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The Missing Link Between Molecular Triplets and Spin-Polarized Free Radicals: Room Temperature Triplet States of Nanocrystalline Radical Pairs

Natalia V. Lebedeva,[†] Valery F. Tarasov,[‡] Marino J. E. Resendiz,[§] Miguel A. Garcia-Garibay,[§]
Ryan C. White,[†] and Malcolm D. E. Forbes*,[†]

*Caudill Laboratories, Department of Chemistry, CB #3290, University of North Carolina,
Chapel Hill, North Carolina 27599-3290, Semenov Institute of Chemical Physics, Kosygin St. 4,
Moscow 119991, Russia, and Department of Chemistry, University of California at Los Angeles,
405 Hilgard Avenue, Los Angeles, California 90095*

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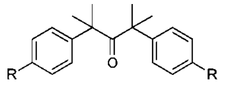
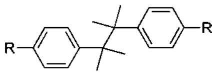
Chemical transformations of organic molecules in the solid state often proceed in high yields to give a single product without generating volatile organic solvent waste,[1] which renders them ideal for the development of green chemistry technologies.[2] In addition, reactions in solids have attracted the attention of mechanistic organic chemists and spectroscopists because of the unconventional pathways followed by reactive molecules when faced with the constraints of a well-defined and rigid environment.[3] An example of such reactivity is the quantitative conversion of dicumylketone (**1H**) to 2,3-dimethyl-2,3-diphenylbutane (**2H**), which takes place upon UV light irradiation of aqueous suspensions of organic nanocrystals (Scheme 1).[4] Although the reaction is believed to proceed by α-cleavage of the triplet state ^{3}**1H***,[5] neither the triplet state nor the free radicals resulting from bond cleavage have been detected heretofore. Indeed, the spectroscopic signatures of triplet states and ensuing reactive intermediates in nanocrystalline materials are largely unexplored.[6] Molecular nanocrystals suspended in liquids possess properties in transition between supramolecular systems and bulk solids. As such, they provide an avenue for the study of solid-state reactivity using methodology normally reserved for free solution samples.



1 (R = H, OMe)

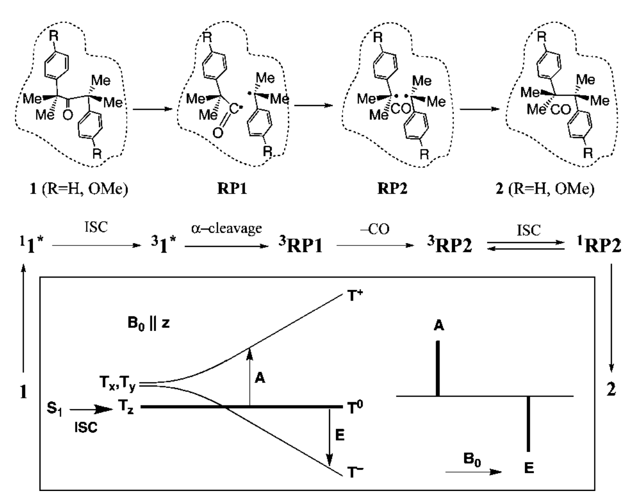


2 (R = H, OMe)

In this communication, we report the first spectroscopic observation of a nanocrystalline radical pair triplet state, created by laser flash photolysis of aqueously suspended nanocrystals of a *para*-methoxy substituted dicumylketone analogue (**1OMe**, shown above). The time-resolved electron paramagnetic resonance (TREPR) spectrum of these radical pairs (RPs) provides a unique signature for the photochemistry of dicumyl ketones in this unusual physical state. The results reported here are novel in two distinct ways: (1) triplet state TREPR spectra are observed at room temperature, a highly unusual situation; (2) strong electron spin polarization (ESP) is observed.

The photochemistry and TREPR spectroscopy of **1OMe** nanocrystals is outlined in Scheme 1. The nanocrystals are prepared by the reprecipitation method.[7] It should be noted that no disproportionation products were found when this photochemical reaction is carried out with nanocrystals, yet these products account for more than 50% of the total yield in free solution or in micelles. The photochemistry in Scheme 1 most likely takes place through sequential radical pairs (RP1 and RP2 in Scheme 1). The quantitative conversion of **1OMe** to a single recombination product in the nanocrystalline state suggests that RP2 can interconvert between triplet and singlet states within its lifetime. Geminate recombination of RP1 has no effect on the outcome of the reaction since it regenerates the starting material; decarbonylation must take place to produce **2OMe**.[8]

Scheme 1



The magnetic properties of triplet states are strongly influenced by electron dipole−dipole interactions (*D*), which depend on the distance between the two unpaired electrons and their orientation relative to the externally applied magnetic field. Since dipole−dipole interactions are averaged to zero by molecular motion, which also provides an efficient relaxation pathway, triplet states are rarely observed in fluid solution. In contrast, organic triplet states are easily observed in frozen solution because motional averaging of *D* ceases and electron spin relaxation becomes very slow.[9]

The TREPR spectra of randomly oriented (frozen) organic triplet states has been studied in detail by many researchers, and the paper of Murai et al.[10] provides an excellent example of how the assignments are made. Following the energy level diagram at the bottom of Scheme 1, the initial photochemical excitation of the ketone takes place in the singlet manifold (S_1) to make ^{1}**1OMe***. Intersystem crossing (ISC) to ^{3}**1OMe*** takes place in the molecular frame, where the triplet is best defined using a zero field basis set (T_x, T_y, and T_z). The ISC process populates the three triplet levels unevenly, resulting in nonequilibrium electron spin state populations. The magnitude of this selective population in the laboratory frame depends on the direction of the externally applied magnetic field B_0. This is indicated in Scheme 1 using a heavy line specifically for the T_z sublevel in the molecular frame, which correlates with T_0 in the high field basis set. To calculate a spectrum, the transition frequencies, transition probabilities, and

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[†] University of North Carolina.
[‡] Semenov Institute of Chemical Physics.
[§] University of California at Los Angeles.

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population differences must be sampled over all possible orientations of the molecule relative to B_0. The molecular orbital symmetry elements of the triplet state ultimately determine the observed phase of the TREPR spectrum.

The energy levels are shown in Scheme 1 for only one such direction, i.e., B_0 aligned parallel to the *z*-axis of the molecular frame. The allowed single-quantum transitions, T^+ to T^0 and T^0 to T^-, will exhibit enhanced absorption (**A**) and emission (**E**) respectively. Intense signals can be observed if electron spin relaxation processes are slower than the time scale of observation (~100 ns). Spin relaxation in molecular excited triplet states can be very fast at room temperature in liquid solution (1−10 ns) but long in frozen glasses (1−100 μs). The electron spin relaxation properties of radical pair triplet states in nanocrystals at room temperature were not known, but as will be demonstrated below, they are much more in line with solid state than liquid state behavior. This provides fortuitous circumstances for the detection of RP2 by TREPR.

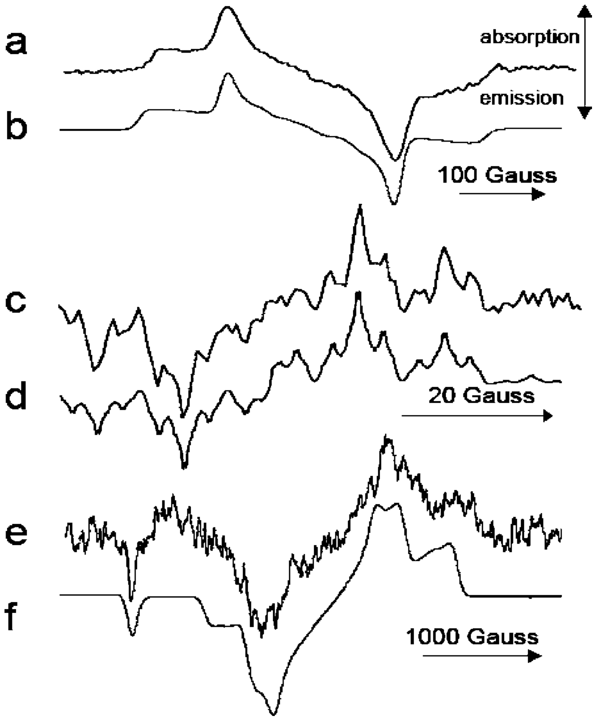

Figure 1. (a) X-band TREPR spectrum obtained 500 ns after 308 nm laser flash photolysis of an aqueous suspension of **1OMe** nanocrystals (~200 ± 30 nm diameter). (b) Simulation of the spectrum in (a) using $D = 243$ G, $E = 11$ G, and $J = -45000$ G. (c) X-band TREPR spectrum obtained 500 ns after 308 nm laser flash photolysis of a 0.1 M toluene solution of **1OMe**. (d) Simulation of the spectrum in (c) using the following parameters: 6H ($2 \times CH_3$) = 15.92 G, 2H(ortho) = 4.63 G, 2H(meta) = 1.54 G, 3H (*para*-OCH_3) = 0.56 G. These values are nearly identical to the literature values for the *p*-methoxycumyl radical reported by Arnold et al.[12] (e) X-band TREPR spectrum obtained 400 ns after 308 nm laser flash photolysis of a frozen toluene solution of **1OMe** at 100 K. (f) Simulation of (e) using the following parameters for the randomly oriented triplet state: $D = 1140$ G, $E = 85$ G.

Figure 1a shows the X-band TREPR spectrum acquired 500 ns after 308 nm laser flash photolysis of an aqueous suspension of **1OMe** nanocrystals. The spectrum shows strong spin polarization at all delay times. The spectrum bears little resemblance to the normally observed TREPR spectra of noninteracting radicals in liquid solutions or interacting radical pairs in micelles (sharp lines with resolved hyperfine couplings). Instead, Figure 1a exhibits spectral features commonly associated with a randomly oriented triplet state: broad lines with a phase of **AAAEEE**. Three phases are reported for the low field side (T^+-T^0) and three for the high field side (T^0-T^-) of the spectrum in accordance with the abrupt changes in the transition probabilities for these two transitions when B_0 is parallel to any of the three canonical axes of the molecule. These abrupt changes in intensity are common to steady state EPR spectra of a triplet state;[9] however the phase information (**E** or **A)** is only available from TREPR.[10] The splitting between the outermost lines (= 2*D*) is ~480 G. This would represent a zero-field splitting parameter of ~240 G, which is too small for a molecular photoexcited triplet state. Computer simulation of the spectrum in Figure 1a is shown in Figure 1b, which will be discussed in detail below.

To support the spectral assignment of Figure 1a to RP2, several control experiments were run, the first of which was to detect free radicals from **1OMe** after photolysis in free solution. Figure 1c shows TREPR spectra acquired 500 ns after 308 nm laser excitation of **1OMe** in benzene at 25 °C. The spectrum is narrow (note the magnetic field scale compared to Figure 1a) with resolved hyperfine lines showing **E**/**A** chemically induced electron spin polarization (CIDEP) from the radical pair mechanism (RPM).[11] Computer simulation of the spectrum in Figure 1c, shown in Figure 1d, was obtained using literature parameters for the methoxycumyl radical[12] and RPM polarization. It should be noted that the free solution TREPR spectrum does not resemble, in any fashion, the nanocrystal spectrum shown in Figure 1a.

The photoexcited *molecular* triplet states of the dicumyl ketone can be examined independently at low temperatures in dilute frozen matrices. Figure 1e shows the molecular triplet state TREPR spectrum for **1OMe** acquired in toluene at 100 K. Note the wide sweep width of this spectrum (4000 G), the phase (**EEEAAA**), the presence of half-field transitions, and the very broad line widths. The simulation in Figure 1f gives *D* and *E* values of 1140 and 85 G, respectively. All of the spectral features in Figure 1e are highly characteristic of a localized carbonyl triplet state.[13] It should also be noted that this spectrum has drastically different features (phase and sweep width) compared to the spectrum acquired in the nanocrystalline state (Figure 1a) and to the spectrum obtained for the methoxycumyl radicals in free solution shown in Figure 1c.

It can be argued that the nanocrystalline spectrum may represent the partially rotationally averaged spectrum of the molecular triplet state. Because of the large size of the nanocrystals, they do not have significant rotational freedom in the aqueous suspension. For particles of diameters near 200 nm, rotational correlation times longer than microseconds are reasonable. For this reason, the nanocrystals can be treated as a randomly oriented powder. If only molecular triplet states were being observed, no bond cleavage and decarbonylation would take place, and no species other than the starting ketone would be observed in the product analysis.

It is possible that, on our time scale of observation (~0.5 μs), the partially averaged molecular triplet state is the primary paramagnetic species observed and that the RP1 and/or RP2 are created later in time. However, it should be noted that the phase of the frozen triplet state spectrum (**EEEAAA**, Figure 1e) is opposite to that of the nanocrystalline TREPR spectrum (**AAAEEE**, Figure 1a). A rotational averaging process cannot lead to changes in the phase of the transitions, only to motional narrowing of the overall spectral width (with a lower observed *D* value), and perhaps changes in the intensity of the transitions.

There is a marked difference in line width, line shape, spectral width, and polarization patterns in all three systems presented here (nanocrystal suspensions, liquid solutions, and frozen triplet states). Coupled with the absence of any disproportionation products that would be observed in mobile spin-correlated radical pairs such as those confined to micelles (or escaped from micelles after a short confinement), the spectra in Figure 1 provide strong evidence for the existence of a spin-polarized "contact" radical pair triplet state in the nanocrystal suspensions. This state is intermediate between the molecular triplet state and the resulting free (noninteracting) monoradicals and can be thought of physically as the “missing link” between these two familiar states (triplet states and free radicals) from the photochemistry literature. The spectra show different spin−spin interactions than those for the parent triplet state, clearly assignable to an intermediate radical pair rather than the reactant or product. The spectral features of this “contact” radical pair are not observable in liquid solutions.

There have been earlier reports of confined radical pairs produced in single crystals and in inclusion compounds, most notably by Bartlett and McBride,[14] Hollingsworth et al.,[15] Modarelli and co-workers,[16] and Casal et al.[17] Additionally, Rao and co-workers showed that long-lived radical pairs can be observed in cyclodextrin inclusion complexes.[18] However, all of these reports focused on steady state EPR or IR experiments with Boltzmann spin state populations, and all those experiments were carried out at low temperatures. The spectra reported here for nanocrystalline RPs are very different from those reported previously for other RPs. For example, the RPs in Scheme 1 are not created or detected in macroscopic single crystals or inclusion compounds. Also, they are detected at room temperature, a condition under which triplet state EPR spectra are notoriously difficult to obtain. Finally, they exhibit strong ESP, a feature not observable by steady-state EPR methods. The ESP provides insight into the detailed molecular structure of the nanocrystal; correlation of crystal packing geometries with our TREPR data is a long-term future goal.

The simulation in Figure 1b implements a dipolar interaction ($D = 243$ G) between the unpaired electrons, and an axial symmetry parameter $E = 11$ G. Notably, an isotropic exchange interaction J is also included. The experimental spectrum shows a net emission, observed on the high field side of the spectrum, that is accounted for by the large J value. The D value reflects a distance between the unpaired electrons of $\sim$5 Å, which seems very reasonable for a confined benzylic radical pair with a CO molecule between them. The J value of $-45\,000$ G may seem high at first glance, but from many previous studies of radical pairs in confined media or biradicals, it is not unreasonable for an inter-radical separation of 5 Å.[19] The D value of 243 G is substantially smaller than that observed for the frozen triplet states, as expected. The small E value of 11 G may reflect a small amount of rotational averaging by nanocrystal tumbling in the suspension. For comparison, we note that Abe and co-workers reported low temperature steady-state EPR spectra of RPs created from the lophine dimer, with a D value of $\sim$140 G for an inter-radical separation of $\sim$6.3 Å and an E value of 0.[20]

The simulation in Figure 1b is sensitive to both electronic coupling parameters. Varying D changes the overall spectral width, while different J values alter the amount of net emission observed in the spectrum. This strong sensitivity to both isotropic and anisotropic parameters is unusual. There are other reports in which both J and D have been observed in a solid-state RP. By angular rotation of single crystals, Casal et al. were able to separate contributions from J and D for a bis(alkyl) RP included in urea channels at low temperatures.[17] Flossman et al. examined RPs created by radiation of 1-methyluracil at low temperature.[21] They proposed that $|J| > |D|$ in their system, leading to a temperature-dependent level crossing. Ikoma et al. reported J and D values for a radical ion pair in a polymer matrix, but the spectrum was poorly resolved and no temperature value was given.[22]

In conclusion, the observation of spin-polarized radical pair triplet state EPR spectra at room temperature implies that there exists a coalition of favorable features of the spin physics, photophysics, and supramolecular dynamics of the nanocrystals. Specifically, it implies that the ISC rate in the molecular excited state of the parent ketone is fast, as is the rate of decarbonylation of RP1. If the ISC rate were slowed down, geminate recombination would be fast in RP1, the TREPR signals would be much less intense, and the reaction efficiency would be lower.[8] If the decarbonylation rate were slowed down, we would observe RP1, which would exhibit a much larger D value due to its closer inter-radical distance. The observed ESP is strong, implying high selectivity for one of the three triplet levels in the molecular frame, and there is slow electron spin relaxation due to the small D value and the slow tumbling rate of the nanocrystals in the aqueous suspension.[23] It is quite remarkable that all of the possible factors that could influence the possibility of detection of triplet states at room temperature coincide favorably in this system. Further work on the temperature dependence, substituent effects, and nanocrystal size effects in these novel paramagnetic systems is currently in progress.

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References

(1) (a) Scheffer, J. R. In *Solid State Organic Chemistry*; Desiraju, G. R., Ed.; VCH: Amsterdam, 1987; pp 1−45. (b) MacGillivray, L. R.; Papaefstathiou, G. S.; Friscic, T.; Hamilton, T. D.; Bucar, D.-K.; Chu, Q.; Varshney, D. B.; Georgiev, I. G. *Acc. Chem. Res.* **2008**, *41*, 280–291. (c) Zimmerman, H. E.; Nesterov, E. E. *J. Am. Chem. Soc.* **2002**, *124*, 2818–2830. (d) Natarajan, A.; Mague, J. T.; Ramamurthy, V. *J. Am. Chem. Soc.* **2005**, *127*, 3568–3576. (e) Fomitchev, D. V.; Bagley, K. A.; Coppens, P. *J. Am. Chem. Soc.* **2000**, *122*, 532–533. (f) Garcia-Garibay, M. A. *Acc. Chem. Res.* **2003**, *36*, 491–498. (ff) Mortko, C. J.; Garcia-Garibay, M. A. *Top. Stereochem.* **2006**, *25*, 205–228.

(2) (a) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998. (b) Poliakoff, M.; Fitzpatrick, J. M.; Farren, T. R.; Anastas, P. T. *Science* **2002**, *297*, 807–810.

(3) (a) Chin, K. K.; Natarajan, A.; Gard, M. N.; Campos, L. M.; Johansson, E.; Shepherd, H.; Garcia-Garibay, M. A. *Chem. Commun.* **2007**, *41*, 4266–4268. (b) Gesquiere, A. J.; Uwada, T.; Asahi, T.; Masuhara, H.; Barbara, P. F. *Nano Lett.* **2005**, *5*, 1321–1325. (c) Matsune, H.; Asahi, T.; Masuhara, H.; Kasai, H.; Nakanishi, H. *Mater. Res. Soc. Symp. Proc.* **2005**, *846*, 263. (d) Kim, H. Y.; Bjorklund, T. G.; Lim, S.-H.; Bardeen, C. J. *Langmuir* **2003**, *19*, 3941–3946.

(4) (a) Veerman, M.; Resendiz, M. J. E.; Garcia-Garibay, M. A. *Org. Lett.* **2006**, *8*, 2615–2617. (b) Resendiz, M. J. E.; Garcia-Garibay, M. A. *Org. Lett.* **2005**, *7*, 371–374.

(5) Ketone photodecarbonylations may also occur in the singlet state when the radical intermediates are highly stabilized: Resendiz, M. J. E.; Family, F.; Fuller, K.; Campos, L. M.; Khan, S. I.; Lebedeva, N. V.; Forbes, M. D. E.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2009**, *131*, 8425–8433.

(6) Ryzhkov, L. R.; McBride, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 4826–4833.

(7) Kasai, H.; Nalwa, H. S.; Oikawa, H.; Okada, S.; Matsuda, H.; Minami, N.; Kakuta, A.; Ono, K.; Mukoh, A.; Nakanishi, H. *Jpn. J. Appl. Phys. 2* **1992**, *31*, L1132–L1134.

(8) The estimated quantum yield of reaction is $F = 0.33$ based on the known quantum yield of **1H** (ref 4a) and the relative yield of **1OMe** (ref 4b).

(9) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772.

(10) Murai, H.; Imamura, T.; Obi, K. *Chem. Phys. Lett.* **1982**, *87*, 295–298.

(11) Harbron, E. J.; Forbes, M. D. E. In *Encyclopedia of Chemical Physics and Physical Chemistry*; Moore, J. H., Spencer, N. D., Eds.; Institute of Physics Publishing: Philadelphia, 2001; Chapter *B1.16*, pp 1389−1417.

(12) Arnold, D. R.; Nicholas, A. M.; de, P.; Snow, M. S. *Can. J. Chem.* **1984**, *63*, 1150–1155.

(13) Tominaga, K.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1990**, *94*, 4425–4431.

(14) Bartlett, P. D.; McBride, J. M. *Pure Appl. Chem.* **1967**, 89–108.

(15) Hollingsworth, M. D.; Harris, K. D. M.; Jones, W.; Thomas, J. M. *J. Inclus. Phenom.* **1987**, *5*, 273–277.

(16) Modarelli, D. A.; Lahti, P. M.; George, C. *J. Am. Chem. Soc.* **1991**, *113*, 6329–6330.

(17) Casal, H. L.; Griller, D.; Kolt, R. J.; Hartstock, F. W.; Northcott, D. M.; Park, J. M.; Wayner, D. D. M. *J. Phys. Chem.* **1989**, *93*, 1666–1670.

(18) Rao, V. P.; Zimmt, M. B.; Turro, N. J. *J. Photochem. Photobiol. A: Chem.* **1991**, *60*, 355–360.

(19) (a) Rajca, A. *Chem. Rev.* **1994**, *94*, 871–893. (b) Tarasov, V. F.; Forbes, M. D. E. *Spectrochim. Acta A* **2000**, *56*, 245–263.

(20) Abe, J.; Sano, T.; Kawano, M.; Ohashi, Y.; Matsushita, M. M.; Iyoda, T. *Angew. Chem.* **2001**, *113*, 600–602.

(21) Flossman, W.; Westhof, E.; Muller, A. *Phys. Rev. Lett.* **1975**, *34*, 959–962.

(22) Ikoma, T.; Nakai, M.; Akiyama, K.; Tero-Kubota, S.; Ishii, T. *Angew. Chem.* **2001**, *113*, 3334–3336.

(23) Sato, H.; Kathirvelu, V.; Spagnol, G.; Rajca, S.; Rajca, A.; Eaton, S. S.; Eaton, G. R. *J. Phys. Chem. B* **2008**, *112*, 2818–2828.

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