

## Preliminary communication

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### PRIMARY REACTIONS IN THE PYROLYSIS OF ALLYLTRIMETHYLSILANE

IAIN M.T. DAVIDSON\* and IAN T. WOOD

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

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#### Summary

The pyrolytic conversion of allyltrimethylsilane to vinyltrimethylsilane is rate determined by a bimolecular reaction; the main initial unimolecular step is silicon—allyl bond rupture.

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Whilst many reactions can occur in the pyrolysis of allylsilanes [1], the main products from pyrolysis of allyltrimethylsilane in flow systems at relatively high pressure are vinyltrimethylsilane, tetramethylsilane, and trimethylsilane [1,2]. It has recently been shown in an elegant labelling experiment [1] that the vinyltrimethylsilane is formed by loss of methyl attached to silicon in the original allyltrimethylsilane and not by extrusion of methylene from the allyl group, as previously proposed [2]. The suggested mechanism [1] consists of reaction 1 followed by rearrangement of the resulting allyldimethylsilyl radical.



Although the ensuing rearrangement sequence [1] is entirely reasonable, reaction 1 is improbable as it stands, since the weakest bond towards unimolecular homolysis in allyltrimethylsilane should be silicon—allyl and not silicon—methyl. A further complication, previously noted [1], is that under apparently similar conditions the retro “ene” reaction 2 has been reported [3].



The characteristic product of this reaction is 1,1,3,3-tetramethyl-1,3-disilacyclobutane, the dimer of the silaethene intermediate.

Thus, there are unresolved problems with this pyrolysis and we have sought to clarify the initial stages of the mechanism by applying our low pressure pyrolysis (LPP) technique, in which ca. 0.2 mmHg of allyltrimethylsilane is pyrolysed in a static system with analysis in situ by mass spectrometry. This

technique has been effective in establishing the nature and kinetics of the primary reactions in a number of complex pyrolyses in silicon chemistry [4]. Between 580 and 730°C the main products were almost equimolecular amounts of propene and trimethylsilane, accounting for at least 90% of the allyltrimethylsilane decomposed. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane and vinyltrimethylsilane were minor products. The main reaction was first order, with an Arrhenius *A* factor of  $10^{15.9 \pm 0.4} \text{ s}^{-1}$  and an activation energy of  $304 \pm 7 \text{ kJ mol}^{-1}$  (ca.  $73 \text{ kcal mol}^{-1}$ ).

These findings are consistent with the main primary process in the pyrolysis of allyltrimethylsilane being silicon-allyl bond rupture, followed by hydrogen abstraction. Under LPP conditions the hydrogen abstraction reactions occur



at the surface of the reaction vessel, a gas-phase chain reaction is not propagated, and the observed activation energy is that of reaction 3, i.e. it is the silicon-allyl bond dissociation energy,  $D[(\text{CH}_3)_3\text{Si}-\text{C}_3\text{H}_5]$  (cf.  $D[(\text{CH}_3)_3\text{Si}-\text{CH}_3]$  355 [5];  $D[\text{C}_2\text{H}_5-\text{CH}_3]$  355 [6];  $D[\text{C}_2\text{H}_5-\text{C}_3\text{H}_5]$  303 [6]  $\text{kJ mol}^{-1}$ ). In our LPP experiments the retro "ene" reaction 2 [3] also occurs to a small extent, but the route to vinyltrimethylsilane is of little importance, in sharp contrast to earlier work [1,2]. We have found that this difference arises because the course of the pyrolysis depends strongly on the pressure of allyltrimethylsilane; in a series of pyrolyses in sealed tubes ca. 550°C, increasing the initial pressure of allyltrimethylsilane increased the relative yield of vinyltrimethylsilane, until by 30 mmHg it was a major product.

We conclude that the rearrangement of allyltrimethylsilane to vinyltrimethylsilane is not rate-determined by a sequence of unimolecular reactions, as previously suggested [1,2]. The main primary unimolecular reaction in the pyrolysis is not silicon-methyl bond rupture [1] or methylene extrusion [2], but silicon-allyl bond rupture. At low pressure, as in our experiments, this leads simply to the formation of trimethylsilane and propene; but at higher pressures [1,2] radicals formed in this initial step must react bimolecularly with allyltrimethylsilane to initiate a sequence of reactions resulting instead in the formation of vinyltrimethylsilane and tetramethylsilane. Whilst the detailed mechanism is still speculative, we think it likely that the vital bimolecular step is addition of a trimethylsilyl radical to allyltrimethylsilane:



The radical resulting from reaction 4 could then undergo unimolecular rearrangement and elimination to form tetramethylsilane and the allyldimethylsilyl radical; the latter could then form vinyltrimethylsilane, as previously suggested [1]. This outline scheme is, of course, consistent with the results of the labelling experiments [1].

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## References

- 1 S.M. Neider, G.R. Chambers, and M. Jones, Jr., *Tetrahedron Letters*, (1979) 3796.
- 2 H. Sakurai, A. Hosomi, and M. Kumada, *J. Chem. Soc. Chem. Commun.*, (1970) 767.
- 3 W.J. Bailey and M.S. Kaufman, *Abstr. 157th. Amer. Chem. Soc. Meeting, Minneapolis, (1969), Org. 57.*
- 4 I.M.T. Davidson, N.A. Ostah, D. Seyferth, and D.P. Duncan, *J. Organometal. Chem.*, 187 (1980) 297;  
I.M.T. Davidson and M.A. Ring, *J. Chem. Soc. Faraday Trans. I*, 76 (1980) 1520.
- 5 A.C. Baldwin, I.M.T. Davidson, and M.D. Reed, *J. Chem. Soc. Faraday, Trans. I*, 74 (1978) 2171.
- 6 K.W. Egger and A.T. Cocks, *Helv. Chim. Acta*, 56 (1973) 1516.