Kinetics of the Formation of Dimethylsilanediyl (Dimethylsilylene) in the Pyrolysis of Pentamethyldisilane and Heptamethyltrisilane

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Experimental kinetic data are reported for the pyrolysis of heptamethyltrisilane to form dimethylsilanediyl, trapped by excess 2,3-dimethylbuta-1,3-diene; it is shown by computer modelling that formation of the trapped product is rate-determined by the primary reaction in that pyrolysis and in the pyrolysis of pentamethyldisilane, a conclusion which has thermochemical implications.

Recently, there has been encouraging progress in the use of time-resolved methods to measure the kinetics of reactions of silanediyls (silylenes).[1] Consequently, in the pyrolysis of a hydridodisilane to form a silanediyl and a monosilane, e.g. $Me_3SiSiMe_2H \rightleftharpoons Me_3SiH + Me_2Si:$, it should be possible to combine kinetic data for the forward reaction (obtained by traditional methods) and for the reverse reaction (obtained by time-resolved methods) to derive much-needed thermochemical information. However, Walsh has pointed out that kinetic data from these two types of source seem to be mutually inconsistent.[2] He drew particular attention to the above example, and as we were responsible for the Arrhenius parameters for the forward reaction,[3] we have now undertaken further kinetic experiments and computer modelling to try to cast light on the inconsistency.

We extended previous work[3] by pyrolysing heptamethyltrisilane $Me_3Si(SiMe_2)_2H$ (1), which was believed[4] to be more thermally labile than pentamethyldisilane (2), between 394 °C and 450 °C in the presence of a 5-fold excess of 2,3-dimethylbuta-1,3-diene as a trap for silanediyls.[3] Although 1,3-dienes are convenient traps, some of the inconsistencies noted above may arise[2] because there is now good evidence that their reaction with silanediyls is a complex process involving reversible formation of a silacyclopropane,[5] as shown in Scheme 1.

Pyrolyses were carried out in a stirred-flow (SFR) apparatus[6] with analysis by g.c.–mass spectrometry (HP5995C); there were no other products besides those in Scheme 1, and Me_3SiH was not a primary product. Consequently, primary decomposition of (1) occurs only by a 1,2 H-shift [reaction (1)], with no contribution from a 1,3 H-shift; the latter would give $Me_2Si=SiMe_2$ (which would be trapped by the butadiene or would rearrange to stable disilacyclobutanes[7,8]) together with some directly formed Me_3SiH. The absence of tetrasilanes indicated efficient silanediyl trapping by the butadiene. Although the silacyclopentene (4) came from $Me_2Si:$ formed in reaction (3) as well as reaction (1), a simple kinetic expression can be derived by considering the mass balance in

the SFR,[9] ignoring the reverse reactions (2) and (4) because of the observed efficiency of trapping by the butadiene. Thus, the mass balances for (2) and $Me_2Si:$ are shown in equations (i) and (ii), respectively, where v is the volume of the reaction vessel and u is the volumetric flow rate. Adding equations (i) and (ii) gives equation (iii), where $\tau = v/u$, the time constant of the SFR.[6] Hence if compound (4) is a measure of the $Me_2Si:$ formed then k_1 is given by equation (iv).

$$k_1 v (1) - k_3 v (2) - u (2) = 0 \qquad (i)$$

$$k_1 v (1) + k_3 v (2) - u (Me_2Si:) = 0 \qquad (ii)$$

$$k_1 = [(2) + Me_2Si:]/2\tau (1) \qquad (iii)$$

$$k_1 = [(2) + (4)]/2 \tau (1) \qquad (iv)$$

First-order rate constants calculated from g.c. peak areas according to equation (iv) gave $\log A = 11.8 \pm 0.4$, $E = 175 \pm 5$ kJ mol^{-1}.

To see if these Arrhenius parameters could be assigned to reaction (1), and if those obtained earlier by us in similar experiments[3] corresponded to reaction (3), we modelled Scheme 1 by numerical integration,[8] with the Arrhenius parameters for individual reactions given in Table 1. Our estimates for reactions (5)—(8) are the same as those recently shown to account for the kinetics of the closely related pyrolysis of 1,1-dimethylsilacyclopent-3-ene with excess 2,3-dimethylbuta-1,3-diene.[10]

We simulated the pyrolysis of (1) with a 5-fold excess of 2,3-dimethylbuta-1,3-diene, calculating rate constants according to equation (iv). The resulting Arrhenius parameters were identical to the experimental values reported above, implying that these were rightly attributed in Table 1 to reaction (1). Likewise, simulating the pyrolysis of (2) with a 10-fold excess of 2,3-dimethylbuta-1,3-diene[3] gave Arrhenius parameters for the formation of (4) identical to those in Table 1 for reaction (3). The computed amount of (1) produced from (2) was very small, in agreement with experiment.[11] Hence, notwithstanding the complexity and reversibility of the reactions in Scheme 1, our belief[3] that formation of (4) in the pyrolysis of (2) is
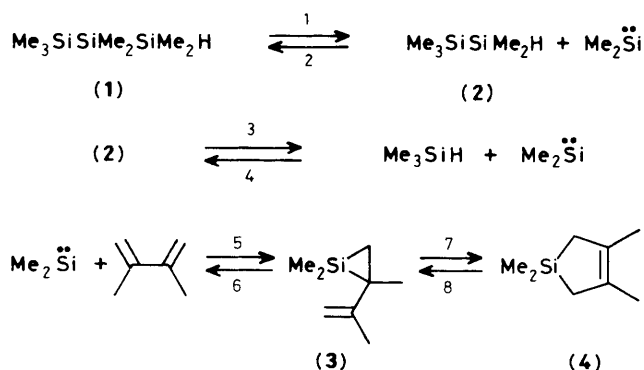
Scheme 1

Table 1. Arrhenius parameters for reactions in Scheme 1.

Reaction	$\log (A/s^{-1})$	$E/kJ\,mol^{-1}$	Source
1	11.8	175	a
2	9.5	0	b
3	13.3	203	c
4	9.5	0	b
5	10.7	0	d
6	13.0	111	d
7	12.5	108	d
8	12.2	232	d

[a] This work. [b] Ref. 2. [c] Ref. 3. [d] Ref. 10.

rate-determined by reaction (3) appears to be confirmed. Walsh[2] suggested that the most reasonable way to reconcile the pyrolysis of (2) with time-resolved kinetics and his thermochemical estimates was to revise the Arrhenius parameters for reaction (3) upwards to $\log A = 15.3$ and $E = 228$ kJ mol^{-1}. The evidence reported here in support of the original Arrhenius parameters[3] may be useful in helping to decide between different thermochemical estimates arrived at by Walsh's methods,[2] ab initio calculations,[12] and bond additivity schemes.[13,14] We understand that differences in the most recent estimates[15] relating to reaction (3) are comparable to the difference between the experimental[3] and 'recommended'[2] values of E_3.

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