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SPECTROSCOPIC AND CHEMICAL EVIDENCE FOR METHYLENE SINGLET-TRIPLET INTERSYSTEM CROSSING IN SOLUTION

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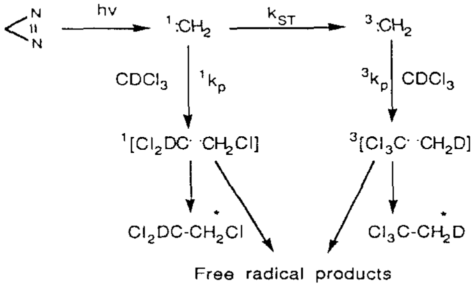
ABSTRACT

Singlet-triplet intersystem crossing of methylene in perfluorohexane solution has been investigated by CIDNP. Evidence of this process is shown by the polarized absorption ^{1}H-NMR signal of Cl_3C-CH_2D, a triplet product, which is obtained upon direct irradiation of diazirine in perfluorohexane solution containing saturated deuteriochloroform. These results are confirmed by product analysis as a function of dilution by perfluorohexane. The rate constant for intersystem crossing for singlet methylene to triplet methylene is evaluated as ca. 8 x 10^8 S^{-1} from the data.

Methylene (CH_2), *the parent carbene, has been studied extensively by chemists,*[1,2] spectroscopists,[3] and chemical physicists.[4,5] Its unique chemistry is primarily due to the substantially different chemical behavior of two low-lying electronic states, the ground triplet state ($^3CH_2$) and the lowest singlet state ($^1CH_2$). The energy difference between the two states has been calculated theoretically, and estimated experimentally to be about 9-10 kcal/mol.[6] Intersystem crossing (ISC) of methylene in the gas phase has been reported.[5,7] The rate of methylene ISC has been obtained directly in the gas phase by monitoring the absorption decay of $^1CH_2$ at 610 nm,[5] and by detecting the growth of the triplet absorption at 141.5 nm,[7] respectively. In contrast to the extensive studies of methylene ISC in the gas phase, the deactivation of singlet-to-triplet CH_2 has not been fully established in solution.[8] The reactivity and the ISC of $^1CH_2$ in solution has been studied mainly by product analysis and not by spectroscopic methods. However, chemically induced dynamic nuclear polarization (CIDNP) has been applied to carbene chemistry to assign spin multiplicities and deduce reaction mechanisms.[9] In this paper we provide evidence of singlet-triplet deactivation of methylene studied using both the CIDNP technique and product analysis.

Photolysis (1000W Xe-Hg lamp, pyrex) of an argon-purged $CDCl_3$ solution containing diazirine at ambient temperature inside an NMR cavity resulted in a polarized ^{1}H-NMR spectrum (Figure 1b). The dominating emission signal is attributed to spin-polarized 1-deuterio-1,1,2-trichloroethane (Cl_2DC-CH_2Cl) consistent with the results reported in the literature.[10] According to CIDNP theory,[11] the radical pair [$Cl_2DC\cdot$ $\cdot CH_2Cl$] must be involved. Dilution with perfluorohexane (saturated $CDCl_3$ in C_6F_{14})[12] resulted in a different polarized ^{1}H-NMR spectrum (Figure 1c). In this spectrum, both a weak emission signal attributed to spin polarized Cl_2DC-CH_2Cl and a strongly enhanced absorption attributed to spin polarized 2-deutero-1,1,1-trichloroethane (Cl_3C-CH_2D), are observed. Thus, two different radical pairs [$Cl_2DC\cdot$ $\cdot CH_2Cl$] and [$Cl_3C\cdot$ $\cdot CH_2D$], were involved in the reaction in dilute solution. The spin states of these two radical pairs were assigned by Roth[10] previously. Singlet methylene has been shown to prefer abstraction of a chlorine atom from $CDCl_3$ to form a singlet radical pair [$Cl_2DC\cdot$ $\cdot CH_2Cl$], which can recombine in the solvent cage to give polarized emission. Triplet methylene abstracts predominantly a deuterium atom from $CDCl_3$ to form a triplet radical pair $[Cl_3C\cdot\ \cdot CH_2D]$, which can undergo spin inversion and recombination to produce polarized absorption. Although, as we shall see below, the reactions are not 100% selective for each spin state, we shall proceed in our discussion to term Cl_2DC-CH_2Cl as the "singlet product" and Cl_3C-CH_2D as the "triplet product". Scheme I summarizes the mechanism assumed to interpret the results of this report.

Scheme 1



The observation of polarized absorption of Cl_3C-CH_2D upon direct photodecomposition of diazirine in C_6F_{14} in the presence of saturated $CDCl_3$ is consistent with singlet-triplet intersystem crossing mechanism of singlet CH_2 in solution. Direct irradiation of diazirine produces singlet methylene which can deactivate via two pathways: reaction with $CDCl_3$ to form the polarized singlet product, or collision with inert solvent molecules to form $^3CH_2$ which then reacts with $CDCl_3$ to produce the polarized triplet product. The fate of $^1CH_2$ depends on the relative rate of the two processes. As shown in Scheme I, these two rates are affected by three variables: k_{ST}, ^1k_p, and the concentration of $CDCl_3$. The k_{ST} and ^1k_p are expected to be constant under the experimental conditions, i.e., constant temperature, pressure, and solvent, etc. Therefore, the major variable is the concentration of $CDCl_3$. In neat $CDCl_3$ solution, singlet methylene which is generated upon direct photodecomposition of diazirine, is trapped quantitatively by $CDCl_3$ to produce the polarized chlorine abstraction product before ISC to $^3CH_2$ can occur. Consequently, no polarized hydrogen abstraction product is observed by CIDNP (Figure 1b). Product analysis of the reaction mixture results in Cl_2DC-CH_2Cl as the major product (>90%). On the other hand, in the presence of large amounts of inert solvent, most of the $^1CH_2$ is collisionally deactivated to ground state $^3CH_2$, which then reacts with $CDCl_3$ to form the polarized hydrogen abstraction product (Figure 1c). Dilution effect has also been observed by product analysis. The yield of C-D insertion product (Cl_3C-CH_2D), a triplet product, increases upon decreasing the concentration of $CDCl_3$ in C_6F_{14}. The CIDNP result is consistent with a mechanism that singlet methylene (rather than methylene precursors) deactivates to the triplet state. However, a quantitative determination of the amount of $^3CH_2$ formed has not bee achieved using CIDNP, because the quantitative polarization of the two radical pairs are not known.

In order to confirm the conclusions derived from the CIDNP investigation, we determined the ratio of products derived from the direct and triplet sensitized photolysis of diazirine and diazomethane with $CDCl_3$ and with $CHCl_3$ as a function of dilution with perfluorohexane. The results are summarized in Figure 2 where one can see that the ratio of singlet to triplet product is a more or less linear function of concentration of chloroform in perfluorohexane. Some comments on the experiments should be made before an analysis of the data is attempted: (1) the extrapolation of the line to neat chloroform does not lead to the experimental value (>20) for the ratio of singlet to triplet products; (2) the maximum solubility of chloroform in perfluorohexane is ca. 0.6 M so that investigations at higher dilutions are not possible; (3) the mass balances for higher concentrations of chloroform are uniformly better than those at lower concentrations; (4) a suitable triplet sensitizer for diazirine was not found.

From Figure 2 the following salient points are apparent: (1) there is no significant isotope effect on the product ratio as a function of dilution; (2) the ratio for triplet sensitized reaction is nearly indistinguishable from the ratio in dilute samples (ca. 0.05M); (3) the ratio of singlet product to triplet product is a (more or less) linear function of chloroform concentration.

The slope of the line in Figure 2 is related to the rate of product formation by reaction of singlet methylene with chloroform to the rate of intersystem crossing of singlet methylene to triplet methylene. Under the simplifying assumption that $Cl_2DC\text{-}CH_2Cl$ is formed mainly from the reaction of $^1CH_2$, and $Cl_3C\text{-}CH_2D$ (ca. 78%) and $Cl_2DC\text{-}CH_2Cl$ (ca. 22%) are formed from $^3CH_2$,[13] the experimental slope of ca. 7 M^{-1} corresponds to the ratio of the rate constant for the $^1CH_2$ reaction with $CDCl_3$ to the rate constant for intersystem crossing. With the additional plausible assumption that the reaction of $^1CH_2$ with $CDCl_3$ is diffusion controlled in perfluorohexane,[14] a value of k_{ST} of ca. 8 x 10^8 S^{-1} is obtained.

In summary, direct irradiation of a dilute solution of diazirine in C_6F_{14} leads to a polarized ^1H-NMR signal from the $Cl_3C\text{-}CH_2D$ produced from the reaction of $^3CH_2$ with $CDCl_3$. This observation of CIDNP from the $Cl_3D\text{-}CH_2D$ product strongly supports the occurrence of an ISC pathway for deactivation of singlet methylene in solution. This result represents the first spectroscopic evidence for singlet-triplet deactivation of methylene in solution, and shows that the behavior is similar to that reported for methylene in the gas phase.[3] These conclusions are confirmed by an investigation of the products formed by the reaction of methylene with chloroform as a function of dilution in C_6F_{14}. From the latter experiments, an estimate of the rate constant of ISC of $^1CH_2$ to $^3CH_2$ of 8 x 10^8 S^{-1} is evaluated.

ACKNOWLEDGEMENT

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12. A solution of C_6G_{14} containing diazirine and saturated $CDCl_3$ was placed in an inner NMR tube, and deuterium oxide was placed in an outer NMR tube in order to lock the FT-NMR signal.

13. Benzophenone triplet sensitized decomposition of diazomethane in neat $CDCl_3$ results in $Cl_2DC\text{-}CH_2Cl$ and $Cl_3C\text{-}CH_2D$ with a ratio of 0.29 ± 0.03.

14. From the viscosity of 1cP for C_6F_{14} at 0°C, the diffusional rate constant is estimated to be $5.0 \times 10^9\ M^{-1}\ S^{-1}$. For the viscosity of C_6F_{14} see: T.J. Brice and R.I. Conn, J. Am. Chem. Soc. 1953, 75, 2921.

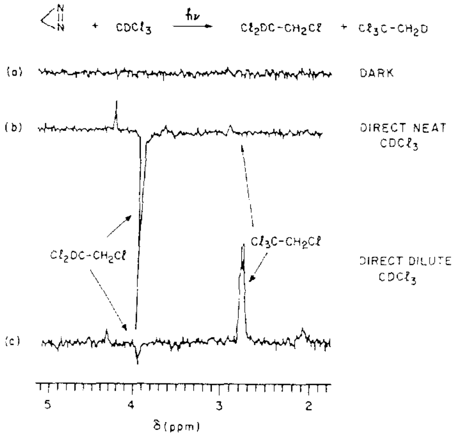

Figure 1. The ^1H-NMR spectra (80 MHz) of diazirine in (b) neat chloroform-d and (c) in C_6F_{14} containing saturated $CDCl_3$ upon direct photolysis (>300 nm). A spectrum of the same region after irradiation is shown in (a).

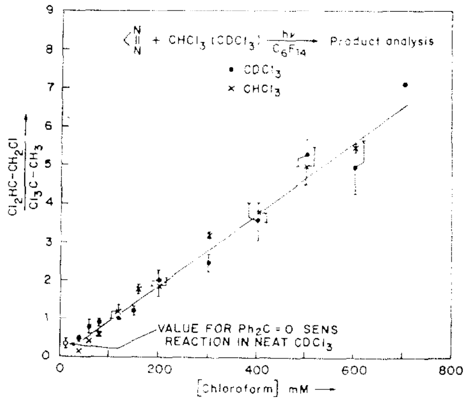

Figure 2. The ratio of the $Cl_2HC\text{-}CH_2Cl$ yield to the $Cl_3C\text{-}CH_3$ yield from the photolysis of diazirine with various concentrations of chloroform (x) or chloroform-d (●) in C_6F_{14} solution at 0°C. (o) represents benzophenone triplet decomposition of diazomethane in neat $CDCl_3$ at 0°C.

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