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A GAS KINETIC STUDY OF THE PYROLYSIS OF OCTAMETHYL-1,2-DISILACYCLOBUTANE

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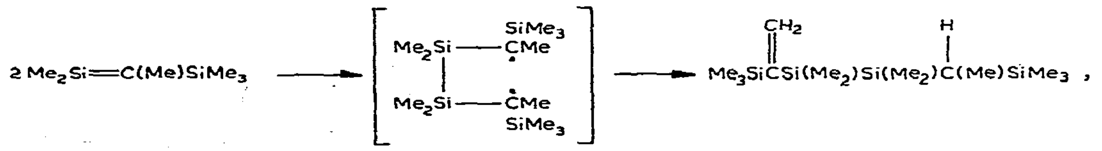
Summary

Pyrolysis of octamethyl-1,2-disilacyclobutane(I) has been shown to proceed by a unimolecular isomerisation involving a biradical which undergoes internal hydrogen-abstraction. Kinetic data were obtained for this pyrolysis and for that of the oxidation product of I, octamethyl-1,3-disila-2-oxacyclopentane(II). A few additional experiments indicated that intermediates with π-bonds to silicon may be generated by photolysis of I. The energetics of these reactions were discussed.

Introduction

In organosilicon chemistry there is considerable current interest in intermediates which can be represented as having π-bonds to silicon [1], viz., silaethenes [2] ($>Si{=}C<$), silanones [3] ($>Si{=}O$), and disilenes [4] ($>Si{=}Si<$). It has been established by inference [1,2] and by direct detection (mass spectrometrically [5,6] or by matrix isolation [7]) that silaethenes are generated in the pyrolysis of silacyclobutanes. Simple silaethenes, e.g. 1,1-dimethyl-1-silaethene, undergo head-to-tail self-combination to form 1,3-disilacyclobutanes [2]. Highly carbon-substituted silaethenes may dimerise head-to-head, followed by internal hydrogen-abstraction rather than cyclisation [8], e.g.

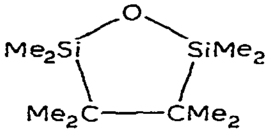


while certain more substituted silaethenes can be stabilised sufficiently to exist as monomers for appreciable times in solution, in equilibrium with the 1,2-disilacyclobutane resulting from their head-to-head dimerisation [9], e.g.

Against this background it is of interest to investigate the pyrolysis of 1,2-disilacyclobutanes to see whether silaethenes, disilenes, or other intermediates are formed. We report here the first kinetic investigation of the gas-phase pyrolysis of a 1,2-disilacyclobutane, octamethyl-1,2-disilacyclobutane.

Experimental

Octamethyl-1,2-disilacyclobutane (I) was prepared as already described [10]. It reacts readily with oxygen to form the siloxane II, and the sample of I used



(II)

in this work contained ca. 8% of II as the only impurity. No attempt was made to remove this impurity, as II was found to be thermally stable over the range of conditions used for the pyrolysis of I. Mass spectra, NMR data, and physical constants of I and II have been published [10].

The pyrolysis apparatus consisted of a quartz reaction vessel housed in an electric furnace with proportional temperature control, and attached to a conventional vacuum line fitted with greaseless stopcocks. The contents of the reaction vessel leaked slowly through a 10 micron hole into the ionisation chamber of a quadrupole mass spectrometer (VG, Q801K), enabling the progress of a pyrolysis to be monitored continuously. Reaction rates were measured by following the decay of a mass spectral peak characteristic of the reactant, decay curves being corrected for the loss of reactant through the 10 micron leak hole.

Mass spectrometric identification of products in the pyrolysis apparatus was supplemented by NMR (Varian EM390). For this purpose, pyrolyses were carried out in a detachable reaction vessel fitted with a greaseless stopcock and greaseless joint, the reaction mixture after pyrolysis being dissolved in benzene for NMR analysis.

Results

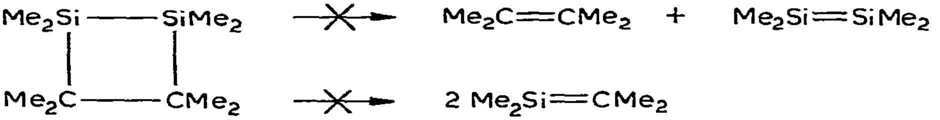
1. Pyrolysis of octamethyl-1,2-disilacyclobutane (I)

Initial pressures of I from 0.04 to 0.25 mmHg were pyrolysed in the main apparatus between 582 and 653 K. The base peak in the mass spectrum of I (m/e 116^+) decreased in intensity on pyrolysis, while peaks at m/e 129^+ and 157^+ (which had intensities ca. 1% of base peak before pyrolysis) rose substantially. At temperatures above 630 K these peaks began to decrease in the later stages of pyrolysis. The intensity ratio of m/e 129^+ to 157^+ was independent of time and temperature. There was little change in the intensity of the molecule-ion m/e 200^+ during pyrolysis, except that it too decreased above 630 K. Characteristic peaks in the mass spectrum of II (m/e 216^+, 133^+, and 117^+) did not change in intensity during runs, indicating that II was thermally stable up to at least 653 K. It was therefore convenient to use the 133^+ peak as an internal standard in the pyrolysis experiments.

Kinetic data were obtained from the time-dependence of the m/e 116^+ peak intensity. As the initial pressure of I was varied 6-fold, the half-life for the disappearance of m/e 116^+ remained constant within 10%; the decomposition of I was therefore first order. First order rate constants were given by:

$$\log_{10} k_I/\mathrm{s}^{-1} = (15.41 \pm 0.41) - (206.9 \pm 4.9)\ \mathrm{kJ\ mol^{-1}}/2.303\ RT.$$

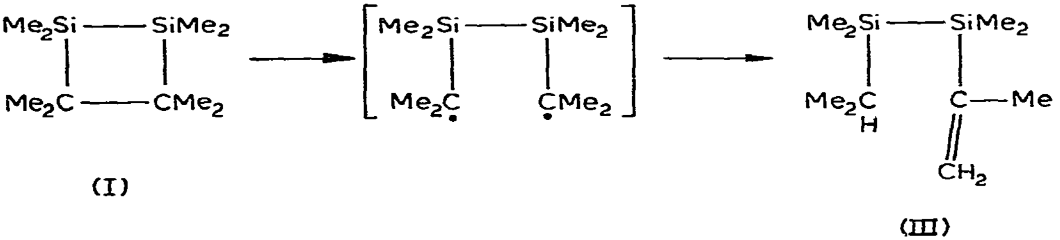
From the above changes in mass spectral peaks on pyrolysis, viz. decrease in 116^+, increase in 129^+ and 157^+, with virtually no change in 200^+, it is clear that I undergoes an isomerisation, and does not dissociate into fragments, i.e.



(1)

(2)

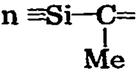
As well as simple fragmentations, the mass spectra of I and II show several rearrangement ions [10]; m/e 129^+ seems to be one such, corresponding to the loss of C_5H_{11} or C_3H_7Si from the isomerisation product. It is therefore not helpful in elucidating the isomerisation. However, m/e 157^+ is more easily understood as resulting from the loss of C_3H_7, suggesting that pyrolysis of I proceeds by:



(3)

(I)

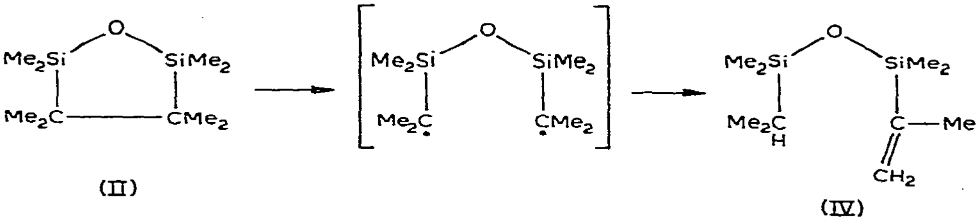
(III)

The isomer III would be expected to give a prominent mass spectral peak at m/e 157^+ by loss of $Me_2\dot{C}H$. Supporting evidence for reaction 3 came from the pyrolysis experiments which were analysed by NMR. After pyrolysis there were new peaks in the NMR spectrum which were entirely consistent [11] with the presence of III, evidence for the configuration  $\equiv Si-C(Me)=CH_2$ being particularly clear. Chemical shifts and assignment of the peaks were (δ, ppm): 5.72 (d_q, 1H), 5.46 (d_q 1H), 1.92 (t 3H), 1.1 (d 6H, $J_{vicinal}$ 16 Hz), 0.32 (s 6H), and 0.18 (s 6H). The only structural feature of III not visible in the NMR spectrum was the isopropyl septet, which was presumably of too low intensity to be detected in the presence of I and II. Irradiation of the methyl triplet at 1.92 ppm removed the *cis*- and *trans*-allylic coupling ($J \sim 1.2$ Hz), leaving the olefinic protons as an AB quartet (J_{gem} 3 Hz).

Further indications of a simple isomerization with no formation of silaethenes came from a few pyrolysis experiments with silaethene traps, which yielded no new products; and from GLC analysis of the reaction mixture, which showed only one new peak.

2. *Pyrolysis of octamethyl-1,3-disila-2-oxacyclopentane (II)*

In view of the presence of a significant quantity of II in the pyrolysis mixture, some pyrolysis experiments were done on pure II (obtained by the deliberate oxidation of I). As noted above, II was thermally stable up to 653 K and indeed a suitable temperature range for kinetic studies was found to be 695 to 752 K. In contrast to I, the molecule-ion (m/e 216^+) decreased in intensity on pyrolysis along with the other characteristic peaks at 133^+ and 117^+. The only significant increase observed was in m/e 173^+, which is the corresponding ion to 157^+ in I. It is likely, therefore, that II decomposes in a similar fashion to I, by reaction 4:



(4)

but that IV then decomposes relatively rapidly between 695 and 752 K to give smaller molecules. Some secondary decomposition of III was observed in the pyrolysis of I above 630 K.

Pyrolysis of II, monitored by following the decrease in m/e 216^+ with time, was first order, with rate constants given by:

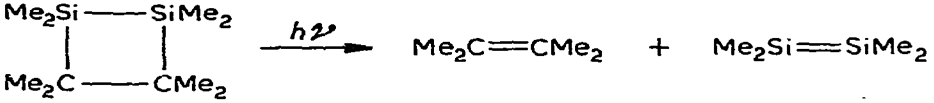
$$\log_{10} k_{II}/\mathrm{s}^{-1} = (15.74 \pm 0.32) - (247.9 \pm 4.4)\ \mathrm{kJ\ mol}^{-1}/2.303\ RT.$$

The ratio of k_{II}/k_I ranges from 10^{-3} at 653 K to 5×10^{-4} at 582 K, confirming the stability of II under the pyrolysis conditions used for I.

3. *Photolysis of octamethyl-1,2-disilacyclobutane I*

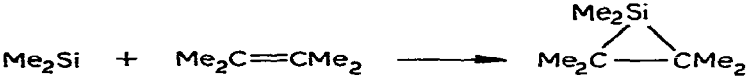
Although reactions 1 and 2 forming a disilene or silaethene did not occur on pyrolysis of I, we thought it possible that these routes might be followed on photolysis. This possibility was investigated in a preliminary way in a few simple experiments. Samples of I, in the detachable reaction vessel used for the NMR analyses, were photolysed at room temperature for ca. 30 min. with an unfiltered medium pressure mercury arc. Analysis was by mass spectrometry.

No peaks at m/e 129^+ and 157^+ were observed, but there were strong new peaks at m/e 69^+, 84^+, 100^+, and 142^+. If reaction 3 occurred on photolysis, it was evidently followed by complete secondary photolysis of the product, III. In any case, the new peaks noted above indicate that at least one other photolytic process occurred. The peaks at 69^+ and 84^+ can be attributed to 2,3-dimethylbut-2-ene and that at 142^+ to hexamethylsilacyclopropane [12], which can reasonably be thought of as being formed thus:



(1)

$$Me_2Si{=}SiMe_2 \longrightarrow 2\,Me_2Si \qquad (5)$$

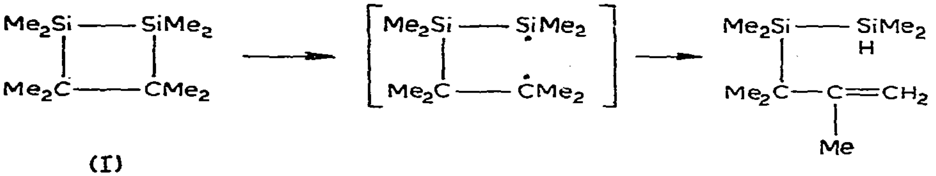


(6)

The peak at m/e 100^+ probably arose from a molecule which we did not identify containing the Me_2SiCMe_2 fragment. This might be an indication that reaction 2 took place, but Me_2SiCMe_2 could also have been formed by secondary photolysis of III. Hence, although we have reasonable evidence for reaction 1 on photolysis of I, we have no clear evidence for reaction 2 and cannot exclude reaction 3.

Discussion

The mass spectral evidence shows clearly that I undergoes isomerisation on pyrolysis, and the combined mass spectral and NMR data provide good evidence that this isomerisation proceeds according to reaction 3, to form III. The only other way to form a product with the two olefinic protons detected by NMR would be by rupture of the silicon—carbon bond, thus:



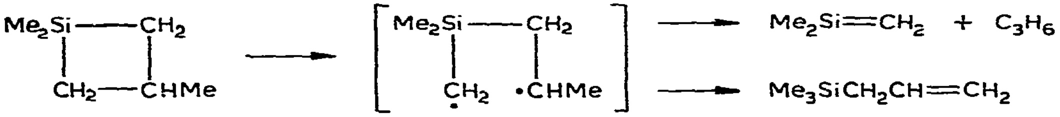
(7)

(I)

(V)

However, V would fit the overall NMR data less well than III and would undoubtedly show a strong m/e 199^+ peak in its mass spectrum, by loss of the hydrogen attached to silicon. Reaction 7 can also be rejected on energetic grounds, as discussed below.

Reaction 3 is consistent with recent developments in the chemistry of cyclic silicon compounds, it being increasingly apparent that radical reactions are important [8,13], as they are in cycloalkane chemistry [14]. There is now considerable evidence that the first step in the pyrolysis of 1,1-dimethyl-1-silacyclobutane is the formation of a biradical [6,15], as in the pyrolysis of cycloalkanes [14], while an isomerisation by internal hydrogen-abstraction by such a radical, as in reaction 3, has recently been reported as a minor parallel route to the formation of a silaethene in the pyrolysis of 1,1,3-trimethyl-1-silacyclobutane [16]:



The Arrhenius parameters obtained in this work are listed with those for the pyrolysis of the silacyclobutanes described above in Table 1.

$\log_{10}A$ values of ca. 15.6 obtained in the pyrolysis of cyclobutanes have been shown to be consistent with biradical formation [14]. Clearly the same interpretation can be put on the A factors obtained in this work. The activation energies measured by us in the pyrolysis of I and II are significantly lower than the other activation energies in Table 1, which can be understood in terms of the bond strengths and strain energies in I and II, as follows.

Considering first the pyrolysis of I, we have to estimate the strengths of the bonds in the ring. Each of these will equal the bond dissociation energy in the corresponding acyclic molecule minus the ring strain energy, E_S. For the silicon—silicon bond in I, a good analogy is $D(Me_3Si{-}SiMe_3)$ in hexamethyldisilane, which is known [17] to be 337 kJmol^{-1}; for carbon—carbon, the analogy is $D(Me_3C{-}CMe_3)$ in "di-t-butyl", which is 288 kJmol^{-1} [18]. For silicon—carbon there is no close analogy, the nearest being $D(Me_3Si{-}Me)$ in tetramethylsilane [19] which is 355 kJmol^{-1}. In hydrocarbons [18] $D(Me{-}Me)$ is 27 kJmol^{-1} greater than $D(Me{-}CMe_3)$. The analogous difference in organosilanes is likely to be less [20], hence $D(Me_3Si{-}CMe_3) \geqslant 328$ kJmol^{-1}. Consequently, the weakest bond in the ring of I is carbon—carbon, in keeping with the evidence for reaction 3 from product analysis.

There is no value available for the ring strain energy in I, E_S, but it may be estimated from the activation energy for reaction 3 and the carbon—carbon bond strength, thus:

$$E_3 = D(C{-}C) - E_S$$
$$207 = 288 - E_S$$
$$\therefore E_S = 81 \text{ kJ mol}^{-1}.$$

This relationship has been shown to hold in the pyrolysis of 1,1-dimethyl-1-sila-

TABLE I

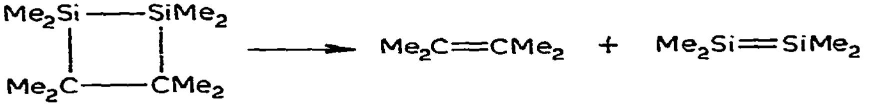
ARRHENIUS PARAMETERS FOR PYROLYSES

Reactant	Reaction	$\log_{10}A(s^{-1})$	E(kJ mol^{-1})	Ref.
1,1-dimethyl-1-silacyclobutane	d	15.6 ± 0.2	262 ± 2	2
1,1,3-trimethyl-1-silacyclobutane	d	16.3 ± 0.3	264 ± 4	16
	i	15.6 ± 0.3	265 ± 3	16
I	i	15.4 ± 0.4	207 ± 5	This work
II	i	15.7 ± 0.3	248 ± 4	This work

d = dissociation to alkene and silaethene
i = isomerisation by internal hydrogen-abstraction

cyclobutane [6] and is likely to be valid here.

To estimate the energetics of reactions 1—3 we also require values of the π-bond energies in alkenes, silaethenes, and disilenes. The π-bond energy in ethene is [18,21] 247 kJmol^{-1} and is 226 kJmol^{-1} in 2,3-dimethylbut-2-ene [21]. In 1,1-dimethyl-1-silaethene the most recent estimate [6] of the π-bond energy is 157 ± 25 kJmol^{-1}, while the silicon—silicon π-bond energy in disilenes has been estimated [22] as 85 kJmol^{-1}. Hence, for reaction 1,



(1)

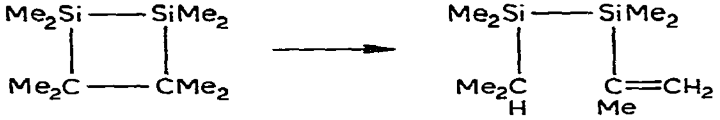
$$\Delta H_1 = 2\,D(\text{Si—C}) - E_S - E_\pi(\text{SiSi}) - E_\pi(\text{CC})$$
$$= 2(\geqslant 328) - 81 - 85 - 226$$
$$\therefore\ \Delta H_1 \geqslant 264\ \text{kJmol}^{-1}$$

For reaction 2,

(2)

$$\Delta H_2 = D(\text{Si—Si}) + D(\text{C—C}) - E_S - 2\,E_\pi(\text{SiC})$$
$$= 337 + 288 - 81 - 2(157)$$
$$\therefore\ \Delta H_2 = 230\ \text{kJmol}^{-1}$$

For reaction 3,



(3)

$$\Delta H_3 = D(\text{C—C}) + D(\text{—CH}_2\text{—H}) - D(\text{=C—H}) - E_\pi(\text{CC}) - E_S$$
$$= 288 + 410 - 381 - 247 - 81$$
$$\therefore\ \Delta H_3 = -11\ \text{kJmol}^{-1}$$ (carbon—hydrogen bond strengths from ref. 18)

Thus, reaction 3 is slightly exothermic, while the endothermicities of reactions 1 and 2 are both greater than the observed activation energy, E_3. Hence, even if —1 and —2 require no activation energy, E_1 and E_2 would be greater than E_3, which accounts for the observed course of the pyrolysis of I. On the other hand, reactions 1 and 2 become feasible on UV photolysis, where energies substantially greater than these endothermicities are available.

In the case of II, if the pyrolysis proceeds according to reaction 4, the ring strain energy in II may be estimated, thus:

$$E_4 = D(\text{C—C}) - E_S$$
$$248 = 288 - \text{E}_S$$
$$\therefore\ E_S = 40\ \text{kJmol}^{-1}.$$

Acknowledgements

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