

A KINETIC STUDY OF THE GAS PHASE THERMAL DECOMPOSITION AND ISOMERIZATION OF 1,1,3-TRIMETHYL-1-SILACYCLOBUTANE

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Summary

The kinetics of the gas phase thermal decomposition and isomerisation of 1,1,3-trimethyl-1-silacyclobutane have been studied in the temperature range of 380–450°C and at a pressure of 20 Torr. The following Arrhenius relationships were obtained:

$$\log K(\text{sec}^{-1}) = 16.39 \pm 0.28 - (63280 \pm 900)/RT \ln 10$$

$$\log K_d(\text{sec}^{-1}) = 16.28 \pm 0.30 - (63200 \pm 950)/RT \ln 10$$

$$\log K_i(\text{sec}^{-1}) = 15.61 \pm 0.25 - (63240 \pm 780)/RT \ln 10$$

The entropy and enthalpy of activation of the total process have been calculated at 450°C: $\Delta S^\ddagger = 12.3 \text{ cal degree}^{-1} \text{ mol}^{-1}$, $\Delta H^\ddagger = 61.9 \text{ kcal mol}^{-1}$.

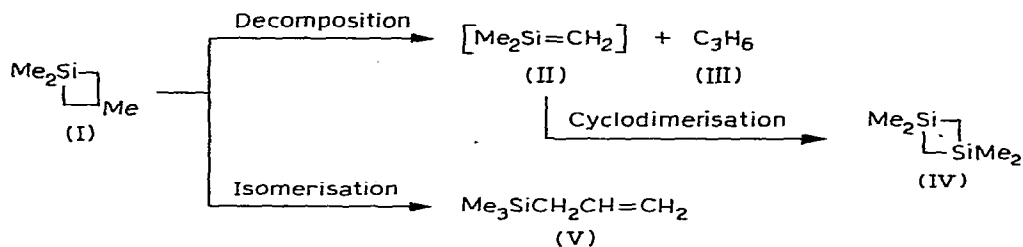
Introduction

A large number of publications [1] have been devoted to the pyrolysis of monosilacyclobutanes as a method of generating the unstable silaalkenes; but only in the case of 1,1-dimethyl-1-silacyclobutane was this process subjected to a detailed kinetic study [2,3].

In this paper we present the results of a study of the kinetics of the gas phase thermal transformation of 1,1,3-trimethyl-1-silacyclobutane (I), which proceeds with formation of propene (III), 1,1,3,3-tetramethyl-1,3-disilacyclobutane (IV) and allyltrimethylsilane (V) [4] (Scheme 1). It is seen from Scheme 1 that decomposition of I proceeds via the unstable intermediate 1,1-dimethyl-1-silaethylene (II), which yields IV by cyclodimerization.

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SCHEME 1



Results and discussion

In accordance with Scheme 1 $[\text{III}]/[\text{IV}] = 1.91 \pm 0.04$, i.e. the ratio of these products is close to the stoichiometric ratio for the decomposition of I. Conversion (x) was calculated according to the formula: $x = ([\text{V}] + 2[\text{IV}])/([\text{I}] + [\text{V}] + 2[\text{IV}])$, where $[\text{I}]$, $[\text{V}]$ and $[\text{IV}]$ are the concentrations of the products shown in Scheme 1. The $\log(1-x)/t$ relationship shown in Fig. 1 indicates that the transformation of I is satisfactorily described by a first order kinetic equation the rate constant of which can be written as the sum of decomposition (K_d) and isomerization (K_i) rate constants:

$$K = K_d + K_i \quad (1)$$

On the other hand:

$$K_d/K_i = 2[\text{IV}]/[\text{V}] \quad (2)$$

The solution of eqs. 1 and 2 gives K_d and K_i . Values of K , K_d and K_i for ten temperatures investigated are listed in Table 1.

Arrhenius relationships for K , K_d and K_i and K_d/K_i are shown in Fig. 2. Least squares treatment of these relationships leads to the following equations:

$$\log K(\text{sec}^{-1}) = 16.39 \pm 0.28 - (63280 \pm 900)/RT \ln 10$$

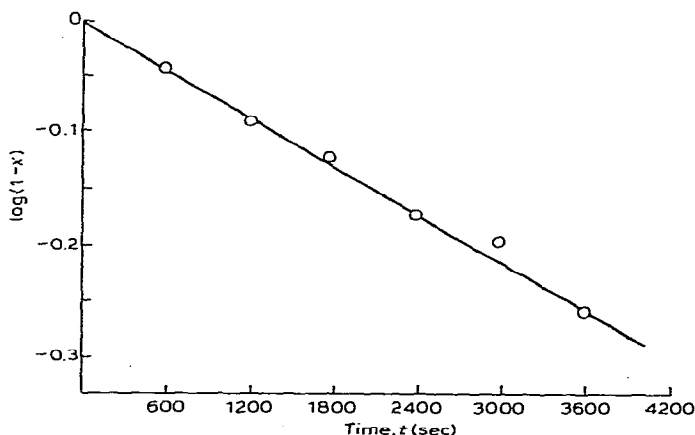


Fig. 1. First order rate plot at 413.6°C.

TABLE I

RATE CONSTANTS FOR TOTAL THERMAL TRANSFORMATION (K), DECOMPOSITION (K_d), ISOMERIZATION (K_i) AND THE RATIO K_d/K_i FOR 1,1,3-TRIMETHYL-1-SILACYCLOBUTANE

Temperature (°C)	$K \times 10^4$ (sec ⁻¹)	$K_d \times 10^4$ (sec ⁻¹)	$K_i \times 10^4$ (sec ⁻¹)	K_d/K_i	Number of determinations
382.0	0.180 ± 0.008	0.149 ± 0.007	0.031 ± 0.001	4.85 ± 0.100	3
390.0	00.400 ± 0.032	0.330 ± 0.022	0.068 ± 0.004	4.84 ± 0.121	3
398.7	0.690 ± 0.018	0.570 ± 0.016	0.120 ± 0.007	4.86 ± 0.180	4
399.5	0.670 ± 0.018	0.560 ± 0.022	0.110 ± 0.006	5.09 ± 0.43	3
410.0	1.32 ± 0.070	1.09 ± 0.060	0.230 ± 0.010	4.80 ± 0.220	5
413.0	1.65 ± 0.040	1.37 ± 0.040	0.280 ± 0.008	4.83 ± 0.180	10
420.0	2.80 ± 0.200	2.32 ± 0.100	0.470 ± 0.030	4.95 ± 0.180	3
432.0	5.83 ± 0.520	4.82 ± 0.480	1.01 ± 0.050	4.74 ± 0.320	7
440.0	11.29 ± 0.260	9.41 ± 0.210	1.88 ± 0.050	4.98 ± 0.250	3
449.4	18.01 ± 0.270	14.97 ± 0.260	3.04 ± 0.110	4.96 ± 0.210	6

$$\log K_d(\text{sec}^{-1}) = 16.28 \pm 0.30 - (63200 \pm 950)/RT \ln 10$$

$$\log K_i(\text{sec}^{-1}) = 15.61 \pm 0.25 - (63240 \pm 780)/RT \ln 10$$

$$\log K_d - \log K_i = 0.67 - 0/RT \ln 10$$

Pyrolysis of four-membered cyclic compounds by a biradical mechanism which is widely accepted to explain the course of the gas phase thermal transformation of cyclobutanes [6], in the case of monosilacyclobutanes involves different ways of forming biradicals: the first starts with Si—C bond cleavage and the second with C—C bond cleavage (Scheme 2).

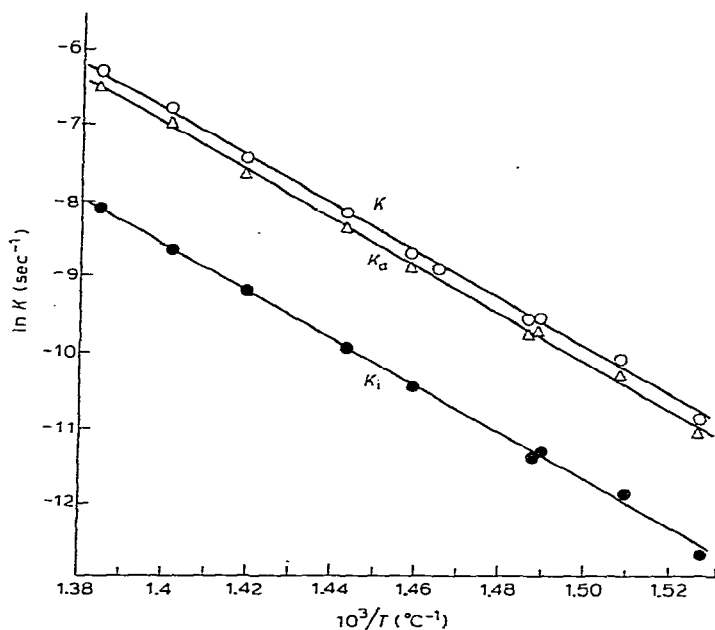
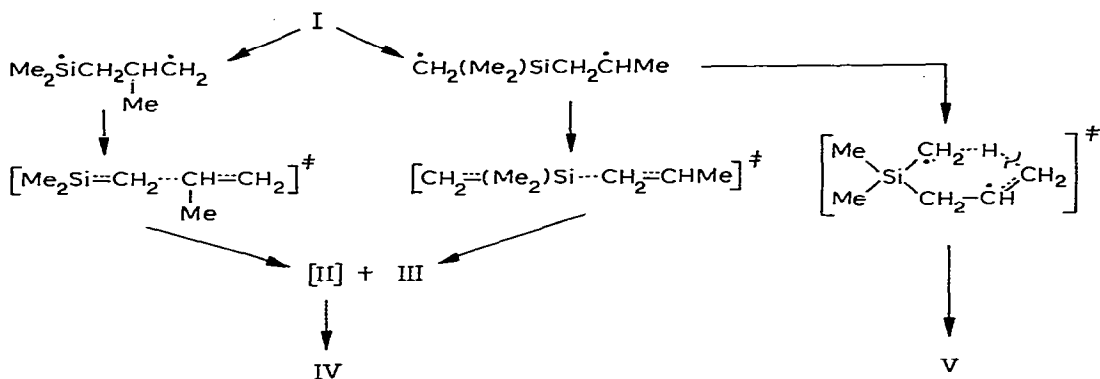


Fig. 2. Arrhenius plot for K , K_d and K_i .

SCHEME 2



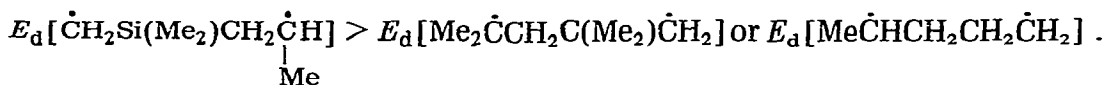
It is seen from Scheme 2 that the decomposition $\text{I} \rightarrow \text{II} + \text{III}$ is explained equally well by the formation of either biradical, whereas the isomerization $\text{I} \rightarrow \text{V}$ definitely indicates C—C bond cleavage in the monosilacyclobutane ring. According to recent data [7,8] the bond dissociation energy of Si—C is slightly higher (85–90 kcal/mol) than that of C—C bond (82 kcal/mol) [9] and, therefore, the process which starts with the cleavage of C—C bond will proceed at a higher rate.

The cleavage of C—C bond in the monosilacyclobutane ring is probably favoured also by some stabilization of the β -radical center formed in this case [10–12]. The preferred cleavage of the C—C bond of the monosilacyclobutane ring has been shown by Barton [13] and Sommer [14] who studied the thermal decomposition of 1,1,2-trimethyl-1-silacyclobutane. The rupture of Si—C bonds apparently proceeds parallel to C—C bond cleavage, but at a lower rate.

It is interesting to note that pyrolysis of I results in larger quantities of unsaturated isomers than the analogous pyrolysis of methyl-substituted cyclobutanes. In Table 2 we compare the values of K_d/K_i for methylcyclobutane, 1,1,3,3-tetramethylcyclobutane and I.

According to the data listed in Table 1 the activation energies of decomposition and isomerization of I are equal (K_d/K_i is independent of temperature). Therefore, the difference in the rates of these processes will be wholly determined by entropy restrictions, which seem to be more pronounced in the case of isomerization, because this process involves formation by the biradical $\dot{\text{C}}\text{H}_2\text{Si}(\text{Me}_2)\text{CH}_2\dot{\text{C}}\text{HCH}_3$ of a rigid six-membered cyclic transition state ($\Delta S_d^\ddagger - \Delta S_i^\ddagger = 3.1 \text{ cal/degree}^{-1} \text{ mol}^{-1}$).

It is doubtful whether entropy limitations differ significantly in the similar processes of isomerization of $\text{Me}_2\dot{\text{C}}\text{HCH}_2\text{CH}_2\dot{\text{C}}\text{H}_2$ and $(\text{Me}_2)\dot{\text{C}}\text{CH}_2\text{C}(\text{Me}_2)\dot{\text{C}}\text{H}_2$ biradicals. The less pronounced contribution of isomerization of these biradicals may best be explained by the lesser energy of activation of their decomposition than that derived from I.



Thus, the lifetime of the biradical $\dot{\text{C}}\text{H}_2\text{Si}(\text{Me}_2)\text{CH}_2\dot{\text{C}}\text{HMe}$ should be greater

TABLE 2

RATIO OF DECOMPOSITION AND ISOMERIZATION RATE CONSTANTS FOR CYCLOBUTANES AND MONOSILACYCLOBUTANES









Compound	Decomposition products	Isomerization products	K_d/K_i	Ref.
Me 	MeCH=CH ₂ + CH ₂ =CH ₂	MeCH ₂ CH ₂ CH=CH ₂	>50	15
Me ₂ 	2 Me ₂ C=CH ₂	Me ₃ CCH ₂ C(Me)=CH ₂	27	16
Me ₂ Si 	[Me ₂ Si=CH ₂] + CH ₂ =CHMe	Me ₃ SiCH ₂ CH=CH ₂	4,9	This work

TABLE 3

KINETIC AND THERMOCHEMICAL DATA OF THE GAS PHASE THERMAL TRANSFORMATION OF METHYL-SUBSTITUTED MONOSILACYCLOBUTANES AND CYCLOBUTANES

Compound	log A (sec ⁻¹)	E (kcal mol ⁻¹)	K × 10 ⁴ (sec ⁻¹) 450°C	ΔS [‡] (cal degree ⁻¹ mol ⁻¹) 450°C	ΔH [‡] (kcal mol ⁻¹) 450°C	References
Me ₂ Si 	15.68	62.3	4.0	9.46	6.09	3
Me ₂ Si 	16.3	63.3	15	12.3	61.9	This work
Me 	15.64 15.38 16.27	62.0 61.2 63.1	8.02 7.75 15.91	9.28 8.1 11.0	60.6 59.8 61.7	18 19 15
Me ₂ 	15.68	61.0	17.7	9.5	59.6	20
Me ₂ 	16.87 16.31	64.8 65.2	4.55 4.04	12.0 12.3	63.35 63.8	16 21

than the lifetime of biradicals Me₂ĊCH₂C(Me₂)ĊH₂ and MeĊHCH₂CH₂ĊH₂ *. This, apparently, facilitates the isomerization reaction in the case of pyrolysis of I.

That K_d/K_i is independent of temperature is observed in this work seems to disagree with the estimated [13] increased contribution of the initial cleavage of silicon-carbon bond in 1,1,2-trimethyl-1-silacyclobutane at higher pyrolysis temperatures. Presumably, it is due to the different temperature ranges (380–450 and 520–680°C, respectively) of these studies. Indeed, in the case of 1,1,2-trimethyl-1-silacyclobutane [13] an increase in pyrolysis temperature from 520 to 570°C did not change the ratio of reaction products due to initial cleavage of C-C and Si-C bonds.

In Table 3 are compared the thermochemical and kinetic data of gas phase thermal transformation of methyl-substituted monosilacyclobutanes and cyclobutanes. It is seen from the values of rate constants listed in Table 3 that thermal transformation of I proceeds ~4 times faster than the analogous process for 1,1-dimethyl-1-silacyclobutane. Both the processes have almost the same activation

* The lifetime of the tetramethylene biradical is estimated as 10⁻¹⁰ sec [17].

energy, but have different preexponential factors: in case of I the entropy of activation is greater by 3 e.u.

A similar increase in the entropy of activation was observed in the series of cyclobutanes having methyl substituents at position 3. However, the rate of decomposition in this case decreased due to the increase in the activation energy of the reaction.

Experimental

Materials

1,1,3-Trimethyl-1-silacyclobutane was prepared as described in ref. 5, a pure sample for kinetic study was obtained by GLC and by drying over calcium hydride powder.

Apparatus

Experiments were carried out in a static system at 380–450°C and at 20 Torr in an "aged" quartz vessel of volume 453 cm³. Dead space of the reactor was 1.8 cm³ (0.4%). The vapours of the substance under study were fed into the reactor through a stainless steel shut-off valve with Teflon packing. The reactor was heated in an SKB INKHS-1534 electric furnace with a massive steel block ensuring a temperature gradient of less than 1°C. Temperature (with accuracy ±0.1°C) was maintained by an SKB INKHS-1499 proportional thermoregulator working with a TSP-712 platinum resistance thermometer.

Analysis

The composition of the reaction mixture was determined by chromatography (LKHM-8Md model 5, flame ionization detector, column 3 m X 3 mm: 10% 1,2,3-tris(β-cyanoethoxy)propane, Chromosorb W). The gaseous sample was injected through a heated inlet valve. The areas of chromatographic peaks were normalized over the following coefficients: I, 1.0; III, 1.42; IV, 0.726; V, 1.06.

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