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Photochemistry of the photoinitiator 4-[2'-*N*,*N*-(diethylamino)ethoxy]-benzophenone. Spectroscopy, radical generation and quenching

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Abstract

The photochemistry at 308 nm of the photoinitiator 4-[2'-*N*,*N*-(diethylamino)ethoxy]-benzophenone was studied. The phosphorescence emission and lifetime of the lowest triplet state were characterized. The 4-alkylaminoketyl radical was generated in the ground state through hydrogen atom abstraction by the lowest triplet state of the initiator. The intermolecular vs. intramolecular character of this process was analysed. The radical was excited to the first doublet excited state using 340 nm pulses from a dye laser. The temporal evolution of the radical concentration in the ground and excited states was followed by laser-induced fluorescence (LIF) and fluorescence intensity measurements respectively. The quenching of the ketyl radical in the ground and excited states by its precursor, O_2, methyl methacrylate and styrene was determined. The effect of the solvent on the quenching of the ketyl radical was studied. Detailed studies on the radical fluorescence were also performed.

Keywords: Photoinitiators; Laser spectroscopy; Laser radical generation

1. Introduction

The synthesis of tailor-made photoinitiators for specific applications requires the ability to predict the relationship between molecular structure and properties. Aromatic carbonyl compounds have been proposed as photoinitiators because their triplet states, formed at high yield on UV irradiation, can abstract hydrogen atoms and produce radicals [1,2]. Photoinitiators containing aromatic carbonyl groups as chromophores have been studied extensively to determine the behaviour of intermediates which may play a significant role in free radical polymerization [3,4]. A complete understanding of a chemical or photochemical reaction requires a detailed knowledge of any transient intermediates. A thorough comprehension of the reaction mechanism will provide the means to control the undesired processes that may take place.

Increased requests for improved photoinitiators have motivated the synthesis of novel organic molecules, e.g. a series of 4-alkylaminobenzophenone derivatives which include in their molecular structure a polymerization coinitiator as the tertiary amine group [5]. Some aspects of their photochemistry and photopolymerization activity have been analysed [6]. This initial study has revealed the important influence of the ionization potential and degree of charge transfer induced by the substituent on the photoinitiator efficiency [6b]. Likewise, Allen et al. [7], applying microsecond and nanosecond flash photolysis techniques, have studied the formation mechanism of the ketyl radical from the photolysis of 15 4-alkylaminobenzophenone initiators. The UV photolysis of these compounds leads to the formation of ketylamino radicals through hydrogen atom abstraction by the lowest triplet state of the initiator. The analysis of the products of photolysis and the kinetic behaviour of the triplet state of the initiator in different solvents suggests that the excited 4-alkylaminobenzophenone initiator abstracts hydrogen from the solvent when this is a good hydrogen atom donor. In the case of non-hydrogen atom donor solvents, e.g. acetonitrile, the ketylamino radical formation may be due to an intramolecular hydrogen atom abstraction reaction from the amino substituent of the photoinitiator. This radical formation mechanism involves an electron transfer process, suggesting the existence of a triplet exciplex. Nevertheless, the role of an intermediate exciplex appears to be the subject of much debate [8,9].

In order to determine the quality and efficiency of the 4-alkylaminobenzophenone derivatives as photoinitiators, it is

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convenient to analyse in detail the photophysics and photochemistry of the corresponding ketyl radicals. Most of this interest is prompted by the relationship between the reactivity of the ketyl radical and its role in the photoinitiated processes. In addition, this study, together with the results obtained in work carried out with other free radicals, particularly benzophenoneketyl radical [10–16], diphenylmethyl radical [17] and a few related species [18,19], may clarify the dependence of the radical reactivity on its structure.

The investigation of the reactivity of the 4-alkylaminoketyl radical can be accomplished with high sensitivity using two lasers with different wavelengths: one is used for the "photosynthesis" of the radical in the ground state and the second is used to promote the radical to its excited state at a wavelength at which all other reagents are transparent. Accurate and reliable timing of the lasers is critical, since the delay between the pulses must be adjusted depending on the lifetime of the intermediate and its rate of formation. In this way, the detection of the fluorescence emission from the excited state enables the intermolecular reactivity of the radical to be studied in the ground state using laser-induced fluorescence (LIF) techniques [17,19,20].

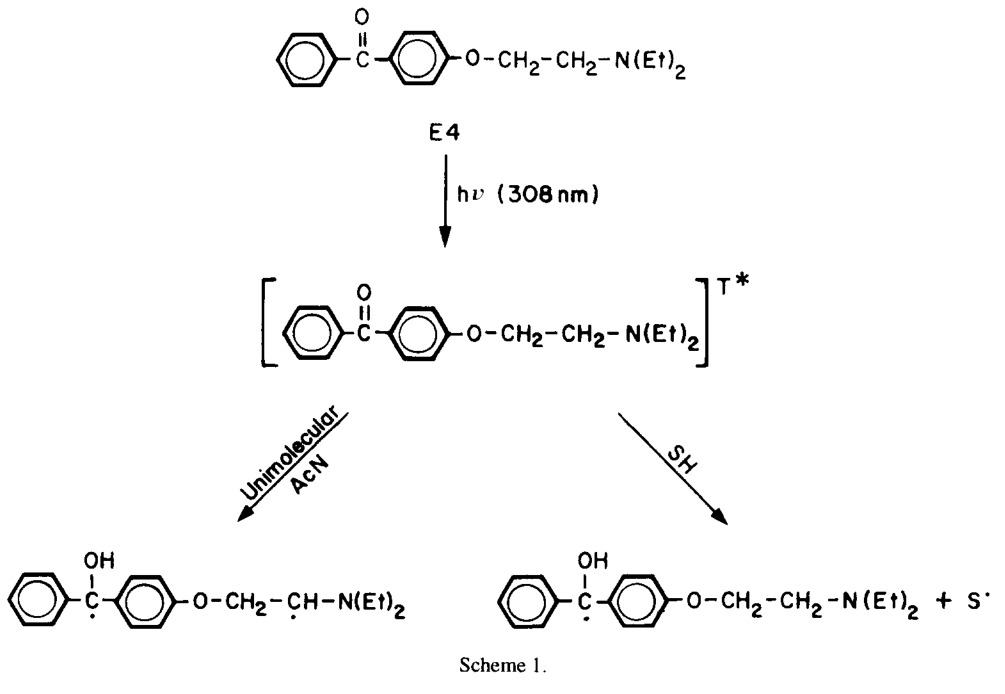
In this paper, we have studied, under conditions of two-photon laser excitation, the photochemistry of the polymerization initiator 4-[2′-*N*,*N*-(diethylamino)ethoxy]-benzophenone, hereafter called E4 following the nomenclature of previous work [5,6]. The 4-alkylaminoketyl radical was generated in the ground state through hydrogen atom abstraction by the lowest triplet state of the initiator (see Scheme 1). The intermolecular vs. intramolecular character of this process was analysed for solutions of E4 in acetonitrile (AcN), 1,4-dioxan and tetrahydrofuran (THF). In addition, the quenching of the ground and excited states of the ketyl radical with a series of substrates was studied. The photoinitiator, O_2, methyl methacrylate (MMA) and styrene were used as radical quenchers. The monomers were selected in an attempt to relate the quenching of the ketyl radical in the ground state to the corresponding yield of polymerization.

2. Experimental details

2.1. Techniques and apparatus

The photolysis of the photoinitiator E4 was carried out using a commercial XeCl excimer laser (MPB-150) supplying up to 120 mJ of energy in approximately 30 ns full width at half-maximum (FWHM) pulses at 308 nm. A quartz beam splitter selected approximately 10% of the laser output to be directed towards the 1 cm silica cell containing the solutions to be studied. A 1 m focal length spectrosil B spherical lens focused the photolysis light onto the cell, and a 2 mm iris diaphragm, placed before the cell, selected the central part of the rectangular laser beam, ensuring spatial uniformity of the light illuminating the cell. The total energy of the pulse impinging on the cell was estimated to be approximately 1 mJ. Part of the laser light passing through the beam splitter was collected by an optical fibre and directed towards a photodiode (RS-BPX-65). The signal from this photodiode was used to monitor the power of the photolysis laser.

The radicals generated during photolysis were excited by a pulsed dye laser (Oxford Lasers EDL-1) pumped by a home-built XeCl excimer laser which delivered 40 mJ of energy in approximately 12 ns FWHM pulses at 308 nm. The selected dye (*p*-terphenyl in cyclohexane) produced about 2 mJ per pulse of visible light in the region 322–350 nm with a bandwidth of approximately 0.5 nm. The excitation wavelength was fixed at 340 nm. The photolysis and excitation



Scheme 1.

laser beams entered the cell collinearly and were spatially overlapping. The probe laser power was monitored by a fast photodiode. The electrical signal so produced was divided and part of it was used to trigger the detection system. The time delay between the photolysis and excitation laser was controlled by a delay generator (Tektronix DD-501) combined with a pulse generator (Tektronix PG-502, 250 MHz). The time delays used ranged from 36 μs (minimum delay, determined by the trigger unit of the home-built excimer laser [21]) to 3 ms, with a jitter of ±2 μs.

The phosphorescence of the E4 triplet state and the fluorescence of the excited radical, monitored at right angles to the path beam, were imaged, after passage through a cut-off filter to eliminate scattered light from both lasers, onto the input slit of a monochromator (MacPherson-2035, 0.35 m) and detected by a photomultiplier (EMI 9816-QB). Phosphorescence and fluorescence spectra were recorded by feeding the signal to a box-car (Stanford SR-250) to be integrated before being digitized by an SR-245 A/D converter. A personal computer was used to record the signal as well as to control and synchronize the experiment via a ComputerBoard DASH-8 interface. The details of the system operation have been described elsewhere [16,22].

The phosphorescence spectra from E4 samples at 77 K were recorded on a Perkin–Elmer LS-5 spectrophotometer.

The lifetimes of the E4 triplet state and the excited radical were obtained from the time-resolved phosphorescence and fluorescence emissions recorded with a 500 MHz digital oscilloscope Tektronix TDS-520 (rise time, 1 ns; vertical resolution, 8 bits). In addition, the lifetime of the E4 triplet state was analysed with a time-correlated, single-photon-counting spectrometer [23] built using ORTEC 583 and 473 A discriminators and a 457 time-to-amplitude converter. In this case, the samples were excited with a thyratron-gated nanosecond flash lamp (Edinburgh Instruments EI199) filled with N_2. The emission was passed through a bandpass filter (Schott KV-408) and detected with a Phillips XP2020Q photomultiplier. The kinetic parameters (lifetime and amplitude) of the fluorescence decay were determined using a fitting routine based on the non-linear, least-squares convolution technique [24].

The kinetics of the ketyl radical in the ground and excited states were analysed by recording the time-resolved fluorescence emission with a 40 MHz digital oscilloscope Tektronix 2430A (rise time, 10 ns; vertical resolution, 8 bits) for different time delays between photolysis and probe lasers. Typically, 32 decay traces were averaged for each time delay.

In all experiments, a static sample was photolysed. The uncertainties in the concentrations of the photoinitiator and quenchers could then be obtained, because of the depletion of these species in solution and the buildup of reaction products during the course of a photolysis run. It was checked that the absorption of each sample at 308 nm changed by less than 10% after irradiation with the number of laser shots required in each experiment. The absorption spectrum of the photoinitiator solution was recorded using a Shimadzu UV-2100 UV–visible spectrometer.

2.2. Materials and sample preparation

AcN (Scharlau, far UV high performance liquid chromatography (HPLC) grade), 1,4-dioxan (Merck Uvasol, 99.5%) and O_2 (Argon, 99.999%) were used as received. THF (FEROSA, HPLC grade) was purified by passage through a column of activated alumina in order to eliminate the peroxides and, after microfiltration, was degassed in an ultrasonic bath. MMA (Merck) was washed three times with portions of 10 vol.% aqueous sodium hydroxide to remove the inhibitor and then twice with distilled water. The monomer, dried over anhydrous $MgSO_4$, was then distilled under reduced pressure before use. Commercial styrene was washed with aqueous 5% NaOH to remove the inhibitor, followed by distilled water, dried for several hours with $MgSO_4$ and distilled under reduced pressure (boiling point (b.p.), 41–42 °C/18 mm). The pre-purified monomer was stored at low temperature (−4 °C) in the dark and kept anhydrous with Linde type 5A molecular sieve; it was fractionally distilled immediately before use. The photoinitiator E4 was synthesized and purified as described previously [5].

Sample concentrations were prepared by standard methods. Degassing of the samples was accomplished by the freeze–thaw method pumping down to pressures below 10^{-4} Torr. The experiments were carried out at room temperature.

O_2 was added to deaerated E4 solution cooled at −73 °C (ethanol/N_2 liquid slush). A capacitance manometer (MKS Baratron, 10^{-3}–1 Torr) was used to measure oxygen pressures ranging from 200 to 900 mTorr. The corresponding concentrations were calculated using the solubility of oxygen in AcN [25] and assuming the same value for the other two solvents, THF and 1,4-dioxan. Indeed, for the common organic solvents, the oxygen concentration for air-saturated solutions at 25 °C changes by less than 10% [25].

3. Results and discussion

The E4 structure is characterized by a lack of electronic conjugation between the amino group and benzophenone; thus no charge transfer state occurs, the lowest excited state being an n–π* transition. The absorption spectrum of E4 exhibits certain differences with respect to that corresponding to unmodified benzophenone due to the presence of one oxygen atom attached to the benzene ring (see Fig. 1). The dependence of the E4 absorption spectrum on the solvent (maximum wavelength and extinction coefficient) is small, with changes of less than 10% [5].

3.1. Assignment of the emission observed at 460 nm. Formation of the E4 triplet state

Pulsed laser irradiation at 308 nm of a solution of E4 induces spectral emission characterized by a broad band in

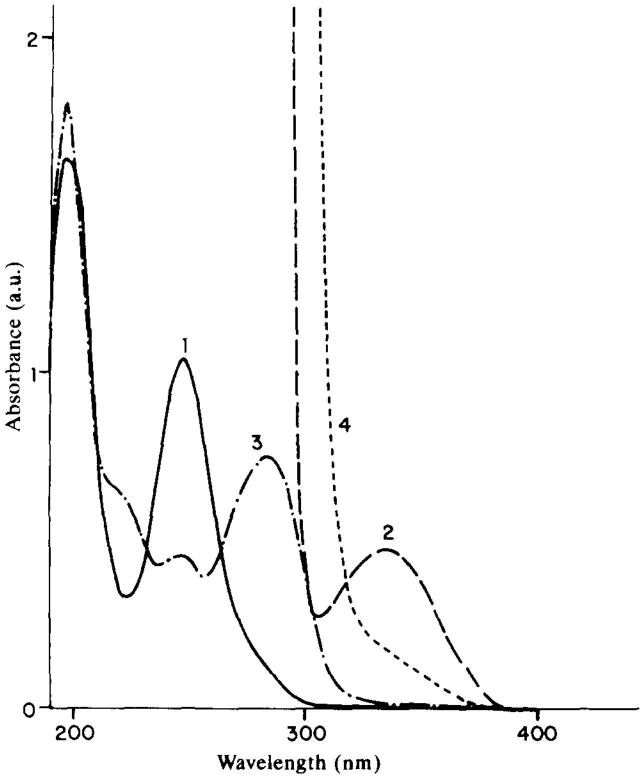


Fig. 1. Absorption spectra in AcN solutions of benzophenone at low (6×10^{-5} M, 1) and medium (3.7×10^{-3} M, 2) concentrations and E4 at low (4×10^{-5} M, 3) and medium (4×10^{-4} M, 4) concentrations.

the range 400–500 nm (see Fig. 2(A)). This spectrum is similar to that observed from the benzophenone triplet state generated under similar experimental conditions [16]. The main feature of the E4 spectrum matches the emission registered with the fluorometer in a 5×10^{-4} E4 solution in AcN cooled at 77 K; the emission is characterized by a relatively short lifetime, $\tau=6$ ms, in good agreement with previously measured values [5]. This result also agrees with the classical value reported for the lifetime of the phosphorescence emission from the benzophenone triplet state at 77 K, $\tau=6$ ms [26], as well as with a more recent measurement, $\tau=6.4$ ms [27]. Therefore the E4 emission centred at 460 nm can be assigned to the phosphorescence from the $^3(n,\pi^*)$ triplet state of the E4 molecule.

This observation, together with previous studies [7], indicates that the triplet state of the 4-alkylaminobenzophenone initiator, E4(T), is generated by fast intersystem crossing from the singlet excited state, E4(S_1), which, in turn, is produced by the E4(S_0) absorption of a 308 nm photon from the photolysis laser. Thus the processes involved in the formation and kinetics of E4(T) can be represented as follows

$$\mathrm{E4(S_0)} \xrightarrow{I_{308\,\mathrm{nm}}} \mathrm{E4(S_1)} \xrightarrow{k_{\mathrm{isc}}{}^{\mathrm{S}}} \mathrm{E4(T)} \qquad (1)$$

$$\mathrm{E4(T)} \xrightarrow{k_\mathrm{p}} \mathrm{E4(S_0)} + h\nu_\mathrm{p} \qquad (2)$$

$$\mathrm{E4(T)} \xrightarrow{k_{\mathrm{isc}}{}^{\mathrm{T}}} \mathrm{E4(S_0)} \qquad (3)$$

$$\mathrm{E4(T)} + \mathrm{Q} \xrightarrow{k_\mathrm{Q}{}^{\mathrm{T}}} \text{quenching} \qquad (4)$$

$$\mathrm{E4(T)} \xrightarrow{k_{\mathrm{int}}} \text{quenching} \qquad (5)$$

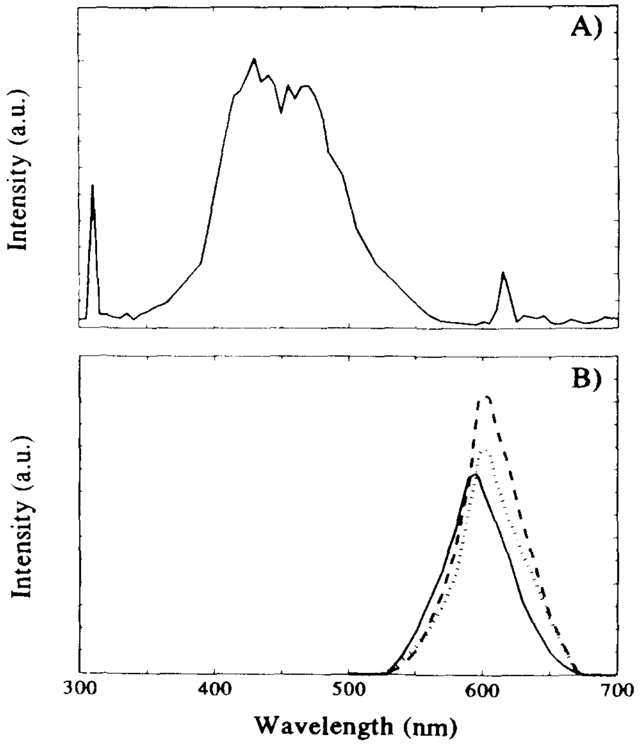


Fig. 2. (A) Phosphorescence spectrum from the triplet state of E4 in a 5×10^{-4} M AcN solution after laser irradiation at 308 nm. (B) Fluorescence spectra of the excited ketyl radical in AcN (full line), 1,4-dioxan (dotted line) and THF (broken line). The radical was produced by the 308 nm photolysis of a 5×10^{-4} M E4 solution and was excited by absorption of a 340 nm photon. The time delay between the pump and probe lasers was 36 μs.

where $k_{\mathrm{isc}}{}^{\mathrm{S}}$ and $k_{\mathrm{isc}}{}^{\mathrm{T}}$ are the rate constants for intersystem crossing from E4(S_1) and E4(T) respectively, k_p is the rate constant for the phosphorescence emission, $k_\mathrm{Q}{}^{\mathrm{T}}$ is the rate constant for the quenching induced by Q and k_{int} is the rate constant for the intramolecular quenching which will be discussed later. When Q is a solvent which is an efficient hydrogen atom donor (THF or 1,4-dioxan), reaction (4) takes over and the rate of the quenching process increases (see below).

No delayed fluorescence from E4(S_1) was observed; therefore the triplet–triplet annihilation reaction

$$\mathrm{E4(T)} + \mathrm{E4(T)} \longrightarrow \mathrm{E4(S_0)} + \mathrm{E4(S_1)}$$

can be neglected [28]. This result agrees with the short E4(T) lifetime measurements discussed below.

3.2. Lifetime of E4 triplet state

The temporal evolution of the phosphorescence emission at room temperature reveals that the lifetime of the E4 triplet state is, in all cases, 30 ns or less. An absolute value for the lifetime could not be determined because it is convoluted with the time profile of the photolysis laser. This phosphorescence lifetime is shorter than that corresponding to the benzophenone triplet state ($\tau=27$ μs) generated in AcN under similar experimental conditions [16]. The temporal behaviour of the phosphorescence emission, analysed using the time-correlated, single- photon-counting technique, yields a lifetime of 4 ns in a 5×10^{-4} M solution of E4 in AcN. When AcN is substituted by 1,4-dioxan or THF, the phosphorescence lifetime decreases below the temporal resolution of the system, approximately 1 ns. In these two cases, proton transfer is probably the predominant contribution to triplet E4 decay, and both the ketyl radical ($R^{\cdot}$) and the radical corresponding to the solvent molecule involved ($S^{\cdot}$) should be formed in a direct manner (see Scheme 1).

The origin of the difference observed between the triplet state lifetimes of E4 and benzophenone in AcN must be ascribed to the kinetic effects (quenching) induced by the substituent present in the E4 structure. Essentially, these effects can take place through an intramolecular (unimolecular) or intermolecular (bimolecular) process. A crude estimation of the maximum diffusion-controlled rate k_{dif} for the bimolecular quenching process yields a value of 5×10^{6} s^{-1} for the term $k_{\mathrm{dif}}\times[\mathrm{E4}]$; this would give an E4 triplet state lifetime of approximately 200 ns at room temperature, i.e. orders of magnitude above the experimentally obtained value. Therefore it is reasonable to conclude that the E4 triplet state lifetime in AcN is controlled by a unimolecular, intramolecular process. It is well documented that the lifetime of this triplet state decreases when there is a substituent in the aromatic ring which is able to transfer a hydrogen atom intramolecularly, as is the case, for example, for 2-methylbenzophenone [29,30]. However, the participation of a fast triplet decay induced by an electron transfer mechanism cannot be ruled out.

Taking into account the above arguments, we conclude that the main contribution to the experimental decay rate of the E4 triplet state in AcN, $k_{\mathrm{int}}=2.5\times10^{8}$ s^{-1}, is intramolecular hydrogen atom abstraction. This rate constant should provide a good approximation to the rate constant for diphenylketylamino radical generation (see Scheme 1) as long as the quantum yield of this unimolecular reaction is close to unity, as is expected [5]. Given that a biradical ($BR^{\cdot}$) is formed and the minimum delay between pump and probe lasers is 36 μs, it is possible that short-lived biradicals have completely disappeared by this point in time [31] and that the radicals monitored are actually true monoradicals ($R^{\cdot}$) which would have a tendency to survive for a much longer time. In this sense, reaction (5) may be the main process in AcN solution. However, a minor component giving true monoradicals may be most important in terms of the long delay phenomena examined at time scales longer than 36 μs.

Under the experimental conditions selected to study ketyl radical quenching, the initiator triplet state is not significantly quenched by any substrate (E4, O_2 and monomers); the phosphorescence signal observed immediately after the photolysis laser pulse does not decrease as the quencher concentration increases.

3.3. Formation of the ketyl radical in the ground and excited states

The excited 4-alkylamino initiator, abstracting a hydrogen atom from the solvent, its substituent or a neighbouring substituent, leads to the formation of the ketyl radical in the ground state [7]. This species exhibits absorption maxima at 340 and 560 nm, the extinction coefficient of the first transition being approximately 15 times higher than that of the second [7]. It was for this reason that the dye laser wavelength chosen to probe the radicals was 340 nm, corresponding to the first doublet state excitation of the radical. According to Allen et al. [7], the triplet–triplet (T_1–T_n) absorption of this 4-alkylamino initiator occurs at nearly the same wavelength, but under the experimental time delay conditions selected in the present work (minimum delay between pump and probe lasers, 36 μs), the first triplet state of the initiator has already disappeared when the probe dye laser is applied.

The scheme corresponding to the formation and kinetics of the ketyl radical in the ground and excited states can be represented as

$$\mathrm{E4(T)} \xrightarrow{k_{\mathrm{int}}} \mathrm{BR}^{:} + \mathrm{E4} \xrightarrow{k_{\mathrm{BR}}} \mathrm{R}^{\cdot} + \mathrm{E4}^{\cdot} \tag{5}$$

$$\mathrm{E4(T)} + \mathrm{SH} \xrightarrow{k_{\mathrm{SH}}} \mathrm{R}^{\cdot} + \mathrm{S}^{\cdot} \tag{5'}$$

$$\mathrm{R}^{\cdot} + \mathrm{R}^{\cdot} \xrightarrow{k_{\mathrm{dim}}} \text{dimer} \tag{6}$$

$$\mathrm{R}^{\cdot} + \mathrm{E4} \xrightarrow{k_{\mathrm{E4}}} \text{quenching} \tag{7}$$

$$\mathrm{R}^{\cdot} + \mathrm{Q} \xrightarrow{k_{\mathrm{Q}}} \text{quenching} \tag{8}$$

$$\mathrm{R}^{\cdot} \xrightarrow{I_{340\ \mathrm{nm}}} \mathrm{R}^{\cdot *} \tag{9}$$

$$\mathrm{R}^{\cdot *} \xrightarrow{k_{\mathrm{f}}} \mathrm{R}^{\cdot} + h\nu \tag{10}$$

$$\mathrm{R}^{\cdot *} \xrightarrow{k_{\mathrm{ic}}} \mathrm{R}^{\cdot} \tag{11}$$

$$\mathrm{R}^{\cdot *} + \mathrm{Q} \xrightarrow{k_{\mathrm{Q}}{}^{*}} \text{quenching} \tag{12}$$

where k_{int} is the rate constant for the generation of the biradical $\mathrm{BR}^{:}$, k_{BR} is the rate constant for the biradical transformation reaction, k_{SH} is the rate constant of proton transfer in donor solvents SH, k_{dim} is the rate constant for the dimerization reaction of $R^{\cdot}$, k_{E4} and k_{Q} are the quenching rate constants for removal of $R^{\cdot}$ by E4 and by an added quencher Q respectively, k_{f} is the rate constant for the fluorescence emission from the radical in the excited state $R^{\cdot *}$, k_{ic} is the rate constant for $R^{\cdot *}$ internal conversion and $k_{\mathrm{Q}}{}^{*}$ is the rate constant for the quenching of $R^{\cdot *}$.

The fluorescence spectra of the radical excited state ($R^{\cdot *}$) generated from E4 solutions in AcN, 1,4-dioxan and THF are shown in Fig. 2(B). The fluorescence emission reaches a maximum at 590, 600 and 603 nm in AcN, 1,4-dioxan and THF respectively. These maxima are red shifted with respect to the fluorescence emission of the non- substituted ketyl radicals, which is to be expected as it is known that substitution in the aromatic ring leads to a red shift in the corresponding emission spectrum [15]. This effect has already

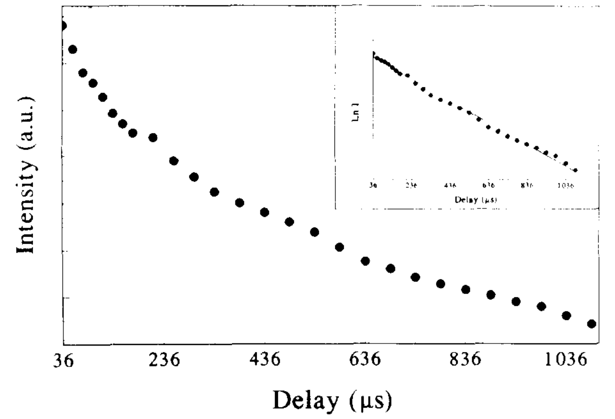


Fig. 3. Fluorescence intensity dependence on the delay between the pump and probe lasers observed during the photolysis of a 3.9×10^{-3} M solution of E4 in AcN. The inset shows the logarithm of this signal as a function of the time delay. The straight line corresponds to the best fit of the data points.

been observed in the fluorescence spectrum of the substituted diphenylmethyl radical [32].

The fluorescence maximum wavelength of the ketyl radical is relatively insensitive to the nature of the solvent. The dependence of the fluorescence emission on the laser intensity at 308 and 340 nm is linear with a slope of unity, which corresponds to a single-photon absorption process in both cases.

In the absence of 340 nm light, the emission centred around 600 nm does not appear. In addition, excitation light at 340 nm does not lead to fluorescence emission unless it is preceded by 308 nm photolysis pulses. This result provides further support to the assignment of the emission spectrum to the fluorescence from the excited ketyl radical.

The quenching of the ketyl radical in the ground and excited states was determined from the dependence of the fluorescence emission at the maximum wavelength on the time delay between the photolysis and probe lasers and the quencher concentration. Stern–Volmer-type treatments were used in both cases.

Table 1
Quenching of the ketyl radical in the ground (k_Q) and excited ($k_Q{}^*\tau^*$) states by various quenchers at room temperature and the relative efficiencies of ketyl radical generation in different solvents ($\mathrm{Eff_{sol}/Eff_{THF}}$)

Quencher	k_Q ($M^{-1}\,s^{-1}$)	$k_Q{}^*\tau_0{}^*$ (M^{-1})	$\mathrm{Eff_{sol}/Eff_{THF}}$
E4/AcN	$(2.4\pm0.3)\times10^5$	10 ± 2	0.3
O_2	$(7.5\pm0.8)\times10^8$	42 ± 8	
MMA	$(6.5\pm0.7)\times10^4$	4.0 ± 0.4	
Styrene	$(10\pm1)\times10^5$	18 ± 4	
E4/1,4-dioxan	$(5.9\pm0.7)\times10^5$	20 ± 5	0.6
O_2	$(2.2\pm0.3)\times10^9$	50 ± 9	
MMA	$(1.2\pm0.2)\times10^5$	5.2 ± 0.5	
Styrene	$(3.8\pm0.5)\times10^6$	30 ± 4	
E4/THF	$(1.2\pm0.2)\times10^6$	30 ± 7	1
O_2	$(5.0\pm0.6)\times10^9$	56 ± 9	
MMA	$(2.0\pm0.3)\times10^5$	6.8 ± 0.9	
Styrene	$(6.0\pm0.7)\times10^6$	46 ± 7	

3.4. Quenching of the ketyl radical in the ground state

The quenching of the ground state of the ketyl radical generated during the photolysis of E4 was studied by analysing its time-dependent concentration decay by LIF. Provided that the laser intensities and the observation solid angle are not varied, proportionality between the fluorescence intensity and the radical concentration is ensured, because the other LIF parameters are identical in each of the cases studied.

In the presence of a sufficiently high concentration of a quencher Q, the decay of the radical becomes pseudo-first-order because $k_{E4}\times[E4]$ and $k_Q\times[Q]$ are much greater than $k_{dim}\times[R^\bullet]$ and, consequently, the temporal dependence of the fluorescence intensity can be written as

$$I_f=I_0\exp(-\tau^{-1}t) \tag{13}$$

where I_0 is the initial fluorescence intensity, I_f is the intensity at time t and τ^{-1} is the experimental decay rate constant under the given conditions. A typical example of the dependence of the excited ketyl radical fluorescence on the time delay between the two lasers is shown in Fig. 3. The fluorescence decay follows pseudo-first-order kinetics over a time range which decreases from 1400 μs at an E4 solution concentration of 5×10^{-4} M to 300 μs when the E4 concentration is increased to 1×10^{-2} M. This behaviour is the same in the three solvents used in the present work.

The pseudo-first-order rate constants τ^{-1} can be experimentally determined from the slope of the logarithm of the fluorescence signal vs. the delay time (see inset in Fig. 3). This decay rate constant can be written as a function linearly dependent on the quencher concentration in the cell

$$\tau^{-1}=\tau_0{}^{-1}+k_{E4}\times[E4]+k_Q\times[Q] \tag{14}$$

where τ_0 is the lifetime of the ketyl radical in the ground state and k_{E4} and k_Q are the experimental rate constants for quenching by the precursor E4 and any added quencher respectively. Values of the rate constants and τ_0 can be obtained from Stern–Volmer plots of the experimentally determined τ^{-1} vs. [E4] or [Q]. Table 1 summarizes the values determined for the quenching rate constant of the ketyl radical in the ground state by its precursor in solutions of AcN, 1,4-dioxan and THF. It is found that this rate constant increases by a factor of five in the above sequence.

The analysis of the intercepts with the ordinate axis in the Stern–Volmer plots yields radical lifetimes of 2.9 ± 0.4, 3.6 ± 0.5 and 3.1 ± 0.4 ms for AcN, 1,4-dioxan and THF respectively. The radical lifetime is not significantly modified by the change in solvent. However, it seems that this parameter shows a tendency to decrease as the solvent viscosity decreases, suggesting the influence of diffusion in radical decay, as observed previously [7]. Allen et al. [7] have determined a lifetime of 5 ms for the ground state of this 4-alkylaminobenzophenone radical using propan-2-ol as solvent. Our experimental data seem to be in agreement with this result because the viscosity of propan-2-ol is much higher than that of the solvents selected in this work [33].

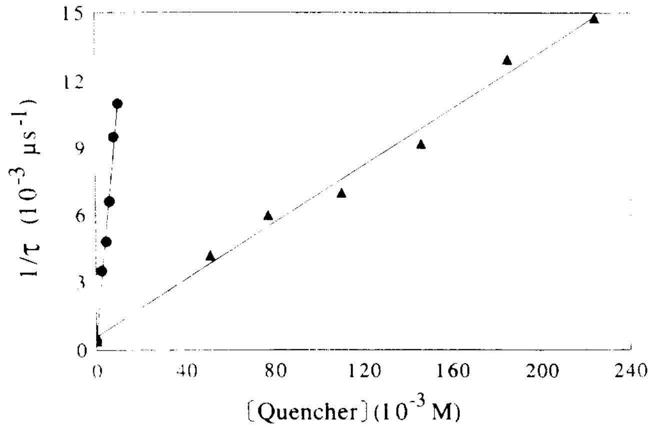


Fig. 4. Experimental decay rate constant of the ketyl radical in the ground state as a function of the quencher concentration: MMA (▲) and styrene (●) added to a constant 5×10^{-4} M solution of E4 in AcN.

The bimolecular rate constants for the quenching of the ketyl radical in the ground state by O_2, MMA and styrene were determined following the procedure described above. In these experiments, the precursor concentration [E4] was kept constant at 5×10^{-4} M. The selected quencher concentrations were high enough to ensure pseudo-first-order kinetics: $[\mathrm{MMA}]=(55\text{–}200)\times10^{-3}$ M, $[\mathrm{styrene}]=(1\text{–}10)\times10^{-3}$ M and $[O_2]=(1\text{–}10)\times10^{-6}$ M. In addition, these concentrations ensure that the values obtained for the quenching rate constants are not contaminated by the reaction of the radical with its precursor, since this reaction is at least 30 times slower than that induced by the other quenchers.

Fig. 4 shows the linear dependence of the radical decay rate constants on the MMA and styrene concentrations added to a constant 5×10^{-4} M solution of E4 in AcN. In these two cases, the intercept with the ordinate axis represents the sum of two terms, τ_0^{-1} and $k_{E4}\times[E4]$, for the selected concentration. The corresponding quenching rate constants can be deduced from the slope of the lines; these kinetic data are included in Table 1.

In accordance with the kinetic behaviour observed for the reaction of the ketyl radical with its precursor, the quenching of this radical in the ground state by O_2, MMA and styrene seems to be solvent dependent. As the solvent is changed, quenching of the ketyl radical increases in the order: AcN > 1,4-dioxan > THF. This is an indication of solvent participation in the photochemically induced reactions [34].

In each of the solvents used, oxygen is the most efficient substrate studied, quenching the radical at near diffusion rates. The ketyl radical may react with the two monomers, MMA and styrene, via double bond addition [35]. The quenching rate constants of the radical with styrene are clearly higher than those with MMA. This different efficiency seems to suggest that the addition of the ketyl radical to an olefinic double bond is favoured when this olefinic bond is conjugated with the aromatic ring [36]. This argument implies a reactive mechanism of quenching for which we have no experimental evidence. However, it is difficult to think of an alternative mechanism for a thermodynamically stable species such as the radical in the ground state.

3.5. Quenching of the ketyl radical in the excited state

The excited state of the ketyl radical is generated by the absorption of a 340 nm photon by the previously prepared ground state. The lifetime of the excited radical is very short, below the temporal resolution of our experimental apparatus which is limited by the pulse duration of the excitation laser (approximately 10 ns FWHM). For this reason, the photochemical kinetics of the excited radical with different partners could not be determined from the dependence of the lifetime on the quencher concentration. Therefore an alternative Stern–Volmer method, based on the relative fluorescence efficiencies vs. quencher concentration, was employed [37]. Under identical conditions of irradiation geometry, initiator concentration, excitation intensity and wavelength and detector sensitivity, and provided that the samples are optically thin at the wavelength used, the ratio of the fluorescence efficiencies equals the ratio of the fluorescence intensities

$$\frac{I_0}{I_f}=1+k_Q{}^*\tau_0{}^*[Q] \qquad (15)$$

where I_0 is the initial fluorescence intensity in the absence of quencher, I_f is the same parameter at a quencher concentration [Q] and $\tau_0{}^*=(k_f+k_{ic})^{-1}$ is the lifetime of the radical in the excited state. In our case, I_0 and I_f are the fluorescence intensities extrapolated to zero time delay for a 5×10^{-4} M E4 solution (I_0) and for each quencher concentration added to this initiator solution (I_f).

Two cases can be distinguished in the kinetic analysis of the radical in the excited state. In the first and more common, Q is a substance which does not participate in ketyl radical formation. In the second, the quencher is the precursor of the ketyl radical. In the first case, I_0 and I_f can be determined experimentally from the intercepts with the ordinate axis in plots of the logarithm of the fluorescence intensity vs. the delay time between the lasers; the plot I_0/I_f as a function of [Q] is straightforward. In the second case, when $Q\equiv E4$, it is not possible to determine experimentally the parameter I_0; an alternative way to determine this parameter is to plot $1/I_f$ vs. [E4] and obtain I_0 by extrapolation to zero concentration.

For all the substrates analysed, including E4, the Stern–Volmer plots are strictly linear. As an example, Fig. 5 shows the dependence of the ratio I_0/I_f on the MMA concentration added to a 5×10^{-4} M solution of E4 in AcN, 1,4-dioxan and THF. The values of the product $k_Q{}^*\times\tau_0{}^*$, derived from the slope of the lines fitting the experimental data, are summarized in Table 1.

The values obtained for $k_Q{}^*\times\tau_0{}^*$, corresponding to the quenching of the excited radical with its precursor, can be affected by two factors working in opposite ways. First, as the E4 concentration increases, the generated radical concentration and therefore the fluorescence intensity increase. Second, as the precursor concentration increases, the region of

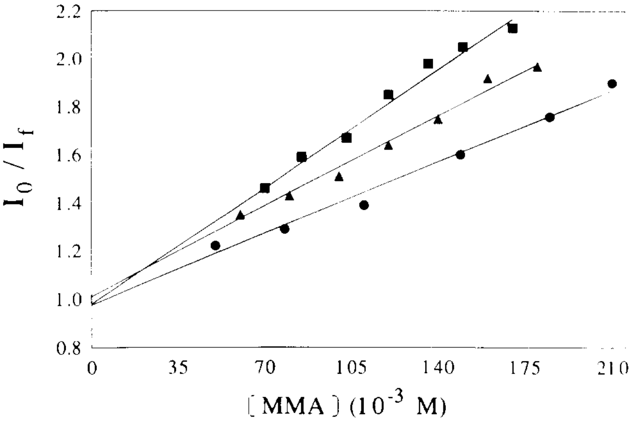


Fig. 5. Stern–Volmer plot for the quenching of the excited ketyl radical induced by MMA added to a constant 5×10^{-4} M E4 solution in AcN (●), 1,4-dioxan (▲) and THF (■).

the sample in which the absorption takes place becomes narrower, leading to a reduction of the fluorescence collection solid angle and, consequently, the fluorescence intensity.

The unknown lifetime of the excited ketyl radical prevents the determination of absolute values for the quenching rate constants $k_Q{}^*$ and their comparison with the values reported for other excited diphenylketyl radicals [12]. It has been observed, however, that substitution in the aromatic ring of the radical has a modest effect on the lifetime of the excited state [13,39]. Therefore, for the excited radical, a lifetime similar to that determined for other excited ketyl radicals [15] can be assumed, i.e. a lifetime in the range 1–4 ns. This would yield, for the quenching rate constants $k_Q{}^*$ in the three different solvents, values ranging from 1×10^9 to 3×10^{10} M^{-1} s^{-1}, characteristic of diffusion control. This may explain why the dependence of $k_Q{}^*$ on the nature of the substrate is less marked in the excited state than in the ground state. Thus, for the excited ketyl radical, the highest rate constant is only about 15 times larger than the smallest, whereas this factor is approximately 10^5 for the kinetics of the ground state radical.

The quenching of the ketyl radical in the excited state by E4, MMA and styrene is at least 10^4 times greater than in the ground state. The kinetics with O_2 follow the same behaviour, but are less marked, because the induced quenching process for the ground state is already governed by a high rate constant. The enthalpy of the excited state of the ketyl radical is approximately 50 kcal mol^{-1} above that of the ground state. Assuming that electron transfer energy processes do not occur, since both the singlet and triplet energies of the quenchers are greater than 70 kcal mol^{-1} [39], the excitation energy determines that fluorescence quenching processes, such as electron transfer and addition reactions, are favoured in the excited state of the radical and, consequently, characterized by higher rate constants than those obtained for the radical in its ground state. Therefore the characteristics typical of an excited state dominate the free radical properties, as has been previously observed for other excited ketyl radicals [17].

3.6. Relative efficiencies of generation of the ketyl radical from the photolysis of E4 solution in AcN, 1,4-dioxan and THF

Radical generation is the generally accepted mechanism of photoinitiator-induced polymerization. Therefore the determination of the efficiency of radical generation during 308 nm photolysis of E4 solutions is of importance to evaluate the capability of this organic molecule as a polymerization initiator. Unfortunately, LIF techniques cannot provide reliable absolute yields. However, the dependence of the efficiency of radical generation on the initiator solvent can be determined relatively.

At low probe laser intensities, where saturation effects can be neglected, the LIF signal is proportional to the concentration of ketyl radicals in the absorbing level under the low optical absorption conditions used. Thus when E4 solutions of equal absorbance at the photolysis laser wavelength in two different solvents are probed, the ratio of the two LIF signals can be evaluated

$$\frac{I_f^1}{I_f^2} = \frac{[R^\cdot]_2\,\epsilon_1}{[R^\cdot]_2\,\epsilon_2} \qquad (16)$$

where the indices 1 and 2 refer to two selected solvents, $[R^\cdot]$ is the ketyl radical concentration generated in each solvent and ϵ is the extinction coefficient of the radical at the probe laser wavelength in each solvent. This relation is valid as long as the laser intensities, quantum yield of excited level generation and fluorescence emission quantum yield are not solvent dependent, which is probable since a common radical transition is probed.

According to Eq. (16), the relative efficiency of ketyl radical generation, Eff_1/Eff_2, can be determined directly as $[R^\cdot]_1/[R^\cdot]_2$ from the ratio of the measured fluorescence intensities corrected by the extinction coefficients ϵ_1/ϵ_2. The dependence of ϵ on the E4 solvents used is unknown. However, based on previous work [17], which reveals changes of less than 10% in the lifetime of the excited diphenylmethyl radical for the solvents methanol, THF, cyclohexane and AcN, it can be assumed that the extinction coefficient ϵ of the ketyl radical does not change significantly for the E4 solvents selected in the present work.

Under these assumptions, the relative efficiencies of ketyl radical generation in the ground state by 308 nm photolysis of E4 solutions in AcN and 1,4-dioxan, normalized to the value for an E4–THF solution, can be calculated. The results obtained are reported as Eff_{sol}/Eff_{THF} in Table 1. These values are determined for a fixed delay of 36 μs between the lasers and for the same E4 concentration, 5×10^{-4} M, in each solvent. The efficiency of generation of ketyl radicals during the photolysis of E4 in THF is 1.7 times higher than in 1,4-dioxan and 3.5 times higher than in AcN. This trend in efficiency should be directly related to the hydrogen atom donor capability of the solvent.

From a practical point of view, a comparison of the kinetic data reported in this work with the quantum yield of polymerization initiated by E4 in MMA and styrene would establish the relative weight that factors, such as the radical reactivity, monomer structure, nature of the solvent and substituent effects in the initiator molecule, have in the polymerization process. Work in this direction is in progress.

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