137

ROLE OF β-PHENYL RINGS IN THE DEACTIVATION OF AROMATIC KETONE TRIPLETS

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Summary

The four aromatic ketones investigated were shown to be photostable in solution. Laser flash photolysis experiments show that this photostability is the result of highly efficient triplet deactivation processes that lead to very short triplet lifetimes; for example for β-phenylpropiophenone the triplet lifetime in toluene at room temperature is about 1.0 ns. Structural effects on the nature and lifetime of the triplet state indicate that its deactivation requires the interaction of the carbonyl chromophore with the π system in the β-phenyl ring; a short-lived charge transfer intermediate may be involved in the process.

1. Introduction

The photochemistry of carbonyl compounds has been the subject of numerous studies. While many different types of behaviour are observed, in general they can be grouped into a relatively small number of categories, *i.e.* bond scission (such as the Norrish type I reaction) [1], hydrogen abstraction (*e.g.* photoreduction and Norrish type II reaction) [1 - 4], electron transfer (*e.g.* quenching by amines) [5], addition to double bonds (*e.g.* oxetane formation) [1, 6] and quenching by aromatic rings [7 - 16]. The last group is the least understood process although it is known to play a major role in the deactivation of carbonyl triplets in many common systems. For example, in a deaerated solution of benzophenone in benzene the triplet lifetime is controlled almost exclusively by quenching by the solvent [7, 9, 12]. While the phenomenon has been known for a number of years, little is known about the intermediates involved in the deactivation process. In the benzophenone–diphenyl ether system [13] we have been able to establish

the intermediacy of a relatively long-lived transient ($\tau \approx 13\,\mu s$) which is presumably a biradical. More recently, Wilson and Halpern [17] have examined the interaction of cyclohexanone triplets with o-xylene and observed the intermediacy of a short-lived exciplex ($\tau \approx 60\,ns$). These seemingly contrasting pieces of evidence are in fact compatible with the idea that charge transfer interactions may be of importance in the reaction path leading to the biradical [13]. While products are occasionally formed from this biradical [18], regeneration of the parent carbonyl compound can occur from either the biradical or its precursor.

The same type of interaction can occur in an intramolecular fashion. Reports by Wagner *et al.* [19], Whitten and Punch [20] and Stermitz *et al.* [21] have demonstrated that this process is extremely efficient in aromatic as well as aliphatic ketones and leads to a dramatic shortening of the triplet lifetime when the aromatic ring is in the β position with respect to the carbonyl group, as in the case of β-phenylpropiophenone. When the aromatic ring is further removed from the carbonyl function, the Norrish type II reaction involving attack at the γ position can become predominant [2, 4, 22]. In contrast, when the ring is moved closer to the carbonyl group (as in the case of benzyl ketones) the Norrish type I reaction involving α bond scission tends to take over [23].

In this work we have used laser flash photolysis techniques to examine the photochemistry of a series of molecules I - IV (Fig. 1) which contain β-phenyl groups. An examination of the role of steric and geometric factors helps us to understand the reaction mechanism. In addition, since earlier studies have shown that efficient deactivation pathways such as photoenolization [24, 25] can be used as polymer photostabilizers, it was of interest to examine the potential of carbonyl triplet deactivation by phenyl rings using a variety of model molecules.
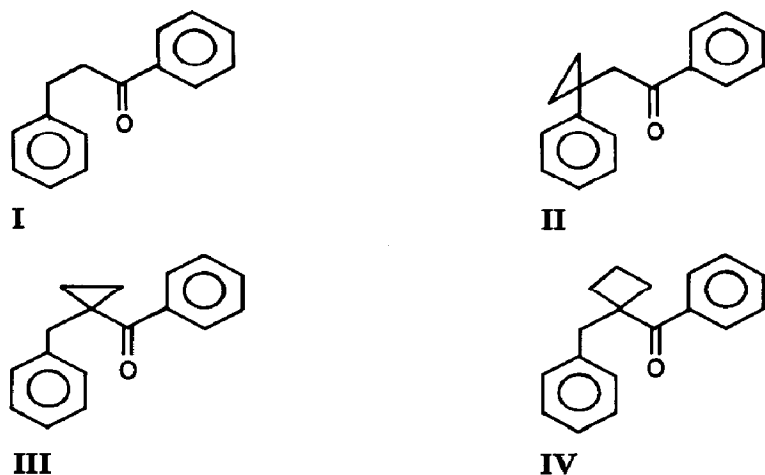

Fig. 1. The structures of compounds I - IV.

2. Experimental details

2.1. Materials

Benzene (Aldrich, Gold Label) was purified and dried by the same procedure as in earlier work [26]. Acetonitrile (Fisher, high pressure liquid chromatography grade) and toluene-d_8 (Merck, Sharp and Dohme) were used as received. The β-phenylpropiophenone (I) used in the initial experiments was a generous gift from Mr. Tom Paine and another batch was prepared according to a literature procedure. The preparation of II has been reported earlier [27].

2.2. 1-benzyl-1-benzoyl-cyclopropane (III)

A slurry of 3.07 g (27.4 mmol) of potassium tert-butoxide in 15 ml of anhydrous benzene was placed under nitrogen in a flame-dried three-necked round-bottomed flask of volume 100 ml. A solution of 2.00 g (13.7 mmol) of cyclopropyl phenyl ketone and 4.69 g (27.4 mmol) of benzyl bromide in 10 ml of anhydrous benzene was added dropwise for a period of 15 min. The mixture was stirred for 1 h, refluxed for 12 h and cooled to room temperature. 20 ml of 15% HCl was then added and the layers were separated. The organic phase was washed with 100 ml of H_2O and the combined aqueous layers were extracted with 100 ml of ether. The combined organic layers were then washed with 100 ml of 5% Na_2CO_3, dried over $MgSO_4$ and evaporated in vacuo. Removal of the majority of excess benzyl bromide and unreacted phenyl cyclopropyl ketone by vacuum distillation gave 1.46 g of the crude product which was chromatographed on a 2.5 cm $\times$ 10 cm silica gel slurry packed with 10% ethyl acetate in hexane; 10 ml fractions were collected. Fractions 8 - 11 yielded 0.965 g (30%) of 1-benzylcyclopropyl phenyl ketone (boiling point, 132 °C at 0.35 Torr). The IR spectrum (neat) was as follows: 3085, 3060, 3030, 2925, 1675, 1600, 1580, 1500, 1450, 1360, 1220, 1176, 1080, 1035, 1009, 974, 780, 750 and 700 cm^{-1}. The ^{1}H nuclear magnetic resonance (NMR) spectrum showed the following bands in parts per million relative to tetramethylsilane (solvent, CDCl$_3$): 0.90, multiplet (m) (2 H); 1.14, m (2 H); 3.11, singlet (s) (2 H); 6.91 - 7.80, broad multiplet (brm) (10 H). For the mass spectrum the exact calculated m/e was 236.120 108 and the observed m/e was 236.120 807.

2.3. 1-benzyl-1-benzoylcyclobutane (IV)

A slurry of 5.60 g (50.0 mmol) of potassium tert-butoxide in 30 ml of anhydrous benzene was placed under nitrogen in a flame-dried three-necked round-bottomed flask of volume 250 ml. A solution of 2.00 g (12.5 mmol) of cyclobutyl phenyl ketone and 8.50 g (50.0 mmol) of benzyl bromide in 15 ml of anhydrous benzene was then added dropwise for a period of 15 min. The mixture was stirred for 1 h, refluxed for 20 h and cooled to room temperature. 50 ml of 15% HCl was then added and the layers were separated.

The aqueous phase was extracted with 100 ml of ether and the combined organic layers were dried over $MgSO_4$ and evaporated *in vacuo*. Vacuum distillation of the crude product produced 1.76 g (56%) of 1-benzylcyclobutyl phenyl ketone (boiling point, 127 - 130 °C at 0.16 Torr). The IR spectrum (neat) was as follows: 3090, 3070, 3040, 2950, 1675, 1600, 1580, 1500, 1450, 1330, 1250, 1230, 1030, 1008, 979, 945, 760 and 710 cm^{-1}. The ^{1}H NMR spectrum showed the following bands in parts per million relative to tetramethylsilane (solvent, $CDCl_3$): 1.72 - 2.93, brm (6 H); 3.30, s (2 H); 6.82 - 7.83, brm (10 H). For the mass spectrum the exact calculated *m/e* was 250.135 757 and the observed *m/e* was 250.136 324.

2.4. Steady state photolysis

Irradiations were carried out using a Rayonet reactor equipped with 16 RPR-3000 lamps. The samples (1 ml) in Pyrex tubes were irradiated in a carousel to ensure equal doses.

2.5. Laser flash photolysis

The samples were excited with the pulses (337.1 nm; up to 10 mJ; about 8 ns) from a Molectron UV-24 nitrogen laser. Transient signals, initially acquired by an R-7912 Tektronix transient digitizer, were processed using a dedicated PDP-11/23 computer which also controlled the experiment and provided suitable storage and hardcopy facilities. Further details have been given elsewhere [28].

3. Results

Molecules III and IV are new substances, and so their synthesis and characterization have been presented in some detail in Section 2.

Compound II has been prepared in connection with another investigation [27] and has previously been shown to be photostable to light with $\lambda > 300$ nm in benzene [29].

All the photochemical experiments were carried out under oxygen-free conditions. The rest of this section is divided into steady state and laser flash experiments.

3.1. Steady state irradiation

Solutions of ketones I - IV (typically 0.01 - 0.05 M in benzene) were irradiated (see Section 2) for periods of between 2 and 16 h. All samples were photostable. In order to put this statement into a somewhat more quantitative perspective, we irradiated valerophenone which is known to yield acetophenone with $\Phi = 0.30$ under the same conditions [30]. Short irradiation periods (10 - 15 min) were sufficient to lead to significant acetophenone yields. We estimate that the quantum yield of ketone consumption for I - IV is substantially less than 0.001.

3.2. Laser flash photolysis

It is clear from Section 3.1 that product formation cannot be expected to play a relevant role in determining the type of transient phenomena observed.

Laser excitation of ketones I and II in benzene at room temperature does not lead to any detectable transients in the region monitored (345 - 650 nm). The corresponding triplets would be expected to be easily detectable at $\lambda < 400$ nm [31]. In the case of III and IV very short-lived signals are detectable and will be discussed later.

In order to obtain an estimate of the triplet lifetime for all substrates, we carried out a series of experiments in which the carbonyl triplets were quenched by 1-methylnaphthalene. Experiments of this type have been shown to be very informative in a number of related studies [32 - 34]. Briefly, 1-methylnaphthalene is transparent at the excitation wavelength (337 nm) and thus it does not interfere with the absorption of light by the substrate. Quenching of triplet ketone leads to the long-lived and easily detectable triplet state of 1-methylnaphthalene; its formation was monitored by its characteristic absorption at about 420 nm [35]. If the substrate has only one triplet state, the quantum yield Φ_N of 1-methylnaphthalene triplets follows a Stern−Volmer type of dependence with the quencher concentration [N]:

$$\frac{1}{\Phi_N} = \frac{1}{\Phi_{isc}} \left(1 + \frac{1}{k_q \tau_T [N]} \right) \tag{1}$$

where Φ_{isc} is the quantum yield of intersystem crossing for the substrate, τ_T is the triplet lifetime and k_q is the rate constant for triplet quenching. The value of Φ_N can be replaced by the transient optical density at 420 nm if a suitable constant α is introduced provided that triplet 1-methylnaphthalene is the only species showing significant absorptions at this wavelength, i.e.

$$\frac{1}{A_N} = \alpha + \frac{\alpha}{k_q \tau_T [N]} \tag{2}$$

The Stern−Volmer slope $k_q \tau_T$ can be obtained from the intercept-to-slope ratio of a plot of A_N^{-1} versus $[N]^{-1}$. Further, comparison of the intercept for one of the substrates of interest with that for a ketone of known Φ_{isc} (such as acetophenone) leads to the estimation of the quantum yield of intersystem crossing. This approach was successfully applied to ketones I, III and IV, and the corresponding data are summarized in Table 1. A representative plot is shown in Fig. 2. When similar experiments were carried out with II the plots were systematically non-linear. In fact it is well recognized that curvature in these plots is indicative of the presence of two or more distinct triplets [32 - 34], i.e. at low quencher concentrations mainly the long-lived triplets are quenched leading to the region with a small slope while large quencher concentrations lead to the steep region near the intercept. Figure 2 also includes a representative plot. Proper kinetic analysis

TABLE 1

Kinetic parameters obtained from quenching studies using 1-methylnaphthalene

Substrate	Solvent (temperature (K))	$k_q\tau_T$ (M^{-1})	Φ_{isc} [a]
I	Toluene (207)	10.9	—
I	Toluene (300)	9.8	—
I	Methanol (300)	10.3	—
I	Benzene (300)	4.4	0.91
II (short)	Benzene (300)	7.5 ⎫	(0.90)
II (long)	Benzene (300)	180 ⎭	
III	Acetonitrile (300)	214	—
III	Benzene (300)	300	1.07
IV	Acetonitrile (300)	300	—
IV	Benzene (300)	420	0.93

[a]Measured using acetophenone as the standard; error, ±10%.
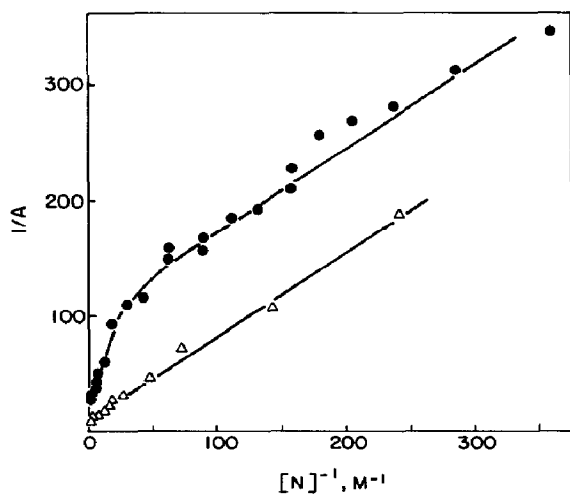
Fig. 2. Reciprocal plots of the yield of 1-methylnaphthalene triplets for different quencher concentrations: ●, II in benzene; △, I in methanol.

[34] of the slopes and intercepts from both regions leads to the $k_q\tau_T$ values for both triplets as well as to an estimate of their relative abundances. For II in benzene at 300 K the $k_q\tau_T$ values for the short- and long-lived triplets are 7.5 M^{-1} and 180 M^{-1} respectively, and they are formed in a relative abundance of 81:19. Table 1 also includes the data for this system. A few exploratory experiments were carried out in other solvents as well as at lower temperatures in the case of I (see Table 1).

As pointed out earlier, ketones III and IV gave detectable, though weak, signals during direct irradiation of their solutions. The transient spectrum obtained for IV is shown in Fig. 3. The lifetime of these signals was
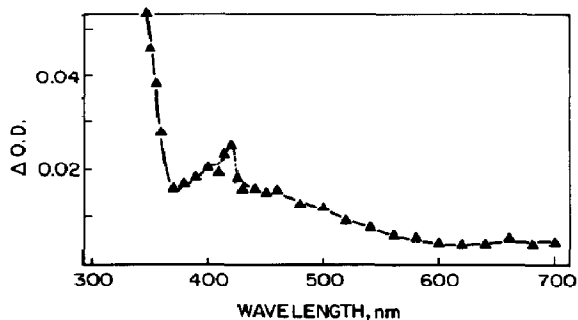
Fig. 3. Transient spectra obtained upon laser irradiation of IV at 209 K in toluene-d_8 based on absorbance measurements between the end of the laser pulse and 1 μs thereafter.
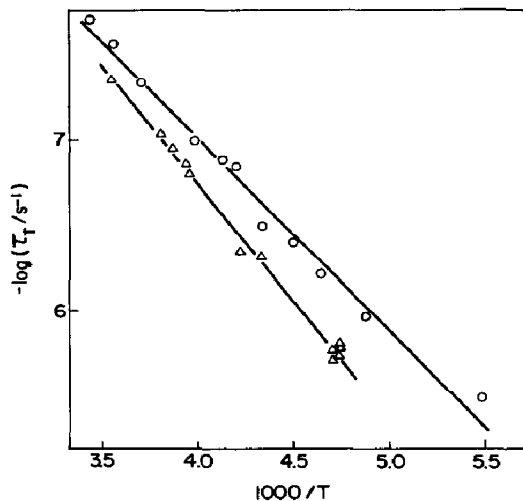
Fig. 4. Arrhenius plots for the decay of the triplet states of III (O) and IV ($\triangle$) in toluene-d_8.

monitored over a temperature range in toluene-d_8 as solvent. Figure 4 shows Arrhenius plots for both substrates which lead to

$$-\log(\tau_T)_{III} = 11.45 \pm 0.36 - \frac{5080 \pm 380}{\theta}$$

$$-\log(\tau_T)_{IV} = 12.24 \pm 0.30 - \frac{6260 \pm 320}{\theta}$$

where $\theta = 2.3RT$ cal mol^{-1}.

The signals observed and the Arrhenius parameters given above are assigned to the triplet state of the corresponding ketones. Addition of a typical triplet quencher such as 1,3-octadiene leads to triplet quenching, and a plot of τ_T^{-1} *versus* [1,3-octadiene] leads, from the slope, to $k_q = 1.8 \times 10^9$ M^{-1} s^{-1} at 225 K for IV in toluene-d_8. This measurement supports the assignment of the results shown in Figs. 3 and 4 to the triplet state. In general the lifetimes measured using direct detection are in satisfactory agreement with the Stern–Volmer slopes given in Table 1.

In the experiments with ketones II, III and IV we also observed very weak long-lived signals following triplet decay at $\lambda < 450$ nm. These could not be characterized in any detail, and while it may be tempting to attribute them to biradicals this would involve more speculation than would seem justifiable.

An exploratory experiment was also carried out using substrate V (Fig. 5). The value of $k_q\tau_T$ for triplet quenching by 1-methylnaphthalene in chlorobenzene was 10.9 M^{-1} at 300 K, suggesting a triplet lifetime of about 2 ns. The value is in line with the lifetimes for the other substrates; however,
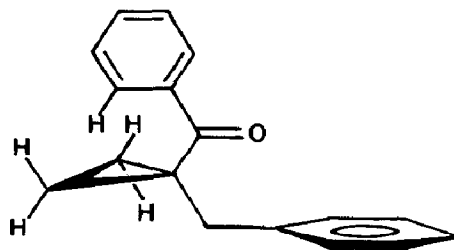
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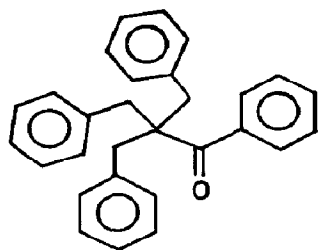
V

Fig. 5. The structure of compound V.

Fig. 6. Proposed conformation for triplet decay in compound III.

steady state photolysis experiments indicated that this substrate does undergo some photodecomposition, presumably as a result of Norrish type I cleavage [36, 37].

4. Discussion

Our experiments conclusively show that the efficient deactivation of triplet aromatic ketones by β-phenyl groups is a very general phenomenon. The high efficiency of the process contrasts with the photostability of ketones I - IV. Perhaps the clue to the understanding of the interactions involved can be found in the relatively long lifetimes and high activation energies for ketones III and IV. Drieding models of these two compounds show that the conformation with the minimum distance between the carbonyl group and the π system in the β-phenyl ring (assuming that the benzoyl group is planar in the triplet state [38]) is one in which the plane of the benzoyl group bisects the cyclopropane (or cyclobutane) ring and involves considerable interaction between the *ortho* hydrogen atom and the α hydrogen atoms in the small ring (Fig. 6). We believe that this conformation is unfavourable, and the kinetic parameters measured probably reflect the repulsion that needs to be overcome in order to reach what we assume to be the transition state for quenching of the carbonyl triplet of the aralkyl side chain. In I the molecule is probably flexible enough for the transition state configuration to be reached easily. Interestingly, in the photochemistry of *N,N*-dimethyl-4-[3-(9-anthryl)propyl]aniline Chuang *et al.* [39] have concluded that it takes 900 ps for the internal orientational motion of this molecule to take place (leading to a charge transfer complex); the time scale is comparable with the lifetime measured for triplet I.

The involvement of two triplets in the case of II is reminiscent of the photoenolization of *o*-alkyl-substituted aromatic ketones [30, 40 - 43] where Wagner and coworkers [40, 41] have proposed the involvement of two triplet conformers with different triplet lifetimes, a mechanism that is now well established. In this particular case, examination of Drieding models does not suggest the type of repulsion shown earlier for III. The two conformers are tentatively attributed to the following structures:
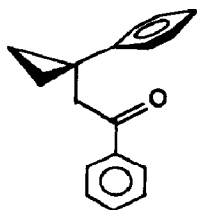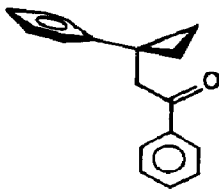
IIA   **IIB**

where **IIA** is assumed to be the short-lived species and **IIB** (for which other conformations could be written) is believed to have to interconvert to **IIA** for decay to occur. According to this model, the rate of decay of **IIB** reflects the interconversion to the reactive species **IIA**.

The choice of structures where the carbonyl group interacts directly with the π system in the β-phenyl ring as those responsible for triplet decay deserves some comment. In principle we could propose two different conformational arrangements that merit consideration. In addition to the one mentioned above, we could envisage an interaction between the two aromatic rings in a transition state where they would be approximately parallel. Examination of the models shows that this conformation would be easy to achieve in all the molecules examined; it would therefore be hard to understand what would make the lifetimes of **III** and **IV** substantially longer than that of **I**. In addition, Whitten and Punch [20] have clearly shown that two aromatic rings are not necessary, but in fact β-phenyl substitution in aliphatic ketones leads to the same effect.

Another question that deserves consideration is whether the rapid triplet deactivation observed in this work leads to the formation of a biradical such as **VI** (Fig. 7) and whether charge transfer interactions are of importance along the reaction path.

We favour a mechanism in which an exciplex or charge transfer intermediate is efficiently formed and leads to a biradical very inefficiently, if at all. This preference is based on the following arguments.

(a) We would expect a transient such as **VI** to be detectable in a flash experiment if its lifetime was longer than about 20 ns. No such transient was detected in the case of **I** even if in other systems [13] (*e.g.* benzophenone–diphenyl ether) where similar transients have been characterized the lifetimes are in the microsecond time domain. In the case of **III** and **IV** weak long-lived signals have been detected which, even if they corresponded to a biradical (and this seems questionable), would be indicative of a very low quantum yield.
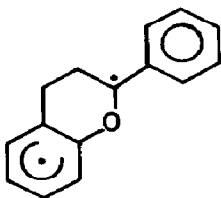
VI

Fig. 7. The structure of biradical VI.

(b) The pre-exponential factors observed (around 10^{12} s^{-1}) seem rather high to correspond to ring formation.

(c) The absence of detectable transients seems compatible with the short-lived intermediates reported by Wilson and Halpern [17] in the quenching of aliphatic ketone triplets by alkyl benzenes.

In summary we favour a mechanism in which the rapid deactivation of the triplet state of ketones I - IV is due to interaction of the carbonyl group with the β-phenyl ring leading to a short-lived intermediate which predominantly decays to regenerate the parent ketone. Some decay to a biradical cannot be ruled out, but it is unlikely to be a major pathway for this intermediate.

An interesting consideration is that, since Wilson and Halpern [17] have demonstrated that exciplexes of this type are excellent energy donors, an alternative way of interpreting the involvement of two different kinds of triplets would be the following. The long-lived species observed in ketones II - IV is due, as in the mechanism proposed earlier, to the carbonyl triplet being in an unfavourable conformation for intramolecular quenching. The short-lived species could be attributed to the exciplex itself. In other words, rather than representing a triplet in adequate conformation and already committed to quenching, it would in a way be the already quenched species detectable with 1-methylnaphthalene because the exciplex is also a good energy donor. Experiments in the time domain accessible to our instrument cannot distinguish the subtle differences between the two mechanisms, and at this point the choice remains a matter for speculation.

Finally it seems clear that processes of the type discussed here could find application in polymer chemistry as photostabilizers [25]; the choice of the best structures for this purpose would require a careful examination of conformational effects since these seem to play a critical role in determining triplet lifetimes and their temperature dependence.

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