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New intermediates in the reaction of benzophenone photoreduction by hydrogen donors

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Abstract

The influence of various factors on the photoreduction of benzophenone by benzhydrol and triethylamine was studied using flash photolysis and steady state spectroscopic techniques. As a result of the investigations conducted, it has been shown that one of the intermediates formed in the reaction is a ketyl radical complex. The second component of the complex is a hydrogen-donor radical. A benzophenone–triethylamine ground state complex is also produced. This affects the properties of the detected radical complex. The spectral and kinetic characteristics of the observed intermediates are presented and the mechanism of the photoreduction is proposed. The mechanism includes the formation of a long-lived exciplex and its decay in two competitive processes: photochemical reaction of the triplet exciplex leads to a ketyl radical and thermal reaction of the exciplex leads to a ketyl radical complex.

Keywords: Benzophenone; Photoreduction; Hydrogen donor

1. Introduction

Benzophenone photoreduction by hydrogen donors has been studied for some time. Nevertheless, the nature of the nascent intermediates of the reaction and their dynamics continue to give rise to much controversy [1–4]. One intermediate of this interaction is a ketyl radical. Its mechanism of formation is controversial [2,3], although its spectral and kinetic characteristics are well known [5,6]. On investigation of benzophenone photoreduction by triethylamine in hydrocarbons, using the flash photolysis technique [7], we discovered that, under certain irradiation conditions, the decay kinetics of non-stationary absorption in the millisecond region were complex and inconsistent with the behaviour of a ketyl radical or other intermediates described in the literature. This motivated a more detailed investigation which is the subject of this paper.

2. Experimental details

Benzophenone was purified by triple recrystallization from ethanol. Triethylamine was repeatedly vacuum distilled. Benzhydrol was recrystallized from a petroleum ether–benzene mixture (2:1). Hydrocarbons were pur-

ified by stirring with oleum, followed by rinsing with concentrated sulphuric acid, water, weak sodium hydroxide solution and again water. They were dried over potassium hydroxide and then distilled.

In all the experiments, the benzophenone concentration was 3×10^{-3} M and that of benzhydrol was 6×10^{-2} M. In the flash photolysis experiments, solutions were vacuum treated using three freezing–evacuation–defrosting cycles. The cuvette thicknesses in the flash photolysis and steady state spectroscopy experiments were 7.8 and 0.1 cm respectively.

2.1. Flash photolysis methods

The spectra and decay kinetics of the intermediates of benzophenone photolysis in the presence of triethylamine or benzhydrol were investigated in the microsecond to millisecond time interval. Irradiation of the solutions was performed using two flash lamps with light filters ($\lambda_{max\ transparency} = 330$ nm). The pulse duration was 40 μs. The flash energy was varied within the range 1.0–8.0 J. For monitoring, use was made of focused visible light (400–700 nm) from an incandescent (175 W) lamp. Under the conditions of the experiment, the intensity of the probe beam incident on the cuvette was varied in the range 0.1–1.0 W cm^{-2}. Automated,

computerized data acquisition was used. The initial recording point was 35 μs after termination of the flash.

2.2. Non-stationary absorption signal processing technique

To reduce the error of the experiment, non-stationary absorption signals were stored and averaged over 10–15 flashes. The averaged signal was smoothed by the spline interpolation technique. The experimental time dependence of the optical density of non-stationary absorption was approximated with linear first- and second-order reactions. If approximation with simple kinetic first- and second-order equations proved inadequate, experimental relationships were approximated with more intricate equations. In each particular application, the following conversions were addressed:

(1) the concurrent progress of (a) ketyl radical dimerization and (b) interaction between the ketyl radical and the hydrogen donor or solvent;

(2) the concurrent progress of (a) ketyl radical dimerization and (b) interaction between the ketyl and aminoalkyl radicals in the volume of the solvent;

(3) the concurrent observation of two light-absorbing intermediates, one of which decays by a first-order reaction and the other, the ketyl radical, in a dimerization reaction.

The differential equation (in the case of (1)) and the set of differential equations (in the case of (2)) were solved by the Runge–Kutta and/or Gear methods. In the case of (3), the Hooke–Jeeves optimization method was adopted for solving the equation

$$D(t) = D_{01} \exp(-k_1 t) + D_{02}/(1 + 2k'_2 D_{02} t) \qquad (1)$$

where D_{01} and D_{02} are the optical densities at the initial instant of time (t) for the intermediate components of the mixture, k_1 is the rate constant of the first-order reaction and k'_2 is associated with the magnitude of the second-order reaction rate constant k_2 by the relation $k'_2 = k_2/\epsilon l$, where $\epsilon = 4340$ M^{-1} cm^{-1} [8] is the extinction coefficient of the ketyl radical and l is the length of the cuvette. If not otherwise stated, data on non-stationary absorption kinetics are attributed to $\lambda = 545$ nm. In all cases, kinetic curves with a 10–20-fold decrease in optical density were investigated.

2.3. Procedure of evaluation of the quantum efficiency of benzophenone consumption

Relative values of the quantum efficiency of benzophenone consumption were determined spectrophotometrically from the decreasing steady state absorption of the solution in the region $\lambda = 344$ nm. Solutions were irradiated using the same pulsed radiation sources as in the kinetic measurements of non-steady state absorption. The decrease in the optical density of a

benzophenone solution in decane, irradiated with 100 pulses in the absence of probe radiation, was taken as a unit. Prior to irradiation, solutions were evacuated by three freezing–evacuation–defrosting cycles. On irradiation, to avoid the interference of light-absorbing, long-lived intermediates on the quantities being measured, the solutions were thoroughly shaken in the presence of air (oxygen) and held for 24 h. The optical density was measured in cuvettes (thickness, 1 cm).

3. Results

Benzophenone irradiation in the presence of triethylamine leads to ketyl radical formation with high quantum efficiencies [3,6]. The ketyl radical exhibits an absorption spectrum with a maximum around $\lambda = 545$ nm and decays via a second-order reaction with a rate constant of the order of 10^9 M^{-1} s^{-1} [5,6].

Fig. 1 shows the non-stationary absorption spectrum and decay kinetics obtained for an intermediate of photolysis of a benzophenone solution in hexane in the presence of 5 mM triethylamine. The spectrum shape, maximum location ($\lambda = 545$ nm) and decay kinetics of the non-stationary absorption are in good agreement with the spectral and kinetic characteristics of the ketyl radical. Allowing for the fact that the rate constants of interaction between the triplet state of benzophenone and amine, on the one hand, and hydrocarbon, on the other, are about 3.0×10^9 M^{-1} s^{-1} [6] and 3.5×10^5 M^{-1} s^{-1} [9] respectively, it may be supposed that, under the conditions of the experiment, the ketyl radical is mostly formed in the reaction with amine.

The observation that the kinetic parameters of the process are dependent on the intensity of the probe radiation incident on the measuring cuvette proved totally unexpected. This is revealed at reduced flash energies. As follows from the data listed in Table 1,
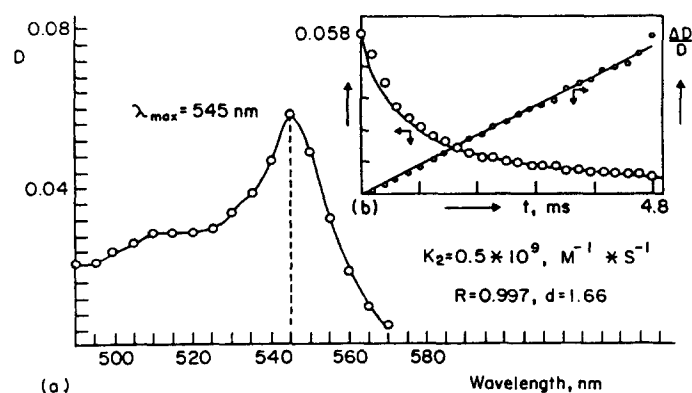

Fig. 1. Absorption spectrum (a) and decay kinetics (b) for an intermediate of benzophenone photoreduction in hexane in the presence of triethylamine (5 mM). Flash energy, 2.2 J. Probe beam intensity, 1.0 W cm^{-2}. D is the optical density, R is the correlation coefficient and d is the root-mean-square deviation.

Table 1

Influence of the probe beam intensity on the kinetics of decreasing optical density of non-stationary absorption during the photolysis of a hexane solution of benzophenone in the presence of triethylamine (5 mM). Flash energy, 1.1 J. Approximation with linear kinetic equations for first- and second-order reactions

Monitoring beam intensity (W cm^{-2})	Approximation parameters					
	R^a	d^a	$k \times 10^{-3\,a}$ (s^{-1})	R^b	d^b	$k \times 10^{-9\,b}$ (M^{-1} s^{-1})
0.10	0.999	0.01	2.49	0.957	7.74	–
0.45	0.969	0.13	–	0.993	2.99	–
1.00	0.915	0.18	–	0.998	1.08	1.8

[a]First order.
[b]Second order.

when the probe beam intensity decreases, the parameters of the decay kinetics of non-stationary absorption vary regularly. At an intensity of 0.1 W cm^{-2}, the decay of the photolysis species obeys a kinetic first-order equation with a rate constant of 2.5×10^3 s^{-1}; the optical density at the initial point of measurement remains practically unchanged.

The result obtained is hard to explain from the available literature data. It is evident that the photochemical reactions of the ketyl radical, described in the literature [10], have nothing to do with these results. More specifically, for the conditions of our experiment, at high irradiation intensities, the appearance of non-stationary absorption and the decay kinetics are easily accounted for by the properties of the ground state of the ketyl radical (see Fig. 1). It is not until the irradiation intensity is decreased that the first-order reaction is observed.

In Ref. [5], diffusion was assumed to play a large role in the kinetics of ketyl radicals. To study the influence of the diffusion parameters of the medium on the decay of benzophenone photolysis intermediates, we investigated the effect of the solvent viscosity on the kinetic parameters of the process.

A comparatively small increase in the solvent viscosity results in a large change in the decay process of the photolysis intermediates (Table 2). Indeed, in hexane, there is a satisfactory correlation between the analytical curve and the experimental data only for a second-order kinetic equation; in n-tetradecane, the decay curve follows first-order kinetics; therefore with increasing viscosity of the solvent, the variation of the correlation coefficient and the standard deviation invariably fits a rigorous pattern. The figure at the bottom of Table 2 illustrates the results of the approximation of the experimental data by various kinetic equations for a solution in n-tetradecane. The value of the first-order decay rate constant, calculated from these data, is 2.2×10^3 s^{-1}, approaching that quoted in Table 1. This

indicates that, in both cases, the same reaction is in evidence.

Let us consider the possible processes that may lead to the kinetic regularities presented in Tables 1 and 2. The reaction of geminate recombination between the ketyl and aminoalkyl radicals can be ruled out. Such processes, although proceeding as first-order reactions, are observed in the nanosecond region in media of high viscosity (10^2–10^4 cP) [11], and their rate constant is three to four orders of magnitude larger than that obtained here.

First-order kinetics may underlie the interaction between a ketyl radical and the solvent or amine to form benzhydrol. A ketyl radical–donor radical reaction may also significantly affect the kinetics of non-stationary absorption decay [6]. With increasing viscosity of the solvent, the diffusion rate of the ketyl radical decreases to a greater extent than that of amine or aminoalkyl radicals. The above reactions must therefore compete with ketyl dimerization. By and large, this is in accord with the data in Table 2. However, such an assumption does not explain the results regarding the influence of the probe beam intensity (Table 1). Nevertheless, the possibility of these reactions was taken into account when constructing mathematical models to describe the variation in the optical density of non-stationary absorption for complex processes. All the kinetic curves used in the calculations, portrayed in Tables 1 and 2, were examined as described in Section 2.2 (items (1) and (2)). The results of these calculations proved unsatisfactory.

We have therefore assumed that there are two types of intermediates with optical absorption in the same spectral region but different reactivity. The relative concentrations of the intermediates are a function of the solvent viscosity and the probe radiation intensity. When one of the intermediates prevails, the kinetic changes are simple and obey a first- or second-order reaction. With more complex concentration ratios, more complicated decay kinetics are observed.

Tables 3 and 4 show the approximation of the kinetic data given in Tables 1 and 2 by Eq. (1). The results presented in these tables show that all the kinetic curves fully obey Eq. (1). In all the applications, the correlation coefficient approaches unity, and the magnitude of the standard deviation is small, such that the rate constants k_1 and k_2 of the elementary reactions agree, within acceptable limits, with the corresponding values listed in Tables 1 and 2 and are independent of the irradiation conditions and diffusion parameters of the medium. However, with increasing probe beam intensity and solvent viscosity, the composition of the intermediates shows a regular variation.

Spectral investigations provide additional evidence in favour of the above assumption. Fig. 2 shows the

Table 2
Influence of the solvent viscosity on the kinetics of decreasing optical density of non-stationary absorption during the photolysis of a solution of benzophenone–triethylamine (5 mM). Flash energy, 1.1 J. Probe beam intensity, 1.0 W cm^{-2}. Approximation with linear kinetic equations for first- and second-order reactions

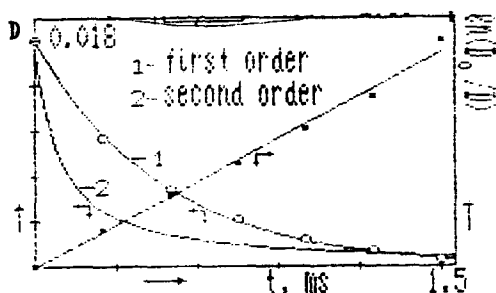| Solvent viscosity (cP)	Approximation parameters					
	R^a	d^a	$k \times 10^{-9\,a}$ $(M^{-1}\ s^{-1})$	R^b	d^b	$k \times 10^{-3\,b}$ (s^{-1})
Hexane/0.32	0.990	18	1.8	0.925	0.32	–
Nonane/0.73	0.580	1966	–	0.963	0.41	–
Undecane/1.20	0.552	2824	–	0.974	0.38	–
n-Tetradecane/2.19	0.823	153	–	0.997	0.009	2.15

^{a}Second order.
^{b}First order.

Table 3
Influence of the probe beam intensity on the kinetics of decreasing optical density of non-stationary absorption during the photolysis of a hexane solution of benzophenone in the presence of triethylamine (5 mM). Flash energy, 1.1 J. Approximation with Eq. (1)

Monitoring beam intensity (W cm^{-2})	D_{01}/D_{02}	$k_1 \times 10^{-3}$ (s^{-1})	$k_2 \times 10^{-9}$ $(M^{-1}\ s^{-1})$	R	$d \times 10^3$
0.10	81	2.6	1.0	1.000	0.16
0.45	3.0	2.9	1.2	0.999	0.24
1.00	0.00003	2.6	2.2	0.999	0.33

absorption spectra of the intermediates of benzophenone photolysis in the presence of triethylamine (5 mM) in hexane solution at a flash energy of 1.1 J. Comparing spectrum 1 (Fig. 2) with that presented in Fig. 1, it can be seen that its shape varies somewhat with decreasing flash energy. There is a maximum at $\lambda = 510$ nm and a peak at $\lambda = 525$ nm. Still greater spectral

changes occur (curve 2, Fig. 2) with decreasing probe beam intensity. In comparison with spectrum 1, the optical density declines appreciably in the region $\lambda = 500$ nm, signalling a variation in the composition of the photolysis intermediates exhibiting optical absorption in the spectral region explored.

Let us discuss the nature of the intermediates detected. All the evidence shows that one of them is a ketyl radical. The nature of the second is unknown.

During the course of the reaction, an aminoalkyl radical is formed [6,12]; however, it does not absorb light in this particular spectral region. The lifetime of the triplet state of benzophenone in hydrocarbons is several microseconds [9] and, in the presence of triethylamine, it should be even less [6]. Therefore the triplet state of benzophenone cannot be detected under our experimental conditions. The anion radical of benzophenone exhibits a broad absorption band in the visible region [2,4]. It may be formed in the reversible reaction of ketyl radical deprotonation by triethylamine

Table 4
Influence of the solvent viscosity on the kinetics of decreasing optical density of non-stationary absorption during the photolysis of a solution of benzophenone–triethylamine (5 mM). Flash energy, 1.1 J. Probe beam intensity, 1.0 W cm^{-2}. Approximation with Eq. (1)

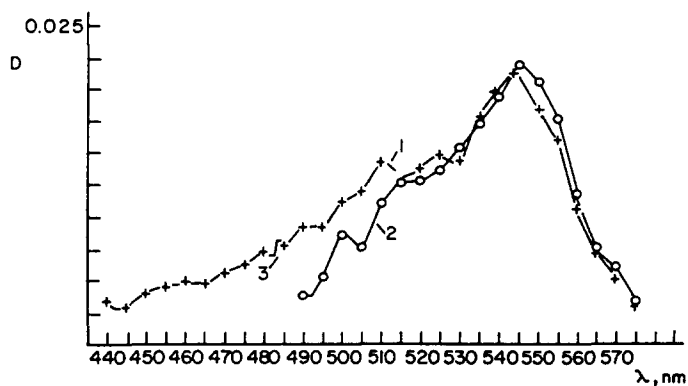| Solvent viscosity (cP)	D_{01}/D_{02}	$k_1 \times 10^{-3}$ (s^{-1})	$k_2 \times 10^{-9}$ $(M^{-1}\ s^{-1})$	R	$d \times 10^3$
Hexane/0.32	0.00003	2.6	2.2	0.999	0.33
Nonane/0.73	75	1.83	0.9	0.998	0.22
Undecane/1.20	71	2.02	1.0	0.999	0.25
n-Tetradecane/2.19	20000	2.11	1.0	0.999	0.16

Fig. 2. Non-stationary absorption spectra for intermediates of benzophenone photoreduction in hexane. Triethylamine concentration, 5 mM. Flash energy, 1.1 J. Probe beam intensity, 1.0 W cm^{-2} (spectrum 1) and 0.1 W cm^{-2} (spectrum 2). The confidence interval for the optical density is also shown (3).

[2]. However, in a medium of low polarity, this reaction can only be expected for polyfluorobenzophenones exhibiting a high electron deficiency of the carbonyl group [13]. Furthermore, this cannot account for the results presented in Tables 1 and 3.

Our results indicate that the absorption spectrum and lifetime of the second intermediate are comparable with those of the ketyl radical. Thus it is possible that this species is a ketyl radical complex. It decays via a first-order reaction with a rate constant of $(2–3) \times 10^3$ s^{-1} and forms at low irradiation intensities. At elevated irradiation intensities, a ketyl radical is formed.

Remarkably, variations in the composition of the mixture of intermediates may occur under the action of the probe radiation in the visible region, which is not absorbed by the precursors. This indicates that the ketyl radicals detected under the conditions of these experiments are formed as a product of a secondary photochemical reaction. Therefore, among the products of the primary photochemical reaction, there must be an intermediate preceding the formation of the ketyl radical which exhibits photochemical activity when irradiated with visible light. Simple analysis reveals that about 0.5 ms is needed for the formation of the observed number of ketyl radicals (about 1×10^{15} ketyl molecules in a cell volume of 8 ml at $D \approx 1 \times 10^{-2}$) under the action of the probe light with an intensity of 1 W cm^{-2}. In this case, to observe an influence of the probe light intensity on the composition of the intermediates, it should be assumed that the quantum yield of the reaction is close to unity.

On investigation of benzophenone photoreduction in hydrocarbons at higher triethylamine concentrations, we observed similar regularities. Variations in the radiation intensity and viscosity of the medium were accompanied by changes in the decay kinetics of non-stationary absorption (see Tables 1–4). A number of

peculiarities regarding the progress of the reaction were revealed, which merit detailed discussion.

On photolysis of benzophenone solution in hexane in the presence of 0.5 M triethylamine (or lower concentrations), the photolysis intermediate decays by a first-order reaction at low irradiation intensities (Fig. 3). However, the decay rate constant is an order of magnitude lower $(4.4 \times 10^2$ $s^{-1})$.

With increasing concentrations of triethylamine, the non-stationary absorption spectrum of the photolysis species changes markedly. In Fig. 4, curves 1 and 2 correspond to the absorption spectra of the intermediates obtained on photolysis of a benzophenone solution in hexane at different triethylamine concentrations. As can be seen, spectrum 2 is somewhat broadened compared with the ketyl radical absorption spectrum (curve 1). The absorption band maximum shows a 10 nm shift to the long-wavelength region, with a decrease in the band intensity. As the concentration of triethylamine is increased further, the location of the maximum
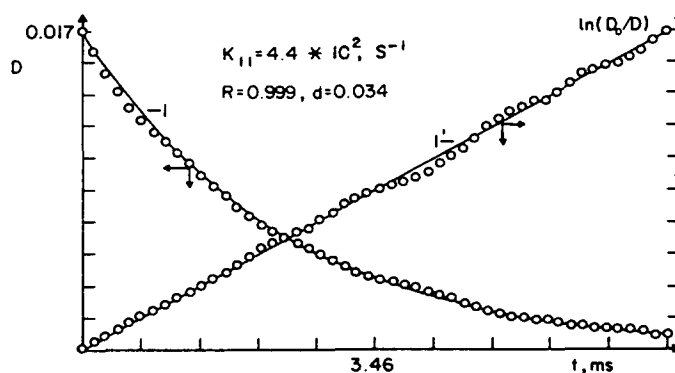

Fig. 3. Decay kinetics of photolysis intermediate of benzophenone–triethylamine (0.5 M) in hexane solution. Flash energy, 1.1 J. Probe beam intensity, 0.1 W cm^{-2}.
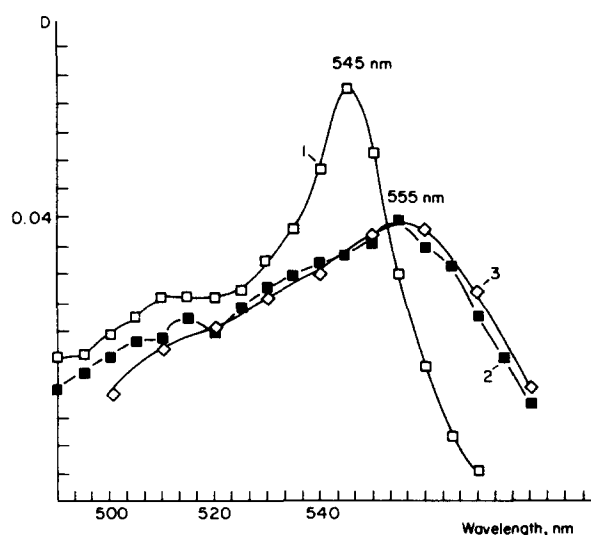

Fig. 4. Non-stationary absorption spectra of products of benzophenone photolysis in the presence of 5 mM (1) and 0.5 M (2,3) triethylamine. Spectra 1 and 2 were obtained in hexane, spectrum 3 in n-tetradecane. Flash energy, 2.2 J. Probe beam intensity, 1.0 W cm^{-2}.

at 555 nm remains unchanged. The decay kinetics of non-stationary absorption are complex and cannot be described by a simple kinetic equation. However, the kinetics obey Eq. (1), yielding the values $k_{\parallel} = 4.2 \times 10^2$ s^{-1} and $k_2 = 2.2 \times 10^9$ M^{-1} s^{-1} (at $D_{01}/D_{02} = 0.54$, $R = 0.997$ and $d = 0.5 \times 10^{-3}$). These magnitudes are comparable with the corresponding values from a linear approximation of the kinetic curves presented in Figs. 1 and 3. The rate constant k_2 apparently characterizes the process of ketyl radical recombination. No component with a decay rate constant of $(2-3) \times 10^3$ s^{-1} was detected over the wavelength range of the spectrum. Spectrum 2 is composed of two main absorption bands: those of the ketyl radical and a species decaying in a first-order reaction with a rate constant k_{11}.

Changes in the absorption spectrum also occur when the viscosity of the medium is increased. Spectrum 3 was obtained on photolysis of benzophenone and triethylamine in n-tetradecane (at the same concentrations of the reagents). In comparison with spectrum 2 (Fig. 4), there is a decrease in the optical density in the 500 nm region and a slight increase in the long-wavelength region. An analysis of the kinetics of decreasing optical density in spectrum 3 reveals no component with a second-order decay. The decay of the non-stationary absorption is uniform over the entire wavelength range, following the kinetics of a first-order reaction with a rate constant of $(3.5-5.5) \times 10^2$ s^{-1}. Presumably, this signals the detection of only one intermediate. Its decay rate constant is close to the k_{11} value obtained in the analysis of spectrum 2 and the k_{11} value obtained by linear approximation of the data presented in Fig. 3. The same intermediate is detected in these cases.

Thus, as expected, a ketyl radical is detected among the intermediates during the photolysis of a benzophenone solution in hydrocarbons in the presence of 0.5 M triethylamine. Under our experimental conditions, it forms at elevated irradiation intensities and is detected in the non-stationary absorption spectrum. The absorption spectrum may also include a second component decaying by a first-order reaction with $k_{11} = (3.5-5.5) \times 10^2$ s^{-1}. This intermediate is formed predominantly if photolysis is performed at reduced radiation intensities (probe and excitation) or in a high viscosity medium. The non-stationary absorption spectrum of this intermediate is observed with $\lambda_{max} = 555$ nm. We believe that this intermediate is a ketyl radical complex as its absorption spectrum and lifetime are comparable with those of a ketyl radical.

The difference between the spectral and kinetic features of the ketyl radical complexes monitored at diverse concentrations of triethylamine was studied in more detail.

An increase in amine concentration can lead to the formation of a ground state complex with benzophenone.

This may affect the pattern of elementary photoreaction processes [1,4], with attendant variations in the quantitative and qualitative compositions of the nascent intermediates [14,15].

To explore the possibility of the formation of a ground state complex between benzophenone and triethylamine, we investigated the steady state absorption spectra of benzophenone solution in heptane at different triethylamine concentrations. Similar investigations have been carried out [6,16,17], with no conclusion being reached about the formation of the complex. This may be because only the $n \to \pi^*$ region of the spectral absorption band of benzophenone was studied. However, it is common knowledge that, as amines possess an undivided pair of n electrons, they are capable of forming donor–acceptor complexes of the $n-\pi$ type, acting as an electron donor [18]. This is accompanied by the appearance of a new spectral absorption band in the $\pi-\pi^*$ transition region of the electron-acceptor molecule [19]. The results of the spectral investigations are shown in Fig. 5.

It follows from Fig. 5(a) that, in the $\pi-\pi^*$ region of the benzophenone absorption band, the optical density of the benzophenone–triethylamine mixture (spectrum 3) exceeds the sum of the spectra of the separate components (spectrum 4). This indicates the formation of a benzophenone–triethylamine complex. No spectral
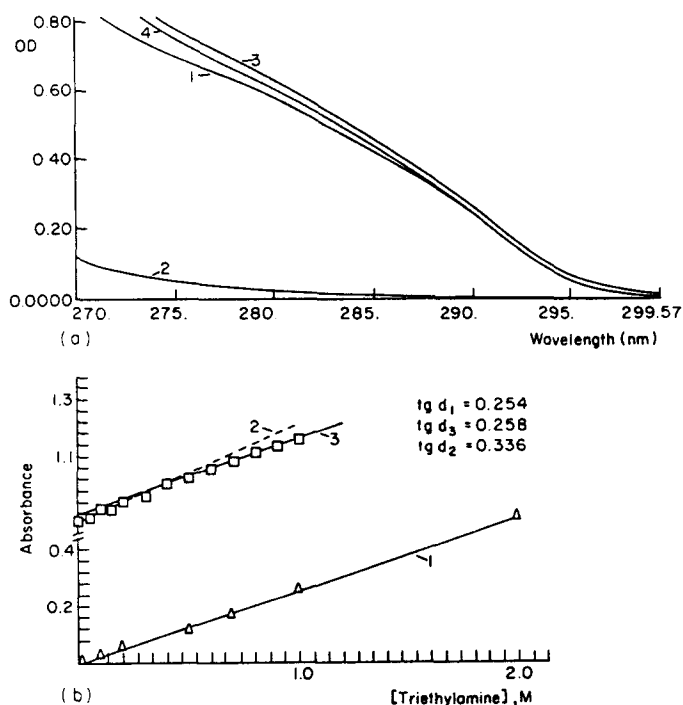

Fig. 5. (a) Steady state absorption spectra of solutions of benzophenone (1), triethylamine (0.5 M) (2) and their mixture (3) in heptane. Curve 4 is the algebraic sum of spectra 1 and 2. (b) Optical density variation of a heptane solution of triethylamine at increasing concentrations ($\lambda = 270$ nm) in the absence (1) and presence (2 and 3) of benzophenone.

changes were observed in the n–π* region of the benzophenone absorption band.

Results supporting the formation of a ground state complex were also obtained on investigation of the effect of the presence of benzophenone on the variation of the optical density of triethylamine solution at increasing concentrations (Fig. 5(b)). In the absence of benzophenone, the optical density of the solution is linearly dependent on the triethylamine concentration (straight line 1). On introduction of benzophenone into the solution, curvature is observed in the 0.3 M triethylamine region. A linear approximation of these data by the least-squares technique shows that, in the presence of benzophenone, the optical density of the solution above the point of curvature (last seven points, straight line 3) increases as in the absence of benzophenone. The slopes of the corresponding straight lines are equal within the limits of experimental error. Below the point of curvature (the first five points, straight line 2), the optical density increases much more rapidly, which is symptomatic of the formation of a complex. Its composition is apparently 1:1. The formation of a complex was also verified by computations. Results of processing by the TRIANG program [20] of the concentration dependences presented in Fig. 5(b) for the 270–300 nm wavelength region demonstrated the formation of a benzophenone–triethylamine complex.

We estimated the stability constant of the complex from the data presented in Fig. 5(b): 5.5 M^{-1}. The corresponding value for a benzophenone–cyclohexylamine complex in benzene, obtained on analysis of the photochemical data by the Stern–Volmer equation, is 8 ± 1 M^{-1} [15]. Thus, at a triethylamine concentration of 0.5 M, virtually all of the benzophenone is present in the solution as a ground state complex with amine. Perhaps the changes in the spectral and kinetic characteristics of the ketyl radical complex can be related to the involvement of the benzophenone–triethylamine complex in the photoreduction process.

Fig. 6(a) shows the results of an investigation of the effect of temperature on the composition of the intermediates during the photolysis of a benzophenone–triethylamine solution at the initial point of observation. The latter was determined by analytical treatment of the kinetic decay curves of the optical density by Eq. (1). As can be seen from the figure, an increase in temperature promotes ketyl radical complex formation and impedes free ketyl radical formation. The nature of the influence of temperature on the formation of the ketyl radical and its complex indicates that these intermediates are formed from one precursor as a result of competitive reactions. From the data of Fig. 6(a), it also follows that the reaction of ketyl radical complex formation is endothermic. Therefore the complex cannot be an association product as this would
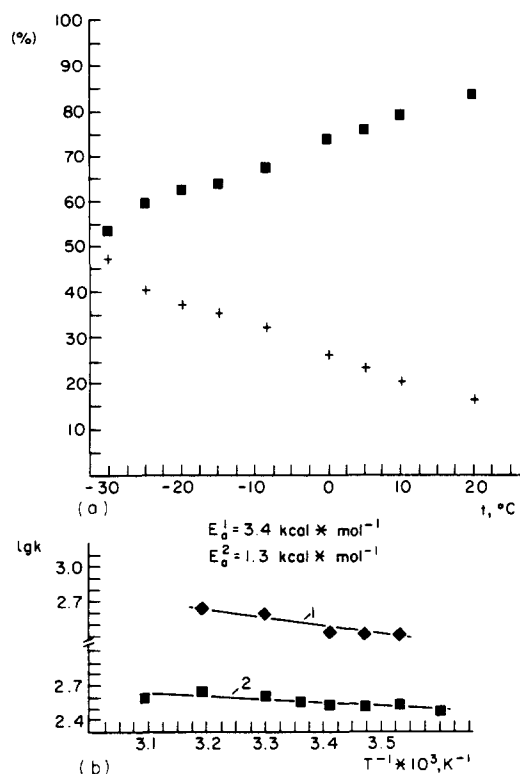

Fig. 6. (a) Effect of temperature on the yield of intermediates during the photolysis of a benzophenone–triethylamine solution in hexane at the initial point of observation. Triethylamine concentration, 0.5 M. Flash energy, 1.1 J. Probe beam intensity, 1.0 W cm^{-2}. Ketyl radical (+). Ketyl radical complex (■). (b) Arrhenius dependence of the first-order reaction rate constant for: 1, decay of the intermediate of benzophenone solution photolysis in hexane in the presence of 0.5 M triethylamine; 2, decay of the intermediate of benzophenone solution photolysis in benzene in the presence of benzhydrol.

be accompanied by a reduction in entropy, which is impossible in terms of thermodynamics.

Fig. 6(b) shows the influence of temperature on the rate constant of decay of the ketyl radical complex formed in the photoreaction of benzophenone and triethylamine (0.5 M) in hexane (dependence 1). These data show a linear relationship in terms of the Arrhenius equation. An approximation of the data by a least-squares technique yields the magnitude of the activation energy of the process ($E_a = 3.4$ kcal mol^{-1}) for a pre-exponential value of about 10^5. The resulting low values are quite revealing. This has been observed for reactions of certain triplet state complexes [9,21]. Thus the possibility that the observed intermediate has a spin multiplicity of three cannot be ruled out.

Results similar to those presented in Fig. 6(a) were also obtained during benzophenone photoreduction in the presence of 5 mM triethylamine. Presumably, the reaction mechanism does not change critically with varying concentration of the amine.

Results concerning the effect of the photolysis conditions on the quantum efficiency of benzophenone

consumption are listed in Table 5. We determined the relative values of the quantum efficiencies spectrophotometrically as described in Section 2. Errors in the values determined, related to the formation of long-lived, light-absorbing intermediates, are apparently not critical [15,22].

As shown in the table, an increase in intensity of the probe radiation leads to an increase in the quantum efficiency of benzophenone consumption. A control experiment has demonstrated that prolonged irradiation of the solution with a probe light source only does not result in a change in the benzophenone concentration. This result cannot be explained by photochemical reactions of the ketyl radical. In this case, the quantum efficiency of benzophenone consumption would decrease with increasing intensity of visible radiation [10].

Conversely, the quantum efficiency of benzophenone consumption decreases with increasing viscosity of the medium. Comparing the data in Tables 1-5, we can conclude that the formation of a ketyl radical complex is accompanied by a decreasing quantum efficiency of benzophenone consumption. Supposedly, the decay process of this complex results in benzophenone regeneration.

Similar results were found on investigation of benzophenone photoreduction by triethylamine in acetonitrile. The decay kinetics of non-stationary absorption of the photolysis intermediates were also dependent on the probe radiation intensity, although to a lesser degree. An increase in triethylamine concentration led to the formation of a ground state benzophenone-amine complex. In acetonitrile, the stability constant of the complex was 2.8 M^{-1}. The ketyl radical complex had a decay rate constant of $(8-10) \times 10^2$ s^{-1} for a triethylamine concentration of 0.5 M.

The essential question is how general are the results presented here. In this connection, we investigated the benzophenone photoreduction by benzhydrol in benzene. This photoreaction is well known, and has been adopted for chemical actinometry [23] and also as a

model system for the investigation of free radical activities [24]. Only one type of radical product, the ketyl radical, is formed, and exhibits non-stationary optical absorption in the millisecond time interval [5,6].

Fig. 7 (curve 1) shows the absorption spectrum of the photolysis intermediate of the solution under investigation. It is identical in form and maximum location ($\lambda = 540$ nm) to the spectrum of ketyl radical absorption in benzene [6]. However, a decrease in the intensity of the probe beam leads to perceptible spectral changes; the optical density in the 470-510 nm region decreases and in the maximum region increases (curve 2). The typical convexity on the curve in the 510 nm region disappears. An investigation of the dynamics of the spectral variation with time reveals that the maximum tends to shift to the long-wavelength region (curve 3).

The results of the spectral measurements (Fig. 7) indicate that, as in the case of triethylamine, the composition of the intermediates of the photoreaction is a function of the intensity of the probe beam and varies with time. The latter doubtless points to the different decay kinetics of the intermediates observed.

We investigated the variation with time of the optical density of non-stationary absorption. Four experimental dependences corresponding to absorption at 540 and 560 nm for probe light intensities of 1.0 and 0.1 W cm^{-2} were treated analytically. In all cases, kinetic curves with a 20-fold decline in optical density were examined.

According to Refs. [5,6], the decay kinetics of the ketyl radical in benzene obey a second-order reaction. The same result was observed in Ref. [25] for benzophenone photoreduction in cyclopentane. However, in our runs, none of the investigated experimental time dependences of optical density satisfies a second-order reaction. This is illustrated by Fig. 8(a), where curve 2 is consistent with a linear approximation of the experimental data by a second-order reaction. The

Table 5
Effect of the irradiation conditions and the medium viscosity on the relative value of the quantum efficiency of benzophenone consumption, on photoreduction in hydrocarbons in the presence of 0.5 M triethylamine

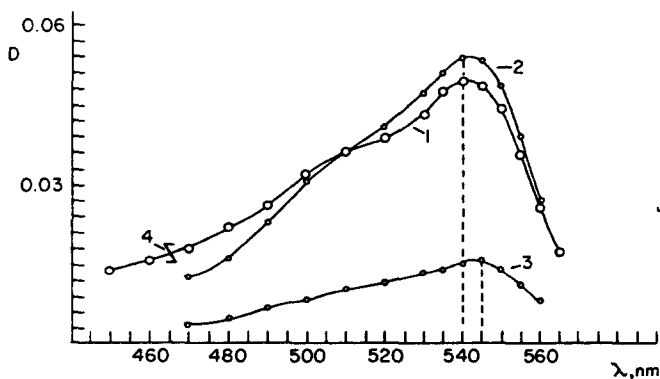| Solvent, condition of irradiation	Viscosity (cP)	Relative value of quantum yield
Decane, $I_{prob} = 0$ W cm^{-2}	0.92	1.00
Decane, $I_{prob} = 1.0$ W cm^{-2}	0.92	1.82
n-Tetradecane, $I_{prob} = 1.0$ W cm^{-2}	2.19	0.76

Fig. 7. Spectra of the non-stationary absorption of products of benzophenone photolysis in benzene in the presence of benzhydrol: 1,2, immediately after the flash; 3, after 2.14 ms. Spectra 2 and 3 were taken at a probe beam intensity of 0.1 W cm^{-2}, spectrum 1 at 1.0 W cm^{-2}. The confidence interval for the optical density is also shown (4). Flash energy, 2.2 J.
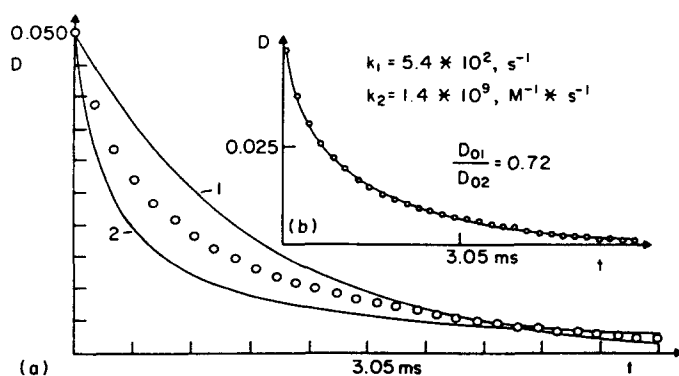
Fig. 8. Decay kinetics of non-stationary absorption of the intermediates formed during the flash photolysis of a benzene solution of benzophenone in the presence of benzhydrol in the region $\lambda = 540$ nm. Flash energy, 2.2 J. Probe beam intensity, 1.0 W cm^{-2}.

approximation by a first-order kinetic equation (for example, curve 1, Fig. 8(a)) also yields an unsatisfactory correlation between the analytical curves and the experimental data.

The results of our kinetic investigations do not fully agree with the literature data [5,6,25], but support the hypothesis advanced above on the intricate composition of the intermediates detected.

As in the case of the benzophenone–triethylamine photoreaction, we have assumed that the spectral and kinetic dependences are related to the formation and decay of two intermediates: one which decays via a first-order reaction and one which decays via a second-order reaction (ketyl radical). Proceeding from these assumptions, we executed applicable analyses using Eq. (1).

We found that the correlation between the analytical curves and the experimental data was good. In all four applications, the maximal absolute departure of the analytical data from the experimental values was within 10% of the minimal value of the optical density (the last point of the kinetic curve), with the magnitudes of the desired parameters being independent of the magnitude of the initial approximation. The results of such an analysis for one of the investigated dependences are presented in Fig. 8(b).

The value of the rate constant of the first-order reaction was $(4.2–5.5) \times 10^2$ s^{-1}. Within the limits of experimental error, this is equal to the value for the decay of the ketyl radical complex observed on benzophenone photoreduction in the presence of 0.5 M triethylamine in hexane. According to our measurements, the magnitude of the rate constant of the second-order ketyl recombination reaction is $(1.1–1.4) \times 10^9$ M^{-1} s^{-1}, which is in good accord with Refs. [5,6].

In addition, the analysis verifies the correctness of the assumption regarding the dependence of the photolysis intermediates on the intensity of the probe radiation. As the latter increases from 0.1 to 1.0 W

cm^{-2}, the D_{01}/D_{02} ratio in the region $\lambda = 540$ nm decreases from 0.85 to 0.72. Changes in the composition of the photolysis intermediates are also expected to be a function of the pulse source intensity. Indeed, when there is a fivefold increase in the pulse irradiation intensity, the decay of the optical density obeys a simple second-order reaction with $k_2 = (1.0–1.4) \times 10^9$ M^{-1} s^{-1}. Probably, no intermediate decaying by a first-order reaction is formed under these conditions.

As in the case of triethylamine, the temperature dependence of the rate ·constant of the first-order reaction can be readily linearized in terms of the Arrhenius equation (Fig. 6(b), dependence 2). The linear approximation of the dependence by a least-squares technique yields the values of 1.3 kcal mol^{-1} and about 10^4 for the activation energy of the process and the preexponential respectively.

Thus it can be concluded that the formation of a ketyl radical complex also occurs in the photoreduction of benzophenone by benzhydrol. It is similar to the ketyl radical complex observed in the photoreduction of benzophenone by triethylamine.

4. Discussion

The possibility of the formation of various complexes by the ketyl radical has been repeatedly debated in the literature (electron spin resonance (ESR) spectroscopy [26] and laser flash photolysis techniques [6,16]).

In Ref. [16], changes in the non-stationary absorption spectrum of the intermediates of benzophenone solution photolysis, with an increase in triethylamine concentration, were ascribed to the formation of a ketyl radical–amine complex with a hydrogen bond. An absorption spectrum of the complex was obtained by subtracting the ketyl radical absorption spectrum from that observed. Its shape and maximum location (555 nm) are identical with the spectrum obtained here (Fig. 4, spectrum 3). There is reason to believe that the same intermediate is present. Also, we can interpret the nature of the intermediates detected as ketyl radical complexes by virtue of their spectral and kinetic characteristics. However, as has been mentioned above, the formation of the complexes does not stem from the specific interaction between the ketyl radical and triethylamine. We believe that a better explanation for the results presented here can be provided by the assumption that a ketyl radical–hydrogen-donor radical complex is formed, with the radicals resulting from the same encounter complex.

Let us address the possible conversion dynamics of the intermediates of this photoreaction that could result in these complexes. To this end, we shall consider a scenario involving benzophenone photoreduction by triethylamine.

Irradiation of a benzophenone solution with UV light leads to the rapid formation (within picoseconds) of the triplet excited state of benzophenone [3] (step 1 in Scheme 1). This state interacts with triethylamine by charge transfer [6,27,28], although the nature of the nascent intermediate is controversial. For instance, it has been reported that the interaction involving charge transfer between triplet excited benzophenone and triethylamine in acetonitrile results in a complex with a strong charge transfer structure [2,29]. This conclusion was drawn from picosecond spectral measurements which revealed absorption symptomatic of benzophenone anion radicals. Such an interpretation of the data [2,29] is at odds with the view that charge transfer occurs only partially [27,28]. The reason for this contradiction may originate from the fact that the analyses in Refs. [2,29] were based on very large concentrations of the reagents (10–100 mM benzophenone and 1–3 M triethylamine). In this case, according to our findings, a considerable portion of the benzophenone will be present in the solution as a ground state complex. The benzophenone anion radical is effectively formed from the singlet excited state of this complex [1,4]. Thus, in our opinion, the assignment of the structure with strong charge transfer to benzophenone triplet excited state reaction products [2,29] is erroneous.
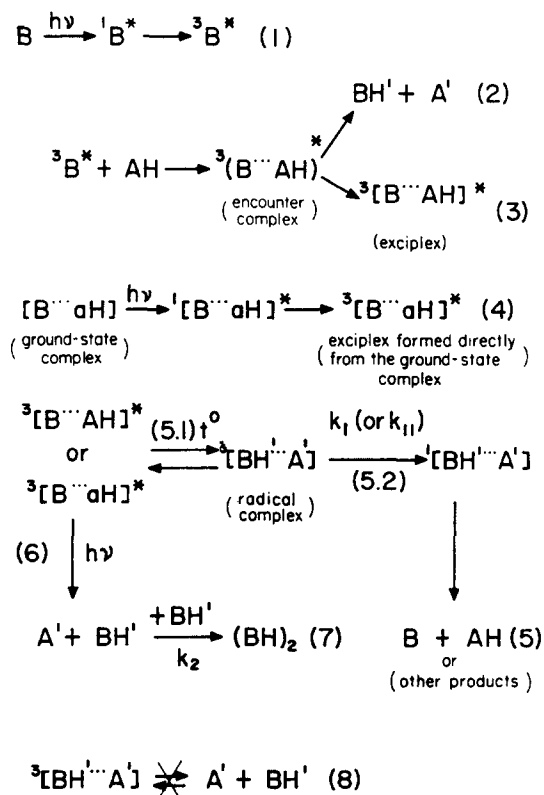
In Refs. [27,28], a complex with partial charge transfer (we shall call it an exciplex) is considered to be a prime product of the interaction between triplet excited benzophenone and triethylamine.

The next step of the reaction is the formation of ketyl radicals. In Refs. [3,4,6,17], it is presumed that this is a transient process and that exciplex formation cannot be observed in either nanosecond or picosecond measurement ranges. This is often invoked to prove the direct mechanism of ketyl radical formation (step 2, Scheme 1). Our findings do not allow us to deny the possibility of such a process. However, we believe, as does Jaques [28], that the key point for subsequent conversions is exciplex formation (step 3, Scheme 1).

From the discussion of the experimental results given above, it has been concluded that a photochemically active intermediate is formed in the reaction of benzophenone photoreduction by triethylamine. The absorption of light from the probe source by this intermediate triggers ketyl radical formation. The above properties can be exhibited by a triplet exciplex. Presumably, the exciplex is also a precursor for the formation of a ketyl radical complex, as shown by the temperature dependence of the composition of the intermediates. The possible structure of the exciplex, and its formation and decay mechanisms are considered below.

The reaction of triethylamine and triplet excited benzophenone begins with charge transfer interaction [6,27]. This occurs between a nitrogen atom possessing an undivided n electron pair and acting as donor and an oxygen atom showing electron deficiency and serving as an acceptor (steps 1 and 2, Scheme 2). Only partial charge transfer takes place. This has already been
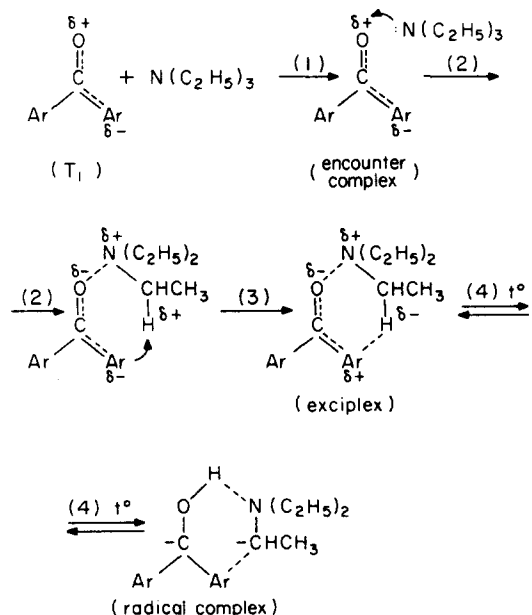
Scheme 1.

Scheme 2.

discussed above. In a triethylamine molecule, there is strong interaction between the n electrons of the nitrogen atom and the electronic cloud of the α-C–H bond [30]. Therefore, a decrease in electron density on the nitrogen atom will probably lead to an electron density deficit on the α-C–H bond hydrogen atom (step 2, Scheme 2). The latter may be located in sufficiently close proximity to the π^* system of a triplet molecule of benzophenone on which there is some surplus electron density [31]. This may result in an additional donor–acceptor interaction where the excited molecule of benzophenone will act as a donor. The ability of triplet exited benzophenone to act as an electron density donor was shown in Ref. [32]. The involvement of the α-C–H bond hydrogen atom in the primary event of the photoreaction has been repeatedly addressed in the literature [6,27].

Scheme 2 shows the structure of the nascent exciplex. Such two-centre coordination in the complex between an amine molecule and excited benzophenone will yield an exciplex of low polarity, and charge transfer interaction will play a key role in the formation of such a structure. This is in good agreement with literature data.

While the interaction between molecules in the exciplex is weak, two-centre coordination must considerably enhance the stability of the exciplex. Therefore we can presume that its lifetime will be sufficiently large for the effective progress of a secondary photochemical reaction of ketyl radical formation (step 6, Scheme 1). We perceive the mechanism of the reaction to be as follows.

Light quantum absorption by the exciplex may cause its structure to be polarized to the point of ion species formation [33]. Charge redistribution is accompanied by conformational change and very rapid proton transfer in the exciplex. The coordination between the complex fragments is disturbed and the radicals thus formed diffuse into the bulk solvent. The ketyl radicals then recombine in a second-order reaction with a rate constant k_2 (step 7, Scheme 1). Increasing viscosity prevents conformational change and, consequently, depresses ketyl radical formation. This is consistent with the results of Tables 2 and 4. Refs. [34,35] confirm the possibility of such a reaction mechanism. In Ref. [34], isomerization of the excited state of 1,1'-diethyl-4,4'-cyanine was observed. This activity was depressed with increasing viscosity of the solvent (within 0.2–2.5 cP), which is in accord with the data obtained in our work. In Ref. [35], the influence of solvent viscosity on the back electron transfer rate in the dicyanoanthracene–dimethylaniline exciplex was described. This was ascribed to electron transfer leading to conformational change.

Presumably, the photochemical consumption of the triplet exciplex by the probe radiation significantly

reduces its lifetime. This was observed in Ref. [34] for the excited state of cyanine. Perhaps this is one of the reasons why a triplet exciplex of benzophenone and triethylamine has not been detected optically. Optical detection of this species may be hard to accomplish for yet another reason. We believe that the electronic structure of the triplet exciplex will not differ significantly from those of triplet excited benzophenone and the ketyl radical. Therefore the spectral responses of all three species will be similar. The possibility of the formation of a ketyl radical complex which absorbs in the same spectral region should also be taken into account. All these intermediates are attributed to one common sequence of reactions which proceeds extremely rapidly. Therefore the absorption spectra will be difficult to resolve in time.

From the data presented in Fig. 6(a), we have concluded that the photochemical consumption of the exciplex competes with the formation of a ketyl radical–hydrogen-donor radical complex (step 5.1, Scheme 1). This process may proceed as hydrogen transfer in the exciplex with two-centre coordination and the initial spatial orientation of the molecular fragments will be retained (step 4, Scheme 2). Presumably, the nature of the bonding between the fragments of the complex varies somewhat. This bonding may be based on a donor–acceptor interaction. This interaction may occur between the nitrogen atom and the –OH group hydrogen atom in terms of a hydrogen bond [26]. The second bond may stem from interaction of the unpaired electron of the aminoalkyl radical with the phenyl ring [36]. Such an interaction between radicals in the complex prevents the process of diffusion separation (step 8, Scheme 1). The spin multiplicity of such a complex will apparently equal three. This assumption was made on the basis of the parameters of the Arrhenius equation for decay of the complex. The limiting step of the decay process may be spin inversion (step 5.2, Scheme 1). This is followed by reverse transport of the hydrogen atom, leading to precursor regeneration (step 5, Scheme 1). However, it is possible that other products of the reaction are also formed, e.g. a long-lived photoproduct with an enol structure of the isobenzopinacol type.

The formation of a combined triplet state in the photoreduction of benzophenone was discovered for the first time by ESR spectroscopy [37]. It was ascribed to the formation of two neighbouring radicals when a ground state benzophenone–dimethylamine complex was photoexcited in methyltetrahydrofuran solution at 77 K. Significantly, the non-stationary absorption spectrum of the photolysis species, obtained under the same conditions, displayed a maximum at $\lambda = 555$ nm. Supposedly, the detection of this product was possible due to the high viscosity of the solvent at 77 K. This is in good agreement with our data. As has been demonstrated (Tables 2 and 4), an increase in the viscosity of the solvent is one of the requirements for observation

of a ketyl radical complex. We assume that it possesses a combined triplet state.

The experimental results obtained indicate that two different ketyl radical complexes are observed among the products of benzophenone photoreduction by triethylamine. At low amine concentrations, a radical complex with a decay rate constant of $k_1 = (2–3) \times 10^3$ s^{-1} (Tables 1–4) is detected. No component with such a rate constant is found on examination of the decay kinetics of non-stationary absorption of benzophenone solution photolysis at high triethylamine concentrations (Figs. 3 and 4). In this case, the radical complex decays with a rate constant $k_{11} = (3.5–5.5) \times 10^2$ s^{-1}. The absorption spectrum of the radical complex formed at low triethylamine concentrations is comparable with that of the ketyl radical in the maximum region ($\lambda = 545$ nm), but different in the region around 500 nm (Fig. 2). The ketyl radical complex formed at high triethylamine concentrations has a spectrum with $\lambda_{max} = 555$ nm (Fig. 4).

In our view, there are several possible explanations regarding the influence of the amine concentration on the properties of the ketyl radical. The formation of a benzophenone–triethylamine ground state complex is the most critical factor. In this case, on formation of the locally excited benzophenone triplet state, the relative orientation of the interacting molecules and the spacing between them will be more favourable for the formation of bonds in the exciplex. Such an exciplex and the radical complex forming from it will be stable. This assumption is verified by the data in Ref. [38], which show the dependence of the stability (decay rate constant) of a triplet benzophenone–diethylamine exciplex on the relative orientation of the molecules in the precursor ground state complex.

Alternatively, we may suppose that charge transfer occurs in the singlet state of the complex [1,4]. Such an activity may lead to a stronger charge transfer. The bond between the fragments of the triplet exciplex will then be more durable. This will affect the properties of the radical complex.

Both scenarios considered above provide for the involvement of a triethylamine molecule incorporated into a ground state complex. However, this molecule may be non-reactive [15]. In this case, the following explanation of the increasing stability of the radical complex and its varying spectral characteristics is possible.

During the formation of a ground state complex, charge transfer from the nitrogen atom onto the benzophenone molecule π electron system will lead to a decrease in the electron density on the α-C–H bond of the triethylamine molecule [30]. This may set the stage for formation of a hydrogen bond between the triethylamine hydrogen atom and the oxygen atom of the carbonyl group of benzophenone. During the formation of this bond, the oxygen atom acquires additional electron deficiency. On excitation of such a complex, the electron deficiency will increase further. Interaction between this exciplex and a second triethylamine molecule may yield a triplex. This process and the process of radical complex formation may occur as indicated in Scheme 2. However, the strength of the bond between the radical complex fragments will be greater due to the greater charge transfer state contribution in the initial step of the process. The shift in the absorption spectrum maximum to $\lambda = 555$ nm may then be ascribed to the additional coordination of the triethylamine molecule to the π system of the ketyl radical.

References

[1] H. Miyasaka and N. Mataga, Bull. Chem. Soc. Jpn., 63 (1990) 131.

[2] C. Devadoss and R.W. Fessenden, J. Phys. Chem., 95 (1991) 7253.

[3] N.A. Borisevich, N.A. Lysak, S.V. Tihomirov, S.A. Melnichuk and G.B. Tolstorozhev, Dokl. Akad. Nauk SSSR, 295 (1987) 900.

[4] N.A. Borisevich, N.A. Lysak, S.V. Tihomirov, S.A. Melnichuk and G.B. Tolstorozhev, Zh. Prikl. Spektrosk., 49 (1988) 653.

[5] J.A. Bell and H. Linschitz, J. Am. Chem. Soc., 85 (1963) 528.

[6] S. Inbar, H. Linschitz and S.G. Cohen, J. Am. Chem. Soc., 103 (1981) 1048.

[7] A.Yu. Tarasyuk, V.M. Granchak and I.I. Dilung, Dokl. Phys. Chem., 316 (1991) 96.

[8] F. Wilkinson and A. Garner, Photochem. Photobiol., 27 (1978) 659.

[9] M.R. Topp, Chem. Phys. Lett., 32 (1975) 144.

[10] L.J. Johnston, D.J. Lougnot, V. Wintgens and J.C. Scaiano, J. Am. Chem. Soc., 110 (1988) 518.

[11] V.A. Kuzmin, P.P. Levin and I.V. Khudyakov, Izv. Akad. Nauk SSSR, Ser. Khim., 4 (1987) 998.

[12] S. Arimitsu, H. Masuhara, N. Mataga and H. Tsubomura, J. Phys. Chem., 79 (1975) 1255.

[13] K.S. Chen, T. Foster and K.S. Wan, Can. J. Chem., 58 (1980) 591.

[14] S.G. Cohen, A.H. Parola and G.H. Parsons, Chem. Rev., 73 (1973) 141.

[15] A.H. Parola, A.W. Rose and S.G. Cohen, J. Am. Chem. Soc., 97 (1975) 6202.

[16] Y. Kajii, H. Itabashi, K. Shibuya and K. Obi, J. Phys. Chem., 96 (1992) 7244.

[17] H. Ohtani, T. Kobayoshi, K. Suzuki and S. Nagakura, Nippon Kagaku Kaishi, 10 (1984) 1479.

[18] J. Rose, Les Complexes Moléculaires, Dunod, Paris, 1971, p. 176.

[19] J.O. Singh, J.D. Anunziata and J.J. Silber, Can. J. Chem., 63 (1985) 903.

[20] F. Hartley, C. Burges and R.M. Alcock, Solution Equilibria, Mir, Moscow, 1983, p. 313 (Russian translation).

[21] E.I. Kapinus and M.M. Aleksankina, Zh. Fiz. Khim., 64 (1990) 2625.

[22] V.M. Granchak, P.A. Kondratenko and I.I. Dilung, Teor. Eksp. Khim., 20 (1984) 43.

[23] B. Borderie, D. Lavabre, G. Levy, G.P. Laplante and J.C. Micheau, J. Photochem. Photobiol. A: Chem., 56 (1991) 13.

[24] S. Kazanis, A. Azarani and L.J. Johnston, *J. Phys. Chem.*, *95* (1991) 4430.

[25] P.J. Wagner, R.J. Truman and J.C. Scaiano, *J. Am. Chem. Soc.*, *107* (1985) 7093.

[26] R.S. Davidson and R. Wilson, *J. Chem. Soc., B*, *1* (1970) 71.

[27] J.B. Guttenplan and S.G. Cohen, *J. Am. Chem. Soc.*, *94* (1972) 4040.

[28] P. Jaques, *J. Photochem. Photobiol. A: Chem.*, *56* (1991) 159.

[29] C.G. Schaefer and K.S. Peters, *J. Am. Chem. Soc.*, *102* (1980) 1566.

[30] M. Rosi, R. Cambi, R. Fantoni, R. Tiribelli, M. Bottomei and A. Giardini-Guidono, *Chem. Phys.*, *116* (1987) 399.

[31] R.M. Hochstrasser and L.J. Noe, *J. Mol. Spectrosc.*, *38* (1971) 175.

[32] V.M. Granchak, P.A. Kondratenko, V.P. Sherstyuk and I.I. Dilung, *Vysokomol. Soedin., Ser. A*, *22* (1980) 1865.

[33] G.B. Sergeyev and I.A. Leyekson, *Usp. Khim.*, *41* (1972) 1566.

[34] U. Aberg and V. Sundstom, *Proc. Indian Acad. Sci., Chem. Sci.*, *103* (1991) 441.

[35] E. Vauthey and D. Phillips, *Chem. Phys.*, *147* (1990) 421.

[36] V.D. Pokhodenko, L.S. Degtyarov, V.G. Koshechko and V.S. Kuts, *Problems of the Chemistry of Free Radicals*, Naukova Dumka, Kiev, 1984, p. 231.

[37] S. Arimitsu and H. Tsubomura, *Bull. Chem. Soc. Jpn.*, *44* (1971) 2288.

[38] M. Hoshino, H. Seki, M. Kaneko, K. Kinoshito and H. Shizika, *Chem. Phys. Lett.*, *132* (1986) 209.