

## Kinetics of the Pyrolysis of 1-Methyl-1-vinyl-1-silacyclobutane; Some Observations on the Stability of Vinyl Silyl Radicals and Silabutadienes

Iain M. T. Davidson,\* Andrew M. Fenton, Peter Jackson, and F. Timothy Lawrence

Department of Chemistry, The University, Leicester LE1 7RH, U.K.

Pyrolysis of the title compound to give ethene and a silabutadiene has the same Arrhenius parameters as pyrolysis of 1,1-dimethyl-1-silacyclobutane, whence the allylic stabilisation in a vinyl silyl radical is estimated to be  $\leq 29$  kJ mol<sup>-1</sup>; some comments are also made on the stability of silabutadienes.

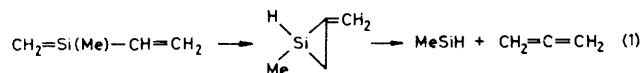
Recently there have been two independent studies on silabutadienes, CH<sub>2</sub>=Si(R)-CH=CH<sub>2</sub>, which extend our knowledge of currently interesting sila-alkene intermediates. From pyrolysis and electron-impact experiments on 1-methyl-1-vinyl-1-silacyclobutane (MVS) Auner and Grobe<sup>1</sup> inferred that it gave 2-methyl-2-silabuta-1,3-diene (MSB), which both dimerised and isomerised. Having detected allene as a product, they suggested that the isomerisation was to a siliran [reaction (1)]. Bertrand *et al.*<sup>2</sup> studied the decomposition of vinyl-silacyclobutanes in the gas phase and in solution in the presence of trapping agents. They concurred that MSB isomerises, but suggested that the isomerisation product in the gas phase was 1-methyl-1-silacyclobut-1-ene. They also concluded from their experimental results and from calculations that MSB has significant conjugative stabilisation.

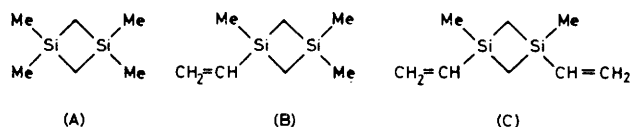
In the pyrolysis of cyclobutanes, considerable insight into the mechanism and into the stability of intermediates has been gained from gas kinetic studies. Thus, in vinylcyclobutane the ring would be expected to open adjacent to the vinyl group to form a biradical with allylic stabilisation, reducing the activation energy relative to cyclobutane by an amount equal to the

allylic stabilisation energy ( $53 \pm 4$  kJ mol<sup>-1</sup>), and reducing the *A* factor approximately ten-fold because of the loss of hindered rotation in the vinyl group.<sup>3</sup> Frey and Pottinger have shown that the kinetics of pyrolysis of vinylcyclobutane to give ethene and butadiene are entirely in accordance with these expectations and furthermore that there is a concurrent ring expansion to form cyclohexene, resulting from delocalisation of the initially formed biradical.<sup>4</sup>

Accordingly, we have studied MVS by low pressure pyrolysis (LPP)<sup>5</sup> to compare its kinetic behaviour with that of 1,1-dimethyl-1-silacyclobutane (DMS), which is well known<sup>6</sup> to decompose unimolecularly to ethene and Me<sub>2</sub>Si=CH<sub>2</sub> ( $\log_{10} A = 15.64$  and  $E/\text{kJ mol}^{-1} = 261.5$ , identical Arrhenius parameters to those for pyrolysis of cyclobutane<sup>7</sup>). Me<sub>2</sub>Si=CH<sub>2</sub> is a sila-alkene intermediate which dimerises head-to-tail to give 1,1,3,3-tetramethyl-1,3-disilacyclobutane; its  $\pi$ -bond energy is approximately<sup>8,9</sup>  $175 \pm 25$  kJ mol<sup>-1</sup>.

Kinetic measurements were made by co-pyrolysis of equimolar mixtures of MVS and DMS, to acquire relative rate data directly and to investigate the fate of intermediates. Between 761 and 900 K the first-order rate constants for the decomposition of MVS and DMS were identical within experimental error, in striking contrast to the cyclobutanes, where the vinyl substituent would<sup>4</sup> have increased the rate constant at 761 K by a factor of nearly 600.





LPP of MVS alone gave ethene and 1,3-dimethyl-1,3-divinyl-1,3-disilacyclobutane, as expected. Likewise, in the co-pyrolysis experiments all three expected disilacyclobutanes (A)—(C) were formed in the proportions of 1 : 0.54 : 0.04 (not 1 : 2 : 1, as might have been expected from the kinetic results). Mass spectrometric analysis gave no further unambiguous information on product formation, so MVS was also pyrolysed in a flow system between 758 and 884 K, with analysis by g.l.c.<sup>10</sup> Allene and its thermally produced isomer, propyne, were found in agreement with earlier work;<sup>1</sup> the activation energy for formation of these products was higher than that for formation of ethene by  $35 \pm 6$  kJ mol<sup>-1</sup>. Allene and propyne amounted to 3% of the ethene produced at 758 K, increasing to 6.5% at 884 K.

It has generally been assumed in the pyrolysis of DMS that the ring is opened by carbon-carbon bond rupture;<sup>6,8</sup> there is now little doubt that this is so, as the silicon-carbon bond has recently been estimated<sup>9</sup> to be up to 32 kJ mol<sup>-1</sup> stronger than the carbon-carbon bond in the silacyclobutane ring. Since pyrolysis of MVS had identical Arrhenius parameters, it too must proceed by carbon-carbon bond rupture. Hence, an upper limit can be placed on the 'allylic' stabilisation in the vinyl silyl radical,  $\dot{\text{S}}\text{i}-\text{CH}=\text{CH}_2$ ; if such stabilisation occurs, the *A* factor would be reduced to  $10^{14.9}$  s<sup>-1</sup>, for the same reason as in vinylcyclobutane;<sup>3,4</sup> if the rate constant for silicon-carbon bond breaking is assumed to be no more than 10% of that observed for carbon-carbon rupture, a lower limit of 265 kJ mol<sup>-1</sup> may be calculated for the activation energy of the former process. This is 3 kJ mol<sup>-1</sup> higher than the observed activation energy for breaking a bond which is 32 kJ mol<sup>-1</sup> weaker than the unstabilised silicon-carbon bond, so the maximum possible 'allylic' stabilisation in  $\dot{\text{S}}\text{i}-\text{CH}=\text{CH}_2$  is 29 kJ mol<sup>-1</sup>. From bond-dissociation energy measurements in

phenylsilane, Walsh<sup>9</sup> has estimated the 'benzylic' stabilisation in  $\text{Ph}\dot{\text{S}}\text{iH}_2$  to be no more than 8 kJ mol<sup>-1</sup>.

It is obvious from the relative yields of the disilacyclobutanes in the co-pyrolysis experiments that there are major alternative reactions of MSB besides formation of disilacyclobutanes. The production of allene and propyne supports the isomerisation of MSB previously suggested,<sup>1</sup> but the involvement of the alternative silacyclobutene isomer<sup>2</sup> cannot be ruled out. In any case, isomerisation seems to be a relatively minor reaction judging by the small yields of the C<sub>3</sub>H<sub>4</sub> products relative to ethene, and our results may confirm that MSB is conjugatively stabilised<sup>2</sup> to an extent which reduces its tendency to combine with other sila-alkenes enough for much of it to diffuse out of the gas phase in LPP experiments.

We thank Professor J. Grobe and Dr N. Auner of Westfälische Wilhelms-Universität for a generous gift of MVS, and the S.E.R.C. for support.

Received, 20th April 1982; Com. 437

## References

- 1 N. Auner and J. Grobe, *J. Organomet. Chem.*, 1980, **197**, 13.
- 2 G. Bertrand, G. Manuel, P. Mazerolles, and G. Trinquier, *Tetrahedron*, 1981, **37**, 2875.
- 3 H. M. Frey and R. Walsh, *Chem. Rev.*, 1969, **69**, 103; S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 2nd Edn. 1976, p. 125.
- 4 H. M. Frey and R. Pottinger, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 1827.
- 5 I. M. T. Davidson and M. A. Ring, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1520.
- 6 M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 1968, 419.
- 7 R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, 1963, **67**, 1370.
- 8 I. M. T. Davidson, P. Potzinger, and B. Reimann, *Ber. Bunsenges. Phys. Chem.*, 1982, **86**, 13.
- 9 R. Walsh, *Acc. Chem. Res.*, 1981, **14**, 246.
- 10 A. C. Baldwin, I. M. T. Davidson, and A. V. Howard, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 972.