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

PRELIMINARY COMMUNICATION

COMPARISON OF THE REACTIVITY OF TETRAMETHYLSILANE AND NEOPENTANE TOWARDS FREE RADICAL ATTACK

E.R. MORRIS and J.C.J. THYNNE

Chemistry Department, Edinburgh University, Edinburgh (Great Britain)

(Received March 14th, 1969)

Recently, Chaudhry and Gowenlock[1] have measured the Arrhenius parameters for the reaction of methyl radicals with a series of Group IV tetramethyls and concluded that the central atom affected the reactivity of the C–H bonds towards methyl radical attack.

We have studied the abstraction of hydrogen atoms from tetramethylsilane by methyl and trifluoromethyl radicals; comparison of our data with the analogous reactions for neopentane should yield information regarding (1) the effect of substitution of the central carbon atom by silicon upon the Arrhenius parameters for the reactions:

$$CH_3 + (CH_3)_4X \rightarrow CH_4 + (CH_3)_3XCH_2$$

$$CF_3 + (CH_3)_4X \rightarrow CF_3H + (CH_3)_3XCH_2$$

and (2) the effect of the polar radical upon the C–H bond reactivity in these compounds.

Below we summarise the Arrhenius parameters and velocity constants at 164° (where 2.303 RT is 2000) for the neopentane and tetramethylsilane systems.

Reaction	Log A ($mole^{-1} \cdot cm^3 \cdot sec^{-1}$)	E ($kcal \cdot mole^{-1}$)	log k (164°) ($mole^{-1} \cdot cm^3 \cdot sec^{-1}$)	ref.
CH_3+$(CH_3)_4Si$	11.5 ± 0.2	10.3 ± 0.4	6.35	this work
CH_3+$(CH_3)_4C$	11.3	10.0	6.3	2
CF_3+$(CH_3)_4Si$	12.0 ± 0.1	7.6 ± 0.2	8.2	this work
CF_3+$(CH_3)_4C$	11.8	7.6	8.0	3

It is apparent that, for attack by the same radical, the Arrhenius parameters and velocity constants are identical, within experimental error, for neopentane and tetramethylsilane. We therefore conclude that substitution of the central carbon atom by silicon has little effect upon the reactivity of the adjacent C–H bonds.

Comparison of the abstraction reactions of the methyl and trifluoromethyl radicals with the same substrate shows that the effect of the polar radical is to markedly increase the velocity constant, there being a pronounced lowering ($\sim$ 2.5 $kcal \cdot mole^{-1}$) of the activation energy requirements in both cases; this is in accord with results reported previously for hydrocarbon systems by Pritchard[4].

REFERENCES

1 A.V. Chaudhry and B.G. Gowenlock, *J. Organometal. Chem*, 16 (1969) 221.
2 A.F. Trotman-Dickenson, J.R. Birchard and E.W.R. Steacie, *J. Chem. Phys.*, 19 (1951) 163.
3 G.O. Pritchard, H.O. Pritchard, H.I. Schiff and A.F. Trotman-Dickenson, *Trans. Faraday Soc.*, 52 (1956) 849.
4 G.O. Pritchard, G.H. Miller and J.K. Foote, *Canad. J. Chem.*, 40 (1962) 1830.