Reaction of Hydrogen Atoms with Halogeno-Methanes

Part 3.*-Chloroform, Deuterochloroform and Bromodichloromethane

BY D. T. CLARK † AND J. M. TEDDER ‡

Dept. of Chemistry, The University, Sheffield 10

Received 30th June, 1965

The reaction of hydrogen atoms with chloroform, deuterochloroform and bromodichloromethane has been investigated. The mechanisms of the reactions are similar to those discussed in parts 1 and 2 only the reactions are complicated by the occurrence of hydrogen (or deuterium) abstraction as well as halogen-atom abstraction. The initially formed trihalogenomethyl and dihalogenomethyl radicals combine with hydrogen atoms to form vibrationally excited halogenomethanes. From the results it has been possible to compare the relative rates of abstraction of hydrogen and halogen and to deduce the fate of the different vibrationally excited molecules.

The results of parts 1 and 2 together with the results from the present paper are combined and the following relative rates of the initial abstraction steps are deduced : (i) the relative rates of abstraction of chlorine from different halogenomethanes CCl₂Br—Cl, 1; CDCl₂—Cl, 1·2; CCl₃—Cl, 1·3; CCl₂F—Cl, 2·0; (ii) the relative rates of halogen (or hydrogen) abstraction from the same molecule k_{Br}/k_{Cl} , 1·5-1·6; $k_{H(D)}/k_{Cl}$, 3·3-3·4; k_{Cl}/k_{F} , 4·7. In a similar way the stabilization/decomposition ratios of the various vibrationally excited molecules are compared.

Part 1 described the study of hydrogen atoms, generated in a Woods' tube with CCl₄.¹ In part 2 this study was extended to bromotrichloromethane and fluorotrichloromethane.² It is the purpose of the present paper to describe the extension of these studies to molecules containing hydrogen and deuterium, and chloroform, deuterochloroform and bromodichloromethane have been investigated. No previous quantitative study of these reactions could be found.

EXPERIMENTAL

MATERIALS

Commercial chloroform was purified by preparative gas chromatography on an Aerograph Autoprep apparatus using a 20 ft. $\times \frac{3}{8}$ in. diam. column packed with 10 % silicone oil on Celite 60/80 mesh at 20°C. The purified material was stored in the dark in an atmosphere of nitrogen. Deuterochloroform was obtained from Messrs. Light and Co., and was stated to contain 2 % of the protium compound as the only impurity. Gas chromatographic analysis showed only one peak and mass and infra-red spectroscopic analysis indicated 2·1 parts of CHCl₃ to 100 parts CDCl₃. The preparation of bromodichloromethane is described in part 2.

* This paper is also considered to be part 10 of a general series entitled, Free Radical Substitution in Aliphatic Compounds.

† present address: Department of Chemistry, California Institute of Technology, Pasadena, U.S.A.

‡ present address : Department of Chemistry, Queen's College, Dundee.

METHOD

The apparatus and basic methods have been described in part 1. In the study of deuterochloroform, alternative methods of analysis were required in order to estimate chloroform in the presence of deuterochloroform. Both infra-red and mass spectroscopy were used and both required some modification to the experimental procedure. At the end of a run the reaction products were transferred to a small trap as before (see part 1); from here they were trap-to-trap distilled on to phosphorous pentoxide to remove traces of moisture and then distilled back to the original trap. The discharge in the Woods tube tended to become unstable if the run was prolonged over 2 h, and this meant that the amount of product available for analysis was limited to *ca*. 0.2 cm³ even when high chloroform flow rates were used. This small product was divided into four portions (i) $3 \times 4 \mu l$. for gas chromatographic analysis, (ii) $40 \mu l$. for infra-red spectrum of total product. The remaining product was injected into the preparative gas chromatograph (10 ft. $\times \frac{3}{8}$ in. diam. 10 % Carbo-wax on Celite 60/80 mesh at 20°) and the chloroform peak isolated. This was used (iii) $40 \mu l$. for infra-red spectrum of the chloroform fraction and (iv) the remainder for mass spectrum of the chloroform fraction.

INFRA-RED SPECTROSCOPIC ANALYSIS

Bands at 1218 cm⁻¹ in the chloroform spectrum and at 2270 cm⁻¹ in the deuterochloroform spectrum were used for analysis.³ Because the deuterochloroform contained some of the protium compound it was necessary to make up a series of mixtures of the starting deuterochloroform to which increasing amounts of chloroform had been added. Let there be *a* moles of CHCl₃ as impurity in every 100 moles of CDCl₃. Then, if the solution is made up of 1 mole of pure CHCl₃ in *x* moles of impure CDCl₃,

$$\frac{[\text{CDCl}_3]}{[\text{CHCl}_3]} = \frac{x \times 100}{(x+1)a+100}$$

Assuming Beer's Law it was possible to obtain the ratio of the two apparent extinction coefficients,

$$\epsilon_{\text{CDCl}_3}^{2290 \text{ cm}^{-1}} / \epsilon_{\text{CHCl}_3}^{1218 \text{ cm}^{-1}} = 3.8 \pm 0.1 \times 10^{-2}$$

and to calculate the concentration of the protium compound in both the starting material and the reaction products. In a similar way, solutions of methylene dichloride in deuterochloroform were made up and the ratio of the extinction coefficients of the absorption band at 2270 cm^{-1} for deuterochloroform and at 1260 cm^{-1} for methylene dichloride was determined

$$\varepsilon_{\text{CDCI}_3}^{2270 \text{ cm}^{-1}} / \varepsilon_{\text{CH}_2\text{CI}_2}^{1260 \text{ cm}^{-1}} = 3.4 \pm 0.2 \times 10^{-2}.$$

Monodeuteromethylene dichloride is reported to have absorption bands at 1218 cm^{-1} coincident with that of chloroform and at 2270 cm^{-1} coincident with that of deuterochloroform. However, the ratio [CDCl₃]/[CHCl₃] determined from the reaction mixture was identical to the same ratio determined from the separated chloroform fraction of the reaction product. It was assumed, therefore, that the concentration of CHDCl₂ was too small to affect this ratio, and could be neglected.

MASS SPECTROSCOPIC ANALYSIS

Mass spectra were determined on an A.E.I. Ltd., M.S.10 instrument using an ionizing voltage of 35 V. Because the instrument gave poor resolution for masses greater than 70, the peaks 35, 36, 37, 38 and 39 were studied. These were attributed to Cl_{35}^{+} , HCl_{35}^{+} , DCl_{35}^{+} , Cl_{37}^{+} , HCl_{37}^{+} , DCl_{37}^{+} . In the mass spectrum of pure chloroform the intensity ratios of the

mass peaks 35/37 and 36/38 were 3.17 as expected. It was assumed that the ratios $DCl_{35}^{+}/HCl_{35}^{+}$ and $DCl_{37}^{+}/HCl_{37}^{+}$ were proportional to the ratio of the concentrations of chloroform and deuterochloroform in the mixture, i.e.,

peak intensity 37 (due to DCl_{35}^+)/peak intensity $36 = K[CDCl_3]/[CHCl_3]$,

peak intensity 39/peak intensity 38 = K'[CDCl₃./[CHCl₃]]

K and K' were determined by making up mixtures of the impure deuterochloroform and pure chloroform in a similar manner to the infra-red spectra calibration. The values of a (the concentration of CHCl₃ in the starting CDCl₃) determined by infra-red spectra were 2.05 ± 0.06 moles/100 moles of mixture and by mass spectra 2.1 ± 0.36 moles/100 moles. The close agreement of the two methods of analysis is satisfactory.

RESULTS

The experimental results including analysis by both methods are tabulated in table 1 (chloroform) table 2 (deuterochloroform) and table 3 (bromodichloromethane).

IADLE I
I ADLL 1

current in secondary mA	A×104	<i>B</i> ×10 ⁴	C×10 ⁵	relative co CCl ₃ H	oncentrations CCl ₂ H ₂	of products CClH ₃	apparent % reaction	no. of runs
300 300	4∙9 4∙9	2·1 2·1	1·8 5·5	$\begin{array}{c} 17 \cdot 9 \pm 0 \cdot 7 \\ 30 \cdot 6 \pm 0 \cdot 5 \end{array}$	1 1	$\begin{array}{c} 0.081 \pm 0.003 \\ 0.076 \pm 0.001 \end{array}$	5∙7 3∙4	3 5

TABLE 2

current in secondary mA	A×104	B ×104	C×105	relative CCl ₃ D+ CCl ₃ H	concentration CCl ₂ DH+ CCl ₂ H ₂	ns of products CCIDH ₂ + CCIH ₃	apparent % reaction	no. of runs
300	5·1	2·4	$2 \cdot 1$	22 ± 0.20	1	0.073 ± 0.001	4·6	2

A, flow rate of hydrogen through discharge tube, moles/min;

B, flow rate of hydrogen through bubbler, moles/min;

C, flow rate of reactant, moles/min.

All measurements at room temperature and pressure; pressure in the reactor 0.22-0.23 mm Hg in all runs.

TABLE 3

current in secondary mA	A×104	<i>B</i> ×10 ⁴	C×105	CCl ₂ BrH	relative concentratio CClBrH ₂	ons of produc CCl ₂ H ₂	cts CBrH ₃	no. of runs
300	5.0	2.7	2.3	$23 \cdot 5 \pm 1 \cdot 2$	1.22 ± 0.01	1.00	0.47 ± 0.02	3
300	5.0	3.0	2.6	29.6 ± 1.2	1.28 ± 0.08	1.00	0.48 ± 0.02	2
200	5.0	2.7	2.3	49.5 ± 2.2	1.26 ± 0.08	1.00	0.44 ± 0.01	3

A, flow rate of hydrogen through discharge tube, moles/min;

B, flow rate of hydrogen through bubbler, moles/min;

C, flow rate of reactant, moles/min.

All measurement at room temperature and pressure; pressure in the reactor 0.22-0.23 mm Hg in all runs.

REACTION OF HYDROGEN ATOMS

DISCUSSION

It would be possible to derive the reaction sequence from the product ratios as was done in part 1. Instead a similar mechanism will be assumed which can be summarized as follows:



Following the convention adopted in part 2, composite two-stage processes (e.g., the recombination of a halogenomethyl radical with a hydrogen atom to give a vibrationally excited halogenomethane followed by collisional deactivation) are represented by dotted arrows.

The above reaction sequences neglect the following reactions,

$$CCl_2DH^* \rightarrow CCl_2D \cdot + H \cdot$$
$$CCl_2DH^* \rightarrow CCl_2H \cdot + D \cdot$$
$$CCl_2DH^* \rightarrow CCl_2: + HD$$

i.e., CCl_2HD^* is assumed either to be stabilized by collision (k_3) or decompose unimolecularly to yield $CDCl + HCl(k_4)$, or $CHCl + DCl(k_5)$. Experimental support for these ideas is provided by the fact that the ratio $[CHCl_3]/[CH_2Cl_2]$ is, within experimental error, the same as that determined in part 1. Making the same assumptions about steady-state concentrations in the main part of the reactor as before (cf. parts 1 and 2) we can derive the following rate expressions (concentrations refer to product concentrations):

$$[CCl_{3}H]/[CCl_{2}H_{2}] = k_{6}M/k_{7},$$

([CClDH_{2}]+[CClH_{3}])/[CCl_{2}DH] = $(k_{4}+k_{5})/k_{3}M,$
[CCl_{3}H]/[CCl_{2}DH] = $k_{2}\left(1+\frac{k_{4}}{k_{3}M}+\frac{k_{5}}{k_{3}M}\right)/k_{1}\left(1+\frac{k_{7}}{k_{6}M}\right)$

The ratio $k_6M/k_7 = 4.2$ was obtained from the experiments with carbon tetrachloride (part 1) and the same value is obtained in table 2A confirming the absence

current in						relative o	oncentrations of pr	oducts		ratio	no. of	%
secondary mA	$A \times 10^4$	$B \times 10^4$	$C \times 10^{5}$	CCI3D	CC	зн	CCI ₂ H ₂	CCl ₂ DH	CCIH ₃ + CCIDH ₂	CCI ₃ H CCI ₂ H ₂	runs	reaction
300	5.0	1-94	5.2	31・7 ±	1·8 0·74	±0.19 0.	176 ± 0.045	0.82 ± 0.05	0.077 ± 0.001	4.2	7	5.4
300	5.1	2:4	2.1	21·2±(0.2 0.83 :	±0.05 0.	198 ± 0.015	0.80 ± 0.02	0.073 ± 0.001	4.2	2	<u>0</u> 6
300	5.0	2.8	7.5	81·3±	1·3 0·87	±0.15 0.	20 ±0·06	0·80±0·06	0.071 ± 0.001	$4\cdot 3\pm 0\cdot 9$	2	2·3
						T	ABLE 2B					
current in secondary mA	$A \times 10^4$	$B \times 10^4$	$C \times 10^5$	$\frac{\rm HCl}{\rm H_2} \times 10^2$	ccl ₃ D	CCI3H	CCl ₂ H ₂	CCl2DH	CCIH ₃ +CCIDH ₂ CCIDH ₂	CCI3D CCI3D CCI3H	no. of runs	% reaction
300	5-0	1.8	4.8	11.0	31 ·9±0·1	1.17 ± 0.07	0.16 ± 0.03	0.84 ± 0.03	0.046 ± 0.003	7-4 ±1-2	7	6.4
A, flow	rate of 1	ıydrogen	through	ı discharge	tube, moles/1	nin;						

D. T. CLARK AND J. M. TEDDER

B, flow rate of hydrogen through bubbler, moles/min; *C*, flow rate of reactant, moles/min. All measurements at room temperature and pressure; pressure in the reactor 0.22-0.23 mm Hg in all runs.

409

TABLE 2A

410

REACTION OF HYDROGEN ATOMS

of isotopic exchange. From the present results we also have

$$\frac{[\text{CCl}_2\text{DH}]}{[\text{CClDH}_2] + [\text{CClH}_3]} = 10.9, \quad \therefore \frac{k_3M}{k_4 + k_5} = 10.9 = \frac{\text{stabilization}}{\text{decomposition}} \text{ ratio of CHDCl}_2^*,$$
$$\frac{[\text{CCl}_3\text{H}]}{[\text{CCl}_2\text{DH}]} \approx 1, \quad \therefore \frac{k_2}{k_1} \frac{(1 + 0.238)}{(1 + 1/10.9)} = 1.1.$$

We next consider the effect of adding hydrogen chloride. The ratios $[CCl_3H]/[CCl_2H_2]$ and $[CCl_2DH]/[CClDH_2] + [CClH_3]$ increase markedly and we account for this by considering the following additional reactions (cf. part 1):

 $CCID:+HCl \rightarrow CCl_{2}HD$ $CCIH:+HCl \rightarrow CCl_{2}H_{2}$ $CCIH:+HCl \rightarrow CCl_{2}H_{2}$ $CCl_{2}:+HCl \rightarrow CCl_{3}H.$ row become

The steady-state expressions now become

$$\frac{[\text{CCl}_2\text{DH}]}{[\text{CClDH}_2] + [\text{CClH}_3]} = \frac{\frac{k_3M}{k_4} + \left(1 + \frac{k_8[\text{H}_2]M}{k_{11}[\text{HCl}]}\right)^{-1}}{\left(1 + \frac{k_{11}[\text{HCl}]}{k_8[\text{H}_2]M}\right)^{-1} + \frac{k_5}{k_4}\left(1 + \frac{k_{12}[\text{HCl}]}{k_9[\text{H}_2]M}\right)^{-1}}$$
$$\frac{[\text{CCl}_3\text{H}]}{[\text{CCl}_2\text{H}_2]} = \frac{\frac{k_6M}{k_7} + \left(1 + \frac{k_{10}[\text{H}_2]M}{k_7}\right)^{-1} + \frac{k_6}{k_4}\left(1 + \frac{k_{10}[\text{H}_2]M}{k_{13}[\text{HCl}]}\right)^{-1}}{\left(1 + \frac{k_{13}[\text{HCl}]}{k_{10}[\text{H}_2]M}\right)^{-1} + \frac{k_4}{k_2}\left(1 + \frac{k_6M}{k_7}\right)\left(1 + \frac{k_9[\text{H}_2]M}{k_{12}[\text{HCl}]}\right)^{-1}\left(1 + \frac{k_3M}{k_5} + \frac{k_4}{k_5}\right)^{-1}}$$

These expressions are too unwieldy and some further simplifying assumptions are necessary. First, we equate k_4 with k_5 . This assumes a negligible isotope effect in the reactions:

$$CCl_2DH^* \rightarrow CClD: + HCl$$

 $CCl_2DH^* \rightarrow CClH: + DCl;$

which is supported by the observations of Shilov and Sabirova who only found a small isotope effect in the pyrolysis of chloroform (this involves a similar mechanism).⁴ The second simplification we make is to assume

$$k_9M/k_{12} = k_8M/k_{11}.$$

This only involves neglecting secondary isotope effects. The simplified expressions are now:

$$\frac{[\text{CCl}_2\text{DH}]}{[\text{CCIDH}_2] + [\text{CCIH}_3]} = \frac{1}{2} \left[\frac{k_3M}{k_4} \left(1 + \frac{k_{11}[\text{HCl}]}{k_8[\text{H}_2]M} \right) + \frac{k_{11}[\text{HCl}]}{k_8[\text{H}_2]M} \right]$$
$$\frac{[\text{CCl}_3\text{H}]}{[\text{CCl}_2\text{H}_2]} = \frac{\frac{k_6M}{k_7} + \left(1 + \frac{k_{10}[\text{H}_2]M}{k_{13}[\text{HCl}]} \right)^{-1}}{\left(1 + \frac{k_{13}[\text{HCl}]}{k_{10}[\text{H}_2]M} \right)^{-1} + \frac{k_1}{k_2} \left(1 + \frac{k_6M}{k_7} \right) \left(1 + \frac{k_8[\text{H}_2]M}{k_{11}[\text{HCl}]} \right)^{-1} \left(2 + \frac{k_3M}{k_5} \right)^{-1}}$$

Inserting the experimental values $k_3M/k_4 = 21.8$ and $[HCl]/[H_2] = 11 \times 10^{-2}$ into the first of the above expressions we obtain

$$k_{11}/k_8M = 5.9.$$

The ratio $k_{13}/k_{10}M$ is 6.3 from part 1. The whole of the right-hand side of the second expression may now be calculated giving a value of 6.9 which can be compared with the experimental ratio [CCl₃H]/[CCl₂H₂] of 7.4. Within experimental error these are the same and this provides strong evidence for the proposed reaction sequence.

The reaction of hydrogen atoms with bromodichloromethane can lead to three different abstraction processes. (To avoid confusion with the reactions of hydrogen atoms with chloroform discussed above we use primes to distinguish rate constants involving bromodichloromethane.)



The subsequent reactions of CCl_2Br (produced in reaction (1')) and $CHCl_2$ (produced in reaction (2')) are known from the work described in part 2 and in the present paper. The ratio of products obtained from the reactions of vibrationally excited bromodichloromethane ($CCl_2Br + H$), described in part 2 was

$$CCl_2BrH$$
, 0.72; CCl_2H_2 , 0.04; $CClBrH_2$, 0.19; $CBrH_3$, 0.05,

and the ratio of the products from vibrationally excited methylene dichloride $(CHCl_2 + H)$ was

$$CCl_2H_2$$
, 0.91; $CClH_3$, 0.09.

The CHClBr radical produced in reaction (3') will combine with a hydrogen atom to yield vibrationally excited bromochloromethane. In part 2 we had a vibrationally excited bromochloromethane produced by the reaction of bromochloromethylene with a hydrogen molecule.

CClBr:+H₂
$$\rightarrow$$
CClBrH^{*}₂, $\Delta H \approx -65$ cal/mole.

In this case the stabilization/decomposition ratio was equal to 3.8. The excess energy in that case was ca. 65 kcal/mole compared with the present case where it is likely to be ca. 90 kcal, i.e.,

CClBrH·+H·
$$\rightarrow$$
CClBrH^{*}₂, $\Delta H \approx -90$ kcal/mole.

The stabilization/decomposition ratio is likely to be smaller in this case and we assume a value of 3.0. Taking this value we calculate a product ratio

$$CClBrH_2, 0.67; CBrH_3, 0.33.$$

Each of these ratios refer to the products from reactions (1'), (2') and (3') separately. Allowing for statistical probabilities and taking into account the results with chloroform we expect $k'_1 > k'_2 > k'_3$. By a process of trial and error we obtain a ratio of $k'_1 : k'_2 : k'_3$ equal to $3 \cdot 4 : 1 \cdot 6 : 1$ for statistically weighted rate constants, which gives a product spectrum of

 $CClBrH_2$, 1·24; CCl_2H_2 , 1; $CBrH_3$, 0·52;

compared with the experimental values 1.25, 1, 0.47, respectively. The rate constants are clearly of the right magnitude although we must not put too much reliance on their absolute values considering the approximate way in which they were derived. Nonetheless, it is interesting to compare the relative rates of hydrogen chlorine and

bromine abstraction from bromotrichloromethane, chloroform and bromodichloromethane.

	$k^{H(D)}/k^{Cl}$	$k^{\mathrm{Br}}/k^{\mathrm{Cl}}$
CCl ₃ Br		1.5
CCl ₃ D	3.3	
CCl ₂ BrH	3.4	1.6

We thus find that hydrogen abstraction from both chloroform and bromodichloromethane is faster than halogen abstraction when allowance is made for the statistical expectation that halogen abstraction is favoured to hydrogen abstraction in both these molecules by a factor of 3. Both abstraction reactions are exothermic but deuterium (or hydrogen) abstraction is exothermic to ca. 14 kcal/mole whereas chlorine abstraction is exothermic to approximately 30 kcal/mole. This is not the first occasion on which hydrogen abstraction has been found to be preferred to halogen abstraction. Szwarc estimated hydrogen abstraction from chloroform by methyl radicals at 60° to be 200 times faster than chlorine abstraction. The thermochemistry of both reactions is similar and Szwarc attributed the difference to coulombic repulsion between the single electron in the $2p_z$ orbital of the carbon atom of the methyl radical and the non-bonded electron pairs of the halogen. In hydrogen atom reactions this coulombic repulsion would be expected to be less, since the smaller size of the hydrogen 1s orbital would allow closer approach to the halogen atom and partial formation of the hydrogen halogen bond will offset the coulombic repulsion. A reaction perhaps more similar to the present experiments is that of hydrogen atoms with hydrogen bromide. The activation energy for the abstraction of hydrogen from hydrogen bromide, and bromine from molecular bromine by hydrogen atoms is approximately 2 kcal/mole :

> $H \cdot + HBr \rightarrow H_2 + Br \cdot$, $\Delta H \approx -16$ kcal/mole, $H \cdot + Br_2 \rightarrow HBr + Br \cdot$, $\Delta H \approx -40$ kcal/mole,

for both reactions in spite of the large difference in their exothermicity.⁶ As well as offering a possible explanation of the preferential abstraction of hydrogen (or deuterium) in the present results, coulombic repulsion is likely to be an important factor in determining the relative rates of abstraction of different halogen atoms, described in parts 1 and 2. The coulombic repulsion would be expected to decrease with a decrease in the size of the halogen atom.

CONCLUSIONS

If we compare the results reported in parts 1 and 2 as well as the present paper we find that the percentage reaction, in experiments in which the hydrogen atom concentration was constant but the halogenomethane concentration was varied, was approximately proportional to the ratio of the [hydrogen atom]/[reactant] ratio, i.e.,

% reaction \propto [H•]/[reactant].

The extent of reaction must also depend on the rate constant from the abstraction reaction $(CX_4 + H \cdot \rightarrow CX_3 \cdot + HX)$,

 \therefore % reaction = $Kk^{a}[H \cdot]/[reactant].$

If we now compare two different reactants A and B studied under the same conditions we have

 $k_{\rm A}^a/k_{\rm B}^a = (\% \text{ reaction of } A \times \text{flow rate } A)/(\% \text{ reaction of } B \times \text{flow rate } B);$

413

e.g., from parts 1 and 2, we have

$$\therefore k^a_{\text{CCl}_4}/k^a_{\text{CCl}_3\text{Br}} = 3.3 \times 4.2/11.6 \times 1.0.$$

Now $k_{CCl_4}^a = 4k_{CCl_4}^{Cl}$, where $k_{CCl_4}^{Cl}$ is the rate constant for abstraction per chlorine atom. Similarly

$$k_{\rm CCI_{3}Br}^{a} = 3k_{\rm CCI_{3}Br}^{\rm CI} + k_{\rm CCI_{3}Br}^{\rm Br}$$

From part 2 we have

$$k_{\rm CCl_3Br}^a = 4.5 k_{\rm CCl_3Br}^{\rm Cl}$$
$$k_{\rm CCl_4}^{\rm Cl} / k_{\rm CCl_3Br}^{\rm Cl} = 1.34.$$

Carrying the same argument through for the other reactions we obtain a series of relative rates of chlorine abstraction from the different halogenomethanes :

 CCl_2Br —Cl, 1; $CDCl_2$ — $Cl, 1\cdot 2$; CCl_3 — $Cl, 1\cdot 3$; CCl_2F — $Cl, 2\cdot 0$.

The accuracy of these calculations is unlikely to be high. Nonetheless, it is interesting to observe how small the variation in the rate of chlorine abstraction is. Taking the two extremes CCl_2Br —Cl and CCl_2F —Cl the greater reactivity of the fluoro compound is the reverse to that expected on thermochemical grounds and suggests that polar forces may play a significant role in the transition state.

The relative rates of abstraction of different atoms from the same molecule are tabulated below.

halogenomethane	relative rate constant	numerical value
CCl ₃ Br	$k_{\rm Br}/k_{\rm Cl}$	1.5
CCl_3D	$k_{\rm D}/k_{\rm Cl}$	3.3
CCl ₃ F	$k/_{\rm F}k_{\rm Cl}$	0.21
CCl ₂ HBr	$k_{\rm Br}/k_{\rm Cl}$	1.6
CCl ₂ HBr	kH/kCl	3.4

The relative stabilization/decomposition rates for the vibrationally excited halogenomethanes are tabulated together with an approximate value of their excess energy.

excited molecule	stabilization decomposition	approx. vibrational energy, kcal mole ⁻¹
CCl ₃ H	4.2	90
CCl ₂ DH	10.9	90
CCl ₂ BrH	2.6	90
CCl ₂ FH	1.8	90
CClBrH ₂	3.0	90
CCl_2H_2	very large	65
CClFH ₂	very large	65

The modes of unimolecular decomposition of some of these molecules to yield a carbene and a molecule of hydrogen halide are summarized below.

excited molecule	approx. vibrational energy, kcal mole ⁻¹	products	relative rate
CCl ₂ BrH	90	$CCl_2 + HBr$	1
		CClBr+HCl	6
CClBrH ₂	65	CClH+HBr	1
		CBrH+HCl	5-10
CCl ₂ FH	90	CClF+HCl	1
		CCl ₂ +HF	1.3

REACTION OF HYDROGEN ATOMS

One feature of the present investigation has been the discovery of the generality of the unimolecular decomposition of molecules of the type CX_2YH (X = halogen, Y = hydrogen or halogen) by the carbene route. It seems probable that this decomposition will have a lower activation than the alternative reaction involving simply C-X or C-Y bond fission. On the other hand, the carbene route will involve a cyclic transition state and probably therefore a lower pre-exponential factor. This means that at low temperatures, as in the present study, decomposition will be almost exclusively by the carbene route. At very high temperatures, the reverse will be At intermediate temperatures there is likely to be a duality of mechanism and true. this may account for the complexity of many pyrolytic studies (e.g., ref. (7)).

¹ Clark and Tedder, Trans. Faraday Soc., part 1.

² Clark and Tedder, Trans. Faraday Soc., part 2.

³ Shimanouchi and Sukui, J. Mol. Spectr., 1962, 8, 222.

⁴ Shilov and Sabirova, Russ. J. Physics. Chem., 1960, 34, 408.

⁵ Fox, Evans and Szwarc, Trans. Faraday Soc., 1961, 57, 1915. ⁶ Britton and Cole, J. Physic. Chem., 1961, 65, 1302.

⁷ Sehon and Szwarc, Proc. Roy. Soc. A, 1951, 209, 110.