Mechanism of alkyl phenylglyoxylates photoreaction in the presence of oxygen[☆]

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Abstract

The rate of starting material disappearance for phenylglyoxylate esters possessing a reactive γ-hydrogen is not significantly influenced by the presence of oxygen. However, the products produced and their yields are quite different. A mechanism involving trapping of the 1,4-biradical intermediate by ground state oxygen following the triplet state γ-hydrogen abstraction is proposed. Rate constants for the various processes are deduced from literature values and from laser flash photolysis of the starting phenylglyoxylates. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The photochemistry of phenylglyoxylate esters has been extensively studied in inert atmospheres [1], and the mechanisms responsible for free radical formation during their use as photoinitiators for acrylate polymerization elucidated [2]. Initiator performance is not significantly affected by the presence of atmospheric oxygen, [1] an unexpected result considering that oxygen normally quenches the reactive triplet state of carbonyl compounds [3,4] and that the initiation reaction of phenylglyoxylates derives from the triplet state of the carbonyl chromophore [2]. In an earlier study, Pirrung and Tepper reported that the yield of the photochemically produced carbonyl product derived from the alkyl moiety of alkyl phenylglyoxylates in the presence of oxygen does not differ from that in the absence of oxygen [5]. We, therefore, conducted this study to confirm the role of oxygen in the photoreaction of alkyl phenylglyoxylates.

2. Experimental section

2.1. General

Benzene (Aldrich) was dried over sodium benzophenone ketyl under argon. Other chemicals obtained from commer-

cial sources were used as received. NMR spectra were taken with either a Varian Gemini 200 NMR spectrometer or a Varian Unity Plus 400 NMR spectrometer. Chemical shifts are in ppm with TMS as the internal standard. GC measurements were carried out on a Hewlett-Packard(HP) 5890 Gas Chromatography with a $30\,m \times 0.253\,mm$ ID $\times 0.25\,\mu m$ film thickness DB-1 column (J and B Scientific) and a flame ionization detector. GC/MS were taken on a Hewlett-Packard 5988 mass spectrometer coupled to an HP 5880A GC with a $30\,m \times 0.25\,mm$ ID $\times 0.25\,\mu m$ film thickness DB-5 ms column (J and B Scientific), interfaced to an HP 2623A data processor. Infrared spectra were taken with a Galaxy™ series 6020 FTIR Spectrometer. High resolution mass spectra were carried out at the University of Illinois at Urbana-Champaign.

2.2. Irradiation in the presence of oxygen

Before irradiation, a solution of the alkyl phenylglyoxylate in benzene was flushed with an appropriate gas (air or oxygen) ($\sim$10 ml min^{-1}) for 15 min. The flushing gas was passed through a CO_2 trap and dried before it was passed through the sample solution. Following irradiation, the sample solution was further flushed with CO_2-free dry argon for 1 h while the exit gases were passed through two CO_2 traps containing a saturated aqueous solution of barium hydroxide. The precipitated barium carbonate was weighed and the yield of CO_2 determined. Reaction mixtures were then immediately washed three times with saturated $NaHCO_3$, and the aqueous solutions combined and acidified

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with dilute HCl solution before being extracted three times using ethyl acetate. The combined ethyl acetate layers were dried over $MgSO_4$. Benzoic acid was obtained after the solvent was evaporated in vacuo.

When the rate of starting material disappearance was compared, samples (0.01 M) were irradiated in test tubes situated parallel to one another on a 'merry-go-round' apparatus. The concentration of starting material remaining was periodically monitored by withdrawing a small aliquots from the reaction mixture and subjecting them to NMR measurements. In the quantitative NMR experiments, the pulse delay was set at 3 s and the pulse repetition time was above 16.

The synthesis and characterization of the starting alkyl phenylglyoxylates has been described earlier [6,7].

2.3. Time-resolved laser flash photolysis

Nanosecond laser flash photolysis was carried out on a setup described by Ford and Rodgers [8] using the third harmonic of a Q-switched Nd : YAG laser (Continuum, YG660) as the excitation source. The sample solution (0.0005 M) in a quartz curette was purged by argon for 10 min before and during the experiment. The samples were excited with 355 nm pulses (pulse width ca. 7 ns). Light from a 200 W xenon lamp was focused into the sample solution and then into a SPEX1680 0.22 mm double spectrometer. A computer controlled kinetic spectrophotometer (Kinetic Instruments) was used in its absorption mode to obtain transient spectra and kinetic data. The spectrometer was interfaced with a digital oscilloscope (Le Croy 9450, 350 MHz bandpass).

Methyl *O*-benzoylmandelate (**6a**) was synthesized by adding an equimolar amount of triethylamine to a solution of benzoyl chloride and methyl mandelate in chloroform. The mixture was stirred at room temperature for 8 h and then washed with 0.5 N HCl solution and three times with water. The organic layer was dried over $MgSO_4$. Evaporation of the solvent gave **6a** in 92% yield. This compound was also isolated in a photoreaction of **1a** in the presence of O_2; ^{1}H NMR (400 MHz, CDCl$_3$) $\delta = 3.73$ (s, 3H), 6.17 (s, 1H), 7.40–7.47 (m, 5H), 7.53–7.61 (m, 3H), 8.10–8.14 (m, 2H); ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 52.58$, 74.76, 127.55, 128.35, 128.77, 129.10, 129.21, 129.86, 133.41, 133.85, 165.75, 169.19; MS *m/z* (EI, 70 eV) 40 (15), 77 (23), 105

(100), 121 (0.8), 211 (1.4), 238 (1.1), 270 (M$^+$, 0.2); HRMS *m/e* calcd 270.0892: Found : 270.0893.

Cyclohexyl *O*-benzoylmandelate (**6b**) was synthesized by the same method as was **6a** except the starting material was cyclohexyl mandelate. The latter was obtained in almost quantitative yield by refluxing mandelic acid in dry HCl saturated cyclohexanol. The identification of **6b** as a photoproduct of **1b** was made by comparing the retention times on two GC columns and the MS cracking patterns of the photoproduct with the synthesized authentic sample. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.23$–1.39 (m, 4H), 1.42–1.55 (m, 3H), 1.65–1.72 (m, 2H), 1.81–1.88 (m, 1H), 4.85 (heptet, $J = 7.6$ Hz, 1H), 6.14 (s, 1H), 7.37–7.66 (m, 8H), 8.10–8.16 (m, 2H). ^{13}C NMR (50 MHz, CDCl$_3$): $\delta = 23.16$, 23.30, 25.23, 30.98, 31.26, 73.97, 75.13, 127.50, 128.36, 128.68, 129.01, 129.51, 129.87, 130.50, 133.27, 134.41, 165.82, 168.11. MS *m/z* (EI, 70 eV): 40 (20), 55 (15), 77 (20), 83 (13), 105 (100), 211 (4.1), 238 (0.7), 338 (M$^+$, 0.02). HRMS *m/e* Calcd 338.1518; Found: 338.1522.

3. Results and discussion

3.1. Photoreaction and products

Various alkyl phenylglyoxylates (

Chart

1 **a:** —R = —CH$_3$

b: —R = (cyclohexyl)

c: —R = (cyclopropylmethyl)
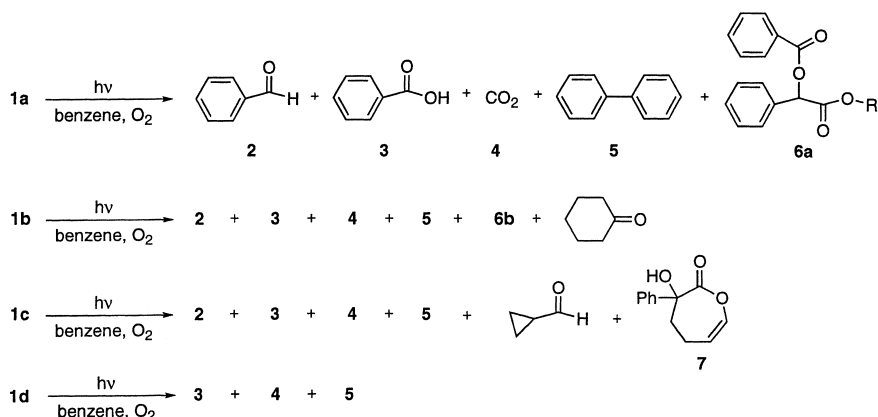
d: —R = C(CH$_3$)$_3$
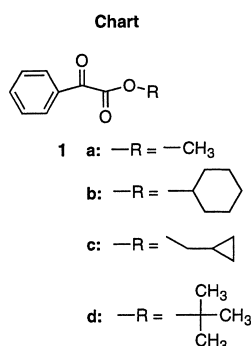
) were irradiated in benzene solutions saturated with CO_2 free oxygen or air. The reaction rate was compared with a parallel reaction under the same conditions (initial concentration of starting material 0.01 M in dry benzene solution) in the absence of oxygen. Disappearance of starting material was monitored by NMR, Table 1 [9]. For alkyl phenylglyoxylates having γ-hydrogens (**1a–c**), the rate of starting

Table 1
Photolysis results in the presence of O_2

Substrate	Condition	Relative quantum yield of starting material disappearance	Yield[a] of **3**	Yield[a] of **4**	Yield[a] of **6**	Relative yield[b] of **5**
1a	No O_2	1	0	0	8%	1
	Under O_2	1 ± 0.08	31%	22%	32%	4
1b	No O_2	1	0	0	0	1
	Under O_2	1 ± 0.1	63%	30%	11%	9

[a] Isolated yields.
[b] From normalized (against signals from all photoproducts) GC signals.

$$1a \xrightarrow[\text{benzene, O}_2]{h\nu} 2 + 3 + CO_2 + 5 + 6a$$

$$1b \xrightarrow[\text{benzene, O}_2]{h\nu} 2 + 3 + 4 + 5 + 6b + \text{(cyclohexanone)}$$

$$1c \xrightarrow[\text{benzene, O}_2]{h\nu} 2 + 3 + 4 + 5 + \text{(7)}$$

$$1d \xrightarrow[\text{benzene, O}_2]{h\nu} 3 + 4 + 5$$

Scheme 1.

material disappearance in the presence of oxygen is almost identical ($\pm 10\%$) to that in the absence of oxygen. The photoproducts produced [10] are shown in Scheme 1. The CO_2 produced was determined gravimetrically. Compounds **6a** and **6b** were isolated and their structures confirmed by independent synthesis. *Tert*-butyl phenylglyoxylate, **1d**, lacks a γ-hydrogen and is virtually photostable in deareated benzene solutions [1]. A slow decomposition of **1d** (reaction rate is about 1% of that of **1a**) was observed in the presence of oxygen and the photoproducts are also displayed in Scheme 1.

When methyl phenylglyoxylate (**1a**) was irradiated, the yield of adduct **6a** was about four times higher in the presence of oxygen than in its absence, indicating that more benzoyl radical is produced when the photolysis is carried out under oxygen. The yield of biphenyl is also significantly higher in O_2 than in an O_2 free environment for reactions of both **1a** and **1b**. Biphenyl, the major product when **1d** was irradiated under O_2, has been proposed to result from the addition of a phenyl radical to the solvent, benzene [1]. The phenyl radical in turn came from decarbonylation of a benzoyl radical. The higher yield of biphenyl under O_2 is therefore also in agreement with the notion that more benzoyl radicals are produced under oxygen. Benzoic acid and CO_2 are only observable when the reactions are carried out under O_2, though benzoic acid may be a secondary product resulting from oxidation of benzaldehyde (the primary photoproduct in the absence of O_2) or it may be a primary photoproduct resulting from O_2 participation in the process. On the other hand, CO, not CO_2, was among the **1a**–**c**, irradiated in the absence of O_2 [6]. However, CO_2 was produced in modest yields when **1a**–**c** were irradiated in the presence of O_2 suggesting that O_2 is directly involved in the photoreaction process furnishing CO_2 as a primary product because CO cannot be oxidized to CO_2 by oxygen under the reaction conditions [11].

We further observed that benzaldehyde, the product resulting directly from the Norrish type II process, is also produced in the reactions carried out in the presence of O_2, indicating that the normal α,β-fragmentation of the biradical intermediate after γ-hydrogen abstraction in the triplet excited state also occurred under the present conditions.

3.2. Mechanism

The literature describes O_2 trapping of biradicals derived from the Norrish type II reaction of phenylketones [12]. We propose, therefore, that O_2 interacts with the biradical intermediate resulting from γ-hydrogen abstraction in alkyl phenylglyoxylates, Scheme 2. Normally, excited carbonyl compounds are quenched by oxygen with rate constants of around $4 \times 10^{-9}\,M^{-1}\,s^{-1}$ [12]. Since in most organic solvents the concentration of oxygen is about $2 \times 10^{-3}\,M^{-1}$ at saturation, this leads to a pseudo-first order rate constant of about $8 \times 10^6\,s^{-1}$ for saturated oxygen quenching of triplet phenylglyoxylates (**T**). The rate constant of γ-hydrogen abstraction in triplet alkyl phenylglyoxylates has been shown to be on the order of $10^6\,s^{-1}$ [6], which is competitive with the quenching of the triplet by oxygen. The triplet biradical, ^{3}**B** resulting from intramolecular γ-hydrogen abstraction can undergo α,β-fragmentation to normal Norrish type II photoproducts, the rate constant of which is between 5×10^7–$5 \times 10^8\,s^{-1}$ and is estimated from the lifetime of the biradical in the absence of oxygen [7,13]. Meanwhile, triplet biradical (^{3}**B**) may interact with ground state O_2. The rate constant of a typical 1,4-biradical reacting with O_2 as measured by laser flash photolysis is about $7 \times 10^9\,M^{-1}\,s^{-1}$ [12]. Taking this value and the saturation concentration of O_2 in common organic solvents, the rate of ^{3}**B** trapping by O_2 is estimated to be on the order of $1 \times 10^7\,s^{-1}$. This is of the same order of magnitude as the normal decay rate of ^{3}**B** to the Norrish type II products, resulting in the situation where the oxygen trapping process and the normal fragmentation reaction are competitive. The fact that the photoproducts observed in the presence of oxygen clearly derive from both processes reinforces the measured rate constant values herein. The photoproducts observed in the presence of oxygen may not be accounted for by the trapping of the biradical by O_2 alone as had been
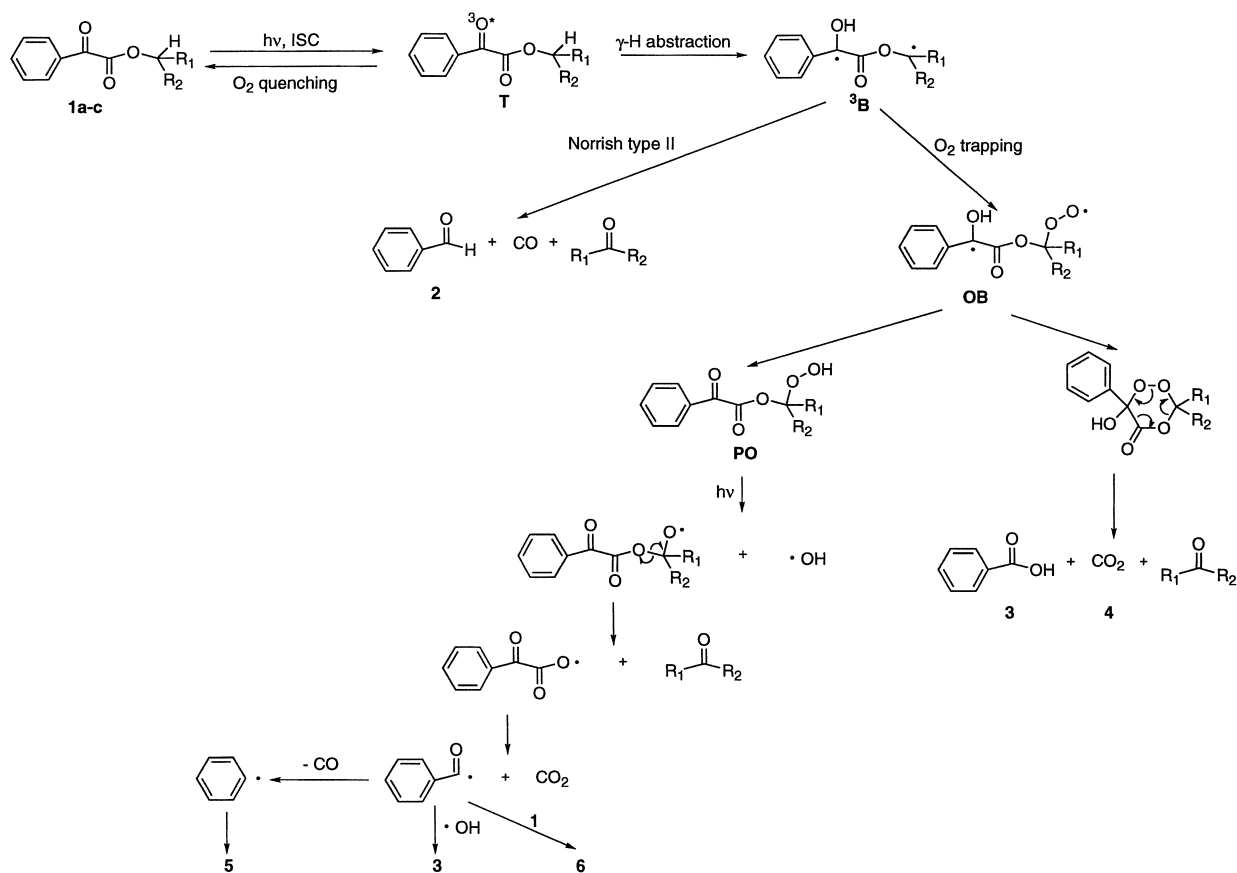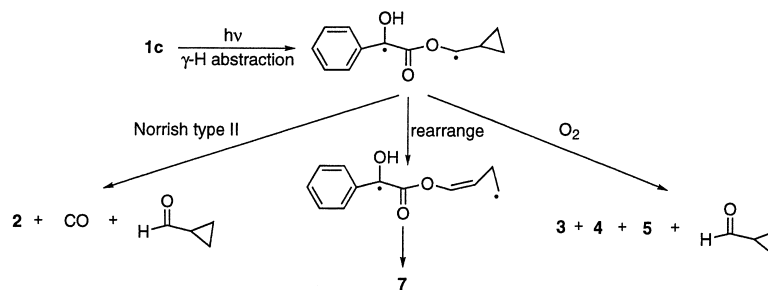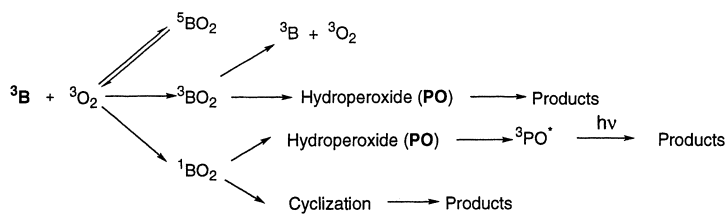
Scheme 2.

proposed earlier [5]. This is further evidenced from the observation that compound **7**, the product putatively resulting from the cyclopropylmethyl radical ring opening in the biradical stage [7], is also formed when the irradiation is carried out in the presence of O_2, Scheme 3. Had O_2 trapped the biradical exclusively, cyclopropyl ring opening would not have occurred. Therefore, the photoproducts observed in the presence of O_2 are derived from both the direct fragmentation of the 1,4-biradical and its trapping by O_2.

Peroxy biradical (**OB**) results from the oxygen trapping of triplet biradical, ^{3}**B**. Such biradicals are short-lived, and earlier laser flash photolyses failed to detect any signal

attributable to this ketyl chromophore [12]. On the other hand, the subsequent hydrogen shift in **OB** to form hydroperoxide (**PO**) is expected to be a facile process since it is exothermic by $\sim$55 kcal mol^{-1} [14]. However, attempts to detect **PO** directly were not successful even though analogous hydroperoxide products had been observed in an earlier study of the 1,4-biradicals derived from phenylketones [12]. This is understood by considering that **PO** is believed to be quite photoactive. **PO** thus produced can be in its ground state or triplet state (vide infra). The ground state was promoted to its excited triplet state by further irradiation. An efficient energy transfer from the excited carbonyl group

Scheme 3.

Scheme 4.

to the peroxy functionality is expected based on the results of earlier work on similar compounds [15]. This leads to immediate fission of the peroxy bond. β-scission of the resulting alkoxyl radical produces a benzoylformyloxy radical and the carbonyl product (an aldehyde or a ketone) [16–22]. Decarboxylation of the benzoylformyloxy radical furnishes a benzoyl radical and CO_2. Benzoic acid results from the coupling reaction between a benzoyl radical and a hydroxyl radical. Compound **6** results when a benzoyl radical adds to the starting phenylglyoxylate [6]. A benzoyl radical also decarbonylates forming a phenyl radical, which adds to the solvent molecule producing **5**. The fact that the yields of **5** and **6** are significantly higher when the reaction is carried out in the presence of oxygen is explained by the greater concentration of benzoyl radical produced from the oxygen trapping of ^{3}**B**.

Biradical **OB** was proposed to undergo a cyclization process followed by electron reorganization to account for, exclusively, the formation of benzoic acid, CO_2, and the carbonyl product derived from the alkyl moiety of the α-keto ester [5]. This mechanism is incomplete because it fails to account for the formation of all the observed photoproducts. A complete identification of all the photoproducts was not pursued in the early study, and this prevented the full elucidation of the reaction mechanism.

According to the spin statistical factors that govern the probabilities of oxygen quenching of the triplet state [23], three different states result from the interaction of a triplet biradical (^{3}**B**) and oxygen ($^3O_2$), Scheme 4. The quintet state, $^5BO_2$, (the probability of its formation is 5/9) is dissociative in nature and does not lead to any observable chemical changes. The triplet state, $^3BO_2$, (the probability of its formation is 3/9) would be expected to rearrange to triplet **PO** since the cyclization in the triplet biradical is not spin allowed. The singlet state, $^1BO_2$, (the probability of its formation is 1/9) can cyclize followed by electron reorganization as proposed [5] or rearrange to ground state **PO**, which is further activated to produce final products. Because of competition between these processes, the quantum yield of starting material disappearance is not significantly perturbed by the presence of O_2 [24]. There are many previous examples in which oxygen apparently has no affect on the Norrish type II reaction of excited carbonyl compounds [25–29].

3.3. Time resolved laser flash photolysis

Time resolved nanosecond laser flash photolysis of **1a** in benzene under oxygen saturation reveals a transient absorption maximizing at around 440 nm, Fig. 1. This is attributed
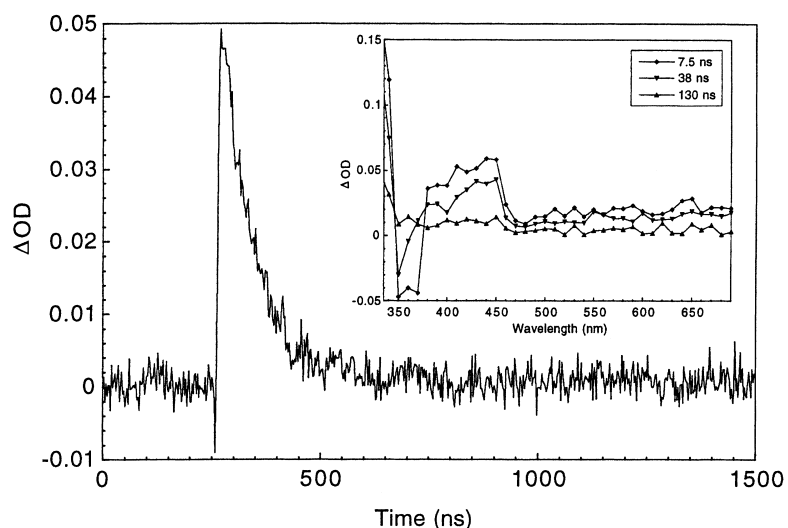
Fig. 1. Transient absorption and decay trace monitored at 440 nm after an oxygen saturated benzene solution of **1a** (0.02 M) was flashed by a 350 nm laser pulse.

to the triplet excited state based on the similarity between this absorption spectrum and that detected for the triplet of **1a** in the absence of oxygen [6]. The triplet decays rapidly with a lifetime of 75 ns under the present conditions. The pseudo first-order rate constant of O_2 quenching of the triplet of **1a** can be calculated by assuming that the rate of γ-hydrogen abstraction in the triplet state of **1a** under O_2 is the same as that measured in the absence of O_2 ($8.6 \times 10^5\,s^{-1}$) [6]. The quenching rate constant so calculated is $1.1 \times 10^7\,s^{-1}$, very close to the value of $8 \times 10^6\,s^{-1}$ estimated from the data derived from other typical triplet carbonyl compounds (vide supra).

The slow photolysis of **1d** in the presence of O_2 cannot be explained by the mechanism elucidated herein involving a 1,4-biradical intermediate since there is no γ-hydrogen in compound **1d**. The reaction responsible for the disappearance of **1d** is inefficient (the rate of disappearance of **1d** in low). A mechanism involving electron transfer from the excited α-keto ester to ground state oxygen leading to a peracid intermediate was suggested in early studies of similar compounds [30–33], and this can account for the photo decomposition of **1d**. However, this process is insignificant if it exists at all.

4. Conclusions

In summary, O_2 interacts at several stages of the photoreaction of alkyl phenylglyoxylates. Interaction of ground state oxygen with the 1,4-biradical intermediate derived from γ-hydrogen abstraction in the triplet excited state leads to significantly higher yields of radical addition products. Since more benzoyl radical is produced in the presence of oxygen than in its absence when alkyl phenylglyoxylate containing γ-hydrogens are irradiated, alkyl phenylglyoxylates are expected to be more efficient in initiating polymerization reactions in the presence of oxygen.

5. Acknowledgements

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[9] The aromatic proton signals of the reaction mixture were used as the internal standard. The downfield aromatic signal (~8.0 ppm) is representative of the starting material and its integration was used to indicate the amount of the remaining starting material.

[10] Products **2** and **5** were identified by comparing the retention times and mass fraction patterns with authentic samples in GC/MS analyses.

[11] A more direct indication that O_2 was involved in the photoreaction is that a negative pressure was developed in the sealed reaction vessels when the benzene solutions of **1a** and **1b** were irradiated in the presence of O_2, evidencing that O_2 is consumed in this process. When the photolysis was carried out in the absence of O_2, a positive pressure was observed due to the CO produced.

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