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INDIRECT OBSERVATION OF SPIN POLARIZATION IN TRIPLET FLUORENYLIDENE AT ROOM TEMPERATURE

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Abstract: The spin polarization of triplet fluorenylidene has been observed indirectly at room temperature via CIDEP spectroscopy. The observed absorptive polarization is in agreement with direct observations of the spin polarization of diphenylmethylene at low temperature.

Introduction

When spin-orbit coupling provides a mechanism for intersystem crossing (ISC) in excited species, symmetry selection rules are imposed such that the interconversion between singlet and triplet states occurs via only one of the triplet sublevels. Such selection rules manifest themselves in both initial triplet population and depopulation processes.[1] In real molecules, these selection rules are not perfect, but often more than 90% of initially populated triplets are to be found in only one sublevel.[2] The phenomenon of sublevel selective population is commonly referred to as spin polarization. Such spin polarization is usually a "forgotten" step in the mechanistic thinking of organic chemists, but can be important in the detailed dynamics of organic species with unpaired spins.

Spin polarization is most directly demonstrated at low temperature where relaxation between the triplet sublevels is sufficiently slow, usually by electron spin echo (ESE), optically detected magnetic resonance (ODMR), or electron-nuclear double resonance (ENDOR) spectroscopies.[1,2] Triplet sublevel polarization has been indirectly observed at room temperature via the Chemically Induced Dynamic Electron Polarization phenomenon of time resolved esr (CIDEP), in which non-Boltzmann spin distributions are observed in the radicals which are products of fast triplet state reactions.[3] If a radical-generating reaction occurs from a triplet overpopulated in, for instance, the lowest triplet sublevel faster than spin thermalization occurs, radicals are generated with excess β-spin. The excess β-spin is seen as an absorptive esr signal when observed without field modulation and within the electronic relaxation time (T_1) of the typically much longer (*ca.* 10^{-5} - 10^{-6} s) than that of the triplet (*ca.* 10^{-8} - 10^{-9} s). Conversely, triplets produced in the upper triplet sublevel generate radicals with emissive esr signals.

CIDEP has also been observed at room temperature under conditions where no net chemical reaction need occur by taking advantage of the phenomenon of spin exchange.[4] In these experiments, a stable radical, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is used to probe the spin population of transient triplets. When TEMPO and the polarized triplet collide, they may undergo spin exchange[5] and the net result is transfer of spin polarization from the triplet to TEMPO. This technique makes indirect observation of spin polarization of unreactive triplets (e.g., phenanthrene[4]) possible.

Previous CIDEP studies have focused mainly on the polarizations of the excited states observed on photolysis of ketones and aza-aromatics. We were interested in extending this technique to the observation of polarization of carbene systems because they are ground state triplets with orbitals analogous to the previous systems. *A priori*, diphenylmethylene and fluorenylidene seemed like logical candidates since their precursors are easy to prepare and handle and they are probably the most thoroughly studied of the aromatic carbenes.[6]

On direct photolysis of either diazofluorene or diphenyldiazomethane, the singlet excited diazo compound decomposes to yield the corresponding singlet carbene. Intersystem crossing to the ground state triplet then occurs after loss of nitrogen, mainly via spin orbit coupling. There is substantial evidence that thermal equilibration occurs between the singlet and triplet states of each of these carbenes, but the symmetry selection rules hold for each intersystem crossing step. Doetschman has shown via low temperature ESE experiments that >93% of the diphenylmethylene triplets are "born" into the lowest triplet sublevel (Scheme 1).[7] With such a model, we expected to observe absorptive CIDEP polarization upon photolysis of triplet carbene precursors.

Scheme 1. An energy level diagram of the photolysis of diphenyldiazomethane adapted from reference 7. The energy levels are approximately to scale, except for the triplet sublevel splittings, which are greatly exaggerated for clarity. The wiggly lines indicate the most probable pathways.

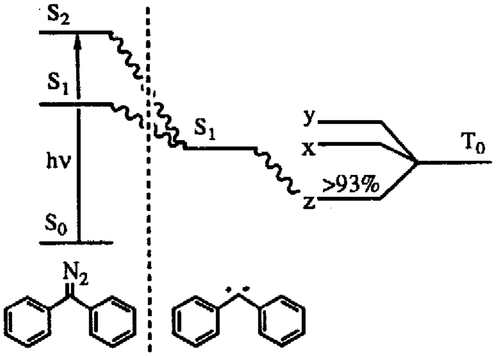
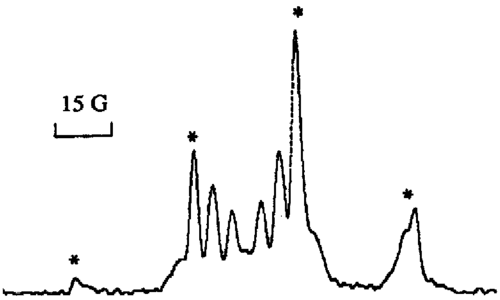


Figure 1. Absorptively polarized 9-fluorenyl radical spectrum observed on photolysis of diazofluorene in cyclohexane. The 4 peaks with stars are the superposition of the spectrum of cyclohexane-1-yl.

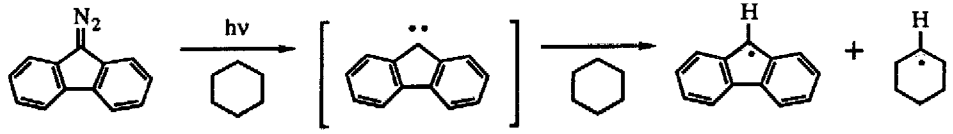


Results

On 266 nm photolysis (4th harmonic Nd:YAG, ca. 10 mJ/pulse, 15 ns pulse width, 20 Hz) of an argon saturated, flowing solution of diazofluorene[8] (5 mM) in cyclohexane in the cavity of a Bruker ER100D esr (modified for direct detection[9]) at time delays of the order of .25 to 5 µs, an absorptive signal characteristic of the 9-fluorenyl radical[10] was observed (Figure 1). The 9-fluorenyl (formed by the reaction in scheme 2) signal is superposed with a signal derived from the cyclohexane-1-yl radical, which shows an E/A* polarization. Very weak absorptive signals were detected using chloroform and triethylsilane as solvents. No signal was observed using carbon tetrachloride or acetonitrile. Photolysis of air saturated cyclohexane diazofluorene solutions or cyclohexane solutions of 9-fluorenone yielded broad, structureless emissive signals with identical g-values that were larger than for the 9-fluorenyl radical (Figure 2). These latter signals are attributed to the fluorenone ketyl; the emissive signal from the air-saturated solutions is assigned to secondary photolysis of fluorenone formed as a result of the reaction of O_2 and fluorenylidene.

Attempts were also made to observe diphenylmethylene spin polarization via analogous hydrogen abstraction reactions using cyclohexane, cumene, triethylsilane, and 1,4-cyclohexadiene, all without success. Attempts to observe

Scheme 2. Hydrogen abstraction from cyclohexane by fluorenylidene.



diphenylmethylene spin polarization using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as either an O atom donor[11,12] or spin exchange probe[4] were complicated by the formation of benzophenone as a reaction product.[11] All signals observed in the diphenyldiazomethane/TEMPO system were due to emissively polarized TEMPO and benzophenone ketyl. Figure 3 shows the spectrum obtained from a cyclohexane solution of diphenyldiazomethane (10 mM) and TEMPO (10 mM) under conditions where the ketyl signal is minimized (addition of air or isoprene).

Attempts to use TEMPO specifically as a spin polarization probe were made using dimesityldiazomethane.[13] Flash photolysis experiments showed that dimesitylmethylene reacts with TEMPO with a rate constant whose upper limit is about 5×10^4 $M^{-1}s^{-1}$, which is clearly too slow to allow for the formation of polarized radical products. However, IR analysis of the photolysis products showed the formation of dimesityl ketone, and the signals observed on photolysis of argon saturated dimesityldiazomethane/TEMPO and dimesityl ketone/TEMPO solutions were identical emissively polarized signals such as in figure 3. These results were consistent over a wide variety of concentrations.

Figure 2. Emissively polarized fluorenone ketyl signal observed on photolysis of fluorenone or air saturated solutions of diazofluorene in cyclohexane.

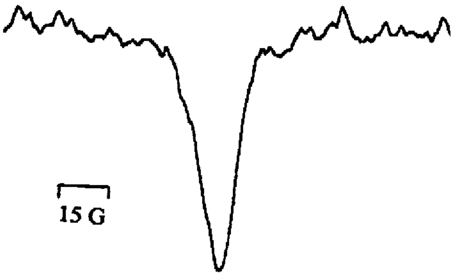
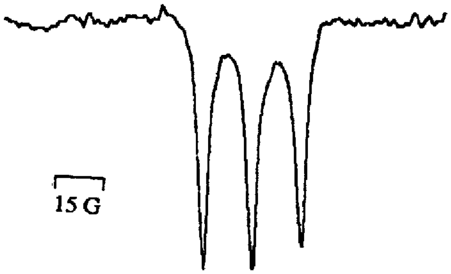


Figure 3. Emissively polarized TEMPO signal observed on photolysis of carbene precursors in the presence of TEMPO in cyclohexane.



Discussion

The rate constant for hydrogen abstraction from cyclohexane (Scheme 2) by fluorenylidene is 8.3×10^7 $M^{-1}s^{-1}$,[14] which is anomalously high for triplet aromatic carbenes. In neat cyclohexane (9.3 M), the pseudo-first order rate constant is 7.7×10^8 s^{-1}. This is in contrast to diphenylmethylene, which has a first order decay rate of 5.7×10^5 s^{-1} in cyclohexane.[15] While the electronic spin lattice relaxation times for diphenylmethylene and fluorenylidene at room temperature are not known, it is reasonable to assume that they are very similar. Thus, with such disparate abstraction rates, it is certainly not surprising that spin polarization is observed only in the fluorenylidene case. The observed absorptive polarization shows that the carbene is initially populated in the lowest triplet sublevel. Although the direct observation of the spin polarization of fluorenylidene has not been reported, the qualitative result is expected to be the same for fluorenylidene, diphenylmethylene and most other diphenyl-type carbenes. Such consistency is generally observed among aliphatic ketones, aromatic ketones, n,π^* aza-aromatics, and "pure" aromatic hydrocarbons. We have shown that triplet fluorenylidene is largely populated in the lowest triplet sublevel, as expected from previous diphenylmethylene results.

Product analysis studies have shown that triplet hydrogen abstraction by fluorenylidene is a relatively minor pathway, and that most of the products appear to be formed by reactions of thermally populated singlets.[16] CIDEP does not allow us to determine the fraction of reactions occurring by the singlet pathway, but it does show that the triplet pathway for fluorenylidene is substantially faster than for diphenylmethylene and must be moderately competitive with the singlet route.

The emissively polarized signals obtained from photolysis of diphenyldiazomethane-TEMPO mixtures are probably due to secondary photolysis of benzophenone. Imamura, *et al* showed that triplet benzophenone can transfer emissive polarization to TEMPO via either spin exchange or energy transfer.[4] While we cannot eliminate direct carbene-TEMPO interaction completely, it seems very unlikely, as it requires an inversion of the triplet sublevels or selection rules for intersystem crossing between liquid helium and room temperatures. The possibility that the signal is derived from the reaction of the carbene and TEMPO to give ketone and amino radical[11] is eliminated by the observation of polarized signal in the dimesitylmethylene case.

Conclusions

We have extended the CIDEP method into a new class of compounds, and have run into some of its limitations as well. Other fast radical-producing reactions of carbenes may be expected to reveal the spin polarizations of the carbene involved. Such studies are continuing in this laboratory.

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