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Supplementary Material Available: Supplementary Figure SF1 and caption, crystallographic summary, and tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters (5 pages); table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

Magnetic Field Effect on Reactions of Radical Pairs Possessing Large Spin–Orbit Coupling Constants

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In several previous reports, we have described how free radical chain reactions can be initiated by UV laser photolysis in thin solid films at cryogenic temperatures.[1-11] In this communication, we report that application of an external magnetic field during photolysis has a dramatic effect on the measured quantum yield for the solid-state reaction of chlorine with methylcyclopropane.

A typical experiment of this type begins with deposition of a mixture of gaseous chlorine and a simple hydrocarbon from the vapor onto a CsI window at 77 K in a high-vacuum Dewar vessel. The thin solid film is then irradiated with a pulsed nitrogen laser (337 nm) to dissociate a small fraction of the chlorine molecules to atoms. This begins a sequence of free radical chain propagation reactions forming HCl and a chlorinated hydrocarbon; e.g., for photochlorination of methylcyclopropane,[12]

$$Cl_2 + h\nu \leftrightarrow 2Cl^\bullet \qquad (1)$$

$$Cl^\bullet + \text{cyclo-}C_3H_5CH_3 \rightarrow HCl + \text{cyclo-}C_3H_5CH_2^\bullet \qquad (2)$$

$$\text{cyclo-}C_3H_5CH_2^\bullet + Cl_2 \rightarrow \text{cyclo-}C_3H_5CH_2Cl + Cl^\bullet \qquad (3)$$

The concentrations of reactants and products are monitored by FTIR spectroscopy as a function of incident cumulative laser fluence. In this way, we are able to determine the photochemical quantum yield or number of product molecules formed per UV laser photon absorbed by the sample. The details of this procedure are described elsewhere.[12]

As illustrated in Figure 1, application of a magnetic field causes the quantum yield to drop sharply from 180 ± 20 (the zero-field value) to a minimum of 70 ± 10 at about 300 G. Thereafter, the yields increase with applied field, reaching a plateau of 120 ± 10 above 1000 G. No experiments were conducted above 3000 G.

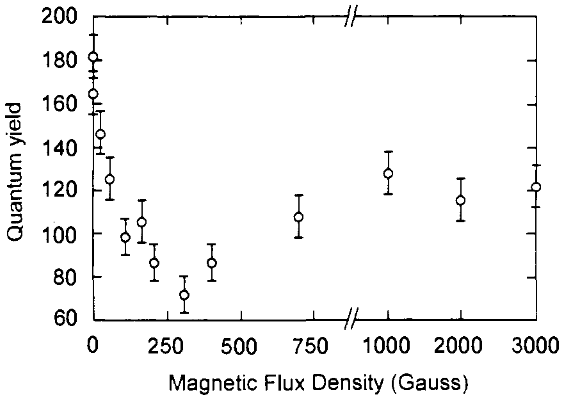

Figure 1. Photochemical quantum yield for solid-state photochlorination of methylcyclopropane versus magnetic flux density.

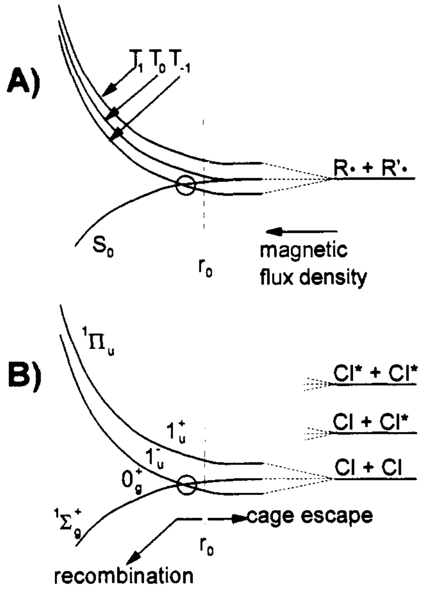

Figure 2. Schematic diagram of potential energy surfaces responsible for magnetic field effects in (A) molecular radicals with small spin–orbit coupling constants (or heavy-atom radicals with ill-defined orbital angular momenta) and (B) molecular chlorine surfaces relevant to this study. The magnetic components of the 1_u spin–orbit state are labeled + or − according to the value of M_J (+1 or −1, respectively), whereas the + on the 0_u^+ term symbol denotes positive reflection symmetry. A complete correlation diagram for the chlorine radical pair states is presented in ref 31.

It is now well established that magnetic fields can affect chemical reactions in solids[13] and in solution[14-19] by altering the rate of radical recombination, the reverse of reaction 1, relative to cage escape and reaction. An external magnetic field can shift the potential energy surfaces of the radical pair, causing crossings between repulsive and attractive surfaces in the asymptotic region. A typical scheme for this is pictured in Figure 2A, where the crossing of interest is circled. The position of the crossing can be less than, greater than, or equal to the radical pair contact distance (indicated schematically in Figure 2 by r_0), depending on the applied magnetic flux density. At the crossing, the two states can be coupled by the nuclear hyperfine interaction, which provides a mechanism for transferring the system from a repulsive

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† Alfred P. Sloan Research Fellow, 1990–94.

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to an attractive surface (or vice versa). Since the probability of this transition depends on the position of the crossing relative to r_0, changes in the magnetic flux density indirectly alter the net rate of reaction. Another commonly cited mechanism for magnetic effects, the so-called Δg mechanism, will not be considered here.[14]

It is widely believed that spin–orbit mixing of the singlet and triplet states provides an additional mechanism for electronic relaxation, thereby diluting the magnetic field effect.[20-22] Because spin–orbit coupling constants[23] are nearly always larger than nuclear hyperfine coupling constants[24] (particularly in heavy atoms),[25] one might conclude that heavy-atom magnetic field effects should be difficult to observe.[26] We believe that this view is false and misleading because it fails to recognize that, in the adiabatic limit, relaxation between spin–orbit states of heavy-atom radicals occurs only as a result of other perturbations (e.g., hyperfine or radiative coupling or rotation of the radicals).

Our study outlined above is one of a growing number in which heavy-atom magnetic field effects have been observed.[20,27-29] In this communication we present an explanation for the large magnetic effect involving reaction of Cl atom pairs. The argument is extended to explain the observation of magnetic effects in other heavy-atom systems.

A schematic diagram of potential energy surfaces relevant to reactive Cl atom pairs generated in reaction 1 is presented in Figure 2B. Photodissociation near 337 nm is known to occur mainly by excitation from the ground $^1\Sigma_g^+$ state to the repulsive $^1\Pi_u$ surface.[30,31] As the atoms separate and these two surfaces approach each other to within the spin–orbit coupling constant (about 900 cm^{-1}), spin and orbital angular momentum become ill-defined, and the surfaces are instead characterized by total spin–orbit angular momentum Ω, which is quantized along the interatomic axis. Thus, while the *characters* of the surfaces change, they nonetheless retain a distinct identity. Transitions between attractive and repulsive surfaces may be induced by nuclear hyperfine coupling[32] at crossing points such as that denoted by the circle in Figure 2B. This is analogous to the scheme represented by Figure 2A. The crossings depicted in Figure 2B are quite general for pairs of atoms having magnetic nuclei.[33] Therefore, magnetic effects in heavy-atom systems may be just as strong and prevalent as for light atoms.

In cases where a heavy-atom radical center is located in a molecule rather than an isolated atom, the electronic state is often orbitally nondegenerate (e.g., $^2A_1$ instead of ^2E), so that the asymptotic states are (essentially) degenerate despite the fact that spin and orbital motions of the unpaired electron are strongly coupled. The correlations of the asymptotic states with the valence states of the radical pair precursor are usually well-defined, and magnetic effects can be interpreted by the scheme represented by Figure 2A.

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3-*o*-Carboranylcarbenes: Linear, Ground-State Triplets[†,1]

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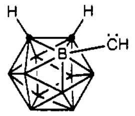
We have recently described the generation and reactions of the first boron-substituted carbenes, **1** and **2**.[2] In these papers we argue from considerations of reactivity for the special prominence of triplet-state reactions of these carboranylcarbenes.[3] Here we report the EPR spectra of **1** and **2** and show that the triplets are the ground states of these probably linear reactive intermediates.



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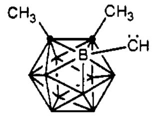

2

Degassed solutions (~10 mM) of the diazo compound precursors[2] of **1** and **2** in methylcyclohexane were frozen at 10 K, and the glasses were irradiated through Pyrex in the EPR cavity with a 200-W high-pressure mercury arc for 30 min. The resulting spectra were persistent at low temperature, but disappeared irreversibly at about 32 K. For **1**, a plot of peak height vs $1/T$ was linear over the range 14–30 K. Thus the Curie law is obeyed, and the ground state of **1** (and presumably the other 3-carboranylcarbenes) is the triplet. At most, the triplet may lie only a few calories above the singlet.

The zero-field splitting parameter, $|D/hc|$, for **1** and **2** is 0.657 and 0.661 cm^{-1}, respectively. This matches well the values of 0.6860 and 0.6920 cm^{-1} reported by Hutton, Roth, and Chari for two carbon-substituted carboranylcarbenes, **3** and **4**.[4] $|D/hc|$ is

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[†] This paper is dedicated to the memory of Professor Gerhard L. Closs, 1928–1992.

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