

SINGLE PULSE TWO-PHOTON LASER-ASSISTED REDUCTION OF BENZOPHENONE BY TRIETHYLAMINE TO FORM EXCITED BENZOPHENONE KETYL RADICAL

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The pulsed laser photolysis at 308 nm of the benzophenone-triethylamine system in acetonitrile solution has been studied at room temperature. In the absence of triethylamine, phosphorescence emission of triplet benzophenone centred at 460 nm and with a lifetime of $\tau = 27 \pm 1 \mu\text{s}$ is observed. Addition of triethylamine results in quenching of the benzophenone phosphorescence. Quenching rate constants k_Q have been determined from emission intensities and from experimental decay rate constants. The values $k_Q = (2.6 \pm 0.3) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $k_Q = (4.0 \pm 0.5) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively, are obtained. On the addition of triethylamine, benzophenone phosphorescence diminishes and simultaneously a new emission with a fast decay rate and centred at 575 nm develops. This signal has been identified as emission from the excited benzophenone ketyl radical. A single pulse two-photon absorption mechanism responsible of the emission at 575 nm has been identified and a kinetic model based on this mechanism has been developed. The model gives a satisfactory quantitative account of both our experimental results and those reported in the literature (quantum yield of radical formation and behaviour of the system as photoinitiator).

KEY WORDS: Laser Photochemistry, two-photon excitation.

INTRODUCTION

The present interest in tailor-made photoinitiators for specific applications requires the prediction of the relationship between molecular structure and properties. Aromatic carbonyl compounds have been proposed as photoinitiators because of the ability of their triplet state, formed at high yield on ultraviolet irradiation, to abstract hydrogen atoms and produce radicals.^{1,2} In addition, photoinitiators containing aromatic carbonyl functions as chromophores have been widely studied in order to determine the behaviour of intermediaries which can 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 intermediary. A thorough comprehension of the reaction mechanism will provide the means to control the undesired processes that can take place.

The benzophenone photoreduction by amines has been studied for a long time. Part of the observations related to the present work were published in the classical papers of Cohen *et al.*⁵⁻⁷ and of Wagner *et al.*⁸ Several authors have published reviews on the subject.^{9,10} The proposed mechanism for the photoreduction of benzophenone involves an electron transfer from amine to benzophenone followed by a proton transfer^{11,12} that forms the benzophenone ketyl radical; the possibility of an ion-pair or a charge transfer complex as intermediaries was included. The mentioned conclusions were arrived at before lasers were incorporated in the flash-photolysis techniques. Later studies accepted that spectral detection of a benzophenone anion or a amine cation warranted the intermediacy of a charge transfer process in the photoreduction process. The majority of the initial studies on the benzophenone (BZ)-triethylamine (TEA) system, using nano- and pico-second techniques, were unable to provide evidence on the participation of polar intermediaries.¹³⁻¹⁶ Only Schaefer *et al.*¹⁷ reported the identification of a complex but the enormous amine concentrations used cast some doubts on its intermediacy under ordinary photoreduction conditions. More recently, Devadoss and Fesseden¹⁸ also favoured the mentioned mechanism, although based on indirect evidence. Gas phase results of Matsushita *et al.*¹⁹ showed that neither the formation of a long lived complex nor the contribution of the solvent molecules are necessary for the hydrogen abstraction.

In most of the modern work the benzophenone ketyl radical (BK^{*}) has been analyzed by LIF, a second laser promoting the transition from the ground to the excited state of the radical.²⁰⁻²⁶ As far as we know only in one previous work the possibility of biphotonic absorption has been reported.²⁷

In this work we have simultaneously followed the time integrated intensity of both benzophenone phosphorescence centred at 460 nm and fluorescence of the excited benzophenone ketyl radical at 575 nm. Both emissions have been readily identified in this work from their spectra and lifetimes.

The data obtained have allowed us to report a case in which a single 308 nm laser pulse of modest energy (a few millijoules) is able to generate an excited benzophenone ketyl radical, in a solution of benzophenone and triethylamine in acetonitrile, through a process that may be defined as a two-photon single pulse assisted reaction. Evidence on the biphotonic character of the process is presented and a kinetic model based on those premises built. The model gives a satisfactory quantitative account of both the data here reported and those reported in the literature (quantum yield of radical formation and behaviour of the system as photoinitiator).

Although photo or laser-assisted reactive collisions is an extremely active field of research (see ref. 28 for a review), we are not aware of any well documented report of single pulse two-photon laser-assisted reaction in the liquid phase.

EXPERIMENTAL SYSTEM

A home-made XeCl excimer laser supplying up to 40 mJ energy in ~12 nsec FWHM pulses at 308 nm was used as the excitation source. A quartz beam splitter selected ~10% of the laser output to be directed towards the 1 cm silica cell containing the solutions. A 1 m focal length spectroil B spherical lens focused mildly the excitation light onto the cell and a 2 mm iris diaphragm placed before the cell selected the central part of the rectangular laser beam assuring spatial uniformity of the light illuminating the cell. The total energy of the pulse impinging in the cell was estimated as ~1 mJ. A 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 for triggering the detection system. The luminescence (monitored at right angles to the exciting beam) was imaged, after the passage through a cut-off filter to eliminate 308 nm scattered light, onto the input slit of a monochromator (MacPherson-2035, 0.35 m) and detected by a photomultiplier (EMI 9816-QB). The signal from the photomultiplier was either displayed directly on a digital oscilloscope (Tektronix 2430) for real time measurements or, for spectra recording, fed to a box-car (Stanford SR-250) to be integrated before being digitized by a SR-245 A/D converter. A personal computer was used to record the signal as well as to control and synchronise the whole experiment. The details of the operation of this system have been described elsewhere.²⁹ In short, the monochromator stepper motor was controlled by the computer by means of a driver card D100 from Berger Lahr and the SR-245 interface from Stanford Research. The "busy" output provided by the box-car synchronised the signal coming from the detection system (cell, monochromator, photomultiplier and box-car) with its acquisition, and conducted it to the computer through the RS 232 interface, to be stored with the corresponding wavelength. The process was repeated at the same wavelength as many times as necessary to obtain an acceptable S/N ratio. Next, the monochromator moved to a new wavelength ($\lambda + \Delta\lambda$) and the whole process was repeated until the final wavelength was reached.

Experiments were performed in order to study the dependence of the emissions at 460 and 575 nm on incident laser intensity. The pump laser intensity was attenuated in a controlled way by intercalating in the pumping beam path different numbers of microscope cover glasses.

Materials and sample preparation

Benzophenone (Aldrich, 99%) and Acetonitrile (Scharlau, far UV HPLC grade) were used as received. Triethylamine (Scharlau) was distilled and stored under nitrogen. Sample concentrations were prepared by standard methods. Degassing of the samples was accomplished by the "freeze and thaw method" pumping down to pressures below 10^{-4} torr.

RESULTS AND DISCUSSION

Irradiation of benzophenone (BZ) in acetonitrile (ACT) at 308 nm gives a spectrum (Fig. 1a) that can be identified as belonging to phosphorescence of the benzophenone triplet state (experimental conditions are described below). It shows clearly the vibrational progression typical of this emission, and the maximum at 460 nm coincides with the reported values.^{30,31a} The dependence of the triplet benzophenone (BZT) lifetime on BZ concentration in ACT, in a range from 1.5 to approximately 20 mM, was studied in the first place in order to find the more favourable experimental conditions for further work. It was found that the change in the BZT lifetime was practically negligible for concentrations between 2 and 4 mM. So, in the experiments described below the BZ concentration was maintained between 3.6 and 3.9 mM. The emission intensity decay under these conditions (i.e. BZ concentration = 3.9 mM) is shown in Figure 1b. It exhibits a clear unimolecular behaviour with a lifetime $\tau = 25 \pm 1 \mu\text{s}$ in good agreement with literature values.^{32,33} In all cases the error quoted corresponds to two standard deviations from the mean.

Under the above experimental conditions, [BZ] = 3.6–3.9 mM, the addition of triethylamine (TEA) in concentrations of the order of 50 mM inhibits completely the BZT phosphorescence and causes the appearance of a strong signal whose spectrum is identical to that reported for the fluorescence emission of the excited benzophenone ketyl radical (BK^{•*}). Its lifetime is below our quantitative detection limits (i.e. below 10 ns), which is consistent with the values reported in the literature.^{19,34–37} At lower TEA concentrations both the BZT phosphorescence and this new emission with the maximum centred at 575 nm are simultaneously seen (Fig. 2). At first, the new emission appears just as a shoulder on the BZT phosphorescence. Then, its intensity increases as TEA concentration is raised until finally, at high TEA concentrations, it is the only observable emission.

The emission intensities at 460 nm and at 575 nm, referred to the water Raman band at 340 nm as internal standard, have been plotted against TEA concentration in Figure 3. The benzophenone phosphorescence decays very fast, a TEA concentration of less than 1 mM is enough to reduce the emission to a level indistinguishable from the experimental background. The emission growth at 575 nm presents a completely different pattern. It increases slowly and for high TEA concentrations seems to reach a plateau.

In what follows, the laser intensity dependence of the two emissions will be analyzed in the first place. Afterwards, the BZT phosphorescence kinetic behaviour and the 575 nm band will be studied; finally a mechanism of reaction will be described and modelled in a context that includes all the available information.

Laser intensity dependence of the 460 nm and 575 nm emissions

The probability of biphotonic absorption W in a sequential process is quadratically dependent³⁸ on the laser incident intensity (I),

$$W \propto I^2.$$

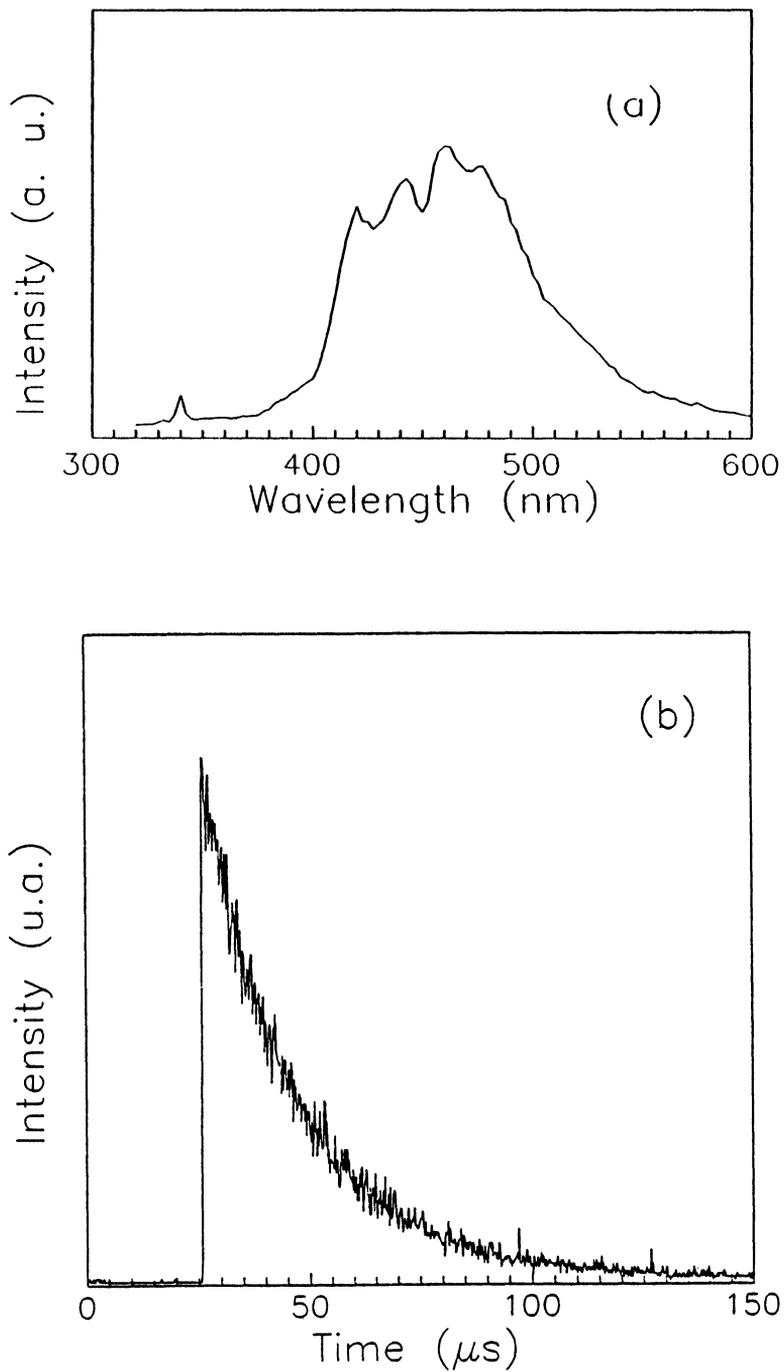


Figure 1 Phosphorescence spectrum (a) and temporal decay of the emission intensity at 460 nm (b) of a solution of benzophenone in acetonitrile 3.9 mM after laser irradiation at 308 nm.

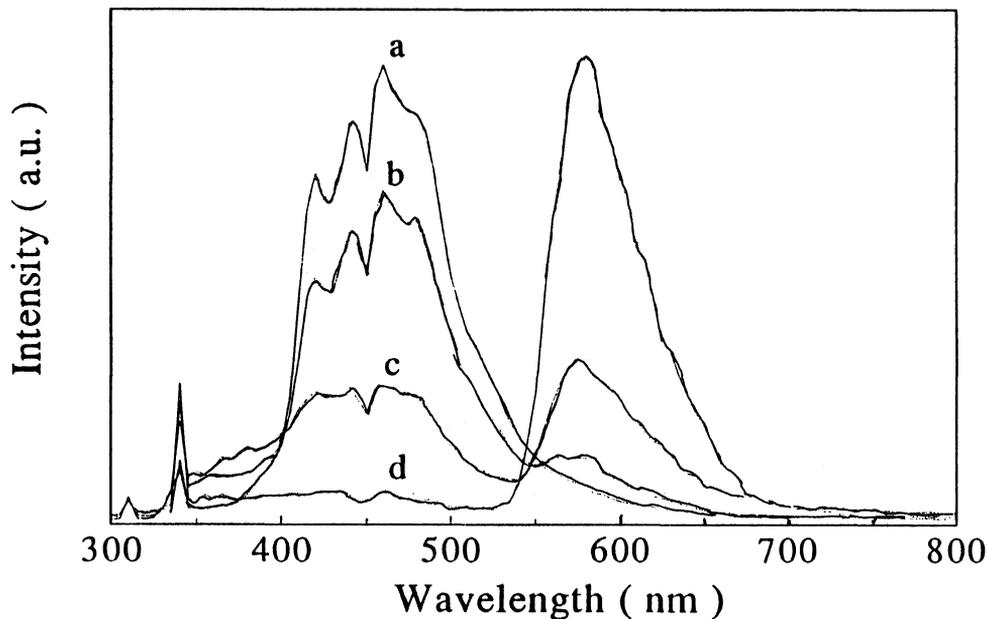


Figure 2 Emission spectra of a solution of benzophenone in acetonitrile 3.9 mM after laser irradiation at 308 nm with different triethylamine concentrations: a) 0 mM, b) 0.02 mM, c) 0.7 mM, and d) 50 mM.

The laser intensity dependence of the 460 nm emission has been measured in a solution of BZ (3.7 mM) in ACT while the corresponding study of the emission at 575 nm was carried out in a solution of BZ/TEA (4/50 mM) in ACT. These concentrations provide the best possible S/N ratio. The observed extremely fast quenching of the 460 nm emission by TEA prevents the analysis of this emission in the presence of even minute amounts of quencher.

The natural logarithms of the observed emission intensities at 460 nm and 575 nm have been plotted against the natural logarithm of the incident pumping laser intensity in Figure 4. According to the above equation a sequential biphotonic absorption should yield a straight line with slope 2. The experimentally obtained slope for the 575 nm emission is 1.88 ± 0.06 , close to the theoretically expected value. The error quoted corresponds to one standard deviation of the mean. The discrepancy is of the expected magnitude in this type of measurements in which the pump beam is mildly focused.^{39,40} Thus, we can safely conclude that the formation of the excited benzophenone ketyl radical is consequence of a single pulse two photon sequential absorption.

The behaviour of the 460 nm emission is totally different. The value found for the slope, 0.51 ± 0.03 , is below the single photon absorption value of 1. Absorption by the initially formed benzophenone triplet could explain the observed result.⁴¹ In the absence of TEA, the BZT lifetime is of the order of tenths of microseconds, allowing the fast build up of a relatively high transitory concentration of BZT, making the possibility of the pulsed light absorption by BZT facile.

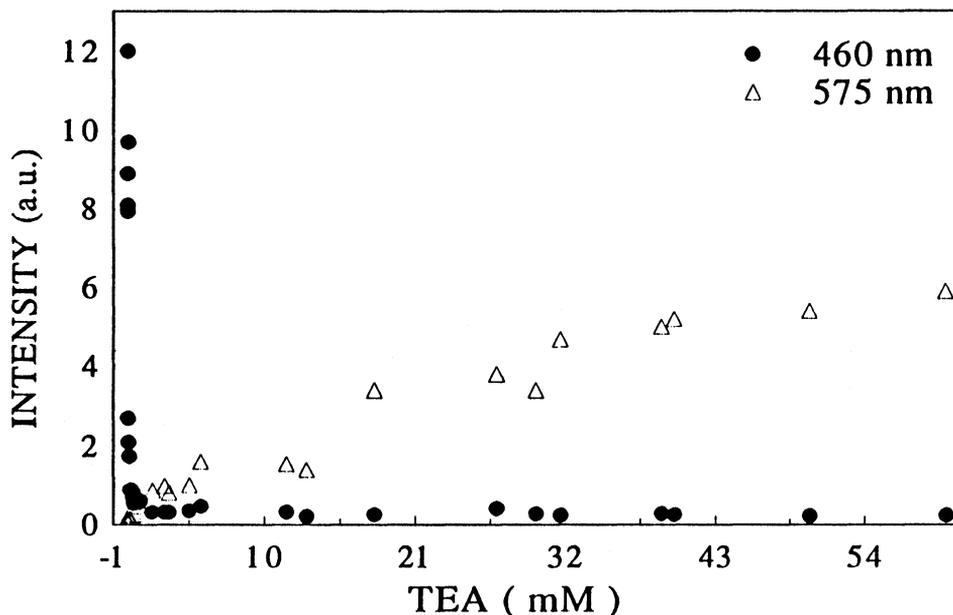


Figure 3 Intensities of the emission from laser irradiated (308 nm) benzophenone in acetonitrile with added triethylamine at 460 nm and 575 nm v.s. triethylamine concentration. The water Raman band at 340 nm was used as internal standard.

In the experiment with high TEA concentration, where the 575 nm emission has been analyzed, the quenching of BZT induced by TEA should reduce its lifetime to a few nanoseconds impeding the BZT population build up, and consequently making the absorption by the triplet very unlikely and therefore, its influence negligible.

Experimental determination of the triplet benzophenone quenching rate constant by triethylamine

a) Quenching rate constant determination from emission intensities at 460 nm.

The quenching rate constant can be calculated from the emission intensity values using the well known Stern-Volmer equation^{31b}

$$I_0 / I = 1 + k_Q[Q]/\Sigma k$$

where I_0 is the emission intensity at 460 nm in absence of TEA, I is the intensity at each different TEA concentration, k_Q is the TEA quenching rate constant, $[Q]$ is the quencher concentration, and Σk is the sum of deactivation rates in absence of TEA. From the experimentally observed lifetime in absence of TEA Σk can be evaluated, $\Sigma k = 1/\tau_0 = (37 \pm 2) \times 10^3 \text{ s}^{-1}$.

The Stern-Volmer representation (i.e. I_0/I vs. $[Q]$) is shown in Figure 5. It can be observed that the least squares fit of the experimental results produces a straight line with reasonable point scattering. The intercept, 0.7 ± 0.1 , is not far from one, the

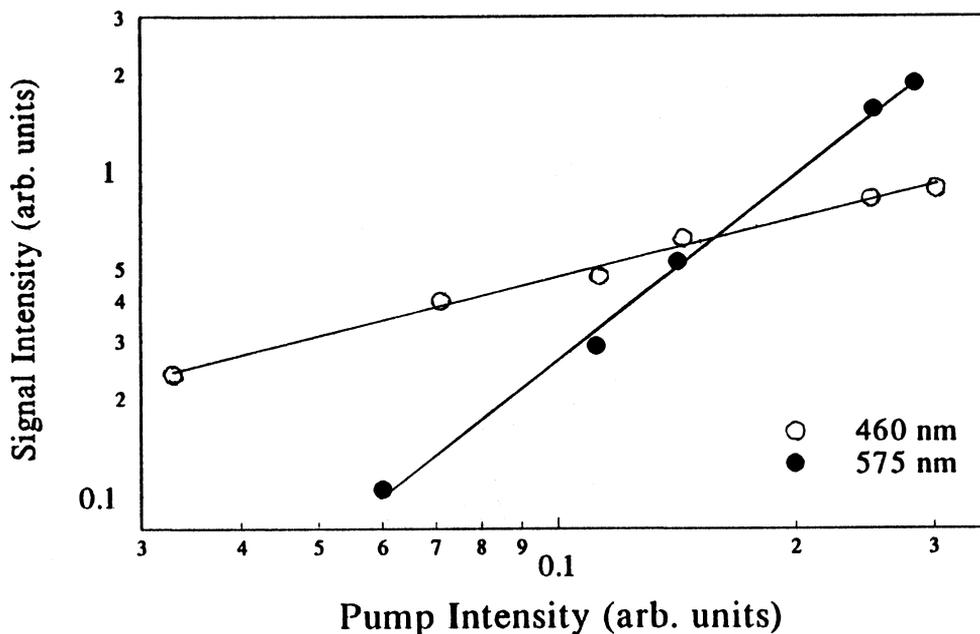


Figure 4 Pump laser intensity dependence of the emission at 460 nm (○) and 575 nm (●).

expected value according to the above equation, and the calculated slope is $k_Q/\Sigma k = (7.1 \pm 0.7) \times 10^4 \text{ M}^{-1}$. From this value and the previously evaluated Σk the following quenching rate constant of BZT by TEA is obtained, $k_Q = (2.6 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is in good agreement with those found in the literature, see below.

b) Quenching rate constant determination from experimental phosphorescence decay rates at 460 nm.

In this case, the Stern-Volmer equation can be written as:

$$k_{\text{exp}} = \Sigma k + k_Q[Q]$$

where k_{exp} is the experimentally determined decay rate constant for each quencher concentration $[Q]$ (i.e. $[\text{TEA}]$), and Σk , as previously defined, is the experimental rate of decay in absence of quencher. The representation (Fig. 6) of k_{exp} against TEA concentration and the least square fit of the experimental results gave the following result, $k_Q = (4.0 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The ordinate intercept provides the value $\Sigma k = (35 \pm 6) \times 10^3 \text{ s}^{-1}$, in good agreement with the above calculated figure.

The discrepancy in the quenching rate constant values obtained by each method could be ascribed to the different systematic errors introduced in each case. Therefore, the preferred figure for the evaluated quenching rate constant of benzophenone triplet phosphorescence by triethylamine would be the averaged value $(3.3 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

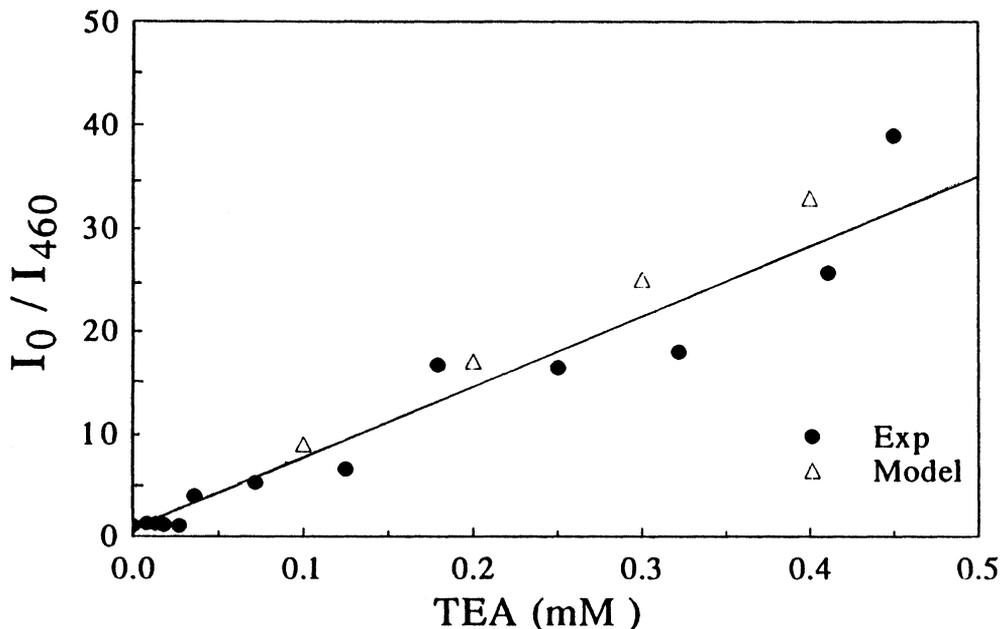


Figure 5 Stern-Volmer representation of the 460 nm phosphorescence intensity quenching. Full circles “●” correspond to experimental data and triangles “△” to model calculated data.

The values above mentioned are within the range of values quoted in the literature, $3.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ by Devadoss *et al.*¹⁸ and $3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ reported by Cohen *et al.*⁴² Turro^{31c} gave a value of $2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ but, in this case, benzene was the solvent. In gas phase, Matsushita *et al.*¹⁹ found a faster rate constant, $7.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. This surprising value may indicate that solvation effects may be unnecessary for the electron transfer process in this particular case.

Analysis of the emission at 575 nm

As previously explained, both the spectrum and lifetime ($\tau < 10 \text{ ns}$, our quantitative detection time limit) of the emission centred at 575 nm agree with those of the transition of the benzophenone ketyl radical from its first electronically excited state to the ground state.

The intensity of the emission at 575 nm (I_{575}) normalized by its maximum value (I_{max}), corresponding to the highest TEA concentrations (50–60 mM), has been plotted in Figure 7 against TEA concentration. The behaviour of this emission (Figures 2, 3) is quite peculiar. It appears when most of the BZT phosphorescence has disappeared, and slowly increases as TEA concentration is raised until it reaches a quasi saturation for high TEA concentrations. It is evident from the figures that no correlation exists between the BZT emission decay and the BK** emission growth.

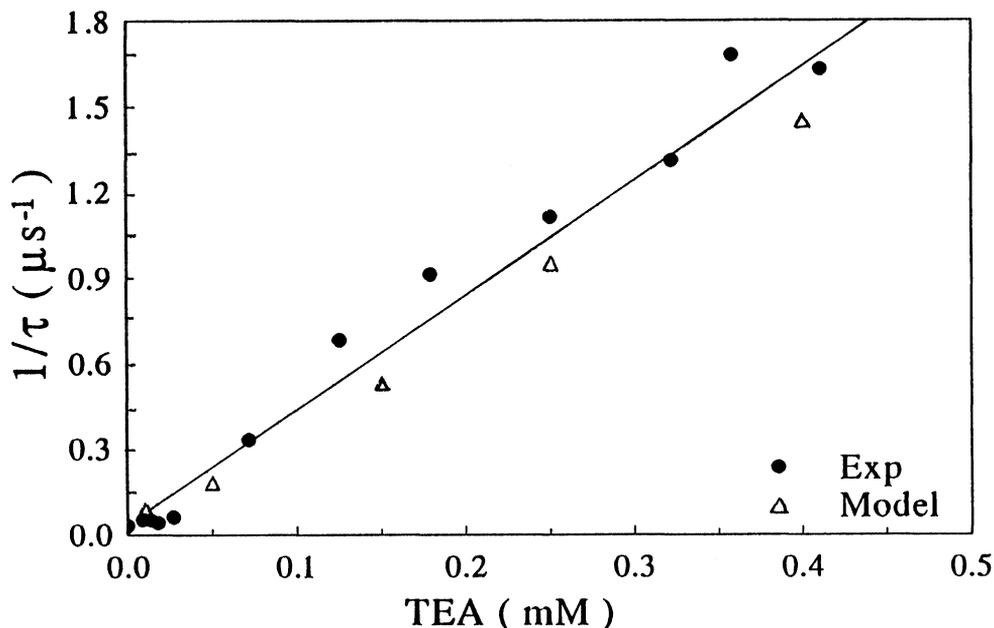


Figure 6 Stern-Volmer representations of experimental decay rates at 460 nm. Full circles “●” correspond to experimental data and triangles “Δ” to model calculated data.

Mechanistic interpretation and modelling

An attempt to develop a kinetic model has been carried out. In principle the model should fulfil the following requirements:

1. The excited benzophenone ketyl radical must be formed by a single pulse two-photon absorption assisted reaction process.
2. The quantum yield of benzophenone ketyl radical formation should be the unity under proper conditions (i.e. high enough TEA concentration).^{17,43-45}
3. The model must reproduce within reasonable accuracy the experimental intensities of BZT phosphorescence against TEA concentration (Figure 3).
4. The model should provide BZT intensity decay rates for the different TEA concentrations in reasonable agreement with the experimentally calculated data (Figure 5).
5. The model should give theoretical intensities at 575 nm (i.e. benzophenone ketyl radical emission) in agreement with those found experimentally (Figure 3).

Several attempts were made before an acceptable model was found. The first requirement reduces the time available for the absorption of the second photon to the duration of the laser pulse.

The second requirement rejects the possibility of any bifurcation in the BZT to BK* path giving a product different from the ketyl radical. On the other hand, the high BZT quenching rate precludes a fast enough return of the charge transfer com-

radical TEA^{*}. The BK^{*} can absorb a second 308 nm photon from the laser pulse with rate k_{ab} forming the excited benzophenone ketyl radical BK^{**}, that emits at 575 nm with rate k_f .

The above mechanism was modelled as follows. The sum of BZT decay rates by internal conversion k_{ic} and phosphorescence k_{ph} can be reasonably approximated by the experimental decay of BZT in ACT without added TEA, $k_0 = \tau^{-1} = (37 \pm 2) \times 10^3 \text{ s}^{-1}$, previously evaluated. The partial contribution of each rate constant is difficult to evaluate exactly for a given set of experimental conditions. Matrix phosphorescence lifetimes³⁰ may provide some criteria for partitioning; however, the possible increase of the phosphorescence by specific interactions, between BZT and solvent should be taken into account⁴⁴. The values used in the model have been $k_{ph} = 8.4 \times 10^3 \text{ s}^{-1}$ and $k_{ic} = 2.9 \times 10^4 \text{ s}^{-1}$. The BZT quenching rate constant used in the model was close to the averaged value previously calculated using the two different Stern-Volmer approaches, $k_Q = 3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The protonation rate constant was fixed at $k_p = 6.7 \times 10^{10} \text{ s}^{-1}$.^{17, 45} The laser pulse was estimated as a triangular area corresponding to the total number of 308 nm laser pulse photons incident into the cell and a width (FWHM) of about 10ns. The absorption rate constant was evaluated from the known benzophenone ketyl radical extinction coefficient $\epsilon = 3700 \text{ M}^{-1} \text{ cm}^{-1}$ at 308 nm.⁴⁶ The excited benzophenone ketyl radical emission rate constant was obtained from the already mentioned emission lifetime.

The integration of the differential equations set was accomplished by the ACUCHEM program⁴⁷ that is based in the well known variable order, variable step DDRIV integrator,⁴⁸ and provides all the facilities needed. A compatible PC computer was used.

Analysis of the model behaviour

The model so developed accomplishes all the requirements demanded.

The quantum yield of benzophenone ketyl radical calculated as $\phi = k_Q [\text{TEA}] / (k_Q [\text{TEA}] + k_{ph} + k_{ic})$, and using model values for the different rate constants, is $\phi = 0.986$ for a TEA concentration of 1 mM, and reaches 0.9998 for concentrations of 10 mM. These figures are in good agreement with the reported value $\phi = 1$.

Some calculated values, I_0/I_{460} have been represented along with the experimental data in the Stern-Volmer plot of the phosphorescence intensity quenching (see Fig. 5). The deviations from the experimental least squared Stern-Volmer straight line are within the experimental errors. Model calculated intensity decay rates, $1/\tau$, also show a good behaviour, as can be seen in Figure 6.

The model calculated intensity at 575 nm, represented as a full line in Figure 7, also is in good agreement with the experimental results.

According to the evidence presented so far, it seems that the biphotonic absorption mechanism properly explains the experimental data obtained for the 308 nm laser photolysis of benzophenone in the presence of TEA. The model includes, and therefore agrees with, most of the known available data about the system: BZT quenching rate constants, extremely high protonation rate of the intermediate complex, and formation of the BZ ketyl radical. However, the model says little about how the

included charge transfer complex is formed. The model discards the sometimes mentioned return back to the initial state. This fact coupled with recent gas phase results¹⁹ may indicate that the charge transfer stabilization is really unimportant in this particular system, and perhaps it could be responsible for the sound behaviour of the system as polymer photoinitiator. Somehow the lack of C.T. stabilization may provide the driving force that induces the fast and efficient protonation pathway leading to the radicals.

The mechanistic description of the single pulse two-photon assisted reaction allows a simple evaluation of the minimum rate constant values involved in the process. Thus, the reaction sequence: absorption of the first photon, formation of the excited singlet BZ, intersystem crossing to the BZT, electron transfer and biradical ion formation, proton transfer, and final BZ ketyl radical absorption of the second photon must occur in less than 10 ns. The possibility of using the single pulse two photon sequential absorption assisted reaction scheme for the investigation of extremely fast reactions could be of interest.

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