931. *Gas-phase Reactions of Sodium. Part I. Rates of Reaction of Methylchlorosilanes and the Analogous Carbon Compounds*

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The rates of reaction with sodium atoms of the three methylchlorosilanes, silicon tetrachloride, and the analogous carbon compounds have been measured. The gradations in velocity constant along the series are discussed in terms of bond dissociation energies, effects of substituents on the energy of the transition state of the reaction, and of the $(p \longrightarrow d)\ \pi$ contribution to the Cl–Si bond.

THE extensive investigations of the rates of reaction of sodium atoms with organic halides by the diffusion-flame technique, which have been summarised by Polanyi,[1] and Bawn,[2] and Warhurst [3] relate to aliphatic halides; later studies [4] extended this technique to aromatic halides. It is generally agreed that, although 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 gradations, or ratios, of the rate constants give essentially correct reflections of the relative reactivities of the different halides.

The simple diffusion-flame technique has been limited to measurement of the reaction rates of a number of carbon–halogen compounds and inorganic halides. There are no rate measurements for organometallic or organo-element halides. We have applied the diffusion-flame technique to the reactions of sodium atoms with the silicon compounds Me_nSiCl_{4-n} and, for comparative purposes, the analogous carbon compounds Me_nCCl_{4-n} ($n = 0$—3).

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[1] M. Polanyi, " Atomic Reactions," Williams and Norgate, London, 1932.
[2] C. E. H. Bawn, *Ann. Reports*, 1942, **39**, 36.
[3] E. Warhurst, *Quart. Rev.*, 1951, **5**, 44.
[4] F. Riding, J. Scanlan, and E. Warhurst, *Trans. Faraday Soc.*, 1956, **52**, 1354.

Literature values are available for silicon tetrachloride,[5] t-butyl chloride,[6] and carbon tetrachloride;[5-8] two of the values for carbon tetrachloride [5,6] were obtained before the Heller [7] conditions for the determination of rate constants were established, and are thus of lower accuracy. The accuracy of the rate constants obtained for carbon tetrachloride, the basis of the simple diffusion-flame expression, is admittedly poor, and various attempts [9-13] have been made to obtain more rigorous expressions for the bimolecular velocity constant. It appears, however, that for a slow reaction, such as for the silicon compounds, the simple diffusion-flame expression results in relatively small errors. An additional advantage is that of comparison with the available published values most of which are calculated on this simple basis.

EXPERIMENTAL AND RESULTS

Preparation and Purification of Materials.—Oxygen-free nitrogen was purified by standard methods.[4] Sodium was purified and prepared as described by Riding, Scanlan, and Warhurst.[4] The halides were all available commercially, and some were of a stated high purity. All the halides were tested for purity by gas–liquid chromatography before distillation. No traces of impurity were found in t-butyl chloride, 1,1,1-trichloroethane and carbon tetrachloride, and these were thus used without fractionation. 2,2-Dichloropropane was found to be 98·4% pure and repeated fractional distillation raised this to 99·6%, the remaining impurity being less volatile than the main component. Commercial trimethylchlorosilane contained 15% dimethyldichlorosilane; repeated fractional distillation reduced this amount to <0·2%. Dimethyldichlorosilane contained 8% trimethylchlorosilane; repeated fractional distillation reduced this amount to <0·3%. Trichloromethylsilane contained about 2% of each of the two other methylchlorosilanes; repeated fractional distillation eliminated these impurities. Silicon tetrachloride contained trace amounts of chlorine and hydrogen chloride, which were eliminated by alternately evacuating the sample at −78°, and warming it to room temperature, the cycle being repeated several times. Bromobenzene was dried, distilled through an efficient column, and the fraction with boiling range 155·5—156° was collected; this was redistilled and the same fraction again collected. Gas-chromatographic analysis showed the absence of impurities.

Apparatus.—We are indebted to Dr. E. Warhurst for the gift of the reaction vessel used for the studies of reaction rates of aromatic halides.[4] The apparatus was essentially the conventional diffusion-flame apparatus [8,14] and two standard methods for the introduction of the halogen-containing compounds were adopted Liquids with a boiling point above 100° were introduced by the Warhurst double-trap system,[15] and the more volatile halides by direct vaporisation and passage through one of a number of suitable fine capillaries. Vapour pressures were determined by separate calibration experiments.

Results.—The values of the bimolecular velocity constant, k, have been calculated from the simple diffusion-flame expression

$$k = \frac{\left(\ln \frac{P_{\mathrm{Na}}}{P_0} - \ln \frac{R}{r}\right)^2}{(R - r)^2} \frac{\delta}{C_{\mathrm{Hal}}}$$

where C_{Hal} is the concentration of the halide in the reaction vessel, R the radius of the flame zone, r the internal radius of the nozzle tube, δ the diffusion constant of the sodium vapour in the carrier gas, P_{Na} the pressure of the sodium vapour at the nozzle mouth, and P_0 the pressure

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[5] W. Heller and M. Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633.

[6] H. von Hartel, N. Meer, and M. Polanyi, *Z. phys. Chem.*, 1932, *B*, **19**, 139.

[7] W. Heller, *Trans. Faraday Soc.*, 1937, **33**, 1556.

[8] J. N. Haresnape, J. M. Stevels, and E. Warhurst, *Trans. Faraday Soc.*, 1940, **36**, 465.

[9] R. J. Cvetanovic and D. J. LeRoy, *Canad. J. Chem.*, 1951, **29**, 597.

[10] R. J. Cvetanovic, *Canad. J. Chem.*, 1956, **34**, 54.

[11] F. Smith, *J. Chem. Phys.*, 1954, **22**, 1605.

[12] J. F. Reed and B. S. Rabinovitch, *J. Phys. Chem.*, 1955, **59**, 261; 1957, **61**, 598.

[13] E. D. Kaufman and J. F. Reed, *J. Phys. Chem.*, 1963, **67**, 896.

[14] H. von Hartel and M. Polanyi, *Z. phys. Chem.*, 1930, *B*, **11**, 97.

[15] E. Warhurst, *Trans. Faraday Soc.*, 1939, **35**, 674.

of the sodium vapour at the visible edge of the flame zone. The value adopted for P_0 is 5×10^{-6} mm., in agreement with Riding, Scanlan, and Warhurst [4] whose reaction conditions were similar to ours. In all the experiments the values of v/δ where v is the linear flow of the carrier gas through the nozzle, were within, or only slightly removed from the range recommended by Heller.[7]

The results are given in Table 1, and are based upon six, seven or eight separate runs carried out on different days; a run consisted of a series of velocity-constant determinations extending over about 2 hr. The values of the velocity constants given are the averages of all the values obtained corrected to 520°K as by Warhurst *et al.*[4]

TABLE 1

Bimolecular velocity constants (ml. mole^{-1} sec.$^{-1}$)

Halide	PhBr	Me_3CCl	Me_2CCl_2	$MeCCl_3$	CCl_4	Me_3SiCl	Me_2SiCl_2	$MeSiCl_3$	$SiCl_4$
$10^{-11}k$	11·5	2·76	42·3	393	2260	0·0249	0·0204	0·0587	6·95

DISCUSSION

Our value for the rate constant for bromobenzene falls within the range of the published values.[4,15]

We have already indicated that the absolute accuracy of the rate constants for the relatively fast reactions such as carbon tetrachloride–sodium is highly questionable, and it is also necessary to note that the rate constants are overall rate-constants, in that the differential equation used by Hartel and Polanyi [14] implies that there is only one reaction per halide molecule. For any polychlorinated molecule there must be more than one dechlorination step,[13] and thus a further degree of approximation enters into the rate constants obtained. This limitation notwithstanding, there are some important correlations which can be established from our results.

By using a collision number of $5 \cdot 10^{14}$ ml.mole^{-1} sec.$^{-1}$, the collision yields can be calculated. In Table 2, the results for the carbon compounds are compared with literature values [5,7] for a similar series. It is interesting to note the reasonable agreement for the carbon tetrachloride values and the similar trend in collision yield along the series. As is to be expected, the methyl compounds regularly react faster than the corresponding hydrogen compounds.

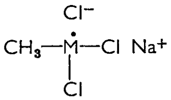
TABLE 2

Collision yields

			Collision yield	
Reactant	Collision yield	Reactant	(Ref. 5)	(Ref. 8)
Me_3CCl	1 in 1810	CH_3Cl	1 in 7100	—
Me_2CCl_2	1 in 118	CH_2Cl_2	1 in 310	1 in 760
$MeCCl_3$	1 in 13	$CHCl_3$	1 in 22	1 in 50
CCl_4	1 in 2	CCl_4	1 in 2	1 in 5

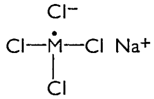
A notable difference is apparent between the analogous carbon and silicon compounds. In passing along the series $Me_3MCl \longrightarrow MCl_4$, successive increase in the number of chlorine atoms results in an increase of reaction-rate by a factor of about 10, when M is carbon. This regular increase is absent when M is silicon, the first two compounds having approximately the same rate of reaction and the trihalide being two to three times faster. The notable increase of reaction rate occurs only when four chlorine atoms are attached to the central atom. It is possible that the reason for this is connected with the $(p \rightarrow d)$ π contribution to the Cl–Si bonds. It may be suggested that this back-co-ordination effect reaches a maximum when three donating groups are attached to the one silicon atom, and that the bonding to the fourth atom is thus weaker. This would then imply that the D(Si–Cl) values are approximately equal for the methylchlorosilanes and greater than $D(Cl_3Si\text{–}Cl)$.

The only values [16,17] are $D(\mathrm{Me_3Si{-}Cl}) = 120$ kcal. mole^{-1} and $D(\mathrm{Cl_3Si{-}Cl}) = 106$ kcal. mole^{-1}, the uncertainties in these values being relatively large. Combination of these two values and of the activation energies calculated on the assumption of the $5{\cdot}10^{14}$ ml.mole^{-1} sec.$^{-1}$ collision number gives $\alpha = 0{\cdot}33$ in the $\Delta E = \alpha\Delta D$ relationship, a value that is similar to the values obtained by other workers.[18] It should be noted, however, that a similar difference in bond dissociation energies operates for t-butyl chloride and carbon tetrachloride, where back-co-ordination effects are absent. Alternative explanations of changes in reaction-rate invoke the negative-group effect, which arises from the stabilisation of the transition state by the presence in the halide molecule of one or more negative groups (*i.e.*, groups with a high electron affinity) in addition to the reacting halogen atom. If this is to be accepted as the explanation for the gradation of reaction rate, it implies that structure (I) is unimportant in the transition state when M = Si, and important when M = C. On the other hand, in order to account for the large increase in rate constant for silicon tetrachloride, structure (II) will be important for M = both C and Si.



$\mathrm{CH_3{-}\underset{\textstyle Cl}{\overset{\textstyle Cl^-}{\dot{M}}}{-}Cl\ Na^+}$

(I)



$\mathrm{Cl{-}\underset{\textstyle Cl}{\overset{\textstyle Cl^-}{\dot{M}}}{-}Cl\ Na^+}$

(II)

It is of interest to see whether the analogous germanium and tin compounds are similar to the carbon or silicon cases. The tetrachlorides react at about the same rate as the carbon tetrachloride.[7,19] We hope to extend these measurements to the methylchlorogermanes and methylchlorostannanes.

It has been suggested [20] that the changes in reaction rate in the methylchlorosilanes and silicon tetrachloride will be reflected in changes of the stretching force-constants for the Si–Cl bond in these molecules. This would parallel the earlier correlation suggested for the chloromethanes.[8] Force constants, obtained by using Urey–Bradley potential functions, are available for the methylchlorosilanes.[21] These values are the same and are identical with the Shimanouchi value [22] for silicon tetrachloride. The variations in the force constant for Si–Cl in the tetrachloride calculated by different workers imply that it may be difficult to establish any correlation.

The only other suggestion that has been made for the variation in rates of sodium-flame reactions is due to Pritchard,[23] who suggests that internal degrees of freedom contribute to the activation process. Successive substitution of a methyl group by a chlorine atom would reduce the number of effective oscillators, and thus reduce the rate along the series, whereas the observed trend is in the opposite direction. It appears, therefore, that this effect can operate only in conjunction with some other effect.

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[16] G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, 1964, **86**, 3174.

[17] W. C. Steele, L. D. Nichols, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1962, **84**, 4441.

[18] N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," vol. 1 (transl. J. E. S. Bradley), Pergamon, London, 1958, p. 27.

[19] N. J. Friswell and B. G. Gowenlock, unpublished results.

[20] E. A. V. Ebsworth, personal communication.

[21] K. Shimizu and H. Murata, *Bull. Chem. Soc. Japan*, 1959, **32**, 46; *J. Mol. Spectroscopy*, 1960, **4**, 201, 214.

[22] T. Shimanouchi, *Pure Appl. Chem.*, 1963, **7**, 131.

[23] H. O. Pritchard, *Rec. Trav. chim.*, 1955, **74**, 779.