7776 *J. Am. Chem. Soc.* **1987**, *109*, 7776-7781

Kinetics of the Reaction of Organosilyl Hydrides with Carbenium Ions in an Inert Solvent. Silicocation Intermediacy. Single Electron Transfer versus Synchronous Hydride Transfer

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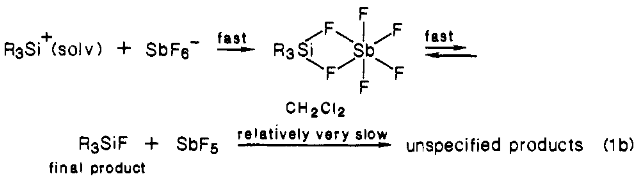
Abstract: The rate of reduction of carbenium center with various organosilyl hydrides and one organogermyl hydride in methylene chloride solution was studied. Triphenylmethylium and cycloheptatrienylium salts having metal-halogen complex anions were used as the carbenium substrates. Although the net result of the process at silicon and germanium centers is the formal substitution of H⁻ by halide ion originating from the decomposition of halometallate ion, this substitution proceeds stepwise and one or more silicocation (germanium cation) intermediates are formed. It is possible that one of them has a structure of silylenium (germylenium) ion $\equiv Si^+$ ($\equiv Ge^+$), which may be modified by interaction with solvent. The process which occurs at the carbon center is the hydride-transfer reduction. The kinetic data indicate that the single electron transfer pathway involving the radical silicocation intermediate is followed rather than a synchronous H⁻ transfer from silicon to the carbenium center.

Some years ago we found that the reaction of triorganosilyl hydrides with triphenylmethylium hexafluoroantimonate in methylene chloride proceeds by a stepwise mechanism.[1] Evidence was provided that the final silicon product of this reaction, i.e., the corresponding triorganofluorosilane, was formed as a result of a process consecutive to the formal hydride transfer to the carbenium ion. The following mechanism was proposed

$$R_3SiH + Ph_3C^+ \xrightarrow{slow} R_3Si^+(solv)^2 + Ph_3CH \text{ final product} \quad (1a)$$



(1b)

Although the above equations explain our previous results well, they should be considered rather as a convenient working hypothesis, which requires further verification and more accurate defining. Our present interest centers on eq 1a, which can be conveniently followed with UV spectroscopy. There are good reasons for which further studies leading to a better understanding of this step could be of value.

Silyl hydrides (hydrosilanes) are commonly applied in organic synthesis as reagents for selective reduction.[4-7] The key reduction step in these processes is often formulated as the hydride transfer from silicon to a transient carbenium center.[6,7] The reaction 1a, which can be followed independently of the consecutive reaction 1b, may serve as a convenient model in studies directed toward the elucidation of the hydride-transfer reduction with the hydrosilane reagents.

Table I. The Second-Order Rate Constant Observed for the Reaction of Triethylsilyl Hydride with Carbenium Ions Having Various Complex Counterions[b]

carbenium ion	counterion	silyl hydride	k,[a] $dm^3 \cdot mol^{-1} \cdot s^{-1}$
Ph_3C^+	SbF_6^-	Et_3SiH	139
	AsF_6^-		120
	PF_6^-		117
	BF_4^-		110
	$SbCl_6^-$		120
	$FeCl_4^-$		120
$C_7H_7^+$	SbF_6^-		0.046
	PF_6^-		0.037
	BF_4^-		0.031
Ph_3C^+	SbF_6^-	Et_3GeH	2780
	AsF_6^-		3050
	$FeCl_4^-$		3200
$C_7H_7^+$	BF_4^-		2.63

[a] The k value for Ph_3C^+ is reproducible within better than ±10%. [b] In methylene chloride at 25 °C.

There is also another aspect in which more detailed studies of the process 1 seem to be of interest. For a long time the reaction of triorganosilyl hydride with carbenium ion has been explored with the purpose of generation of silylenium ion, the silicon analogue of carbenium ion. Although first attempts were unsuccessful as reviewed by Corriu and Henner,[8] more recently, however, Lambert and Schulz[9] claimed to synthesize by this method tris(2-propylthio)silylenium perchlorate, which was fairly stable in methylene chloride solution. Although evidence came from both electrical conductance as well as from ^{13}C and ^1H NMR spectroscopy, Olah et al.[10] presented an opinion that more convincing proofs were needed. Quite recently Lambert and coworkers provided some new evidence in favor of their concept claiming to synthesize ionic triphenylsilylenium perchlorate[11] which was in contrast to earlier reports of covalent structures of triorganosilyl perchlorates.[12] Earlier observations by Sommer and Baumann[13] on the same system also seemed to indicate the gen-

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(1) Chojnowski, J.; Wilczek, L.; Fortuniak, W. *J. Organomet. Chem.* **1977**, *135*, 13.

(2) Formation of this complex was suggested as a result of the interaction of R_3SiF with SbF_5 by Olah et al. (Olah, G. A.; Mo, Y. L. *J. Am. Chem. Soc.* **1971**, *93*, 4942). We suppose that the complex remains in equilibrium with its components which lies well to the side of the complex. However, SbF_5 is slowly converted as a consequence of its reaction with the solvent which leads to R_3SiF as the final product.

(3) The reaction of SbF_5 with CH_2Cl_2 may begin somewhat analogously to that of $AlCl_3$ with CH_2Cl_2 as described by Bock et al. (Bock, H.; Lechner-Knoblauch, U. *J. Organomet. Chem.* **1985**, *294*, 295).

(4) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworth: 1981; p 329.

(5) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: 1983; p 273.

(6) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633.

(7) Fleming, I. *Organic Silicon Chemistry in Comprehensive Organic Chemistry*; Barton, O.; Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, p 541.

(8) Corriu, R.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1.

(9) Lambert, I. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671.

(10) Olah, G. A.; Laali, K.; Faroog, O. *Organometallics* **1984**, *3*, 1337.

(11) Lambert, J. B.; McConnell, I. A.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 2482.

(12) (a) Wannagat, U.; Liehr, W. *Angew. Chem.* **1957**, *69*, 783. (b) Barton, T. J.; Hovland, A. K.; Tully, C. R. *J. Am. Chem. Soc.* **1976**, *98*, 5695. (c) Barton, T. J.; Tully, C. L. *J. Org. Chem.* **1978**, *43*, 3649.

(13) Sommer, L. H.; Bauman, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 7045.

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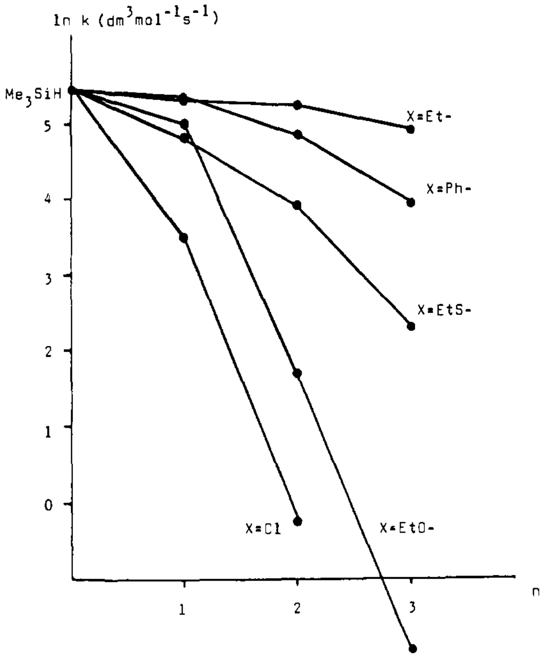


Figure 1. Structure-reactivity dependence for the reaction of $Ph_3C^+SbF_6^-$ with silyl hydrides of general formula $X_nMe_{3-n}SiH$. X = Et-, Ph-, EtS-, EtO-, Cl-. Rate constants in methylene chloride at 25 °C.

eration of the silylenium ion. They reported that the stereochemical outcome of the reaction of silyl hydride with trityl halides depended critically on the solvent used, and a completely racemic product was obtained in methylene chloride solution. We hoped that more detailed studies of the kinetics of the reaction of silyl hydrides with stable carbenium salts in an inert solvent of low nucleophilicity like CH_2Cl_2 might give some information relevant to the silylenium ion question. It should be mentioned that earlier kinetic studies of carbenium ion–silane hydride transfer were performed in a solvent taking part in the reaction as a nucleophile attacking the silicon center.[14]

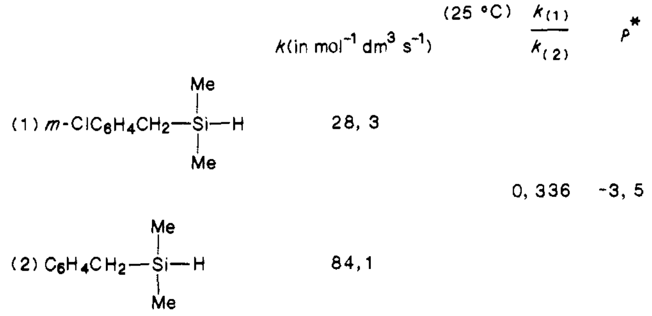
Results and Discussion

General Kinetic Features of the Process. The kinetic studies of the reaction of silyl hydrides with stable triphenylmethylium (trityl) salts in methylene chloride solution[1] have been extended to include more silyl hydride and carbenium salt structures. Some attempts to extend this study to germanium and tin analogues were also made. The rate of the disappearance of carbenium ion was investigated following its VIS absorption. The formation of final products was in some cases monitored by gas chromatography. Results confirmed our previous observations.[1,15] In particular, stoichiometric (one-to-one) amounts of substrates were used. The reaction led to stoichiometric formation of the addition product of the hydride ion to the carbenium ion. The silicon product was the corresponding halosilane. The rate was virtually independent of the structure of the carbenium counterion which was demonstrated here in a series of kinetic experiments with trityl salts having different anions (Table I). It should be mentioned that in the range of the initial salt concentration used (10^{-3}–10^{-4} M) free ions coexisted with ion pairs.[16] Ion pairing had no evident influence on the rate. In general, in all cases the same kinetic law was observed (eq 2).

$$-\frac{d[\equiv C^+]}{dt} = k[\equiv C^+][\equiv SiH] \qquad (2)$$

Systematic kinetic studies included also the reaction of the silyl hydride with tropenylium (cycloheptatrienylium, $C_7H_7^+$) salts having various complex anions. Although the tropenylium ion shows much lower electron affinity in comparison with Ph_3C^+,[17] the reaction takes an analogous course, and the kinetic eq 2 is obeyed. The decrease of the absorbance of tropenylium ion and the increase of the absorbance due to cycloheptatriene were observed at the same time. The rate of the cycloheptatriene formation was confirmed to be the same as the rate of the tropenylium conversion. However, it should be mentioned that the reproducibility of the results of the kinetic experiments with the tropenylium salts were somewhat worse than those with the Ph_3C^+ salts. Solution of the $C_7H_7^+$ salts in CH_2Cl_2 undergoes rather fast ageing, which may lead to a deviation in the course of the reaction. To avoid this trouble the solution of the salt was prepared on a high vacuum line and used within a short period of time.

The comparison of the rate of the silane substrates having various groups attached to a silicon atom permits to conclude that substituents modify markedly the reactivity. The influence of their structure on the rate constant could be interpreted in terms of a combination of polar, resonance, and steric effects. Electron-withdrawing substituents through the inductive $-I$ effect considerably decrease the rate, which is evident from the comparison of the rate of benzyldimethylsilyl hydride with its meta chloro derivative.



	(25 °C) k(in mol^{-1} dm^3 s^{-1})	$\frac{k_{(1)}}{k_{(2)}}$	ρ^*
(1) $m\text{-}ClC_6H_4CH_2\text{—}SiMe_2\text{—}H$	28, 3		
		0, 336	-3, 5
(2) $C_6H_4CH_2\text{—}SiMe_2\text{—}H$	84,1		

The sensitivity of the process to the polar effect is also reflected in almost 200-fold reduction of the rate of Me_3SiH on the substitution of chlorine atom in the methyl group[1] and in complete inertness of Cl_3SiH.

Resonance effects manifest themselves as a variation of reactivity in series of $X_nMe_{3-n}SiH$ reactions, where X is a group having electrons available to a π-conjugation. Results are presented in Figure 1.

The rate of the reaction decreases on substitution with the first X group less than it does on substitution with the subsequent groups. Since the inductive effect is expected to be more or less additive, this behavior is best interpreted by the contribution from the resonance effect, which, when referred to the single X group, becomes less effective with the increasing n (see, for example[18]).

If someone assumed that a parallellism exists between the substituent effect on the stability of the transition state and on the stability of the product, i.e., silylenium ion, then our data would not confirm the expectation of others[9] that three mercapto substituents at silicon atom exert a particularly high stabilizing effect on the silylenium ion structure nor would the data confirm that the triphenylsilyl structure is particularly convenient for the generation of the silylenium ion as it was suggested in.[11] Actually, the carbenium ion disappears evidently faster in the presence of Me_3SiH than of Ph_3SiH or $(EtS)_3SiH$. The data in Figure 1 indicate also that the mercapto group stabilizes the partial positive charge on silicon by resonance effect less effectively than the alkoxy group.

Steric effect does not seem to be very important for most substrates studied here. It becomes meaningful only if a silane bearing very bulky groups is used. For example, tri-(*tert*)-butylsilane reacts so slowly with Ph_3C^+ that its rate cannot be measured with a reasonable precision. However, a good example of a low sensitivity of the reaction to the substituent steric effect

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(14) Carey, F. A.; Wang Hsu, C. L. *J. Organomet. Chem.* **1969**, *19*, 29.

(15) Chojnowski, J.; Mazurek, M.; Wilczek, L. *Analyst* **1976**, *101*, 286.

(16) Gogolczyk, W.; Słomkowski, S.; Penczek, S. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1729.

(17) Harmon, K. M. In *Carbonium Ions*; Olah, G. A., von Schleyer, D. R., Eds.; Wiley-Interscience: New York, 1973; Vol. 4, p 1579.

(18) Truong, T.; Gordon, M. G.; Boudjouk, P. *Organometallics* **1984**, *3*, 484.

Table II. Rate Constants (25 °C) and Activation Parameters for Reactions of Trialkylsilyl Hydrides with the Triphenylmethylium Hexafluoroantimonate in CH_2Cl_2

silane	k, $dm^3 \cdot mol^{-1} \cdot s^{-1}$	ΔH^{*}, $Kcal \cdot mol^{-1}$	ΔS^{*}, $cal \cdot mol^{-1} \cdot deg^{-1}$
Me_3SiH	223	5.8	−28
Et_3SiH	139	7.0	−25
n-Pr_3SiH	175		
n-Bu_3SiH	279	6.3	−26
n-Hex_3SiH	256		

is increase of the rate in the series $Et_3SiH < Pr_3SiH < Bu_3SiH \approx Hex_3SiH$ (see Table II).

The reaction shows a low value of activation enthalpy and a rather high negative value of the activation entropy (Table II). The transition state has a loose structure as indicated by the negative value of ρ^{*} and a low sensitivity to steric effects of substituents. Therefore, the highly negative activation entropy is perhaps partly connected with the reorganization of the solvation shell of the substrates on coming to the transition state. Further discussion is delayed to the next section.

The reaction of triethylgermyl hydride with carbenium ion was studied by using both hydride acceptors, i.e., Ph_3C^+ and $C_7H_7^+$. The reaction proceeds in an analogous way. In particular, eq 2 is obeyed in the concentration range in which free ions dominate, and the rate does not seem to change with changing the counterion. Thus, there is no reason to suppose that any deeper difference exists in the reaction mechanism between silicon and germanium analogues. The reaction of the germanium hydride is evidently faster than that of the corresponding silyl hydride by a factor of about 25 and 60 for Ph_3C^+ and $C_7H_7^+$, respectively (Table I). The attempts to follow the rate of the corresponding reaction of trialkyl tin hydride were unsuccessful because of its high rate. The process proceeded faster at least by a factor of 10^5 as compared with the reaction of silicon analogue.

Before coming to the more detailed mechanistic interpretation of the formal hydride transfer step of eq 1 we consider it necessary to emphasize that this study fully confirms the nonsynchronous course of the replacement process of the hydrogen substituent at silicon in result of the interaction with carbenium salts. The body of evidence which we collected here and in the previous study[1] (Table III) leaves no room for any argument for a S_N2 Si pathway. However, such a statement seems worthwhile in the light of universality of S_N2 mechanisms in organosilicon chemistry and also since a synchronous four center mechanism has been postulated for somewhat similar reaction systems involving triorganosilyl hydrides.[14,19,20a] In particular, F. A. Carey and C. L. Wang Hsu[14] have done comprehensive kinetic studies on the silane–carbenium hydride transfer in acetic acid. This solvent being a nucleophile can attack silicon and actually participates in the reaction, since the corresponding acetoxysilane is the final silicon product. The authors postulate that the acetoxy group substitutes the silicon and that the H^- is transferred to carbenium ion in one concerted step involving a four centered transition state.

The absence of any anion effect on the rate shows that the rate-determining step is quite different from the silicon product-determining step. Since any mechanism involving the formation of a neutral silyl radical intermediate does not seem feasible and since we showed that we are dealing with a nonsynchronous formation of the final silicon and carbon products, we must conclude that a transient silicocation must appear in the system. It is not unreasonable to postulate that the silicocation species has a form of silylenium ion with silicon having formal coordination number three. However, in considering the silicon coordination, allowance must be made for the interaction of this intermediate with the solvent.[20b] Methylene chloride has a low nucleophilicity and is a routine solvent for studies of carbenium ions. Nevertheless, in view of a high ability of silicon to coordinate electron–rich species, the silylenium ion structure may be affected by the solvation with CH_2Cl_2 to a larger extent than the structure of its carbon analogue. The transient formation of the silylenium ion in this process would be in agreement with Schulz–Lambert interpretation of the behavior of some carbenium perchlorate–hydrosilane systems[9,11] and with stereochemical results of Sommer and Baumann.[12]

Single Electron Transfer Pathway Versus Synchronous Hydride Transfer. The reaction studied here falls into the broad group of processes which are a subject of a sharp controversy. Many classic reactions long thought to proceed via pure polar mechanism are now considered to involve radical-ion intermediates.[21-24] Processes resulting in the transfer of a hydrogen atom with an electron pair from tetrahedral carbon to carbenium ion center are well-known in organic chemistry. They have often been considered to involve a synchronous one-step pathway.[25] The synchronous hydride transfer (eq 3) could be considered as one possibility of the mechanism of carbenium center reduction with a silyl hydride.

$$\equiv Si - H + {}^{+}C\equiv \rightleftharpoons [\equiv \overset{\delta+}{Si} \text{----} H \text{----} \overset{\delta+}{C} \equiv] \rightarrow \equiv Si^{+} + HC\equiv \qquad (3)$$

However, silicon shows, in some respects, a close similarity to metal elements. Mechanisms, which are characteristic of reductive processes with metal compounds are those involving single electron transfer (SET).[26-29] A few years ago Klinger, Mochida, and Kochi[30] postulated such a mechanism for the addition of triorganostannyl hydride and their germanium and silicon analogues to tetracyanoethylene (TCNE). A somewhat analogous pathway for the reaction of silyl hydrides with carbenium ions could also be formulated (eq 4).

$$R_3SiH + C^+ \rightleftharpoons \underset{\text{CTor encounter complex}}{[R_3SiH\ {}^{+}C\equiv]} \xrightarrow{\text{rate limiting}} \underset{\text{free radical pair}}{\{R_3Si^{+}\dot{H}\ \dot{C}\equiv\}} \rightarrow R_3Si^{+} + HC \qquad (4)$$

The rate-limiting electron-transfer step according to Kochi and co-workers takes place within a charge-transfer complex. To our knowledge, no evidence of the formation of the CT complex of silyl hydrides with carbenium ions exists; however, the transfer may occur here within an encounter complex as well. Radical pair decay is likely to proceed as a cage process, and thus the radical intermediates cannot be detected by EPR technique.[31]

Recently the reaction of hydrosilylation of olefin was postulated to occur via a radical silicocation.[32] One of the possible ways of further conversion of this intermediate was suggested to be its fragmentation to silylenium ion and hydrogen radical, which is in a close analogy to the pathway presented in eq 4.

The most important evidence for the SET mechanism according to Kochi and co-workers[30] could be provided by deuterium kinetic isotope effect (KIE) studies.

On the substitution of $\equiv SiH$ with deuterium, the synchronous hydride transfer should lead to a primary kinetic isotope effect of a rather high value. Instead, the electron-transfer mechanism

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(19) Corey, J. Y.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2430.

(20) (a) Austin, J. D.; Eaborn, C. A. *J. Chem. Soc.* **1964**, 2279. (b) Eyler, J. R.; Silverman, G.; Battiste, M. *Organometallics* **1982**, *1*, 477.

(21) Eberson, L. In *Advances in Physical Organic Chemistry*; Gold, V., Bethel, D., Eds.; Academic Press: London, 1982; Vol. 18, p 79.

(22) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

(23) Okhlobistyn, O. Yu.; Berberova, N. T. *Zhurn. Obshch. Khim.* **1981**, *17*, 88.

(24) Chanon, M.; Tobe, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1.

(25) See, for example: Deno, N. C.; Peterson, H. J.; Saines, G. S. *Chem. Rev.* **1960**, *60*, 7 or ref 14.

(26) Kochi, J. K. In *Organometallics Mechanisms and Catalysis*; Academic Press: New York, 1978.

(27) Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139.

(28) Gould, E. S. *Acc. Chem. Res.* **1985**, *18*, 22.

(29) Cannon, R. D. *Electron Transfer Reactions*; Butterworth: London, 1980.

(30) Klinger, R. J.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6626.

(31) Our preliminary effort to detect free radicals in the reaction system studied here was unsuccessful.

(32) Khapitcheva, A. A.; Berberova, H. T.; Klimov, E. C.; Okhlobistyn, O. Yu. *Zhurn. Obshch. Khim.* **1985**, *55*, 1533.

Table III. Evidence for Nonsynchronous Mechanism Involving a Silicocation[a] Intermediate

observed features of the reaction being against S_N2 Si but in favor of the transient formation of a silicocation[a]	results expected for a synchronous bond making and bond breaking to silicon
1. product R_3SiF from the reaction of $R_3SiH + Ph_3C^+SbF_6^-$ forms after the disappearance of Ph_3C^+ and the formation of Ph_3CH[1]	R_3SiF and Ph_3CH form synchronously
2. the reaction is of the first order with respect to the salt, when free ions are dominating species[1]	the second order in the salt
3. the rate is independent of the structure of complex anion (Table I)	a considerable variation of the rate with changing of counterion
4. the same rate in CH_2Cl_2 and in CH_2Cl_2-*n*-heptane system[1]	increasing of the rate on coming to a medium of lower polarity
5. low sensitivity to steric effect of substituents (Table II)	rather a high sensitivity to the steric effect
6. electron-withdrawing substituents considerably decrease the rate	rather a low sensitivity to polar effects
7. *n*- and π-electron substituents exert a special effect on the rate (Figure 1)	rather no particular effect of *n*- and π-electron substituent
8. strained ring substrates show almost the same rate as their cyclic analogues (Table V)	a considerable rate enhancement for strained ring substrates
9. small amounts of water and fortuitious nucleophiles do not affect the rate[1]	nucleophiles stronger than the counterions should increase the rate

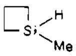
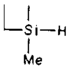
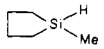
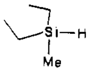
[a] A positively charged silicon species valency, coordination of Si, and spin of the species are not considered at the moment.

Table IV. Deuterium Kinetic Isotope Effect of the Reaction of Triorganosilyl Hydrides with Triphenylmethylium and Tropenylium Salts in Methylene Chloride at 25 °C

carbenium salt	silane	rate constant, dm^3 mol s^{-1}	k_H/k_D
$Ph_3C^+SbF_6^-$	$PhMe_2SiH$	210	1.49
	$PhMe_2SiD$	141	
$C_7H_7^+SbF_6^-$	$PhMe_2SiH$	$3.46\ 10^{-2}$	1.45
	$PhMe_2SiD$	$2.38\ 10^{-2}$	
	Et_3SiH	$4.67\ 10^{-2}$	1.41
	Et_3SiD	$3.32\ 10^{-2}$	

should give rise only to a secondary KIE with upper limit k_H/k_D of about 1.5.[30] The values obtained in this study are falling within the range predicted for the SET pathway (Table IV). However, the low value of the observed KIE could also be attributed to an unsymmetrical structure of the transition state for the synchronous H^- transfer. As a matter of fact, the substratelike transition state might have been anticipated here on the basis of theoretical calculations implying a higher stability of silylenium ion as compared to their carbon analogues.[33,34] To check this possibility the KIE was studied in the reaction with both triphenylmethylium and tropenylium substrates. The latter carbenium ion is a much weaker electrophile than the former one. The difference in acidity of Ph_3C^+ and $C_7H_7^+$ measured in pK_{R^+} units is almost as high as 11.5, the value of which may be deduced from the data in ref 35 and 36. The difference in reactivity toward $\equiv$SiH, though not so high, is still considerable, since the rate constant is reduced by a factor of 10^4 in going from Ph_3C^+ to $C_7H_7^+$. Consequently, the transition state in the synchronous process should be more symmetrical for the tropenylium ion, which should lead to a higher KIE value for $C_7H_7^+$ than for Ph_3C^+. The KIE value observed remains, however, at the same low level for both of these ions (Table IV) thus supporting the SET mechanism.[37] It should be noted that a highly unsymmetrical transition-state structure with a little hydride transfer could be in disagreement with a rather high negative value of Hammett's ρ observed for this reaction.

Table V. Comparison of Rate Constants and Activation Parameters of the Reaction of Some Ring Strained Hydrosilanes and Their Acyclic Analogues with Triphenylcarbenium Ion in Methylene Chloride

silane	temp, °C	*k*, $dm^3 \cdot mol^{-1} \cdot s^{-1}$	$\Delta H^\ddagger$, $Kcal \cdot mol^{-1}$	$\Delta S^\ddagger$, $cal \cdot mol^{-1} \cdot deg$
	+25	163		
	−25	13.0	7.0	−25
	+25	164		
	−20	21.4	6.3	−27
	+25	139		
	−20	16.2	6.6	−26
	+25	138		
	−20	18.3	6.2	−28

Another approach to the SET pathway problem, which we exploited, was the study of the reaction rate of a silyl hydride having the silicon atom being a part of a strained ring and the comparison with the rate of the reaction of its acyclic analogue. Any synchronous hydride transfer should be very sensitive to the ring strain. A considerable reactivity enhancement of the strained cyclic substrate is expected for a mechanism involving a five coordinate silicon transition state due to the release of the strain in the formation of a trigonal bipyramid.[38] On the other hand, a process involving bond breaking with no bond making at silicon in a rate-limiting step should lead to a considerable reduction of reactivity for a strained cyclic structure. This is because the transition-state structure would be lying somewhere between the tetrahedral structure of the substrate and the trigonal structure of the enium ion product. Now, considering the single electron transfer pathway, there is no major change in geometry of the bonds around the silicon atom in going to the transition state, which is represented in eq 5.

$$[\equiv\mathrm{Si}—\mathrm{H}\cdots{}^{+}\mathrm{C}\equiv \leftrightarrow \equiv\mathrm{Si}^{+}\dot{—}\mathrm{H}\cdots\dot{\mathrm{C}}\equiv]^{\ddagger} \qquad (5)$$

Therefore, this pathway is anticipated to be less sensitive to the ring strain. 1-Methylsilacyclobutane and 1-methylsilacyclopentane as well as their ring-opened analogues were studied. The data are collected in Table V.

The strained ring silanes show the same reactivity as their acyclic analogues. This observation is unusual in the light of the known reactivity enhancement during the substitution of the exocyclic group bound to silicon in the silacyclobutane ring.[38] It is also better understood on the basis of SET mechanism than assuming a direct hydride transfer.

The low sensitivity of the reaction to the steric hindrance, in connection with a highly negative entropy of activation, can also

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(33) Doering, W. E.; Knox, L. H. *J. Am. Chem. Soc.* **1954**, *76*, 3203.

(34) Deno, N. C.; Jaruzelski, J. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044.

(35) Hopkinson, A. C.; Lien, M. H. *J. Org. Chem.* **1981**, *46*, 998. Hopkinson, A. C.; Lien, M. H. *J. Mol. Struct.* **1983**, *104*, 303.

(36) Truong, T.; Gordon, M. S.; Boudjouk, P. *Organometallics* **1984**, *3*, 484.

(37) Carey and Wang-Hsu (ref 14) performed similar experiments in their system receiving somewhat similar results. For the reaction of Ph_3SiL (L = H, D) with phenyl-*p*-tolyldeuteriomethylium, 9-(*p*-methoxyphenyl)xantylium, and tris(2,6-dimethoxyphenyl)methylium in acetic acid or trifluoroacetic acid medium they obtained k_H/k_D = 1.51, 1.89, and 1.89, respectively. The values for the carbenium ions of lower electron affinity exceeded the limit predicted for the SET pathway. However, it is possible that the general picture of the reaction is similar to that in methylene chloride, when it is considered in terms of a continuous mechanistic spectrum involving as limiting cases the SET and the synchronous process with the solvent participation as nucleophile.

(38) Prince, R. H. In *Reaction Mechanisms in Inorganic Chemistry*; Tobe, M. L., Ed.; Butterworths: London, 1972; Vol. 9, Part 1, p 353.

be interpreted in terms of the SET pathway. Only part of this lost entropy may be explained by the bimolecularity of the process. The remaining part must be largely due to the solvent reorganization in the transition-state formation. Since the net charge here is the same in the transition state and in the initial reactant state, the highly negative $\Delta S^{\ddagger}$ value cannot be ascribed to a lowering of the solvent entropy in the formation of the activation complex. Instead, according to the Marcus theory[21,39] the basic requirement for the electron transfer is that the two forms of the transition state, the one with electronic structure of the reactants and the other having electronic structure of the products (eq 5), have the same energy. This requirement is met if the solvent molecules around the activated complex are oriented in some nonequilibrium configuration, which may lead to a marked negative value of activation entropy.[39]

It should be pointed out that all the other features of the process studied here and explained in terms of the direct H^- transfer could be understood on the basis of single electron transfer mechanism as well. The kinetics of the reaction studied here show a striking similarity to that of the addition to TCNE of triorganotin hydrides extended to their germanium and silicon analogues, for which strong evidence for the electron-transfer pathway was provided.[30] In particular, both reactions show an analogous kinetic law, similar values of deuterium kinetic isotope effect, and a similar reactivity change in the Si, Ge, and Sn analogue series. They both are also sensitive to the polar effect of substituents and show a low sensitivity to the steric effects.

According to Pross[22] the main criterion for the SET pathway of a given reaction is the possibility of coupling of two spin-paired electrons following the electron shift. Therefore, the stability of free radical intermediates is of primary importance. Triphenylmethyl and cycloheptatrienyl radicals are strongly stabilized by resonance. The extra resonance energies found were 24 and 16 kcal/mol, respectively, compared to the value for benzene 36 kcal/mol.[40] This is the additional argument for the SET mechanism.

Finally, it should be mentioned that kinetic studies in the gas phase of the reaction of organosilyl hydrides with carbenium ions proved that the electron-transfer process may compete with the hydride-transfer process.[41]

Thus, the single electron transfer pathway should be seriously taken into consideration in the reaction of an organic silyl hydride with a carbenium center. The rate-limiting step would be electron transfer resulting in the formation of tetracoordinate silicon radical–cation, while later steps were not defined by the kinetic experiments.

Experimental Section

Materials. Hydrosilanes used in kinetic studies are all well-known compounds, and they were mostly obtained according to synthetic methods described in literature. For example, 1-methylsilacyclobutane was obtained in a three-step synthesis including the following: hydrosilylation of allyl chloride with methyldichlorosilane,[42] Grignard cyclization of γ-chloropropylmethyldichlorosilane,[43] and reduction of 1-chloro-1-methylsilacyclobutane with $LiAlH_4$. 1-Methylsilacyclopentane was synthesized by Grignard halocondensation of 1,4-dibromobutane with methyldichlorosilane followed by Grignard cyclization.[44] Ethylmercaptohydrosilanes $(EtS)_nMe_{3-n}SiH$ ($n = 1, 2, 3$) were obtained in the reaction of corresponding chlorosilanes with ethyl mercaptan.[45] Some of hydrosilanes used here were commercial products, and some others had been synthesized in other laboratories. The hydrosilanes were carefully purified by distillation over an efficient column or by recrystallization. Their purity checked by gas–liquid chromatography was high, in most cases better than 99%.

Triethylgermanium was synthesized by methylation of $GeCl_4$ with Grignard reagent followed by the equilibration of tetraethylgermanium with $GeCl_4$ in the presence of $AlCl_3$ and then by a reduction of triethylchlorogermanium with $LiAlH_4$.[46]

Triphenylmethylium salts were reagent grade products of Ozark Mahoning, Ventron, or Fluka. They were purified by redissolving in prepurified methylene chloride, filtrating and precipitating with CCl_4, and these operations were performed on high vacuum line (hvl) similar to those described in ref 45. Weighed samples were prepared in vacuum spreading the salts into small thin glass wall ampoules which were then fused out of the hvl.

Tropenylium hexafluoroantimonate was obtained from $Ph_3C^+SbF_6^-$ and cycloheptatriene according to.[48] It was purified under vacuum by redissolving in SO_2 and filtrating and precipitating with CCl_4. SO_2 was prepurified by driving SO_2 gas through bubblers with H_2SO_4 and a column with P_2O_5 to an ampoule with a Rotaflo stopcock and was cooled in solid carbon dioxide–propanol bath. Then the ampoule was installed on the hvl to be used for the salt purification procedure. Tropenylium-hexafluorophosphorane, Aldrich reagent grade, was purified with SO_2 as described above. Tropenylium tetrafluoroborate, Willow Brook Labs Inc., was purified by recrystallization from a large volume of ethyl acetate. For all of these tropenylium salts, a weighed sample preparation procedure was performed on hvl.

The solvent, methylene chloride Fluka pure, was shaken, refluxed with 30% oleum, washed with water and a water solution of Na_2CO_3, and dried over $CaCl_2$. Then it was refluxed 24 h with CaH_2 and distilled from a fresh portion of CaH_2 into a dark ampoule fitted with a Rotaflo stopcock. Air was removed on the hvl. Methylene chloride used for hvl kinetic experiments was additionally purified on the hvl with sodium mirror as in.[47]

Kinetic Study. Most of kinetic experiments were performed under pure nitrogen. Vacuum kinetic experiments in which atmospheric oxygen and water were almost entirely excluded were done in the case of runs carried out at low temperatures and in some chosen rate measurements at 25 °C to verify results obtained under inert gas conditions. This verification seemed to us important in the light of the unstableness of some solutions of the carbenium salts and because of a low concentration of carbenium substrates used in kinetic studies, which in most cases was 10^{-3}–10^{-4} mol dm^{-3}. The hvl kinetic experiments were performed in a similar manner to that described in our earlier paper.[1] The level of water concentration in the system studied under vacuum was well below 10^{-4} mol dm^{-3}. The agreement of the data obtained under nitrogen atmosphere with those obtained under high vacuum confirmed that traces of oxygen and fortuitous nucleophiles were not important.

The solution of the salt was prepared in a 50-mL flask with a tight closure, which had been purged with nitrogen. The small ampoule containing the weighed sample of the salt was placed and broken under the surface of methylene chloride. The solution was diluted if necessary. Its concentration was determined spectroscopically having known molar absorbance of the carbenium ion used. The solution of tropenylium salt was always freshly prepared for each day of the kinetic experiment series. A known volume of the solution of carbenium salt was placed in a cylindrical reactor having a quartz cell in the bottom, and the reactor was closed with Teflon key stopcock. The reactor had been thoroughly rinsed with pure nitrogen. The solution was thermostatted in a specially designed compartment mounted on Specord UV–vis spectrometer of Jena–Zeiss. After the initial absorbance was read, a known amount of hydrosilane solution was quickly introduced by means of Hamilton hypodermic syringe. From this moment the time of reaction was measured. The decrease of absorbance was recorded at 435 nm for Ph_3C^+ or at 281 nm for $C_7H_7^+$. In some cases of $C_7H_7^+$ reaction the increase of the absorbance of cycloheptatriene formed was followed at 256 nm.

Most kinetic experiments with tropenylium salts were done under the pseudo-first-order condition with use of a considerable excess of SiH reactant. The reaction was checked to be of the first external order with respect to the silane by performing a series of runs at variable initial silane concentration. Relatively fast reactions of the trityl salts were performed by using an excess of the carbenium ion over the Si–H reactant. Rate constants were determined based on the last portion of the kinetic curve. It was possible since the reaction in its final stage proceeded always to a high precision in accord with the kinetic law represented by eq 2. Rate constant values presented here are mostly averages determined from at least three independent runs. Reproducibility of the rate constant observed in most cases was better than ±10%. Gas–liquid

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[39] Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

[40] Wincow, G.; Dauben, H. J., Jr.; Hunter, F. R.; Volland, W. V. *J. Am. Chem. Soc.* **1969**, *91*, 2823.

[41] Goodloe, G. W.; Lampe, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 5649.

[42] Mironov, W. F.; Nepomnina, W. W.; Leyters, L. A. *Izv. Akad. Nauk SSSR Ser. Khim. Nauk.* **1960**, 461.

[43] Vdovin, W. M.; Nametkin, N. S. *Dokl. Akad. Nauk SSSR* **1963**, *150*, 799.

[44] Chruściel, J. Ph.D. Thesis, Technical University of Lódź, 1978.

[45] Woliński, Z.; Tickelmann, H.; Post, H. W. *J. Org. Chem.* **1951**, *16*, 395.

[46] Anderson, H. H. *J. Am. Chem. Soc.* **1957**, *79*, 326.

[47] Słomkowski, S.; Penczek, S. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1718.

[48] Cowell, G. W.; Ledwith, A.; White, A. C.; Woods, H. J. *J. Chem. Soc. B* **1970**, 228.

J. Am. Chem. Soc. **1987**, *109*, 7781–7785

chromatographic analyses were done in a manner similar to that described in.[1]

Acknowledgment. We are grateful to Prof. Manfred Weidenbruch of the Technical University of Aachen F.R.G. (presently at the University of Oldenburg) for providing us with a sample of t-Bu_3SiH. We also express gratitude to Dr. Jerzy Chruściel and Prof. Zygmunt Lasocki from Politechnika Łódzka for the gift of samples of $PhMe_2SiD$ and Et_3SiD. This was Research Project CPBP 01.13.

Registry No. $Ph_3C^+SbF_6^-$, 437-18-3; $Ph_3C^+AsF_6^-$, 437-15-0; Ph_3C^+-PF_6^-, 437-17-2; $Ph_3C^+BF_4^-$, 341-02-6; $Ph_3C^+SbCl_6^-$, 1586-91-0; Ph_3C^+-$FeCl_4^-$, 34690-18-1; $C_7H_7{}^+SbF_6^-$, 29630-12-4; $C_7H_7{}^+PF_6^-$, 29663-54-5; $C_7H_7{}^+BF_4^-$, 27081-10-3; Et_3SiH, 617-86-7; Et_3GeH, 1188-14-3; Me_3SiH, 993-07-7; n-Pr_3SiH, 998-29-8; n-Bu_3SiH, 998-41-4; n-Hex_3SiH, 2929-52-4; $PhMe_2SiH$, 766-77-8; $PhMe_2SiD$, 22034-19-1; Et_3SiD, 1631-33-0; $(CH_2)_3Si(Me)H$, 765-33-3; $EtMe_2SiH$, 758-21-4; $(CH_2)_4Si(Me)H$, 765-41-3; Et_2MeSiH, 760-32-7.

1,3-Nitrogen Shift Reaction in Sulfur–Nitrogen Chemistry. Preparation and Interconversion of *exo*- and *endo*-Trithiatetrazocines

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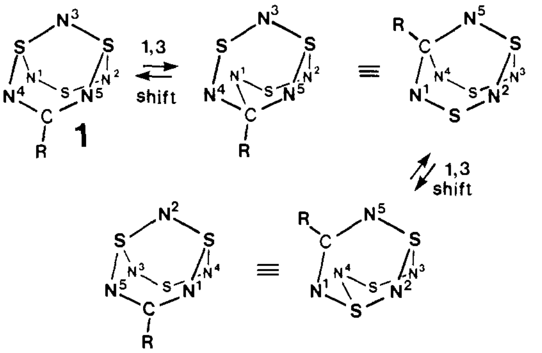
Contribution from The Guelph Waterloo Centre for Graduate Work in Chemistry, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and the Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701. *Received May 20, 1987*

Abstract: The reaction of the 1,3-NSN-bridged 5-phenyl-1,3,2,4,6-dithiatriazine $PhCN_5S_3$ with tertiary phosphines [PPh_3, PCy_3, PPh_2Me, $P(o\text{-}tol)_3$] and triphenylarsine has been studied by ^{31}P and ^{15}N NMR spectroscopy. The mechanism of formation of the final product, the *endo*-3-imino-5-phenyl-1,3,5,2,4,6,8-trithiatetrazocines $PhCN_4S_3(NER_3)$ (E = P, As), involves the intermediacy of a rapidly formed 1-substituted 5-phenyl-1,3,2,4,6-dithiatriazine, which then transforms to either the *exo*- or *endo*-$PhCN_4S_3(NER_3)$ derivative. The exo isomer is kinetically preferred but slowly converts at room temperature to the thermodynamically more stable endo modification. The interconversion of the two isomers is suggested to occur in a stepwise process involving ring contraction (1,3-shift), ligand rotation, and ring expansion (1,3-shift). The importance of the 1,3-nitrogen shift reaction as a pathway for structural rearrangements in cyclic sulfur nitrogen systems is discussed.

Recent developments in the chemistry of heterocyclic thiazenes have provided a much clearer picture of the electronic factors that control the basic reactivity patterns of molecules containing conjugated —S=N— units.[2] Recognition of the electronic similarities between unsaturated cyclothiazenes and organic π-systems has been particularly useful and has led to the identification of several mechanistic parallels. Simple frontier orbital models, for example, successfully account for the rates and regiochemistries of olefin cycloadditions[3] and also provide insight into the stereochemistries of oxidative addition reactions.[4,5]

There remains, however, a vast array of chemistry whose mechanistic interpretation has never received any systematic analysis. Notable within this latter category are the reactions of S_4N_4 with nucleophiles (e.g., cyanide, azide, and sulfide ions, amines, phosphines, phosphinimines, diazomethanes),[6-9] which all result in cleavage of the S_4N_4 unit. Depending on the reagent involved, open-chain, cyclic, and cage species can be formed; usually a mixture of products is generated and, in the absence of any convenient and fast spectroscopic probe, the observation and characterization of the reaction intermediates represents a difficult if not impossible task.

Scheme I



In order to address these important mechanistic issues we are examining the reactivity of heterocyclic thiazenes with nucleophiles. The advantages are several. First, the mixed organic/inorganic rings are generally more kinetically stable than their purely binary sulfur–nitrogen counterparts, reacting more specifically and more slowly with nucleophiles. Second, many of these compounds can be prepared with ^{15}N labels at specific sites, a feature that allows the use of ^{15}N NMR spectroscopy as an analytical tool. The bicyclic derivative $PhCN_5S_3$ (**1**;[10,11] iso-

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(1) (a) University of Guelph. (b) University of Arkansas.
(2) Oakley, R. T. *Prog. Inorg. Chem.*, in press.
(3) Liblong, S. W.; Oakley, R. T.; Cordes, A. W.; Noble, M. C. *Can. J. Chem.* **1983**, *61*, 2062.
(4) Oakley, R. T. *Can. J. Chem.* **1984**, *62*, 2763.
(5) Boeré, R. T.; Cordes, A. W.; Craig, S. L.; Oakley, R. T.; Reed, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 868.
(6) (a) Bojes, J.; Chivers, T. *Inorg. Chem.* **1978**, *17*, 318. (b) Bojes, J.; Chivers, T.; Drummond, I.; MacLean, G. *Inorg. Chem.* **1978**, *17*, 3668.
(7) Bojes, J.; Chivers, T.; MacLean, G.; Oakley, R. T.; Cordes, A. W. *Inorg. Chem.* **1981**, *20*, 16.
(8) Ruppert, I.; Bastian, V.; Appel, R. *Chem. Ber.* **1974**, *107*, 3426.
(9) Fluck, E.; *Z. Anorg. Allg. Chem.* **1961**, *312*, 195.
(10) Boeré, R. T.; Cordes, A. W.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1985**, 929.

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