Some Observations on the Thermal Interconversion of Silanediyls (Silylenes) and Sila-olefins (Silenes)

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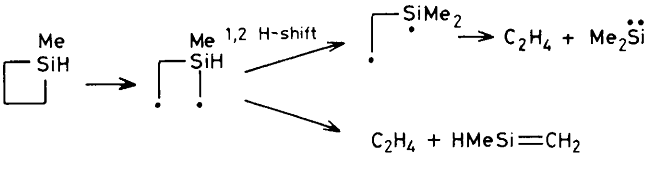
New experiments on thermally-generated $\mathrm{Me_2\ddot{S}i}$ are interpreted in terms of a reversible silanediyl $\rightleftharpoons$ sila-olefin isomerization, as predicted theoretically; earlier apparently conflicting results are shown to be consistent with this explanation.

The interconvertibility of sila-olefins and silanediyls, exemplified by reactions (1) and (−1), is a question of some current interest and controversy. Pyrolysis of 1,1-dimethylsiletane[1] is a clean source of 2-methyl-2-silapropene ($\mathrm{Me_2Si{=}CH_2}$), which dimerizes to a 1,3-disiletane; 1-methylsiletane would likewise be expected to be a source of 2-silapropene, but its pyrolysis, alone and with butadiene and trimethylsilane as trapping agents at 925 K, gave clear evidence for dimethylsilanediyl. It was concluded that reaction (1) went to completion under these conditions.[2] Similar evidence for the analogous reaction (2) was found in the pyrolysis of siletane.[3] On the other hand, 2-silapropene generated from another precursor at 673 K dimerized efficiently, or was trapped by added butadiene,[4] with no evidence for $\mathrm{Me_2\ddot{S}i}$. It was pointed out that a possible alternative to reaction (1) is a 1,2-hydrogen shift in the initial biradical, as in Scheme 1. Walsh[5] has advanced a kinetic argument which would reconcile the foregoing results if reaction (1) had an activation energy approximately equal to the theoretically-calculated barrier (*vide infra*) and if $\log A_1 =$ *ca.* 13.5, but which took no account of the reversibility of reaction (1).

$$\mathrm{HMeSi{=}CH_2 \rightleftharpoons Me_2Si{:}} \qquad (1), (-1)$$

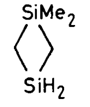
$$\mathrm{H_2Si{=}CH_2 \rightarrow {:}SiHMe} \qquad (2)$$

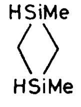


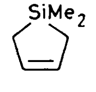
Scheme 1

The considerable theoretical activity in this field has been critically reviewed.[6] Reaction (2) is calculated to be approximately thermoneutral, with a barrier to isomerization of *ca.* 170 kJ mol^{-1}. Recent calculations[7] indicate that the same should be true for reactions (1) and (−1). The thermoneutrality is consistent with experimentally-based estimates of bond dissociation energies and enthalpies of formation.[8] We estimate that ΔS_1 is also about zero; the entropy of $\mathrm{Me_2\ddot{S}i}$ should approximately equal that of $\mathrm{Me_2S}$ (286 J mol^{-1} K^{-1})[9] or $\mathrm{Me_2SiH_2}$ (304 J mol^{-1} K^{-1}),[10] which has the same symmetry, while the entropy of $\mathrm{HMeSi{=}CH_2}$ may be estimated as *ca.* 302 J mol^{-1} K^{-1} from the entropy of propene corrected for the effect of silicon-substitution on the group additivity terms and the π-bond frequency.[9,10] Hence, reaction (1) should not go to completion, but should reach equilibrium, equally accessible from $\mathrm{Me_2\ddot{S}i}$ as from $\mathrm{HMeSi{=}CH_2}$, with an equilibrium constant of close to unity. We have therefore sought to shed some light on reactions (1) and (−1) by carrying out some experiments, with and without trapping, on thermally-generated $\mathrm{Me_2\ddot{S}i}$.

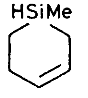
The sources of $\mathrm{Me_2\ddot{S}i}$ were chloropentamethyldisilane[11] between 810 and 924 K, and the more thermally labile methoxypentamethyldisilane between 720 and 830 K. A


(1)


(2)


(3)


(4)


(5)

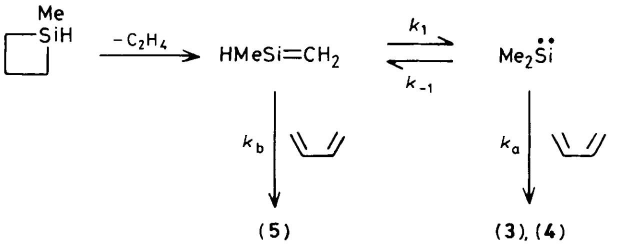
stirred-flow apparatus was used, with analysis by g.l.c.[12] Between 780 and 860 K, pyrolysis of the appropriate disilane without any trapping agent gave 1,1-dimethyl-1,3-disiletane (**1**) and 1,3-dimethyl-1,3-disiletane (**2**); the ratio of (**1**) to (**2**) varied from *ca.* 1.4 : 1 at 780 K to *ca.* 0.5 : 1 at 860 K. Some trisilane and tetrasilane insertion products were also observed with the methoxydisilane, but not with the chlorodisilane, which is not surprising[13] considering that the energy barriers for the former disilane are at least as low as in pentamethyldisilane.[14]

In pyrolyses with a 10-fold excess of butadiene between 720 and 924 K, formation of (**1**) and (**2**) was completely suppressed, as was formation of any tri- or tetra-silanes. The only significant products other than decomposition products of butadiene at higher temperature, and of course the monosilane produced concomitantly with the $Me_2\ddot{Si}$, were the adducts of $Me_2\ddot{Si}$ to butadiene, (**3**) and (**4**). The adduct of $HMeSi{=}CH_2$, (**5**) was at most a minor product (<1%).

In separate experiments under the same conditions, (**5**) was found to decompose to give (**1**)—(**4**) and butadiene; the extent of decomposition was <10% up to 850 K, but rose to *ca.* 60% at 924 K.

In our experiments with *ca.* 6 Torr of butadiene (*i.e.* 10^{-4} mol dm^{-3}), reaction (-1) clearly did not compete with addition of $Me_2\ddot{Si}$ to butadiene. At 930 K addition of $\ddot{Si}H_2$ to butadiene has the same rate constant as insertion of $\ddot{Si}H_2$ into the silicon–hydrogen bond of trimethylsilane (and some lower temperature data support the argument);[15] the rate constant for insertion of $Me_2\ddot{Si}$ into trimethylsilane has been estimated[16] as 10^9 dm^3 mol^{-1} s^{-1}, with zero activation energy. If the Arrhenius parameters for reaction (-1) are log A = *ca.* 13.5 and E = *ca.* 170 kJ mol^{-1}, then k_{-1} = *ca.* 7.8×10^3 s^{-1} at 924 K and the relative rates of addition and isomerization are given by: $(10^9 \times 10^{-4}/7.8 \times 10^3) = 13$ which is entirely consistent with experiment. Addition is even more favoured over isomerization at lower temperatures.

On the other hand, reactions (1) and (-1) should be fully equilibrated in the absence of butadiene, even at 780 K (the calculated half-life for isomerization at 780 K is 25 ms, while the residence time in the reactor was 7 s). We believe that the observed yields of (**1**) and (**2**) confirm that expectation. Both (**1**) and (**2**) are known[17] to be formed from rearrangement of $Me_2Si{=}SiMe_2$, initiated[18] by its isomerization to $Me_3Si\ddot{Si}Me$. The ratio of (**1**) to (**2**) was 3 : 1 from $Me_2Si{=}SiMe_2$ at 633 K[17] and 1.9 : 1 from $Me_3Si\ddot{Si}Me$ at 973 K.[18] Conlin and Gaspar[19] generated $Me_2\ddot{Si}$ from a similar precursor to ours, but at temperatures (873 to 973 K) which corresponded to extensive decomposition of it. They reasonably interpreted the formation of (**1**) and (**2**) as evidence for dimerization of $Me_2\ddot{Si}$ to $Me_2Si{=}SiMe_2$. However, in their experiments, as in ours, significantly more (**2**) was formed than in experiments starting from Me_4Si_2 [their ratio of (**1**) to (**2**) was 0.86 : 1 at 873 and 0.59 : 1 at 973 K]. With remarkable insight they suggested that some (**2**) could come from dimerization of $HMeSi{=}CH_2$. We agree with that suggestion, which we believe to be the first recognition of the possibility that a silanediyl could rearrange to a sila-olefin. In their experiments and in ours, we envisage rapid equilibration by reactions (1) and (-1), giving equimolecular concentrations of $Me_2\ddot{Si}$ and $HMeSi{=}CH_2$, which are then withdrawn from the equilibrium mixture by dimerization [this argument is not weakened by neglect of 'cross-combination' of $Me_2\ddot{Si}$ and $HMeSi{=}CH_2$, which would merely lead to one of the intermediates proposed[18] in the rearrangement of Me_4Si_2 to (**1**) and (**2**)].



Scheme 2

The experiments of Conlin and Wood on 1-methylsiletane[2] may be reinterpreted in similar terms. Generation of $HMeSi{=}CH_2$ in the absence of butadiene between 898 and 925 K gave ratios of (**1**) to (**2**) *ca.* 0.55 : 1, as expected if reactions (1) and (-1) were equilibrated, but not if $HMeSi{=}CH_2$ had been fully converted to $Me_2\ddot{Si}$. Their experiments with added butadiene at 925 K, which gave no (**5**), appear to invalidate our argument, but we believe that result to be a consequence of the nature of the trapping experiment. The relevant reactions are shown in Scheme 2. $Me_2\ddot{Si}$ is the secondary intermediate, which reacts rapidly with butadiene and may be assumed to be in a steady state. Hence the expression in equation (3).

$$[(\mathbf{5})]/[(\mathbf{3}),(\mathbf{4})] = (k_{-1}k_b/k_1k_a) + (k_b[C_4H_6]/k_1) \qquad (3)$$

Walsh[5] has suggested Arrhenius parameters for k_b of log A = *ca.* 7 and E = *ca.* 30 kJ mol^{-1} from the relative rates of dimerization and adduct formation in the CO_2 laser-induced decomposition of 1,1-dimethylsiletane.[20] However, the effective temperature in these experiments was uncertain, so in view of the thermal instability of sila-olefin adducts to butadiene we think it safer to rely on the observation[4] that at 673 K, with extensive decomposition of the precursor, butadiene completely suppressed dimerization of $HMeSi{=}CH_2$; hence $k_b > 10^6$ dm^3 mol^{-1} s^{-1} at 723 K. We suggest log A_b = *ca.* 7 and E_b = *ca.* 10 kJ mol^{-1}. With that estimate, those given above for k_1, k_{-1}, and k_a, and a butadiene concentration of $10^{-4.5}$ mol dm^{-3}, $[(\mathbf{5})]/[(\mathbf{3}),(\mathbf{4})]$ = *ca.* 0.01 at 925 K (Walsh's estimate for E_b would give an even lower result); since (**5**) decomposes significantly at 925 K, a negligible amount would be observed. The high efficiency of reaction (a) prevented equilibration, just as it did in our experiments. The experiments at 925 K with added trimethylsilane[2] gave a similar ratio of (**1**) to (**2**) as in the neat pyrolysis because trimethylsilane is not an effective trap under these conditions; the half-life of pentamethyldisilane is[14] only 12 ms at 925 K.

When $HMeSi{=}CH_2$ was generated at 673 K in an excess of butadiene,[4] trapping would have been *ca.* 30 times faster than reaction (1) according to our estimates of k_1 and k_b, in good agreement with experiment, and with a similar calculation by Walsh.[5] Indeed, we have found that when 1-methylsiletane was pyrolysed with butadiene as carrier gas, the large excess of trapping agent caused (**5**) to be the major product even at 873 K.

We conclude that in all of the high-temperature pyrolyses discussed above an equimolecular equilibrium mixture of $HMeSi{=}CH_2$ and $Me_2\ddot{Si}$ was produced in the absence of butadiene, irrespective of the direction from which the equilibrium was approached. This conclusion was obscured in earlier experiments with added butadiene[2] by the large difference between k_a and k_b. The theoretical estimates[6] of the energetics of reactions (1) and (−1) are thus entirely consistent with experiment. The reported isomerizations in a matrix at 100 K[21] are now believed to occur by an indirect mechanism.[22] Finally, it should be noted that our conclusion neither confirms nor invalidates the suggestion embodied in Scheme 1, which remains an open question.

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