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GAS PHASE REACTIONS OF SODIUM
IV. RATES OF REACTION OF METHYLCHLOROGERMANES AND -STANNANES

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SUMMARY

The rates of reaction with sodium atoms of the compounds Me_3MCl and Me_2MCl_2 ($M = Ge, Sn$) have been measured. The gradations in velocity constants along the Group IV series Me_3MCl ($M = C, Si, Ge, Sn$) are discussed in terms of bond dissociation energies. It is concluded that the reaction rate of trimethylchlorostannane is high and reasons for this behaviour are discussed.

INTRODUCTION

There have been a large number of investigations of the rates of reaction of sodium atoms with organic halides using the diffusion-flame technique but there is only one report of measurements where an organo-element halide is compared with the analogous carbon compound namely the study of Me_nSiCl_{4-n} and Me_nCCl_{4-n} ($n = 0$–3) reported by Gowenlock and Thomas[1]. It was thought appropriate to extend this study to the remainder of the Group IV elements in order to correlate the effects of the change of the central atom with the rates of reaction obtained. Such an extension is in keeping with the fact that whereas the limits of error for individual rate constants may be high, in a series of reactions where the major variable is the partial pressure of the halide, the relative values of the rate constants give an essentially correct reflection of the relative reactivities of the halides used.

EXPERIMENTAL

Materials

Trimethylchlorogermane was prepared by the redistribution reaction[2] (1).

$$(CH_3)_4Ge + GaCl_3 \rightarrow (CH_3)_3GeCl + CH_3GaCl_2 \quad (1)$$

The initial manipulations were carried out in a glove box under a positive pressure of dry nitrogen: Gallium trichloride (10 g, 0.057 mole) was placed in a trap and tetramethylgermane (7.4 g, 0.056 mole) was added rapidly. The solid gallium trichloride

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dissolved over a period of 5 min during which time the trap became warm. After 10 min the trap was stoppered and transferred to the vacuum line, the contents were cooled to −196°, evacuated, degassed and then distilled to give a colourless liquid mixture of approx. composition $Me_3GeCl/Me_4Ge = 4/1$. Trap-to-trap distillation *in vacuo* from −30° to −78° removed most of the tetramethylgermane and prolonged pumping at −85° removed the remainder leaving a gas chromatographically pure sample of trimethylchlorogermane.

Dimethyldichlorogermane was a commercial sample (Alfa). It was shown by GLC to contain a very small quantity of a more volatile impurity which was removed by repeated trap-to-trap distillation *in vacuo* retaining the middle fraction on each occasion. Trimethylchlorostannane was a commercial sample (Fluka). GLC showed the absence of any impurity. Dimethyldichlorostannane was prepared by Smith and Rochow's method[3]. The major product was a white crystalline solid which condensed separately from small amounts of a viscous liquid. The solid was purified by vacuum sublimation and had m.p. 106° (lit.[3] 106°). All liquid materials were intensively degassed and stored in the dark at liquid nitrogen temperatures when not in use for kinetic purposes. The purities of all materials were re-checked by gas chromatography: no impurities were observed. The purification and storage of the nitrogen carrier gas are as previously reported[1] and the purification of the sodium followed the standard method[4]. The apparatus is as described in Part I[1].

RESULTS AND DISCUSSION

The procedure for the measurement of the velocity constant is as described in Part I[1] and the values are calculated from the simple diffusion flame equation. The values of the velocity constants given in Table 1 are based upon between five and eight separate runs carried out on different days, a run consisting of a series of velocity constant determinations extending over two or more hours. The values are corrected to 520°K as by Warhurst *et al.*[4].

TABLE 1

BIMOLECULAR VELOCITY CONSTANTS ($ml \cdot mole^{-1} \cdot sec^{-1}$)

Halide	$10^{-11} k$	Halide	$10^{-11} k$
Me_3GeCl	0.50	Me_3SnCl	66.0
Me_2GeCl_2	209	Me_2SnCl_2	585

In the first paper of this series[1] we emphasised that for any polychlorinated molecule there must be more than one dechlorination step and that consequently the velocity constant obtained in such a case is an overall velocity constant. This limitation notwithstanding some correlation of results is possible. In passing along the Group IV series $Me_3MCl \rightarrow Me_2MCl_2$ there is an increase in rate by a factor of 15(C), 420(Ge), 9(Sn) but for silicon there is no increase in rate. In this we may note that silicon is exceptional. It is possible that the enhanced rate of increase for germanium may be due to increased stability of the $Me_2M\colon$ product relative to silicon and tin but this conclusion is highly tentative.

$$Me_3MCl + Na \rightarrow Me_3M + Cl^-Na^+ \qquad (2)$$

The most striking feature relates to the relative rates of the reaction for the trimethyl Group IV halides. If the mechanism of reaction (2) is identical then the series should show the simple relationship[5] (3).

$$\Delta E = -\alpha \cdot \Delta(\Delta H) \text{ (where } E \text{ is the activation energy)} \qquad (3)$$

An alternative form of this relationship is shown in eqn. (4) (where a and b are constants). This will hold if the pre-exponential term of the Arrhenius equation is

$$\log k = a \cdot D(Me_3M\text{–}Cl) + b \qquad (4)$$

constant. Evidence is available[6] for the approximate equality of the pre-exponential factors of sodium "flame" reactions and consequently it is of interest to examine the equation as given. Bond dissociation energy data are given in Table 2. It should be noted that although a range of values is available for $D(Me_3Sn\text{–}Cl)$ there is general agreement that this bond is stronger than the C–Cl bond in tert-butyl chloride.

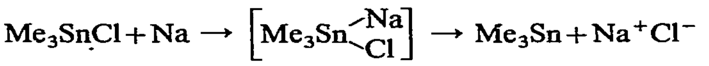
TABLE 2

INTERCOMPARISON OF VELOCITY CONSTANTS AND BOND DISSOCIATION ENERGY DATA FOR Me_3MCl

M	10^{-11} k (ml·mole^{-1} sec^{-1})	$D(Me_3M\text{–}Cl)$ (kcal/mole)
C	2.76 (ref. 1)	79 (ref. 7), 80 (ref. 8)
Si	0.0249 (ref. 1)	88 (ref. 9), 91 (ref. 8)
Ge	0.50 (this work)	
Sn	66.0 (this work)	98[a], 89 (ref. 8), 85 (ref. 10)

[a] From $\Delta H_f^0(Me_3Sn)_g = 27.0$ kcal/mole (ref. 11), $\Delta H_f(Me_3SnCl)_{liq} = -53.0$ kcal/mole (ref. 12) and $\Delta H_V(Me_3SnCl)_{liq} = 11.0$ kcal/mole estimated from Wheland's expression[13].

It is therefore necessary to emphasise that the rate constant for the reaction of sodium with trimethylchlorostannane is many times larger than expected on the basis of eqn. (4) and it seems probable that an alternative reaction pathway is responsible. We suggest that the reaction may follow either pathway (5) or (6), *i.e.*, "harpooning" of the tin in place of the chlorine The first of these implies the possibility



$$Me_3SnCl + Na \rightarrow \left[Me_3Sn\begin{smallmatrix}\nearrow Na\\ \searrow Cl\end{smallmatrix}\right] \rightarrow Me_3Sn + Na^+Cl^- \qquad (5)$$

$$Me_3SnCl + Na \rightarrow [Me_3Sn^- \cdots Cl \cdots Na^+] \rightarrow Me_3Sn + Na^+Cl^- \qquad (6)$$

of a pentavalent intermediate, a suggestion similar to that recently proposed[14] for reaction of trifluoromethyl radicals with tetramethyltin (eqn. 7) whereas the second

$$Me_4Sn + CF_3 \rightarrow [Me_4SnCF_3] \rightarrow Me_3SnCF_3 + CH_3 \qquad (7)$$

suggestion is similar to that recently proposed for the molecular beam study of the reaction of potassium vapour with trifluoromethyl iodide[15]. It is, of course, possible that the two proposals (5) and (6) are much more similar than the above formalism would suggest. In an attempt to confirm the above suggestion an attempt was made to study the reaction of sodium vapour with tetramethyltin. Some reaction occurred in that a "flame" was obtained but the reaction was very slow ($k < 10^8$ ml · mole^{-1} · sec^{-1}). Consequently, if either of the suggested mechanisms is correct it appears to be dependent primarily upon the presence of the halogen atom in the molecule and the resultant partial charge separation $Sn^{\delta+}-Cl^{\delta-}$. The very rapid reaction of the dichloride is also consistent with this observation.

It is apparent that our suggestions of reaction pathways (5) and (6) are analogous to the proposals of Boué, Gielen and Nasielski[16] that the accessibility of the empty *5d* orbitals of tin play an important role in radical substitution reactions of tetraalkyltins. Further studies are required to substantiate our suggestions and, in particular, it would be useful to investigate the temperature variation of the velocity constants for the silicon, germanium and tin compounds by means of the competitive technique[7] so as to check our assumption that the anomalous behaviour of the tin compound is due predominantly to an activation energy effect and not to abnormally large variations in the pre-exponential factor.

It is particularly unfortunate that little or no thermochemical data are available for trimethylchlorogermane. By intercomparison with the data for C and Si using eqn. (4) we predict $D(Me_3Ge\text{–}Cl) = 83 \pm 3$ kcal/mole.

All attempts to measure the rate of reaction of the corresponding lead compounds failed due to the involatility of the crystalline solids. Similarly, extension to the cases of the analogous compounds triphenylchlorostannane and triphenylchlorogermane was also impossible due to involatility.

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REFERENCES

1 B. G. Gowenlock and K. E. Thomas, *J. Chem. Soc.*, (1965) 5068.
2 H. Schimidbaur and W. Findeiss, *Chem. Ber.*, 99 (1966) 2187.
3 A. C. Smith Jr. and E. G. Rochow, *J. Amer. Chem. Soc.*, 75 (1953) 4103.
4 F. Riding, J. Scanlan and E. Warhurst, *Trans. Faraday Soc.*, 52 (1956) 1354.
5 E. Warhurst, *Quart. Rev.*, 5 (1951) 44.
6 J. A. Kerr, *Chem. Rev.*, 66 (1966) 465.
7 J. A. Kerr, E. A. Lissi and A. F. Trotman-Dickenson, *J. Chem. Soc.*, (1964) 1673.
8 R. A. Jackson, *Advan. Free-Radical Chem.*, 3 (1969) 231.
9 B. G. Gowenlock and J. Stevenson, *J. Organometal. Chem.*, 13 (1968) P13.
10 W. P. Neumann, *Angew. Chem. Int. Ed. Engl.*, 8 (1969) 288.
11 J. B. Pedley, personal communication.
12 G. A. Nash, H. A. Skinner and W. F. Stack, *Trans. Faraday Soc.*, 61 (1965) 640.
13 G. W. Wheland, *Resonance in Organic Chemistry*, Wiley, New York, 1955.
14 T. N. Bell and A. E. Platt, *Chem. Commun.*, (1970) 325.
15 P. R. Brooks, *J. Chem. Phys.*, 50 (1969) 5031.
16 S. Boué, M. Gielen and J. Nasielski, *J. Organometal. Chem.*, 9 (1967) 481.