

Kinetics of Addition of 2-Methyl-2-silapropene to Hydrogen Chloride, Hydrogen Bromide, and Oxygen

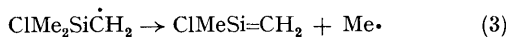
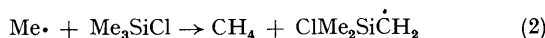
By IAIN M. T. DAVIDSON,* CHRISTOPHER E. DEAN, and F. TIMOTHY LAWRENCE

(Department of Chemistry, The University, Leicester LE1 7RH)

Summary 2-Methyl-2-silapropene adds rapidly to hydrogen chloride and to hydrogen bromide in the gas phase to form the corresponding trimethylsilyl halide, and to molecular oxygen to form dimethylsilanone; Arrhenius parameters for these reactions have been measured.

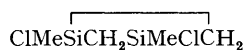
THERE is considerable interest in the chemistry of silaethenes, but little quantitative information on the reactions of these important intermediates. We report Arrhenius parameters for the gas-phase addition of hydrogen chloride, hydrogen bromide, and oxygen to 2-methyl-2-silapropene.

The experiments with hydrogen halides arose from our work on the pyrolysis of trimethylchlorosilane, studied by a low-pressure pyrolysis (L.P.P.) technique.¹ By analogy with the pyrolysis of tetramethylsilane,² we expected the mechanism in Scheme 1.



SCHEME 1.

In practice, methane was indeed formed with essentially the same kinetic parameters as in the pyrolysis of tetramethylsilane, but there was no evidence for

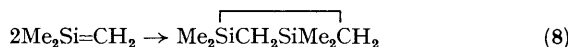
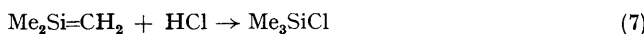
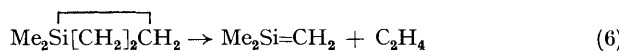


whereas dimethyldichlorosilane was a significant product.

Since some hydrogen chloride is inevitably present during experiments with trimethylchlorosilane, a reasonable explanation for these findings is that pyrolysis proceeds by reactions (1) to (3), followed by reaction (5) instead of reaction (4).



This prompted us to investigate the kinetics of addition of a silaethene to hydrogen chloride, by generating 2-methyl-2-silapropene from 1,1-dimethyl-1-silacyclobutane³ in our L.P.P. apparatus¹ in the presence of hydrogen chloride. The products were those expected (Scheme 2). Reaction



SCHEME 2.

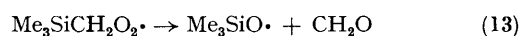
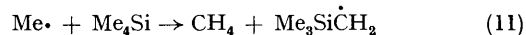
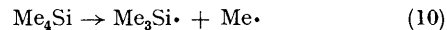
(7) was very fast, to the extent that conditions could not be found for the simultaneous occurrence of reactions (7) and (8), the latter only being observed when most of the hydrogen chloride had been used up. Consequently, the normal kinetic method of measuring k_7 relative to $(k_8)^{1/2}$ could not be used. Instead, progress curves were plotted for the reactants and products in a series of experiments between 773 and 813 K with constant initial amounts (ca. 0.5 mmHg) of a 3:1 mixture of dimethylsilacyclobutane and hydrogen chloride. A plot of the time required for the onset of reaction (8) against the time for a fixed percentage decomposition of the dimethylsilacyclobutane at each temperature was approximately linear, suggesting that reactions (7) and (8) had approximately equal activation energies. This result was refined by computer-aided numerical integration,² using the well established literature data³ for reaction (6) and the latest estimate⁴ for reaction (8), viz. $k_8 = 10^{6.55} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, with zero activation energy. The best computed fit to the experimental data gave $\log_{10} k_7/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (7.5 \pm 0.5) - (10 \pm 7 \text{ kJ mol}^{-1})/2.303 RT$.

Similar experiments were carried out with hydrogen bromide instead of hydrogen chloride over the same temperature range, but with a 2:1 mixture of dimethylsilacyclobutane and hydrogen bromide. Analogous results were obtained, with reaction (9) instead of reaction (7).



Reaction (9) was sufficiently slow for it and reaction (8) to occur simultaneously, but there were still difficulties in measuring the kinetics because trimethylbromosilane decomposed rapidly in our apparatus, probably by heterogeneous hydrolysis. An approximate measure of the rate of reaction (9) was obtained from the rate of disappearance of hydrogen bromide, leading to an estimate of k_9 which was then refined by computer-aided numerical integration. The best computed fit to the most reliable experimental measurements, viz. the rates of reactions (6) and (8), gave $\log_{10} k_9/(\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) = (7.4 \pm 0.5) - (36 \pm 7 \text{ kJ mol}^{-1})/2.303 RT$.

The experiments with oxygen arose from our gas kinetic study of the thermal reaction between tetramethylsilane and oxygen.⁵ The mechanism of this reaction is complex, but the essential features of the oxidation of tetramethyl-



SCHEME 3.

silane are that kinetically it resembles the oxidation of methane, it is initiated by the thermal dissociation of tetramethylsilane, and the main silicon-containing products are cyclic dimethylsiloxanes, the precursor to which is dimethylsilanone,⁶ Me₂Si=O. Taking into account the distinctive chemistry of silicon, these features could be explained by the sequence in Scheme 3. However, the Me₃SiCH₂• radical is known² to dissociate to give a silaethene, which in the presence of oxygen might then react as in Scheme 4.



SCHEME 4.

The reactions in Scheme 4 would achieve the same ultimate result as reactions (12)–(14), and reaction (16) is plausible in view of the known instability of silaoxetans.⁷

A mixture of 1,1-dimethyl-1-silacyclobutane with oxygen in the ratio of 7:1 was pyrolysed between 733 and 793 K in the L.P.P. apparatus, at total initial pressures of 0.2 to 0.6 mmHg. The silicon-containing products, identified

mass spectrometrically, were all cyclic: Me₂SiCH₂SiMe₂CH₂, (Me₂SiO)₃, (Me₂SiO)₄, {[Me₂SiO]₂Me₂SiCH₂}₂, and {Me₂SiO-(Me₂SiCH₂)₂}. Formaldehyde and ethene were also formed. These findings are consistent with the occurrence of reactions (6), (16), and (8) with various cyclization reactions of Me₂Si=O and Me₂Si=CH₂ to give the other cyclic products. The rate constant k_{16} was estimated relative to $(k_8)^{1/2}$ in the conventional way, using the formation of formaldehyde

as a measure of the rate of reaction (16). Hence, $\log_{10} k_{16}/(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}) = (7.6 \pm 0.3) - (15 \pm 5 \text{ kJ mol}^{-1})/2.303 RT$.

The relative rates of formation of {Me₂SiO(Me₂SiCH₂)₂}, {(Me₂SiO)₂Me₂SiCH₂}, and (Me₂SiO)₃ varied from 0.2:0.5:1 at 736 K to 1.6:1.2:1 respectively at 793 K. Computer-aided numerical integration showed that this trend could be entirely accounted for by the temperature-dependence of reaction (6), indicating that the activation energies for all of these cyclization reactions are probably approximately equal and close to zero, like E_6 .

Our results are summarised in the Table, along with an example of the only previous kinetic work on addition reactions of silaethenes known to us, in which Gowenlock, John, and co-workers studied the kinetics of silaethene addition to olefins by conventional methods.⁸

TABLE. Arrhenius parameters for silaethene addition (relative to $k_8 = 3.55 \times 10^6 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$).

Reactants	$\log_{10} A$	$E/\text{kJ mol}^{-1}$	k (800 K)
Me ₂ Si=CH ₂ + HCl ^a	7.5 ± 0.5	10 ± 7	7.0 × 10 ⁶
Me ₂ Si=CH ₂ + O ₂ ^a	7.6 ± 0.3	15 ± 5	4.2 × 10 ⁶
Me ₂ Si=CH ₂ + HBr ^a	7.4 ± 0.5	36 ± 7	1.1 × 10 ⁶
Me ₂ Si=CH ₂ + C ₃ H ₆ ^b	5.2 ± 0.6	35 ± 4	8.2 × 10 ²

^a This work. ^b Ref. 8.

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