

In conclusion, high-pressure Raman spectra of  $[\text{Me}_3\text{S}][\text{HgCl}_3]$  provide evidence for a pressure-induced transition at 1.2 GPa, with major involvements on vibrational modes. The best evidence lies in the Hg-Cl stretching region, which is the most significant for the identification of a local structural change around mercury. We suggest a transition from planar trigonal  $\text{HgCl}_3$  to tetrahedral, or pseudotetrahedral,  $\text{HgCl}_4$  units sharing two apexes or one edge along the chain. This phase change is reversible, confirming the larger stability, at ambient pressure, of the trigonal planar with respect to the tetrahedral form of coordinated mercury. Although

phase transitions of tri- and tetrachloromercurate compounds have been known for some time to occur by changing temperature,<sup>16-18</sup> to our knowledge this is the first example of a pressure-induced coordination change in this class of materials.

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## Combined Effect of Isotopic Substitution, Temperature, and Magnetic Field on the Lifetimes of Triplet Biradicals

Jin-Feng Wang, V. Pushkara Rao, Charles Doubleday, Jr.,\* and Nicholas J. Turro\*

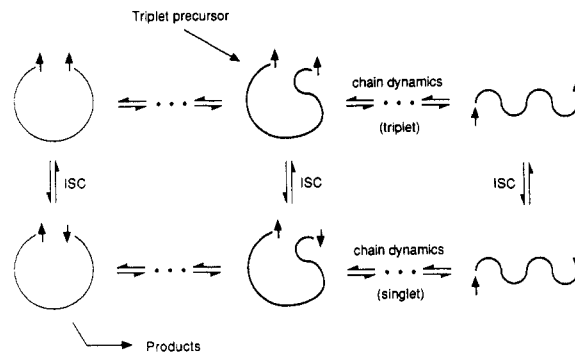
Department of Chemistry, Columbia University, New York, New York 10027 (Received: July 5, 1989)

Lifetimes  $\tau$  for decay of triplet biradicals derived from 2-phenylcycloalkanones were measured by nanosecond transient absorption under conditions designed to probe the contribution of intersystem crossing and chain dynamics to the observed decay. The temperature dependence of  $\tau$  was measured at both 0 and 2 kG magnetic field, and also in the presence of 0.004 M  $\text{MnCl}_2$ . Under a variety of conditions of temperature, solvent viscosity, and magnetic field, the lifetime of the biradical derived from 2-phenylcyclohexanone was compared with its perdeuterated analogue and with a 1:1 mixture of 1,2- $^{13}\text{C}_2$  and 1,12- $^{13}\text{C}_2$  isotopomers. The magnetic isotope effect on  $\tau$  and the temperature dependence of  $\text{Mn}^{2+}$  quenching support chain dynamics as the rate-limiting step at  $-85^\circ\text{C}$  and intersystem crossing as the rate-limiting step at room temperature. However, the magnetic field effect on  $\tau$  reaches a maximum around  $-50^\circ\text{C}$  and persists even at  $-99^\circ\text{C}$ , in contrast to the magnetic isotope effect and  $\text{Mn}^{2+}$  quenching, which are absent at low temperature. The significance of this observation is discussed.

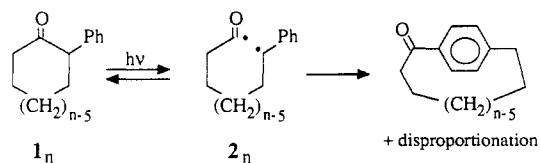
Flexible triplet biradicals offer an excellent opportunity to study the effect of chain motions and chain conformations on the electron spin dynamics. In the general description shown in Scheme I, triplet biradical decay is due to a competition between intersystem crossing (ISC) and chain dynamics.<sup>1</sup> The other major process in Scheme I, product formation from the singlet biradical, is assumed to be much faster than ISC or chain dynamics.<sup>1</sup> To understand the dynamics of triplet biradicals, our procedure is to change ISC or chain dynamics in a well-defined way and observe the effect on the triplet biradical lifetime  $\tau$ . An important parameter is the relative contribution of spin dynamics vs chain dynamics to  $\tau$  under given conditions. The goal is a comprehensive model of the total dynamics, which would, for example, allow one to predict the optimum conditions for isotopic enrichment.

Two limiting cases of Scheme I are clear. If chain motions are much faster than ISC, e.g., at high temperature and low viscosity, then  $\tau$  is determined only by ISC and  $\tau^{-1}$  is the conformationally averaged ISC rate constant. If chain motions are much slower than ISC, e.g., at low temperature or very high viscosity, then  $\tau$  is essentially a measure of the rate at which the biradical can adopt a conformation poised for product formation. The transition from rate-limiting ISC to rate-limiting chain dynamics is not expected to be sharp, and under a broad range of conditions both are expected to contribute to  $\tau$ . Because of this inherent complexity, we have examined five different methods of probing the interplay of spin and chain dynamics: the effect on  $\tau$  of variations in temperature, solvent viscosity, external magnetic field, paramagnetic nuclei, and bimolecular encounters with paramagnetic ions. We have reported extensively on the temperature dependence of  $\tau$  in the earth's magnetic field<sup>2</sup> and the magnetic field effect

### SCHEME I



### SCHEME II



at room temperature.<sup>3</sup> In this paper we report unexpected results obtained from varying both temperature and magnetic field together, as well as results on isotopic substitution, increase in solvent viscosity, and paramagnetic ion quenching. Lifetimes of biradicals  $2_n$  were measured, derived from type I photolysis of ketones  $1_n$  (Scheme II), where  $n$  is the number of carbons in the biradical chain. The products were previously reported.<sup>4</sup>

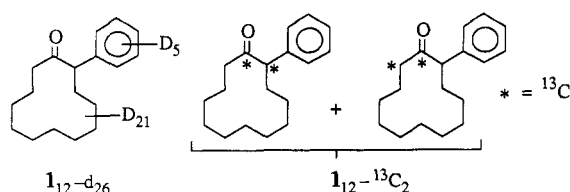
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## SCHEME III



To a first approximation, viscosity and temperature are expected to affect only chain dynamics; an external magnetic field, paramagnetic nuclei, and paramagnetic ions are expected to affect only ISC. In a magnetic field large enough that the Zeeman splitting is much larger than the singlet-triplet gap, the outer two triplet levels are sufficiently far in energy from the singlet that only  $T_0 \rightarrow S$  ISC is important, so the ISC rate constant decreases relative to zero field.<sup>3</sup> The hyperfine coupling (HFC) of nuclei to the electron spin is a major ISC mechanism and is obviously influenced by isotopic substitution that changes the total HFC in the biradical. Paramagnetic ions are well-known to interact with radicals by electron spin exchange and have been found to accelerate ISC in biradicals. Each of these probes—magnetic field effect, magnetic isotope effect, and paramagnetic quenching—is sensitive to the contribution of ISC to the overall dynamics, but since the probes are different they may yield different information. Thus we employ all of them.

## Experimental Section

Unlabeled ketones  $\mathbf{1}_6$  and  $\mathbf{1}_{12}$  were synthesized as previously reported.<sup>5</sup> Labeled ketones (Scheme III) were synthesized as follows.  $\mathbf{1}_{12}\text{-}d_{26}$  (95% perdeuterated by NMR) was prepared in 75% yield from  $\mathbf{1}_{12}$  by reaction with excess  $D_2O$  in an autoclave at 250 °C and 1000 psi for 3 days, in the presence of  $D_2$ -reduced  $PtO_2$  and  $Na_2O_2$ .<sup>6</sup> A 1:1 mixture of  $\mathbf{1}_{12}\text{-}1,2\text{-}^{13}C_2$  and  $\mathbf{1}_{12}\text{-}1,12\text{-}^{13}C_2$  was obtained from 1,10-dibromodecane via the following sequence:<sup>7</sup> (1)  $K^{13}CN$ ; (2) hydrolysis; (3) esterification; (4) acyloin condensation; (5) 2 equiv  $Br_2/AcOH$ ; (6) 2 equiv  $LiCuPh_2$ .

Triplet biradicals were generated by photolysis of ketones at 308 nm with a Lambda Physik excimer laser (ca. 18 ns fwhm, <10 mJ per pulse). Lifetimes were measured by nanosecond transient UV absorption monitored at 320 nm. Analyzing light was generated by pulsing a 150-W Xe high-pressure lamp (PRA Model 301 power supply, PRA Model 305 pulser) and detected through an ISA H 10 monochromator using six dynodes of an RCA 4840 photomultiplier tube. Signals were digitized with either a Biomation 4500 digital oscilloscope or a Tektronix 7912 AD programmable digitizer. Data analysis was performed on a PDP 11/23 or a Macintosh. The excitation/detection geometry was right angle, except for the magnetic field dependence in which crossed beams, 35°, were used.

Magnetic field studies were performed using a permanent 2-kG magnet. Variable-temperature studies were performed using an optical Dewar and chilled or heated  $N_2$  gas. Temperature readings were made on an Omega Digicator with constantan thermocouple, which was attached directly to the cell holder in the Dewar.

As measured by GC, the product distribution was insensitive to changes in external magnetic field, isotopic substitution, and solvent.

## Results and Discussion

Table I shows magnetic isotope effects on  $\tau$  for isotopically substituted  $\mathbf{1}_{12}$  as a function of magnetic field, solvent viscosity, and temperature. The top row shows the isotope effects in methanol at room temperature in the earth's magnetic field. Qualitatively, the results are in the direction expected from the relative HFC. One can attempt a more quantitative interpretation

TABLE I: Lifetimes of Biradicals  $\mathbf{2}_{12}$ ,  $\mathbf{2}_{12}\text{-}d_{26}$ ,  $\mathbf{2}_{12}\text{-}^{13}C_2$ , and  $\mathbf{2}_6$ 

solvent	T, °C	mag field, kG	lifetime, ns			
			$\mathbf{2}_{12}$	$\mathbf{2}_{12}\text{-}d_{26}$	$\mathbf{2}_{12}\text{-}^{13}C_2$	$\mathbf{2}_6$
methanol	22	0	69	83	50	65
methanol	22	2.0	84	89	72	65
glycerol	20	0	760	760	760	100
glycerol	20	2.0	770	750	765	100
methanol	-85	0	570	560	580	235
methanol	-85	2.0	630	660		230
mixture <sup>a</sup>	-99	0	790			
mixture <sup>a</sup>	-99	2.0	890			
mixture <sup>a</sup>	-135	0	20100			
mixture <sup>a</sup>	-135	2.0	20000			

<sup>a</sup> 64.5 vol % pentane, 24.4 vol % methylcyclohexane, 11.1 vol % 1-propanol.

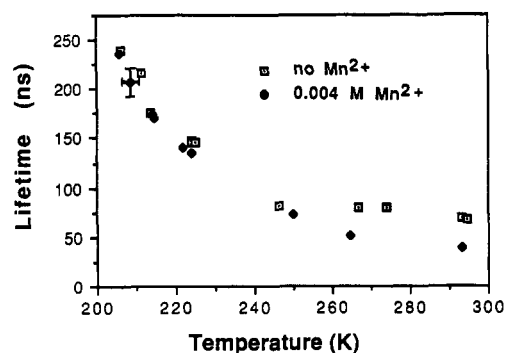


Figure 1. Lifetimes (ns) for decay of  $\mathbf{2}_{12}$  in methanol as a function of temperature in the presence of 0.004 M  $MnCl_2$  and in its absence. Error bars in upper left are typical of data below 240 K. Above 240 K, error bars are about the size of the data symbols.

by assuming that  $\tau^{-1}$  is proportional to the square of an effective HFC given by<sup>8</sup>  $\langle HFC \rangle^2 \propto \sum_i A_i^2 S_i(S_i + 1)$ , where  $A_i$  is the HFC of nucleus  $i$  with spin  $S_i$ . Substituting the known values<sup>9</sup> of  $A_i$ , one calculates relative lifetimes for  $\mathbf{2}_{12}$ ,  $\mathbf{2}_{12}\text{-}d_{26}$ , and  $\mathbf{2}_{12}\text{-}^{13}C_2$  of 1.0:15.8:0.055 instead of the observed ratio of 1.0:1.2:0.72. The simplest explanation for the discrepancy is that HFC is only a minor ISC mechanism in these biradicals, so that isotopic substitution makes little difference in the lifetime. This is consistent with previous evidence<sup>2a,10,11</sup> that supports spin-orbit coupling (SOC) as the dominant ISC mechanism in acyl-benzyl biradicals such as  $\mathbf{2}$ .

The second row of Table I shows the magnetic isotope effect at 2 kG. As expected, all lifetimes are increased relative to the 0 kG results as a result of removing the  $T_{\pm 1}$  states from the singlet, and the relative values are still qualitatively consistent with the relative HFC. We attempted to fit the relative values of the six lifetimes for  $\mathbf{2}_{12}$  in the first two rows of Table I by adopting an infinite temperature model in which  $\tau^{-1} = \sum_i f_i \tau_i^{-1}$ , where  $f_i$  is the equilibrium population of biradical conformer  $i$  and  $\tau_i^{-1}$  is the ISC rate constant of conformer  $i$ . Using an analytical form for the biradical end-to-end distribution function<sup>8a</sup> and reasonable models for  $\tau_i^{-1}$  and the dependence of SOC<sup>12</sup> and the singlet-triplet gap<sup>13</sup> on the end-to-end distance, we were unable to fit all six data points within experimental error. (The 0 kG results could be fit, but inclusion of a magnetic field presented problems.) We suspect that the rapid but finite stochastic motion of the chain must be

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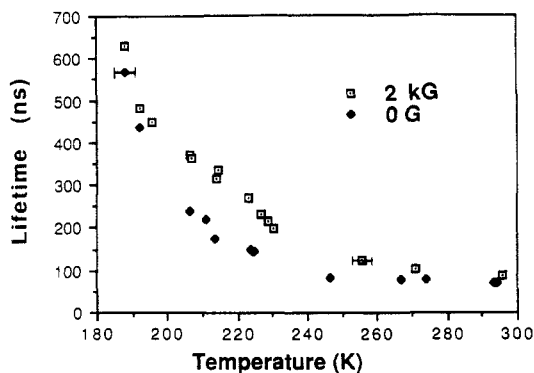
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**Figure 2.** Lifetimes (ns) for decay of  $2_{12}$  in methanol as a function of temperature in the earth's magnetic field and in a 2-kG magnetic field. As explained in ref 17 of the text, temperature variation accounts for most of the uncertainty (error bars).

taken into account to give a proper quantitative treatment.<sup>14</sup>

At low temperature  $T$  or high solvent viscosity  $\eta$ , chain dynamics becomes the rate-limiting step for biradical decay. At that point, the magnetic isotope effect, magnetic field effect, and the effect of paramagnetic ions are expected to vanish. Figure 1 confirms this expectation for the effect of added paramagnetic  $Mn^{2+}$  ions. For  $T < -20$  °C the addition of 0.004 M  $MnCl_2$  has no effect on  $\tau$  for  $2_{12}$ , and above this temperature  $\tau$  decreases in the presence of  $Mn^{2+}$ , apparently as a result of bimolecular spin exchange<sup>15</sup> with the biradical.<sup>16</sup> As a control we measured the effect of  $Mn^{2+}$  on the lifetime of  $2_6$ , whose chain is short enough that ISC is still rate limiting even at  $-90$  °C.<sup>2b</sup> For  $2_6$  in methanol at  $-82$  °C we found  $\tau = 165$  ns in the absence of  $Mn^{2+}$  and  $\tau = 120$  ns in the presence of 0.004 M  $MnCl_2$ . This confirms that when  $Mn^{2+}$  should have an effect at low temperature, it does.

Table I shows that at 20 °C in glycerol ( $\eta = 1400$  cP) the magnetic field effect and magnetic isotope effect vanish, as expected for high viscosity where chain dynamics are rate limiting. At  $-85$  °C in methanol, however, we found that, although the magnetic isotope effect vanishes as predicted, a *small magnetic field effect still persists*. This finding was unexpected, and we averaged many measurements before concluding that the effect is real.<sup>17</sup> In fact, the temperature dependence of  $\tau$  in methanol between +20 and  $-85$  °C (Figure 2) shows that the magnetic field effect actually increases as  $T$  is lowered and is at a maximum around  $-50$  °C. Table I shows that the magnetic field effect still persists at  $-99$  °C (in a solvent mixture) and finally disappears by  $-135$  °C. For comparison we include lifetimes for  $2_6$  (last column of Table I), a biradical with rate-limiting ISC<sup>2b</sup> under all conditions so far examined, but whose short chain length gives it such a large singlet-triplet gap that  $\tau$  is not affected by a 2-kG field.

The magnetic field effect at low temperature is particularly striking in view of our previous study of the temperature dependence of  $\tau$  at 0 kG,<sup>2b</sup> which showed that the Arrhenius parameters for decay of  $2_{12}$  below  $-50$  °C ( $E_a = 3.6$  kcal,  $\log A/s^{-1} = 10.6$ ) are typical of chain dynamics, and are considerably different from those above 0 °C ( $E_a = 1.2$ ,  $\log A = 8.1$  s<sup>-1</sup>), which correspond to rate-limiting ISC. This gives a remarkable set of results: the  $T$  dependence of  $\tau$  at 0 kG<sup>2b</sup> and the magnetic isotope effect in Table I both support rate-limiting chain dynamics at  $-85$  °C, but

the magnetic field effect in Table I shows that ISC is important at  $-85$  °C!<sup>18</sup>

That ISC affects the biradical decay rate even at low temperature is not unreasonable. In a strict sense, the transition from rate-limiting ISC to rate-limiting chain dynamics never really takes place. Over practical temperature ranges, the dynamics are always a mixture of ISC and chain dynamics. In Scheme I, ISC becomes the exclusive rate-limiting step only at infinite temperature, and chain dynamics becomes exclusively rate limiting only when ISC is infinitely faster (complete singlet-triplet equilibration in each biradical conformer). In a simulation of our data for the  $T$  dependence of  $\tau$  at 0 kG for  $2_{12}$ ,<sup>2b</sup> the eigenvectors of the matrix of rate coefficients showed that the singlet and triplet states are ca. 90% equilibrated at  $-85$  °C.<sup>19</sup> Thus even at this low temperature about 10% of the lifetime is due to ISC, and in principle  $\tau$  can be affected by magnetic fields, paramagnetic ions, and magnetic isotopes. However, it is *only the magnetic field effect* that actually persists.

In Figure 2, the unusual temperature dependence of the magnetic field effect is probably due to the increased importance of electron spin relaxation as the temperature is lowered, which has its own characteristic  $T$  dependence. Although a proper discussion must await a stochastic Liouville simulation including relaxation terms, we offer the following qualitative suggestions.  $T_1$  relaxation processes connect all three triplets with the singlet and  $T_2$  processes connect  $T_0$  with S. The frequency-dependent part of the relaxation rate constant is proportional to  $\tau_0/(1 + \omega^2\tau_0^2)$ , where  $\tau_0$  is the correlation time and  $\omega$  is the frequency,<sup>20</sup> equal to 5.6 GHz at 2 kG. At room temperature  $\tau_0$  is short enough that  $\omega^2\tau_0^2 \ll 1$ , and spin relaxation makes a negligible contribution to the biradical lifetime  $\tau$ .<sup>1</sup> At this temperature, the small magnetic field dependence<sup>3</sup> is due solely to the change in the triplet Zeeman levels with respect to the singlet level. Below 260 K the magnetic field effect on  $\tau$  increases. As the temperature decreases  $\tau_0$  increases and the condition  $\omega^2\tau_0^2 = 1$  (at 2 kG) is approached, where  $T_1^{-1}$  makes its maximum contribution to ISC and the field dependence of spin relaxation becomes significant. With a significant contribution of relaxation to ISC below 260 K, one sees a larger magnetic field effect on the observed lifetime  $\tau$ . Even though an increase in  $T_1^{-1}$  makes ISC faster, the biradical decays more slowly at lower temperature, because the effective decay rate becomes increasingly dominated by conformational interconversion rather than ISC. As the temperature gets even lower, approaching  $-100$  °C, the field dependence of spin relaxation increases without bound, but the magnetic field effect on  $\tau$  eventually decreases, for at least two reasons. First, the contribution of the frequency-dependent part of spin relaxation to ISC decreases when  $\omega^2\tau_0^2 \gg 1$ . Second, and probably more important, the contribution of ISC to the observed  $\tau$  becomes very small at  $-100$  °C because chain motions mainly determine the biradical decay. Ultimately, at  $-135$  °C, the contribution of ISC is negligible and no magnetic field effect remains. In this model, the low-temperature magnetic field effect is due to the frequency-dependent part of electron spin relaxation. There is no analogue of this effect for the magnetic isotope effect; therefore the isotope effect is absent at low temperature.

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**Registry No.**  $1_6$ , 1444-65-1;  $1_{12}$ , 50717-87-8;  $2_6$ , 98737-15-6;  $2_{12}$ , 98720-30-0;  $^{13}C$ , 14762-74-4;  $MnCl_2$ , 7773-01-5;  $D_2$ , 7782-39-0.

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