

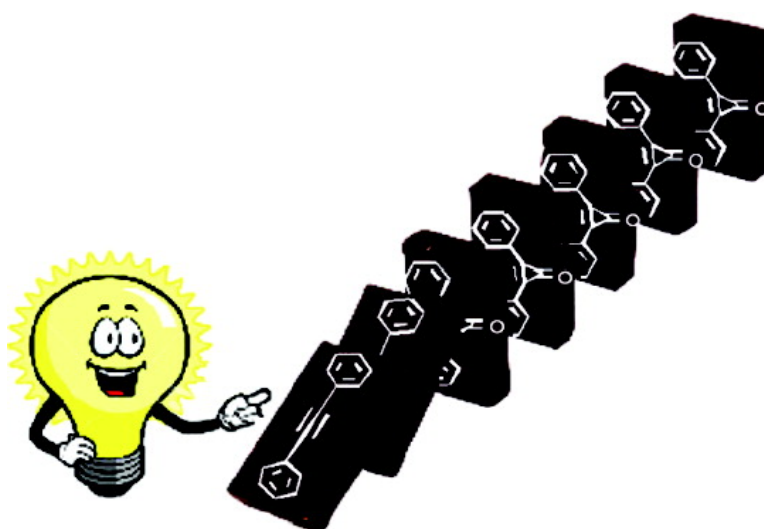
Communication

Solid-State Photodecarbonylation of Diphenylcyclopropenone: A Quantum Chain Process Made Possible by Ultrafast Energy Transfer

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Solid-State Photodecarbonylation of Diphenylcyclopropenone: A Quantum Chain Process Made Possible by Ultrafast Energy Transfer

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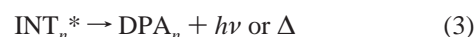
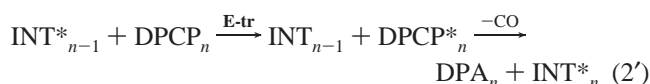
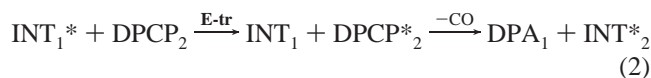
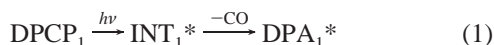
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Robust reactivity models, progress in crystal design, and the use of specimens in the nanometer scale have led to remarkable advances in the photochemistry of crystals.¹ While it is well appreciated that the crystalline environment “allows” for certain excited-state processes and reaction pathways, as suggested by the topochemical postulate,² recent views place more emphasis on the structure of the reactant, which ultimately determines its chemical fate.^{3,4} For example, on the basis of simple structural considerations, even without predicting its crystal packing, one can predict whether the photodecarbonylation of a crystalline ketone may occur in the solid state!^{3–5} The reaction has been recently exploited in the synthesis of structures with adjacent quaternary stereogenic centers, including the total synthesis of (±)-herbertenolide⁶ and optically pure (–)- and (+)-α-cuparenone.⁷

The feasibility of the solid-state reaction relies on α-substituents (R₁–R₆, Scheme 1a) that lower the bond dissociation energies of the bonds being cleaved. The reaction starts by excitation and is followed by sequential cleavage of the two α-bonds to form radical pairs RP-1 and RP-2. However, as indicated in Scheme 1a, efficient α-cleavage is necessary but not sufficient for the reaction to occur since RP-1 can return to the starting ketone. For that reason, the dissociation of CO from RP-1 becomes the product formation determining step.

Exploring new avenues for the solid-state photodecarbonylation reaction, we sought out structures that facilitate the first bond cleavage and make the second one unavoidable. Notably, these conditions should occur in small ring ketones where the release of a large amount of strain energy after the initial α-cleavage makes the return to the ground state unfavorable. To test this, we choose diphenylcyclopropenone (DPCP, Scheme 1b),⁸ which has a well-documented solution photochemistry^{9,10} and has been shown to dissociate adiabatically along the S₂ surface to form CO and diphenylacetylene (DPA). While there is some debate on whether de-excitation occurs in the final product⁹ or along the reaction surface,¹⁰ we reasoned that ultrafast energy transfer in crystals would favor an otherwise very unlikely quantum chain process.¹¹ Ideally, excitation to (S₂) DPCP* would lead to the irreversible formation of an excited intermediate or product INT*, which would transfer energy (E-tr) to a neighboring DPCP, form another INT*, and so on, until the *n*th intermediate finally deactivates (eqs 1–3).

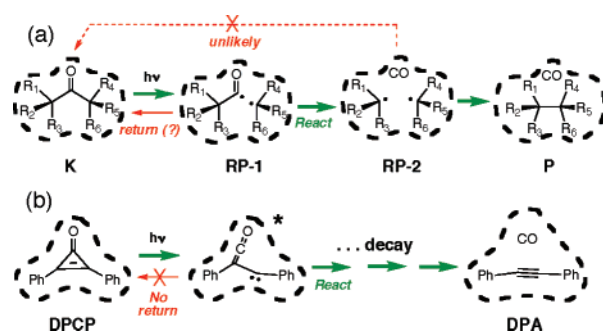


Experiments with large single crystals of DPCP monohydrate¹² showed that the solid-state photoreaction occurs with remarkable efficiency. In a strong indication of a quantum chain process, crystals crumbled within a few minutes into a fine powder of pure DPA (Figure 1 and Supporting Information).¹³ The large amount of mechanical energy released in this process is consistent with a very efficient reaction, a large and positive reaction volume, and the loss of CO gas.

In order to explore the adiabaticity of the reaction, we set out to measure its quantum yield, Φ_{DPCP}, defined as the moles of product formed per mole of photons absorbed. A quantum chain would require Φ_{DPCP} > 1.0. While it is difficult to measure the number of photons absorbed by dry solids, we recently showed that aqueous nanocrystalline suspensions may trap all of the photons from a light source so that one can use a chemical actinometer.¹⁴ Having established a Φ_{DCK} = 0.2 for the decarbonylation of nanocrystalline dicumyl ketone (DCK), we decided to use it as an internal actinometer for DPCP by measuring their relative reactivities within the same container. Independent nanocrystalline suspensions of DCK and DPCP prepared by the reprecipitation method¹⁵ were mixed, exposed to low-intensity RPR-3000 (λ = 312 ± 15 nm) lamps, and their products quantified. We confirmed that centrifuged and filtered nanocrystals of DPCP and DPA correspond to the same phases as their corresponding macroscopic samples. A representative run of the conversion versus time data in Figure 2 shows the parallel time evolution of the two reactions and a remarkable factor of 50 between the two conversion scales.

The amounts of diphenyl acetylene DPA (N_{DPA}) and dicumene (N_{DC}) were measured at various time intervals (Figure 2) in triplicate experiments for various loading ratios using suspensions with (CTAB and SDS) and without surfactants. With >50 independent

Scheme 1



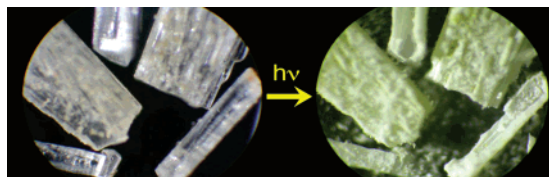


Figure 1. Two micrograph frames illustrating the conversion of crystalline DPCP to powder DPA. For a series of frames illustrating the entire transformation into a fine powder within 15 min.¹²

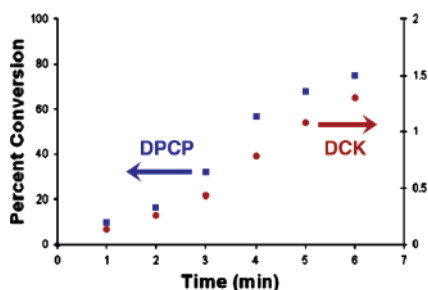


Figure 2. Representative plot of conversion versus time for a suspension with equimolar DPCP and DCK in H₂O/CTAB. The 50-fold difference in reactivity is due to a ca. 3.4 times greater absorbance by DPCP, and a 16-fold difference in quantum yield ($\Phi_{\text{DCK}} = 0.2$ and $\Phi_{\text{DPCP}} = 3.30 \pm 0.35$).

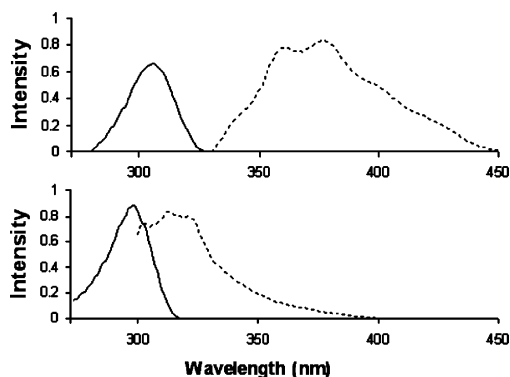


Figure 3. Fluorescence excitation (heavy line) and emission (dotted line) of (top) a nanocrystalline suspension of DPA with submicellar CTAB/H₂O and (bottom) a micellar solution of DPA in CTAB/H₂O.

experiments, taking into account the different absorbances (A) of DPCP and DCK, and using the formula

$$\Phi_{\text{DPCP}} = (A_{\text{DPCP}}/A_{\text{DCK}})(N_{\text{DPA}}/N_{\text{DC}})\Phi_{\text{DCK}}$$

we obtained $\Phi_{\text{DPCP}} = 3.30 \pm 0.35$.¹⁶ Incidental evidence that no reaction takes place in solution or in micelles was obtained by fluorescence analysis. While DPCP is not emissive, the fluorescence emission of DPA formed in solid suspensions was nearly identical to that obtained from a bulk solid, which is readily distinguishable from that obtained from experiments carried out in solution or in micelles (Figure 3).

A quantum yield greater than 1.0 is consistent with an adiabatic barrierless reaction involving a species capable of transferring energy to the ground-state reactant before deactivation. While there is some disagreement on the series of events leading to the ground state,^{9,10} femtosecond excitation of DPCP to S_2 in solution leads to ring opening within ca. 200 fs to give an excited-state species with a lifetime of ca. 8 ps before relaxing to S_1 . Given that singlet excitons in crystals have hopping times of ca. 1–2 ps,¹⁷ our results

are consistent with every photon initiating the ring-opening reaction of no more than 4–8 molecules (i.e., 3.30 molecules per photon in this case). It should be noted that the reaction is exothermic by ~ 10 kcal/mol, and that each mole of 300 nm photons injects ~ 75 kcal/mol into the sample. A large fraction of this energy may lead to the vaporization of H₂O, which requires the cleavage of several hydrogen bonds, and to the recrystallization of the product. To test this hypothesis, we investigated the photochemistry of solvent-free crystals grown from dry benzene.¹⁸ While the reaction was also fast at ambient temperature, the samples melted and recrystallized in situ.¹³ It was also of interest to see whether suspended nanocrystals of the hydrate have a mechanical response that is similar to that of macroscopic specimens.¹⁹ Indeed, using dynamic light scattering, we found that the average crystal size changed from 1000 nm before reaction to 220 nm at 100% conversion.

In conclusion, the release of ring strain upon α -cleavage is a viable strategy to engineer decarbonylation reactions in crystals. With quantum yield values of $\Phi_{\text{DPCP}} = 3.30 \pm 0.35$, our results indicate that DPCP undergoes an efficient quantum chain reaction in the crystalline state. Given that the product is a highly emissive chromophore, this remarkable reaction may be used to design strategies for signal amplification.

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Supporting Information Available: Photochemical procedures, reaction data, and fluorescence spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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