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Conformational Control of the Photochemistry and Photophysics of Diphenylacetone

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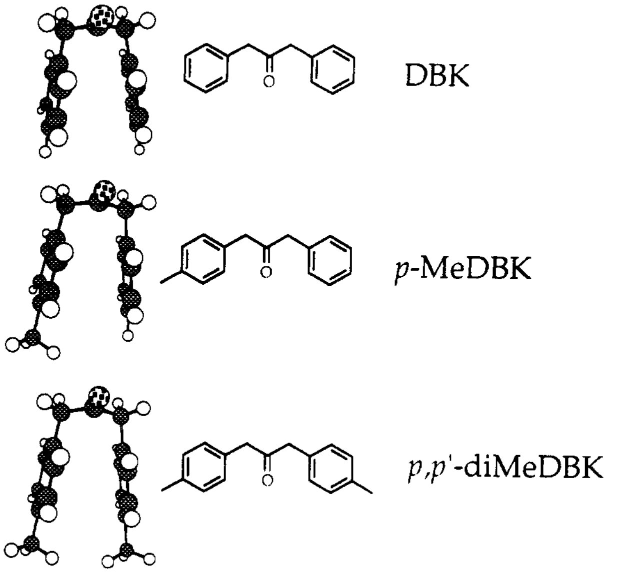
We report the direct observation of the lowest triplet states of 1,3-diphenylacetone (DBK) and two methylated derivatives by direct detection time-resolved electron spin resonance (TRESR) at 15 K in methylcyclohexane glass. The spectral features are broad with multiple peaks in the $\Delta M_2 = 2$ region, which we assign to a multitude of conformations frozen into the glass. Successive experiments on a single sample provide evidence that certain of these conformations can be photochemically removed. DBK and 1-*p*-tolyl-3-phenylacetone (*p*-MeDBK) give single-exponential fluorescence lifetimes of 2.7 ns. 1,3-di-*p*-tolylacetone (*p,p'*-diMeDBK) gives a multiexponential fluorescence decay. ZFS parameters, triplet sublevel populating rates, and rates of triplet-state α-cleavage appear to be more sensitive functions of conformation than would be expected for nominally aliphatic ketones. We conclude that a significant portion of the unpaired electron density of the triplet state of DBK (and its derivatives) is delocalized into the phenyl rings and propose that this delocalization is responsible for the previously observed change in rate of triplet-state α-cleavage with substitution in the phenyl rings.

1. Introduction

We have shown in previous reports[1,2] that triplet-state characteristics of benzophenone (BP) such as reactivity toward hydrogen abstraction, phosphorescence lifetime, and zero-field splitting parameters are sensitive to the conformation of the phenyl ring relative to the carbonyl moiety. In fact, when the *para* positions of the phenyl rings are tied together with an eight-methylene tether, the reactivity of BP toward hydrogen abstraction decreases by 3 orders of magnitude. We explained these findings by showing that such a conformational change moves unpaired triplet electron density out of the nonbonding orbital of the oxygen and into the π^*-orbital of the carbonyl and the π-orbital of one phenyl ring. BP, though, is a conjugated aromatic ketone, and such an effect is not surprising.

More surprising, perhaps, is a report by Wagner et al.[3] in which the conformation of the phenyl ring of α-phenylcyclohexanone relative to the carbonyl serves as an on/off switch for triplet-state α-cleavage. In this system, the carbonyl and aromatic moieties are not conjugated. We will present evidence that an analogous conformational "switch" also controls the triplet photochemistry of diphenylacetone (DBK) (Chart 1), and as was the case for BP, the effect is due to the movement of unpaired electron density from the carbonyl into the phenyl rings as a function of conformation.

CHART 1: Ketones Used in this Study Shown in the Low-Energy Conformations Found by MM2



The first reports of the photochemistry and photophysics of DBK concluded that its triplet energy was roughly equivalent to that of acetone.[4-6] The effect of the phenyl rings was to increase the stability of the products of α-cleavage, yielding a benzyl radical rather than the methyl radical from acetone, thereby lowering the activation energy to this cleavage and increasing the quantum yield of radical formation to 1. Literature reports have shown that the triplet states of acetone and DBK are, in certain respects, qualitatively different. For example, TRESR studies have shown that, in solution at room temperature, the triplet state of acetone is emissively triplet mechanism polarized,[7-9] while that of DBK is absorptively polarized. However, the basis for these differences, as far as we are aware, has not been definitively elucidated. The one report in which the triplet state of a substituted derivative of DBK is shown to fundamentally differ from that of an aliphatic ketone is by Robbins et al.,[5,6] in which they show that 1,3-bis(*p*-cyanophenyl)acetone yields no benzyl radicals upon photoexcitation. They attribute this result to intramolecular triplet energy transfer.

One other literature report relevant to these issues is a CIDNP study of monosubstituted DBKs[10] in which *para* methyl substitution to DBK was claimed to increase the rate of triplet α-cleavage *ca.* 1.5 times and *para* methoxy substitution *ca.* 3 times. Johnston et al.[10] fit their data to Hammett plots and concluded that the transition state for cleavage of DBK is polar and is stabilized by electron-donating aromatic substitution. We will provide evidence that the effect for *para* methyl substitution may not be due to any change in activation energy but to the same conformational "switch" that Wagner et al.[3] reported previously.

2. Experimental Details

2.1. Reagents and Solvents. DBK from Aldrich (~99% pure, yellow liquid) was further purified by either multiple precipitations from dry ice cooled diethyl ether or recrystallization from EtOH/H_2O. Both methods yield crystalline DBK that is >99% pure by

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GC. The syntheses of all of the DBK derivatives used are reported elsewhere[11-13] and were >99% pure by gas chromatography (HP5890, SE30 column, flame ionization detection).

2-Propanol, which was employed for room temperature time-resolved electron spin resonance (RT-TRESR), was from Aldrich. Low-temperature TRESR (LT-TRESR) was run in Aldrich Spectro-Grade methylcyclohexane, further purified by distillation. The cyclohexane for single photon counting (SPC) experiments from Burdick and Jackson Laboratories was further purified by passage through a silica column and found to have no light-emitting impurities in blank SPC runs.

All flash photolysis and radical quenching was run in Aldrich spectrophotometric grade MeOH. $BrCCl_3$ was 99% pure from Aldrich. Dodecane, used as an internal standard for product analysis, was from Aldrich.

2.2. Room Temperature Time-Resolved Electron Spin Resonance. Our solution-phase TRESR experiments have been described previously,[9,14] and we include only a brief description here. The conventional square cavity tunes to approximately 9.7 GHz, and we employ 9.9 mW of microwave power. The fourth harmonic (266 nm) of a DCR II Nd:YAG laser (0.3 W, 5-ns fwhm, 20 Hz) both excites the ketones and triggers the experiment via a fast photodiode. We sweep the magnetic field without modulation from 3423 to 3523 G in 500 s. During that time we collect 512 points which yields a spectral resolution of approximately 0.2 G. We typically accumulate data in a window from 500 to 1000 ns after laser excitation. The instrumental response time is limited by the preamplifier and is ~60 ns.

Samples were 0.01 M ketone in 2-propanol and were flowed with a syringe pump (1.5 mL/min) through a ~0.3 mm thick quartz flat cell.

2.3. Time-Resolved ESR of Triplets in a Glassy Matrix. The low-temperature direct detection time-resolved ESR experiment on molecules in their photoexcited triplet states has been described previously.[2] We employ a Bruker ESR spectrometer (ESP380) with a dielectric ring cavity (ESP380-1052 DLQ-H) tuned to approximately 9.7 GHz, an Oxford cryostat (GFS300) at ~15 K, a Lambda-Physik XeCl excimer laser (LPX100 ~14 ns fwhm at 308 nm) fired at 30 Hz, and a Princeton Applied Research boxcar averager (Model 4420) to time average the signal over a 5 μs window beginning 1 μs after the laser pulse. We measure the strongest transient signals at a microwave power of 166 μW.

Solutions of the ketones were approximately 0.1 M in methylcyclohexane. We place the samples in 5 mm quartz ESR tubes and, without deoxygenation, place them into the liquid helium cooled cavity. Immersion in liquid nitrogen prior to insertion into the cavity had no effect on the spectra.

We sweep the magnetic field 6000 G over 1000 s and during that time acquire 256 points, giving a resolution of about 25 G. The acquisition of a single spectrum with acceptable signal to noise requires about 30 000 laser pulses.

2.4. Single-Photon Counting. Our SPC experiments have been reported in detail previously.[15] Excitation was achieved with a Nd:YAG pumped dye laser which excites the samples at 310 nm. We monitor the decays at both 380 and 440 nm. The reported uncertainties are given as two standard deviations in the fit. The change in monitoring wavelength has no effect on the results for DBK and *p*-MeDBK. The quantum yield of fluorescence from DBK is less than 1%,[4,11] so the SPC experiment is extremely sensitive to efficiently fluorescing impurities. It is recognized that *p,p'*-diMeDBK, following photocleavage, yields metastable products that emit when photoexcited. Under no conditions were we able to achieve an acceptable single-exponential fit to the fluorescence decay of *p,p'*-diMeDBK, although stirring the sample and slowing the repetition rate of the laser yielded a decay that was nearer to one exponential.

The instrument response function (fwhm) is 42 ps.

2.5. Laser Flash Photolysis. We recently upgraded our nanosecond flash photolysis system and have reported a detailed description of this instrument elsewhere.[16] The 308-nm output of a XeCl excimer laser (LambdaPhysik, Lextra 50, ~15 mJ/pulse impinging on sample, ~14 ns fwhm) excites the sample in a 1 × 1 cm quartz cell. Typically, 10–15 laser pulses were averaged to produce each experimental trace. We monitored growth kinetics of the doublet–doublet absorption of the benzyl radical by direct detection at 317 nm.

TABLE 1: Room Temperature Fluorescence Lifetimes Recorded at 440 nm in Cyclohexane[a]

ketone	A_1	τ_1 (ns)	A_2	τ_2 (ns)
DBK	1	2.72 ± 0.01		
p-MeDBK	1	2.70 ± 0.01		
p,p'-diMeDBK	19	0.31 ± 0.04	81	1.39 ± 0.06

[a] Excitation at 310 nm.

Samples were prepared so as to exhibit ground-state optical density of 0.3–0.6 at 308 nm in MeOH. $BrCCl_3$ was used at concentrations of 0.1, 0.05, and 0.01 M.

Temperature was controlled with a Bruker 4111 VT variable temperature unit cooled by a liquid nitrogen reservoir. Samples were bubbled with argon gas throughout the experiment. Experiments were run at temperature intervals of 10 K from 231 to 291 K.

Data was fit using nonlinear least-squares regression, and reported uncertainties are given as two standard deviations in the fit.

2.6. Quenching Studies. Samples were 0.01 M *p*-MeDBK in MeOH, 0.1 M $BrCCl_3$ as quencher, 0.005 M dodecane as internal standard, photolyzed with a medium-pressure mercury lamp. We bubbled the samples with N_2 during photolysis both to remove oxygen and to stir the samples. Temperature was controlled with a Bruker 4111 VT variable temperature unit cooled by a liquid nitrogen reservoir. Photolyses were carried to ~20% conversion.

GC analyses were perrformed on an HP5890 gas chromatograph equipped with an SE30 column and flame ionization detector. The reported values are the average of two photolyses and two injections for each photolysis. Peaks were identified by co-injection with the known materials. Methyl phenylacetate was from Aldrich. Methyl tolylacetate was synthesized from tolylacetic acid (Aldrich) by conversion to the corresponding acyl chloride with $SOCl_2$, followed by addition to MeOH and purification by preparative TLC.

3. Results

3.1. Room Temperature Fluorescence Lifetimes. Table 1 lists the singlet lifetimes of DBK, *p*-MeDBK, and *p,p'*-diMeDBK (Chart 1) as measured by single-photon counting (SPC). The quantum yield of fluorescence for DBK is less than 1%,[4,11] so the multiexponential lifetime we report for *p,p'*-diMeDBK may be due to efficiently fluorescing impurities. Two other possibilities, conformationally distinct singlet states, each state with its own lifetime, or an intramolecular charge transfer state degenerate with the classical singlet excited state, may also explain the results, but we feel it unlikely that *p,p'*-diMeDBK would behave in such a manner when *p*-MeDBK does not.

3.2. RT-TRESR. Figure 1 shows the TRESR spectra of the benzyl radicals formed upon photolysis of DBK, *p*-MeDBK, and *p,p'*-diMeDBK in 2-propanol. The spectrum from DBK has been reported previously.[9] The spectra were satisfactorily simulated using literature values for the hyperfine couplings[17] and a *g*-factor of 2.0026, adding net polarization to triplet precursor (*E*/*A*) radical pair mechanism (RPM) polarization. The net polarization is absorptive for DBK and emissive for *p*-MeDBK and *p,p'*-diMeDBK. We assign this net polarization to the triplet mechanism (TM) and note that it is reasonable for TM polarization to be observed for these radicals given the short lifetime of their triplet precursors.[18]

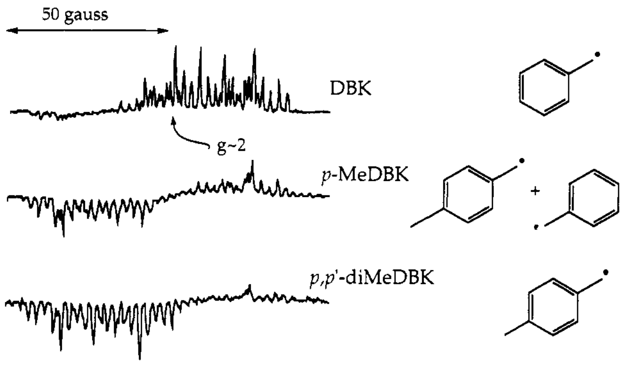
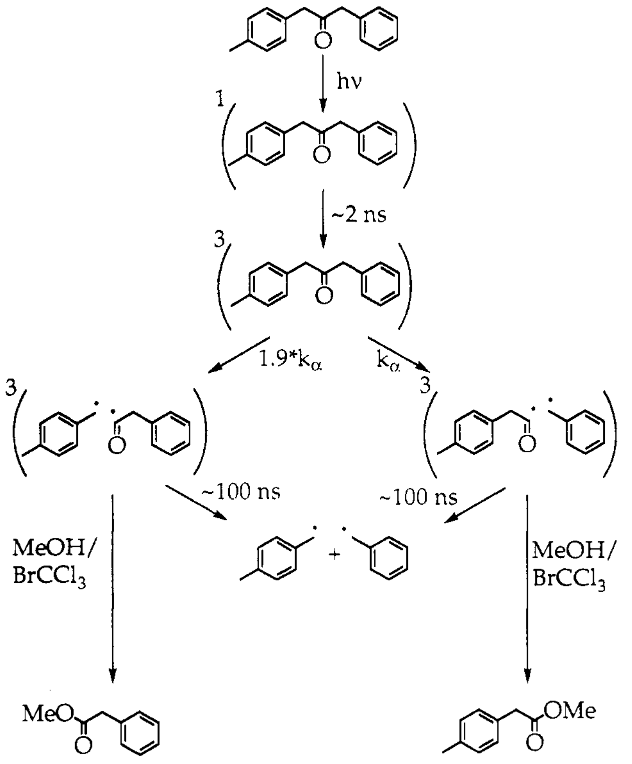


Figure 1. Room temperature TRESR spectra recorded during a 0.5 μs window, 0.5 μs after 266-nm excitation. Samples are 0.01 M ketone in 2-propanol.

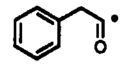
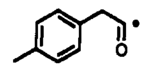
CHART 2: Scheme of the Photochemistry of *p*-MeDBK



3.3. Quenching of the Phenylacetyl and Tolylacetyl Radicals. The scheme for the photochemistry of *p*-MeDBK is shown in Chart 2. The acyl radicals are quenched by reaction with $BrCCl_3$ in MeOH. The acyl bromide first formed is rapidly transformed into the corresponding methyl ester by solvent. We measure the relative yield of the stable and readily analyzed methyl phenylacetate to methyl tolylacetate by gas chromatography. Assuming the trapping and conversion to ester is quantitative, the ratio of the two esters represents the ratio of cleavage pathways. The ratio of these two esters is graphed in Figure 2 as a function of temperature. Each data point is the average of two experiments, two GC injections per experiment. Errors, calculated as the standard deviation of the four GC injections, are ~5%. The flame ionization response factors of the two esters differed by 3%, and we did not correct for them.

If these two reaction pathways were activation controlled and displayed identical Arrhenius prefactors, then the ratio at any temperature would yield the difference in activation energy for the two paths (see the Discussion). From the ratio at one temperature, the ratio of products at all temperatures could be predicted. Starting from the ratio at 241 K, this prediction is graphed in Figure 2.

TABLE 2: Activation Parameters for the Decarbonylation of the Acyl Radicals Shown

radical	log A (s^{-1})	E_A (kcal/mol)
	10.5 ± 1.0	6.0 ± 0.6
	11.7 ± 1.2	7.4 ± 0.7

3.4. Laser Flash Photolysis. As controls, we monitored the rate of decarbonylation of the phenylacetyl/tolylacetyl radical (i.e., the growth of the second benzyl/*p*-Me-benzyl radical) both as a function of added $BrCCl_3$ and as a function of temperature. The former was to confirm that $BrCCl_3$ quenches the phenylacetyl radical faster than 10^8 M^{-1} s^{-1}. At room temperature, we were unable to see the growth of the second benzyl radical at quencher concentrations of 0.01 M and higher. For us not to be able to see the appearance of the second benzyl radical, the $BrCCl_3$ must quench the phenylacetyl radical some 10 times faster than the phenylacetyl radical decarbonylates. Since the phenylacetyl radical decarbonylates at ~1 × 10^6 s^{-1},[19,20] the $BrCCl_3$ must quench it at some rate greater than 1 × 10^8 M^{-1} s^{-1}.

We ran the latter control experiment to ensure that the rates of decarbonylation of the phenylacetyl and tolylacetyl radicals are comparable over the entire range of temperatures. The activation parameters we have derived are listed in Table 2. Representative kinetic traces are shown in Figure 3. The values for the decarbonylation of the phenylacetyl radical have been previously reported.[19,20a] Differences between previously reported values and our present values will be discussed below.

3.5. TRESR at Cryogenic Temperatures. Figure 4 shows the LT-TRESR spectra of the three ketones photoexcited in methylcyclohexane glass at ~15 K. The peak at center field (g ~ 2) is ascribed to radicals formed within the time scale of the laser pulse. Because this is a direct detection experiment with no modulation of the magnetic field and the signal passes through an ac preamplifier, this signal cannot be due to a steady-state concentration of radicals. Although the signal appears intense, we note that the integrated intensity is small relative to the rest of the spectrum. The nominal $\Delta M_s = 2$ forbidden transitions are labeled. We are unable to find any single set of zero field splitting (ZFS) parameters that will simulate the multiple peaks observed in this region.

Figure 5 shows successive TRESR spectra taken of a single sample of ketone frozen in methylcyclohexane glass at ~15 K. Note the gradual disappearance of certain peaks in the $\Delta M_s = 2$ region with no corresponding increase in the intensity of the remaining peaks.

3.6. Calculations. A Monte Carlo search with the MM2 force field of Macromodel for the global minima of the three ketones yields the conformations shown in Chart 1. For DBK, we processed 20 000 conformers, found 174 in the lowest 10 kJ, and found the four lowest conformers of DBK, all isoenergetic, more than 1 000 times. Of the conformations found in the lowest 10 kJ of energy, none had the phenyl rings in any conformation other than the "eclipsed" form shown in Chart 1. We note that in this "eclipsed" form, the 1-positions of the phenyl rings of DBK are slightly more than 3 Å apart. The Boltzmann distributions of conformations for the three ketones are similar and broad to below 100 K.

Figure 6 shows the electron spin distributions for the triplet states of the three ketones as calculated by unrestricted Hartree–Fock on the low-energy ground-state conformations found by molecular mechanics. AM1 does not optimize the structures for the triplet state.[20b]

4. Discussion

Besides some recent discussion about possible singlet-state photocleavage, the photochemistry of the three ketones (Chart

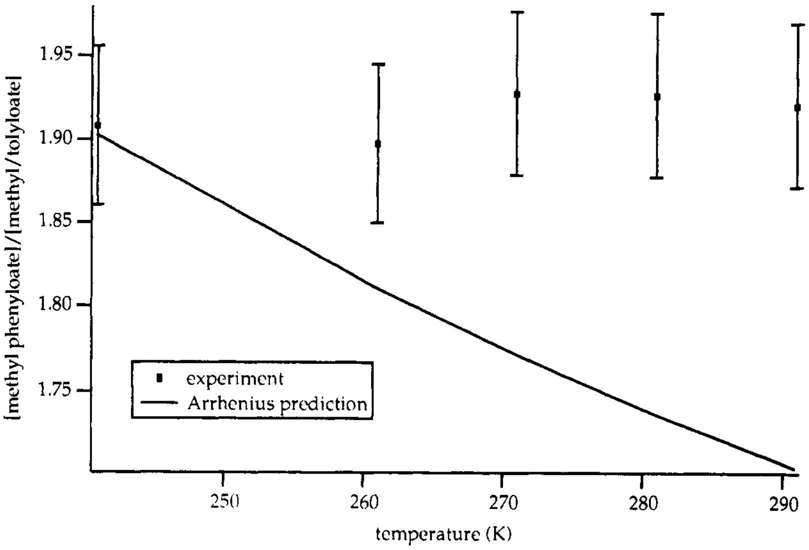


Figure 2. Experimental ratio of α-cleavage products and the "Arrhenius" prediction versus temperature.

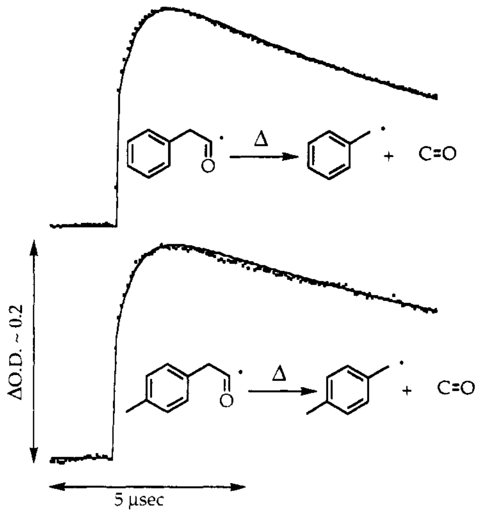


Figure 3. Kinetic traces taken at 291 K, with fits, of the benzyl radicals shown, monitored at 317 nm. Initial laser excitation at 308 nm.

1) is well established.[4-6,11,12] We show a representative scheme for the photochemistry of *p*-MeDBK in MeOH in the presence of $BrCCl_3$ in Chart 2 and report the first fluorescence lifetime measurements for DBK and *p*-MeDBK (Table 1) as 2.7 ns. These numbers are in good agreement with those previously reported for DBK by Arbour and Atkinson[18] as measured by transient absorption spectroscopy. These authors concluded that since the triplet state of DBK was not experimentally observed, either DBK's photochemistry occurs from its singlet state or its triplet lifetime is shorter than a few hundred picoseconds. Magnetic resonance results and quenching studies, though, show that a significant percentage of DBK's photochemistry comes from its triplet state,[21] so it appears that photoexcited DBK, as stipulated by Arbour and Atkinson, reacts via an exceedingly short lived triplet.

Although we conclude in this paper that the triplet states of the ketones examined in this work differ measurably, the rates of intersystem crossing (ISC) (as determined by fluorescence lifetimes) of DBK and *p*-MeDBK are identical. We have previously shown for a family of cyclophanobenzophenones that significant changes in triplet behavior including large changes in relative triplet sublevel populating rates are often accompanied by only small changes in singlet lifetimes.[22]

The room temperature solution TRESR of the benzyl radicals formed from these triplet states are composed of both triplet precursor radical pair mechanism polarization (E/A) and net

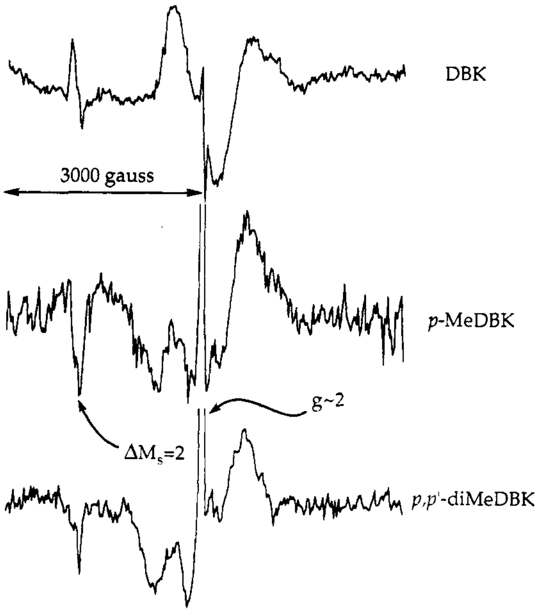


Figure 4. LT-TRESR spectra recorded during a 5-μs window, 1 μs after 308-nm laser excitation. Samples are 0.1 M, frozen in methylcyclohexane glass at ~20 K.

polarization from the triplet mechanism (Figure 1). That this net polarization is from the triplet mechanism is reasonable given the sub-nanosecond triplet lifetime suggested by Arbour and Atkinson.[18] DBK yields slightly absorptively polarized radicals, *p*-MeDBK yields slightly emissively polarized radicals, and *p,p'*-diMeDBK yields radicals that are somewhat more strongly emissively polarized than those from *p*-MeDBK.

The sign of triplet mechanism polarization is given by

$$P = D(2\mathrm{PopZ} - (\mathrm{PopX} + \mathrm{PopY})) \qquad (1)$$

where P is the sign of polarization ($P > 0$ = absorptive), D is the sign of the ZFS D parameter, and PopX, PopY, and PopZ are the relative triplet sublevel populating rates. We suggest that the change in sign of the polarization on going from DBK to the methyl-substituted DBKs is due to small changes in the relative triplet sublevel populating rates rather than any reordering of triplet sublevels. Van Willigen et al.[23] have recently shown that, for acetone photolyzed in 2-propanol, the RPM polarization is of comparable magnitude to Boltzmann distribution of spins. Since the net absorptive polarization from DBK is of the same magnitude as its RPM polarization, the radicals are formed with

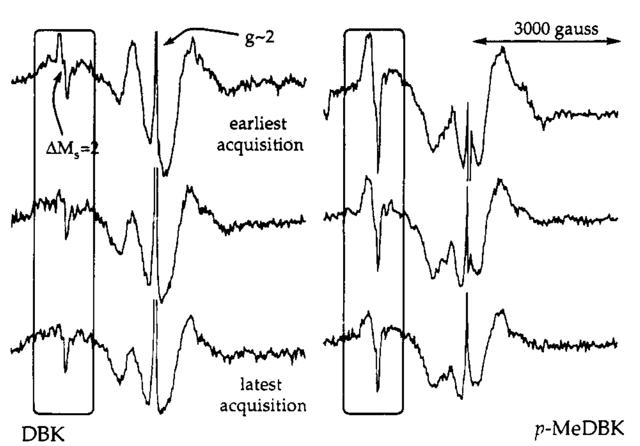


Figure 5. Successive TRESR spectra taken of a single sample, each recorded during a 5 μs window, 1 μs after 308 nm excitation. Samples are 0.1 M, frozen in methylcyclohexane glass at ~20 K. Time between acquisition ~ 5 min.

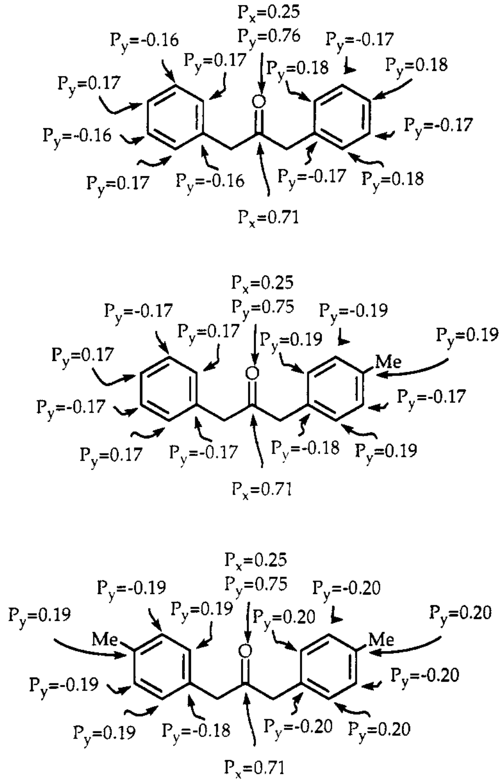


Figure 6. Spin density distribution in the lowest triplet state as calculated by unrestricted Hartree–Fock, parametrized with AM1. The conformations are minima on the ground-state surface, not on the triplet surface.

near Boltzmann distribution of spins. Thus, only small changes in the relative triplet sublevel populating rates (a few parts in a thousand) are needed to invert the signal.

From MM2 calculations on the three ketones studied, it appears that the small changes in triplet character are due to the electronic effects of substitution, not steric effects. *Para* methyl substitution of DBK neither changes its lowest energy ground-state conformation nor its distribution of conformers.

Triplet *p*-MeDBK cleaves via two pathways, one to form a *p*-Me-benzyl/phenylacetyl radical pair, the other to form a benzyl/tolylacetyl radical pair (Chart 2). Johnston et al.[10] used CIDNP to conclude that the former pathway is some 1.5 times faster than the latter. We repeated their measurements as a function of temperature by the more precise method of radical scavenging with $BrCCl_3$ followed by gas chromatographic analysis. The observed ratio of 1.9 does not change over the 50 K window from 241 to 291 K. If the difference in rates were due to a difference in activation energies and both processes displayed identical Arrhenius prefactors, then the ratio of rates would yield the difference in activation energy between the two reaction pathways.

$$k_1/k_2 = \exp(E_2 - E_1)/RT \tag{2}$$

This equation predicts that a ratio of 1.9 at 241 K would drop to 1.7 at 291 K. Since this clearly is not the case (Figure 2), ***the difference in rates for the two major reaction pathways of triplet p-MeDBK is not due to a difference in activation energies.***

We ran two control experiments to ensure that the ratios we measure are due to differences in the initial rates of reactions rather than to subsequent differences in decarbonylation rates for the acyl radicals. The first such experiment showed, as measured by laser flash spectroscopy, that $BrCCl_3$ concentrations as low as 0.01 M scavenge all the phenylacetyl radicals formed by photolysis of DBK. This implies that $BrCCl_3$ quenches the phenylacetyl radical at $>1 \times 10^8$ M^{-1} s^{-1}, in agreement with earlier magnetic resonance results.[24]

For the second control experiment, we measured the activation parameters for decarbonylation of the tolylacetyl radical and remeasured those for the phenylacetyl radical. As seen in Figure 3, the initial formation of a single equivalent of benzyl radicals is followed by the slower growth of a second benzyl radical. This slower growth gives the rate of decarbonylation of the acyl radical.

The two previous reports on the decarbonylation of the phenylacetyl radical[19,20] fit the early portion (after the initial step function but before decay of the radicals takes over) of the kinetics as a single-exponential growth, setting the asymptotic limit manually. Due to decay of the radicals, though, this limit is not reached and is therefore difficult to set. The system can be reasonably described as

$$A \rightarrow B \rightarrow C$$

where A is the phenylacetyl radical, B is the benzyl radical that we monitor, and C is products. For $A_0 = B_0 = 1$, which is correct for this system, and sufficient oxygen in the experiment such that B decays with a pseudo-first-order rate, the kinetics of B can be described by[25]

$$B = e^{-k_b t} + \frac{k_a}{k_b - k_a}(e^{-k_a t} - e^{-k_b t}) \tag{3}$$

We found eq 3 to fit the kinetics well, yielding standard deviations in the fit of less than 10%. Of perhaps equal importance, *eq 3 also fits the height of the initial step relative to the maximum growth.* The activation parameters for the decarbonylation of the phenylacetyl radical differ somewhat from those reported previously[19,20] and from those for the tolylacetyl radical. However, the rates of decarbonylation of the phenylacetyl and tolylacetyl radicals are similar enough not to affect our scavenging results.

The TRESR spectra (Figure 4) of the three ketones frozen into methylcyclohexane glass at ~15 K represent, we believe, the first direct detection of these triplet states. An early report on the photochemistry of DBK concluded that triplet emission (Phosphorescence) could not be observed at 77 K over the emission of impurities.[4]

All three spectra show a sharp peak at $g \sim 2$ due to radicals formed from triplet cleavage. Organic radicals are expected to give such a sharp transition,[26] and since such aliphatic ketones as acetone, cyclohexanone, and cyclopentanone give no such signal under similar conditions,[7] it is unlikely that the radicals are formed as a result of hydrogen abstraction from the solvent.

The signals are weak, which corresponds to our findings from the room temperature experiments that the triplets are formed with little spin polarization. We suggest that the broad spectra and multiple maxima at $\Delta M_s = 2$ are due to multiple conformations frozen into the matrix, each conformation yielding a triplet with a different set of ZFS parameters. Benzophenone is another triplet state that yields a broad spectrum,[2,26] but benzophenone is an aromatic ketone and calculations[27] have shown that its ZFS parameters are extremely sensitive to conformation. Literature reports of the triplets of aliphatic ketones show much sharper spectra. Davidson et al.[28,29] have calculated the ZFS parameters for two different possible conformers of triplet formaldehyde and have shown that the parameters are especially sensitive to the ability of the carbonyl moiety to pyramidalize. Tominaga et al.[7] showed that it is possible to control the ability of the triplet state of aliphatic ketones to pyramidalize by control of the substituents around the carbonyl.

Cyclohexanone and cyclopentanone represent an extreme case of the effect of substitution around the carbonyl on the ZFS parameters of the triplet state. The cyclohexanone and cyclopentanone ground-state conformations differ in the C—C—C carbonyl bond angle (α) by about 6° and in the planarity of the carbonyl (θ) by nearly 2°.[30] The same forces that lead to such different conformations in the ground state should lead to quite different conformations in the excited state. But although the overall appearance of the spectra is different,[7] the positions of their transitions, especially their $\Delta M_s = 2$ transitions, are quite similar. The extrema of their $\Delta M_s = 2$ transitions differ by less than 5 G.

Both the observation of multiple transitions at $\Delta M_s = 2$ and of such broad spectra for the three ketones investigated here can be straightforwardly explained if they show extremely broad distributions of conformations around the carbonyl moiety when frozen in a glass. With this possibility in mind, we used molecular mechanics to calculate the Boltzmann distributions of α and θ for DBK and *p,p'*-diMeDBK. The glass transition temperature of methylcyclohexane—corresponding roughly to the temperature at which the viscosity, η, is $\sim 10^{11}$ P—is reported to be 87 K,[31] but the precise temperature at which the various conformers of DBK can no longer interconvert at any meaningful rate is not clear. We therefore calculated the Boltzmann distributions of α and θ for these ketones at both 200 and 100 K. At both temperatures, the distributions of α and θ are sharp, well less than 1° in breadth. The difference in α and θ between the ketones is also less than 1°.

From the breadth of these distributions, we conclude that if the triplet state of DBK were similar to those of cyclohexanone and cyclopentanone—which possess localized carbonyl triplets—it would not show multiple extrema for the $\Delta M_s = 2$ transition and the spectrum as a whole would be sharper. Also, if the triplet states of DBK, *p*-MeDBK, and *p,p'*-diMeDBK were localized to the carbonyl, then the conformations they display around the carbonyl would be so similar that the three ketones should display extremely similar spectra. Since neither of these is the case, we conclude that *the three ketones exhibit triplet states which are not localized to the carbonyl, but are delocalized into the phenyl rings; small changes in the orientation of the phenyl rings relative to the carbonyl and to each other lead to large changes in the amount of delocalization*, thus leading to broad spectra.

Figure 5 shows three successive spectra (a, b, and c, where a is the earliest) taken of a single sample of DBK frozen in methylcyclohexane glass at 15 K. In the earliest spectrum, the $\Delta M_s = 2$ transition has an absorptive/emissive shape. We postulate that the absorptive transitions are due to one set of conformers frozen in the glass, the emissive to another set. In the two later spectra, the absorptive part of the $\Delta M_s = 2$ transition gradually disappears.

Certain features of the spectrum decrease in intensity with successive laser shots with no corresponding increase in the intensities of any other features. From the conformational heterogeneity we postulated in the previous paragraph, we conclude that the laser is burning a hole in the sample, removing one set of conformers from the experiment. Thus, we conclude that *the triplet cleavage of certain conformations of these ketones is enthalpically activationless*. The $\Delta M_s = 2$ transitions of the "reactive" conformations are downfield from those of the "unreactive" conformations. If the triplet state of DBK resembled that of an aromatic hydrocarbon, we would conclude that the more reactive triplet states are those with less electron delocalization.[32,33] Carbonyl triplet states, however, are more complex. Calculations have shown that both spin–spin and spin–orbit components contribute to their ZFS parameters,[27–29] and the relative and absolute contributions of these two components are a sensitive function of conformation.

Unrestricted Hartree–Fock AM1 calculations are used to model the delocalization of the triplet states. While it is clear that the triplet excited states of these ketones should have different low-energy conformations than do their ground states—most notably the pyramidalization of the carbonyl moiety—they should not be able to explore these conformations when frozen into a glass at 15 K. The broadness of our spectra confirms that the excited states are unable to fully explore their conformational space; otherwise, they would all find single minima. We therefore run the calculations on the low-energy conformers we find for DBK and its derivatives by molecular mechanics. We do not minimize the conformations since we do not know which degrees of freedom the molecule is able to explore. Figure 6 shows the results of the AM1 calculations. All atoms with negligible (less than 0.1) electron density from the calculations are unlabeled. The total electron density should add to 2.

For DBK, most of the unpaired electron density is localized in the $n\pi^*$-orbitals of the carbonyl, but a significant amount can be found in the phenyl rings, alternating from carbon to carbon between spin-up and spin-down electrons. Notably, one ring displays slightly more electron density than the other, the result of slightly different orientations of the rings relative to the carbonyl.

As is the case for triplet DBK, most of the electron density for *p*-MeDBK is $n\pi^*$ on the carbonyl, with a significant residual density on the phenyl rings. In fact, the methyl-substituted ring has more electron density than either ring of DBK. For *p,p'*-diMeDBK, each ring has slightly more density than do those of DBK, and as for DBK, the two rings do not have identical densities.

Extensive experimental work[34,35] has been reported on the triplet electron distribution of the aromatic ketone benzophenone (BP). ^{3}BP, like ^{3}DBK, has most of its unpaired spin localized to the carbonyl, with about half the unpaired electron density localized to a nonbonding orbital on oxygen, about a quarter of the density on the carbonyl carbon, and the rest delocalized over the phenyl rings. Both calculations[27] and experiment[2] indicate that the spin distribution of ^{3}BP is a sensitive function of conformation.

Conclusions. We draw the following conclusions from our experiments.

(1) There are conformations of DBK and its derivatives from which the triplet cleaves with little or no activation energy.

(2) Different conformations of DBK have different ZFS parameters and different amounts of unpaired electron density in the phenyl rings.

(3) Methyl substitution of the phenyl ring of DBK does not change the conformation of the ketone, but changes the triplet ZFS parameters, increases the unpaired electron density in the substituted phenyl ring, and increases the rate of triplet cleavage. This increase in rate is not due to a decrease in activation energy.

DBK appears to cleave from only certain conformations of its triplet state. These "reactive" conformations are those with increased unpaired electron density in a phenyl ring. Methyl substitution of a phenyl ring increases the percentage of conformations with sufficient unpaired electron density in that phenyl ring and therefore increases the rate of triplet cleavage.

These results are consistent with the work of Wagner et al.[3] in which the conformation of the phenyl ring of α-phenylcyclohexanone relative to the carbonyl serves as an on/off switch for triplet-state α-cleavage.

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