465

A. B. D. CASSIE AND S. BAXTER

THE RATE OF REACTION OF SODIUM ATOMS WITH POLYHALOGENATED METHANE DE-RIVATIVES.

By J. N. HARESNAPE, J. M. STEVELS AND E. WARHURST.

Received 1st December, 1939.

Up to the present date relatively few measurements have been made of the velocity of reactions of Na atoms with organic halides which contain more than one halogen atom. The few existing measurements of Hartel, Meer and Polanyi¹ and Heller and Polanyi² are exclusively concerned with chlorine derivatives. These authors have measured the rate of reaction of Na atoms with the compounds of the series CH₃Cl, CH₂Cl₂, CHCl₃, CCl₄, and found a marked progressive increase in reaction rate on passing along the series from CH₃Cl to CCl₄. Heller and Polanyi²

¹ Hartel, Meer and Polanyi, Z. physik. Chem., B, 1933, 19, 139.

² Heller and Polanyi, Trans. Faraday Soc., 1936, **32**, 633.

RATE OF REACTION OF SODIUM ATOMS

drew attention to the fact that this increase in reaction velocity runs parallel to a decreasing force constant for the C-Cl bond. It has been shown by one of us (J.M.S.^{3, 4}) that in the case of the above series, increase of the number of Cl atoms causes an increase in the atomic refractions and polarisabilities of the individual Cl atoms. Thus, this increase in polarisability runs parallel to the increase in the velocity of the reaction with Na atoms. A general method has been developed^{3, 4} for the calculation of the atomic refraction of any halogen atom in any polyhalogenated methane derivative. In the case of the mixed methane derivatives containing C, H, Cl and Br certain well marked trends in polarisability of the halogen atoms are noticeable, and in view of this it is of considerable interest to measure the rates of reaction of these derivatives with sodium atoms in order to correlate trends of reaction rates with these trends in polarisability. The field chosen for investigation consisted of ten of the possible fourteen methane derivatives which contained chlorine or bromine or both halogens together. The compounds CCl₂Br₂ and CClBr₃ were omitted because of their instability and CBr₄ on account of its low vapour pressure; CH₃Cl was also not included. In addition to these ten compounds, two methane derivatives containing F and Br, viz. CHFBr, and CFBr₃ have been dealt with, together with methyl iodide.

Experimental.

The halides were prepared in the Physical Chemistry Department of the University of Leiden; the methods of preparation and purification are described elsewhere.⁵ Two different experimental methods were employed to measure the reaction rates, (a) the Life Period Method ⁶, ⁷ with the modifications described recently by one of the authors, ⁸ and (b) the Diffusion Flame Method as modified by Heller.* In both cases the halides were used in pairs, *i.e.* in the same run the reaction rates of halides A and B were measured, and in the next run the rates of B and C, and so on. From the ratios of the rates so obtained, by choosing one halide as standard, a gradation of relative velocities along a series could be obtained. In this way the effect of errors which might vary haphazardly from run to run was eliminated as far as possible. This was essential since in some cases the difference in reaction rates is not very great. This procedure gives an accurate gradation of velocity constants, the accuracy being independent of any uncertainties in the absolute values of the constants. The purity of all the compounds was checked before use by refractive index measurements.

The Life Period Method.

The technique employed was that which has been described for measurements of the rate of reaction of Na atoms with bromobenzene.⁸ Hydrogen was the carrier gas and its rate of flow was regulated in all experiments so that $v/\delta \sim 13 \times 10^{-2}$ where v is the linear streaming velocity of the carrier gas at the nozzle mouth in metres/per sec., and δ is the diffusion constant of the Na vapour in the carrier gas at the pressure in the reaction vessel $(\sim 3 \text{ mm.}).$ The temperature of the Na boat was usually about 192° C. These conditions are within the range which has been shown by one of us * to lead to very reliable results with the Life Period Method. The majority

³ Stevels, Trans. Faraday Soc., 1937, 33, 1381. 4 Ibid., 1938, 34, 429.

⁵ Stevels, Dissertation, Leiden, 1937. ⁶ Frommer and Polanyi, Trans. Faraday Soc., 1934, **30**, 519.

⁶ Frommer and Polanyi, 1700. 1 (1935, 31, 987. ⁷ Fairbrother and Warhurst, *ibid.*, 1935, 31, 987. ⁹ Heller, *ibid.*, 1937, 33, 1556.

J. N. HARESNAPE, J. M. STEVELS AND E. WARHURST 467

of the velocity constants diverged from the mean value by less than \pm 10%; in a few cases greater di- TABLE I.—REACTION VESSEL TEMPERATURE 255° C.

cases greater divergencies were ob-In some tained. experiments velocity constants were determined over a range of flame sizes corresponding to 14 % to 20 % absorption. No drift in the value of the constant was apparent. In the case of CHFBr, the constant was determined with a sodium temperature of 191° C. and subsequently with temperature of а 220° C., corresponding to more than a five-fold increase in sodium vapour pressure. The two

	1		
Compound.	% Absorption of Flame.	Temp. of Sodium °C.	Velocity Constant $k(\times 10^{-12})$ cc. mol ⁻¹ , sec. ⁻¹
CH_2Cl_2	16.9	192	0.60
	17.0	192	0.20
CH_2ClBr	15.6	192	17.8
-	14.5	192	16.6
	20.8	192	16.4
	10.0	192	18.7
CH ₃ Br ₃	17.5	192	31.0
	18.0	102	31.4
	13.3	102	25.0
	14.0	102	20.8
CHFBr.	10.0	102	18.5
0111 212	21:0	192	40 5
	17.5	192	41.7
	1/5	191	59.0
	17.2	191	57.5
	17.3	220	40.0
	19.0	220	45.0
	18.8	220	43.0
CFBr ₃	15 ·1	224	91.0
	13.9	224	89.7

sets of values were in good agreement. A typical batch of results is shown in Table I, which illustrates the points mentioned above.

The Diffusion Flame Method.

The first experiments were carried out using nitrogen as carrier gas at pressures ranging from 3-15 mm., and sodium temperatures of about 240° C. The results obtained under these conditions were unsatisfactory, the velocity constants showing a pronounced decrease with increase of nitrogen pressure in the reaction vessel (see Table II).

TABLE II.-CHClBr₂. REACTION VESSEL TEMPERATURE 250 °C.

Nitrogen pressure, P_{N_2} in mm.	2.6	4.0	4.0	3.9	5.0	5.1	7.2	7.5	11.3
Vel. const. $k \times 10^{-12} \frac{\text{cc}}{\text{mol.sec.}}$	42	22	19	20	16	14	10.6	10.3	6.9

This drift of k with P_{N_a} was most marked for the halides which reacted fastest. The explanation of this drift lies in the fact that the flames prove to be far from ideal since they largely consisted of a central core of unreacting sodium atoms into which no halide was able to diffuse (" core " flames), because the ratio of the partial pressure of halide, P_{Hal} , to the sodium pressure, P_{Na} , at the nozzle mouth was very small (~ 1/3). In order to change this state of affairs a modification in experimental technique was made. The velocity constant of the reaction is given by

$$k = \frac{\left(\ln \frac{P_{\text{Na}}}{P_{\text{Na}}^0} - \ln \frac{R}{r}\right)^2}{(R-r)^2} \frac{\delta}{P_{\text{Hal}}}$$

where P_{Na} is the sodium pressure at the nozzle mouth, P_{Na}^{0} the limiting pressure of sodium visible, R the radius of the flame, r the radius of the

RATE OF REACTION OF SODIUM ATOMS

nozzle, δ the diffusion constant of sodium vapour, and P_{Hal} the partial pressure of halide in the reaction vessel. Thus, other things being equal an increase in P_{Hal} necessitates a proportional increase in δ for the same stationary state (i.e. flame diameter) to be maintained. A considerable increase in the ratio of $P_{\rm Hal}/P_{\rm Na}$ was brought about by a twenty fold increase in δ . This was achieved by using hydrogen instead of nitrogen as carrier gas at very low pressures (as low as 0.4 mm.) in the reaction vessel. The correct value of v/δ was maintained by using very high speeds of flow of carrier gas; such speeds were made possible by placing a reaction vessel on the low pressure side of three mercury vapour circulation pumps working in parallel. The tendency to form "core" flames was further reduced by lowering the sodium pressure at the nozzle mouth from 2 imes 10-3 to 4×10^{-4} mm.

The results with the new conditions for CHCl₂Br, a very reactive compound, are shown in Table III, for various carrier gas pressures, $P_{\rm He}$, in the reaction vessel. Although the results vary considerably, on account

TABLE III.—TEMPERATURE	OF	Reaction	VESSEL	250°	C.
------------------------	----	----------	--------	------	----

$P_{\mathbf{H_2}}$ in mm.	o·43	0·4 6	o· 46	o·47	0.24	0.22	0.55	0.71	o ·94
$k \times 10^{-12}$	115	132	130	174	124	104	97:3	130	88.4

of increased difficulty in measuring accurately flames of such low intensity, there is no apparent drift in the value of k over a more than two-fold increase in $P_{\mathbf{H}_{2}}$. The value of the ratio of $P_{\text{Hal}}/P_{\text{Na}}$ in this case was ~4. The new value of k for CHClBr₂ (the early results for which are shown in Table II) proved to be 180×10^{12} . On account of the decreased dazzling effect on the eye of the central zone of the resonance flames in these experiments at low Na pressures we consider that the appropriate value for P_{Na}^0 is 7 \times 10⁻⁶ mm.

The results obtained by the Life Period and Diffusion Flame Methods

Compound.	Collision Yield Life Period Method.	Collision Yield Diffusion Flame Method.
CCl ₄ CCl ₃ Br CHCl ₃ CHCl ₃ Pr CHClBr ₂ CHClBr CH ₂ Cl ₂ CH ₂ Cl ₂ CH ₂ ClBr CH ₂ Br ₂ CH ₃ Br CH ₄ Br CHFBr ₂ CFBr ₃ CH ₃ I	5:3 5:3 13:5 9:0 6:3 833 28 17:0 — 11 5:5 10:6	$5.5 \\ 1.7 \\ 50 \\ 4.4 \\ 2.8 \\ 1.4 \\ 760 \\ 26 \\ 13.2 \\ 135 \\ - \\ 2.3 \\ 11.4$

TABLE IV.

are given in Table IV and are shown schematically in In Table V the Table V. figure underlined above each compound is the collision yield, *i.e.* the average number of collisions per effective collision; the values are those of \mathbf{the} Diffusion Flame Method. In calculating these collision yields the value of the collision cross-section of 3.5×10^{-15} cm.² given by Hartel and Polanyi 10 was This value is probably used. somewhat high for monohalogenated compounds.8 The collision yield for methyl chloride (marked*) has been taken from the work of Heller and Polanyi.² The figure

below each compound is the atomic refraction calculated by the method developed by one of the authors.^{3, 4} In the cases of CH₃Cl, CH₂Cl₂, CHCl₃ and CCl₄ the refractions given are per chlorine atom; in all other cases

10 Hartel and Polanyi, Z. physik. Chem., B, 1930, 11, 97.

J. N. HARESNAPE, J. M. STEVELS AND E. WARHURST 469

the refractions are per bromine atom since, in these cases, the reaction consists in the removal of a bromine atom. The values for the two series $CH_3Cl \rightarrow CCl_4$ and $CH_3Br \rightarrow CBr_4$ have been published previously by one of us.³



TABLE V.

Discussion of Results.

In view of the polyhalogenated nature of these compounds the possibility of multiple reactions involving substituted radicals could not be ignored. In connection with this it was noticed that some of the compounds (CCl₃Br, CHCl₂Br, CHClBr₂, CHBr₃ and CFBr₃) showed a faint chemiluminescence in the early experiments with the diffusion flame apparatus, when a high nozzle pressure of sodium and a low concentration of halide were used. These chemiluminescent zones emitted the D line of sodium. It is unlikely that the primary reaction in any of these instances is sufficiently exothermic to excite the D line, since this would necessitate the assumption of improbably low values for the C--Cl and C--Br bond strengths. The luminescence is very probably due to a secondary reaction involving the halogenated radical, the heat of reaction in this case being greater than $48\cdot3$ k.cal./mol., e.g.

$$CCl_3Br + Na = -CCl_3 + BrNa + Q < 48.3$$
 k.cal.

followed by

$$CCl_3 + Na = : CCl_2 + CINa + Q > 48.3$$
 k.cal.

The heat change of the latter reaction may be large because it probably includes the energy change of a quadrivalent carbon atom to a divalent carbon atom (~ 37 k.cal./mol.).¹¹ When one of this group of halides, CHCl₂Br, was introduced by means of a nozzle into a large excess of sodium vapour in a "highly dilute flame" apparatus,¹² the D line of sodium was strongly emitted and a dark deposit, presumably carbon, was formed on the sides of the reaction vessel. In this case the carbon atom is probably stripped of all its halogen atoms.

If the rate of such a secondary reaction were of the same order, or faster than the corresponding primary reaction, then, in a case where the secondary reaction were occurring to an appreciable extent, the experimental value of the velocity constant would be greater than the true value for the primary reaction. This effect will arise when the value

¹¹ Norrish, Trans. Faraday Soc., 1934, **30**, 110; Heitler and Hertzberg, Z. Physik, 1929, **53**, 52.

¹² M. Polanyi, Atomic Reactions, 1932.

RATE OF REACTION OF SODIUM ATOMS

of $P_{\text{Hal}}/P_{\text{Na}}$ is small and will increase as this ratio decreases. Thus, in order to minimise the influence of any secondary reaction in the flame zones the ratio $P_{\text{Hal}}/P_{\text{Na}}$ was maintained as large as possible in both methods. A comparison of the early results for CHBr₃, CHCl₂Br and CHClBr₂ obtained on the diffusion apparatus (when $P_{\rm Hal}/P_{\rm Na} \sim \frac{1}{4}$) and those obtained later (when $P_{\rm Hal}/P_{\rm Na} \sim 4$) showed that the former values of k are smaller than the latter as is to be expected when there is an increasing tendency to form core flames at low values of $P_{\rm Hal}/P_{\rm Na}$; an increasing preponderance of secondary reaction, on the other hand would be expected to cause an increase in the value of k for the low values of The authors consider that the above facts indicate that the $P_{\rm Hal}/P_{\rm Na}$. collision yields given in this paper are determined by the rates of the primary reaction. The discrepancy between the collision yields given by the two methods in certain instances is at the moment unexplained. The discrepancy, however, is not relevant to the main point made here because it does not introduce contrary trends in reaction rates or influence our correlation of these trends with trends in atomic refraction.

The previous results for polychlorinated methane derivatives are shown in Table VI.

The values given in column 4 are those obtained by the diffusion flame

Compound.	Collison	Collison	Collision
	Yield. ¹	Yield. ²	Yield.
CH ₃ Cl CH ₂ Cl ₂ CHCl ₃ CCl ₄	10,000 900 100 25	7100 310 22 2	760 50 5'5

TABLE VI.

method in the present investigation. Although our results show appreciable divergencies from the earlier results of Hartel, Meer and Polanyi¹ the gradation of collision yields shown by our results is very close to that shown by the results of Heller and Polanyi² The

actual values of the collision yields are, however, a factor of 2-3 times larger than the corresponding yields given by Heller and Polanyi (col. 3).

In a review of the diffusion flame method, Heller⁹ has concluded that the range of collision yields over which the method can be used with accuracy, is 50-5000. The agreement between the results of the diffusion flame and life period methods in our experiments indicate that with the modified experimental conditions the range of the diffusion flame method can be extended to collision yields as low as ten, and perhaps five. This extension is due to the use of low carrier gas pressures (high values of δ) which enable the ratio of $P_{\rm Hal}/P_{\rm Na}$ to be maintained at substantially high values even for very fast reactions, which would otherwise tend to give " core " flames.

In the schematic presentation of the results (Table V) the triangle for the halides which contain C, H, Br and Cl can be divided into a number of series by taking compounds lying along any particular straight line. The arrows indicate trends of decreasing collision yields, *i.e.* increasing reaction velocity, or increasing atomic refraction per bromine or chlorine atom as explained above. It can be seen that the whole of the results are embraced by the generalisation that an increase in atomic refraction goes parallel to a decrease in collision yields. Particular instances of this are :—

(a)
$$\begin{array}{ccc} 7^{100} & \mathbf{I35} & \mathbf{I1\cdot4} \\ \mathrm{CH}_{3}\mathrm{Cl} \longrightarrow \mathrm{CH}_{3}\mathrm{Br} \longrightarrow \mathrm{CH}_{3}\mathrm{I} \\ \mathbf{6\cdot 19} & \mathbf{8\cdot 19} & \mathbf{I3\cdot 26} \end{array}$$

J. N. HARESNAPE, J. M. STEVELS AND E. WARHURST 471

In this case the actual reaction changes along the series; a different halogen atom is removed by the reaction in each case.

(b) In a homogeneous series, *i.e.* only one halogen involved, increase of the number of halogen atoms causes an increase in atomic refraction per halogen atom and a decrease in collision yield, e.g.



This parallelism has been pointed out previously by one of the authors in the case of the series of chlorides.³ The same effect is exhibited in the case of mixed halides, e.g.

$$\begin{array}{ccc} 26 & 2 \cdot 8 \\ \mathrm{CH}_2\mathrm{ClBr} & \longrightarrow & \mathrm{CHClBr}_2 \\ 8 \cdot 42 & 8 \cdot 94 \end{array}$$

Presumably $CClBr_3$ where there is a further increase in the atomic refraction per bromine atom, would react faster than $CHClBr_2$.

(c) In the case of a series of mixed halides each containing bromine increase in the number of chlorine atoms causes an increase in atomic refraction per bromine atom and a decrease in collision yield.

 $\begin{array}{c} {}^{135}_{\mathrm{CH_3Br}} \longrightarrow {}^{26}_{\mathrm{H_2ClBr}} \longrightarrow {}^{4\cdot4}_{\mathrm{CHCl_2Br}} \longrightarrow {}^{1\cdot7}_{\mathrm{CCl_3Br}}_{8\cdot19} \longrightarrow {}^{1\cdot7}_{\mathrm{CCl_3Br}}_{8\cdot65} \longrightarrow {}^{1\cdot7}_{\mathrm{S\cdot88}} \\ {}^{13\cdot2}_{\mathrm{CH_2Br_2}} \longrightarrow {}^{2\cdot8}_{\mathrm{CHClBr_2}}_{\mathrm{S\cdot71}} \longrightarrow {}^{2\cdot8}_{\mathrm{S\cdot94}} \end{array}$

(d) Replacement of H by F, F by Cl, or Cl by Br in a bromide results in an increased atomic refraction per bromine atom and a decreased collision yield, e.g.

13·2 CH ₂ Br ₂ - 8·71	$\xrightarrow{11}^{*} \text{CHFBr}_2 \longrightarrow \underset{8.92}{\overset{8.92}{}}$	$\rightarrow \begin{array}{c} 2 \cdot 8 \\ \text{CHClBr}_2 \\ 8 \cdot 94 \end{array}$	$\rightarrow \begin{array}{c} {}^{1\cdot4} \\ {\rm CHBr}_{3} \\ 9^{\cdot23} \end{array}$
4∙4 CHCl₂Br 8∙65	$\xrightarrow{2\cdot8} CHClBr_2 - 8\cdot94$	$\xrightarrow{I\cdot4} CHBr_3 \\ 9\cdot23$	
26 CH ₂ ClBr 8·42	$\xrightarrow{I3\cdot 2} CH_2Br_2 \\ \xrightarrow{8\cdot 71}$		

The parallelism between the decreasing force constant for the C—Cl bonds and the increasing reaction rate, along a series $CH_3Cl \rightarrow CCl_4$ has already been pointed out.² It has also been shown that there is a progressive increase in atomic refraction of the chlorine atoms along this series.³ Our results show that there is a parallelism between the increase

* This value is the collision yield given by the Life Period Method.

472 PROTECTIVE OXIDE FILMS ON METALS, II

in reaction rate and atomic refraction which extends over all the polyhalogenated methane derivatives. In the case of the series $CH_3Br\rightarrow CBr_4$ we have a further instance of a progressive decrease in force constant of the C—Br bond along the series from CH_3Br to CBr_4 .⁵ It seems probable, therefore, that in all these polyhalogenated methane derivatives, increase in atomic refraction or reaction velocity will run parallel to decreasing force constants for the particular C—Hal bonds. Furthermore, it has been pointed out by Sidgwick ¹³ that there is a small decrease in the C—Cl bond strengths in the series $CH_3Cl \rightarrow CCl_4$, the values being 74.7, 72.5 and 72.6 k.cal./mol. for CH_3Cl , $CHCl_3$ and CCl_4 respectively. In view of this it might be concluded that the increases in reaction rate and atomic refraction also run parallel to a decrease in bond strength throughout the whole series of methane derivatives. However, there is, at present, no further bond strength data to confirm such a conclusion.

At the present moment it is not possible to deal with these parallelisms in a quantitative manner with any degree of certainty, and further clarification must await advances in the theoretical methods available for treating reactions involving such polyatomic molecules.

In conclusion, the authors wish to thank Professor Polanyi for much helpful advice during the work, Professor Van Arkel, of Leiden University, for the organic halides, and the D.S.I.R. for a research grant to one of us (J.N.H.).

Department of Chemistry, The University, Manchester.

13 Sidgwick, The Covalent Link in Chemistry, p. 121.