Methyl Phenylglyoxylate as a Photoinitiator

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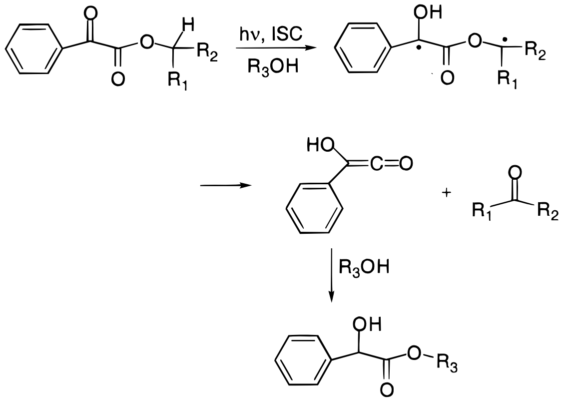
ABSTRACT: α-Cleavage reactions do not occur from the excited states of methyl phenylglyoxylate.

Introduction

The earliest study of the photochemical reactions of the phenylglyoxylate chromophore appeared in the early 1950s,[2] when Schönberg and his group in Cairo reported that phenylglyoxylic acid underwent reductive dimerization in isopropyl alcohol in sunlight. Huyser and Neckers later reported the photoreduction of alkyl esters of phenylglyoxylic acid,[3] first observing the formation of the mandelic esters from the alcohols used as the solvents. This ester exchange was proposed to come from solvent alcohol trapping of the intermediate α-hydroxyphenylketene formed from an intramolecular γ-hydrogen abstraction reaction by the triplet carbonyl group, eq 1.[3]



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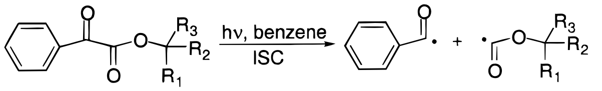
A later study on the photochemistry of α-keto esters, including that of ethyl phenylglyoxylate in benzene, suggested an α-cleavage mechanism, eq 2.[4]



(2)

These contradicting literature reports prompted a comprehensive reinvestigation of the photochemistry of methyl phenylglyoxylate and its analogues under a variety of experimental conditions[5,6] in which it was established that reaction results from the γ-hydrogen abstraction process. There were no circumstances under common lamp irradiation conditions in which the reactions observed derived from an α-cleavage.[5,6]

Alkyl phenylglyoxylates have also long been used as photoinitiators for vinyl polymerization,[7−10] and are the subject of current commercial interest.[11] Methyl phenylglyoxylate (**MP**) has numerous industrial applications, however the mechanism by which it initiates vinyl polymerization is only partially understood due to the conflicting literature on its photochemical reactions. For example, Dietliker grouped **MP** with other initiators known to function by an α-cleavage mechanism.[12] More recently, Allen et al reported observing benzoyl radical transient signals when **MP** was irradiated in isopropyl alcohol and suggested that it initiates radical polymerization following α-cleavage.[13]

The latter report contradicts the well-established mechanism of the photochemical reactions of alkyl phenylglyoxylates,[5,6] and caused us to reinvestigate the transient spectroscopy of the title compound. We now report additional experiments on the photochemical reactions of methyl phenylglyoxylate that pertain to its ability to initiate vinyl polymerization.

Results and Discussion

A systematic study of the photochemical reactions of methyl phenylglyoxylate and its analogues in benzene under argon revealed a plurality of concentration dependent reactions with intramolecular γ-hydrogen abstraction (Norrish type II) predominating at lower concentrations. Intermolecular hydrogen abstraction induced radical reactions compete with the intramolecular process at higher concentrations.[5] The Norrish type II reaction mechanism was further supported by radical trapping experiments,[14,15] but there was no evidence for an α-cleavage reaction.[6]

Though most practical polymerization systems that employ **MP** usually contain compounds with reactive hydrogen atoms, we have studied **MP** initiated polymerization reactions of a monomer lacking reactive hydrogens.[16] We observed that equal concentrations of benzoyl radicals and phenyl radicals were the initiating species, and suggested that such radicals result from a bimolecular, self-quenching reaction between **MP** triplet and **MP** ground state.[5]

The phenylglyoxylate chromophore has been shown[2] to exclusively undergo reductive dimerization to dihydroxydiphenylsuccinates (eq 3)[3,17] in the presence of H atom donors,[18,20] in a reaction that is formally analogous to the photoreduction of benzophenone. A critical intermediate obviously formed during the process is the methyl phenylglyoxylate ketyl radical, **K**.

In the recent report,[13] it was suggested that a signal detected when **MP** was irradiated in isopropyl alcohol was that of the benzoyl radical **B**, eq 4. The published microsecond laser flash photolysis of **MP**[13] was carried out in dilute isopropyl alcohol solution (1.0×10^{-5} M) under nitrogen, and it was the transient absorption

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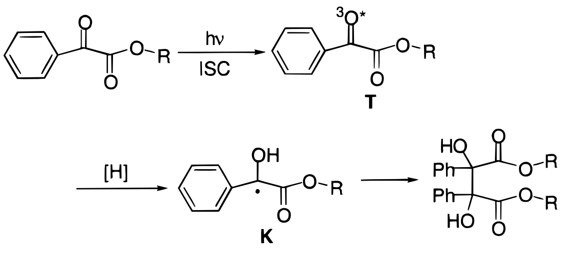
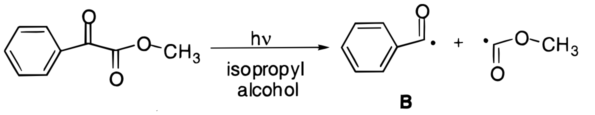


(3)

spectrum at unspecified delay time (Figure 1) which was assigned.[13]



(4)

Since the shape of the spectrum (Figure 1) does not resemble the absorption spectrum of benzoyl radicals recorded at a low temperature (Figure 2)[20] or the transient spectra of benzoyl radicals obtained from photolysis of various aryl ketones (Figure 3),[21] we were confused by the result. The absorption is far too intense since the benzoyl radical has been reported to be weakly absorbing ($\epsilon \sim 150$ M^{-1} cm^{-1} at $\lambda_{max} = 370$ nm).[21–23]

Accordingly we repeated the nanosecond laser flash photolysis of methyl phenylglyoxylate in isopropyl alcohol under the reported conditions.[13] Transient absorption spectra at different delay times were recorded, Figure 4, and the decay trace of the transient species was monitored at 440 nm, Figure 5. The spectra obtained do not match those of the benzoyl radicals in either shape or intensity.

On the basis of the known photochemical reactions of alkyl phenylglyoxylates in hydrogen-donating solvents,[3,17] we hypothesized the transient spectra in Figure 4 were most likely to be attributed to the methyl phenylglyoxylate ketyl radical (**K**). The spectra are clearly not due to the α-hydroxy radical derived from isopropyl alcohol following hydrogen atom abstraction by the triplet, because this radical does not absorb significantly above 300 nm.[21,24] However since the gross features of the spectra in Figure 4 also resemble those of an alkyl phenylglyoxylate triplet,[5,6] the possibility of they being the spectra of the triplet (**T**) cannot be immediately ruled out.

MP triplets are quenched by isopropyl alcohol with a rate constant of 3.6×10^6 M^{-1} s^{-1},[17] so the calculated triplet lifetime of **MP** in *pure isopropyl alcohol* is less than 20 ns. Since 20 ns is at the resolution limit of our laser flash photolysis instrumentation, it is impossible that the transient species detected is the triplet (**T**). Further supporting the assignment that the spectra in Figure 4 are due to the methyl phenylglyoxylate ketyl radical (**K**) is that the decay trace in Figure 5 can only be perfectly fitted with second-order kinetics. It has been found that there is no cross coupling between **K** and the α-hydroxyl radical derived from the solvent molecule,[3,17] and that methyl phenylglyoxylate ketyl radicals (**K**) self-couple exclusively forming dimethyl 2,3-dihydroxy-2,3-diphenylsuccinate. Had a cross coupling reaction proceeded to any measurable degree, the ketyl radical (**K**) would decay with a mixed first/second-order kinetics. Were the absorption due to **MP** triplets (**T**), the decay trace should follow first-order kinetics.

The ketyl radical signals decay with a first half time of 14.8 μs under the present experimental conditions.

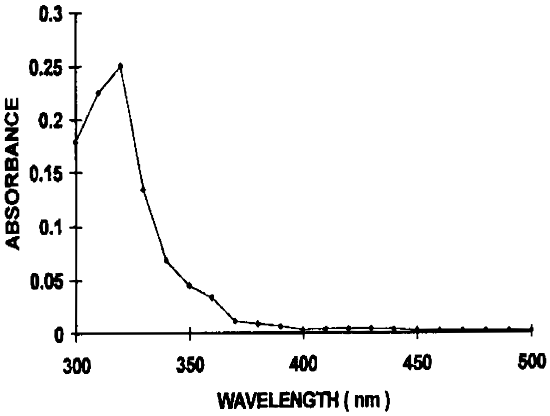


Figure 1. Transient absorption spectrum of a **MP** solution in isopropyl alcohol (1.0×10^{-5} M) under nitrogen atmosphere. Reprinted with permission from ref 13. Copyright 1999 Elsevier Science.

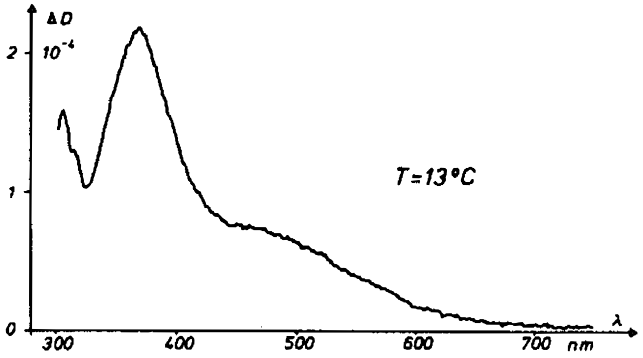


Figure 2. Absorption spectrum of benzoyl radicals recorded at 13 °C in 3-methyl-3-pentanol.[20] Reprinted with permission from ref 20.

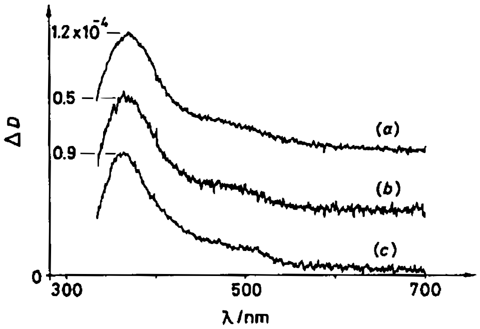


Figure 3. Transient spectra of benzoyl radicals obtained from the photolysis of various aryl ketones.[21] Reprinted with permission from ref 21. Copyright 1990 The Royal Society of Chemistry. Key: (a) 2-methoxyl-2-methyl-1-phenylpropan-1-one, (b) 2-hydroxy-2-methyl-1-phenylpropan-1-one, and (c) 1-hydroxycyclohexyl phenyl ketone.

Assuming the absorption coefficient of **K** at 440 nm is close to that of the benzil ketyl radical (2000 M^{-1} cm^{-1}),[25] the self-coupling rate constant of **K** can be calculated to be about 7.0×10^9 M^{-1} s^{-1}.

It is thus concluded that Allen et al.[13] misinterpreted the ketyl radical signal to be that of the benzoyl radical.

When **MP** is irradiated in monomers with reactive hydrogens, photoreduction is the expected reaction, eq 3. This is depicted in Scheme 1 using triethylene glycol diacrylate as a typical monomer.[6]

In the absence of reactive hydrogen donors, and based on the photochemistry observed under such conditions (*vide supra*), benzoyl radicals resulting from the self-

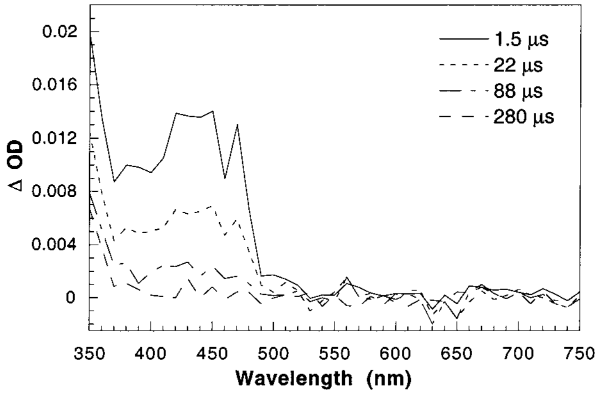


Figure 4. Transient absorption spectra recorded at different delay times after laser flash photolysis of an isopropyl alcohol solution of **MP** (0.005 M) under argon atmosphere.

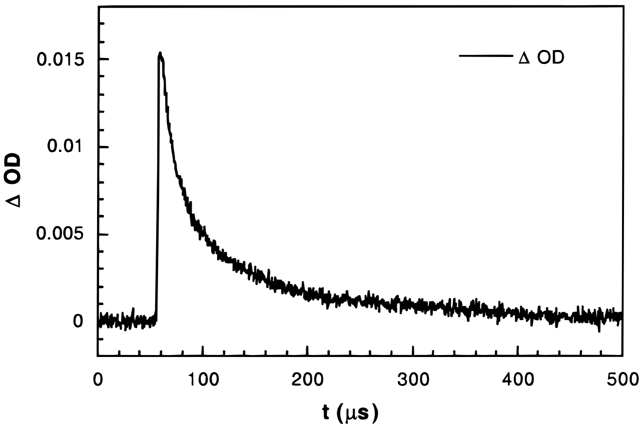
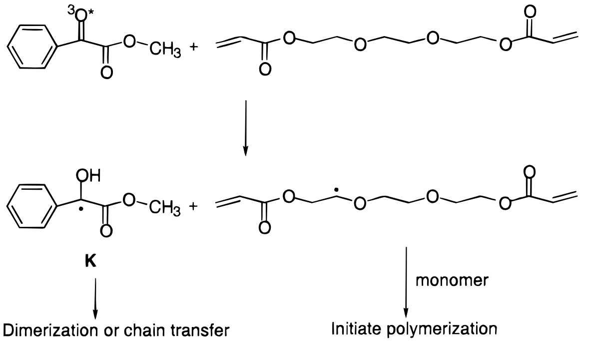


Figure 5. Transient decay trace monitored at 440 nm after laser flash photolysis of an isopropyl alcohol solution of **MP** (0.005 M) under argon atmosphere.

Scheme 1



quenching reaction of **MP** become the initiating radicals.[16] We further observed oxygen trapping of the intermediate 1,4-biradical when the reaction is carried out under oxygen producing more benzoyl radicals than under inert atmosphere.[6] It is thus to be expected that **MP** will be a more efficient initiator under oxygen than under an inert atmosphere.[6]

Irradiation of an oxygen-saturated isopropyl alcohol solution of **MP** leads to rapid disappearance of the starting material following an inhibition period. This can easily be followed from the absorption spectrum of **MP**, Figure 6. A parallel reaction carried out on a solution saturated with argon was similarly monitored. Dimethyl dihydroxydiphenylsuccinate is the only photoproduct in both cases.

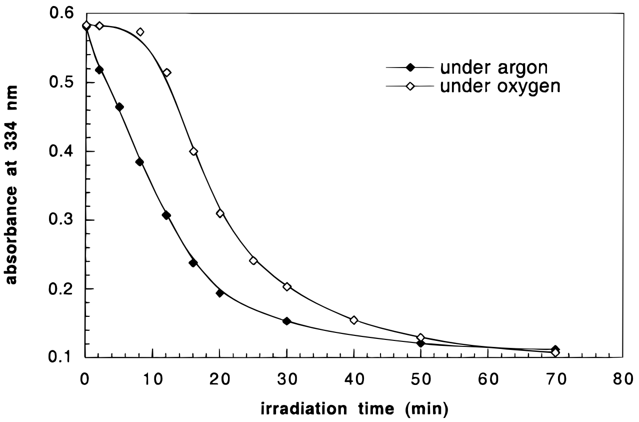


Figure 6. Rate of **MP** disappearance in isopropyl alcohol under oxygen and argon atmosphere.

When an oxygen-saturated isopropyl alcohol solution of **MP** (0.005 M) was subjected to laser flash irradiation under similar conditions, the triplet lifetime is further shortened in comparison to the 20 ns lifetime estimated under argon because of oxygen quenching of the triplet state. That the triplet will avoid the detection in our transient experimental setup is therefore expected. The fact that we detected no ketyl radical transient signal in the presence of oxygen reveals that the radical is also efficiently trapped by oxygen and its lifetime further shortened so as to not be detectable with the current laser flash photolysis instrument. The product resulting from oxygen trapping of the ketyl radical dissociates because no new photoproduct can be detected other than the self-coupling product of the ketyl radicals.

Conclusions

In non-hydrogen-donating solvents, methyl phenylglyoxylate, when irradiated, undergoes primarily Norrish type II reactions. The extent of intermolecular hydrogen abstraction depends on concentration. In the presence of compounds furnishing abstractable hydrogens, the triplet excited state of methyl phenylglyoxylate abstracts a hydrogen atom from the donor molecule and forms the ketyl radical, which exclusively couples. When methyl phenylglyoxylate is used to initiate the polymerization of a monomer containing reactive hydrogens, the triplet state abstracts hydrogens from monomer molecules. The monomeric radical resulting therefrom is the initiation species. If the monomer lacks reactive hydrogens, self-quenching and intermolecular hydrogen abstraction among methyl phenylglyoxylates leads to initiating radicals. When the initiation reactions are carried out in an oxygen atmosphere, oxygen trapping of reaction intermediates occurs and the initiation mechanism is altered accordingly.

The reactivity of an initiation system cannot be revealed from measuring only the quantity of reactive radical produced from the primary reaction of the photoinitiator. A comprehensive consideration of a host of photochemical processes and the characteristics of the reactive species is necessary when comparing the initiation abilities of photoinitiation systems.

Experimental Section

Materials. Methyl phenylglyoxylate and isopropyl alcohol are the purest commercial products purchased from Aldrich and were used as received. UV–visible spectra were obtained using an HP 8452 diode array spectrophotometer. Routine GC measurements were carried out on a Hewlett-Packard (HP) 5890 gas chromatograph with a 30 m × 0.253 mm ID × 0.25 μm film thickness DB-1 column (J & W 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 × 0.25 mm ID × 0.25 μm film thickness DB-5 ms column (J & W Scientific), interfaced to an HP 2623A data processor.

Laser Flash Photolysis. Nanosecond laser flash photolysis was carried out on a set up described by Ford and Rodgers[26] using the third harmonic of a Q-switched Nd:YAG laser (Continuum, YG660) as the excitation source. Solutions of **MP** were prepared at concentrations such that the optical density was about 0.3 at the excitation wavelength employed. The sample solution in a quartz cuvette was purged with argon or oxygen for 5 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 nm 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 band-pass).

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