The Reaction of Dimethylsilylene with Carbon Tetrachloride in Solution Studied by Means of Spin Chemistry and Laser Pulse Photolysis Methods

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The interaction between dimethylsilylene (Me$_2$Si, DMS) generated through the photolysis of 7,7′-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene (**I**) and carbon tetrachloride has been studied by means of laser pulse photolysis and spin chemistry methods. The reactions of dimethylsilylene in excited triplet and ground singlet states have been described. From the analysis of magnetic effect, the interaction of triplet dimethylsilylene with carbon tetrachloride has been demonstrated. The laser pulse photolysis experiments have shown that the reaction of singlet dimethylsilylene with CCl$_4$ proceeds via the intermediate formation of a donor−acceptor complex (Me$_2$Si/ClCCl$_3$, λ_{max} = 334 nm). Its decay is supposed to occur via the reaction with **I** (k = 1.26 × 10^7 M^{-1}·s^{-1}) and via the disproportionation process ($2k_{bim}/\epsilon$ = 1.07 × 10^6 cm·s^{-1}). The lifetimes of different spin states of DMS have been estimated in the frames of the proposed kinetic scheme ($\tau_S \leq 3.2 \times 10^{-7}$ s, $\tau_T \leq 1.4 \times 10^{-7}$ s).

Introduction

At present, organometallic compounds attract growing attention, especially in connection with their wide practical application. The organometallic compounds with elements of group 14, Si, Ge, and Sn, and their divalent derivatives play a significant role among them. For example, they are used as sources of different organometallic synthons in complex organic syntheses. Therefore, it is necessary to understand the mechanisms of their chemical reactions comprehensively (i.e., to identify elementary stages and reactive short-lived intermediates involved in the processes under investigation). This was the subject of very intensive studies during last few decades.[1−3]

Among the reactive organometallic intermediates with group 14 element atoms, the heavy carbene analogues (silylenes, germylenes, stannylenes) occupy a significant place. These highly reactive species, the so-called carbenoids, have two unpaired electrons, which could be located in either a single orbital ($^1A_1$) or two orbitals ($^3B_1$), see Scheme 1.

They are widely used in various organic syntheses to introduce organometallic fragments into molecules because the insertion reactions are very characteristic of carbenoids.[4−7] It is known[8] that the majority of carbenoids are characterized by the singlet ground state ($^1A_1$); however, in contrast to carbon analogues, there is no experimental information about the reactivity of the ground and excited states. The only exception is the results obtained by spin chemistry methods that will be described below.

Another chemical process that is very characteristic of carbenoids is the complexation with the Lewis bases. In this case, there is a weak interaction between the vacant molecular orbital of a singlet carbenoid and the electron pair of a molecule

SCHEME 1: Singlet and Triplet Excited Dimethylsilylene
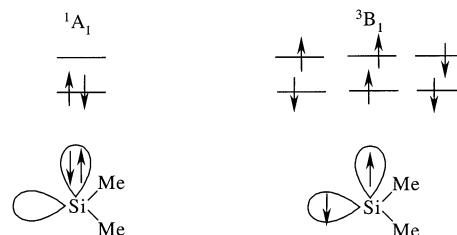
SCHEME 2: Complexation of Singlet Me$_2$Si with Lewis Base B
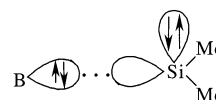
donor (Scheme 2).[6,7,9−11] The similar complexation significantly changes the reactivity of carbenoids and could sometimes radically change the direction of chemical processes.[7,9,12,13]

Despite a great number of reports devoted to the processes in which carbenoids are considered to be involved,[1−3] there are only certain systems for which the mechanisms of elementary stages have been especially investigated. The major part of these data was obtained by means of spin chemistry and laser pulse photolysis methods.[14−16] These are, first of all, the phototransformations of sila- and germanorbornadiene derivatives that are widely used as the sources of silylenes and germylenes[14−18] (Scheme 3).

At present, the reactions of carbenoids from their ground states with various scavengers have been widely investigated by chemically induced dynamic nuclear polarization (CIDNP).[14,15,19,20] However, until now, there have been three examples of the reactions of carbenoids from the excited triplet state: those with thiocycloheptine,[21] 7-silanorbornadiene (**I**),[22]

SCHEME 3: Generation of Carbene Analogs from 7-Heteronorbornadienes

Tetraphenylnaphthalene
(TPN)   E = Si, Ge
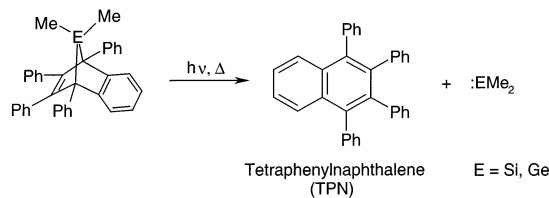
and carbon tetrachloride.[22,23] Besides these, they described two cases of the influence of electron-donor molecules (PPh$_3$ and CHBr$_3$) on the lifetime of triplet dimethylsilylene generated during the photolysis of **I**.[16,22] All of these data on the chemical behavior of triplet carbenoids were obtained using spin chemistry methods: CIDNP and magnetic field effect (MFE) in combination with the laser pulse photolysis.

To continue investigation of the reactivity of the triplet state of dimethylsilylene (DMS), we have studied its reaction with carbon tetrachloride by laser pulse photolysis and magnetic field effects. In the present paper, we have investigated the laser pulse photolysis of 7,7′-dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene (**I**) in a solution in the presence of CCl$_4$ in magnetic fields of different strengths.

Experimental Section

Materials. 7,7′-Dimethyl-1,4,5,6-tetraphenyl-2,3-benzo-7-silanorbornadiene (**I**) was synthesized as described in ref 24. The solvents (*n*-hexane and carbon tetrachloride, UV-grade purity) were used without repurification. All experiments were performed at room temperature and at atmospheric pressure.

Instrumentation. The nanosecond laser pulse photolysis setup includes a XeCl excimer laser ($\lambda = 308$ nm, pulse duration 15 ns, average pulse energy ca. 10 mJ, delay time 50 ns) as an excitation light source. The exciting and probing light beams fall on the quartz optical cell (10 mm thickness) at a small angle ($\sim 2°$). The beam area on the sample is about 10 mm^2. Because the ratio between the beam area and the entire volume of the sample is about 1/200, we could make 20−30 measurements without serious degradation of the sample. The photomultiplier signal was recorded on a digital oscillograph Tektronix 7912AD connected to an IBM PC computer. The kinetic curves could be recorded in the regime of both the single measurement and the summing. All experimental results were normalized to laser pulse intensities. A detailed description of this setup can be found in ref 25.

MFE Measurements. In these experimental series, the concentration of **I** in hexane solution was over the range $C = 7 \times 10^{-4}$ to 1×10^{-3} M. It was controlled spectrophotometrically by a Specord UV−vis spectrometer (Karl Zeiss). The concentration of oxygen was determined by its natural solubility in a solvent. The concentration of CCl$_4$ was varied within the range 10^{-2} to 10 M. The photodecomposition of **I** was monitored by the yield of stable reaction product, 1,2,3,4-tetraphenylnaphthalene (TPN). The TPN yield was detected by a change in the optical density of the sample (ΔD), measured after a single laser pulse at the wavelength $\lambda = 334$ nm at 200 μs. Magnetic field was applied by permanent Sm−Co magnet with the moving pole ensuring the variation of the magnetic field. MFE was determined according to the following formula:

$$\text{MFE} = \left(\frac{\Delta D - \Delta D_{\text{H}}}{\Delta D}\right)100\%$$

where ΔD (ΔD_{H}) is the absorbance change detected under geomagnetic (external) field. According to the proposed formula, MFE > 0 with the TPN yield decreasing in the external magnetic field and MFE < 0 with TPN yield increasing. The points of the magnetic field dependencies are the results of the statistical treatment of 7−10 kinetic traces. The standard experimental error of MFE measurements was estimated not to exceed 2%.

Kinetic Measurements. In these experimental series, the initial concentration of reagents was **I** $C = 1 \times 10^{-3}$ M and CCl$_4$ $C = 5$ M. All experiments were performed in the presence of oxygen dissolved in hexane because preliminary experiments have shown the identity of the kinetic traces of the reaction between dimethylsilylene and CCl$_4$ detected both in aerated and deaerated solvents. In all kinetic experiments, the wavelength of probing light was the maximum of absorption of transient species, $\lambda = 334$ nm. To extract the effective reaction rate constants, the processing of the kinetic traces of the decay of transient absorption was performed by an in-house computer program. The resulting kinetic curves were treated using nonlinear regression by the least-squares fit for the kinetics of the first, second, and combined (first and second) orders. To determine the order of decay reactions, we have varied the initial amplitude of the signal under investigation by the diminution of laser pulses intensities through the set of glass filters.

Results and Discussion

To investigate the interaction between DMS and CCl$_4$, we have watched the two aspects of this process: the reaction of dimethylsilylene with this scavenger and the influence of CCl$_4$ on the yield of 1,2,3,4-tetraphenylnaphthalene (TPN). Earlier we have reported about the influence of external magnetic field on the yield of TPN during the photodecomposition of **I**.[22] It has been demonstrated that only the fraction of TPN formed in the bulk through the reaction of the triplet and singlet dimethylsilylene with initial **I** changes under the action of magnetic field. The mechanism of this process is presented in Scheme 4. Earlier based on the CIDNP data analysis,[23] the following scheme was proposed for the dimethylsilylene reaction with carbon tetrachloride (Scheme 5). In the presence of these two scavengers (**I** and CCl$_4$), carbon tetrachloride is expected to be an effective concurrent with **I** in their reaction with triplet dimethylsilylene. Because the MFE measurements allow one to reliably determine the spin state from which silylene reacts with **I**,[22] it is of great interest to trace experimentally this competition by the alteration of MFE sign and magnitude with varying CCl$_4$ concentration.

Indeed, in the system under study, we have experimentally registered the influence of the external MF on TPN yield. Figure 1 shows the MFE dependence detected during the photolysis of **I** on the carbon tetrachloride concentration. During these measurements, all sample solutions contained dissolved oxygen in the equilibrium concentration (i.e., the samples were not subjected to deaeration, see Experimental Section). All of these experiments were performed at fixed magnetic field strength, $H = 560$ G. Earlier,[22] it was shown that this MF magnitude corresponds to the extremum of field dependencies measured in the presence of oxygen. Figure 1 demonstrates that the variation of CCl$_4$ concentration leads to the alteration of MFE sign. At the initial part of this dependence (when CCl$_4$ concentration does not exceed 0.5 M), the sign of MFE corresponds to the triplet state of TPN paramagnetic precursor−1,6-biradical **III**. The MFE of the same sign was registered in the photodecomposition of **I** without any scavengers.[22] Indeed,

SCHEME 4: Photodecomposition of 7-Silanorbornadiene, I
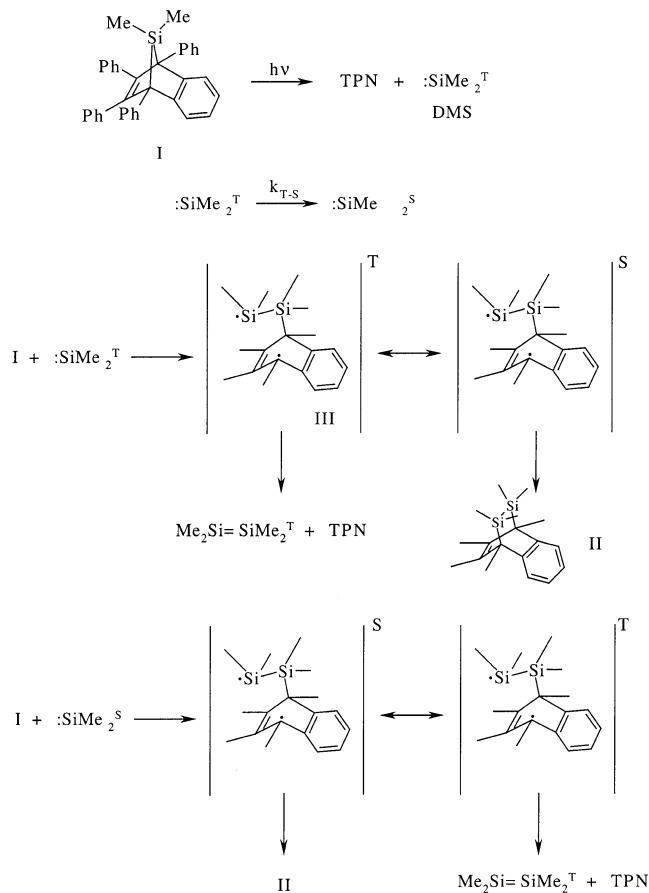
SCHEME 5: Mechanism of DMS Reaction with CCl$_4$ According to CIDNP Analysis^a
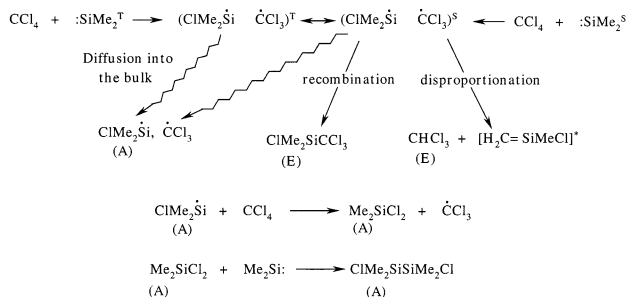
^{a} A and E denote the signs of the observed CIDNP effects, absorption and emission, respectively. The ∗ denotes an unstable product.

the extremum of MFE dependence corresponds to the minimal TPN yield because, in this case, the rate of T−S conversion into 1,6-biradical **III^T** would be maximal and the resulting singlet 1,6-biradical **III^S** provides the formation of another reaction product **II** (see Scheme 4). As the CCl$_4$ concentration increases, the MFE sign changes. According to the MFE theory,[26] the alteration of MFE sign testifies that under these conditions the MFE is formed already in the singlet biradical precursor.

The alteration of MFE sign reliably confirms the competition between **I** and CCl$_4$ in their reaction with triplet silylene. In the extremum of obtained dependence (Figure 1), the concentration of carbon tetrachloride is 5 M, that is, greater than that of norbornadiene **I** by 3 orders of magnitude. Remember that the reaction of dimethylsilylene with **I** is characterized by the rate constant close to the diffusion control limit, $k = 5.7 \times 10^9$
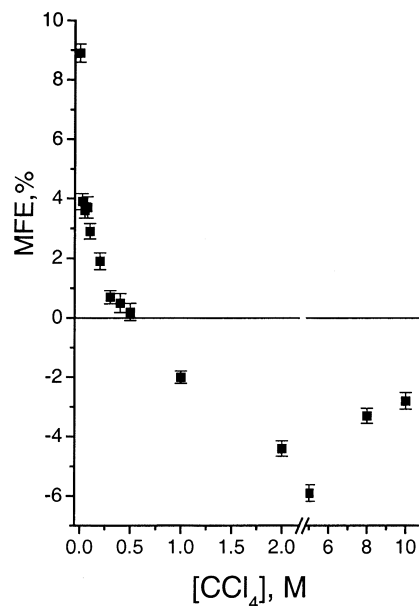

Figure 1. MFE dependence on carbon tetrachloride concentration during the photolysis of **I** ($C = 7 \times 10^{-4}$ M) in the presence of oxygen at MF strength $H = 560$ G.
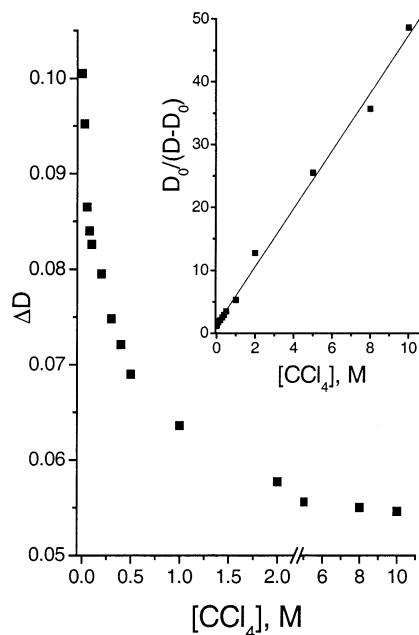

Figure 2. The dependence of TPN yield measured at $\lambda = 334$ nm on CCl$_4$ concentration in the photolysis of **I** ($C = 7 \times 10^{-4}$ M) in the presence of oxygen. The insert shows the dependence of $D_0/(D - D_0)$ on CCl$_4$ concentration.

M^{-1}·s^{-1}.[16] Therefore, the rate of the silylene reaction with CCl$_4$ should be greater than 10^7 M·s^{-1}; the rate constant of DMS reaction with CCl$_4$ should be on the order of 10^6 M^{-1}·s^{-1}. The analysis of CIDNP effects and chromatography data allowed identification of the end products of the interaction of DMS and CCl$_4$. However, CCl$_4$ is a potential complexing agent for dimethylsilylene, and the channels of its influence on the yield of TPN will be discussed below.

The presence of carbon tetrachloride strongly affects the TPN yield (Figure 2). For example, when the photodecomposition of **I** is carried out in pure CCl$_4$, the TPN yield is only 54% of that in the absence of a halogen-containing reagent. The dependence of TPN yield on CCl$_4$ concentration cannot be

Reaction of Me$_2$Si with CCl$_4$ in Solution

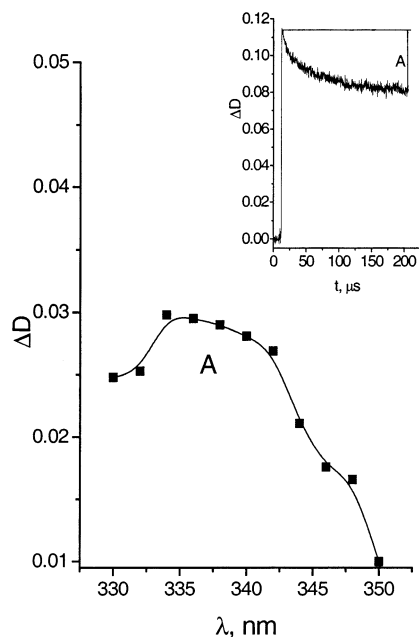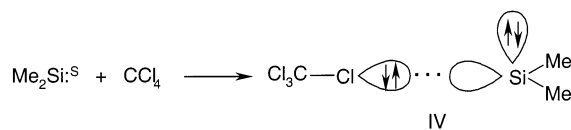*J. Phys. Chem. A, Vol. 107, No. 20, 2003* **4099**

Figure 3. The absorption spectrum of the silylene complex with CCl$_4$ ($C(\mathbf{I}) = 9 \times 10^{-4}$ M, $C(\text{CCl}_4) = 2$ M in the presence of oxygen). The insert shows the time profile of intermediate absorption at $\lambda = 334$ nm.

SCHEME 6: DMS Complexation with CCl$_4$

linearized in the frames of either the Stern–Volmer or Perrin plots (in contrast to the influence of triphenylphospine or bromoform on TPN yield[16,22]). In both cases, the influence of scavengers was explained by the quenching of the triplet state of DMS. Therefore, the present experimental result can testify that the processes of the physical quenching of triplet dimethylsilylene do not occur in the system under study. The similar influence of carbon tetrachloride on the TPN yield cannot be related to the interception of laser quanta because CCl$_4$ has no absorption at $\lambda = 308$ nm. Then we should to explain the registered dependence taking into account the competition between **I** and CCl$_4$ in their reaction with dimethylsilylene. TPN forms from the first reaction only. Thus, the contribution of the second process leads to a decrease in the TPN yield (see Schemes 4 and 5). Naturally, this competition is assumed to occur for both the triplet and singlet states of dimethylsilylene.

An additional transient absorption was recorded in the presence of CCl$_4$. Its typical time profile and absorption spectrum with a maximum at $\lambda = 334$ nm are presented in Figure 3. By analogy with bromoform,[16] it should be reasonable to ascribe this absorption to the formation of the intermediate donor–acceptor complex (**IV**) of dimethylsilylene with carbon tetrachloride (Scheme 6). Certainly, the similar complexation through the vacant p-orbital of carbenoid is possible for the singlet dimethylsilylene only. Some examples of similar complexation in matrixes between the germylenes and chlorine-containing reagents (chlorobenzene and chlorocyclohexane) are given in ref 17.

The characteristic time of the appearance of absorption under study is shorter than 50 ns. Therefore, it is impossible to reliably determine the rate constant of complex formation from the experimental data.
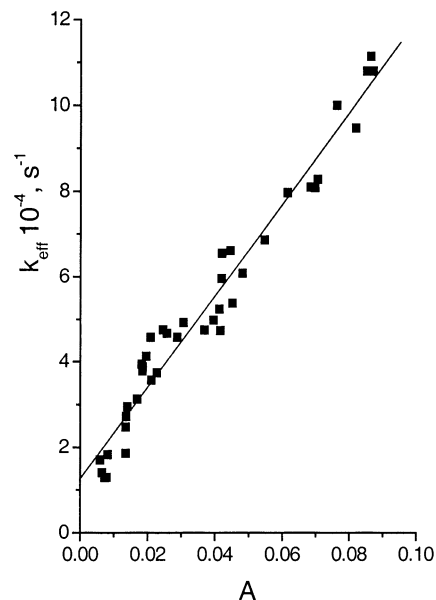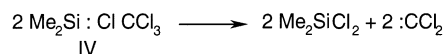

Figure 4. The dependence of k_{eff} on the initial amplitude of the transient absorption of complex **IV** ($C(\mathbf{I}) = 1 \times 10^{-3}$ M, $C(\text{CCl}_4) = 5$ M in the presence of oxygen).

SCHEME 7: Disproportionation Reaction of Complex IV

Independently of the reaction order, the effective rate constant of the intermediate decay is determined, in the general case, as follows:

$$k_{\text{eff}} = -(1/C_0)(dC/dt)|_{t \to 0}$$

where C_0 is the initial concentration of intermediate. For the first-order reaction, $k_{\text{eff}} = k_{\text{mono}}$, for the second-order reaction, $k_{\text{eff}} = 2k_{\text{bimol}}C_0$, and in the case of mixed order (first and second), $k_{\text{eff}} = k_{\text{mono}} + 2k_{\text{bimol}}C_0$.

To determine the decay reaction order, the dependence of k_{eff} on the initial amplitude of transient absorption was measured. The obtained dependence is represented in Figure 4. The effective rate constant of absorption decay demonstrates the linear dependence on laser pulse intensities and intercepts the ordinate axis. The similar dependence is characteristic of the reaction of the mixed order (first and second).

The slope of linear dependence in Figure 4 allows one to determine the bimolecular rate constant, $2k_{\text{bimol}}/\epsilon = (1.07 \pm 0.04) \times 10^6$ cm·s^{-1}. By analogy with the silylene complex with bromoform,[16] the disproportionation reaction between the two molecules of complex **IV** followed by the formation of dichlorocarbenes is assumed (Scheme 7).

The first-order reaction decay of this complex is explained in the same manner as that of the complex of silylene and PPh$_3$,[22] that is, by the reaction with initial norbornadiene **I**. The numerical value of this reaction rate constant ($k_{\text{mono}} = (1.26 \pm 0.17) \times 10^7$ M^{-1}·s^{-1}) is 2 orders of magnitude smaller than that of free dimethylsilylene.[16] This confirms the well-known statement that complexation considerably decreases the reactivity of heavy carbene analogues.[7]

Additional data on the fine details of the processes that occur during the photolysis of **I** in the presence of CCl$_4$ could be obtained also from the analysis of magnetic field dependence. The magnetic field dependence of magnetic effect was measured
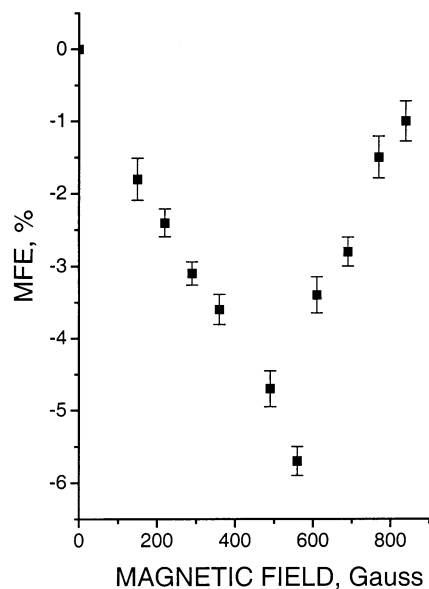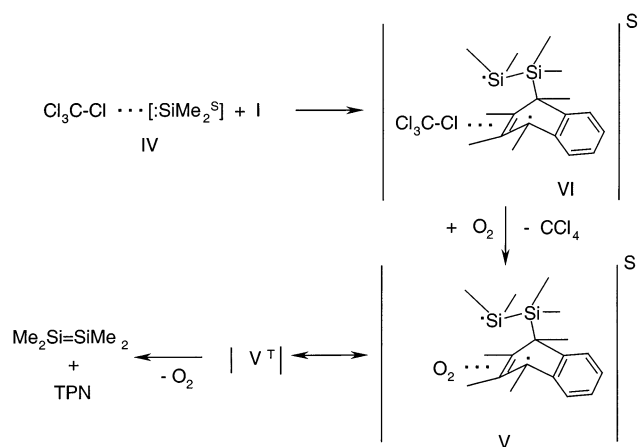
Figure 5. MFE on TPN yield in the photolysis of **I** ($C = 1 \times 10^{-3}$ M) in the presence of oxygen and carbon tetrachloride CCl_4 ($C = 5$ M).

SCHEME 8: Reaction of Complex IV with 7-Silanorbornadiene (I)

at the fixed CCl_4 concentration (5 M) and in the presence of oxygen (Figure 5). The shape of the obtained dependence is identical to those of the field dependence measured in the presence of triphenylphosphine, PPh_3, and oxygen.[22] In the presence of oxygen, the extrema of both of the MF dependencies are located at 560 G. This proves that in both cases, MFE originates from the same paramagnetic intermediate despite the presence of additional silylene scavengers. We have proposed [22] that the reversible complex (**V**) formed by silicon-centered 1,6-biradical **III** and oxygen may be considered as a similar intermediate. We have considered the formation of **V** in the presence of PPh_3 and oxygen to be a result of two consecutive reactions: first the reaction of DMS complex containing PPh_3 with **I** through the biradical intermediate and second the substitution of PPh_3 by O_2 from the last intermediate.[22] Then by analogy with the case of PPh_3,[22] we have suggested Scheme 8 for the decay reaction of dimethylsilylene complex **IV** in reaction **I**.

In conclusion, we have attempted to make estimates of the reaction rate constants of the processes under study and to compare the results of the application of spin chemistry techniques and laser pulse photolysis data. To estimate the rates of essential processes presented in Schemes 4–6, we have

SCHEME 9: DMS Reactions with Two Scavengers[a]
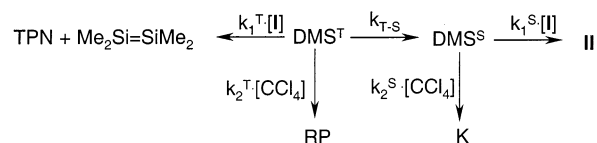
[a] K is the complex of CCl_4 and DMS.

proposed Scheme 9 for silylene reactions with two scavengers (**I** and CCl_4) on the basis of MFE and CIDNP data.

The rate constants of silylene reaction with initial **I** from different spin states are denoted as k_1^T and k_1^S, and those with CCl_4 are designated as k_2^T and k_2^S. The order of all of these reactions is pseudo-first-order, because the concentrations of these scavengers are several orders of magnitude greater than that of silylene. k_{T-S} is the monomolecular rate constant of T–S conversion of dimethylsilylene. k_{T-S} is assumed to be independent of the presence of CCl_4. The process of silylene generation (the first reaction in the Scheme 4) is considered to be an instantaneous one. Thus, initially, at $t = 0$, the triplet silylene and TPN are presented in this system in equal concentrations $[T_0] = [TPN_0]$. The initial concentrations of other intermediates are zero.

To simplify the kinetic analysis in the frames of the scheme proposed we assume 100% TPN yield in the reaction of triplet silylene with initial **I** and 100% yield of **II** in the same reaction of singlet silylene (compare with Scheme 4). In the framework of the competitive reactions scheme, the TPN concentration is described by the following expression:

$$[TPN] = \frac{k_1^T[\mathbf{I}][T_0]}{(k_1^T[\mathbf{I}] + k_2^T[CCl_4] + k_{T-S})}(1 - e^{-(k_1^T[\mathbf{I}] + k_2^T[CCl_4] + k_{T-S})t})$$

Taking into account the amount of TPN formed at the initial moment (according to the first stage of Scheme 4) and omitting the temporal factor in this expression (because the TPN concentration was determined at 200 μs, when all reactions are considered to be completed), we can get the final formula for the TPN yield:

$$[TPN] = \left(1 + \frac{k_1^T[\mathbf{I}]}{k_1^T[\mathbf{I}] + k_2^T[CCl_4] + k_{T-S}}\right)[TPN_0]$$

Then, in the limiting case in which the concentration of halogen-containing reagent tends to infinity $[CCl_4] \to \infty$, entirely triplet silylene will react with CCl_4, that is, the silylene reaction with **I** will be fully suppressed. Under these circumstances, TPN will be generated from **I** only at the initial moment. It means that the determination of this limiting TPN concentration ($[TPN_0]$) will allow one to calculate the initial concentration of triplet silylene.

After some simple transformations, this formula is reduced to the linear dependence of the experimentally measured TPN optical density on CCl_4 concentration:

$$\frac{D_0}{D - D_0} = \left(1 + \frac{k_{T-S}}{k_1^T[\mathbf{I}]}\right) + \frac{k_2^T}{k_1^T[\mathbf{I}]}[CCl_4]$$

where D_0 and D are the optical densities of TPN formed at the initial moment ($t = 0$) and at $t = 200$ μs in the result of all reactions, respectively. In this expression, D_0 is also a variable

Reaction of Me$_2$Si with CCl$_4$ in Solution

J. Phys. Chem. A, Vol. 107, No. 20, 2003 **4101**

parameter, depending on which the experimental data can be linearized (frame in the Figure 2). D_0 is determined to be 0.0535. So the initial concentration of triplet silylene produced by the single laser pulse is determined as $[T_0] = 7.4 \times 10^{-5}$ M. Moreover, the fraction of triplet silylene reacting with initial **I** in the absence of additional scavengers is determined as $\alpha = 0.88$. Because the concentration of complex **IV**, the product of consecutive DMS reactions, cannot exceed $[T_0]$, we can obtain the lower estimation for the extinction coefficient of this complex ($\epsilon > 350$ M^{-1}·cm^{-1}) and that for the bimolecular rate constant of its decay, $2k_{\text{bimol}} > 3.7 \times 10^8$ M^{-1}·s^{-1}.

The analysis of the obtained linear dependence (Figure 2) gives the following numerical values for the ratios of rate constants:

$$k_{\text{T}-\text{S}}/k_1^{\text{T}} = 2.4 \times 10^{-4}\,\text{M}, \quad k_2^{\text{T}}/k_1^{\text{T}} = 3.2 \times 10^{-3},$$

$$k_2^{\text{T}}/k_{\text{T}-\text{S}} = 13.3\ \text{M}^{-1}$$

The lifetime of triplet and singlet dimethylsilylene in the absence of additional trapping agents is determined as follows:

$$\tau_{\text{T}} = 1/(k_{\text{T}-\text{S}} + k_1^{\text{T}}[\textbf{I}]); \quad \tau_{\text{S}} = \tau_{\text{T}} + (1/k_1^{\text{S}}[\textbf{I}])$$

Then using the standard concentration of $[\textbf{I}] = 1 \times 10^{-3}$ M and the obtained ratios of rate constants, we can write the lifetime of triplet silylene as $\tau_{\text{T}} = 0.81(1/(k_1^{\text{T}}[\textbf{I}]))$, that is, τ_{T} is determined by the rate of its reaction with **I**, rather than by T−S conversion.

To estimate τ_{T}, we assume that the rate constant of triplet silylene reaction with **I** is either equal to or greater than those measured for singlet silylene, that is, $k_1^{\text{T}} \geq 5.7 \times 10^9$ M^{-1}·s^{-1}. As a result of similar approximation, the lifetime of triplet silylene is determined as $\tau_{\text{T}} \leq 1.4 \times 10^{-7}$ s, and the rate constants of its reactions are estimated as $k_{\text{TS}} \geq 1.4 \times 10^6$ s^{-1} and $k_2^{\text{T}} \geq 1.8 \times 10^7$ M^{-1}·s^{-1}. The lifetime of singlet silylene calculated in the framework of this assumption, $\tau_{\text{S}} \leq 3.2 \times 10^{-7}$ s is in fair agreement with the literature data.[27,28]

Finally, it is of great interest to review the results on the complexes of silylene with bromoform and carbon tetrachloride to discuss the similarity and difference of their reactivities. In the case of bromoform complex, the CIDNP effects are absent. Thus, the decay reaction of the bromoform complex does not involve any radical stages. The product of silylene insertion into the C−Br bond (BrMe$_2$SiCHBr$_2$) was not detected in both GC/MS and NMR spectra. The absence of MFE in this system suggests also the absence of chemical interaction between this complex and initial **I**. So the only pathway for the decay of bromoform complex is the disproportionation process (similar to Scheme 7).[16] At the same time in the case of carbon tetrachloride, there is another decay pathway, that is, the reaction of complex **IV** with **I** deduced from MFE analysis. However, under the conditions of CIDNP experiments, that is, under continuous UV irradiation, complex **IV** can also decay via the radical abstraction pathway with the intermediate formation of radical pair (Scheme 5). The subsequent radical pair recombination results in the product of silylene insertion into the C−halogen bond (ClMe$_2$SiCCl$_3$). It is necessary to emphasize that the CIDNP effects for this recombination product are registered over the entire range of CCl$_4$ concentrations. Therefore, the complex of silylene with CCl$_4$ can also react via the radical pair stage. MFE is observed within the same range of CCl$_4$ concentrations. This proves that silylene can react with initial **I** both from the free state and from the complex with

CCl$_4$. This interpretation allows us to join without discrepancy the data of spin chemistry (CIDNP and MFE) and of laser pulse photolysis.

Conclusions

In the present paper, the reactions between the carbon tetrachloride and dimethylsilylene in both the excited triplet and the ground singlet states have been demonstrated. In the singlet state, DMS forms the donor−acceptor complex with CCl$_4$ that reacts with the initial norbornadiene. From the kinetic analysis of the silylene reactions, it was shown that the complexation decreases the chemical reactivity of DMS. The last statement is consistent with the literature data on the reactions of dimethylgermylene.[2,7]

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