

Kinetics of Photoreactive 4,4'-Dimethylbenzophenone Nanocrystals: Relative Contributions to Triplet Decay from Intermolecular H-Atom Transfer and Reductive Charge Transfer Quenching

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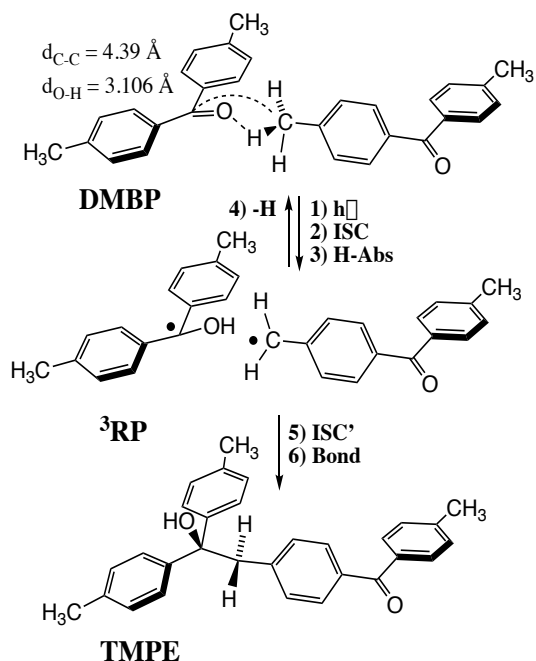
ABSTRACT: Crystals of 4,4'-dimethylbenzophenone (**DMBP**) are known to react by intermolecular H-atom transfer followed by radical pair recombination. To determine the contribution of the H-atom transfer reaction for the deactivation of the triplet ketone, transient absorption spectra and kinetics were obtained using aqueous nanocrystalline suspensions. Single exponential lifetimes of ca. 1185 ns with no deuterium isotope effect and inefficient product formation suggests that the reaction does not contribute significantly to the kinetics of triplet decay. By contrast, the observed lifetime is consistent with previous observations with p, p'-disubstituted benzophenones that undergo efficient self-quenching process by a reductive charge transfer mechanism.

Introduction

Measuring the kinetics of photochemical reactions in crystals using conventional transmission spectroscopy methods has been challenging, primarily due to their high absorption and anisotropic optical properties, which includes strong light scattering, specular reflection, birefringence and dichroism. Recent work from our group has shown that aqueous nanocrystalline suspensions (NCS) of molecular crystals with sizes smaller than the wavelength of light used for excitation (ca. 100-300 nm) are amenable for the use of transmission spectroscopy.¹ Previous investigations into the kinetics of solid-state photochemical reactions have primarily focused on intramolecular processes, such as the Norrish Type-I^{2,3} and Type-II⁴ reactions. Looking to establish expand the scope of the method, we identified the radical-pair mediated dimerization of 4,4'-dimethylbenzophenone (**DMBP**) reported by Ito and coworkers, as a suitable system.⁵

As shown in Scheme 1, the dimerization of **DMBP** is controlled by the way in which two neighboring molecules are arranged in crystal lattice. The reaction starts with molecular excitation followed by rapid intersystem crossing to the triplet state.⁵ Product formation starts by hydrogen atom transfer between the triplet ketone and the methyl group of a neighboring molecule to yield a ketyl-benzyl radical pair (³RP), which occurs in competition with other triplet decay pathways such as thermal decay and intermolecular quenching (not shown). While the bimolecular H-transfer

Scheme 1. Solid-state dimerization of **DMBP** via photoinduced intermolecular H-atom abstraction.



reaction in solution is unfavorable, the reaction is topologically controlled in the crystalline state, with a reactive ketone carbonyl in close proximity of a neighboring methyl group. Once formed, the intermediate ³RP decays by intersystem crossing to the singlet state, potentially going back to the ground state dimer by reverse H-atom transfer, or by formation of a new C-C bond to yield 1,1,2,2-tetrakis(4-methylphenyl)-1,2-ethanediol (**TMPE**) as the only photoproduct. Crystals of **DMBP** in the space group $P2_12_12_1$ were shown to have a structure with the closest hydrogen atom being accessible, but not ideal for H-atom transfer to the carbonyl of a neighboring molecule (Scheme 1). Assuming that the ideal ground state geometry should have strong resemblance to that of the transition state, Scheffer proposed that crystals with van der Waals contact between the H and O atoms and a co-linear orientation between the C-H bond and the H...O vector along the plane of the carbonyl n-orbital

would lead to the fastest triplet reactions.¹² The closest C=O---H-C distance of 3.106 Å in the case of **DMBP** is ca. 15% longer than the sum of the O and H van der Waals radii of 2.72 Å, and the position of the H-atom bond is not in the plane of the active n,π^* state n-orbital, as indicated by a C-C=O---H dihedral of -44.3° , which otherwise would adopt a value of 0° . Furthermore, changes in the distance between the two carbon atoms involved in the reaction must change significantly from an original value of 4.39 Å in the reactants to the normal value of ca. 1.54 Å for C-C sigma bond. In agreement with this less-than-ideal reaction geometry and the substantial structural change required from reactant to product, the reaction is relatively inefficient, reaching a chemical yield of ca. 15% after 1 h of irradiation with a 400 W high-pressure Hg lamp. In the remainder of this paper, we will show that the efficiency of H-atom abstraction from the triplet excited state in this system is indeed very low, and that the kinetics of the excited state ketone in the solid state are consistent with a rate-limiting, intermolecular, self-quenching mechanism.

Experimental Section

Transient absorption spectra and decay kinetics were obtained using an Edinburgh Instruments LP 920 laser flash photolysis system equipped with either the fourth or third harmonic of a Quantel Brilliant B Nd-YAG laser (355 or 266 nm) and a 450W medium-pressure Xe-Hg lamp as the pump and probe sources, respectively. No difference in either lifetime or spectral features was observed when varying the excitation wavelength. Kinetics were measured at 540 nm, which corresponds to the λ_{max} of the transient absorption spectrum. A single-pass flow system was used to minimize nanocrystal aggregation or sedimentation and to remove any photoproducts accumulated between laser pulses. Each measurement consisted of 25 or more consecutive pump-probe scans averaged to minimize noise. Transient spectra were obtained by collecting transient decay measurements between 300-600 nm in 5 nm steps, taking the value of the ΔOD at various time intervals, and plotting this value against the collection wavelength.

Nanocrystalline suspensions were prepared by the precipitation method.⁶ A small amount of a 0.6 mg/mL solution of **DMBP** in acetonitrile was quickly added to water containing sub-micellar concentrations of CTAB (0.1 mM) while vortexing. The resulting suspensions had a ketone loading of ca. 80 μM and had an optical density of approximately 0.15 at 355 nm. Suspensions were added to a reservoir connected to a peristaltic flow system and continuously stirred to prevent aggregation. Multiple suspensions were used for each measurement to minimize variations due to inconsistencies in preparation. Average nanocrystal sizes were 267 ± 41 nm as determined by dynamic light scattering (DLS) analysis (Figure S2). Solution samples were prepared by sparging 250 ml batches of 0.1 mg/ml acetonitrile solutions with argon gas in the sealed reservoir of a peristaltic flow system for 60 minutes before measurements.

Synthesis of **DMBP-d₆** was carried out by a procedure analogous to that of Tie et al.⁷ and is described in the SI section. The extent of deuteration was found by NMR integration to be approximately 99%.

Results and Discussion

Powder X-Ray diffraction analysis was performed to confirm that the reported $P2_12_12_1$ polymorph of **DMBP** was the one present in the nanocrystalline suspensions. Comparison of the experimental spectrum with one simulated from published crystal confirmed the assignment (Figure 1). Preparations of **DMBP** in bulk powder, solution, and nanocrystalline suspension were analyzed by TLC and NMR after 12 h irradiation with a high-power Hg lamp to confirm the identity of photoproducts. Both the bulk powder and nanocrystalline samples were found to exclusively contain **DMBP** and **TMPE**, with no observable side products. Irradiation in solution consisted of **DMBP** and **TMPE** with trace amounts of additional side products in the form of a yellow, insoluble residue that collected on the sides of the reaction vessel. These results confirm that the reaction of **DMBP** proceeds in the same manner in both bulk powder and nanocrystalline samples, with solution-phase samples having access to multiple reaction pathways.

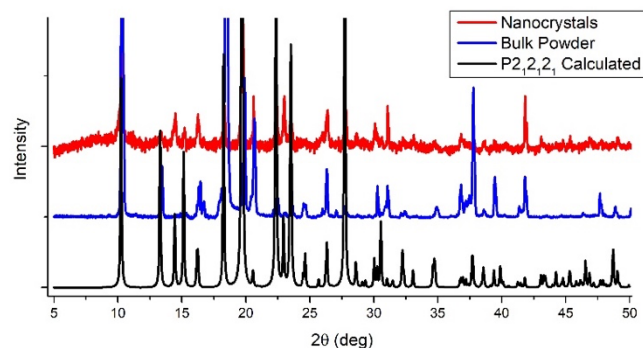


Figure 1. PXRD data of **DMBP** nanocrystals obtained from suspension (red) and bulk powder (blue) compared with calculated spectra for the reported $P2_12_12_1$ polymorph of **DMBP** (black). Further crystallographic information is available in the SI.

Having confirmed that the reaction in nanocrystals proceeds through the mechanism described in Scheme 1, we identified four species that could potentially be observed through laser flash photolysis: the triplet ketone (3K), the individual ketyl and benzyl radicals in solution, and the triplet radical pair 3RP in the solid state. Identification of the transient species began by obtaining time-resolved transient absorption spectra of **DMBP** in both solution and nanocrystalline suspension. In each case, only one transient species was observed, with signals decaying at essentially the same rate across all wavelengths.

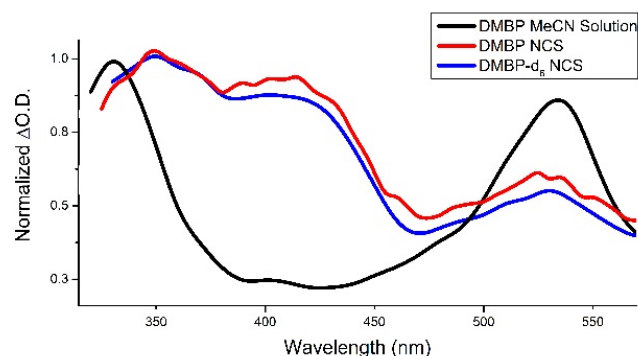


Figure 2. Transient absorption spectra of **DMBP** in acetonitrile solution (black), aqueous nanocrystalline suspension (red), and **DMBP-d₆** in aqueous nanocrystalline suspension (blue). Spectra were recorded 50 ns after laser pulse.

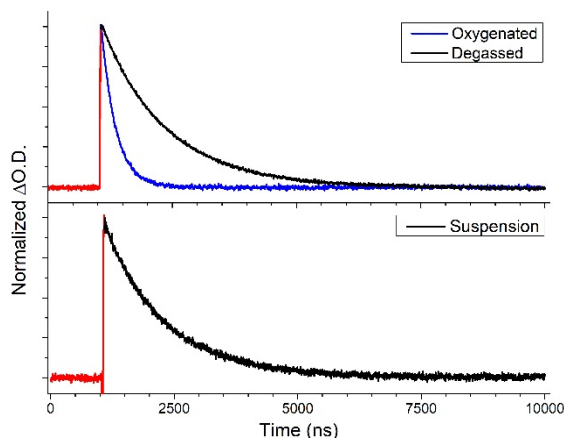


Figure 3. Transient decay measurements collected at 540 nm for **DMBP** in acetonitrile solution (top) and in aqueous nanocrystalline suspension (bottom). Red trace denotes the period before decay begins.

As shown in Figure 2, the absorbance values of the solution-phase spectra closely resemble the triplet ketone reported by Tsubomura et al., with two broad peaks centered around 330 and 540 nm and a smaller transition at ca. 410 nm.⁸ The transient absorbance spectrum for the nanocrystals contains the same general features as in solution, with peaks centered around 340 and 540 nm and the signal at ca. 420 nm displaying a much greater intensity.

Initially, we considered that the peak at 420 nm might originate from the ketyl-benzyl radical pair formed by H-atom abstraction. To test this, the transient absorption spectrum of **DMBP-d₆** nanocrystalline suspension was obtained in search of a potential primary isotope effect that would affect the relative intensities of the triplet ketone and the subsequent radical pair transient. We found the spectra of the deuterated and natural abundance samples to have essentially the same relative intensity, and the two spectra to decay homogeneously, strongly suggesting a unique signal carrier. From these observations, we tentatively assign the identity of the observed transient species in both nanocrystals and solution to the triplet ketone.

Transient decay measurements performed to determine the lifetime of the triplet ketone in solution and in the solid state as aqueous nanocrystalline suspensions (Figure 3) revealed single exponential decay functions with the lifetimes recorded in Table 1. The lifetime of **DMBP** in nanocrystalline suspensions was determined to be 1185 ± 60 ns and was not affected by oxygen. By contrast, decay traces in solution depended strongly on the presence of oxygen as shown in Figure 3, with the longest lifetimes reaching values of $ca. 1302 \pm 165$ ns. In agreement with spectral observations, no kinetic isotope effect could be observed for the lifetime of the nanocrystalline suspension samples, indicating that the rate of triplet deactivation is not determined by H-atom abstraction, but by an alternative triplet-state quenching process.

Table 1. Triplet lifetimes collected at 540 nm for **DMBP/DMBP-d₆** in sparged acetonitrile solution and nanocrystalline suspension.

Ketone	Medium	τ_{obs} (ns)
DMBP	MeCN Solution	1302 ± 165
DMBP	NCS	1185 ± 60
DMBP-d ₆	NCS	1174 ± 30

Previous literature reports on the photophysics of *p,p'*-disubstituted benzophenones uncovered a relatively general and efficient self-quenching mechanism which occurs in both solution and the solid state.^{9,10} Based on the electronic effect of the *p*-substituents on the rate of quenching, it was proposed that the mechanism involves the formation of an n-type donor-acceptor exciplex with the aromatic ring of a ground-state molecule acting as an electron donor to the singly occupied lone-pair orbital of the n,π^* excited carbonyl. As the exciplex has some amount of charge-transfer character, the free energy change for exciplex formation can be expressed as a function of the ionization potential of the donor as well as the electron affinity of the acceptor.¹³ In the case of *p*-substituted benzophenones, the electron affinity of the carbonyl remains essentially unchanged while the ionization potential of the rings varies greatly with substituent effects. Early reports on this mechanism showed a relationship between the rate of self-quenching and the ionization potential of analogous benzene derivatives. Later work opted to use the more generally applicable σ^+ values for the substituents, as they correlated well with the ionization potentials of relevant benzene derivatives.^{9,14}

Using the previously reported ρ value from the Hammett plot for self-quenching of *p,p'*-disubstituted diaryl ketones in the solid state, and the known $\sigma^+ = -0.31$ value for methyl groups, the lifetime of the triplet excited state of **DMBP** is predicted to be on the order of 260 ns.¹⁰ Our experimentally determined value of *ca.* 1185 ns (red star in Figure 4) is not far from this value when one considers the steep slope of the plot given by the relatively large $\rho = -3.08$ value. This

analysis supports our hypothesis that the observed decay is caused primarily by self-quenching.

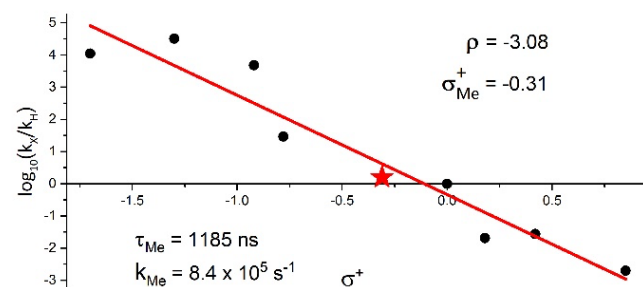


Figure 4. Hammett plot for the triplet decay rate constants of a series of *p,p'*-disubstituted benzophenones in the solid state as reported by Kuzmanich et al.¹⁰ The red star is obtained from the decay rate of **DMBP** measured in this work. Experimental data in the Hammett plot includes the following substituents and substituent constants (σ^+): *p*-NMe₂ (-1.7), *p*-NH₂ (-1.3), *p*-OH (-0.92), *p*-OMe (-0.78), *p*-CH₃ (-0.31), *p*-H (0), *p*-CO₂Me (0.18), *p*-CO₂H (0.42). A data point was included for pyromellitic anhydride, 3,4-(CO₂)O (0.85).

The rate constant describing the deactivation of the triplet state can be written as $k_{obs} = k_{HT} + k_{SQ} + k_i$, where the observed rate constant is equal to the sum of the rate constants for H-atom transfer (k_{HT}), self-quenching (k_{SQ}), and the intrinsic decay for an isolated molecule in solution (k_i).⁹ As we have determined $k_{obs} \gg k_{HT}$, the expression can be rewritten as $k_{SQ} \approx k_{obs} - k_i$ to determine the rate of self-quenching in the solid state. Using an assumed value for the radiative lifetime of ca. 5 ms, along with the observed lifetime, we estimate the self-quenching rate constant to be $8.4 \pm 0.4 \times 10^5 \text{ s}^{-1}$.⁹ As **DMBP** has an approximate concentration on the order of 5 M in the solid state, we estimate a bimolecular rate constant of $1.7 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. By comparison, the rate of **DMBP** self-quenching in solution measured by Wolf and coworkers is $1.8 \pm 0.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, suggesting that the deactivation in the solid state is roughly one-tenth as efficient.

Conclusion

The triplet state of **DMBP** in the solid state was identified through transient absorption spectroscopy, allowing for the determination of its excited state kinetics. The lifetime of the triplet state was found to be $1185 \pm 60 \text{ ns}$, with no difference in the rate observed when **DMBP** was substituted for a methyl-deuterated isotopologue, indicating that H-atom transfer has a minimal contribution towards the deactivation of the excited triplet state. Considering likely alternative triplet decay pathways, we assigned the relatively short lifetime as resulting from a reductive self-quenching mechanism known to be common in substituted benzophenones.¹⁰ The reported self-quenching rate constant of **DMBP** in benzene solution is $1.8 \pm 0.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$, being roughly one order of magnitude larger than the rate constant of $1.7 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ in the solid state. This result suggests that the P2₁2₁2₁ polymorph of **DMBP** is in a less than ideal

configuration to form the exciplex involved in the self-quenching process.^{9,10} If a reliable method can be developed to prepare nanocrystalline suspensions of different polymorphs, a future study comparing the triplet lifetimes of different polymorphs of **DMBP**¹¹ would make it possible to determine the role of molecular packing geometries in the self-quenching mechanism.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Preparation and NMR data of 4,4'-dimethyl-*d*₆-benzophenone, X-ray data, dynamic light scattering and transient absorption and kinetics (PDF).

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ACKNOWLEDGMENT

We thank the National Science Foundation grant CHE-2154210 for support of this work.

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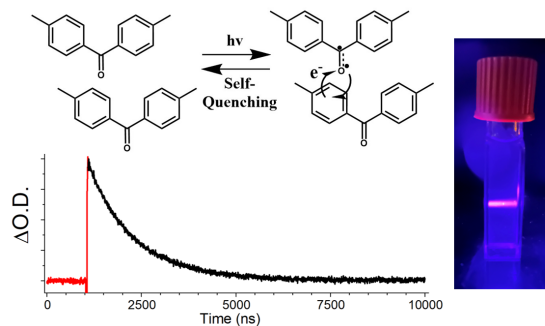
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SYNOPSIS TOC



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