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ARRHENIUS PARAMETERS FOR THE REACTIONS OF METHYL RADICALS WITH GROUP IV TETRAMETHYLS*

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SUMMARY

Arrhenius parameters for the reaction of methyl radicals with $(CH_3)_4M$ (M = Si, Ge, Sn, Pb) have been measured. A direct correlation of the activation energy and velocity constant with $J(^{13}C\text{–}H)$ is proposed. It is shown that there is no correlation between the activation energy or velocity constant and any of the electronegativity values for Group IV elements. It is shown that hydrogen abstraction reactions of various organosilanes also exhibit a coupling constant–velocity constant correlation.

INTRODUCTION

This study was commenced with the aim of obtaining information on two different, but related, topics. The hydrogen abstraction reactions (1) of methyl radicals have been studied for many years and a considerable body of data has accumulated[1] for the Arrhenius parameters of (1) where RH represents hydrocarbons and oxygenated compounds. Gray and Thynne and their collaborators[2,3] have extended such

$$\cdot CH_3 + HR \rightarrow CH_4 + R\cdot \qquad (1)$$

studies to nitrogen containing compounds and have used deuterium labelling to determine the point of attack. It is apparent that there is little accurate information for reaction (1) where RH represents a molecule containing metal or metalloid atoms. We commenced this study to obtain such information. The choice of Group IV tetramethyls was made in order to further comparisons of gas phase reactivity of molecules containing these elements upon which one of us[4] had already initiated studies. Our second, related, aim was to find out whether there was any influence of the electronegativity of M upon the Arrhenius parameters of reaction (2). It was

$$\cdot CH_3 + CH_3M(CH_3)_3 \rightarrow CH_4 + \cdot CH_2M(CH_3)_3 \qquad (2)$$

hoped that some correlation would emerge relating the activation energy with one set of the several, disputed, electronegativity scales for the Group IV elements[5-8].

After this work was begun, we were informed of the related studies of Kerr *et al.*[9,10] for organochlorosilanes. Our data are complementary to those studies and the results will be discussed together.

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EXPERIMENTAL

Materials

Tetramethylsilane was a highly purified sample as used for internal standardisation of NMR spectra. Tetramethylgermane was prepared by the reaction of germanium tetrachloride and methylmagnesium bromide in di-n-butyl ether solution[11]. Tetramethyltin was prepared by the reaction of stannic chloride and methylmagnesium iodide in di-n-butyl ether solution[12]. Tetramethyllead was prepared by the reaction of lead chloride and methylmagnesium iodide in diethyl ether. After distilling off the ether and more volatile products of 70°, the tetramethyllead was then obtained by repeated high vacuum distillation of the residue from $-78°$ to $-196°$. Azomethane was prepared from 1,2-dimethylhydrazine dihydrochloride and cupric chloride in aqueous sodium acetate followed by decompositon of the dried cuprous chloride–azomethane complex at 120–140° under vacuum[13].

All materials were intensively degassed and stored in blackened storage bulbs fitted with a finger which was immersed in liquid nitrogen. The purities of all materials were checked by gas chromatography and in some cases by mass spectroscopy. No impurities were observed.

Apparatus and procedure

Photolyses were carried out in a cylindrical pyrex vessel (98 ml) heated in an electrical furnace controlled to better than $\pm 1°$ during a run. The light source was a tungsten filament 60W car headlight bulb operated on a 12 V a.c. supply. A heat absorbing glass was used to prevent any rise in temperature of the reaction vessel due to incident radiant heat. Where necessary (tetramethyltin) a sheet of sodaglass was inserted between the light source and the reaction vessel to prevent direct photolysis of the organometallic compound. Reactant pressures were measured by a null technique using a glass spiral gauge, with the pointer immersed in silicone oil. Greaseless taps were used throughout the reaction and analytical systems.

Analysis of the nitrogen, methane and ethane products was carried out by gas chromatography. The permanent gases were toeplered from traps cooled by isopentane slush baths, the total quantity measured in a Toepler-gas burette and the gases were then toeplered into a narrow vertical tube fitted with a detachable cup[14]. The mercury plug was frozen on pouring liquid nitrogen into the cup, the tube rapidly sealed off to an appropriate length, and the resultant tube inserted into a crusher device placed in the inlet system of a gas chromatography apparatus. The gas mixture was analysed by temperature programmed gas solid chromatography (F and M 720) using a molecular sieve 5A column length 4 feet, programmed at 4°/min and standardised flow conditions of the helium carrier gas. The method is essentially similar to that given by Burchfield and Storrs[15]. The apparatus was first calibrated for nitrogen, methane and ethane. The calibration graphs of peak areas against micromoles of gas were accurately linear in each case.

RESULTS AND DISCUSSION

The photolysis of azomethane alone

Detailed kinetic information for this photolysis was not sought because recent results from a variety of laboratories[2,3,9,16] have established the kinetic parameters

$$\cdot CH_3 + CH_3N_2CH_3 \rightarrow CH_4 + \cdot CH_2N_2CH_3 \qquad (3)$$

for reaction (3) to a high degree of accuracy. We have therefore used the values[2] $\log_{10}A_3$ (ml·mole^{-1}·sec^{-1}) = 10.93 ± 0.11, E_3 (kcal·mole^{-1}) = 7.84 ± 0.19. We have also used the value[17] $\log_{10}k_4$ (ml·mole^{-1}·sec^{-1}) = 13.34 as used by Gray and Thynne[2] and others.

$$\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6 \qquad (4)$$

The photolysis of azomethane in the presence of tetramethyl compounds

Values of k_2 are determined from the rates of formation of methane and ethane established experimentally and the values of k_3 and k_4 as given previously. From reactions (2), (3) and (4) we obtain the following relation for rates of methane and ethane production in the steady state

$$R_{CH_4(2)} = R_{CH_4(\text{total})} - R_{CH_4(3)}$$

$$\frac{R_{CH_4(2)}}{R^{\frac{1}{2}}_{C_2H_6} \cdot [Me_4M]} = \frac{k_2}{k_4^{\frac{1}{2}}}$$

The Arrhenius parameters are summarised in Table 1. The error limits quoted are based on the 95% confidence limits[18] carried out on a computer.

TABLE 1

Compound	$\log_{10}A_2$ (ml·mole^{-1}·sec^{-1})	E_2 (kcal·mole^{-1})	$\log_{10}k_2$[a] (ml·mole^{-1}·sec^{-1})
$(CH_3)_4Si$	12.6 ± 0.19	11.0 ± 0.34	6.83
$(CH_3)_4Ge$	11.8 ± 0.21	9.6 ± 0.39	6.68
$(CH_3)_4Sn$	11.1 ± 0.13	8.6 ± 0.24	6.50
$(CH_3)_4Pb$	10.2 ± 0.48	7.4 ± 0.88	6.25

[a] The temperature chosen is 140° which is the median temperature for the experiments.

The values for tetramethylsilane may be compared with the corresponding values for the methylchlorosilanes[9,10]. The activation energies are within 0.6 kcal·mole^{-1} but the A factor is lower for tetramethylsilane by a factor varying from 2 (compared with $MeSiCl_3$) to 8 (compared with Me_3SiCl). If the A factor per methyl group (A') is compared we obtain the following values for $\log_{10}A'_2$ (ml·mole^{-1}·sec^{-1}): $(CH_3)_4Si$ 12.0, $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$, CH_3SiCl_3 12.9. Kerr *et al.* suggested that a reason for the relatively high values of the A factors lay in the contribution of ionic states to the transition states. It is tempting to suggest that the absence of the polar Si–Cl bonds leads to a lowering of such ionic contributions and hence to a smaller A factor.

It is immediately evident that the Arrhenius parameters and/or the median value of the velocity constant display no regular relationship to the electronegativity of the central atom in the molecules $(CH_3)_4M$. In particular the alternation implicit in the Allred and Rochow electronegativity values is not reflected in the kinetic data.

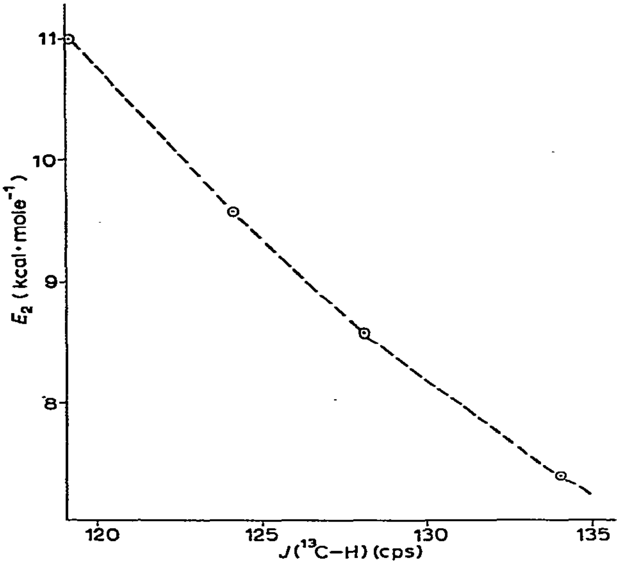

Fig. 1. Relation between E_2 (kcal·mole^{-1}) and $J(^{13}C\text{–}H)$ (Hz).

On the other hand, the constancy of the revised[5] Pauling values is also not reflected in the data. It is, however, apparent that the central atom affects the reactivity of the C–H bond towards methyl radicals. This suggests small but definite changes in the character of the C–H bonds in Group IV tetramethyls. This led us at once to Drago's interpretation[7,8] of hybridisation changes in these molecules. It was then immediately apparent that there was a direct correlation between the activation energy E_2 (or k_2) and the $^{13}C\text{–}H$ coupling constants, $J(^{13}C\text{–}H)$ for the Group IV

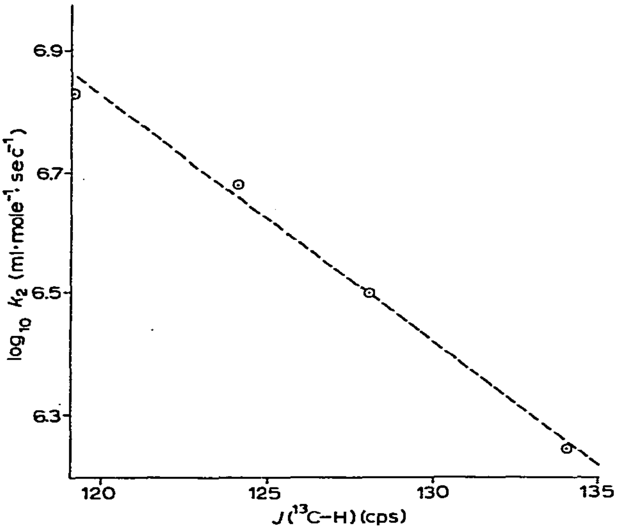

Fig. 2. Relation between $\log_{10}k_2$ (ml·mole^{-1}·sec^{-1}) and $J(^{13}C\text{–}H)$(Hz).

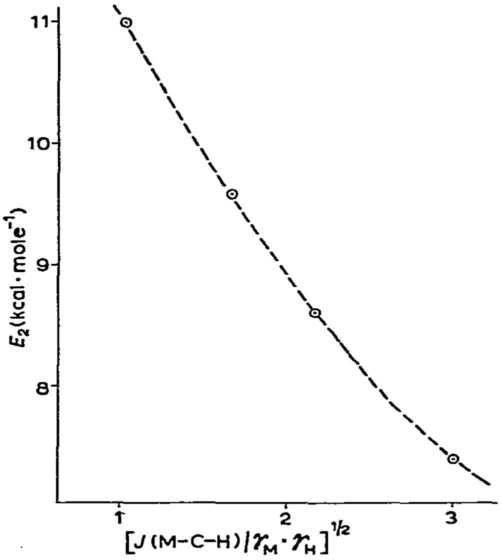

Fig. 3. Relation between E_2 (kcal·mole^{-1}) and reduced coupling constants $[J(\text{M–C–H})/\gamma_M \cdot \gamma_H]^{\frac{1}{2}}$.

tetramethyls (see Figs. 1 and 2). This implies that change in the fraction of *s* character employed by carbon in its bonds to hydrogen is reflected in the energy of activation (and free energy of activation) for a reaction where the bonds broken and formed are of similar polarity. It has been suggested[19] to us that the reduced coupling constants of Reeves[20] $[J(\text{M–C–H})/\gamma_M \cdot \gamma_H]^{\frac{1}{2}}$ should also show a regular variation with the activation energy, E_2 and Fig. 3 shows that this is the case.

Correlations between coupling constants and reactivities have been made for a variety of reactions by Dixon[21] and for chlorination reactions by Mack[22]. A further correlation between CH reactivities to trifluoromethyl radicals and the deshielding of the respective methyl protons in the methylchlorosilanes has been observed by Cheng and Szwarc[23]. In this connection it is relevant to note that similar correlations emerge between SiH reactivities[9,10] for reaction (5) and both the chemical shift of the protons and $J(^{29}\text{Si–H})$ (See Table 2).

$$\cdot\text{CH}_3 + \text{HSiR}_2\text{R}' \rightarrow \text{CH}_4 + \cdot\text{SiR}_2\text{R}' \qquad (5)$$

It is recognised[31] that the factors determining SiH chemical shifts are still ill defined but the smooth trend of these values against $\log_{10}k_5$ is of interest and by

TABLE 2

R	R′	E_5 (kcal·mole^{-1})	$\log_{10}k_5{}^a$ (ml·mole^{-1}·sec^{-1})	$J(^{29}\text{Si–H})$ (Hz)	τ(SiH)
CH_3	CH_3	7.0^{10}	6.92^{10}	184^{24}, 190^{25}	6.01^{29}
Cl	CH_3	7.2^{9}	7.55^{9}	279.5^{26}, 281.1^{27}	4.48^{29}
Cl	Cl	8.5^{9}	8.38^{9}	362.9^{28}	3.93^{30}
F	F	8.7^{10}	7.21^{10}	381.7^{28}	5.47^{30}

[a] The temperature chosen is 370°K which is the median temperature for the data.

analogy with the arguments of Cheng and Szwarc may reflect a correlation between changes in polarity of Si–H and the ease of removal of the hydrogen by the attacking radical.

Correlations between structure and reactivity are desirable but often of limited theoretical significance and it is recognised that such correlations may be fortuitous. A survey of the literature indicates that it is necessary to have a wider range of both kinetic and NMR data for such relationships to be established for other organic and organometallic compounds.

REFERENCES

1 A. F. TROTMAN-DICKENSON, *Advances in Free Radical Chemistry*, Vol. 1, Logos Press, London, 1965, p. 1.
2 P. GRAY AND J. C. J. THYNNE, *Trans. Faraday Soc.*, 59 (1963) 1149.
3 J. C. J. THYNNE, *Trans. Faraday Soc.*, 58 (1962) 1533.
4 B. G. GOWENLOCK AND K. E. THOMAS, *J. Chem. Soc.*, (1965) 5068.
5 H. O. PRITCHARD AND H. A. SKINNER, *Chem. Rev.*, 55 (1955) 745.
6 A. L. ALLRED AND E. G. ROCHOW, *J. Inorg. Nucl. Chem.*, 5 (1958) 269.
7 R. S. DRAGO AND N. A. MATWIYOFF, *J. Organometal. Chem.*, 3 (1965) 62.
8 R. S. DRAGO, *Rec. Chem. Progr.*, 26 (1965) 157.
9 J. A. KERR, D. H. SLATER AND J. C. YOUNG, *J. Chem. Soc.*, *A*, (1966) 104.
10 J. A. KERR, D. H. SLATER AND J. C. YOUNG, *J. Chem. Soc.*, *A*, (1967) 134.
11 D. F. VAN DE VONDEL, *J. Organometal. Chem.*, 3 (1965) 400.
12 W. F. EDGELL AND C. H. WARD, *J. Amer. Chem. Soc.*, 76 (1954) 1169.
13 F. P. JAHN, *J. Amer. Chem. Soc.*, 59 (1937) 1761.
14 H. W. MELVILLE AND B. G. GOWENLOCK, *Experimental Methods in Gas Reactions*, MacMillan, London, 1964, p. 243.
15 H. P. BURCHFIELD AND E. E. STORRS, *Biochemical Applications of Gas Chromatography*, Academic Press, London, 1962, p. 185.
16 M. H. JONES AND E. W. R. STEACIE, *J. Chem. Phys.*, 21 (1953) 1018.
17 A. SHEPP, *J. Chem. Phys.*, 24 (1956) 939.
18 J. BURDON, W. B. HOLLYHEAD, C. R. PATRICK AND K. V. WILSON, *J. Chem. Soc.*, (1965) 6375.
19 J. FEENEY, Private communication.
20 L. W. REEVES, *J. Chem. Phys.*, 40 (1964) 2128.
21 W. T. DIXON, *Tetrahedron Lett.*, (1967) 2531; *Tetrahedron*, 24 (1968) 5509.
22 W. MACK, *Tetrahedron Lett.*, (1967) 4993.
23 W. J. CHENG AND M. SZWARC, *J. Phys. Chem.*, 72 (1968) 494.
24 H. DREESKAMP, *Proc. XVIII Colloque Ampere*, University of Leuven, 1964.
25 H. SCHMIDBAUR, *Chem. Ber.*, 97 (1964) 1639.
26 M. A. JENSEN, *J. Organometal. Chem.*, 11 (1968) 423.
27 W. MCFARLANE, *J. Chem. Soc.*, *A*, (1967) 1275.
28 E. A. V. EBSWORTH AND J. J. TURNER, *J. Chem. Phys.*, 36 (1962) 2628.
29 E. A. V. EBSWORTH AND S. G. FRANKISS, *Trans. Faraday Soc.*, 63 (1967) 1574.
30 E. A. V. EBSWORTH, *Volatile Silicon Compounds*, Pergamon, Oxford, 1963, p. 23.
31 H. J. CAMPBELL–FERGUSON, E. A. V. EBSWORTH, A. G. MACDIARMID AND T. YOSHIOKA, *J. Phys. Chem.*, 71 (1967) 723.