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Silyl Radicals. X. On the Mechanism of Uncatalyzed Reduction of Carbon Tetrachloride with Polysilicon Hydride[1]

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Gilman and Harrell have reported first that polysilicon hydride such as tris(trimethylsilyl)silane reacted smoothly with carbon tetrachloride to give the corresponding chlorosilane without any added catalyst.[2]

The mechanism of the uncatalyzed reduction may be either a molecular reduction involving a four-centered transition state[3,4] or a free-radical chain reactions typically shown in the case of peroxide-catalyzed reduction of carbon tetrachloride with hydrosilanes.[5] The following evidence reported in this paper indicates the latter to be the case.

Both pentamethyldisilane and 1*H*-heptamethyltrisilane, dissolved in carbon tetrachloride, respectively, were converted quantitatively to the corresponding chlorosilanes by heating at 50°C for 38 hr. Addition of a small amount of a free-radical scavenger such as galvinoxyl[6] resulted in complete inhibition of the reduction of carbon tetrachloride with pentamethyldisilane even at 135°C. This is a strong indication of a free-radical nature of the uncatalyzed reaction.

$$\mathrm{Me_3SiSiMe_2H + CCl_4 \longrightarrow Me_3SiSiMe_2Cl + CHCl_3} \qquad (1)$$

$$\mathrm{Me_3SiSiMe_2SiMe_2H + CCl_4 \longrightarrow Me_3SiSiMe_2SiMe_2Cl + CHCl_3} \qquad (2)$$

Uncatalyzed reduction of carbon tetrachloride with monosilanes, such as *n*-propyldimethylsilane and triethylsilane, did not occur at 50°C. However, while triethylsilane alone did not react with an excess of carbon tetrachloride on heating at 80°C, addition of pentamethyldisilane resulted in conversion of both silanes to the corresponding chlorosilanes in good yields, and again the reaction was inhibited by galvinoxyl. These facts suggest a free-radical mechanism for the reaction. The co-chlorination of triethylsilane and pentamethyldisilane may be interpreted by the following sequence of reactions.

$$\mathrm{Me_5Si_2H \longrightarrow Me_5Si_2\cdot + (H\cdot)} \qquad (3)$$

$$\mathrm{Me_5Si_2\cdot + CCl_4 \longrightarrow Me_5Si_2Cl + CCl_3\cdot} \qquad (4)$$

$$\mathrm{Me_5Si_2H + CCl_3\cdot \longrightarrow Me_5Si_2\cdot + CHCl_3} \qquad (5)$$

$$\mathrm{Et_3SiH + CCl_3\cdot \longrightarrow Et_3Si\cdot + CHCl_3} \qquad (6)$$

$$\mathrm{Et_3Si\cdot + CCl_4 \longrightarrow Et_3SiCl + CCl_3\cdot} \qquad (7)$$

Pentamethyldisilane functions as an initiator in this scheme. The reaction of pentamethyldisilane with carbon tetrachloride could not be completed, when the mixture was degassed as thoroughly as possible. Therefore, oxygen plays some role at the initiation

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1) For part IX, see Ref. 7.

2) H. Gilman and R. L. Harrell, *J. Organometal. Chem.*, **5**, 199 (1966).

3) J. Y. Corey and R. West, *J. Amer. Chem. Soc.*, **85**, 2430 (1963).

4) J. D. Austin and C. Eaborn, *J. Chem. Soc.*, **1964**, 2279.

5) Y. Nagai, K. Yamazaki, I. Shiojima, N. Kobori, and M. Hayashi, *J. Organometal. Chem.*, **9**, 21 (1967).

6) P. D. Bartlett and T. Funahashi, *J. Amer. Chem. Soc.*, **84**, 2596 (1962).

step, although the precise mechanism is uncertain.

Pentamethyldisilane can also initiate the S_H2 reaction between an organodisilane and 1,2-dibromoethane.[7] Addition of a small amount of pentamethyldisilane to a mixture of hexamethyldisilane and 1,2-dibromoethane at 80°C resulted in complete conversion of hexamethyldisilane to trimethylbromosilane.

The relative reactivity of pentamethyldisilane to triethylsilane towards chlorination with carbon tetrachloride was determined in the presence and absence of an initiator, respectively. Since it is well established that reactions of silyl radicals with carbon tetrachloride (steps 4 and 7) are very rapid,[8] the steps 5 and 6 determine the relative reactivity which should be invariable regardless of the nature of initiation.

The reactivity ratio of pentamethyldisilane to triethylsilane in the uncatalyzed reaction was found to be 8.3 and 6.5 at 80.0°C. The dibenzoyl peroxide catalyzed reaction gave the value of 6.3 at 80.0°C. These two sets of values agree with each other fairly well although not perfectly.[13]

It is worthwhile to note that pentamethyldisilane is several times more reactive than triethylsilane toward carbon tetrachloride. The difference in the reactivity may arise from the more electron-positive nature of the pentamethyldisilanyl group than the monosilyl group,[9] which may play a role in a possible polar effect in the transition state of chlorine abstraction.[10]

Experimental

Materials. Pentamethyldisilane,[11] 1*H*-heptamethyltrisilane,[11] triethylsilane,[12] and galvinoxyl[6] were prepared according to literatures.

Uncatalyzed Reaction of Pentamethyldisilane with Carbon Tetrachloride in the Absence or the Presence of Galvinoxyl. A mixture of pentamethyldisilane (0.109 g, 0.83 mmol) and carbon tetrachloride (1.19 g, 7.73 mmol) in a sealed tube was placed in a thermostatted oil bath kept at 135±1°C for 1 hr. Inspection of the mixture by glc after addition of *m*-xylene (internal standard) revealed that it contained pentamethylchlorodisilane (0.85 mmol, 102%), chloroform and unchanged carbon tetrachloride. On the other hand, only a trace amount of pentamethylchlorodisilane was detected by glc with another mixture of pentamethyldisilane (0.119 g, 0.90 mmol) and carbon tetrachloride (1.12 g, 7.28 mmol), which contained 0.0057 g (0.014 mmol) of galvinoxyl, after heating at 135±1°C for 1 hr.

Competitive Chlorination of Pentamethyldisilane and Triethylsilane. *a) Uncatalyzed Thermal Reaction*: In small glass ampules (*ca.* 3 *ml*) were placed a solution of pentamethyldisilane and triethylsilane in carbon tetrachloride. Dry nitrogen was bubbled gently through the capilary for about 5 min and then ampules were sealed. These were immersed in an oil bath thermostatted at 80.0°C. After given intervals, ampules were picked up and mixtures were analyzed on glc.

b) Dibenzoyl Peroxide Catalyzed Reactions: Similarly mixtures of pentamethyldisilane, triethylsilane, and dibenzoyl peroxide in carbon tetrachloride were subjected to reaction.

c) Analytical Procedure: Products were identified by glc and NMR. For quantitative analyses an internal standard (*e.g.* *m*-xylene) was used. The relative reactivity was calculated by the equation.

$$(k_A/k_B) = \log([A_0]/[A_t])/\log([B_0]/[B_t])$$

where $[A_0]$ and $[A_t]$ are the concentrations of pentamethyldisilane (A) at the initial and a given time, respectively, and $[B_0]$ and $[B_t]$ have a similar significance for triethylsilane (B). Relative rates were calculated by the least squares method. Data are listed in Table 1.

TABLE 1. COMPETITIVE CHLORINATION OF Me_5Si_2H (A) AND Et_3SiH (B) WITH CCl_4 AT 80.0°

Reactants (mmol)				Reaction time (hr)	$[A_t]$	$[B_t]$	k_A/k_B
$[A_0]$	$[B_0]$	CCl_4	BPO				
2.07	2.10	19.6[a]		12	1.54	2.01	8.2_6
				18	1.41	1.99	
				24	1.37	2.00	
				30	0.93	1.91	
1.04	4.09	19.8		12	0.93	4.04	6.5_2
				18	0.79	3.04	
				24	0.87	3.99	
				30	0.79	3.97	
				36	0.75	3.91	
1.04	4.09	19.8	0.09	10 (min)	0.56	3.81	6.3_1
				20 (min)	0.14	3.10	
				30 (min)	0.13	2.92	

a) Reaction with this mixture in the presence of BPO was too rapid to determine the relative rates.

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[7] A. Hosomi and H. Sakurai, *ibid.*, **94**, 1384 (1972).

[8] A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**, 199 (1969).

[9] H. Sakurai, S. Deguchi, M. Yamagata, S. Morimoto, M. Kira, and M. Kumada, *J. Organometal. Chem.*, **18**, 285 (1969).

[10] R. A. Jackson, *Advan. Free-Radical Chem.*, **3**, 231 (1969).

[11] M. Kumada, M. Ishikawa, and S. Maeda, *J. Organometal. Chem.*, **2**, 478 (1964).

[12] F. P. Price, *J. Amer. Chem. Soc.*, **69**, 2600 (1947).

[13] **Note Added in Proof:** L. H. Sommer and L. A. Ulland, *J. Amer. Chem. Soc.*, **94**, 3803 (1972), reported recently the rate of hydrogen abstraction from $Ph_3SiPhSiMeH$ by trichloromethyl radicals relativeto α-NpPhMeSiH to be 7.1.