218. *The Reactions of Fluorine Atoms with Alkanes.*

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The hydrogen transfer reactions of fluorine atoms with methane, ethane, propane, cyclopropane, n-butane, isobutane, and neopentane have been studied between $-95°$ and $100°$ by a competitive method based on analysis of the fluorides produced. The activation-energy differences are very small. The A factors of the reactions have been discussed in terms of transition-state theory and compared with those found for chlorine atoms.

THE gas-phase reactions of chlorine atoms with saturated hydrocarbons have recently been extensively studied.[1,2] Kistiakowsky, Van Artsdalen, and their co-workers have investigated the reactions of bromine atoms with alkanes.[3] Much less is known about the reactions by which fluorine atoms abstract hydrogen atoms from saturated compounds. These reactions are interesting because they form a unique series involving three similar atomic reactants. The only comparable series of reactions about which much is known is that involving the lower alkyl radicals, but our knowledge of these reactions is still fragmentary. The halogen atoms offer the considerable advantage for theoretical interpretation in that we know the strengths of the bonds involved to a high accuracy. It might therefore be possible to interpret the activation energies or differences in the activation energies of their reactions. There is more hope, however, that the variations in the A factors of the reactions can be understood. The transition states for the reaction of a hydrocarbon with the different halogens differ only in the mass of the attacking atoms and slightly in the lengths of the bonds and their flexibility.

The rate constants for the attack of bromine atoms on hydrocarbons, according to the equation $Br + RH = R + HBr$, have been measured absolutely, though the values obtained for the higher hydrocarbons are doubtful. The chlorinations have been followed competitively both by the study of the relative rates of consumption of two hydrocarbons in a mixture [1] and by measuring the rates of formation of the distinctive products from the reactions [2] $R + Cl_2 = RCl + Cl$. Reactions in solution have been studied in this way for some years. The very small amounts of the products formed in gaseous systems made the analyses difficult until the invention of gas chromatography. Knox [4] first applied this technique to the chlorination of methane, ethane, and propane. He made use of the fact that when the consumption of RH is small the rate constants for the attack of a chlorine atom on two hydrocarbons R^1H and R^2H are given by:

$$\frac{k_1}{k_2} = \frac{R^1Cl}{R^2Cl} \times \frac{[R^2H]}{[R^1H]} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

This approach has the advantage that attack on different positions in a molecule yields different products.

The present work involves the application of this technique to the study of fluorine atoms about which very little is known, though the reactions of fluorine with n-butane and isobutane have recently been investigated.[5] The reactions of fluorine atoms have been neglected partly because of experimental difficulty and partly because the reactions are so exothermic that they have been difficult to control. Consequently the reactions of elementary fluorine have been chiefly studied in ill-defined systems designed to conduct away the excessive heat. The products obtained were usually polyfluorides and the analyses are not susceptible to kinetic evaluation.

[1] Pritchard, Pyke, and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629.
[2] Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937.
[3] For references see Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955.
[4] Knox, *Chem. and Ind.*, 1955, 1631.
[5] Anson, Fredricks, and Tedder, *J.*, 1959, 918.

<div align="center">EXPERIMENTAL</div>

Materials.—Fluorine was generated with an I.C.I. medium-temperature 10 A cell and collected in a soft-glass bulb from which oxygen was removed by flushing with nitrogen. Samples were taken after generation for 5 A-hr. (longer if the cell had not been used for some time). The fluorine was distilled into a soft-glass storage vessel cooled in oxygen boiling under reduced pressure. Fresh samples were taken every 3 days.

The nitrogen (oxygen-free), hydrogen, methane, and cyclopropane were from commercial cylinders. Methane was purified by bulb-to-bulb distillations from liquid oxygen which removed most of the propane, ethane, and ethylene. Carbon dioxide was obtained from a solid block. The butanes were given by the British Petroleum Company and the propane by Imperial Chemical Industries Limited. The ethane and neopentane were of high purity and were obtained from the National Chemical Laboratory. The condensable gases were purified and degassed by bulb-to-bulb distillations and analysed by gas chromatography.

Apparatus.—The high-vacuum system, apart from the fluorine storage vessels, was constructed of Pyrex glass. Stopcocks in contact with fluorine or the reaction products were lubricated with Florube A. The volume of the reaction vessel was 60 c.c. The gas-chromatography system was of standard design with 6 mm. bore columns and a brass thermal conductivity cell with tungsten filaments as detector. Firebrick was of 25—52 mesh.

Procedure.—Small pressures of fluorine were measured on a spoon gauge and introduced by several expansions into a vessel held at the reaction temperature. Either carbon dioxide or nitrogen was mixed with the fluorine as a diluent. The hydrocarbons were measured on a mercury manometer, mixed by convection in a suitable vessel, and expanded into the reaction vessel, the temperature of which was thermostatically controlled by a cooling mixture or vapour jacket. The fluorinating mixture was then expanded into the reaction vessel, where the total pressure was about 16 cm. and the fluorine : hydrocarbon : inert gas ratio was 1 : 20 : 120. The reaction time was varied between 2 and 30 min. without affecting the products. No illumination was required if the fluorine was carefully handled, in agreement with calculations based on the known dissociation constant of elementary fluorine and the probable absolute rate constants of these reactions. The reaction of fluorine with glass, especially Pyrex, yields an inhibitor; oxygen also seems to have some effect. The products were condensed out after passage through a tube of sodium fluoride crystals to remove the hydrogen fluoride.

Hydrogen gas (30—40 cm.^{3} min.$^{-1}$) carried the products to the chromatography columns. The products were identified by their elution times, confirmed for n-butyl fluoride by comparison with a sample kindly supplied by Dr. J. M. Tedder. The amounts of products were found by measurement of peak areas, calibrated by collection of individual products as they came off the column, measurement of their volume on a gas burette, and repassage through the chromatography system to check that there was no loss. Each run yielded about 3 μmoles of fluorides. Within experimental error the sensitivities of the monofluorides were identical with the exception of methyl fluoride which gave a 3% lower response.

*Results.**—Runs were done with the following mixtures and pure hydrocarbons. The ratios of the hydrocarbons in the mixtures were varied between 1·5 : 1 and 1 : 1·5. The fluorine : hydrocarbon ratio was varied between 1 : 10 and 1 : 20. No changes in reactivity accompanied these variations. The fluorine : inert gas ratio was varied between 1 : 70 and 1 : 160, without affecting the results except in the cases noted. The choice of mixtures was determined largely by the ease of analysis. The errors quoted are standard errors throughout, determined by normal statistical procedures.

(1) *Methane–ethane.* 31 Runs were carried out between −75° and 78° with nitrogen as inert gas. Analysis was with 32 ft. columns of 20% nitrobenzene–firebrick. A least-squares treatment of the results shown as an Arrhenius plot in Fig. 1 gave

$$k(\text{ethane})/k(\text{methane}) = (0.38 \pm 0.04) \exp \left[(928 \pm 41)/\textbf{\textit{R}T} \right]$$

This expression is obtained directly from the analyses of ethyl fluoride and methyl fluoride and the equation analogous to (1). No allowance is made in this section for the numbers of hydrogen atoms in the reactant molecules.

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* k^{p}, k^{s}, k^{t} relate to reaction at a primary, secondary, or tertiary carbon atom, respectively. Where all the carbon atoms of a molecule are equal this suffix is omitted.

(2) *Ethane–propane.* 21 runs were carried out at 20° and −60° with carbon dioxide as the inert gas. The columns for analysis were 15 ft. of 25% diethyl phthalate–washed Celite, 2 ft. of 25% nitrobenzene–washed Celite, plus 10 ft. of 25% diethyl phthalate–firebrick. The ratio ethyl fluoride : n-propyl fluoride appeared to fall slightly when the fluorine : carbon dioxide ratio was greater than 1 : 100. It was supposed that this indicated that the ethyl fluoride molecules which are formed by an exothermic reaction were not deactivated sufficiently rapidly at the lower relative pressure of inert gas. Some ethyl fluoride then decomposed to ethylene and hydrogen fluoride. Similar behaviour was observed with cyclopropane. It is not easy to determine very small quantities of an alkene in the presence of large amounts of alkane of the same carbon number but the indications were that in no case did the amount of

FIG. 1. *Arrhenius plots for the reactions of fluorine atoms with ethane–methane* (k_e/k_m; *circles*) *and ethane–propane* (k_e/k_p; *crosses*) *mixtures. The filled circles and widened lines indicate two or more coincident points. The figures indicate the number of runs at each temperature.*
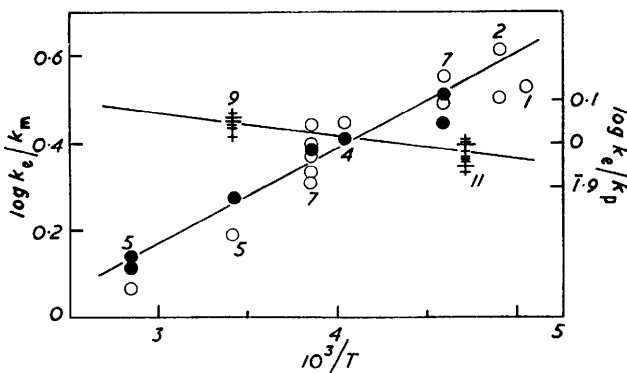
alkene formed exceed 5% of the amount of appropriate alkyl fluoride. The rate constants are again plotted in Fig. 1:

$$k\text{(ethane)}/k^p\text{(propane)} = (1\cdot84 \pm 0\cdot05) \exp\left[-(279 \pm 12)/\boldsymbol{R}T\right]$$

(3) *Propane–n-butane.* 14 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as the inert gas. The columns were 12 ft. of 25% diethyl phthalate–washed Celite, 2 ft. of 25% nitrobenzene–washed Celite plus 5 ft. of diethyl phthalate–firebrick. No activation energy was found.

$$k^p\text{(propane)}/k^p\text{(n-butane)} = 1\cdot11 \pm 0\cdot06$$
$$k^s\text{(propane)}/k^s\text{(n-butane)} = 0\cdot56 \pm 0\cdot04.$$

(4) *Isobutane–n-butane.* 17 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as the inert gas [analysis as for (3)].

$$k^p\text{(isobutane)}/k^p\text{(n-butane)} = 1\cdot57 \pm 0\cdot06$$

(5) *n-Butane–cyclopropane.* 19 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as the inert gas. Columns were 12 ft. of 25% diethyl phthalate–washed Celite plus 5 ft. of 25% diethyl phthalate–firebrick. When the carbon dioxide : fluorine ratio fell below 100 : 1 a three-carbon product other than cyclopropyl fluoride was formed. At a ratio of 60 : 1 it constituted 50% of the C_3 products and at 80 : 1, 30%. It is likely that the unknown product was a fluoride of propene formed by a typical isomerization of the cyclopropane nucleus activated from its exothermic mode of formation. No activation energy was found at high pressures of the inert gas.

$$k^p\text{(n-butane)}/k\text{(cyclopropane)} = 1\cdot02 \pm 0\cdot06$$
$$k^s\text{(n-butane)}/k\text{(cyclopropane)} = 0\cdot80 \pm 0\cdot06$$

(6) *Propane–cyclopropane.* 25 Runs were carried out in the same manner as for (3). The

same dependence of the products on carbon dioxide was found as with (5). Propyl fluorides were not formed by the attack of hydrogen fluoride on cyclopropane.

$$k^{\mathrm{p}}(\text{propane})/k(\text{cyclopropane}) = 1\cdot13 \pm 0\cdot15$$
$$k^{\mathrm{s}}(\text{propane})/k(\text{cyclopropane}) = 0\cdot45 \pm 0\cdot05$$

(7) *Isobutane–neopentane.* 14 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as inert gas. Columns were 12 ft. of 25% diethyl phthalate–washed Celite plus 2 ft. of 25% nitrobenzene–washed Celite.

$$k(\text{neopentane})/k^{\mathrm{p}}(\text{isobutane}) = 1\cdot22 \pm 0\cdot04$$

(8) *Propane.* 74 Runs were carried out (25 with cyclopropane, 21 with ethane, 14 with n-butane) between 36° and −99°. Carbon dioxide and nitrogen were used separately as inert gases with similar results. Columns of 15 ft. of 15% nitrobenzene–firebrick were sometimes used.

$$k^{\mathrm{p}}(\text{propane})/k^{\mathrm{s}}(\text{propane}) = 2\cdot48 \pm 0\cdot08$$

(9) *n-Butane.* 124 Runs were carried out (14 with propane, 17 with isobutane, 19 with cyclopropane) at 25°, −25°, and −60° with carbon dioxide as the inert gas. Columns of 10 ft. of 25% dinonyl phthalate–firebrick plus 2 ft. of 25% nitrobenzene–washed Celite were sometimes used.

$$k^{\mathrm{p}}(\text{n-butane})/k^{\mathrm{s}}(\text{n-butane}) = 1\cdot30 \pm 0\cdot09$$

(10) *Isobutane.* 16 Runs were carried out at 20°, −25°, and −60° with carbon dioxide as inert gas. Columns were 12 ft. of 25% diethyl phthalate–washed Celite plus 5 ft. of 25% diethyl phthalate–firebrick. An amount of olefin equal to about 5% of the fluorides was always formed.

$$k^{\mathrm{p}}(\text{isobutane})/k^{\mathrm{t}}(\text{isobutane}) = 6\cdot41 \pm 0\cdot34.$$

DISCUSSION

The experimental results are summarized in Table 1. For convenience it has been assumed that the reaction of a fluorine atom with a hydrogen atom in one of the higher

TABLE 1. *Reactions of fluorine and chlorine atoms with alkanes.*

Tond Type	$\log_{10} A$ (mole^{-1} cm.^{3} sec.$^{-1}$)	E (kcal. mole^{-1})	E (kcal. mole^{-1})
	Fluorine		Chlorine
H$_2$	13·67	1710[6]	5500 [a]
CH$_4$	13·39	1210	3850[1], 3850[2]
Primary C–H bonds			
C$_2$H$_6$	12·90 *	280	1000[1], 1040[2]
C$_3$H$_8$	12·64	0	1000[2]
n-C$_4$H$_{10}$	12·59	0	790[2]
iso-C$_4$H$_{10}$	12·61	0	820[2]
neo-C$_5$H$_{12}$	12·58	0	920[2]
Secondary C–H bonds			
cyclo-C$_3$H$_6$	12·59	0	4140[2]
C$_3$H$_8$	12·71	0	680[2]
n-C$_4$H$_{10}$	12·67	0	270[2]
Tertiary C–H bond			
iso-C$_4$H$_{10}$	12·76	0	20[2]

The A factors listed are for reactions of individual hydrogen atoms of the standard type.
* Assumed value.
[a] Ashmore and Chanmugam, *Trans. Faraday Soc.*, 1953, **49**, 254. Other references as in text.

hydrocarbons requires no activation energy. It has also been assumed that the logarithm of the A factor for the attack of a fluorine atom on a single hydrogen atom in ethane is 12·90 mole^{-1} cm.^{3} sec.$^{-1}$. All the results for fluorine atoms were obtained in this work with the exception of the results for hydrogen which are taken from Mercer and Pritchard [6]

[6] Mercer and Pritchard, personal communication.

who used Pritchard, Pyke, and Trotman-Dickenson's [1] method to study hydrogen–methane mixtures. They found

$$k(\text{methane})/k(\text{hydrogen}) = 1 \cdot 05 \exp\left[-(500 \pm 200)/RT\right]$$

Hydrogen–methane mixtures were not studied in the present work because the hydrogen fluoride formed could not be determined accurately.

The present results with the butanes are in good agreement with those of Anson, Fredericks, and Tedder [5] who found at 25° that $k^p(\text{n-butane})/k^s(\text{n-butane}) = 1 \cdot 20 \pm 0 \cdot 17$ $(1 \cdot 30 \pm 0 \cdot 09)$ and $k^p(\text{isobutane})/k^t \text{isobutane}) = 6 \cdot 47 \pm 0 \cdot 70$ $(6 \cdot 41 \pm 0 \cdot 34)$; the present values are placed in parentheses.

Activation Energies of Fluorine Atom Reactions.—Although the assumption that fluorine atoms react with no activation energy with the higher hydrocarbons may not be precisely correct, it is unlikely that any of the activation energies are large. First, the absence of any activation-energy difference between the attack on the primary and tertiary hydrogen atoms in isobutane, together with the absence of differences for the other higher hydrocarbons, is an indication that no activation energies are involved. Secondly, there is a marked parallelism between the activation energies for the attack of fluorine and chlorine atoms on hydrogen, methane, and ethane. The activation energies for the attack of chlorine atoms on the higher hydrocarbons are very small, those for fluorine must be smaller. The assumption of zero energies of activation is therefore not likely to be in error by more than a few tens of calories at the most. Too little is known about the factors that determine activation energies for the detailed consideration of these small energies to be profitable.

A Factors of Fluorine Atom Reactions.—According to transition-state theory the A factor for a bimolecular reaction is given by [7]

$$A = e^2 \cdot (kT/h) \exp\left[(\Delta S^{\ddagger}_{\text{tr}} + \Delta S^{\ddagger}_{\text{rot}} + \Delta S^{\ddagger}_{\text{vib}})/R\right]$$

The translational entropy of activation for reaction

$$\text{RH} + \text{F} \rightleftharpoons \text{RHF} \longrightarrow \text{R} + \text{HF}$$

is given exactly by

$$\Delta S^{\ddagger}_{\text{tr}} = 1 \cdot 5R \ln (M^{\ddagger}/M) - 14 \cdot 75 \text{ cal. mole}^{-1}$$

where $M^{\ddagger}$ and M are the molecular weights of RHF and RH respectively and the standard state is 1 mole cm.$^{-3}$.

The rotational entropy of activation may be obtained from

$$\Delta S^{\ddagger}_{\text{rot}} = 0 \cdot 5R \ln (A^{\ddagger}B^{\ddagger}C^{\ddagger}/ABC)$$

where $A^{\ddagger}B^{\ddagger}C^{\ddagger}$ and ABC are the products of the principal moments of inertia of RHF and RH. This value is for reaction at a single hydrogen atom of any type; inclusion of the symmetry numbers in the expression would yield $\Delta S^{\ddagger}_{\text{rot}}$ appropriate to reaction with all the hydrogen atoms of a given type in the molecule. The ABC values can be evaluated graphically with sufficient accuracy by assuming suitable configurations and bond lengths in RH and RHF. C–H and C–C distances have been taken throughout as $1 \cdot 10$ and $1 \cdot 54$ Å except for the half-order bonds in the complexes, *i.e.*, the bonds $\geqslant$C–H–F. After Pauling [8] we have assumed that they are $0 \cdot 18$ Å longer than the corresponding single bonds. All bond angles have been taken as tetrahedral. $A^{\ddagger}B^{\ddagger}C^{\ddagger}/ABC$ is not very sensitive to the exact lengths chosen and increases in the C–F distances by $0 \cdot 1$ Å, for example, lead to increases of only about 3% in the ratio. More serious errors arise from the difficulty of choosing the

[7] Glasstone, Laidler, and Eyring, " Theory of Rate Processes," McGraw Hill Book Co., New York, 1941.
[8] Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, New York, 1940.

correct configuration of the molecules, since any molecule containing three or more carbon atoms in an unlinked chain may have an infinite number of configurations depending upon the degree of rotation about each C–C bond. An approximate method of dealing with the situation is to work out ABC values for a few extreme configurations and to take the average value.[9] Fortunately the errors introduced are probably not greater than $\pm10\%$. For n-propyl fluoride two configurations were chosen with the fluorine atom as near to and as far from the centre of gravity of the propane molecule as possible. The values of $A^{\ddagger}B^{\ddagger}C^{\ddagger}$ were respectively 1.04×10^5 and 0.99×10^5 AMW (Ångström molecular weight units). For 2-methylpropyl fluoride $[(CH_3)_2CH \cdot CH_2F]$ the two configurations chosen were those with the fluorine atom as near to and as far from the tertiary hydrogen atom as possible. Rather more divergent values were obtained, 4.7×10^6 and 3.7×10^6 AMW. For the n-butane molecule an expanded chain and bent chain structure are possible. However, calculations by Knox and Nelson for the corresponding chlorine atom complexes showed that almost identical results were obtained with the two structures. Accordingly the moments of inertia have been calculated only for the extended form of the hydro-carbon and for the complex with the fluorine atom as close to the centre of gravity of the butane molecule as possible.

The calculation of the vibrational entropy of activation is much less certain. It is difficult to assign frequencies to the vibrations in RH but quite impossible to do so accurately for the complexes. However, it is likely that many of the vibrations in RH

FIG. 2.
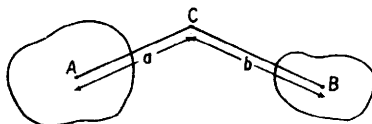
will be little changed by the addition of a fluorine atom and their contributions to $\Delta S^{\ddagger}_{\text{vib}}$ will largely cancel. Only a few vibrations intimately connected with the part of the molecule to which the fluorine atom is attached will give rise to important contributions. These vibrations will be the C–H stretching and C–H wagging in the hydrocarbon which are replaced by five new vibrations in the activated complex. The C–H stretching becomes the reaction co-ordinate and the C–H wagging becomes the wagging of H–F against the rest of the hydrocarbon. The three additional vibrations are the symmetrical stretching of the C–H–F bonds and the doubly-degenerate bending of the C–H–F bonds.

Approximate calculations on this basis have been made by Pitzer[10] and by Wilson and Johnston[11] for various abstraction reactions. They hinge upon the assumption that the force constants for these vibrations do not change with R. Pitzer used the observed A factor of the reaction $Cl + H_2 = HCl + H$ to deduce $\Delta S^{\ddagger}_{\text{vib}}$ and calculated that the probable bending and stretching frequencies in the complex were 560 cm.$^{-1}$ and 1460 cm.$^{-1}$ respectively. Assuming that the force constants for these modes of vibration were the same in the CH_3–H–Cl complex he calculated an A factor for the reaction of chlorine with methane. No account was taken in this calculation of the wagging vibration of the H–Cl against the methyl group in the complex. To calculate the change of frequency due to a change of R, the stretching frequencies are reduced in the ratio of the root of the reduced mass, and the bending frequencies in the ratio of the root of the reduced moment of inertia. For a molecule (see Fig. 2) consisting of two molecular fragments A and B joined to a common atom C the reduced mass is

$$\mu = m_a m_b / (m_a + m_b)$$

[9] Knox and Trotman-Dickenson, *J. Phys. Chem.*, 1956, **60**, 1367.
[10] Pitzer, *J. Amer. Chem. Soc.*, 1957, **79**, 1804.
[11] Wilson and Johnston, *J. Amer. Chem. Soc.*, 1957, **79**, 29.

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The reduced moment of inertia is given by

$$\lambda = J_a J_b/(J_a + J_b)$$

where
$$J_a = \frac{(m_a + m_c)m_b}{(m_a + m_b + m_c)} a^2 + I_a ; \quad J_b = \frac{(m_b + m_c)m_a}{(m_a + m_b + m_c)} b^2 + I_b$$

The m's are the masses of A, B, and C; I_a, I_b are the moments of inertia of A and B about axes through their centres of gravity and perpendicular to the plane of vibration and a and b are the distances of C from the centres of gravity of A and B respectively (Schlapp's formula). When m_c is small in comparison with m_a and m_b (true for all complexes except H–H–F), the formulæ reduce approximately to

$$J_a = \mu a^2 + I_a; \quad J_b = \mu b^2 + I_b$$

Calculations for the RHCl complexes have been carried out by Knox and Nelson [2] and are now extended to the fluorine atom complexes. The values for the various $\Delta S^{\ddagger}_{vib}$ are given in Table 2.

With chlorine atoms the absolute rate constant for the reaction with hydrogen is known over a range 25—700° and Pitzer's calculations refer to the mid-temperature of this range. The discrepancy in Table 2 between the calculated and theoretical values for the reaction

TABLE 2. *A Factors for Fluorine and Chlorine Atom Reactions.*

				F + RH			Cl + RH[2]		
Bond type RH	$\Delta S^{\ddagger}_{tr}$ +14·75	$\Delta S^{\ddagger}_{rot}$	$\Delta S^{\ddagger}_{vib}$	log A (calc.)	log A (exp)	log $\frac{A_{exp}}{A_{calc}}$	log A (calc.)	log A (exp)	log $\frac{A_{exp}}{A_{calc}}$
H$_2$	6·99	4·92	0·8	13·22	13·67	+0·50	13·37	13·60	+0·23
CH$_4$	2·31	5·51	4·8	13·20	13·39	+0·24	13·46	12·78	−0·68
Primary C–H bonds									
C$_2$H$_6$	1·46	3·73	6·1	12·90	12·90	0·00	13·28	13·18	−0·10
C$_3$H$_8$	1·07	2·66	6·6	12·69	12·64	−0·05	12·98	13·23	+0·25
n-C$_4$H$_{10}$	0·84	2·33	6·9	12·62	12·59	−0·03	12·95	13·15	+0·20
iso-C$_4$H$_{10}$	0·84	2·05	6·9	12·57	12·61	+0·04	12·87	13·11	+0·24
neo-C$_5$H$_{12}$	0·68	1·70	7·1	12·52	12·58	+0·06	12·84	13·15	+0·31
Secondary C–H bonds									
cyclo-C$_3$H$_6$	1·11	3·13	6·4	12·76	12·59	−0·17	13·11	12·95	−0·16
C$_3$H$_8$	1·07	2·88	6·6	12·74	12·71	−0·03	13·04	13·56	+0·52
cyclo-C$_4$H$_8$							12·95	13·51	+0·56
n-C$_4$H$_{10}$	0·84	2·33	6·7	12·59	12·67	+0·08	12·84	13·34	+0·50
Tertiary C–H bond									
iso-C$_4$H$_{10}$	0·84	1·99	7·1	12·61	12·76	+0·15	12·82	13·23	+0·41

arises because the calculated value used here was for 25°. For the reactions of fluorine atoms there is no such absolute measurement. Therefore equality between the experimental and theoretical A factors for the reactions of fluorine atoms with ethane has been assumed.

The similarity of the pattern of the A factors for the reactions of fluorine atoms to that for the chlorine atoms is demonstrated by the following points: (1) There is a fall in log (A_{exp}/A_{calc}) from hydrogen to ethane, followed by a slight rise as the hydrocarbons become more complex. This rise may be attributed to the part played by alterations in the frequencies of the chain deformations which have been ignored in the calculations. (2) The values of log (A_{exp}/A_{calc}) are slightly higher for attack on a hydrogen atom attached to a secondary than a primary carbon atom. (3) Cyclopropane has the lowest value of log (A_{exp}/A_{calc}) for hydrocarbon higher than methane.

In general, apart from the apparently anomalous position of methane in the chlorinations, the results for fluorine atoms show similar but less marked trends than those for chlorine. The lower mass of the fluorine atom leads to smaller differences in the

entropies of activation and to smaller errors resulting from assumptions about the vibrational frequencies. The differences between calculated and experimental A factors for reactions of bromine atoms may be more marked than those for reactions of chlorine atoms.