Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

FACTORS INFLUENCING THE FORMATION OF SILYLENES IN THE PYROLYSIS OF SILICON COMPOUNDS

IAIN M. T. DAVIDSON
Department of Chemistry, The University, Leicester LE1 7RH (Great Britain)

(Received April 3rd, 1970)

SUMMARY

Pyrolysis of silicon compounds may yield silyl radicals or silylenes. The thermodynamic and kinetic features of these two modes of decomposition are discussed and the importance of kinetic factors in determining whether any particular silicon compound gives silyl radicals or silylenes on pyrolysis is established. Some pyrolyses which have not yet been fully investigated are discussed in the light of the generalizations which have been developed.

INTRODUCTION

Silicon compounds may dissociate on pyrolysis into silyl radicals [reaction (d)], the reverse reaction (−d) being combination of two monoradicals; or they may eliminate a silylene [reaction (e)], the reverse reaction (−e) being insertion of the silylene into a bond in the molecule formed along with the silylene in reaction (e). Thus, for disilanes:

$$Si_2R_6 \rightleftharpoons 2\,{}^{\bullet}SiR_3 \qquad \text{(d)} \quad (-\text{d})$$

$$Si_2R_6 \rightleftharpoons SiR_2 + SiR_4 \qquad \text{(e)} \quad (-\text{e})$$

As Jackson has pointed out[1], a very fine balance appears to exist between the two modes of decomposition; for example, hexamethyldisilane[2] follows route (d), while 1,2-dimethoxytetramethyldisilane[3,4] follows route (e).

In this paper a simple explanation is proposed of the factors determining whether silyl radicals or silylenes are to be formed pyrolytically.

DISCUSSION

For disilanes, the enthalpy changes (ΔH), activation energies (E), and bond dissociation energies (D) for reactions (d) and (e) are related thus:

$$E_{(d)} = \Delta H_{(d)} + E_{(-d)}$$

$$E_{(e)} = \Delta H_{(e)} + E_{(-e)}$$

$$\Delta H_{(e)} = D(R_3Si\text{–}SiR_3) + D(R_2Si\text{–}R) - D(R_3Si\text{–}R)$$

hence

$$\Delta H_{(e)} = \Delta H_{(d)} - [D(R_3Si\text{–}R) - D(R_2Si\text{–}R)]$$

Irrespective of the nature of R, $D(R_2Si{-}R)$ is likely to be less than $D(R_3Si{-}R)$ because of the relative stability of silylenes[3], and hence $\Delta H_{(d)} > \Delta H_{(e)}$, *i.e.* elimination of silylene will be the thermodynamically favoured process. Also, since recombination of monoradicals requires little or no activation energy, $E_{(-d)}$ is approximately equal to zero. Consequently, the expressions for the activation energies of the two decomposition routes become:

$$E_{(d)} > \Delta H_{(e)}$$

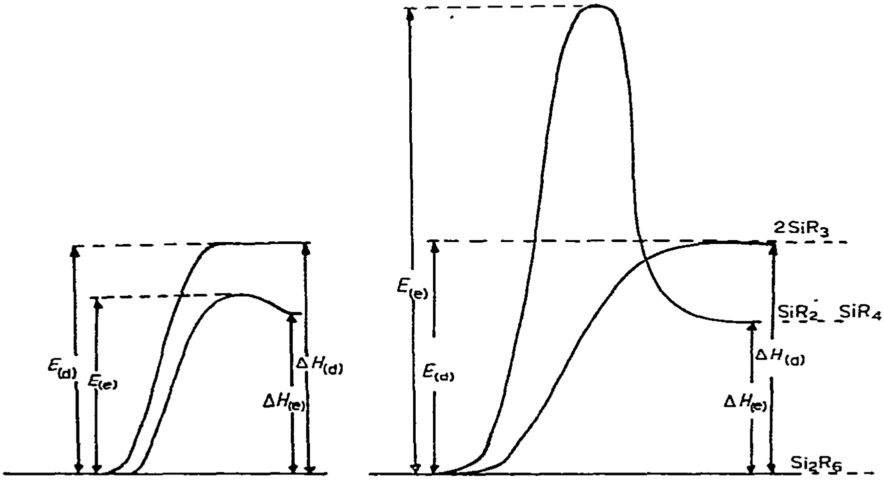
and

$$E_{(e)} = \Delta H_{(e)} + E_{(-e)}$$

Thus, the value of the activation energy, $E_{(-e)}$, for the silylene insertion reaction, (−e), will determine whether $E_{(e)}$ is less than or greater than $E_{(d)}$, and hence whether silyl radicals or silylenes are to be formed in the pyrolysis of any disilane. This point is illustrated by Fig. 1, which contains two energy diagrams:

(*a*) When $E_{(e)}$ is sufficiently small, $E_{(e)} < E_{(d)}$ and the primary decomposition route will be elimination of a silylene.

(*b*) When $E_{(-e)}$ is large, $E_{(d)} < E_{(e)}$ and the primary decomposition route will be dissociation into silyl radicals.



(a) $E_{(d)} > E_{(e)}$ (b) $E_{(d)} < E_{(e)}$

Fig. 1. Energy diagrams showing enthalpy changes (ΔH) and activation energies (E) for dissociation into silyl radicals (d) and elimination of a silylene (e).

Fortunately, a clear distinction can be made in practice between categories (*a*) and (*b*). Silylenes are known[3] to insert rapidly, with little temperature-dependence, into silicon–hydrogen, silicon–halogen, silicon–oxygen, and silicon–nitrogen bonds. Hence, if the disilane would give a monosilane in reaction (e) containing one of these bonds, $E_{(-e)}$ would be small or zero and the disilane would belong to category (*a*), giving silylene on pyrolysis. On the other hand, silylene insertion into silicon–carbon, carbon–hydrogen, and carbon–carbon bonds has not been observed even at high temperatures[3,5] so that $E_{(-e)}$ for silylene insertion into a silane containing these bonds would be high. Consequently, disilanes containing only alkyl or aryl groups belong to category (*b*), giving silyl radicals on pyrolysis.

The validity of the above generalization is shown by the following examples.

Category (*a*):

$Si_2H_6 \rightleftharpoons SiH_2 + SiH_4$ (ref. 5,6)

$Si_2X_6 \rightleftharpoons SiX_2 + SiX_4$ (X is halogen) (ref. 3)

$(MeO)Me_2SiSiMe_2(OMe) \rightleftharpoons SiMe_2 + (MeO)_2SiMe_2$ (ref. 3,4)

In the last example insertion of dimethylsilylene into a methoxymonosilane was found to be slower than into a methoxypolysilane[4], implying that the former insertion requires a somewhat higher activation energy than the latter.

The fact that decomposition route (e) is followed by the above disilanes in category (*a*) confirms the assumption that $\Delta H_{(e)} < \Delta H_{(d)}$, *i.e.* that silylene formation is thermodynamically favourable, in keeping with the expected trend down Group IVB of the Periodic Table[1].

Category (*b*):

$Si_2Me_6 \not\rightleftharpoons SiMe_2 + SiMe_4$ (ref. 2)

$Si_2Me_6 \rightleftharpoons 2\ {}^{\bullet}SiMe_3$

Similar considerations apply to the pyrolysis of monosilanes, where reactions (d) and (e) are:

$SiR_4 \rightleftharpoons {}^{\bullet}SiR_3 + R^{\bullet}$ (d) (−d)

$SiR_4 \rightleftharpoons SiR_2 + R_2$ (e) (−e)

and

$$\Delta H_{(e)} = \Delta H_{(d)} - [D(R\text{–}R) - D(R_2Si\text{–}R)]$$

The activation energy for silylene insertion, $E_{(-e)}$, will again be an important factor, as it was for disilanes, but in addition a high value of D(R–R) relative to $D(R_2Si\text{–}R)$ will be necessary in order to make silylene formation thermodynamically feasible. For example, although silylene formation in the pyrolysis of trimethylsilane would be thermodynamically favourable, trimethylsilane resembles a disilane in category (*b*) above, and forms silyl radicals on pyrolysis[7]:

$Me_3SiH \not\rightleftharpoons SiMe_2 + CH_4$

$Me_3SiH \not\rightleftharpoons HSiMe + C_2H_6$

$Me_3SiH \rightleftharpoons {}^{\bullet}SiMe_3 + H^{\bullet}$

$Me_3SiH \rightleftharpoons {}^{\bullet}SiMe_2H + Me^{\bullet}$

Tetrahalosilanes, unlike trimethylsilane, would have low values of $E_{(-e)}$, because silylenes insert readily into halogen–halogen bonds[3]. However, they give only poor yields of halosilylenes even at high temperature because $\Delta H_{(e)}$ is high as a result of the low value of D(X–X). This thermodynamic obstacle to the formation of halosilylenes from tetrahalosilanes may be overcome in practice by pyrolysing the halosilanes in the presence of silicon[3], which is a less endothermic reaction:

$SiX_4 + Si \rightleftharpoons 2\ SiX_2$

Silane satisfies the thermodynamic requirement for silylene formation, D(H–H) being high, and is believed to give silylene on pyrolysis[8]:

$$SiH_4 \rightleftharpoons SiH_2 + H_2$$

If silylene is indeed formed, the activation energy for silylene insertion into the hydrogen–hydrogen bond, $E_{(-e)}$, must be low. If so, methylsilane might give methylsilylene (but not silylene itself) on pyrolysis:

$$CH_3SiH_3 \rightleftharpoons CH_3SiH + H_2$$

$$CH_3SiH_3 \not\rightleftharpoons SiH_2 + CH_4$$

A recent investigation of the pyrolysis of methylsilane[9] gave products consistent with both of these predictions, as did experiments under substantially different conditions in our laboratory[10]. The latter experiments also provided evidence, both analytical and kinetic, for the occurrence of reaction (d):

$$CH_3SiH_3 \rightleftharpoons CH_3^{\bullet} + {}^{\bullet}SiH_3$$

which indicates that there may be little difference between the activation energies $E_{(d)}$ and $E_{(e)}$ in this particular case. Work is proceeding on the pyrolysis of methylsilane with a view to resolving this question, and on the pyrolysis of other simple silanes to test further the generalizations expounded here.

Finally, it is important to remember that these generalizations apply only to the *pyrolytic* generation of radicals and that silicon compounds which would not give silylenes on pyrolysis may nevertheless do so by other means if sufficient energy is provided. An excellent example illustrating this point is the formation of high yields of the silylenes SiH_2 and CH_3SiH from methylsilane by direct photolysis in the far ultraviolet[11].

ACKNOWLEDGEMENT

Valuable discussions with Professor J. H. Purnell and access to his results before publication are gratefully acknowledged.

REFERENCES

1 R. A. Jackson, *Advan. Free Radical Chem.*, 3 (1969) 231.
2 I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc. A*, (1968) 282.
3 W. H. Atwell and D. R. Weyenberg, *Angew. Chem. Int. Ed. Engl.*, 8 (1969) 469, and references therein.
4 W. H. Atwell, L. G. Mahone, S. F. Hayes and J. H. Uhlmann, *J. Organometal. Chem.*, 18 (1969) 69.
5 M. Bowrey, Ph.D. Thesis, University of Wales, 1969; M. Bowrey and J. H. Purnell, unpublished results.
6 E. M. Tebben and M. A. Ring, *Inorg. Chem.*, 8 (1969) 1787.
7 I. M. T. Davidson and C. A. Lambert, *Chem. Commun.*, (1969) 1276.
8 J. H. Purnell and R. Walsh, *Proc. Roy. Soc. A.*, 293 (1966) 543.
9 J. J. Kohanek, P. Estacio and M. A. Ring, *Inorg. Chem.*, 8 (1969) 2516.
10 K. A. Betesta, I. M. T. Davidson, A. G. Procter, D. G. Smith, I. L. Stephenson, J. F. Thompson and R. Wyvill, unpublished results.
11 K. Obi, A. Clement, H. E. Gunning and O. P. Strausz, *J. Amer. Chem. Soc.*, 91 (1969) 1622.