

Origin of Magnetic Field Effect in the Photolysis of 7-Silanorbornadiene Derivatives in Solution

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Theoretical modeling of the magnetic field effect detected in the photolysis of 7-silanorbornadiene derivatives has clearly demonstrated the involvement of biradical intermediates and confirmed the participation of both singlet and triplet excited states of dimethylsilylene, :SiMe₂.

Introduction

Recent investigations of the photolytic decomposition of a 7,7'-dimethyl-7-silanorbornadiene derivative (**I**) have shown that a stationary external magnetic field affects the yield of one of the main reaction products, tetraphenylanthracene (TPN).¹ The reaction mechanism (see Scheme 1) has been proposed on the basis of a series of investigations of the process by means of spin chemistry techniques^{1,2} and laser pulse photolysis.³

The experimentally observed magnetic effect (ME) is formed in the biradical of the disilabicyclooctadiene derivative (**II**^S and **II**^T, Scheme 1) possessing two silicon atoms; the external magnetic field affects the ratio of triplet (**II**^T) to singlet (**II**^S) states of the biradical, which, according to Scheme 1, are the precursors of different reaction products. The involvement of biradicals in the photolysis of 7-sila(germa)norbornadiene derivatives has been earlier hypothesized,^{4,5} relying on the analysis of the end products of the photodecomposition. Nevertheless, the results of spin chemistry should be regarded as the first independent direct confirmation of the existence of biradicals obtained by means of physicochemical methods. This fact is of primary importance because of the lack of reference data on the structure and properties of short-lived biradicals—postulated intermediates in a number of organic reactions. This is especially true in regard to the reactions of organometallic compounds despite the fact that organoelement chemistry is an intensively developing field of research.⁵ In particular, considerable study is being given to photodecomposition products of 7-sila(germa)norbornadiene derivatives, since these species are the precursors of divalent silicon and germanium derivatives, which are of notable significance in organic synthesis.^{5,6} In the case under study, this is a heavy carbene analogue, dimethylsilylene, :SiMe₂ (stage 2, Scheme 1). The analysis of the magnetic field dependence of the ME¹ has allowed us to obtain data on the reactivity of singlet and triplet states of this carbene analogue. It is significant to note that, as of now, this information is also unavailable in the world literature.

A previous paper¹ has provided a purely qualitative interpretation of the magnetic field dependence of the ME. In view of the fundamental importance⁶ of the basic conclusions made therein,¹ the present work attempts to model the magnetic field dependencies of ME formed in the biradicals and to compare the calculations with the experimental results. Calculations of the magnetic field dependencies are performed in the frames of the exponential approximation of the radical pair theory.^{7,8}

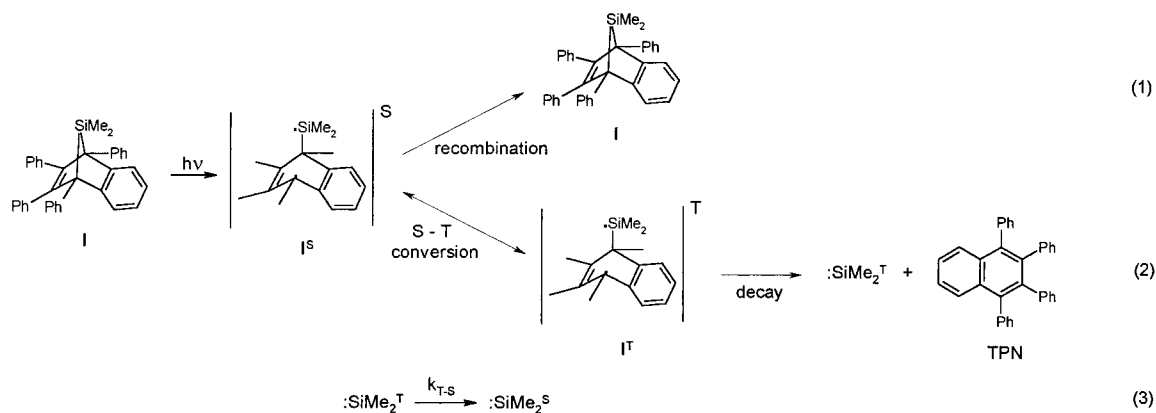
It must be emphasized that biradical species are the most popular subjects of investigation in the area of spin chemistry.⁷ However, the overwhelming majority of papers, as a rule, consider two types of model compounds: the biradicals formed through the photolysis of cyclic ketones with varying length of the hydrocarbon chain, and the compounds where donor and acceptor groups are linked by the said hydrocarbon chain. The geometry, lifetimes, and the multiplicities of the reacting state of these species are generally known in advance.

As for silicon-containing biradicals examined in the present case, their properties are presently unknown. Therefore, we are virtually forced to solve the inverse problem, i.e., to gain the information on the lifetimes and the parameters of electron exchange interaction in the biradicals on the basis of comparison of the calculated magnetic field dependence with the experimental one. Things get worse because of the impossibility of deriving the analytical solution of a system of coupled nonlinear differential kinetic equations descriptive of the process given by Scheme 1. Hence, to construct the theoretical magnetic field dependence, we have considered only three key magnetic sensitive stages.

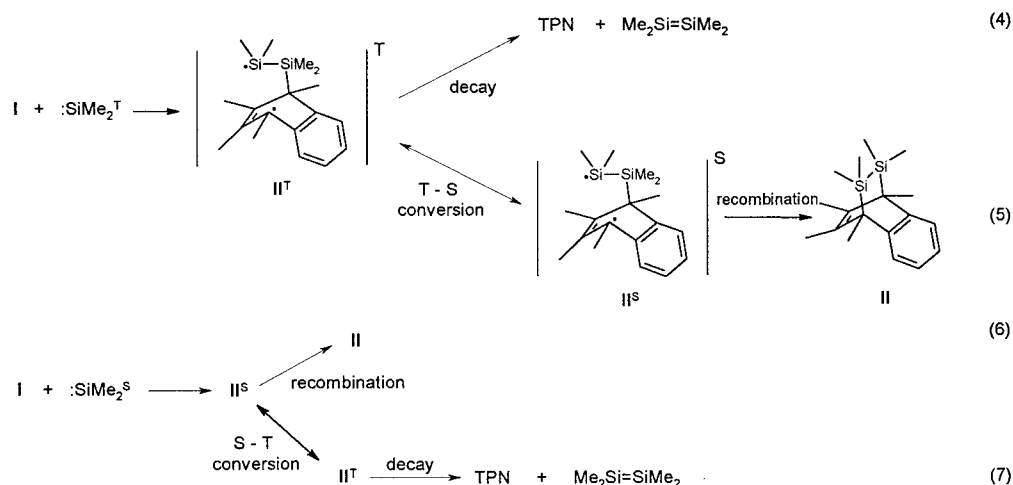
In the present paper, the analysis of the ME magnetic field dependence is used to confirm the earlier suggested mechanism of the photolytic decomposition of **I**.¹ According to previous understanding, the photolysis of **I** includes the triplet to singlet (T → S) conversion of dimethylsilylene and the reaction of both triplet and singlet :SiMe₂ with the initial heteronorbornadiene derivative, resulting in the formation of biradical species. As it has been already stressed, up to the present the reactions of triplet dimethylsilylene have been never mentioned in the literature.

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SCHEME 1



Reactions of $:\text{SiMe}_2^{\text{T}}$ and $:\text{SiMe}_2^{\text{S}}$ with the initial **I** :



Description of the Contributions to Magnetic Field Dependencies

The dependencies of the yield of tetraphenylnaphthalene (TPN), the photodecomposition product of 7-silanorbornadiene derivative **I**, on the external magnetic field (MF) strength in the presence of different scavengers (O_2 and Ph_3P) are shown in Figures 1 and 2. The experimental results¹ reflect the variations of the optical densities of TPN detected by means of laser pulse photolysis. Scheme 1 shows the detailed mechanism of the process proposed on the basis of the analysis of CIDNP and the ME signs.

It has been demonstrated¹ that the MF-dependent fraction of TPN is formed in the bulk as a result of reaction of the starting **I** with the T and S states of dimethylsilylene. According to Scheme 1, this reaction leads to biradicals in the initial triplet and singlet states. The recombination of the singlet biradicals gives rise to the disilabicyclooctadiene derivative (**II**), while the triplet state of the biradical is responsible for TPN formation.

In this case, one might expect that the sign and magnitude of ME will be defined by the balance of the rates of the following processes: $\text{T} \rightarrow \text{S}$ conversion of dimethylsilylene and the reactions of triplet and singlet $:\text{SiMe}_2$ with the starting **I**. Indeed, triplet and singlet biradicals (**II**^T and **II**^S) of disilabicyclooctadiene should be responsible for the formation of ME demonstrating the opposite signs.

To verify the proposed scheme of ME formation, an attempt was made to establish a link between TPN yield and the recombination probabilities of the biradicals.

According to Scheme 1, the fraction of TPN resulting from the decomposition of the starting **I** (stage 2) is defined as $(1 - {}^1P_s)$, where 1P_s is the recombination probability of the singlet biradical **I**^S. The same is true for triplet excited dimethylsilylene, since both TPN and $:\text{SiMe}_2^{\text{T}}$ are simultaneously generated in a single act at stage 2 of Scheme 1. Triplet excited $:\text{SiMe}_2^{\text{T}}$ may undergo $\text{T} \rightarrow \text{S}$ conversion into the singlet (ground state) $:\text{SiMe}_2^{\text{S}}$. It has been shown, however, that the reaction rate of dimethylsilylene with the initial **I** lies in the diffusion time scale.³ Hence, the manifestation of the magnetic field dependencies of the ME, which are opposite in sign in the presence and in the absence of different scavengers of dimethylsilylene (cf. Figure 1 and Figure 2), makes it reasonable to suggest that both triplet and singlet $:\text{SiMe}_2$ enter the reaction with **I**. Let us denote the fraction of triplet dimethylsilylene by α . In principle, the yield of triplet dimethylsilylene $:\text{SiMe}_2^{\text{T}}$ is a function of quantum yield and also depends on the reactions with the scavengers. In the system under study, both the starting **I**, triphenylphosphine, and O_2 play the role of scavengers of dimethylsilylene. According to the model used in the present study, the relative fraction of triplet dimethylsilylene $:\text{SiMe}_2^{\text{T}}$ is denoted by α :

$$\alpha = \frac{[:\text{SiMe}_2^{\text{T}}]}{[:\text{SiMe}_2^{\text{T}}] + [:\text{SiMe}_2^{\text{S}}]}$$

Thus, parameter α varies from 0 to 1, and if singlet dimethylsilylene is solely present in the reaction mixture, $\alpha = 0$. Otherwise, if all dimethylsilylene has triplet multiplicity, $\alpha = 1$.

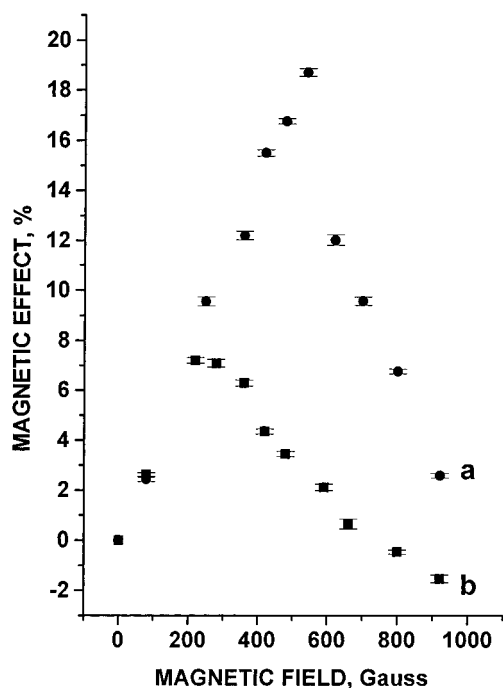


Figure 1. Magnetic field dependencies of the ME originating from triplet biradical II^{T} (Scheme 1): (a) field dependence of ME observed experimentally in the photolysis of **I** in the presence of O_2 ; (b) field dependence of ME observed experimentally in the photolysis of **I** in deaerated solutions.

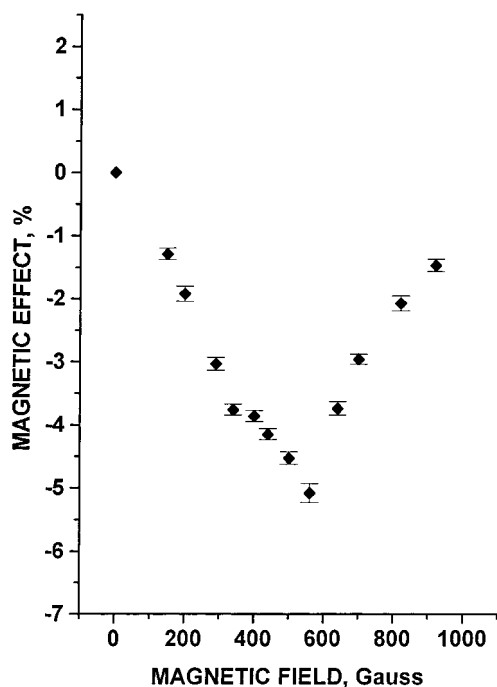


Figure 2. Magnetic field dependencies of the ME originated in singlet biradicals II^{S} (Scheme 1) observed experimentally in the photolysis of **I** in the presence of O_2 and Ph_3P .

The present model does not take into account the dependence of α on the external magnetic field strength, since there is a lack of reference data on the magnetic field influence on intersystem crossing in heavy carbene analogues.

Oxygen enters the complexing reactions with biradicals, and its influence is taken into account through the variation of α and J , the effective electron exchange interaction, which defines the location of the extremes of the field dependence of the magnetic effects.

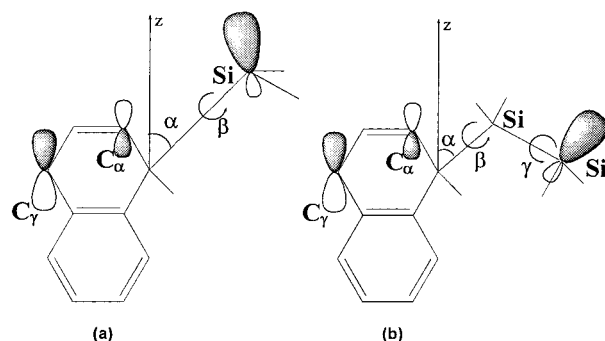


Figure 3. Model systems **Im** (a) and **IIm** (b) and schematic representation of the unpaired electron orbital population therein.

Thus, the amount of triplet $:\text{SiMe}_2$ entering the reaction with the initial **I** will be defined as $\alpha(1 - {}^1P_{\text{S}})$, while that of singlet $:\text{SiMe}_2$ comprises $(1 - \alpha)(1 - {}^1P_{\text{S}})$. In turn, the yield of TPN resulting from the interaction of dimethylsilylene with the starting **I** will be constituted by the sum of TPN fractions formed in the reaction of triplet and singlet $:\text{SiMe}_2$ with **I** (stages 4 and 7 of Scheme 1). These two items are equal to $\alpha(1 - {}^1P_{\text{S}})(1 - {}^{\text{II}}P_{\text{T}})$ and $(1 - \alpha)(1 - {}^1P_{\text{S}})(1 - {}^{\text{II}}P_{\text{S}})$, respectively. Here, ${}^{\text{II}}P_{\text{T}}$ is the probability of singlet recombination of the triplet-born biradical II^{T} , whereas ${}^{\text{II}}P_{\text{S}}$ is the recombination probability of singlet-born biradical II^{S} . Accordingly, the total yield of TPN resulting from all three sources (stages 2, 4, and 7 of Scheme 1) will be defined by the following expression:

$$(1 - {}^1P_{\text{S}})[1 + \alpha(1 - {}^{\text{II}}P_{\text{T}}) + (1 - \alpha)(1 - {}^{\text{II}}P_{\text{S}})]$$

Finally, in the frames of the above reasoning, the experimentally observed magnetic field effect¹⁴ should be approximated by a formula where the fraction of triplet $:\text{SiMe}_2$, α , is a variable parameter:

$$\left\{ 1 - \frac{(1 - {}^1P_{\text{S}})[1 + \alpha(1 - {}^{\text{II}}P_{\text{T}}) + (1 - \alpha)(1 - {}^{\text{II}}P_{\text{S}})]}{(1 - {}^1P_{\text{S}}^0)[1 + \alpha(1 - {}^{\text{II}}P_{\text{T}}^0) + (1 - \alpha)(1 - {}^{\text{II}}P_{\text{S}}^0)]} \right\} \times 100\% \quad (1)$$

Here, the superscript “0” denotes the values of corresponding recombination probabilities in the geomagnetic field.

Calculations of Recombination Probabilities of the Biradicals

It has been already mentioned¹ that it is impossible to perform an adequate description of the experimental dependence of TPN yield on the external magnetic field strength only on the basis of the combined approach of HFI and Δg mechanisms⁷ neglecting the electron interaction (J). It has been also aforementioned that the literature lacks data pertaining to the scale and the sign of J in the biradicals similar to those explored in the present paper. Therefore, the present study attempts to calculate the value of J in several model systems (Figure 3). The choice of these models has been stipulated by the impossibility of estimating J for the real molecule because of the enormous complexity of the calculations.

Unlike long chain biradicals⁹ the biradicals under study are rigid enough. In this case, the main conformational transitions are defined by the rotations around C–Si and Si–Si bonds. Calculated J values are several orders of magnitude greater than those one might expect on the basis of the location of extremes of the experimental field dependencies ($\sim 10^2$ G; see Figures 1 and 2). However, the model case exemplified in Figure 4 shows

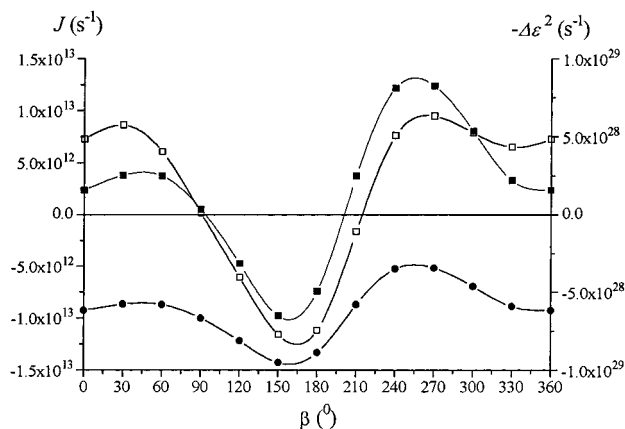


Figure 4. Exchange interaction parameter dependence on the geometry variations for **Im**: (□) J in 3×3 CI approach; (■) optimal J^{eff} ; (●) $\Delta\epsilon^0$.

that depending on the rotation angle of the unpaired electron orbital relative to C–Si and Si–Si, one might observe both positive and negative regions of the electron exchange interaction parameter with a moderate absolute magnitude (Figure 4).

Therefore, under these circumstances, we have rejected the idea of using a common calculation approach employed for long chain biradicals.¹⁰ Instead, to analyze the formation of the magnetic effects in the intermediate biradicals, we have employed a two-positional exponential model.⁸ A biradical possessing two conformations with different exchange interaction has been considered. The transitions between the conformations are treated as first-order processes occurring at a rate K_{jump} . The dynamics of the biradical is described by a system of equations

$$\begin{aligned}\rho_0^1 &= \frac{i}{\hbar} [\hat{H}_1, \bar{\rho}_1] + K_{\text{jump}}(\bar{\rho}_2 - \bar{\rho}_1) + \frac{1}{2} \{\hat{K}, \bar{\rho}_1\} + K_d \bar{\rho}_1 \\ \rho_0^2 &= \frac{i}{\hbar} [\hat{H}_2, \bar{\rho}_2] + K_{\text{jump}}(\bar{\rho}_1 - \bar{\rho}_2) + \frac{1}{2} \{\hat{K}, \bar{\rho}_2\} + K_d \bar{\rho}_2\end{aligned}\quad (2)$$

where the spin density matrices $\bar{\rho}_i$ are given by

$$\bar{\rho}_i = \int_0^\infty \rho_i(t) dt, \quad i = 1, 2 \quad (3)$$

and $\bar{\rho}_i(t)$ is the spin density matrix for the i th biradical conformation at a time t .

For a one-nuclear radical pair with spin $I = 1/2$, the spin Hamiltonian is

$$\begin{aligned}\hat{H}_i &= g_a \beta_e \hbar^{-1} H_0 \hat{S}_{az} + g_b \beta_e \hbar^{-1} H_0 \hat{S}_{bz} + g_a \beta_e \hbar^{-1} A \hat{S}_a \cdot \hat{I} - \\ &\quad J_i \left(\frac{1}{2} + 2 \hat{S}_a \cdot \hat{S}_b \right), \quad i = 1, 2\end{aligned}\quad (4)$$

where g_a and g_b are the isotropic electron g factors of the radicals **a** and **b**, respectively, β_e is the Bohr magneton, H_0 is the magnitude of the external magnetic field, A is the hyperfine constant with the magnetic nucleus, and J_i is the exchange interaction between the unpaired electron spins for the i th biradical conformation.

The cage recombination of the biradical occurs only from the singlet state:

$$\hat{K} = K_S \hat{P}_S \quad (5)$$

where K_S is the first-order singlet recombination rate constant and \hat{P}_S is the projective operator on the singlet manifold. For

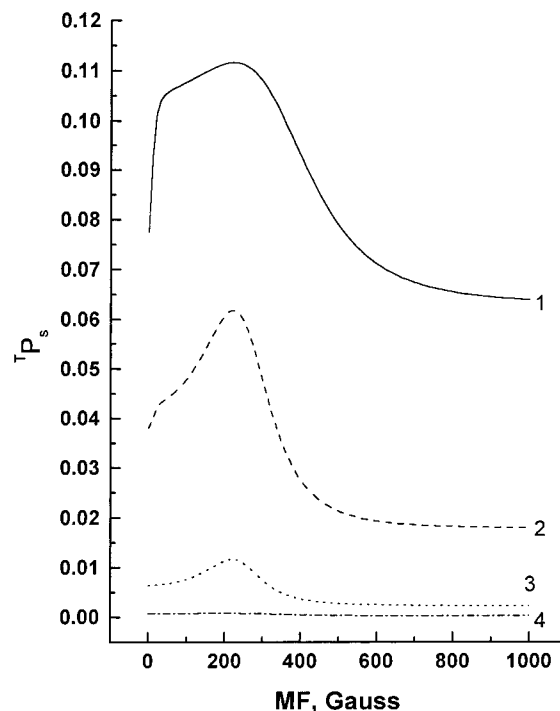


Figure 5. Magnetic field (MF) dependencies of singlet recombination probabilities for triplet precursor (1P_S) calculated by means of two-positional model for various K_S with the following calculation parameters: $\Delta g = 0.0006$, $A_{\text{eff}} = 20$ G, $J_1 = -2.2 \times 10^9$ s $^{-1}$, $J_2 = 2.2 \times 10^9$ s $^{-1}$, $K_{\text{jump}} = 1.4 \times 10^9$ s $^{-1}$, $K_d = 1.4 \times K_S$. For curve 1, $K_S = 10^9$ s $^{-1}$. For curve 2, $K_S = 10^7$ s $^{-1}$. For curve 3, $K_S = 10^8$ s $^{-1}$. For curve 4, $K_S = 10^9$ s $^{-1}$.

simplicity, we consider the singlet recombination rate K_S to be identical for both conformations. The irreversible decay of the biradical resulting in the decomposition products is described by the first-order rate constant K_d (eq 2).

The initial condition ($t = 0$) corresponds to a biradical with equipopulated conformations:

$$\rho_0^i = \frac{1}{2} \hat{\rho}_0, \quad i = 1, 2 \quad (6)$$

Here $\hat{\rho}_0$ is the initial spin density matrix. In our calculations, we have considered the situations of either singlet or triplet biradical precursors with equipopulated α, β nuclear spin states.

The system of equations (2) was solved numerically. The singlet recombination probability, P_S , was calculated as

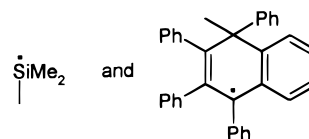
$$P_S = \frac{1}{2} \text{Tr} \{ \hat{K}, \bar{\rho}_1 + \bar{\rho}_2 \} \quad (7)$$

The probability of the decay of biradical, P_d , was calculated as

$$P_d = K_d \text{Tr}(\bar{\rho}_1 + \bar{\rho}_2) \equiv 1 - P_S \quad (8)$$

Derivation of the Calculated Magnetic Field Dependencies of the ME

To calculate the recombination probabilities of the biradicals **I** and **II**, we have employed the magnetic resonance parameters for two structural fragments with unpaired electrons:



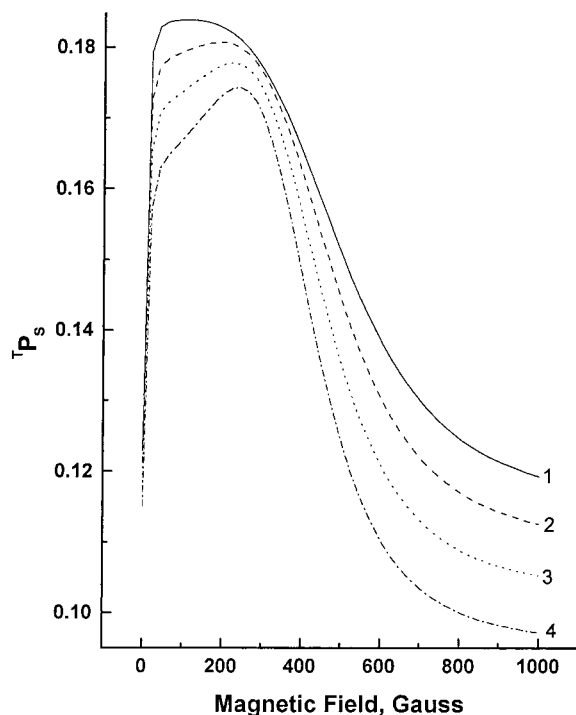


Figure 6. Magnetic field (MF) dependencies of singlet recombination probabilities for triplet precursor (P_s) calculated by means of two-positional model for various K_{jump} with the following calculation parameters: $\Delta g = 0$, $A_{\text{eff}} = 20$ G, $J_1 = -3 \times 10^9$ s $^{-1}$, $J_2 = 3 \times 10^9$ s $^{-1}$, $K_s = 10^6$ s $^{-1}$, $K_d = 1.4 \times 10^6$ s $^{-1}$. For curve 1, $K_{\text{jump}} = 3 \times 10^9$ s $^{-1}$. For curve 2, $K_{\text{jump}} = 2 \times 10^9$ s $^{-1}$. For curve 3, $K_{\text{jump}} = 1.4 \times 10^9$ s $^{-1}$. For curve 4, $K_{\text{jump}} = 10^9$ s $^{-1}$.

For these two structures, g factors are equal to 2.0031 and 2.0025 ($\Delta g = 0.0006$), respectively.¹¹ For hyperfine interaction, our semiempirical estimations have shown that effective HFI (A_{eff})¹⁵ in the biradicals under study could be as high as 20 G. This is in a fairly good agreement with the experimental data for conjugated derivatives of cyclohexadienyl radicals.¹² For electron exchange interactions of two different conformations, to reproduce the location of the extremes of the ME field dependence for the biradical **II** (Scheme 1), we have used $J_1 = -2.2 \times 10^9$ s $^{-1}$ and $J_2 = 2.2 \times 10^9$ s $^{-1}$. To model the shift of the extremes during the photolysis in the presence of O₂ (Figure 1a) the values of J_1 and J_2 have been changed and are -5.5×10^9 and 5.5×10^9 s $^{-1}$, respectively. The influence of K_s and K_{jump} on the calculated recombination probabilities has been shown in Figures 5 and 6, respectively. The best agreement with the experimental data has been attained in the case of $K_s = 10^6$ s $^{-1}$, $K_{\text{jump}} = 1.4 \times 10^9$ s $^{-1}$, $K_d = 1.4 \times 10^6$ s $^{-1}$.

As it has been already mentioned,¹ biradical **I** is not responsible for the formation of the magnetic field effect in the reaction under study. Therefore, for the biradical **I** J_1 and J_2 were set to 0. The value of K_s was 10^9 s $^{-1}$, $K_d = 10^9$ s $^{-1}$.

Thus, substitution of the calculated values of recombination probabilities of the biradicals under study into expression 1 leads to the model field dependencies of the ME shown in Figures 7 and 8.

Discussion

Figure 7 (cf. curves a and c; curves b and d) and Figure 8 (cf. curves a and b) show that the variation of α , in principle, allows us to reproduce the alteration of the sign and magnitude of ME. Unfortunately, we have managed to attain only qualitative agreement between the experimental and calculated field dependencies.

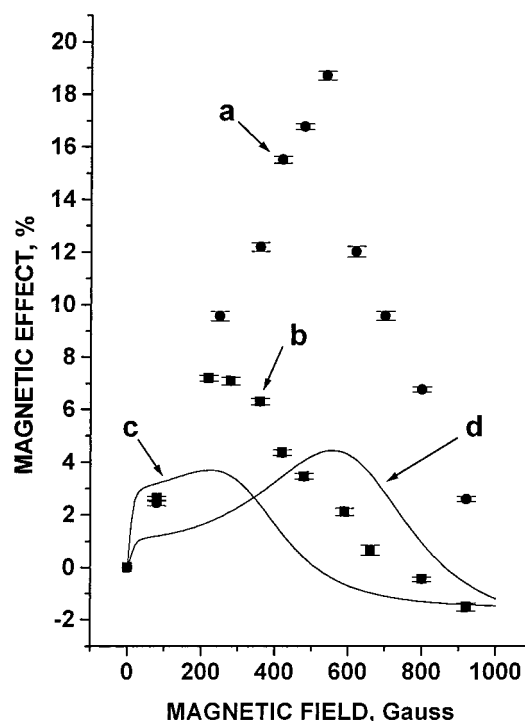


Figure 7. Experimental and simulated magnetic field effects (ME) originating from triplet biradical **II**^T (Scheme 1): (a) field dependence of ME observed experimentally in the photolysis of **I** in the presence of O₂; (b) field dependence of ME observed experimentally in the photolysis of **I** in deaerated solutions; (c) theoretical simulation of the field dependence of ME for case b, with calculation parameters $\Delta g = 0.0006$, $A_{\text{eff}} = 20$ G, $J_1 = -2.2 \times 10^9$ s $^{-1}$, $J_2 = 2.2 \times 10^9$ s $^{-1}$, $K_s = 10^6$ s $^{-1}$, $K_{\text{jump}} = 1.4 \times 10^9$ s $^{-1}$, $K_d = 1.4 \times 10^6$ s $^{-1}$, $\alpha = 1$; (d) theoretical simulation of the field dependence of ME for case a, with calculation parameters $\Delta g = 0.0006$, $A_{\text{eff}} = 20$ G, $J_1 = -5.5 \times 10^9$ s $^{-1}$, $J_2 = 5.5 \times 10^9$ s $^{-1}$, $K_s = 10^6$ s $^{-1}$, $K_{\text{jump}} = 1.4 \times 10^9$ s $^{-1}$, $K_d = 1.4 \times 10^6$ s $^{-1}$, $\alpha = 1$.

Figure 7 presents the magnetic field dependencies (experimental and calculated ones; curves b and d of Figure 7, respectively) of the yield of TPN originating from the disilabicyclooctadiene biradical **II**^T in the initial triplet state. The closest possible agreement between theory and experiment could be obtained when employing the values of recombination probability calculated for $K_s = 10^6$ s $^{-1}$ and $\alpha = 1$.

Another set of experimental data represent the observations during the photolysis of **I** in the presence of equilibrium oxygen concentration in solution. In this case, the remarkable increase in ME magnitude of both signs has been observed (Figure 7a and Figure 8a).

It has been suggested¹ that oxygen is capable of forming short-lived complexes with disilabicyclooctadiene biradicals. In the reaction under study, O₂ displaces triphenylphosphine from the Ph₃P complex with biradical. In this case, it seems likely that the newly formed complex results from the interaction of O₂ and biradical. It is this complex that is responsible for ME formation.

Indeed, the MEs formed during the reactions of singlet and triplet :SiMe₂ in the presence of O₂ demonstrate the field dependencies that are mirror images of each other (cf. Figure 7a and Figure 8a). These observations are best explained under the assumption of the formation of two biradicals with identical structures but different multiplicities.

The experimental field dependencies observed in the presence of oxygen agreed satisfactorily with the calculated ones only for the case of the initial singlet biradical (**II**^S)—modeling of the reaction in the presence of triphenylphosphine.

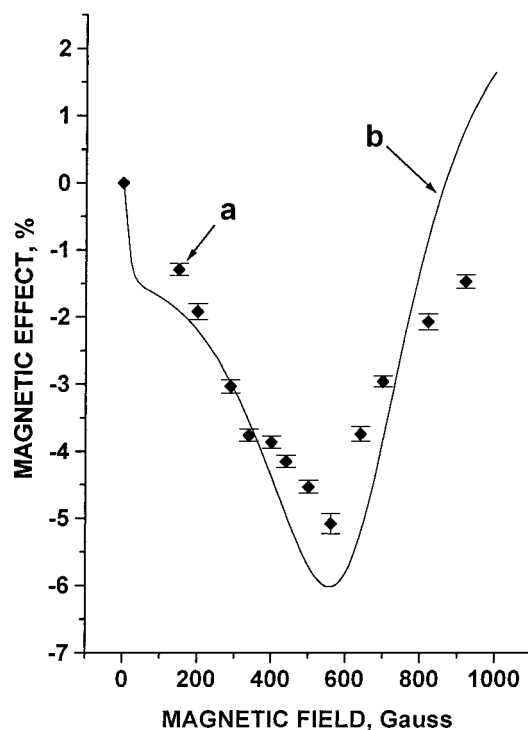


Figure 8. Experimental and simulated magnetic field effects (ME) originating from singlet biradicals Π^S (Scheme 1): (a) field dependence of ME observed experimentally in the photolysis of **I** in the presence of O_2 and Ph_3P ; (b) theoretical simulation of the field dependence of ME for case a, with calculation parameters $\Delta g = 0.0006$, $A_{\text{eff}} = 20$ G, $J_1 = -5.5 \times 10^9 \text{ s}^{-1}$, $J_2 = 5.5 \times 10^9 \text{ s}^{-1}$, $K_s = 10^6 \text{ s}^{-1}$, $K_{\text{jump}} = 1.4 \times 10^9 \text{ s}^{-1}$, $K_d = 1.4 \times 10^6 \text{ s}^{-1}$, $\alpha = 0.25$.

The closest possible agreement is achieved under the following assumptions: $K_s = 10^6 \text{ s}^{-1}$, $\alpha = 0.25$ (see Figure 8b). A value of α other than 1 but greater than 0 implies that the observed ME is still a superposition of the contributions from T and S precursors; i.e., triphenylphosphine has not managed to quench all triplet excited dimethylsilylene species.

When the reaction is mediated by the biradical in the initial triplet state (Π^T) (the reaction is carried out in the absence of triphenylphosphine (Figure 5)), the scale of the calculated effect is substantially lower than the experimental one. In this case, the attempts to improve the agreement by means of simple variation of the parameters of a two-positional model have been unsuccessful. The absence of quantitative consistency between the experimental and calculated field dependencies of ME might imply that, in general, the manifestation of the interaction of oxygen with the biradical is not limited by the variations in the set of the reactive conformations. It is precisely these conformations that are taken into account in the calculations through the variations of the exchange interaction.

The observed effect of oxygen could be possibly related to the so-called spin catalysis—the phenomenon exemplified by the acceleration of the reaction between two paramagnetic species in the presence of a third one due to the variations in spin dynamics.¹³

It is assumed¹³ that this might be a result of the contribution of the paramagnetic relaxation to $S \rightarrow T$ conversion in the radical pair. In the case under study, this could be the $S \rightarrow T$ conversion in the biradical.

Conclusions

Comparison of the experimental field dependencies with the calculated ones provides a confirmation of the earlier made inference¹ about the involvement of biradical intermediates and clearly demonstrates the participation of both triplet and singlet states of dimethylsilylene. The results of the analysis are also consistent with the hypothesis of the formation of the complexes of biradicals, triphenylphosphine, and oxygen.

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Supporting Information Available: Detailed description of ab initio and semiempirical calculations of the exchange interaction parameter in the model biradical systems and semiempirical estimates of the hyperfine interaction constants in the biradicals under study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Experimental magnetic field effect is defined as follows: $(1 - D_H/D_0) \times 100\%$, where D_H and D_0 are the yields (optical densities) of TPN originating from the action of the external magnetic field and from the geomagnetic one, respectively.
- (15) The effective hyperfine interaction is defined as $A_{\text{eff}} = (1/3) \sum_k A_k^2 I_k(I_k + 1)^{1/2}$, where A_k and I_k are the hyperfine interaction constants and nuclear spins of all magnetic nuclei in the radical pair, respectively.