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Exceptionally Long Lifetimes of Strongly Entangled Acyl−Trityl Radical Pairs Photochemically Generated in Crystalline Trityl Ketones

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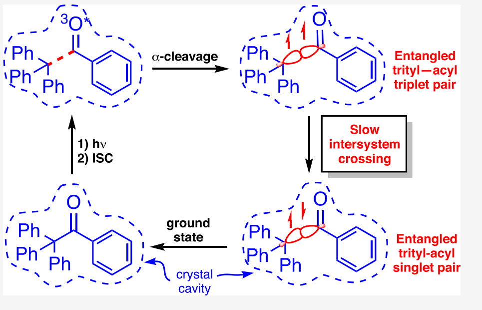
ABSTRACT: Triplet acyl−alkyl radical pairs generated by pulsed laser excitation within the constraints of their nanocrystalline ketone precursors were recently introduced as a potential platform for the robust and repeated instantiation of spin qubit pairs for applications in quantum information science. Here, we report the transient spectroscopy of a series of nanocrystalline trityl−alkyl and trityl−aryl ketones capable of generating correlated triplet radical pairs with persistent triphenylmethyl radicals forced to remain within bonding distances of highly reactive acyl radicals. Whereas triplet trityl−acyl radical pairs decay by competing product-forming decarbonylation and intersystem crossing, triplet trityl−benzoyl radical pairs have lifetimes of up to ca. 4 ms and exclusively regenerate the starting ketone. We propose that these long lifetimes are the result of the short inter-radical distances and the colinear orientation of the two singly occupied orbitals, which are expected to result in large singlet−triplet energy gaps, large zero-field splitting parameters, and a poor geometry for spin-obit coupling. Ketones generating trityl−benzoyl radical pairs demonstrate promising performance along multiple dimensions that are crucial for quantum information science.



INTRODUCTION

Crystalline solids offer opportunities to study previously unchartered regions of chemical dynamics[1,2] and to carry out highly selective reactions.[3,4] Our recent report on the reversible formation of triplet acyl−alkyl radical pairs generated by photochemical excitation of nanocrystalline diphenylmethyladamantyl ketones (Figure 1a, R = adamantyl, $R_1 = R_2 =$ Ph, R_3 = H)[5] suggested a new platform for the repeated generation of qubit pairs with potential applications in quantum information science.[6−8] We confirmed that triplet radical pairs generated by the cleavage of a single bond, and forced to remain nearly static within a bond distance, are strongly correlated as they lack efficient mechanisms for intersystem crossing.[9] Using laser flash photolysis with nanocrystalline samples suspended in water,[10] we showed that triplet acyladamantyl-diphenylmethyl radical pairs (^{3}**RP-A**) have lifetimes in the range of ca. 50−60 μs,[5] which are one to four orders magnitude longer than analogous acyl−alkyl biradicals held close together by short alkyl chains in solution.[11−13]

Recognizing that longer lifetimes will make it possible to execute multiple logical operations by quantum spin-state manipulation,[14] we sought to investigate a series of triphenylmethyl-substituted ketones that may lead to longer-lived triplet pairs by taking advantage of the persistent nature of the triphenylmethyl (trityl) radical (Figure 1a, $R_1 = R_2 = R_3$ = Ph).[15] In a previous publication, we showed that α-trityl ketones enable the solid-state photodecarbonylation of acyl radicals (Figure 1b, step 6), even when they generate highly unstable primary alkyl radicals.[16,17] We surmised that extending the lifetime of the acyl−alkyl radical pair had made it possible for the energetically unfavorable and slower decarbonylation reaction to take place.

As shown in Figure 1b, the expected mechanistic scheme[16,18] starts with electronic excitation (step 1) and is followed by rapid intersystem crossing (ISC, step 2). An α-cleavage reaction yields the triplet acyl−alkyl radical pair ^{3}**RP-A** (step 3), which, depending on the relative rates of decarbonylation (step 6) vs ISC (step 4), proceeds through radical pairs ^{3}**RP-B** or ^{1}**RP-A**, respectively. In solution, these radical pairs will diffuse apart leading to free radicals that undergo nonspecific recombination and disproportionation reactions. In contrast, reactions in crystals occur within the constraints of the reaction cavity (represented by the dotted line in Figure 1), which acts as a barrier for diffusion and severely constrains the conformational dynamics of the radical species.[1−3] As such, ^{1}**RP-A** cannot be considered an open-shell species and its nature should be dictated by a large overlap integral that essentially renders it an elongated sigma bond expected to rapidly reach the equilibrium distance character-

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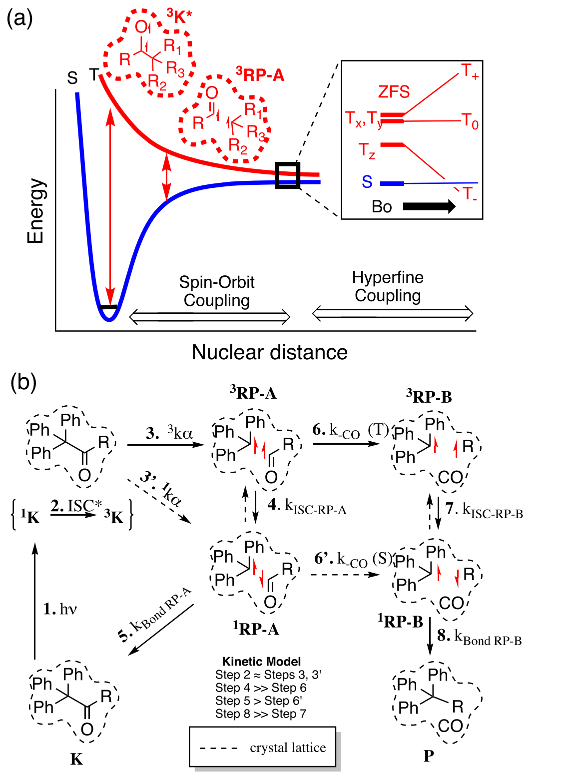


Figure 1. (a) Qualitative energetics of photoexcitation and an α-cleavage reaction in a triplet excited-state crystalline ketone leading to the formation of a triplet acyl–alkyl radical pair ^{3}RP-1. Short inter-radical distances lead to a large singlet–triplet (ST) energy gap and large zero-field splitting (ZFS) that along with the rigidity of the crystal severely limit the potential intersystem crossing mechanisms. (b) General reaction scheme for α-cleavage reaction of trityl ketones in the crystalline state.

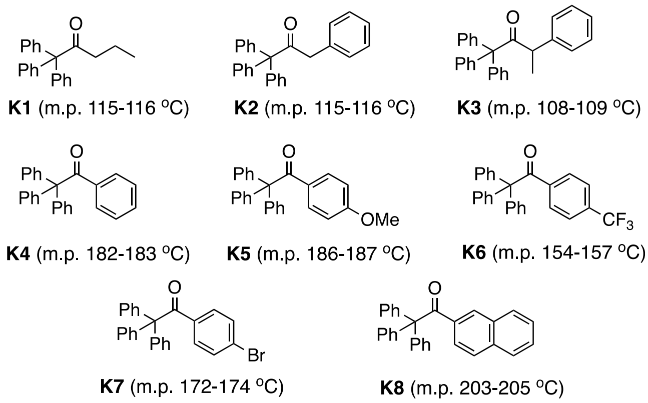
istic of the starting ketone **K**, rendering the photochemical reaction unproductive (step 5). By contrast, ^{3}**RP-B** is expected to form the decarbonylation product **P** by a rate-limiting ISC to ^{1}**RP-B** (steps 7 and 8).[19] Ketones designed to follow the latter path can be used as precursors for the synthesis of challenging structures for compounds with adjacent all-carbon-substituted stereogenic quaternary centers,[20] as it was recently shown for the crystal-mediated total synthesis of the alkaloid psychotriadine.[21]

In this study, we report the product formation, transient absorption spectra, and decay kinetics of the radical pairs from trityl ketones **K1**−**K8** in Scheme 1, both in dilute acetonitrile solutions and in nanocrystalline suspensions. We started with crystalline ketones **K1**−**K4**, which were the subject of our previous report.[15] When laser flash photolysis (LFP) studies on the unproductive trityl phenyl ketone **K4** revealed a radical pair with a remarkably long lifetime in excess of 4 ms, we synthesized additional derivatives **K5**−**K8** to determine its range as a function of various substituents. While **K4** remained the longest-lived triplet radical pair, it was shown that substituent effects on the aromatic ketone can be used to alter the radical pair lifetime.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. Ketones **K1**−**K8** were synthesized from the corresponding alcohols (**1a**−**8a**) by Jones oxidation.[16] The alcohols were prepared by addition of the appropriate aldehyde into a solution of triphenylmethyllithium at 0 °C. Following column chromatography and recrystallization from ethanol, compounds **K1**−**K7** were isolated as colorless, crystalline solids with melting points ranging from 108 to 109 °C (**K3**) up to 203 °C (**K8**, Scheme 1). Compound **K8** was isolated as pale yellow crystals after recrystallization from ethanol. The full description of synthetic procedures and the data from complete experimental and spectral characterization of **1a**−**8a** and **K1**−**K8** is found in the Supporting Information (SI).

Scheme 1. Structures and Melting Points of Crystalline Trityl Ketones Analyzed in This Work



Single-crystal X-ray structures of **K1** and **K2** were previously reported.[16] Crystals of **K6** and **K8** obtained from the ethanol recrystallizations were subjected to single-crystal X-ray diffraction analysis to obtain the molecular structures shown in Figure 2 as representative examples for the molecular conformations adopted by the aryl−trityl ketones.

Diffraction data from crystals of **K6** were solved in the orthorhombic space group Pna2/1 with one molecule per asymmetric unit. The structure of **K6** is characterized by having the carbonyl and *p*-trifluoromethyl-phenyl groups nearly coplanar [D_B (Ph—C=O) = 2.35°) and one of the phenyl groups of the trityl substituent aligned nearly parallel to the carbonyl C=O bond vector, as indicated by a dihedral angle D_A (Ph−C(Ph$_2$)−C=O) = −6.67° (Scheme 2a and Table 2). The structure of **K8** was solved in the triclinic space group P1 bar with rotational disorder where the aromatic naphthyl group occupies two non-equivalent positions defined by rotation about the carbonyl carbon to naphthyl β-carbon bond (Figure 2 and Scheme 2a). The two conformations of **K8** have relative occupancies of 62.7 and 37.3%, and the aromatic and carbonyl groups have dihedral angles of D_B (Naph—C=O) = 12.50° and 23.54° (Table 1). In analogy to **K6**, the rotation of the trityl group is such that one of the phenyl rings is oriented close to parallel to the carbonyl bond vector with D_A (Ph—C(Ph$_2$)—C=O) = −9.09° and −23.12°). The values for D_A in the non-aromatic ketones **K1** and **K2** were − 35.11° and −14.28° (Table 1).

A structural feature that facilitates an efficient α-cleavage reaction in the solid state relates to the resonance stabilization of the nascent alkyl radical center.[16,17] This stabilization is optimal when the plane of the aromatic groups is orthogonal to the bond undergoing α-cleavage, D_C [Ph−C—C(C=O)] ≈ 90°, so that once formed the trityl radical *p*-orbital has maximum overlap with the π-orbital of the α-phenyl groups (Scheme 2b).[22] The persistent nature of the trityl radicals is based in part on the fact that the three phenyl groups in their

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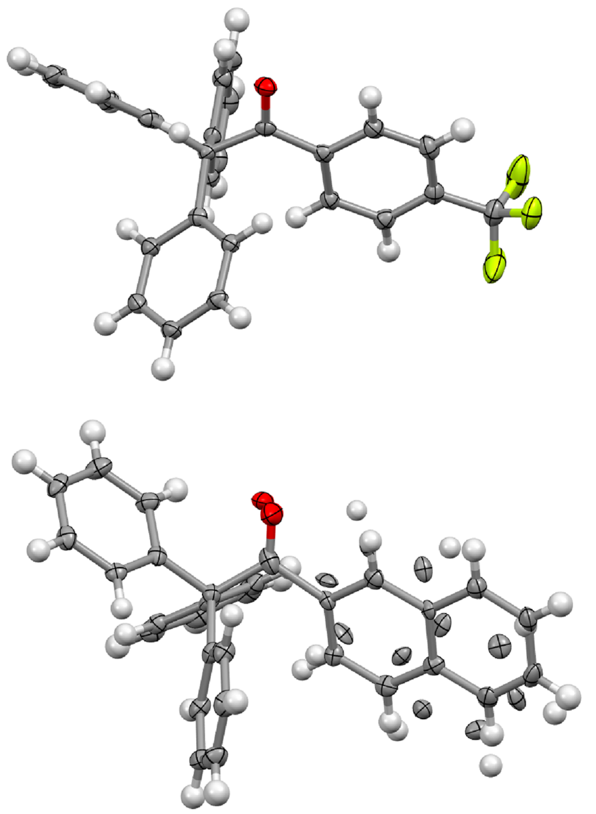

Figure 2. Single-crystal X-ray diffraction structures of **K6** and **K8**, with thermal ellipsoids drawn at the 50% probability level. Please see text and Scheme 2 for a description of the disorder in **K8**.

Scheme 2. Definition of Structural Parameters Affecting the a-Cleavage Reaction of Several Crystalline Trityl Ketones

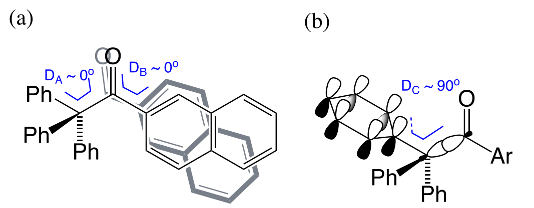

Table 1. Conformational Features Potentially Affecting the Solid-State Reaction of Selected Trityl Ketones

ketone	D_A [Ph−C(Ph$_2$)−C=O] (°)	D_B [Ar−C=O] (°); ideal = 0°	D_C [Ph−C—C(C=O) (°)]; ideal = 90°
K1[a]	−35.11	N.A.	54.79, 60.82°, 31.02°
K2[a]	−14.28	N.A.	19.17°, −52.17°, −69.37°
K6	−6.67	2.35°	15.78°, −52.67°, −55.53°
K8	−9.09, −23.12	12.50°, 23.54°	47.55°, 67.19°, 3.18°

[a]Crystal structures published in ref 16.

structure are able to cooperatively provide resonance stabilization, which is facilitated by the relatively large values of D_C that can be seen for two of the three phenyl rings. Beyond the structural factors that determine the α-cleavage reaction, a crucial feature of these crystals is related to their ability to contain the radical pair within a close-packed environment, and with limited translational, rotational, and conformational dynamics that would otherwise enable various ISC mechanisms available in solution.[9]

Solution and Solid-State Photochemistry. In order to determine the extent of the photodecarbonylation reaction, product analysis studies were conducted for each ketone in acetonitrile solution and in dry solid-state samples. In each case, all eight samples were irradiated simultaneously for 30 min with a 450 W medium-pressure mercury lamp. Solution samples were prepared as equimolar solutions of ∼15 mmol in degassed MeCN-d_3 in Pyrex NMR tubes. Powder samples were ground between microscope Pyrex glass slides (approximately 5 mg spread over ca. 2 square inches).[23] Photoproduct analysis by ^{1}H NMR revealed the percentage conversion values shown in Table 2. All ketones showed significant conversion values in solution, but only **K1−K3** were reactive in the solid state.

Table 2. Photochemical Reactivity of Ketones K1−K8 in Solution and as Dry Powders[a]

ketone	% conversion (dry powder)	% conversion (solution)
K1	3	22
K2	13	61
K3	37	68
K4	0	17
K5	0	29
K6	0	22
K7	0	25
K8	0	41

[a]Samples of each type were irradiated simultaneously for 30 min with a 450 W medium-pressure mercury lamp.

Solution irradiations produced complex mixtures suggestive of all possible recombination products involving acyl, alkyl, and triphenylmethyl free radicals. Their detailed characterization was not attempted. By contrast, ^{1}H NMR samples from powder irradiation gave spectra, which indicated clean conversion of ketones **K1−K3**, respectively, to the corresponding photodecarbonylation products **P1−P3** (Figure 1). Notably, conversion values of 3, 13, and 37% for **K1−K3** are qualitatively consistent with the expected rates of decarbonylation from the intermediate acyl radicals **RP-A**, which are known to correlate with the relative stability of the alkyl radicals formed: propyl (primary) < primary benzylic < secondary benzylic.[24] Samples of **K4−K8** were reactive in solution, leading to products from reactions of the trityl and benzoyl free radicals. By contrast, these ketones were unproductive in the crystalline solid state because the loss of CO to give highly unstable phenyl radicals is extremely unfavorable, such that the only radical−radical combination pathway goes back to the starting ketone.

Transient Absorption Spectroscopy and Kinetics. Transient absorption spectra and decay kinetic measurements were conducted using an Edinburgh Instruments LP920 LFP system equipped with a Quantel Brilliant B Nd:YAG laser at 266 nm. Solution samples were prepared in 100−200 mL batches and degassed by sparging with argon for 30−60 min. Samples were passed through a single-pass flow system to collect spectral data. Nanocrystalline suspension samples were prepared by the reprecipitation method by addition of a concentrated acetonitrile stock solution of the ketone into an aqueous solution of sodium dodecyl sulfate (SDS) at 1/10 of the critical micelle concentration.[25] Average particle sizes in the range of ca. 100−200 nm with a unimodal size distribution

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were determined for all ketones by dynamic light scattering (DLS) and can be found in the SI. We note that DLS data does not provide evidence that these particles are crystalline and may consist of aggregates with varying degrees of crystallinity that may contribute to the variation in the measured kinetic parameters.

Suspension LFP experiments with reactive crystals of **K1**–**K3** were conducted with a single-pass flow system in order to collect spectral and kinetic data with no complications from the presence of accumulated photoproducts. By contrast, samples of the unproductive ketones **K4**–**K8** were conducted with static samples, which were observed to give a higher signal-to-noise ratio. Control experiments with these samples confirmed no photoproduct formation by GC–MS analysis under conditions where products can be easily detected in analogous experiments carried out with static solution samples.

Representative transient absorption and decay curves for solution and suspension samples of **K4** are shown in Figures 3 and 4, respectively. Corresponding spectra for all other ketones are found in the SI section. In each case, the overall sample concentration is noted in the figure caption. For suspension samples, the concentration reflects the overall loading of the ketone in the aqueous medium rather than the much higher local concentration of molecules within the nanocrystals. Decay traces shown in Figures 3 and 4 cover a time window of 8 ms, which is limited by the width of our ca. 10 ms probe pulse. Both solution and nanocrystalline suspensions display non-exponential decays with a residual absorption in the wavelength range of ca. 300–380 nm. Notably, solution spectra are heterogenous with a fast-decaying component visually characterized by a peak with a λ_{max} = 340 nm and a longer-lived, broader spectrum with a λ_{max} = 315 nm that extends up to ca. 350 nm (Figure 3). The initial spectrum is consistent with the known free trityl radicals,[26,27] which exist in equilibrium with the dimer formed by bonding a radical trityl carbon with a *para*-phenyl carbon of another radical, a species known as the Gomberg hydrocarbon (Scheme 3). The latter accounts for the residual spectrum observed at the end of the 8 ms time window.[21]

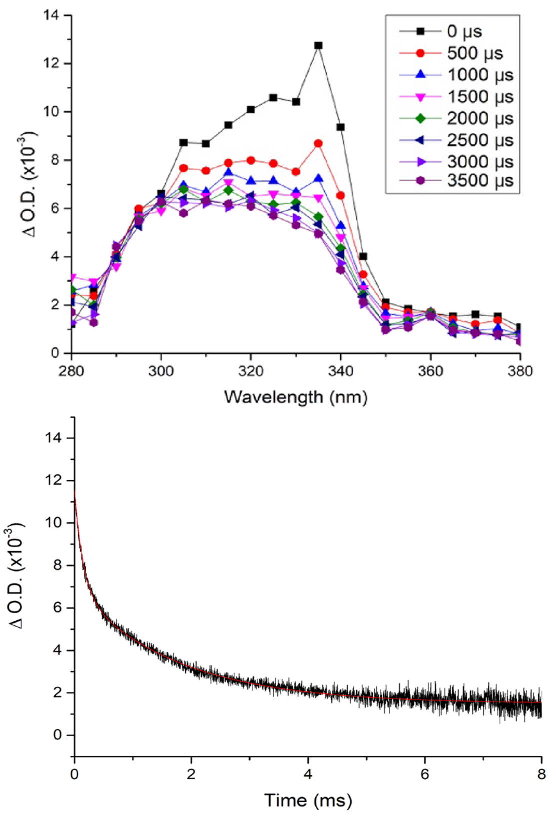


Figure 3. (Top) Transient absorption spectrum of **K4** in degassed MeCN solution (0.013 mg/mL) and (bottom) transient decay measured at 335 nm. The red line represents a double exponential fit with lifetimes τ_1 = 150 ± 30 μs and τ_2 = 2.15 ± 0.34 ms.

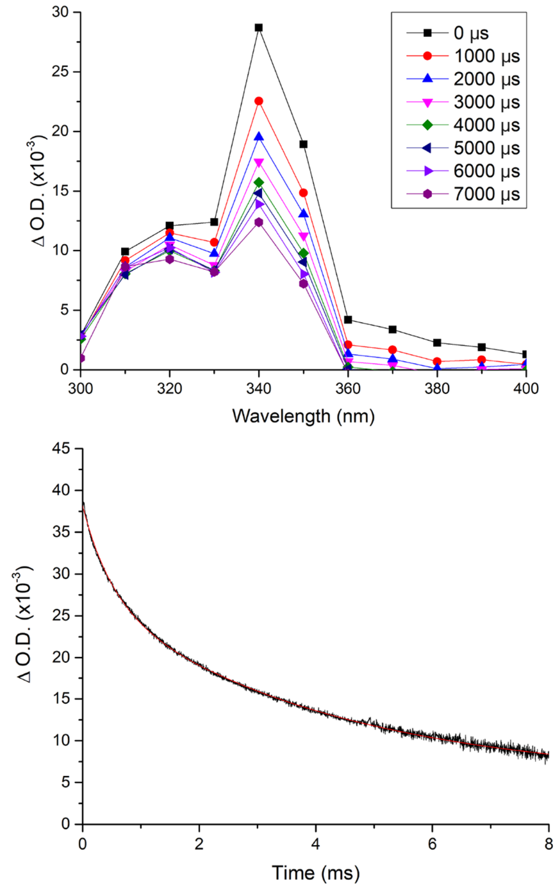
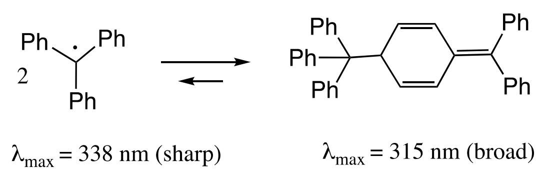


Figure 4. (Top) Transient absorption spectrum of **K4** in aqueous suspension (0.010 mg/mL) and (bottom) transient absorption decay measured at 345 nm. The red line represents a double exponential fit with lifetimes τ_1 = 470 ± 20 ms and τ_2 = 4.22 ± 0.58 ms.

Scheme 3. Dimerization Equilibrium between Two Trityl Radicals and the Gomberg Hydrocarbon



In contrast to solution, and as illustrated in top of Figure 3, transients obtained in the nanocrystalline suspensions decay homogeneously as a single species with a spectrum that is consistent with that of the trityl radical, suggesting that spin–spin interactions in the triplet radical pairs do not have a significant effect on the aromatic π,π^* transitions. It should also be noted that significant variations in the kinetics of the

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Table 3. Lifetimes and Percent Contributions for Radical Pairs Generated from Samples of K1−8 in MeCN Solutions and Nanocrystalline Suspensions

ketone	medium	τ_1 (μs)	τ_2 (ms)	% τ_1	% τ_2
K1	solution	270 ± 30	2.24 ± 0.35	12 ± 2	88 ± 2
	suspension (3)	82 ± 6	0.40 ± 0.05	23 ± 9	77 ± 9
K2	solution	350 ± 100	2.20 ± 0.39	19 ± 5	81 ± 5
	suspension (13)	4.3 ± 1.6	0.14 ± 0.06	11 ± 4	89 ± 4
K3	solution	530 ± 140	3.28 ± 1.26	14 ± 4	86 ± 4
	suspension (37)	4.2 ± 0.3	0.08 ± 0.01	74 ± 7	26 ± 7
K4	solution	150 ± 30	2.15 ± 0.34	11 ± 4	89 ± 4
	suspension	470 ± 20	4.22 ± 0.58	4 ± 1	96 ± 1
K5	solution	250 ± 60	2.75 ± 0.41	15 ± 2	85 ± 2
	suspension	340 ± 330	4.16 ± 0.70	3 ± 2	97 ± 2
K6	solution	300 ± 80	3.55 ± 0.75	17 ± 7	83 ± 7
	suspension	220 ± 80	1.60 ± 0.48	33 ± 5	67 ± 5
K7	solution	200 ± 70	1.88 ± 0.37	10 ± 1	90 ± 1
	suspension	740 ± 140	2.20 ± 0.36	5 ± 4	94 ± 4
K8	solution	150 ± 60	2.30 ± 0.19	17 ± 7	83 ± 7
	suspension	570 ± 420	2.76 ± 0.29	6 ± 4	94 ± 4

solid-state suspension transients highlight the complexity of the samples.

We posit that kinetics in solution reflect components with a relatively fast decay for the observed trityl free radical that are consumed by reaction with the highly reactive alkyl or acyl free radicals co-generated by the laser pulse. The residual absorption in solution is consistent with the one reported for the Gomberg hydrocarbon, which would exist with small equilibrium concentrations of the persistent trityl radicals. In contrast, the absence of diffusion and radical−radical separation and kinetics in the solid state are uniquely related to the triplet radical pair. Decay signals obtained with the ca. 8 ms window showed a residual absorption in a process of slowly decaying, suggesting contributions from fast-, intermediate-, and slow-decaying components with lifetimes that expand from sub-milliseconds to several milliseconds. This interpretation is supported by the fact that transients measured for crystals of **K3**, which is the most reactive ketone, decay almost completely to baseline. The shortest components of their lifetime of 4.2 μs and 0.080 ms are also consistent with an efficient photodecarbonylation reaction that leaves almost no residual absorption, neither in solution nor in the suspended nanocrystals.

As mentioned above, our kinetic observations had a significant variation from experiment to experiment. In order to explore potential sources of error and to document the reproducibility of the decay curves, we analyzed experiments from at least a dozen trials performed on multiple days. The results of this analysis for all of the ketones are included in Table 3. Suspension decays can be fit to double exponentials. The average time constants and standard deviations are shown in Table 3 along with the averages and standard deviations of the percent contributions of the short- and long-lived components of the decays. The λ_{max} values of the transient absorption spectra for all samples were found to be in the range of 330−345 nm, which matches previous reports of the transient absorption spectrum of the trityl radical.[21,28,29] We hypothesize that biexponential lifetimes in solution reflect two different populations of radicals. The short-lived component (τ_1) corresponds to acyl−trityl (^{3}**RP-A**) or alkyl−trityl (^{3}**RP-B**) radical pairs that recombine on a relatively short time scale, whereas the long-lived component (τ_2) reflects the lifetime of the persistent trityl free radicals that remain in equilibrium with the Gomberg hydrocarbon, as shown in Scheme 3. Interestingly, kinetic variations in solution are relatively small across all samples, as both the τ values and relative percent contributions for both components are similar, suggesting that they are determined by recombination kinetics and residual traps, such as O_2.

In contrast to solution experiments, comparison of the radical pair lifetimes in suspension samples suggests an interesting story. As expected, there is a clear distinction between the photoreactive and product-forming alkyl−trityl ketones **K1**−**K3** and the unproductive aromatic-trityl ketones **K4**−**K8** (Table 3). Shorter τ_2 lifetimes in the case of **K1**−**K3** correlate qualitatively with the extent of reaction in the solid state and are consistent with a faster decay of ^{3}RP-A due to contributions from a competing photodecarbonylation reaction to ^{3}RP-B followed by rapid product formation (Figure 1b, steps 6, 7, and 8). In support of this interpretation, we note that weighted average lifetimes in the cases of **K1**−**K3** vary by a factor of 13.8, from 330 to 130 to 24 μs, respectively, while differences in solid-state reactivity for the same compounds range by a factor of 12.3 with product formation values of 3, 13, and 37% under identical reaction conditions (Table 2).

Longer lifetimes with smaller variations in the radical pairs derived from **K4** to **K8** suggest subtle differences that are presumably associated with changes in the rate of intersystem crossing from ^{3}RPA to ^{1}RPA (Figure 1b, step 4), with ^{1}RPA rapidly decaying back to the starting ketone (step 5). The two components in the case of **K4**−**K8** have values that vary much less, from 1.60 ms (**K6**) to 4.22 ms (**K4**) for the longer-lived component τ_2 to ca. 220 to 470 μs for the shorter-lived one τ_1.

Focusing our analysis on the long-lived components, we can see that a lifetime of 4.22 ms for the acyl−alkyl radical pairs in the case of **K4** is a remarkable result, as it surpasses the previous record of 63 μs, previously reported by our group by almost two orders of magnitude.[5] Taking **K4** as the parent ketone, the effects of aryl substituents cause lifetime variations that range from negligible up to ca. 62%. On one end, the electron-donating *p*-methoxy group in **K5** had a very small effect (τ_2 = 4.16 ms) while the electron-withdrawing *p*-trifluoromethyl group in **K6** caused a reduction in lifetime by 62% (τ_2 = 1.60 ms). The *p*-bromo-substituted ketone **K7** also exhibited a 48% reduction in the radical pair lifetime relative to **K4**, which may be attributed in part to the heavy atom effect by the bromine substituent. Lastly, the naphthyl group in **K8** offers an extended conjugated π-system to the acyl radical, which may allow for enhanced spin delocalization that increases the average distance between the radical centers and is reflected by a 35% reduction in the lifetime of the corresponding ^{3}RP-A.

CONCLUSIONS

Photoproduct analysis and LFP experiments conducted on eight trityl ketones (**K1**−**K8**) suggest the potential of triplet trityl−acyl radical pairs as spin qubits for quantum information science. We have shown that electronic excitation of crystalline ketones flanked by a trityl group form triplet acyl−alkyl radical pairs with remarkably extended lifetimes, reflecting the persistent nature of the trityl radicals. While crystalline trityl−propyl and trityl−benzyl ketones **K1**−**K3** undergo efficient triplet-state α-cleavage to generate triplet trityl−acyl radical pairs, subsequent photodecarbonylation leads to product formation and the loss of the radical pair-generating ketone. In contrast, the aryl−trityl ketones (**K4**−**K8**) undergo an α-cleavage reaction to form triplet trityl−benzoyl radical pairs that do not cleave their Ar−CO bond. These trityl−benzoyl triplet radical pairs are characterized by having both unpaired electrons originating from cleavage of a sigma bonding orbital and retaining their original proximity as enforced by the crystal lattice. Close radical−radical proximity leads to large singlet−triplet energy gaps and a large zero-field splitting that cause the triplet radical pairs to remain strongly entangled. Notably, radical pairs generated by fast laser pulses and with lifetimes in the millisecond regime may be amenable to functional operations and readout, followed by decay and recycle, potentially constituting an addressable and reusable qubit pair. However, applications in quantum information science will require a detailed analysis of the nascent polarization of the triplet sublevels, which is known to arise during the ketone intersystem crossing step, as well as a deeper understanding of their equilibrium kinetic and spin evolution, which will be reported in due course. This will require further studies, including the effects of heavy atoms, external magnetic fields and microwaves, and the use of time resolved electron paramagnetic resonance (EPR). In addition, the potential application of these ketones as reusable qubit pairs will benefit from nanocrystals with well-defined size distribution and greater crystallinity, as well as the use of single crystalline specimens to take advantage of expected anisotropies.

ASSOCIATED CONTENT

Data Availability Statement

Single crystal X-ray diffraction data for ketones **K6** and **K8** has been deposited in the Cambridge Crystallographic Data Center as CCDC 2217714 and CCDC 2217715.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c11787.

General methods and synthesis procedures; spectroscopic ^{1}H NMR, ^{13}C{^{1}H} NMR, and IR data; UV−Vis and transient absorption data for solutions and suspensions (PDF)

Accession Codes

CCDC 2217714−2217715 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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