

Time-Resolved Step-Scan Fourier Transform Infrared Spectroscopy of Alkyl Phenylglyoxylates[†]

Andrei V. Fedorov, Eugene O. Danilov,
Michael A. J. Rodgers,* and Douglas C. Neckers*

Center for Photochemical Sciences
Bowling Green State University, Bowling Green, Ohio 43403

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Previous investigations on the photochemical reactivity of alkyl phenylglyoxylates (APG)^{1–5} have outlined two major pathways (Scheme 1). At higher concentrations (>0.1 M), bimolecular (self-quenching) hydrogen abstraction takes place.² At lower APG concentrations, intramolecular γ -hydrogen abstraction prevails yielding a putative 1,4-biradical (2) that rapidly undergoes α - β cleavage (16 ns estimated lifetime⁴) resulting in formation of an aldehyde or ketone and α -hydroxyphenyl ketene (3). The latter presumably undergoes secondary photodecarbonylation forming benzaldehyde. Formation of 3 has been widely accepted and indirectly confirmed by the analysis of photolysis products.^{1–3} Previous time-resolved UV studies of APG in aqueous solutions⁵ also implied the formation of α -hydroxyphenyl ketene. Herein we report the use of time-resolved Fourier transform spectrometry to provide the first direct observation of the mid-IR spectrum of the α -hydroxyphenyl ketene (3) and characterize its reactivity.

Ketenes have been previously observed by time-resolved IR spectroscopy using dispersive methods. α -Methoxynaphthyl ketene was observed from the photolysis of diazonaphthyl acetates in which both singlet⁶ and triplet⁷ carbenes may have been precursors. The time resolution for these studies was 50 ns. Wagner et al.⁸ reported the time-resolved IR spectra and absolute reactivity of various ketenes toward amines in acetonitrile. An instrument response function of 250 ns prevented observation of the growth of the absorption of the ketene. The present report describes the first application of 30 ns time resolution step-scan Fourier transform infrared spectroscopy⁹ for the observation of a ketene intermediate.

A 3-dimensional representation of the TR FTIR spectrum (Figure 1) of a photolyzed hexane solution of methyl phenylglyoxylate (MPG) shows two transient absorptions in the carbonyl region at 1655 and 2100 cm^{-1} . Similar results occurred in benzene. In both cases, the 1655 cm^{-1} transition grew in rapidly (<30 ns) and had completely decayed within 2.5 μs after excitation. The 2100 cm^{-1} signal, in turn, grew in over a few microseconds.¹⁰ The time profiles for the 1655 and 2100 cm^{-1} transitions in both hexane and benzene are presented in Figures 2 and 3, respectively. The decay and growth of the corresponding kinetic profiles are concomitant in both solvents implying the 1655 cm^{-1} species is the precursor for the intermediate absorbing at 2100 cm^{-1} .

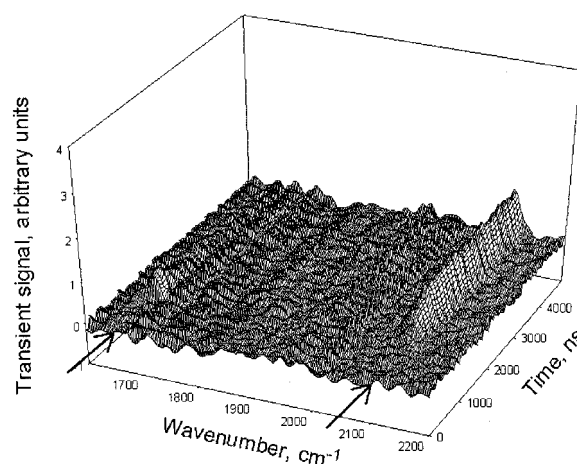


Figure 1. A 3-dimensional representation of the time-resolved step-scan FTIR spectrum of methyl phenylglyoxylate (40 mM) in argon-saturated hexane. Two transient absorptions are observed at 1655 and 2100 cm^{-1} .

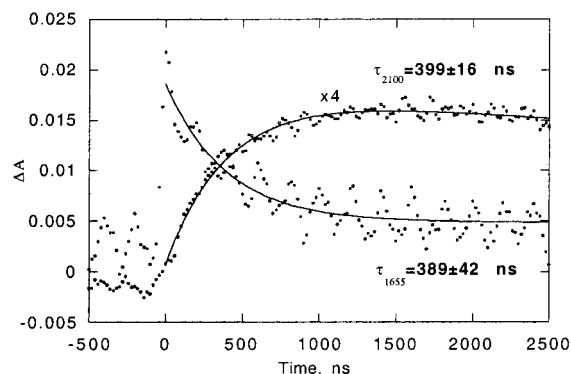
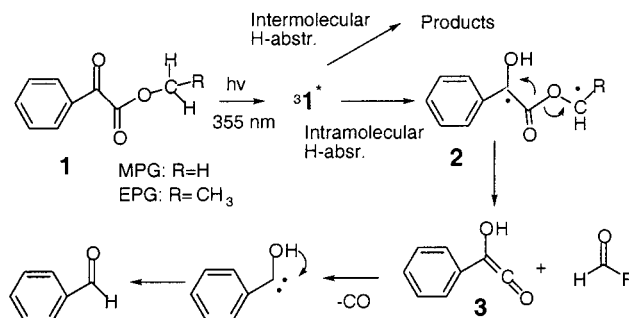


Figure 2. Kinetic traces observed at 1655 and 2100 cm^{-1} following 355 nm laser excitation of methyl phenylglyoxylate (40 mM) in argon-saturated hexane. Dots represent experimental data; lines are calculated best fits to a single-exponential function.

Scheme 1



Examination of 40 mM benzene and hexane solutions of ethyl phenylglyoxylate (EPG) revealed a TR FTIR spectrum similar to that of MPG.

(10) In the absence of the UV excitation, MPG possesses two IR carbonyl fundamentals at 1699 and 1747 cm^{-1} with the higher energy transition belonging to the ester moiety. For the concentration range (20–40 mM) used to provide effective UV excitation, these transitions are saturated making it impossible to observe the transient IR changes within $\pm 15 \text{ cm}^{-1}$ of the MPG IR bands. This explains the absence of the TR IR bands corresponding to the depletion of the starting glyoxylate. The experimental carbonyl frequencies are in good agreement with the B3LYP/6-31G+(d) calculated¹¹ C=O stretches of MPG predicted at 1679 and 1714 cm^{-1} (the scaling factor of 0.96 was used for these and all other calculated frequencies).

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- A brief description of the experimental setup is available as Supporting Information.

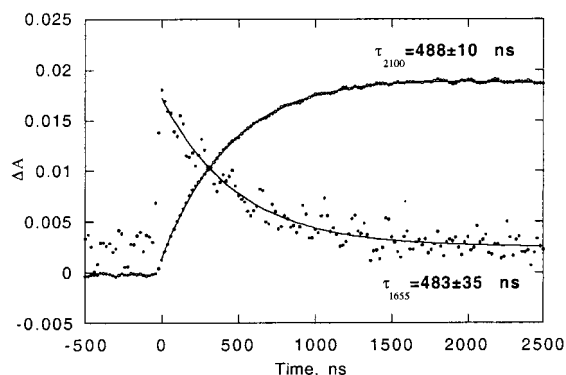


Figure 3. Kinetic traces observed at 1655 and 2100 cm^{-1} following 355 nm laser excitation of methyl phenylglyoxylate (40 mM) in argon-saturated benzene. Dots represent experimental data; lines are calculated best fits to a single-exponential function.

Ketenes are known to display a characteristic antisymmetric C=C=O stretching absorption in the 2085–2197 cm^{-1} region.^{8,12} It therefore appears likely that the 2100 cm^{-1} carbonyl band arises from α -hydroxyphenyl ketene (**3**) formed within several microseconds after photoexcitation of MPG. This assignment is supported by DFT calculations,¹¹ which predict the C=C=O stretch of **3** to absorb at 2096 cm^{-1} .

The C=O stretch fundamental of formaldehyde, which is formed simultaneously with ketene, was not observed for the same reasons as depletion of the starting glyoxylate.¹⁰ This transition, predicted (DFT) to absorb at 1750 cm^{-1} , lies under the carbonyl bands of MPG ground state, making the observation of this peak impossible. The situation is similar for EPG, where the carbonyl fundamental band of acetaldehyde is calculated at 1743 cm^{-1} , in reasonable agreement with the experimental C=O frequency (1736 cm^{-1}) in hexane solution.

In the absence of quencher, the 2100 cm^{-1} signal showed no signs of decay over a time interval of 500 μs . The addition of 2.20 M of methanol to the MPG solution shortened the lifetime of the ketene to tens of microseconds. A similar result occurred when the solution is saturated with oxygen. The interaction of ketenes with alcohols and oxygen has been previously shown¹³ and the results here provide additional confirmation to the assignment of this IR band to the C=C=O fundamental of **3** and not to the carbon monoxide, which has been reported in other situations.¹⁴

As a precursor to ketene, the 1655 cm^{-1} band is formed within the 30 ns response time of the instrument. Though this might be attributed to either biradical (**2**) or MPG triplet, the triplet has been shown to have longer lifetime arguing against its assignment to **2** or any other species derived from the triplet state of **1**.² This band is more likely to be derived from the excited singlet state and correspond to the MPG triplet. When MPG ([40 mM] in benzene) was saturated with O_2 , the decay (72 ± 20 ns) and the

growth (75 ± 5 ns) of two bands were significantly faster than corresponding values in the oxygen-free solutions. This is consistent with the first band being the MPG triplet and its concomitant decay with ketene formation.

To confirm the assignment of the 1655 cm^{-1} transition, the TR FTIR spectrum in hexane of *tert*-butyl phenylglyoxylate (TBPG) was recorded. TBPG has no γ -hydrogens and formation of both **2** and **3** is thereby obviated. Changing the aliphatic group is not expected to significantly alter the C=O fundamental frequency of the TBPG triplet relative to that of MPG. The TR FTIR spectrum of TBPG displays a single weak absorption at 1643 cm^{-1} with a lifetime of about 1 μs ,¹⁵ reasonably attributable to the triplet state of TBPG, and thus confirming the nature of the 1655 cm^{-1} MPG band. The C=O fundamental of MPG triplet is red shifted by 44 cm^{-1} relative to the 1699 cm^{-1} C=O band of the MPG ground state. This shift is much less than the -214 and -370 cm^{-1} C=O fundamental shifts of the $\pi\pi^*$ and $n\pi^*$ triplets of para-substituted acetophenones.¹⁶

Longer triplet lifetimes corresponding to the natural triplet decay of glyoxylates (6.9 μs in hexane, 12.6 μs in benzene) were obtained by UV laser flash-photolysis of quite dilute (1×10^{-4} M) TMPG solutions. From these results and our TR FTIR spectroscopic data, rate constants for the intramolecular γ -hydrogen abstraction of 2.4×10^6 (in hexane) and 2.0×10^6 s^{-1} (in benzene) were obtained.² In agreement with previous studies of glyoxylates,^{2,4,17} these values are lower than rate constants of γ -hydrogen abstraction in simple phenyl ketones.¹⁸ This difference in rate constants can be explained by the conformational issues in APGs where γ -hydrogen can only be abstracted from a less stable^{19,20} E-conformer.

In summary, step-scan TR FTIR spectroscopy of alkyl phenylglyoxylates has confirmed the postulated intramolecular H-abstraction by first direct observation of the time-resolved IR absorptions of glyoxylate triplet states and α -hydroxyphenyl ketene. From the IR data, the intramolecular H-abstraction rate constants have been determined.

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Supporting Information Available: Brief description of experimental setup, details of DFT calculations, and the kinetic trace for the 1643 cm^{-1} band of TBPG (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(15) The kinetic trace observed at 1643 cm^{-1} is available as Supporting Information.

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