

Kinetics of the Thermal Decomposition of Polyfluoroalkylsilicon Compounds

By G. FISHWICK, R. N. HASZELDINE, C. PARKINSON, P. J. ROBINSON, and R. F. SIMMONS

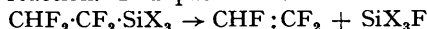
(Chemistry Department, Faculty of Technology, University of Manchester)

STUDY of the kinetics of the pyrolysis of fluoro-alkylsilicon compounds in which fluorine is present

on α -, β -, or γ -carbon relative to silicon has confirmed the two distinct types of mechanism

proposed earlier for the α -¹ and β -^{2,3} substituted compounds, and revealed a third type for γ -substituted compounds. The kinetic data, summarised in the Table, refer to the gas-phase (unless otherwise stated) decompositions of

order reaction. In unpacked vessels the reaction is:



However, the decomposition does not involve β -fluorine elimination. In the presence of equimolar quantities of a hydrocarbon olefin (*e.g.*,

Table

Kinetic Parameters for the Decomposition of Polyfluoroalkylsilicon Compounds

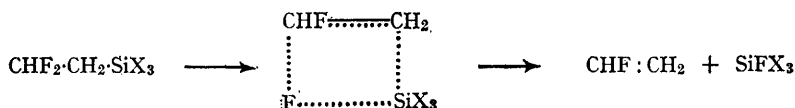
Compound	Temp. (°C)	Order	log ₁₀ A*	E*
CHF ₂ ·CH ₂ ·SiF ₃	150—220	1	12.3	32.7
CHF ₂ ·CH ₂ ·SiMeF ₂	190—240	1	13	36
CHF ₂ ·CH ₂ ·Si(OBu ⁿ) ₃ †	230—270	1	8.5	30.2
CHF ₂ ·CF ₂ ·SiF ₃	130—210	1	11.1	28.7
CHF ₂ ·CF ₂ ·SiMe ₃	310—370	1	13.6	46.9
CF ₃ ·CH ₂ ·CH ₂ ·SiF ₃	550—640	1.5	17.8	74

* Units: A, sec.⁻¹ or ml.¹ mole⁻¹ sec.⁻¹; E, kcal. mole⁻¹.

† In solution in MS 550 silicone oil.

compounds of the type CHF₂·CH₂·SiX₃, CHF₂·CF₂·SiX₃, and CF₃·CH₂·CH₂·SiX₃.

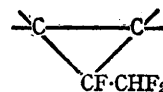
2,2-Difluoroethyl Compounds:—The kinetic study reported³ for the gas-phase decomposition of 2,2-difluoroethyltrifluorosilane into vinyl fluoride and silicon tetrafluoride, has been followed by study of the decompositions of the compounds CHF₂·CH₂·SiMeF₂ (gas-phase) and CHF₂·CH₂·Si(OBuⁿ)₃ (in solution). The decompositions, which take place at fairly low temperatures, are first-order and unaffected by the surface:volume ratio of the reaction vessel or the addition of olefins, so it is concluded that they involve unimolecular transfer of β -fluorine to silicon by a four-centre transition-state:



The successful measurement of the kinetics of decomposition of 2,2-difluoroethyltributoxysilane in solution at temperatures near 250° is noteworthy.

1,1,2,2-Tetrafluoroethyl Compounds:—The compounds CHF₂·CF₂·SiF₃ and CHF₂·CF₂·SiMe₃ also decompose at fairly low temperatures by a first-

propene, but-2-ene), the yield of trifluoroethylene is markedly reduced and can approach zero under certain conditions. Correspondingly a cyclopropane of type (I)



is formed in yields approaching 100%. Despite these apparent complications the silicon compound CHF₂·CF₂·SiX₃ always decomposes at the same rate, which is first-order in reactant concentration and independent of the surface:volume

ratio of the reaction vessel or the presence of an olefin.

A two-step mechanism involving a reactive intermediate formed by homogeneous unimolecular decompositions of a reactant molecule must thus be involved, and α -elimination *via* a three-centre transition state to give a carbene*

* The term "carbene" is not intended here to imply any particular electronic structure of the species.

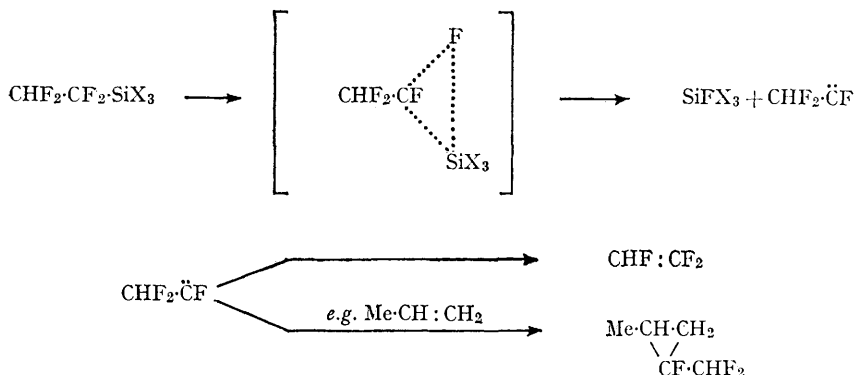
¹ R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 1959, 394; W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. and Ind.*, 1961, 789.

² R. N. Haszeldine, M. J. Newlands, and J. B. Plumb, *Proc. Chem. Soc.*, 1960, 147; T. N. Bell, R. N. Haszeldine, M. J. Newlands, and J. B. Plumb, *J. Chem. Soc.*, 1965, 2107.

³ R. N. Haszeldine, P. J. Robinson, and R. F. Simmons, *J. Chem. Soc.*, 1964, 1890.

$\text{CHF}_2\ddot{\text{C}}\text{F}$ satisfactorily explains all these observations:

mixture of products including SiF_4 , C_2H_4 , CHF_3 , $\text{CF}_3\text{CH}:\text{CH}_2$, $\text{CH}_2:\text{CH}\cdot\text{SiF}_3$, $\text{CH}_3\cdot\text{SiF}_3$, and H_2 .



Replacement of fluorine on silicon by methyl causes a very marked decrease in the rate of decomposition, and this is attributed to the electron-release by methyl to silicon which makes the silicon less electropositive, and less receptive to attack by fluorine. This demonstrates clearly that the thermal stability of organosilicon compounds can be markedly dependent upon the substituents on silicon as well as in the organic group.

3,3,3-Trifluoropropyl Compounds:—The compound $\text{CF}_3\text{CH}_2\text{CH}_2\text{SiF}_3$ decomposes only at temperatures above 550°C , and gives a complex

The reaction has an overall order of about 1.5 and is sensitive to surface conditions and to the presence of nitric oxide and hydrocarbon olefins. The pattern of the formation of the various products is not simple and indicates the early onset of secondary reactions. It is clear from these observations that the decomposition proceeds by a complex radical-chain mechanism, involving homolytic fission of C-C and C-Si bonds, in contrast to the simple mechanisms of decomposition of the α - and β -fluoroalkylsilicon compounds.

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