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Kinetics of the Thermal Isomerization of (Trimethylsilyl)cyclopropane. Evidence for Anchimeric Assistance

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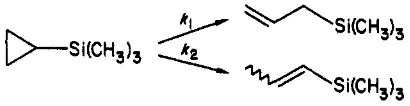
The gas-phase thermal decomposition of (trimethylsilyl)cyclopropane has been investigated over the temperature range 416.4–477.9 °C at pressures near 14 torr. Three products, allyltrimethylsilane (91.9%) and (*E*)- and (Z)-1-propenyltrimethylsilane (8.1%), were formed at 444.3 °C by a first-order decomposition which was unaffected by a 12-fold increase in the surface to volume ratio. The rate constants were for



the formation of allyltrimethylsilane, $\log k_1/\mathrm{s}^{-1} = 14.3 - 57.9\ \mathrm{kcal\ mol^{-1}}/RT \ln 10$, and for the formation of (*E*)- and (*Z*)-propenyltrimethylsilanes, $\log k_2/\mathrm{s}^{-1} = 14.9 - 63.3\ \mathrm{kcal\ mol^{-1}}/RT \ln 10$. The difference between activation energies has been interpreted in terms of anchimeric assistance or the β effect of the silicon atom.

A recent innovation in organic synthesis is the use of silicon as a directing group in the rearrangement of organic ring structures.[1] Cyclopropylsilanes, in particular, have attracted considerable interest not only for synthetic applications[2] but also as theoretical[3] and spectroscopic[4] models for the interaction between a metalloid atom (silicon) and the strained three-membered ring. Intriguingly, the conclusion from both theory and spectroscopy is that the C2–C3 (far) bond of cyclopropylsilane is significantly shorter than the C1–C2 (near) bond. A reasonable if not simplistic deduction would be that the shorter (far) bond is stronger than the longer (near) bond.

Nevertheless, the only thermal study[5] of a cyclopropylsilane in which the ring was not perturbed by additional substituents[6] has been explained by exclusive isomerization to allyltrimethylsilane through cleavage of the shorter (stronger) bond. Thus it was of interest to obtain kinetic parameters for the surprising effect of a silicon atom on the cyclopropane isomerization.

Gas-phase pyrolysis[7] of (trimethylsilyl)cyclopropane (1) (14–30 torr) at 444.3 °C in a 250-mL quartz reaction vessel held in thermostated fused salt bath yielded three new products: allyltrimethylsilane (2, 91.9%) along with (*E*)- and (*Z*)-1-propenyltrimethylsilane (3 and 4, respectively, 8.1%). Rate constants for the decomposition of 1 (Table I) and for the formation of 2 and 3 + 4 (Table II), obtained at eight different temperatures from 416.4–477.9 °C, provided good straight lines as calculated by the method of least squares. The Arrhenius plot (Figure 1) for decomposition of 1 yielded the following activation parameters:

$$\log k_{\mathrm{overall}}/\mathrm{s}^{-1} = 14.8 \pm 0.1 - 59.1 \pm 0.3\ \mathrm{kcal\ mol^{-1}}/RT \ln 10$$

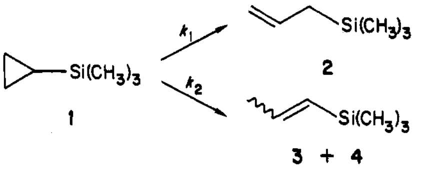


Table I. Rate Constants for Overall Decomposition of 1

T (±0.1), K	10^4K_{overall}, s^{-1}	T (±0.1), K	10^4K_{overall}, s^{-1}
689.6	1.048	721.6	6.990
698.0	1.708	732.5	12.99
705.5	2.642	740.5	20.00
717.5	5.498	751.1	34.93

Table II. Rate Constants for Formation of 2 and 3 + 4

T (±0.1), K	10^4k_1, s^{-1}	10^5k_2, s^{-1}	k_1/k_2
689.6	0.896	0.643	13.9
698.0	1.476	1.193	12.4
705.5	2.280	2.108	10.8
717.5	4.655	4.073	11.3
721.6	5.895	5.223	11.4
732.5	10.77	9.818	11.0
740.5	16.01	16.62	9.63
751.1	28.43	29.69	9.58

Although a direct comparison with the hydrocarbon analogue *tert*-butylcyclopropane is not available, it is of interest that the silylcyclopropane isomerizes approximately 10 times faster than monoalkylated cyclopropanes such as methyl-[8] and ethylcyclopropane.[9]

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[6] Unlike hydrocarbons, replacement of a hydrogen atom on silicon by a methyl group appears to have little effect on bond lengths and energies see: Walsh, R. *Acc. Chem. Res.* **1981,** *14,* 246–252.

[7] Surface effects are minimal as indicated by pyrolysis in a vessel packed with quartz tubes. The difference in rate constants was >5% when the surface to volume ratio was increased twelvefold.

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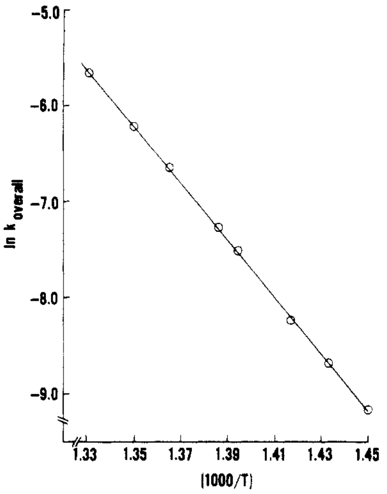


Figure 1. Arrhenius plot of ln k_{overall} vs. 1000/T.

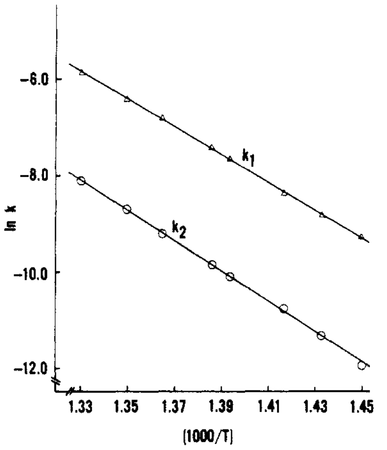


Figure 2. Arrhenius plot of ln k vs. 1000/T.

The plot of rate constants for the formation of the terminal olefin **2** and for the internal olefins **3** and **4** (Figure 2) yielded the following parameters:

$$\log k_1/\text{s}^{-1} = 14.3 \pm 0.1 - 57.9 \pm 0.2 \text{ kcal mol}^{-1}/RT \ln 10$$

$$\Delta H^{\ddagger} = 56.5 \pm 0.2 \text{ kcal mol}^{-1}/RT$$

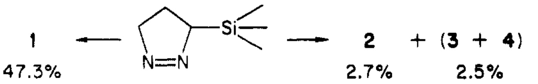
$$\Delta S^{\ddagger} = 3.2 \pm 0.3 \text{ cal/(mol T) at } 447\ {}^\circ\text{C}$$

$$\log k_2/\text{s}^{-1} = 14.9 \pm 0.3 - 63.3 \pm 0.8 \text{ kcal mol}^{-1}/RT \ln 10$$

$$\Delta H^{\ddagger} = 61.9 \pm 0.8 \text{ kcal mol}^{-1}/RT$$

$$\Delta S^{\ddagger} = 5.9 \pm 1.1 \text{ cal/(mol T) at } 447\ {}^\circ\text{C}$$

The assumption that the major product allyltrimethylsilane (**2**) is formed by cleavage of the stronger (far) bond in **1** requires closer scrutiny. Ring opening of the corresponding hydrocarbon methylcyclopropane takes place primarily at the more substituted (near) bond, and the main products 1- and 2-butenes derived from H shifts were formed in similar amounts.[8] By analogy the "conventional" path to **2** would be cleavage of the near bond followed by a hydrogen shift. Evidence against this pathway is that pyrolysis of 3-(trimethylsilyl)pyrazoline, a reasonable precursor to the $Me_3SiCHCH{=}CH$ biradical, produced **2** and **3** + **4** in nearly equal quantities.[11] Since pyrolysis of **1** gave **2** as the major product (90%), we are left with the conclusion that **2** was formed predominantly by ring opening of the far C–C bond and trimethylsilyl migration. Such 1,2-silyl shifts are known for more highly substituted cyclopropylsilanes.[10,14] The absence of 2-(trimethylsilyl)propene in the product mixture implies that the silyl shift is much faster than the hydrogen shift.



The smaller $\Delta S^{\ddagger}$ of formation of **2** compared with that of **3** + **4** is primarily a statistical factor reflecting the lower reaction path degeneracy leading to the transition state.[12] The lower activation barrier for cleavage of the shorter ring bond may be explained by a mechanism in which the silyl group assists the opening of the far carbon–carbon bond. Since the kinetic parameters reported here for the formation of **2** probably include a small contribution from the higher energy cleavage of the near bond, the quoted activation barrier for C2–C3 cleavage represents an upper limit.

The difference between the activation energies of k_2 and $k_3$3, 5.4 kcal/mol, is remarkably close to the stabilization energy ascribed to the conformational preference of β-silyl-substituted ethyl radicals.[15,16] An alternative description is one in which the silyl group migrates as the C2–C3 bond opens. Although such bridging silyl groups are well-known from structural studies of silyl-substituted main-group organometallic compounds,[17] this is the first example for which it is suggested that a silicon atom anchimerically assists carbon–carbon bond homolysis. Whether the thermal cleavage of the far bond involves β-stabilization of the radical centers on C1 and C2 followed by a silyl shift or a bridging silyl group remains an open question.

Experimental Section

General Data. Proton NMR spectra were recorded on a Hitachi Perkin-Elmer R24B 60-MHz spectrometer using methylene chloride as an internal standard and carbon NMR spectra were obtained on a JEOL FX 90Q spectrometer with D_2O or $CDCl_3$ as a lock solvent. All chemical shifts are reported in parts per million downfield from external tetramethylsilane.

Preparative gas chromatography was performed on a Varian 90A GLC (thermal conductivity detector). Analytical gas chromatography was performed on a HP 5840A GLC (flame ionization detector) equipped with a Valco gas sampling port. Mass spectra were determined on a HP 5970A mass selective analyzer coupled to a HP 5790A gas chromatograph.

Cyclopropyltrimethylsilane (**1**) was synthesized as described by Seyferth and Cohen[18] but with a Zn/Cu couple prepared by the method of Rawson and Harrison.[19] Proton NMR (neat): δ -0.30 (1 H, m, HCSi), 0.08 (9 H, s, $(CH_3)_3Si$), 0.12 (2 H, m, CHCH),

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0.52, (2 H, m, CHCH). Carbon NMR (neat): δ −4.88 (d), −3.25 (q), 0.52 (t). MS: *m/e* (% relative intensity) 99 (87), 73 (100), 73 (100), 71 (29), 59 (78), 55 (10), 45 (30), 43 (52).

(*E*)- and (*Z*)-1-propenyltrimethylsilane (**3** and **4**, respectively) were synthesized by the method of Seyferth and Vaughn.[20] Proton NMR and IR data were identical with those previously reported. Carbon NMR of **3** (neat): δ −2.02 (q), 21.59 (q), 130.84 (d), 140.72 (d). MS: *m/e* (% relative intensity) 114 (11), 100 (10), 99 (97), 73 (85), 59 (100), 55 (12), 45 (12), 43 (59), 41 (51). Carbon NMR of **4** (neat): δ −0.65 (q), 18.14 (q), 129.28 (q), 142.09 (d). The mass spectrum of **4** was virtually identical with that of **3**.

Allyltrimethylsilane (**2**) was purchased from Aldrich Chemical Co.

Kinetics Experiments. The thermal decomposition of **1** was carried out in a well-conditioned, spherical quartz reaction vessel of 250-mL capacity which was housed in an insulated 20-L stainless steel beaker containing stirred molten salt (eutectic mixture 40% $NaNO_2$, 7% $NaNO_3$, and 53% KNO_3). The bath temperature was maintained constant to +0.1 °C by a Thermotrol proportional controller (230 V), Model 1083 A (GCA Precision Scientific) with a Model 1153 platinum resistance temperature detector (GCA). Heat was provided by a stainless steel mineral insulated heating element from Chromalox Industrial Products.

Temperature was measured with a Chromel-Alumel thermocouple (Type K) in coordination with a Leeds and Northrup K-2 potentiometer. The thermocouple was immersed in a well which was placed in the center of the salt bath. Temperatures measured from the thermocouple were calibrated with a Brooklyn thermometer (range 298–355 °C). Vapors of the cyclopropylsilane were introduced into the pyrolysis vessel by expansion from a reservoir in the contiguous vacuum line. The starting sample pressure of each kinetic run was measured by a Model PDR-C-2 pressure gauge (MKS Instrument Co.) and a Model 227AHS-A-100 Baratron (MKS).

In a typical kinetic pyrolysis run the pyrolysate was sampled six times into a gas sampling bulb held at liquid-nitrogen temperature by removing an aliquot (approximately 1 torr) of the reaction mixture via expansion into a small section of the vacuum line. Starting pressure of **1** in each experiment was approximately 15 torr. Each point in a rate constant was an average of at least two GC runs. Each rate constant plot contained six points, and all reported rate constants and activation parameters were derived by a least-squared analysis of the data where each such analysis yielded a correlation coefficient of at least 0.999. Reaction of **1** was monitored chromatographically to approximately 50% decomposition, depending on temperature, and was first-order.

The role of surface effects on the course of the isomerization is minimal as suggested by a comparison of rate constants obtained in packed and unpacked reaction vessels at 416.8 °C. With a 12-fold increase in the surface to volume ratio, the change in the rate constant for decomposition was <5%. Pyrolysis of each of the reaction products, **2**, **3**, and **4**, under conditions where **1** decomposed, indicated no secondary reaction. Predetermined response factors were measured with cyclohexane as an internal standard.

The kinetics apparatus and techniques utilized in this work were modeled on the design of Prof. H. M. Frey (Univerisity of Reading, U.K.).

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Registry No. 1, 930-40-5; 2, 762-72-1; 3, 4964-03-8; 4, 4964-02-7.

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Theoretical Study of Silanethione ($H_2Si=S$) in the Ground, Excited, and Protonated States: Comparison with Silanone ($H_2Si=O$)

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To extend knowledge of silicon–sulfur double bonds, several properties of $H_2Si=S$ were investigated and compared with those of $H_2Si=O$ and $H_2C=O$, by means of ab initio calculations including polarization functions and electron correlation. $H_2Si=S$ is found to be kinetically stable enough to its unimolecular destructions such as $H_2Si=S \rightarrow H_2 + SiS$, $H_2Si=S \rightarrow H + HSiS$, and $H_2Si=S \rightarrow HSiSH$, as in the cases of $H_2Si=O$ and $H_2C=O$. Furthermore, it is found that $H_2Si=S$ is thermodynamically stable compared with $H_2Si=O$. Through these comparisons, it is emphasized that silicon is less reluctant to form double bonds with sulfur than with oxygen. The singlet–triplet energy differences in $H_2Si=S$ and $H_2Si=O$ are calculated to be considerably smaller than that in $H_2C=O$. In the protonated states, the S-protonated singlet species H_2SiSH^+ is the most stable, and it is separated by sizable barriers from its isomers H_3SiS^+ and $HSiSH_2{}^+$, as are H_2SiOH^+ and H_2COH^+. Finally, the potential energy surface for the reaction of $H_2Si=S$ with water is calculated to investigate the reactivity toward polar reagents.

Introduction

Compounds that feature double bonding to silicon are of current interest.[1] As the silicon analogues of ethenes, silicon–carbon (silenes)[2] and silicon–silicon (disilenes)[3] doubly bonded compounds have been characterized and isolated in the last few years. In contrast, the study of the formaldehyde analogues seems to be still in the early stages.[1] Recently we have studied the thermodynamic and

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