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Observations of Different Triplet Conformations in Time-Resolved Infrared Spectra of Alkyl Phenylglyoxylates[1]

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Step-scan methodology has facilitated the practicality of time-resolved infrared spectroscopy[2] (TRIR) to follow the chemical structures of short-lived intermediates arising from photochemical events.[3] Few reactions have provided as much information by this method as have the photochemical processes of α-ketoesters[4] such as alkyl phenylglyoxylates (APG).[5,6] In inert solvents, an alkyl phenylglyoxylate (APG) in the triplet state can decay in unimolecular events to the ground state via radiation or radiationless transitions and undergo Norrish Type II photoelimination producing α-hydroxyphenylketene or, in a bimolecular event, abstract a hydrogen atom from another APG molecule.[7] We have obtained the transient spectra of a number of alkyl phenylglyoxylates using the step-scan FTIR setup described previously.[5] The observed spectra change with time and depend on the structure and the concentration of APGs. As an example, a TRIR spectrum of a 0.01 M solution of ethyl phenylglyoxylate in hexane is shown in Figure 1. It features the decaying triplet state peak at 1654 cm^{-1} and concomitantly growing ketene centered around 2105 cm^{-1}. The two negative bands observed at 1697 and 1743 cm^{-1} correspond to bleaching of the ground state.

At enhanced 4 cm^{-1} resolution, in hexane we observed that the triplet band splits into two components **1** and **2**. The transient spectra of methyl phenylglyoxylate (MPG), ethyl phenylglyoxylate (EPG), isopropyl phenylglyoxylate (*i*PPG), and neopentyl phenylglyoxylate (NPG) averaged over 200 ns intervals are shown in Figure 2. The decay of band **2** and the rise of ketene exhibit the same time dependence, indicating that **2** is the ketene precursor. Therefore, **2** corresponds to one triplet state of APG.[5] The lifetime of **1** is approximately an order of magnitude greater than the lifetime of **2**, implying it belongs to a different species, yet the intermediates corresponding to bands **1** and **2** have similar reactivity toward hydrogen atom donors. The rate constants of quenching of ethyl phenylglyoxylate transients by 1,4-cyclohexadiene are 1.0×10^7 M^{-1} s^{-1} for intermediate **1** and 5.5×10^7 M^{-1} s^{-1} for intermediate **2**. Similarly, $^3n\pi^*$ states of 2,4,6-triisopropylbenzophenone and 2,4,6-trimethylbenzophenone are quenched by 1,4-cyclohexadiene with the rate constants of 2.8×10^7 and 3.7×10^7 M^{-1} s^{-1}, respectively, in acetonitrile.[8] Because the difference between the vibrational frequencies of **1** and **2** is small (<10 cm^{-1}), **1** and **2** must be similar in structure. The difference of this magnitude may be accounted for by the presence of two rotamers. For example, in the case of *o*-chlorobenzaldehyde, the difference between the carbonyl stretching frequencies in a rare gas matrix of syn- and anti-conformations is 24 cm^{-1}.[9] Moreover, conformations of the same excited state can exhibit different reactivity[10] (e.g., one isomer may decay via both intramolecular and intermolecular pathways, whereas the other may decay only by the intermolecular route).

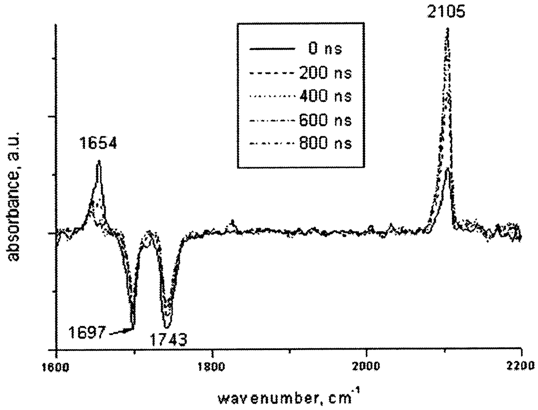

Figure 1. Time-resolved infrared spectra of a 0.01 M solution of ethyl phenylglyoxylate in hexane. The individual spectra are averaged over 200 ns intervals. The resolution is 4 cm^{-1}.

Consequently, we attribute **1** and **2** to the different conformations *E* and *Z* of APG triplets (Figure 3), only one of which (*Z*) is capable of undergoing the Norrish Type II photoelimination.[11−13]

This assignment is further supported by the correlation between the bulkiness of the alkyl substituent of an alkyl phenylglyoxylate and the amplitude of peak **2**. As the size of the alkyl group increases, the amplitude of peak **2** decreases, consistent with fewer APG molecules assuming the sterically hindered limiting conformation *Z*.

Because the spectra shown in Figure 2 were averaged over 200 ns intervals, which is comparable to the transient lifetimes, we must distinguish the influence of the lifetime and the transient concentration on the amplitude of the averaged peak. In diluted solutions, the influence of the time evolution of peak **1** on peak **2** is small; in addition, due to its longer lifetime, over a short time interval the contribution of **1** can be approximated by the baseline correction. The preexponential coefficients of the resulting single-exponential fit of **2** will then reflect the initial concentration of the transient corresponding to the peak. The ratio of the initial transient signal amplitudes in the series MPG:EPG:*i*PPG in 0.01 M solution was 137:115:100. Assuming that the IR extinction coefficient corresponding to the carbonyl group stretching vibration is unaffected by the size of the alkyl substituent, we find that the amount of conformation *Z* decreases as expected.

In the case of *tert*-butyl phenylglyoxylate (*t*BuPG), conformation *Z* would lead to strong repulsion between the terminal methyl groups and the α-carbonyl group, thus making it extremely unfavorable. Indeed, only one peak is observed at 1640 cm^{-1} (Figure 4). Both its lifetime (∼1.1 μs) and its position match those of peaks **1** in other cases. Therefore, *t*BuPG can be used as a model system for investigating the reactivity of peak **1**. Upon the addition of 1,4-

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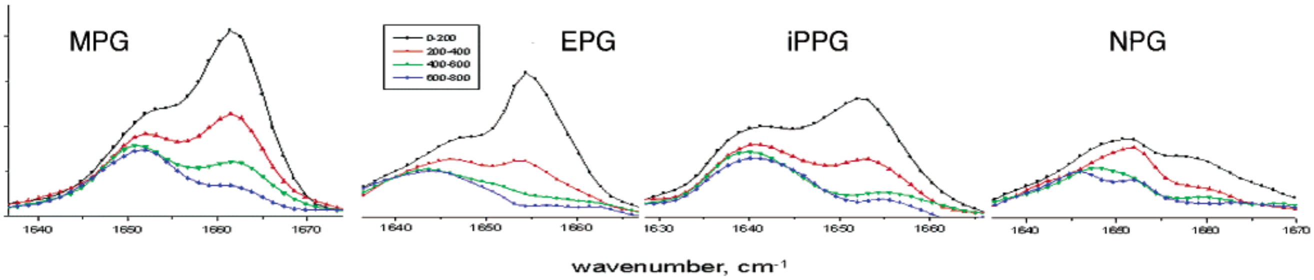
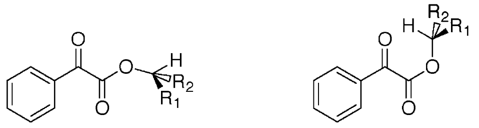


Figure 2. The time-resolved infrared spectra of methyl phenylglyoxylate (MPG), ethyl phenylglyoxylate (EPG), isopropyl phenylglyoxylate (*i*PPG), neopentyl phenylglyoxylate (NPG). Spectra shown are averaged over 200 ns intervals. All APGs are 0.04 M solutions in hexane. Peaks **1** and **2** are the left and right peaks, respectively.



E (1)
Z(2)

Figure 3. *E* (**1**) and *Z* (**2**) isomers of alkyl phenylglyoxylate triplet.

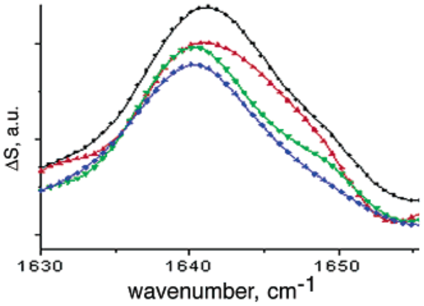


Figure 4. Time-resolved infrared spectra of a 0.01 M solution of *t*BuPG in hexane. The individual spectra are averaged over 1 μs intervals.

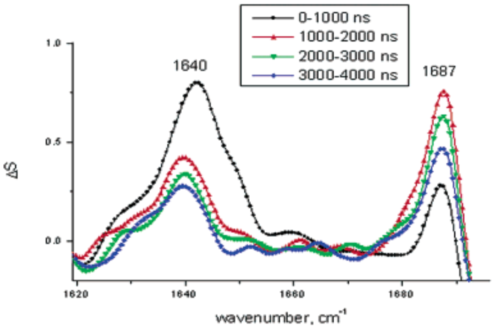


Figure 5. Quenching of *t*BuPG triplet by 0.065 M 1,4-cyclohexadiene. Transient spectra are averaged over 1 μs intervals.

cyclohexadiene, the lifetime of the *t*BuPG triplet state at 1640 cm^{-1} decreases, and a band centered at 1687 cm^{-1} grows in with the characteristic time similar to the lifetime of the triplet (Figure 5). Thus, we attribute the latter band to *t*-butyl mandelate radical. The bimolecular quenching rate of the triplet by 1,4-cyclohexadiene was 2.6×10^7 M^{-1} s^{-1}.

Therefore, one of the observed peaks **2** corresponds to the intermediate *Z* that reacts via both intra- and intermolecular pathways, forming ketene and other products at higher concentrations. Peak **1** corresponds to the intermediate *E* which can only take part in intermolecular processes because its conformation prevents the formation of the chairlike transition state necessary for a Norrish Type II process. We believe this is the first definitive structural evidence of sterically distinguishable nπ* triplet states in a single molecule. We are pursuing the implication in similar species by the practical application of TRIR spectroscopy.

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Supporting Information Available: Synthesis and characterization of NPG. Triplet quenching data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Observed transients are not assigned to nπ* and $\pi\pi$* triplet states because their reactivity towards hydrogen donors is close, whereas the $\pi\pi$* triplet is expected to be virtually unreactive as compared to the nπ* triplet of the same molecule. See refs 13 and 14. Also, alkyl substituents should not have a strong influence on the triplet energy levels of the analogous, but differing, APGs. Yet the spectrum of ^{t}BuPG contains only one triplet transient.
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