Gas-Phase Dyotropic Rearrangement of (Chloromethyl)dimethylsilane

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Studies of the gas-phase isomerization of (chloromethyl)dimethylsilane (I) to trimethylchlorosilane (II) in a static reactor (636–690 K) are reported. The neat reaction is shown to occur by two parallel reaction pathways: a concerted dyotropic rearrangement and a free radical chain. The free radical chain pathway, which appears to be wall initiated, has rate parameters log k_{chain} = 9.42–43 000 cal/2.3RT. The dyotropic rearrangement pathway, isolated by maximal chain quenching with excess propylene, has rate parameters log k_I = 12.99 ± 0.13–52 165 ± 405 cal/2.303RT. An activation energy of 11 kcal for the 1,2-Cl shift reaction $ClCH_2\dot{Si}Me_2 \xrightarrow{2} \cdot CH_2SiMe_2Cl$ relative to the chlorine abstraction reaction $ClCH_2\dot{Si}Me_2 + ClCH_2SiHMe_2 \xrightarrow{8} ClCH_2SiMe_2Cl + \cdot CH_2\dot{Si}HMe_2$ is deduced.

Introduction

The theory and possibility of dyotropic rearrangements where two σ-bonded moieties (atoms or groups) migrate intramolecularly (as in Scheme I) was first explored by Reetz.[1-3] Numerous well-documented examples of such rearrangements have since been reported.[4] Most occur in organosilicon reaction systems and involve the migration of two silyl groups between heteroatoms (e.g., X = Y = SiR_3; a–b = (C–O), (C–S), (N–O), etc). All of these reactions are relatively insensitive to solvent polarity, occur with retention of configuration in the migrating groups and inversion of configuration at the heteroatom centers, and do not produce crossover products in mixed reactant rearrangement systems, which are requirements of the thermally induced dyotropic rearrangements in these systems.[4]

Examples of dyotropic rearrangements involving the exchange of other kinds of groups have also been reported.[5] For example in structures of the form $R_3SiCHR'X$, alkyl and aryl groups (e.g., R = Ph, Me, C_2H_5) exchange with various electronegative groups (e.g., X = F, OTos, OAc, Cl, Br, OMe). [These rearrangements are $R_3SiCHR'X \rightarrow R_2XSiCHR'R$, and the ease of the exchange decreases in the order shown for X. The exchange appears to occur by a consecutive step process involving carbonium ion stabilized inverse ylide intermediates. (Heteroatom centers are Si and C.)]

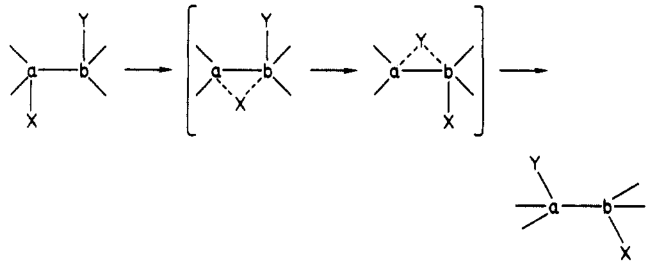
To our knowledge, all examples of dyotropic reactions to date have been in solution or in neat liquids. We now report evidence for the first such gas-phase reaction: (chloromethyl)dimethylsilane (I) isomerization to trimethylchlorosilane (II) (reaction 1, gas phase, 635–690 K).

$$\underset{\text{I}}{ClCH_2SiHMe_2} \xrightarrow{1} \underset{\text{II}}{Me_3SiCl}$$

Experimental Section

Normal and deuterated reactant (I) were prepared by $LiAlH_4$ (or $LiAlD_4$) reduction of (chloromethyl)dimethylchlorosilane (Petrarch) in *n*-butyl ether. Pure I, as indicated by GC, NMR, and MS analyses, in yields exceeding 65%, was separated from minor reaction products (e.g., Me_3SiCl and Me_3SiH in 3–10% yields) by repeated trap to trap distillations on a vacuum line. Other chemicals employed were obtained commercially from standard sources.

Scheme I



Scheme II

chain 1 $ClCH_2\dot{Si}Me_2 \xrightarrow{2} \cdot CH_2SiMe_2Cl$ fast Cl shift

$\cdot CH_2SiMe_2Cl + I \xrightarrow{3} Me_3SiCl + ClCH_2\dot{Si}Me_2$

chain 2 $\cdot CH_2SiMe_2H \xrightarrow{4} Me_3Si\cdot$ fast H shift

$Me_3Si\cdot + I \xrightarrow{5} Me_3SiCl + \cdot CH_2SiMe_2H$

Table I. Initial Rate vs. Initial Concentration-Reaction Order Data[a] for Reaction 1

$ClCH_2SiMe_2H \xrightarrow{1} Me_3SiCl$ T = 682.6 °K

neat I_H[b]			neat I_D[c]		
P, torr	10^8R_0, M/s	$10^4[I]_0$, M	P, torr	10^8R_0, M/s	$10^4[I]_0$, M
4.00	2.132	0.94	15.0	5.72	3.52
5.00	2.614	1.17	13.0	4.87	3.05
10.0	6.609	2.35	28.0	10.36	6.58
16.0	9.118	3.76	60.0	20.47	14.09
26.0	14.31	6.11	14.0	4.93	3.29
40.0	22.49	9.40	5.0	1.73	1.17
			6.0	2.18	1.41

[a] General rate law is $R = k_1[I]^n$ ln R = ln k_1 + n ln [I]. [b] Slope of ln R_0 vs. ln $[I]_0$ for neat I_H is n = 1.018 ± 0.089 to 95% confidence limit. [c] Slope of ln R_0 vs. ln $(I)_0$ for neat I_D is n = 0.993 ± 0.043 to 95% confidence limit.

The reaction was studied statically in two reactors, one Pyrex (400 cm^3) and one Quartz (250 cm^3), immersed in a resistively heated air bath with temperatures maintained to within ±0.1 °C during any given run by a Bayley 124 controller. Product analyses were made on a $^1/_8$ in. × 24 ft stainless column packed with 20% squalene on Supercoport operated at ambient temperatures with a Carle Instruments TC chromatograph (Model 8500) in conjunction with a Hewlett-Packard 3380-A digital integrator.

Results and Discussion

When 200 torr of a I–Ar mixture (14% I with Ar as the internal standard) was reacted at 641.5 K, II was produced essentially quantitatively (i.e., yields > 99%). A reaction

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(2) Reetz, M. T. Angew. *Chem., Int. Ed. Engl.* **1972**, *11*, 131.
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(5) Bassindale, A. R.; Brook, A. G.; Jones, P. F.; Lennon, J. M. *Can. J. Chem.* **1975**, *53*, 332.

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Scheme III

$$\mathrm{I} \underset{-6}{\overset{6}{\rightleftharpoons}} CH_2{=}SiMe_2 + HCl$$

$$HCl + CH_2{=}SiMe_2 \xrightarrow{7} Me_3SiCl$$

Scheme IV

$$\text{initiation} \quad t\text{-}BuO\cdot + \mathrm{I} \longrightarrow t\text{-}BuOH + ClCH_2\dot{S}iMe_2$$

$$\text{chain 3} \quad ClCH_2\dot{S}iMe_2 + \mathrm{I} \xrightarrow{8} ClCH_2SiMe_2Cl + \cdot CH_2SiMe_2H$$

$$\cdot CH_2SiMe_2H + \mathrm{I} \xrightarrow{9} Me_3SiH + ClCH_2\dot{S}iMe_2$$

$$\text{chain transfer} \quad \cdot CH_2SiMe_2H + Me_3SiH \xrightarrow{10} Me_3Si\cdot + Me_3SiH$$

$$ClCH_2\dot{S}iMe_2 + Me_3SiH \xrightarrow{11} Me_3Si\cdot + \mathrm{I}$$

$$\text{chain 4} \quad Me_3Si\cdot + ClCH_2SiMe_2Cl \xrightarrow{12} Me_3SiCl + \cdot CH_2SiMe_2Cl$$

$$\cdot CH_2SiMe_2Cl + Me_3SiH \xrightarrow{13} Me_3SiCl + Me_3Si\cdot$$

order study of initial rates vs. initial reactant concentration (see data of Table I) confirmed that the reaction followed first-order kinetics, and from analyses of sequential aliquots of the reaction up to 54% conversion the first-order rate constant for reactant loss (or product formation) by reaction 1 was found to be $k_1(642\ \mathrm{K}) = 3.25 \pm 0.12 \times 10^{-5}$ s^{-1}. At least three plausible mechanisms can be proposed for this reaction: a dyotropic rearrangement (Scheme I), a free radical mechanism (chain 1 and/or chain 2, Scheme II), and a consecutive step four-center HCl elimination–addition mechanism (Scheme III).

The free radical chain rearrangement of I (as in Scheme II) does occur and has been induced by the thermal decompositions of dimethylmercury and di-*tert*-butylperoxide at 500 K.[6] Additional support for these particular chain processes comes from the changes in reaction character for the free radical induced reaction of I at higher concentrations and lower temperatures (i.e., $T < 409$ K).[7,8] The reaction of I then proceeds as in Scheme IV.

The initial products under these conditions are trimethylsilane and (chloromethyl)dimethylchlorosilane (formed in chain 3). With increasing conversions, yields of these products decrease as the yields of trimethylchlorosilane (formed via chain 4) increase.[7]

To see if our observed thermally induced rearrangement (I → II) was also a free radical process, we investigated the effect of various additives on the reaction pathway and rates.

When a mixture of I in propylene ($C_3H_6/\mathrm{I} \simeq 6$) was pyrolyzed at 642 K at pressures between 50 and 260 torr, good first-order kinetics with rate constants independent of the initial concentrations were still observed. However, in propylene the rate constants were lowered by factors of about two: $k_1(642\ \mathrm{K\ in}\ C_3H_6) \simeq 1.6 \times 10^{-5}\ \mathrm{s}^{-1}$. Increasing propylene concentrations to $C_3H_6/\mathrm{I} = 20$ produced no further rate reductions. Therefore, at least part of the rearrangement of neat I is free radical induced and occurs by Scheme II.

The pyrolysis of deuterated I ($ClCH_2SiMe_2D$, $\mathrm{I_D}$) in excess propylene was studied. Rearrangement of I by Scheme I, by Scheme II, chain 2, or by Scheme III must give deuterated II as product. Reaction by Scheme II, chain 1, however, must give normal II. [In excess propylene reaction 3 would be replaced by the trapping reaction $\cdot CH_2SiMe_2Cl + C_3H_6 \rightarrow Me_3SiCl + CH_2{=}CHCH_2\cdot$.] The product produced (by MS analysis) was exclusively $\mathrm{II_D}$. Thus chain 1 is operative in the uninhibited isomerization of I but is quenched in the propylene inhibited system.

Next the isomerization of $\mathrm{I_D}$ was studied in the presence of excess propylene and methyl bromide ($C_3H_6/CH_3Br/\mathrm{I_D} = 5/8.5/1$) at 195 torr. Reaction rates were unchanged, and no Me_3SiBr was produced for conversion up to 50%. If the propylene inhibited reaction of I occurred by Scheme II, chain 2, then in the presence of methyl bromide, trimethylbromosilane would have to be formed. [The competing reactions are $Me_3Si\cdot + CH_3Br \rightarrow Me_3SiBr + CH_3\cdot$ and reaction 5. Since $[Me_3SiBr] = 8.5[\mathrm{I}]$ and both halogen abstraction reactions have similar exothermicities and presumably similarly low activation energies, the favored product should be Me_3SiBr.] Since the product was exclusively trimethylchlorosilane, we can conclude that the isomerization I → II in excess propylene is not a free radical induced reaction (i.e., does not involve Scheme II in any way) and that it occurs by either Scheme I or Scheme III.

Finally, Scheme III was eliminated as a viable reaction route by studying the isomerization of $\mathrm{I_D}$ under propylene inhibition in the presence of added HCl ($HCl/C_3H_6/\mathrm{I_D} = 1/6/1$) at 80 torr and 677 K. Reaction rates were unchanged by the added HCl, and only $\mathrm{II_D}$ was produced. Reaction via Scheme III would produce only normal II (DCl steady-state concentrations of Scheme III would necessarily be quite low). Thus, the thermal isomerization I → II in the presence of propylene must be a dyotropic rearrangement and occur exclusively by Scheme I.

Kinetics of the Dyotropic Rearrangement I → II. The kinetics of the rearrangement I → II for normal and deuterated I, both neat and in the presence of excess propylene, were studied in the 640–680 K range. Experimental conditions and rate constant results are given in Table II. A least-squares Arrhenius analysis of the data give the results of Table III, where the errors represent the 95% confidence limit. Activation energies in propylene are surprising in that $E(\mathrm{I_D})$ is lower than $E(\mathrm{I})$, suggesting an inverse isotope effect. On the other hand, k_H/k_D in the range 640–680 K $\simeq 1.5$, support a small regular isotope effect. Clearly the errors are such that the differences in the A, E, and k values of the normal and deuterated systems are not very significant. It is interesting to note, however, that the observed A factors under propylene inhibition bracket the thermochemical kinetic estimate[9] for the dyotropic shift: $A \simeq 10^{12.8\pm0.3}\ \mathrm{s}^{-1}$. [An activation entropy of $\Delta S^{\ddagger} \simeq -3.5$ eu is estimated because of the loss of one internal rotation in the bridged transition state; rpd = 1; $A = (ekT/h)e^{\Delta S^{\ddagger}/R}$.]

Free Radical Induced Isomerization of I → II. Since the neat rearrangement of I → II is part unimolecular (dyotropic) and part chain and since the overall reaction accurately follows first-order kinetics, it follows that the chain component also is first order. By subtracting the unimolecular component (i.e., rate constants under propylene inhibition) from the overall rate constant of the neat reaction, one can obtain rate constants for the free radical part of the reaction (k_{FR}). Average values of k_{FR} for I_D, shown in column 5 of Table II, account for about 30 ± 5% of the reaction and are consistent with Arrhenius parameters of $k_{FR} = 10^{9.42} \times e^{-43000/RT}\ \mathrm{s}^{-1}$.

It is interesting to examine in further detail the free radical mechanisms of the thermal reactions of I (i.e.,

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Table II. First-Order Rate Constants for Reaction 1 (I → II)

A. I_H in Propylene: $I_H/C_3H_6 = 1/6$ (Pyrex Reactor)

T, K	10^5k_H, s	P, torr	% convn	yield of II, %	runs
636.0	1.11 ± 0.05	50–105	2.58–28.3	95.0	3
649.1	2.63 ± 0.05	48–215	36.4–44.2	96.5	3
676.0	12.83 ± 0.24	56–260	45.1–46.4	97.0	3
689.6	27.80 ± 0.47	54–184	71.2–72.0	98.0	3
662.8	5.92 ± 0.30	50–220	24.4–25.9	97.0	3

B. I_H in Propylene: $I_H/C_3H_6 = 1/6$ (Quartz Reactor)

T, K	10^5k_H, s	P, torr	% convn	runs
640.7	1.48 ± 0.10	60–110	27–28	3
680.4	16.62 ± 0.45	50–140	40–55	3

C. I_D in Propylene: $I_D/C_3H_6 = 1/6$ (Quartz Reactor)

T, K	10^5k_D, s^{-1}	P, torr	% convn	runs
640.5	1.04 ± 0.07	40–170	23–48	5
680.7	11.08 ± 0.47	40–190	31–46	4

D. I_H in Argon (Pyrex Reactor)

T, K	10^5k_H, s^{-1}	P, torr	% convn	runs
641.7	3.25 ± 0.12	184–224	52–54	2

E. I_D in Argon (Quartz Reactor)

T, K	10^5k_D, s^{-1}	P, torr	% convn	10^5k_{FR}	runs
640.4	1.59 ± 0.15	60–80	23.3, 25.0	0.55	2
680.4	15.09 ± 0.33	50	49.5, 57.3	4.01	2

Table III. Arrhenius Parameters for Rearrangement of Chlorodimethylsilane to Trimethylchlorosilane

reactant	condns	"T" range, K	log A, s^{-1}	E, cal
I_H	$C_3H_6/I = 6^a$	636–690	12.99	52 165 ± 405
I_H	$C_3H_6/I = 6^b$	641–680	13.14	52 682 ± 1380
I_D	$C_3H_6/I = 6^b$	640–680	12.47	51 160 ± 1995
I_D	neat^b	640–680	11.83	48 709 ± 580

[a] Pyrex reactor. [b] Quartz reactor.

Schemes II and IV) and their implications. First, it is clear that under the high concentration and relatively low-temperature conditions employed by Jung and Weber,[7] the (chloromethyl)dimethylsilyl radical reacts bimolecularly by reaction 8 (producing $ClCH_2SiMe_2Cl$) rather than unimolecularly by reaction 2. Under these conditions Scheme IV is followed. Under reaction conditions of somewhat higher temperatures and considerably lower concentrations, $ClCH_2\dot{S}iMe_2$ reacts essentially exclusively by 1,2-Cl shift (reaction 2). Under these conditions trimethylsilane and (chloromethyl)dimethylchlorosilane are either not observed[6] or are at best trace products with yields less than 0.5% (this study). Scheme II is then followed. It is possible to establish the activation energy of the 1,2-Cl shift relative to chlorine abstraction ($E_2 - E_8$) from the above experimental observations and from reasonable estimates of the A factors of the competing reactions. Thus at 436 K, with [I] = 1.2 M,[7] rate 8/rate 2 $\geqslant$ 100. At 642 K, from our data (this study), rate 8/rate 2 $\leqslant 0.01$ with $[I] \simeq 2.5 \times 10^{-3}$ M. Setting $A_2 \simeq 10^{9.0}$ M^{-1} s^{-1} and $A_8 \simeq 10^{12.5}$ s^{-1}, these observations establish $(E_2 - E_8) \geq 10.1$ kcal and $(E_2 - E_8) \leq 12.0$ kcal, respectively. Therefore, $(E_2 - E_8) \simeq 11 \pm 1$ kcal.

At elevated temperatures, where the free radical component of the I → II isomerization proceeds by Scheme II, chain 1, the free radical component of reaction is rate(free radical) = $k_2(\cdot CH_2SiMe_2Cl)(I)$. To be first order in I as observed, the steady-state concentration of the (dimethylchlorosilyl)methyl radical must be a constant. This can only occur if radical initiation occurs zero order at the walls. In a subsequent note we report results on surface and wall initiation effects relative to initial reaction products and to initial and overall reaction rates for this reaction and also for the reaction of methyl chloride with silane. Surface effects can be quite significant in both these systems.

Conclusion

The gas-phase (636–690 K) isomerization of (chloromethyl)dimethylsilane to trimethylchlorosilane has been shown to occur by two parallel and roughly comparable reaction pathways: a concerted dyotropic rearrangement and a free radical chain. The chain reaction is overall first order in reactant, is initiated zero order at the walls, and can be quenched by added propylene. An activation energy difference of 11 ± 1 kcal for the 1,2-Cl shift reaction ($ClCH_2\dot{S}iMe_2 \xrightarrow{2} \cdot CH_2SiMe_2Cl$) relative to the chlorine abstraction reaction ($ClCH_2\dot{S}iMe_2 + ClCH_2SiHMe_2 \xrightarrow{8} ClCH_2SiMe_2Cl + \cdot CH_2SiHMe_2$) is deduced.

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