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# On the yield of intermediates formed in the photoreduction of benzophenone

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**Abstract**

The production of intermediates (light absorbing transients, LAT) has been examined in the photoreduction of benzophenone by different hydrogen donors in inert solvents (acetonitrile and benzene). For 2-propanol in acetonitrile, a branching ratio of 0.3 for the coupling reaction between dimethyl- and diphenylketyl radicals was extracted by computer model simulations considering inner filter effects and the quenching of triplet benzophenone by LAT. Experimental evidence is presented that indicates that LAT could be an efficient H-donor. Steady-state quantum yields for LAT production, $\Phi_{LAT}$, and benzophenone conversion, $-\Phi_{Ph_2CO}$, were determined for the donors 2-propanol, n- and c-hexane, benzhydrol and tetrahydrofuran. The relative quantum yield, $-\Phi_{LAT}/\Phi_{Ph_2CO}$, which indicates the differential partitioning of the products, shows that 2-propanol and tetrahydrofuran are nearly ten times more efficient than alkanes. From the analysis of the mechanism we derived an upper limit for the rate constant for the coupling reaction of two diphenylketyl radicals to yield LAT: $k_{6d} \leqslant 5\times10^5$ M$^{-1}$ s$^{-1}$.

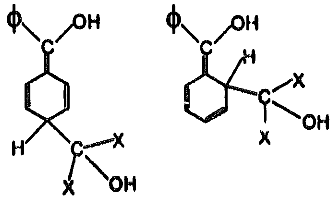
*Keywords:* Photoreduction; Kinetics; Condensed phase; Benzophenone; Light absorbing transients; Intermediates; Ketyl radicals

## 1. Introduction

The photoreduction of benzophenone by H-donors represents a classic example of organic solution photochemistry and it has been widely explored for many years. The mechanistic characterization of this reaction has been the subject of various articles [1–10] including studies carried out not only in solution but also in other media such as micelles [11] and in solid state [12].

Examining the effect of oxygen on the mechanism, Pitts et al. [1] were the first to observe that the irradiation of degassed solutions of benzophenone in 2-propanol produced oxygen-sensitive intermediates which strongly absorb in the 350 nm region, besides the expected benzopinacol and acetone. Since then, various evidence has been presented for the formation of these relatively stable intermediates, which are usually referred to as light absorbing transients (LAT) [1–10].

Bäckström [3], Colman [7] and Demeter [9,10] studied the nature of the LAT produced in the photoreduction of benzophenone by alcohols, discussing their structure, production and decay-kinetics. Besides, the formation of an adduct between ground state benzophenone and diphenylketyl radical [1], or of the charge-transfer complexes of free radicals [3] have been proposed to explain the origin of these intermediates. Unfortunately, attempts to elucidate their structure by NMR have failed [6]. Though somewhat indirect, all the experimental evidence indicates that LAT are ortho- and para-coupling products of diphenylketyl radicals, or of one diphenylketyl radical and the radical derived from the H-donor molecule (see Scheme 1) [4,5,7–9]. However, no build-up of products which absorb in the $n$–$\pi^*$ region (300–400 nm) could be detected when the donor is benzhydrol [10,13]. On the basis of this fact, Demeter et al. favored type II structures, shown in Scheme 1, for the absorbing intermediates in the photoreduction of benzophenone by 2-propanol, being $p$-LAT the major component of the isomer mixture.



I: X = ϕ

II: X = CH$_3$

Scheme 1.

From the analysis of their experiments in terms of the mechanism shown in Scheme 2, they also reported quantum yields for LAT formation [9].

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$$Ph_2CO + h\nu \rightarrow {}^1Ph_2CO \rightarrow {}^3Ph_2CO \tag{1a}$$

$${}^3Ph_2CO \rightarrow Ph_2CO \tag{1b}$$

$${}^3Ph_2CO + Me_2CHOH \rightarrow Ph_2COH\bullet + Me_2COH\bullet \tag{2}$$

$$Me_2COH\bullet + Me_2COH\bullet \rightarrow (Me_2COH)_2 \tag{3a}$$

$$Me_2COH\bullet + Me_2COH\bullet \rightarrow Me_2CHOH + Me_2CO \tag{3b}$$

$$Me_2COH\bullet + Ph_2COH\bullet \rightarrow Me_2C(OH)C(OH)Ph_2 \tag{4a}$$

$$Me_2COH\bullet + Ph_2COH\bullet \rightarrow Me_2CHOH + Ph_2CO \tag{4b}$$

$$Me_2COH\bullet + Ph_2COH\bullet \rightarrow Me_2CO + Ph_2CHOH \tag{4c}$$

$$Me_2COH\bullet + Ph_2COH\bullet \rightarrow LAT \tag{4d}$$

$$Me_2COH\bullet + Ph_2CO \rightarrow Me_2CO + Ph_2COH\bullet \tag{5}$$

$$Ph_2COH\bullet + Ph_2COH\bullet \rightarrow (Ph_2COH)_2 \tag{6}$$

Scheme 2.

Since LAT absorption overlaps the $n$–$\pi^*$ and the $\pi$–$\pi^*$ band regions of benzophenone, the inner filter effects can not be avoided. Also, the probable quenching of triplet benzophenone by LAT might alter the course of the photoreaction. As a consequence, most of the experiments do not provide confident quantitative information, due to insufficient treatment of these subjects [1,2,6,8–10]. Besides, there is a complete lack of reports on the quantum yields for LAT formation by donors other than 2-propanol. It is also not clear whether the enhancement of the LAT yield is a result of the properties of the solvent, or whether it depends on the nature of the H-donor.

In the present work we explored the kinetics of the photoreaction in order to assess the influence of the H-donor and the solvent media on the production of LAT. The understanding of this subject cannot be disregarded when quantitative and mechanistic aspects of the reaction are to be analyzed.

## 2. Experimental details

### 2.1. Materials

Benzophenone (Fluka) was recrystallized from ethanol. 2-propanol (Mallinckrodt, ACS), acetonitrile, tetrahydrofuran, n-hexane, c-hexane and benzene (Carlo Erba, RS) were used as received. Phenylglyoxilic acid (Sigma) was recrystallized from benzene.

### 2.2. Steady-state photolysis

Samples (4 ml) of benzophenone solution were previously degassed by bubbling $N_2$ for 10 min. The stirred solutions were irradiated at 366 nm in a rectangular 1 cm path length cell at room temperature. The light emerging from a high pressure Xe–Hg arc was filtered with a Kratos monochromator within ±5 nm. Fine mesh screens were placed between the monochromator and the sample to attenuate the light. Incident light intensities (photon density per unit time), $I_0$, were measured using phenylglyoxilic acid as an actinometer [14]. The absorption spectra were determined at different time intervals using an UVPC-2101 Shimadzu spectrophotometer.

## 3. Results and discussion

### 3.1. Photoreduction of benzophenone by 2-propanol in inert solvents

We reinvestigated the photoreduction of benzophenone in acetonitrile and benzene, using 2-propanol as the H-donor. In both solvents, it can confidently be assumed that more than 99.99% of the quenching events of triplet benzophenone lead to a dimethylketyl radical. This conclusion is based on the experimental and estimated lifetimes of the triplet benzophenone: $1.8\times10^{-4}$ s in acetonitrile [15], $5\times10^{-8}$ s in 2-propanol [16], and $1.9\times10^{-6}$ s in benzene [15]. The last figure was obtained from the correlation between the ionization potentials of the radical R· and the rate constant of the H-abstraction reaction between ${}^3Ph_2CO$ and a species RH [15].

In addition, control experiments were carried out in each solvent which verified that, under our experimental conditions, no photoreaction takes place when 2-propanol is absent.

#### 3.1.1. Experiments in acetonitrile

Solutions of $5\times10^{-4}$–$1.5\times10^{-2}$ M benzophenone and 0.4 M of 2-propanol in acetonitrile were irradiated for various time intervals ranging between 1–120 min, under continuous stirring. Fig. 1 shows the absorption spectra for a typical run. The sudden rise of the absorbance around 320 nm clearly shows that inner filter effects and possible spatial inhomogeneties during the reaction might be considerable. After 12 min of irradiation, air was admitted into the cell and the solution was kept in the dark until a constant value of absorbance was reached (curve f). A period of about 24 h under

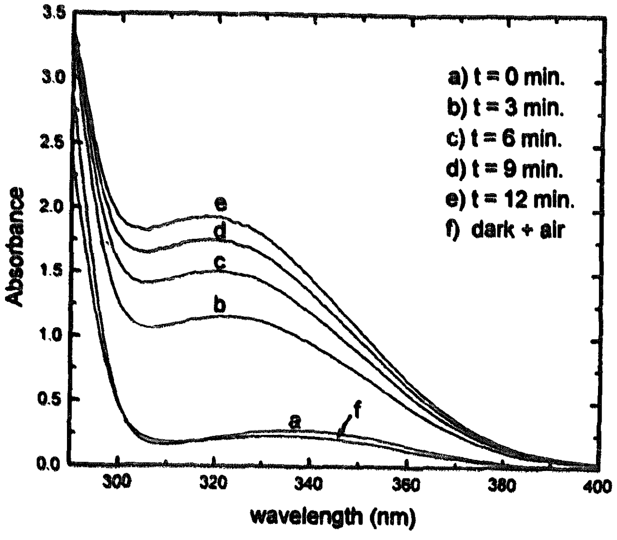


Fig. 1. Absorption spectra of a solution $2\times10^{-3}$ M and 0.4 M 2-propanol in acetonitrile at various irradiation times. a) Initial spectrum; b), c), d), e) after 3, 6, 9, and 12 min of irradiation at 366 nm. Spectrum f) was taken after 24 h in the dark under air-saturated conditions.

air-saturated conditions proved to be enough to ensure complete LAT depletion. As previously shown in a similar experiment, the recovery of the characteristic benzophenone emission indicates that benzophenone does regenerate in this process [5]. Thus, the difference between spectra a and f in Fig. 1 accounts for the amount of benzophenone converted in products other than LAT.

Figs. 2 and 3 show the results at single wavelengths for the two extreme benzophenone concentrations. The different behavior seen when the benzophenone concentration is changed from $5\times10^{-4}$ to $1\times10^{-2}$ M, is related to the decrease in the yield of light absorbing photoproducts and it reflects the competition of reaction (4d) with the H-atom transfer from $Me_2COH\cdot$ to benzophenone (reaction (5)).

For the dilute solution (Fig. 2), the absorbance at 320 nm (LAT's maximum-absorbance wavelength, [9,10]) increases sharply up to ca. 2, reaching a plateau in nearly 30 min. Considering the initial value (0.1), it is obvious that the absorbance is mainly due to LAT. However, for larger benzophenone concentrations (Fig. 3), the competition between LAT production and benzophenone consumption is reflected by the occurrence of the maximum in the absorbance at 366 nm.

In order to further elaborate these data we needed a model mechanism. Thus, we made use of the set of reactions in Scheme 2 [9], adding reaction (7) to take into account the physical quenching of benzophenone triplets by LAT [10,11,15].

$$^3Ph_2CO + LAT \longrightarrow Ph_2CO + {}^3LAT \qquad (7)$$

Rate constants for steps (1) to (6), were taken from Ref. [9], and $k_7$ was set at the diffusion limit $5\times10^9$ $M^{-1}$ $s^{-1}$. The group of differential equations for the full mechanism was solved by using the numerical integration program FACSIMILE [17]. The inclusion of the algebraic restriction $I_a = fI_o$, accounted for the time dependence of the inner filter effects [18]. Here, $I_a$ and $I_o$ stand for the absorbed and incident light intensities (photon density per unit time) respectively. The fraction of light absorbed by benzophenone, as shown in Eq. (8), is obviously a function of time through the concentration of the absorbing species ([$Ph_2CO$] and [LAT]).

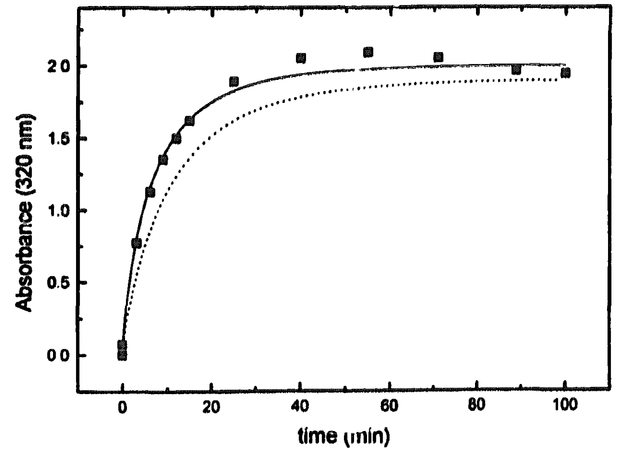


Fig. 2. Absorption profile at 320 nm of a solution $6.5\times10^{-4}$ M and 0.4 M 2-propanol in acetonitrile irradiated at 366 nm. (■) Experimental data. Broken and solid lines are the simulated profiles, with parameters from Ref. [9] and Table 2 respectively (see text).

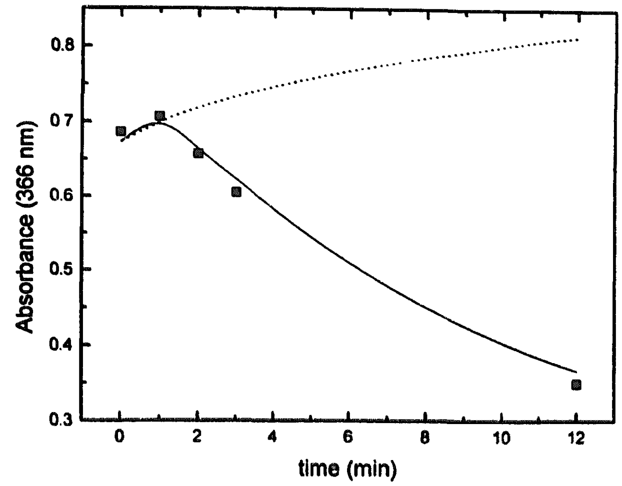


Fig. 3. Absorption profile at 366 nm of a solution $1.2\times10^{-2}$ M and 0.4 M 2-propanol in acetonitrile irradiated at 366 nm. (■) Experimental data. Broken and solid lines are the simulated profiles, with parameters from Ref. [9] and Table 2 respectively (see text).

$$f = \frac{\epsilon^{366}_{Ph_2CO}[Ph_2CO]}{\epsilon^{366}_{Ph_2CO}[Ph_2CO] + \epsilon^{366}_{LAT}[LAT]} \qquad (8)$$

$\epsilon^{366}_{Ph_2CO}$ and $\epsilon^{366}_{LAT}$ being the extinction coefficients at the irradiation wavelength (366 nm) for benzophenone and LAT respectively. Since there is considerable uncertainty in the reported values of $\epsilon_{LAT}$ [5,9,10], we decided to consider it as an adjustable parameter. However, it was impossible within this framework to simulate the experiments for the full range of benzophenone concentrations. Dotted lines in Figs. 2 and 3 show the best fit that could be obtained in these conditions. It is clear that from these figures, that the model is not able to simulate the dependence of LAT formation with benzophenone concentration.

As incorrect treatment of previous data may have introduced errors in the derived values of $k_4$ [9,10], and admitting that the values of $k_5$ in the literature are somewhat disperse [19,20], we made an attempt to fit the experimental results by relaxing these constraints. Still, this proved not to be enough: it seems likely the postulated mechanism is inadequate or at least incomplete.

LAT photolysis, as well as its depletion by a dark process involving benzophenone or assisted by triplet benzophenone, were analyzed as possible sources of the discrepancies. In degassed solvents, LAT is a rather stable species, i.e., we measured a mean lifetime of $2.6\times10^4$ s under dark and oxygen-free conditions at the higher concentrations of benzophenone [21]. Thus, the participation of LAT in an obscure reaction can be neglected under our experimental conditions. In comparison, by supposing that a fraction, $q$, of the light absorbed by LAT induces its decomposition, the results can be improved. However, the values of $q$ required to simulate the experiments increase from $10^{-6}$–$10^{-4}$, on going from benzophenone $5 \times 10^{-4}$–$1.5 \times 10^{-2}$ M suggesting that the analyzed option is not adequate. Besides, the quenching of triplet benzophenone by LAT [10,11], may be due not only to an energy transfer process, but may be as a consequence of the fact that LAT can act as an efficient H-donor (reaction (9)) [21].

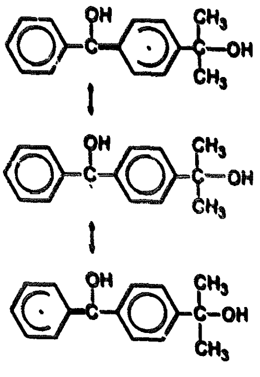
$$^3Ph_2CO + LAT \longrightarrow \cdot LAT + Ph_2COH\cdot \qquad (9)$$

Here ·LAT refers to a radical with the resonant structures shown in Scheme 3.

Finally, rate parameter optimization of the mechanism comprised by reactions (1)–(7) plus (9), leads to the results listed in Table 1. Minimum $\chi^2$ was used as a fitting criterion. Estimated uncertainties in the reported values are also given. This fit was able to reproduce our experiments for $5 \times 10^{-4}$–$1.5 \times 10^{-2}$ M benzophenone and also changing the incident light intensity from $1 \times 10^{-3} - 1.35 \times 10^{-4}$ M min$^{-1}$ (see solid lines in Figs. 2 and 3). It should be noticed that the calculated benzophenone concentration at the end of the photolysis is in accordance with the value arising from the final absorbance on the assumption that one mole of LAT converts into one mole of benzophenone after the dark reaction with oxygen [5].

Most rate constants agree, within a factor of 2.5, with previous reports. The high value of $k_8$ derived in this work, implies that near 30% of the quenching events of triplet benzophenone with LAT lead to H-abstraction. Even when not previously considered, this result is not unexpected since a high efficiency to H-donation was previously found for 1,4-cyclohexadiene, where similar stability resonance effects in the radical may be invoked (see Scheme 3) [11,21,22].

Once the complete set of parameters was derived, we were able to obtain the reaction quantum yields. For each experiment, quantum yields for Ph₂CO consumption, $-\Phi_{Ph_2CO}$ (and LAT formation, $\Phi_{LAT}$) were evaluated at short time intervals (conversion <2%) from the ratio between the moles of Ph₂CO consumed (LAT formed), and the number of photons absorbed by benzophenone. The results are summarized in Table 2. As expected, the yields are very sensitive to light intensity.



Scheme 3.

Table 1
List of parameters used in this work for the mechanism given in Scheme 2

| Parameter [a] | Value | Reference |
|---|---|---|
| $k_{1a}$ | Ia | |
| $k_{1b}$ | $7500 s^{-1}$ | [9] |
| $k_2$ | $2.3 \times 10^6 M^{-1} s^{-1}$ | [9] |
| $k_{3a}$ | $1.2 \times 10^8 M^{-1} s^{-1}$ | [9] |
| $k_{3b}$ | $1.0 \times 10^9 M^{-1} s^{-1}$ | [9] |
| $(k_{4a}+k_{4c})$ [a] | $1.8 \times 10^8 M^{-1} s^{-1}$ | [9] |
| $k_{4b}$ | $(3.1 \pm 0.7) \times 10^8 M^{-1} s^{-1}$ | this work [b] |
| $k_{4d}$ | $(3.6 \pm 0.4) \times 10^8 M^{-1} s^{-1}$ | this work [b] |
| $k_5$ | $(1. \pm 0.3) \times 10^5 M^{-1} s^{-1}$ | this work [b] |
| $k_6$ | $(5.1 \pm 0.7) \times 10^7 M^{-1} s^{-1}$ | this work [b] |
| $k_7$ | $5.0 \times 10^9 M^{-1} s^{-1}$ | this work |
| $k_8$ | $(1.8 \pm 0.4) \times 10^9 M^{-1} s^{-1}$ | this work |
| $\epsilon_{LAT}^{320}$ | $(2.6 \pm 0.1) \times 10^4 M^{-1} cm^{-1}$ | this work |
| $\epsilon_{LAT}^{366}$ | $(2.7 \pm 0.2) \times 10^3 M^{-1} cm^{-1}$ | this work |

[a] Our data do not provide independent values for $k_{4a}$ and $k_{4c}$.

[b] The corresponding rate constants derived in reference 9 are $k_{4b} = 4.9 \times 10^8 M^{-1} s^{-1}$, $k_{4d} = 1.4 \times 10^8 M^{-1} s^{-1}$; $k_5 = 7.3 \times 10^4 M^{-1} s^{-1}$ and $k_6 = 5.9 \times 10^7 M^{-1} s^{-1}$.

Table 2
Calculated quantum yields for benzophenone photoreduction, $-\Phi_{Ph_2CO}$, and LAT formation, $\Phi_{LAT}$, in 0.4 M 2-propanol in acetonitrile, at $I_0 = 1 \times 10^{-3}$ M min$^{-1}$

| [Ph₂CO]/M | $-\Phi_{Ph_2CO}$ | $\Phi_{LAT}$ | $-\Phi_{LAT}/\Phi_{Ph_2CO}$ |
|---|---|---|---|
| $5.0 \times 10^{-4}$ | 1.18 | 0.20 | 0.17 |
| $1.0 \times 10^{-3}$ | 1.22 | 0.16 | 0.13 |
| $2.5 \times 10^{-3}$ | 1.33 | 0.12 | 0.09 |
| $5.0 \times 10^{-3}$ | 1.47 | 0.10 | 0.07 |
| $7.5 \times 10^{-3}$ | 1.53 | 0.08 | 0.05 |
| $1.0 \times 10^{-2}$ | 1.58 | 0.07 | 0.04 |

Table 3
Calculated quantum yields for benzophenone photoreduction, $-\Phi_{Ph_2CO}$, and LAT formation, $\Phi_{LAT}$, for $5 \times 10^{-3}$ M benzophenone in 0.4 M 2-propanol in acetonitrile, at various flux intensities

| $I_0$/M min$^{-1}$ | $-\Phi_{Ph_2CO}$ | $\Phi_{LAT}$ | $-\Phi_{LAT}/\Phi_{Ph_2CO}$ |
|---|---|---|---|
| $1.0 \times 10^{-2}$ | 1.14 | 0.15 | 0.13 |
| $1.0 \times 10^{-3}$ | 1.47 | 0.10 | 0.07 |
| $1.0 \times 10^{-4}$ | 1.78 | 0.05 | 0.03 |

### 3.1.2. Experiments in benzene

Solutions of $10^{-2}$–$10^{-5}$ M benzophenone in benzene were irradiated in the presence of 0.4 M 2-propanol. Strikingly, no oxygen-sensitive light-absorbing photoproducts could be detected under the same experimental conditions used for acetonitrile solution. Neglecting any variation of $\Phi_{LAT}$ with the solvent, we estimate $[LAT] \leqslant 2.6 \times 10^{-6}$ M by considering that a minimal absorbance reduction of 0.05 units could be detected upon the admission of air into the cell.

### 3.2. Influence of the donor in the yields of LATs

LAT formation might be expected to be common for any H-donor. By modifying Scheme 2, the case of a generic donor

RH can be treated. The main difference in the mechanism would arise from the distinctive fate of radicals R· formed upon H-abstraction by triplet benzophenone. Thermochemical data, which are available in most cases, can be used to predict whether the thermal reaction between R· and ground state benzophenone can be neglected or not [23]. It should be noticed that the exclusion of reaction (5), in Scheme 2, makes the mechanism amenable to analytical solution and leads, under the steady state hypothesis for the reactive molecules, to:

$$\Phi_{\mathrm{LAT}}=\Phi_{\mathrm{ISC}}\Phi_{\mathrm{R}}\left[\frac{k^0_{4\mathrm{d}}}{\sum\limits_i k^0_{4i}+2(k_6\sum\limits_i k^0_{3i})^{1/2}}-\frac{k^0_8[\mathrm{LAT}]}{k^0_2[\mathrm{RH}]}\right] \qquad (10)$$

$$-\Phi_{\mathrm{PH2CO}}=\frac{\Phi_{\mathrm{ISC}}\Phi_{\mathrm{R}}[k^0_{4\mathrm{a}}+k^0_{4\mathrm{c}}+k^0_{4\mathrm{d}}+2(k_6\sum\limits_i k^0_{3i})^{1/2}}{\sum\limits_i k^0_{4i}+2(k_6\sum\limits_i k^0_{3i})^{1/2}} \qquad (11)$$

which, at variance with donor 2-propanol, are independent of benzophenone concentration and $I_0$. Here, $\Phi_{\mathrm{ISC}}$ and $\Phi_{\mathrm{R}}$ are the quantum yields for intersystem crossing, and triplet quenching by RH (reaction (2)), respectively. The superscripts in $k_i^o$, the rate constants of reaction $i$ for a donor RH, distinguish them from the analogous for 2-propanol in Scheme 2.

### 3.2.1. *Experiments in acetonitrile*

We investigated the photoreduction of $5\times10^{-3}$ M benzophenone in acetonitrile with different H-donors (between 0.16–0.25 M): benzhydrol, linear and cyclic hexane, and tetrahydrofuran (THF). For all these donors, reaction (5) is too endothermic to contribute to benzophenone consumption, thus Eqs. (10) and (11) can be applied. It follows from these equations that, since $-\Phi_{\mathrm{LAT}}/\Phi_{\mathrm{Ph_2CO}}$ becomes independent of the associated variations in $\Phi_{\mathrm{R}}$ with the donor, this ratio can be taken as a convenient measure of the relative efficiencies of the different systems to produce LAT.

Besides, experimental ratios of quantum yields $-\Phi_{\mathrm{LAT}}/\Phi_{\mathrm{Ph_2CO}}$ can be easily obtained as the rate between the observed variation in LAT and benzophenone concentrations. By assuming that $\epsilon^{320}_{\mathrm{LAT}}$ is independent of the solvent and that the dark decomposition of one mole LAT yields one mole benzophenone, we obtained $-\Phi_{\mathrm{LAT}}/\Phi_{\mathrm{Ph_2CO}}=0.02$, 0.04, and 0.25 for n-hexane, c-hexane, and THF, respectively (see Table 4). However, in agreement with previous results [10,13], we could not find any evidence of an oxygen-sensitive photoproduct in the benzhydrol-benzophenone-acetonitrile system for the full range of photon-fluxes used in this work.

### 3.2.2. *Experiments in benzene*

When similar experiments were performed in benzene, no oxygen-sensitive species could be detected for the donors benzhydrol, n-hexane, and c-hexane. In addition, the quantum yield for LAT formation in THF was considerably depressed and the ratio $-\Phi_{\mathrm{LAT}}/\Phi_{\mathrm{Ph_2CO}}$ dropped to 0.05.

Table 4
Experimental ratios $-\Phi_{\mathrm{LAT}}/\Phi_{\mathrm{Ph_2CO}}$, in $5\times10^{-3}$ M benzophenone at $I_0=1\times10^{-3}$ M min$^{-1}$ for different solvents and H-donors

| Donor | $-\Phi_{\mathrm{LAT}}/\Phi_{\mathrm{Ph_2CO}}$ | |
|---|---|---|
| | Acetonitrile | Benzene |
| benzhydrol (0.25 M) | $<1\times10^{-3}$ | $<1\times10^{-3}$ |
| hexane (0.25 M) | 0.02 | $<1\times10^{-3}$ |
| c-hexane (0.25 M) | 0.04 | $<1\times10^{-3}$ |
| 2-propanol (0.4 M) | 0.06 | $<1\times10^{-3}$ |
| THF (0.16 M) | 0.25 | 0.05 |

## 4. Summary and conclusions

The production of LAT in the photoreduction of benzophenone in acetonitrile was found to be common for all the tested donors, benzhydrol being the only exception. In an attempt to explain the absence of absorbing intermediates in the benzophenone–benzhydrol–benzene system, Bäckström put forward the possibility that LAT could actually be a charge transfer complex. Should this be the case, they will not be formed unless both radicals do differ considerably in their electron affinities and ionization potentials. But this idea was soon disregarded as no ESR signal could be detected in the presence of LAT [5].

However, the absence of LAT arising from the coupling of two diphenylketyl radicals may be analyzed on a kinetic basis. Notice that for benzhydrol, RH = $\mathrm{Ph_2CH_2OH}$, there is only one radical species and thus Eqs. (10) and (11) are reduced to (12) and (13), respectively.

$$\Phi_{\mathrm{LAT}}=\Phi_{\mathrm{ISC}}\Phi_{\mathrm{R}}\left[\frac{k_{6\mathrm{d}}}{\sum\limits_i k_{6i}}-\frac{k^0_8[\mathrm{LAT}]}{k^0_2[\mathrm{RH}]}\right] \qquad (12)$$

$$-\Phi_{\mathrm{PH_2CO}}=\Phi_{\mathrm{ISC}}\Phi_{\mathrm{R}} \qquad (13)$$

At low benzophenone conversions (⩽3%), the ratio of Eqs. (12) and (13) yields the expression (14):

$$-\frac{\Phi_{\mathrm{LAT}}}{\Phi_{\mathrm{PH_2CO}}}\cong\frac{k_{6\mathrm{d}}}{\sum\limits_i k_{6i}} \qquad (14)$$

thus, from our detection limit $-\Phi_{\mathrm{LAT}}/\Phi_{\mathrm{Ph_2CO}}$ and the well-established value of $\Sigma_i k_{6i}=5.9\times10^7$ M$^{-1}$ s$^{-1}$ [9,10], we were able to set $k_{6\mathrm{d}}\leqslant5\times10^5$ M$^{-1}$ s$^{-1}$, i.e., nearly 700 times lower than the value of $k_{4\mathrm{d}}$.

By taking $-\Phi_{\mathrm{LAT}}/\Phi_{\mathrm{Ph_2CO}}$ as a quantitative measure of the relative ability of the donors to produce LATs, we found that THF is much more efficient that n- or c-hexane. It should be noticed that since Eqs. (10) and (11) do not apply for 2-propanol, the comparison with the other donors deserves special attention. As previously stated, the thermal reaction between the ground state benzophenone and the dimethylketyl radicals sets the dependence of the quantum yields on the benzophenone concentration. Hence, in order to adequately compare the relative quantum yields, one should use the values obtained for dilute solutions, where the contribution of reaction (5) is negligible. From Table 2 we obtained $-\Phi_{LAT}/\Phi_{Ph_2CO} \sim 0.2$ in the limit of $-\Phi_{Ph_2CO} = 1$, thus 2-propanol is nearly as efficient as THF.

Finally, the increase in the yields of LAT on going from benzene to acetonitrile, observed for the different donors, is in agreement with the previous findings regarding the influence of the media on the distribution of the products [11]. Nevertheless, this fact does not necessarily reflect a mere increase of $k_{4d}$ in the polar solvent, i.e. the contribution of a structure with a high charge separation in the transition state for LAT formation. Solvent effects in product partitioning may also operate by modifying other rates of radical recombination. Incidentally, the higher value of $k_6$ in benzene compared with that in acetonitrile, suggests that the self recombination of diphenylketyl radicals to give pinacol would compete more efficiently, in this media, with the build-up of the crossed-coupling product (reaction (4d)) [24]. When 2-propanol is the donor, the additional observation that reaction (5) is much faster in benzene than in hydrophilic solvents [25] also contributes to explain our observations.

Summing up, we have shown that, by appropriate treatment of inner filter effects and quenching of the triplets by LAT, it is possible to derive branching ratios for LAT formation in the photoreduction of benzophenone in inert solvents with different H-donors. In order to account for the results at long irradiation times, it was necessary to consider the H-abstraction from LAT by excited benzophenone. We can conclude that the quantum yields for LAT formation are enhanced in polar media. Apparently, also the polarity of the radicals derived from the H-donor may determine the extent of this reaction since the most efficient donors are THF and 2-propanol, in comparison with n- and c-hexane.

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