cation is generated in the same process (ionization), from $PhC^{\bullet}(OMe)_2$, in support of eqn. (3).

The formation of $PhC^{\bullet}(OMe)_2$ from DMPA was used to determine the quantum yield of DMPA decomposition [eqn. (1)] at 248 nm in different solvents, using the $S_2O_8^{2-}$-actinometer.[31] The value for an aqueous solution containing 2% isopropyl alcohol is 0.53, for acetonitrile 0.44, and for methanol 0.60.[46] These numbers are larger than those given in ref. 2 but similar to that reported in ref. 14.

Photolysis with two consecutive pulses (248 and 308 nm)

In order to study the photochemical reactions of $PhC^{\bullet}(OMe)_2$ in aqueous solution in further detail, the radical was produced by 248 nm photolysis of a 0.1 mM solution of DMPA in H_2O, using a low pulse power ($\leqslant$ 12 mJ) to minimize photodecomposition of the primary products. After 2.5 μs, a time sufficient for any e^-_{aq} produced by the pulse to disappear [see Figs. 1 and 3, insets (*b*)], but much too short for $PhC^{\bullet}(OMe)_2$ to decay, a second pulse (20 ns) was fired, this time with 308 nm light. This resulted in depletion of the 275 [see Fig. 3, inset (*a*)] and *ca.* 420 nm bands of $PhC^{\bullet}(OMe)_2$ and in the formation of e^-_{aq}, as evidenced by the broad absorption in the 500 to 700 nm region [Fig. 3 and inset (*b*)]. That this band is due to e^-_{aq} was demonstrated by the effect of typical electron scavengers such as O_2, N_2O or RCl. A dose variation was performed in the range 5 to 30 mJ pulse^{-1} in order to determine the photonity of the e^-_{aq} production from $PhC^{\bullet}(OMe)_2$ by the 308 nm light. It was found that the yield of e^-_{aq} is proportional to the 308 nm light intensity, the process is thus monophotonic, which is different from the case[22] of $Ph_2CH^{\bullet}$, which in acetonitrile and in aqueous solution is ionized in a biphotonic process *via* the electronically excited state of the radical.

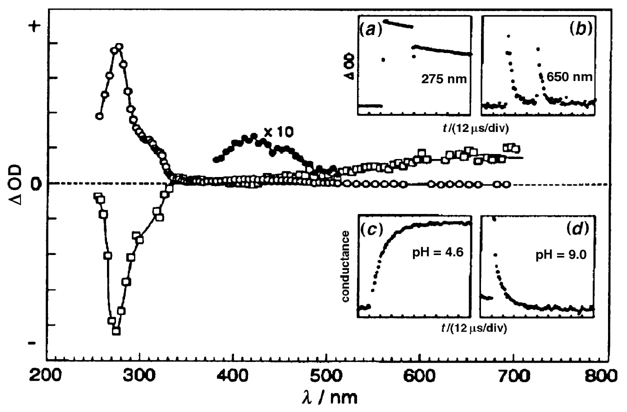


Fig. 3 Open circles: absorption spectrum of $PhC^{\bullet}(OMe)_2$ observed at 100 ns after pulse radiolysis of a N_2O-saturated aqueous solution containing 1mM $PhCH(OMe)_2$ and 0.5 mol dm^{-3} KOH. Full circles: the 420 nm band of $PhC^{\bullet}(OMe)_2$ magnified by a factor of 10. Squares: spectrum from two-colour–two-laser flash photolysis (first pulse: 248 nm, 12 mJ, second pulse: 308 nm, 50 mJ, delay 2 μs, spectrum recorded at 200 ns after the second pulse) of 0.1 mM DMPA in deoxygenated aqueous solution. The spectra are normalized to the 275 nm peak. Insets *a* and *b*: changes of Δ*A* upon two-laser–two-colour photolysis of deoxygenated aqueous 0.1 mM DMPA solutions, showing the formation (by the 248 nm pulse) and depletion (by the 308 nm pulse) of $PhC^{\bullet}(OMe)_2$ at 275 nm (*a*), and the electron formation and decay at 650 nm (*b*). In insets (*c*) and (*d*) the conductance changes (after the 308 nm pulse) recorded using the same solution (containing, however, 0.2% CH_2Cl_2 to scavenge e^-_{aq}) at pH = 4.6 (*c*), and = 9.1 (*d*).

The yield for e^-_{aq} formation, *i.e.* for ionization of $PhC^{\bullet}(OMe)_2$ by the 308 nm light relative to photodecomposition of $PhC^{\bullet}(OMe)_2$ was determined by comparing the amplitude of the (positive) e^-_{aq}-signal at 650 nm ($\varepsilon = 16\,400$ dm^3 mol^{-1} cm^{-1})[47] with the (negative) signal at 275 nm ($\varepsilon = 19\,800$ dm^3 mol^{-1} cm^{-1}, see Table 1; e^-_{aq} has essentially no absorption here). Taking the absorption at 275 nm of the photoproduced cation, $PhC^+(OMe)_2$, into account with ε(275 nm) *ca.* 6500 dm^3 mol^{-1} cm^{-1},[34] the value calculated for the ratio results as 0.40. This means that only 40% of the photodestruction of $PhC^{\bullet}(OMe)_2$ is due to its ionization.[48] In order to determine the quantum yield for ionization, the amplitude of the e^-_{aq}-signal at 650 nm was compared with the absorption at 320 nm from the triplet of acetophenone in acetonitrile solution of the same *A* at 308 nm as that due to $PhC^{\bullet}(OMe)_2$ in the photolysed (with the 248 nm pulse) DMPA solution. The value obtained for the quantum yield for photoionization of $PhC^{\bullet}(OMe)_2$ in aqueous solution (5% isopropyl alcohol) is 0.21. Analogously, from the comparison of Δ*A* due to depletion of $PhC^{\bullet}(OMe)_2$ with the acetophenone triplet signal, the quantum yield for the overall destruction of the radical is 0.51. As pointed out above, 40% of this value is due to photoionization of $PhC^{\bullet}(OMe)_2$, from which the quantum yield results as 0.2, in agreement with the directly determined number.

Previously, the quantum yield for $PhC^{\bullet}(OMe)_2$ decomposition by 308 nm light was estimated to be 0.5 in acetonitrile solvent[5] whereas that reported[6] for destruction in benzene with 420 nm light is 0.8. The reaction was assumed[5,6] to solely result in homolysis to yield $CH_3^{\bullet}$ and methyl benzoate [eqn. (2)]. We have performed experiments also in acetonitrile and we do not see a solvate electron. However, this does not mean that ionization does not occur in this polar solvent. The solvated electron in acetonitrile has a very weak absorption[49] and is thus extremely difficult to detect. In order to see whether photoionization of $PhC^{\bullet}(OMe)_2$ also occurs in solvents other than water, we used methanol and isopropyl alcohol, where $e^-_{solvated}$ has a strong absorption band in the red, like that of e^-_{aq}. Using 40–70 mJ pulses of 248 nm light (one-laser approach), the electron was clearly seen, even in the comparatively weakly polar solvent isopropyl alcohol ($\varepsilon = 18.3$). This shows that photoionization of $PhC^{\bullet}(OMe)_2$ occurs in weakly polar environ-

Table 2 Absorption maxima[a] of PhCH$^{\bullet}$(OR) in H_2O containing 2–5% CH_3CN

R	λ_{max}[b]/nm
Me	225; $\underline{275}$; 305[c]; 315[c]; *ca.* 400[d]
Et	235; $\underline{275}$; 305[c]; 315[c]; *ca.* 410[d]
$CHMe_2$	230; $\underline{277}$; 308[c]; 320[c]; *ca.* 400[d]
CMe_3	230; $\underline{280}$; 305[c]; 315[c]; *ca.* 400[d]

[a] Obtained on 248 nm photolysis of 0.1 mM benzoin ether. Not corrected for depletion of parent. [b] The main peak is underlined. [c] Shoulder. [d] This (weak) band extends from *ca.* 350–520 nm.

Table 3 Rate constants ($k/10^9$ dm^3 mol^{-1} s^{-1}) for reaction of the α-substituted benzyl radicals[a] PhC$^{\bullet}$H(OR), PhC$^{\bullet}$(OMe)$_2$, and 4-$MeC_6H_4C^{\bullet}(OMe)_2$ with oxidants in aqueous solution at 20 ± 1 °C

R	$K_3Fe(CN)_6$[b]	Na_2IrCl_6[c]	$(CF_3OCO)_2IC_6H_5$[b]	O_2[b]
Me	5.6	4.2	0.18	3.2
Et	5.5	4.4	0.19	2.8
$CHMe_2$	6.4	3.7; 4.2[f]	0.14	2.7
CMe_3	6.6	4.2; 3.6[f]	0.15	2.4
PhC$^{\bullet}$(OMe)$_2$	5.2	4.2	0.16	2.4
4-$MeC_6H_4C^{\bullet}$-(OMe)$_2$[d]		4.2[e]		

[a] Produced by 248 nm photolysis of the precursors PhC(O)CH(OR)Ph. [b] Measured by monitoring the decay of the benzyl-type radical as a function of [oxidant]. [c] Measured by monitoring the decay of $IrCl_6^{2-}$ at 490 nm. [d] Obtained by 248 nm photolysis of *p*-$MeC_6H_4C(O)C(OMe)_2$-C_6H_4-*p*-Me. [e] Obtained from monitoring the decay of 4-$MeC_6H_4C^{\bullet}$-(OMe)$_2$ at 305 nm. [f] Determined by conductance at pH *ca.* 4.

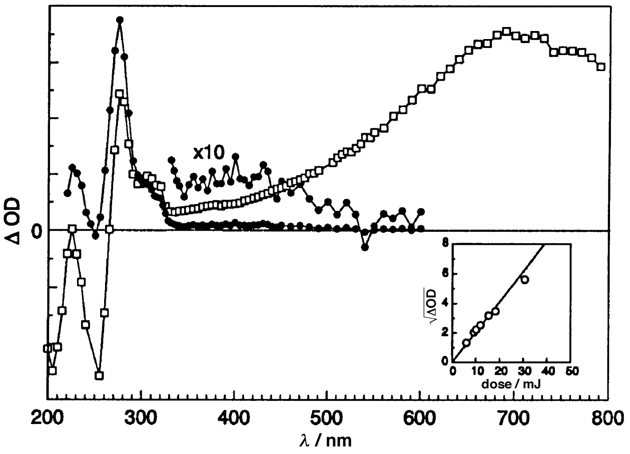


Fig. 4 Circles: absorption spectrum observed at 2 μs on 248 nm photolysis (4 mJ pulse^{-1}) of a deoxygenated aqueous solution containing 0.1 mM PhC(O)CH(OMe)Ph and 3% (v/v) Pr^{i}OH. Squares: same solution. Pulse power increased to 63 mJ pulse^{-1}. Spectrum recorded at 100 ns after the pulse. Inset: square root of the yield of e^-_{aq} (measured at 720 nm) as a function of pulse power (mJ/pulse).

ments. In the strongly polar solvent acetonitrile ($\varepsilon = 35.9$), ionization of PhC$^{\bullet}$(OMe)$_2$ is thus very likely to take place.

Even further evidence for the ionization of PhC$^{\bullet}$(OMe)$_2$ by 308 nm light comes from conductivity studies. After decay of the conductance change resulting from the 248 pulse (see above), the 308 nm pulse was fired. This resulted in a rise of conductance in acidic and a decrease in basic solution [see Fig. 3, insets (*c*) and (*d*)], with the same rate ($k = 1 \times 10^5$ s^{-1}). As already mentioned, this rate is characteristic for the reaction of PhC$^+$(OMe)$_2$ with H_2O,[43] which leads to the production of protons and the hemiorthoester of benzoic acid, eqn. (4).

Benzoin ethers

The study was extended to the family of benzoin ethers PhC(O)CH(OR)Ph, R = Me, Et, Pr^i, Bu^t. On photolysis in aqueous solution with 248 or 308 nm light, the α-alkoxybenzyl radicals PhC$^{\bullet}$H(OR) were seen (Fig. 4, circles; for λ_{max}-values see Table 2). The benzoin ethers thus undergo homolysis of the central bond,[8,29] eqn. (7), which is analogous to eqn. (1).

$$\text{PhC(O)CH(OR)Ph} \xrightarrow{h\nu} \text{PhC}^{\bullet}\text{O} + \text{PhCH}^{\bullet}\text{(OR)} \quad (7)$$

In addition, with pulses of > 10 mJ, production of e^-_{aq} became apparent in a process requiring two photons (see Fig. 4, squares and inset), as in the case of DMPA. The ionization was checked using conductance detection. For this purpose, the deoxygenated solutions contained 0.1 mM benzoin ether and 1.2% (v/v) 2-chloroethanol to scavenge e^-_{aq}. At pH 3.7, a rapidly forming (within 50 ns) conductance increase was observed, whereas at pH *ca.* 10 the signal was negative. The pH-dependent polarity inversion of the conductance signal indicates that a proton is produced, which in basic solution is neutralized by OH$^-$. The amplitude of the conductance rise increased quadratically with the laser power, which shows that the process leading (from the benzoin ethers) to the production of protons requires two photons. Formation of e^-_{aq} was also achieved by photolysing PhC$^{\bullet}$H(OR), generated by 248 nm irradiation of PhC(O)CH(OR)Ph, with 308 nm pulses (two-laser–two-colour approach). With this technique, conductance detection was also applied. It was found that the photolysis of PhC$^{\bullet}$H(OR) results in a conductance change, an increase in acidic and a decrease in basic solution. This change is assigned to reaction of the photochemically formed cations PhC$^+$H(OR) with water generating the hemiacetals PhCH(OH)OR and H$^+$. The conclusion is thus that the α-alkoxybenzyl radicals, PhCH$^{\bullet}$(OR), can be photoionized with 248 or 308 nm light, eqn. (8).

$$\text{PhCH}^{\bullet}\text{(OR)} \xrightarrow{h\nu} \text{PhCH}^{+}\text{(OR)} + e^- \quad (8)$$

Chemical oxidation of PhC$^{\bullet}$H(OR) and of PhC$^{\bullet}$(OMe)$_2$

The radicals PhC$^{\bullet}$H(OR), formed on photolysis of PhC(O)CH(OR)Ph with 248 or 308 nm light, react rapidly with oxidants Ox. The rate of this reaction was measured as a function of [Ox] by the decay of PhC$^{\bullet}$H(OR) or by that of Ox.[50] As oxidants were used $Fe(CN)_6^{3-}$ (reduction potential 0.36 V *vs.* normal hydrogen electrode, NHE), $IrCl_6^{2-}$ (0.86 V *vs.* NHE), PhI^{2+} (unknown potential) and O_2 (−0.33 V *vs.* NHE). The rate constants obtained are listed in Table 3.

The rate constants for reaction of the α-alkoxybenzyl radicals with $Fe(CN)_6^{3-}$ are on average (5.9 ± 0.6) × 10^9 dm^3 mol^{-1} s^{-1}, *i.e.* within experimental error there is no dependence on the structure of R. Surprisingly, the average rate constant for reaction of the stronger oxidant, $IrCl_6^{2-}$, is somewhat lower, (4.2 ± 0.3) × 10^9 dm^3 mol^{-1} s^{-1}. These numbers may be compared to those[51,52] for simple α-alkoxyalkyl radicals, where the reactivity of $IrCl_6^{2-}$ is somewhat larger than that of $Fe(CN)_6^{3-}$.[53] With the α-alkoxyalkyl radicals, the reaction with $IrCl_6^{2-}$ and $Fe(CN)_6^{3-}$ proceeds by electron transfer giving rise to the corresponding α-alkoxycarbenium ions.[52,54] If this mechanism also applies to the reaction between the metallic oxidants and the benzyl radicals, the corresponding cations should be produced. As pointed out above, these species can be identified by their reaction with water, a process in which protons are produced [eqn. (4)]. At low concentrations of oxidant the oxidation of the benzyl radicals should be rate-determining and not the reaction of the cation with water. Under this condition, the reaction rate *k*(PhC$^{\bullet}$ + Ox) can be determined by monitoring the rate of conductance change as a function of [Ox]. At high [Ox], the observed rate should become independent of [Ox], the rate-determining step now being the reaction of the cation PhC$^+$ with water. That this is in fact the case is shown in Fig. 5 for oxidation of PhC$^{\bullet}$(OMe)$_2$ by $Fe^{III}(CN)_6^{3-}$. The rate constant for reaction with water (obtained from the plateau) is,

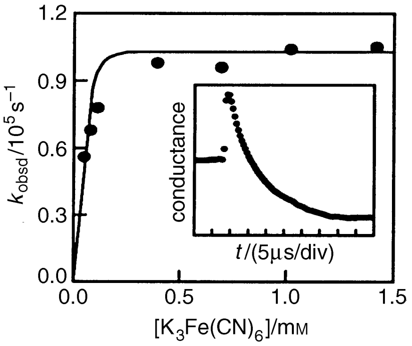


Fig. 5 Dependence of k_{obs} for pseudo-first-order oxidation of $PhC^{\bullet}(OMe)_2$ (produced by 248 nm photolysis of a deoxygenated aqueous solution of 0.1 mM DMPA) on $[K_3Fe(CN)_6]$, measured *via* the conductance decrease at pH 9–10. Inset; the kinetics of conductance change photo-induced in a 0.1 mM DMPA solution at pH 9.2 containing 0.7 mM $K_3Fe(CN)_6$

within experimental error, the same as that observed by the radical photoionization method (see above). The chemical oxidation of $PhC^{\bullet}$ to give PhC^+ is thus a method complementary to that of photoionization of $PhC^{\bullet}$. An obvious disadvantage of chemical oxidation is that it cannot be successfully applied to highly reactive cations since their (second order) formation is likely to be slower than their (first order) decomposition. This seems to be the case for the monoalkoxybenzyl systems, where $k(\text{cation} + H_2O)$ is apparently $> 1 \times 10^6$ s^{-1}. This value is deduced from the observation that there was no plateau in the k_{obs}. *vs.* [Ox] plots up to this number.

As seen from Table 3, the reaction rate constants of the α-alkoxybenzyl radicals with the oxidant $(CF_3CO_2)_2IPh$ are lower by a factor of *ca.* 30 than those for the metallic oxidants $Fe(CN)_6^{3-}$ and $IrCl_6^{2-}$. With the rate constant (1–2) × 10^8 dm^3 mol^{-1} s^{-1}, the reaction is not diffusion, but activation controlled. Nevertheless, there is clearly no dependence on the structure of R. PhI^{2+} belongs to a new class of 'soft' oxidants (hypervalent iodine reagents),[55] whose chemical properties are similar to those of Pb^{IV}, Ti^{III} and Hg^{II} complexes, but which do not have the disadvantage of being toxic.

The rate constants for reaction of the benzyl radicals with O_2 [average $(2.7 \pm 0.3) \times 10^9$ dm^3 mol^{-1} s^{-1}, Table 3] are similar to those measured[56] for simple aliphatic radicals in aqueous solution. There is obviously no dependence on the nature of R. It has been noted that O_2 tends to react by addition to a radical rather than by electron transfer,[57] even in those cases where the difference in redox potential between the reaction partners is sufficient for electron transfer to occur. In order to find out in which way the α-alkoxybenzyl radicals behave, O_2-saturated solutions of PhC(O)CH(OR)Ph at pH 10–11 were photolysed with 248 nm pulses using conductance for detection. If carbocations are formed from the initially produced $PhCH^{\bullet}(OR)$, eqn. (9), they should be detectible *via* their reaction with water,

$$PhCH^{\bullet}(OR) + O_2 \xrightarrow{a} PhCH(OR)O_2^{\bullet} \xrightarrow{b} PhCH^+(OR) + O_2^{\bullet-} \quad (9)$$

analogous to eqn. (4). It was found that on introduction of O_2 into the solutions, the conductance signals observed at pH *ca.* 10 as a result of photoionization (see above) increased in amplitude by the factor 10 ± 2. However, the conductance changes took place on rather a long timescale (400 μs) and the kinetics were not first-order. Also, there was little dependence on the structure of R. This probably means that the heterolytic cleavage of the $C-O_2^{\bullet}$ bond (reaction 9*b*) is slow such that it is interfered with by radical–radical reactions that (also) lead to conductance changes. A low rate of $O_2^{\bullet-}$ elimination from the α-alkoxybenzyl system is in agreement with the relatively high reactivity (low stability) of the α-alkoxybenzyl-type cations, as evidenced by their short lifetimes (< μs) in water.

Conclusions

It has been shown by direct detection of solvated electrons that α-dimethoxy- and α-alkoxy-benzyl radicals are photoionized by 248 or 308 nm light. In the case of the α-dimethoxybenzyl radical, obtained from the industrially important photoinitiator DMPA, the resulting carbocation was identified by optical and conductance measurements and the quantum yield for photoionization determined to be 0.2. On this basis, it is suggested that in industrial applications of this type of photoinitiator, the promotion of polymerization under conditions of high-intensity light may, at least in part, be due to the photochemical production of carbocations. In other words, the effect of high-intensity light may derive from the mechanism changing from free radical to cationic polymerization. Furthermore, the high rate constants for oxidation of the α-alkoxybenzyl radicals by chemical oxidants such as *e.g.* $(CF_3CO_2)_2IPh$ may be the basis of their high efficiency in producing cations as active species in polymerization.

References

1 *Current Address*: Department of Chemical Engineering, FEUP, Rua dos Bragas, P-4050 Porto, Portugal.
2 M. R. Sandner and C. L. Osborn, *Tetrahedron Lett.*, 1974, 415.
3 J. P. Fouassier, P. Jacques, D. J. Lougnot and T. Pilot, *Polym. Photochem.* 1984, **5**, 57.
4 H. J. Hageman, *Progr. Org. Coat.*, 1985, **13**, 123.
5 H. Fischer, R. Baer, R. Hany, I. Verhoolen and M. Walbiner, *J. Chem. Soc., Perkin Trans. 2*, 1990, 787.
6 J. T. Banks, J. C. Scaiano, W. Adam and R. Schulte Oestrich, *J. Am. Chem. Soc.*, 1993, **115**, 2473.
7 R. Kuhlmann and W. Schnabel, *Polymer*, 1977, **18**, 1163; *Angew. Makromol. Chem.*, 1978, **70**, 145.
8 H. G. Heine, H. J. Rosenkranz and H. Rudolph, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 974; F. D. Lewis, R. T. Lauterbach, H. G. Heine, W. Hartmann and H. Rudolph, *J. Am. Chem. Soc.*, 1975, **97**, 1519.
9 J. Kosar, *Light Sensitive Systems*, Wiley, New York, 1965, p. 161.
10 S. Adam, H. Güsten, S. Steenken and D. Schulte-Frohlinde, *Liebigs Ann. Chem.*, 1974, 1831.
11 J. P. Fouassier and A. Merlin, *J. Photochem.*, 1980, **12**, 17.
12 W. Adam and R. Schulte Oestrich, *Chem. Ber.*, 1992, **125**, 2463.
13 F. Jent, H. Paul and H. Fischer, *Chem. Phys. Lett.*, 1988, **146**, 315.
14 The quantum yield for DMPA decomposition in benzene, acetonitrile, *tert*-butyl or isopropyl alcohol by 350 nm light has been estimated to be 0.15–0.25.[2] More recently, a value of 0.5 was given for 365 nm excitation in acetonitrile solution: H. Baumann and H. J. Timpe, *Z. Chem.*, 1984, **24**, 18.
15 D. O. Cowan and R. L. Drisko, *Elements of Organic Photochemistry*, Plenum Press, New York, 1976.
16 E. S. Huyser and D. T. Wang, *J. Org. Chem.*, 1964, **29**, 2720.
17 R. L. Huang, T. W. Lee and S. H. Ong, *J. Chem. Soc.* (*C*), 1969, 40; G. Behrens and D. Schulte-Frohlinde, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 932.
18 S. Steenken, H. P. Schuchmann and C. von Sonntag, *J. Phys. Chem.*, 1975, **79**, 763.
19 J. Bartl, S. Steenken, H. Mayr and R. A. McClelland, *J. Am. Chem. Soc.*, 1990, **122**, 6918.
20 J. L. Faria and S. Steenken, *J. Am. Chem. Soc.*, 1990, **112**, 1277.
21 J. L. Faria and S. Steenken, *J. Phys. Chem.*, 1992, **96**, 10869.
22 W. Adam and R. Schulte Oestrich, *J. Am. Chem. Soc.*, 1992, **114**, 6031.
23 R. W. Redmond, J. C. Scaiano and L. J. Johnston, *J. Am. Chem. Soc.*, 1990, **112**, 398.
24 The IP of benzyl radical is 7.2 eV (F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1978, **100**, 3290). Substitution of a radical at C_α by OMe typically reduces the IP (by 2.8 eV in the case of methyl radical, *cf.* D. Danovich, Y. Apeloig and S. Shaik, *J. Chem. Soc., Perkin Trans. 2*, 1993, 321 and references cited therein). With two OMe groups at C_α, the E_i is thus expected to be $\leqslant 7$ eV.
25 J. F. Rabek, *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers*, Wiley, Chichester, 1987.
26 J. V. Crivello, in *Cationic Polymerization and Related Processes*, ed. E. J. Goethals, Academic Press, London, 1984; pp. 289–305.
27 A. Ledwith, *Makromol. Chem., Suppl.*, 1979, **3**, 348.

28 A. Ledwith, S. Al-Kass and A. Hulme-Lowe, in *Cationic Polymerization and Related Processes*, ed. E. J. Goethals, Academic, London, 1984; pp. 275–287.
29 Y. Yagci and W. Schnabel, *Makromol. Chem., Makromol. Symp.*, 1988, **13/14,** 161; Y. Yagci, J. Borbely and W. Schnabel, *Eur. Polym. J.*, 1989, **25**, 129.
30 J. L. Faria and S. Steenken, *J. Phys. Chem.*, 1993, **97**, 1924.
31 For a description of this actinometer, see ref. 21.
32 H. Lutz, E. Breheret and L. Lindquist, *J. Phys. Chem.*, 1973, **77**, 1758.
33 In contrast to the earlier work,[5] we did not find $C_2H_{6;}$, the dimer of $CH_3^\bullet$. This is probably due to the presence in our solutions of the good H-donor isopropyl alcohol.
34 R. A. McClelland, V. M. Kanagasabapathy and S. Steenken, *Can. J. Chem.*, 1990, **68**, 375.
35 In a similar approach, H-abstraction from $PhCH(OMe)_2$ has been affected with $Me_3CO^\bullet$, *cf.* ref. 6. See also ref. 10.
36 In contrast to $OH^\bullet$, $O^{\bullet -}$ does not add to aromatic double bonds, but it H-abstracts from the side chain.
37 The 232 nm peak was not seen in this pulse radiolysis experiment, due to insufficient analysing light intensity.
38 The value has been corrected for the depletion of $PhCH(OMe)_2$, whose ε at 275 nm is 220 dm^3 mol^{-1} cm^{-1}.
39 K. Sehested, H. Corfitzen, H. C. Christensen and E. J. Hart, *J. Phys. Chem.*, 1975, **79**, 310.
40 The radical produced by H-abstraction from MeO is assumed, based on its aliphatic character, not to absorb above 250 nm.
41 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513.
42 The conductance change was measured using pulses varying in power from 5 to 40 mJ. Even with the weakest pulse, the signal-to-noise was $\geqslant 50$.
43 S. Steenken and R. A. McClelland, *J. Am. Chem. Soc.*, 1989, **111**, 4967.
44 R. A. McClelland and M. Ahmad, *J. Am. Chem. Soc.*, 1978, **98**, 7027.
45 There is precedence for reaction of stabilized cations with N_3^- with rate constants below the diffusion rate: F. L. Cozens, N. Mathivanan, R. A. McClelland and S. Steenken, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2083.
46 The effect of depletion of DMPA was taken into account. The loss of DMPA was taken to be equal to the yield of radical. ε of DMPA is 5300, 2000 and 3500 dm^3 mol^{-1} cm^{-1} in water (2% isopropyl alcohol), acetonitrile and methanol, respectively. The ε of the radical was considered independent of solvent and equal to 19 800 dm^3 mol^{-1} cm^{-1}.
47 G. L. Hug, *Natl. Stand. Ref. Data Ser.*, 1981, **69**, 1.
48 It is reasonable to assume that the remaining 60% are due to O–Me bond cleavage (reaction 2).
49 Y. Hirata, N. Mataga, Y. Sakata and S. Misumi, *J. Phys. Chem.*, 1983, **87**, 1493. See also ref. 30.
50 The benzoyl radical, $PhCO^\bullet$, produced by the photolysis of PhC(O)CH(OR)Ph [see eqn. (7)] may also react with Ox leading to its depletion. If this occurs, the rate constants are either very low ($<10^7$ dm^3 mol^{-1} s^{-1}) or the same as those for reaction of $PhC^\bullet H$-(OR). This is concluded from the fact that there was only one kinetic component visible in the depletion of Ox.
51 S. Steenken and P. Neta, *J. Am. Chem. Soc.*, 1982, **104**, 1244.
52 S. Steenken, J. Buschek and R. A. McClelland, *J. Am. Chem. Soc.*, 1986, **108**, 2808.
53 The observed difference in reactivity between $IrC1_6^{2-}$ and $Fe(CN)_6^{3-}$ is opposite to expectation based on the driving force of the reaction. With the α-alkoxybenzyl radicals $PhC^\bullet H(OR)$ and $PhC^\bullet(OMe)_2$ the oxidation potentials may be very low. The radical $Me_2C^\bullet OH$ may be a suitable model. Its oxidation potential at pH 7 is *ca.* −2 V/NHE (M. Breitenkamp, A. Henglein and J. Lilie, *Ber. Bunsenges. Phys. Chem.*, 1976, **80**, 973. J. Lilie, G. Beck and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 1971, **75**, 458). If a similar number applies to the α-alkoxybenzyl radicals, the driving force for the electron transfer reaction to $IrC1_6^{2-}$ is *ca.* 2.9 V. This value is large enough for Marcus inverted-region behaviour.
54 R. A. McClelland and S. Steenken, *J. Am. Chem. Soc.*, 1988, **110**, 5860.
55 S. Spyroudis and A. Varvoglis, *J. Chem. Soc., Chem. Commun.*, 1979, 615.
56 G.E. Adams and R. L. Wilson, *Trans. Faraday Soc.*, 1969, **65**, 2981. For a review, see P. Neta, R. E. Huie and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1990, **19**, 413.
57 V. Jagannadham and S. Steenken, *J. Am. Chem. Soc.*, 1988, **110**, 2188. S. Steenken, *Free Radicals in Synthesis and Biology*, ed. F. Minisci, NATO ASI Series, C260, Kluwer Academic Publishers, Dordrecht, 1989, p. 213.

Paper 6/07743I
Received 14*th November* 1996
Accepted 12*th February* 1997