Production of Chemically Activated Fluoroalkanes by Direct Fluorination

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Ethane, ethyl fluoride, ethyl chloride and 1,1-difluoroethane have been fluorinated by reaction with molecular fluorine at very large RH/F_2 ratios to give the monosubstituted product in each case. The reaction step

$$R + F_2 = RF^* + F$$

is exothermic enough to deposit in the newly formed fluoride enough energy for it to eliminate hydrogen halide

 $RF^* = alkene + HF$ (and HCl in the case of chlorofluoroalkanes).

Measurement of the rate constants of this reaction as a result of monofluorination of the compounds above gave

RF*	C₂H₅F	CH_2FCH_2F	CH_3CHF_2	CH ₃ CF ₃	CH ₃	CHClF	CH ₂ FCH ₂ Cl	
$\log(k_{\rm a}/{\rm s}^{-1})$	6.8	4.74	7.13	6.5	6.9	6.0	3.4	5.0
				(-HCD	(-HF)	-HCh	(-HF)

assuming that $\omega = 10^7 \text{ s}^{-1}$.

e.g.

The relative rates of attack of fluorine atoms on C(1) or C(2) atoms in C_2H_5Cl , C_2H_5F and 1,1- $C_2H_4F_2$ have also been obtained.

Chemically activated alkyl fluorides have previously been produced mainly by two methods

(a) The combination of radicals 1

$$CH_3 + CH_2F = C_2H_5F^* \tag{1}$$

where $C_2H_7F^*$ has about 375 kJ mol⁻¹ of excess energy.

(b) The insertion reactions of singlet methylene biradicals 2

$${}^{1}\mathrm{CH}_{2} + \mathrm{C}_{2}\mathrm{H}_{5}\mathrm{F} = \mathrm{C}_{3}\mathrm{H}_{7}\mathrm{F}^{*}$$
(2)

where $C_3H_7F^*$ has about 465 kJ mol⁻¹ of excess energy.

A third method for the production of alkyl fluorides containing excess energy greater than the critical energy for elimination has been briefly reported previously.³ This method is based upon the chain fluorination of the alkane or alkyl halide,⁴ e.g. for ethane

$$F_2 = 2F \tag{3}$$

$$\mathbf{F} + \mathbf{C}_2 \mathbf{H}_6 = \mathbf{H} \mathbf{F} + \mathbf{C}_2 \mathbf{H}_5 \tag{4}$$

$$C_2H_5 + F_2 = C_2H_5F^* + F.$$
 (5)

The exothermicity of reaction (5) $\Delta H = D_{F-F} - D_{C_2H_5-F} = 290 \text{ kJ mol}^{-1}$, which is greater than that needed for hydrogen fluoride elimination,

$$C_2H_5F^* = C_2H_4 + HF.$$
 (6)

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P. CADMAN, A. W. KIRK AND A. F. TROTMAN-DICKENSON 1429

A competitive process is the collisional stabilisation of ethyl fluoride

$$C_2 H_5 F^* + M = C_2 H_5 F.$$
(7)

The ratio $R[C_2H_4]/R[C_2H_5F]$ (where R = rate of production) should be a linear function of the reciprocal pressure (or collision frequency ω) if the strong collision assumption holds and the energy distribution is narrow. Previous workers ⁴ did find a variation of yields with pressure but because of the problems of self heating no consistent results were obtained.

In fact the problems of self heating, explosions and extreme reactivity of fluorine have restricted the study of reactions of fluorine atoms to relatively few,^{4, 5} although since this work was originally done there have been some more studies of fluorination.^{6, 7} In this paper we report the experimental techniques which overcome the problems of self heating *etc.* for fluorination experiments and obtain values for the rate of hydrogen halide eliminations from chemically activated ethyl fluoride, 1,1-difluoroethane, 1,2-difluoroethane, 1,1-fluorochloroethane, 1,2-fluorochloroethane and 1,1,1-trifluoroethane.

EXPERIMENTAL

MATERIALS

Ethane (Cambrian Chemicals) had traces of ethylene removed by passing repeatedly through a column of firebrick containing mercuric nitrate and acetate dispersed in ethylene glycol. Ethyl fluoride was prepared by the method of Edgell and Parts² and purified as above. Ethyl chloride (B.D.H.) was purified by distillation. 1,1-Difluoroethane was from Cambrian Chemicals and nitrogen was B.D.C. "white spot". Fluorine was prepared using an I.C.I. 10 A fluorine generator to electrolyse a mixture of 2HF.KF (41 % w/w HF). The evolved gas was pyrolysed at 573 K and collected in a soda glass storage vessel where the gas could be frozen if necessary at temperatures down to 51 K using liquid air evaporated under reduced pressure. Soda glass storage bulbs were used as Fettis⁹ believed that prolonged contact of fluorine with pyrex reduced its reactivity, all taps in contact with fluorine were greased with Kel F grease (3 Ms company). Fluorine pressures were measured, where necessary, using a glass spiral gauge.

TECHNIQUE

Preliminary experiments were done on the fluorination of ethane under similar conditions to those used by Fettis *et al.*⁴ About 1.5 Torr of fluorine was mixed with 200 Torr of nitrogen and expanded into a reaction vessel containing about 40 Torr of ethane. Alternatively the ethane and nitrogen mixtures were expanded into 1 Torr of fluorine. When the pressure was reduced by decreasing the ethane and nitrogen only, the reaction became explosive as considerable self heating took place and both mono- and di-substitution occurred.

To avoid these self heating and explosive reactions the technique for substitution was drastically modified. The pressures of fluorine used were considerably reduced and pressures as low as 0.006 Torr were used. Two different methods were then developed which because of the large RH/F_2 ratios did not need the addition of nitrogen.

(i) 3.06 cm³ doser was filled with ethane at known pressure and expanded into reaction vessel (96 cm³) via a narrow entry tube. The fluorine was then expanded into an intermediate volume and finally into the reaction vessel. The final pressures in the reaction vessel were calculated by accurately calibrating all the volumes involved. Typical pressures obtained in this way were 0.026 Torr F₂ and 0.428 Torr ethane (*i.e.* C_2H_6/F_2 nominally about 16.5). The real ratios were much larger than this (possibly as much as 100:1) due to loss of fluorine with the walls *etc.*

The use of this expansion technique gave several seconds delay from the time the fluorine left the storage vessel until the reactants were finally mixed. This time of delay affected the overall yield of products but not the ratios. The reduced yields were probably due to

reactions of fluorine with grease and glass. Specific variation of the reaction time itself did not affect the results obtained. About 5-10 % yields were found. The results obtained with this technique were reproducible and the reaction did not need initiation by light.

(ii) A second method was developed for lower total fluorine pressures and was generally simpler and quicker than that above. This used an additional doser (0.7 cm^3) used exclusively for the ethane or alkyl halide and a larger reaction volume (340 cm³). Both dosers, each supplied with reactant from separate parts of the apparatus, also had separate entrances into the reaction vessel so that the gases could be admitted soon after one another. Long lengths of connecting tubing, which affected the rate of diffusion into the reaction vessel, were also eliminated.

Typical values of the gas pressures obtained were $F_2 \sim 0.006$ Torr, ethane ~ 0.08 Torr. The results obtained by the two different methods agreed well and at these low fluorine pressures and very large RH/F2 ratios self heating was not a problem as the radical R entering the reaction step (5) is likely to be virtually thermalised having undergone many collisions with RH before colliding with F₂.

Although reaction vessels with very different S/V ratios were not used, no effect attributable to wall reactions was found. Such wall reactions as the formation (bimolecularly) of RF and its subsequent decomposition are unlikely at the low pressures and temperatures used in these experiments.

ANALYSIS

The reactant mixtures were analysed by gas chromatography using a flame ionisation detector. They were first separated by temperature programming on either 2 m columns of Porapak Q or Porapak T. The reaction products were elucidated by comparison of retention times with authentic samples and by mass spectroscopic analysis.

RESULTS

FLUORINE/ETHANE REACTION

Fluorination of ethane was attempted using both methods (i) and (ii). The only products found were ethylene and ethyl fluoride from reactions (3)-(7). The results are shown in fig. 1 and gave linear relationships of $R(C_2H_4)/R(C_2H_5F)$ against



FIG. 1.—The variation of $R(C_2H_4)/R(C_2H_5F)$ with reciprocal collision frequency by method (i) (upper line), \bigcirc , method (ii) (lower line \bullet).

reciprocal collisional frequencies except in method (ii) at pressures below about 0.05 Torr total where deviations from linearity occurred. These points were not used, as multistage deactivation is probably becoming important at these low pressures.

A value of $\omega = 10^7 \text{ s}^{-1} \text{ Torr}^{-1}$ is taken in this paper for the rate of collisional deactivation. More exact calculations using a Lennard-Jones potential and different cross sections gave results which did not differ drastically from $10^7 \text{ s}^{-1} \text{ Torr}^{-1}$. Furthermore deducible parameters such as critical energies are not particularly sensitive to differences in ω (a few kJ mol⁻¹ at most).

The conditions used were

method (i) P_{F_2} 0.019-0.052 Torr; total $P(F_2 + C_2H_6)$ 0.49-6.85 Torr.

method (ii) P_{F_2} 0.004-0.015 Torr; total $P(F_2 + C_2H_6)$ 1.31-26.5 Torr.

The slopes of the plots were method (i) $(5.2\pm3.3)\times10^6$ s⁻¹; method (ii) $(6.6\pm2.6)\times10^6$ s⁻¹, where the errors are standard deviations from least mean square analysis. It was felt that the best value was that obtained from method (ii), as the results are less scattered. From these figures a value of k_6 was obtained;

$$\log (k_6/s^{-1}) = 6.8.$$

FLUORINE/ETHYL CHLORIDE

When the ratio of ethyl chloride/fluorine is kept high it was found the reaction gave only monosubstitution. In this instance there are two monofluorosubstituted chloroethanes which can be formed

$$F + CH_3CH_2Cl \rightarrow CH_3CHCl + HF$$
 (8)

$$F + CH_3CH_2Cl \rightarrow CH_2 - CH_2Cl + HF$$
(9)

$$CH_{3}CHCl + F_{2} \rightarrow CH_{3}CHFCl^{*} + F$$
(10)

$$CH_2CH_2Cl + F_2 \rightarrow CH_2FCH_2Cl^* + F.$$
(11)

These vibrationally excited fluorochloroethanes can decompose to the corresponding olefins by either the elimination of hydrogen fluoride or hydrogen chloride unless deactivated by collision. They both contain energies greater than the critical energies for elimination.

$$CH_3CHFCl^* + M \rightarrow CH_3CHFCl + M$$
 (12)

$$CH_3CHFCl^* \rightarrow CH_2 = CHF + HCl$$
 (13)

$$CH_3CHFCl^* \rightarrow CH_2 = CHCl + HF$$
 (14)

$$CH_2FCH_2Cl^* + M \to CH_2FCH_2Cl + M$$
(15)

$$CH_2FCH_2Cl^* \rightarrow CH_2 = CHF + HCl$$
 (16)

$$CH_2FCH_2Cl \rightarrow CH_2 = CHCl + HF.$$
 (17)

Ethyl chloride was fluorinated by method (ii) in the pressure range 0.014-6 Torr and the products analysed by gas chromatography. 1,2-fluorochloroethane, vinyl fluoride and vinyl chloride were detected as products. Unfortunately 1,1-fluorochloroethane could not be separated from the very large parent ethyl chloride peak but subsequent numerical analysis of the results indicated its presence. Chlorination of ethyl fluoride under the appropriate conditions for monosubstitution also gave two products as expected, one with the same retention time as ethyl chloride.

As both 1,1-fluorochloroethane and 1,2-fluorochloroethane can eliminate hydrogen

chloride and hydrogen fluoride the analysis of reactions (12)-(17) to obtain k_{13} , k_{14} , k_{16} and k_{17} is complicated but can be achieved because the two fluoroalkanes are stabilised in different pressure regions. In the higher pressure region both 1,1-fluorochloroethane and 1,2-difluoroethane are stabilised but in the lower pressure region only 1,2-fluorochloroethane is stabilized to any significant extent.

From eqn (12)-(17) the following relationships (which are derived in the appendix) were obtained. At a given pressure

$$\frac{[\text{total olefin} + \text{CH}_3\text{CHFCl}]}{[\text{CH}_2\text{FCH}_2\text{Cl}]} = \frac{[\text{CH}_3\text{CHFCl}]_{\infty}}{[\text{CH}_2\text{FCH}_2\text{Cl}]_{\infty}} + \frac{1}{f[\text{CH}_2\text{FCH}_2\text{Cl}]_{\infty}} \frac{k_{16} + k_{17}}{\omega}.$$
 (18)

The two compounds, CH_3CHFCl^* and $CH_2FCH_2Cl^*$, are assumed to have the same stabilisation frequency ω , ∞ refers to very high pressure and $f[CH_2FCH_2Cl]_{\infty}$ is the fraction of CH_2FCH_2Cl that would be obtained at infinitely high pressure and is therefore constant.

$$\frac{[\text{total olefin} + \text{CH}_2\text{FCH}_2\text{Cl}]}{[\text{CH}_3\text{CHFCl}]} = \frac{[\text{CH}_2\text{F} - \text{CH}_2\text{Cl}]_{\infty}}{[\text{CH}_3\text{CHClF}]_{\infty}} + \frac{1}{f[\text{CH}_3\text{CHClF}]_{\infty}} \frac{k_{13} + k_{14}}{\omega}$$
(19)

at low pressures
$$\frac{[CH_2=CHF]}{[CH_2FCH_2Cl]_{total}} \rightarrow r_1 + [r_1(k_{16}+k_{17})+k_{16}]\frac{1}{\omega}$$
(20)

and

$$\frac{[CH_2 = CH_2CI]}{[CH_2 FCH_2CI]_{total}} \rightarrow r_2 + [r_2(k_{16} + k_{17}) + k_{17}]\frac{1}{\omega}$$
(21)

where

$$r_{1} = \text{constant} = \frac{[CH_{3}CHFCI]_{\infty} \text{ (eliminating HCl)}}{[CH_{2}FCH_{2}CI]_{\infty}}$$
(22)

$$r_{2} = \text{constant} = \frac{[CH_{3}CHFCI]_{\infty} \text{ (eliminating HF)}}{[CH_{2}FCH_{2}CI]_{\infty}}.$$
 (23)

The following relationships hold;

(a) at low pressures
$$(20) + (21) \rightarrow (18)$$
 (as CH₃CHFCl $\rightarrow 0$)

(b)
$$r_1 + r_2 = \frac{[CH_3CHFCI]_{\infty}}{[CH_2FCH_2CI]_{\infty}}$$

(c)
$$r_1 + r_2 + 1 = \frac{1}{f[CH_2FCH_2Cl]_{\alpha}}$$

(d)
$$r_1/r_2 = k_{13}/k_{14}$$

A plot of the left hand side of eqn (18) against $1/\omega$ (neglecting any 1,1-isomer which, as is indicated, will be very small at low pressures) becomes a straight line intercept $[CH_3CHFCl]_{\infty}/[CH_2FCH_2Cl]_{\infty}$ and slope $(1/f[CH_2FCH_2Cl]_{\infty})$ $(k_{16}+k_{17})$ in this pressure region. This is shown in fig. 2.

Similar graphs can be plotted for (20) and (21) to give r_1 and r_2 (fig. 3). From these results $k_{16} = 2.6 \times 10^3 \text{ s}^{-1}$ and $k_{17} = 9.6 \times 10^4 \text{ s}^{-1}$ and $k_{13}/k_{14} = 8.9$. The latter result is confirmed by plotting [CH₂=CHF]/[CH₂=CHCl] against $1/\omega$ where the same intercept should be and is obtained (fig. 4). The value for k_{16} above is relatively very small and may possibly be zero (*i.e.* CH₂FCH₂Cl* has insufficient energy to eliminate HCl) if the errors involved are considered. The elimination of

P. CADMAN, A. W. KIRK AND A. F. TROTMAN-DICKENSON 1433

hydrogen chloride from the 1,1-isomer is much bigger in marked contrast. Absolute values of k_{13} and k_{14} may be obtained in several ways. The quantities of 1,1-chlorofluoroethanes may be calculated for the high pressure runs using eqn (18) and data already obtained but this method is not particularly accurate. A better way is to contrast calculated values of the product ratio $(CH_2=CHCI)+(CH_2=CHF)/$



FIG. 2.—Plot of R (total olefin)/R(CH₂FCH₂Cl) against reciprocal collision frequency for the fluorination of ethyl chloride. --, curve calculated with $k_{16} = 2.6 \times 10^3 \text{ s}^{-1}$, $k_{17} = 9.6 \times 10^4 \text{ s}^{-1}$ and assumed values of $k_{13} = 8 \times 10^6 \text{ s}^{-1}$ and $k_{14} = 9 \times 10^5 \text{ s}^{-1}$ ($k_{13}/k_{14} = 8.9$).



FIG. 3.—Variation of $R(C_2H_3Cl)/R(CH_2FCH_2Cl)$ (I) and $R(C_2H_3F)/R(CH_2FCH_2Cl)$ (II) with reciprocal collision frequency for the fluorination of ethyl chloride.

 (CH_2FCH_2Cl) with experimental values at different values of $1/\omega$ (in the higher pressure region shown in fig. 2). The previously determined values of k_{16} and k_{11} were used along with estimates of $(k_{13}+k_{14})$ such that $k_{13}/k_{14} = 8.9$. This approach is shown on fig. 2 where the dotted line corresponds to assumed values of

$$k_{13} = (8 \pm 3) \times 10^6 \text{ s}^{-1} \text{ and } k_{14} = (9 \pm 3) \times 10^5 \text{ s}^{-1}$$

The actual fitting was done on a large scale where these values of k_{13} and k_{14} gave

the best fit with the estimated errors shown. From the ratio $[CH_3CHFCl]_{\infty}/[CH_2F-CH_2Cl]_{\infty}$ a value of $k_8/k_9 = 1.73$ or 2.59 (on a per atom basis) was found for the relative rate coefficients for abstraction.

Although the data are not as precise as the other data reported here the sequence $k_{13} \ge k_{14} \ge k_{17} \ge k_{16}$ is firmly established and as a consequence the elimination of hydrogen chloride from 1,2-fluorochloroethane has a higher activation or critical energy than hydrogen fluoride elimination which does not usually occur. RRKM calculations ¹⁰ on 1,2-fluorochloroethane and thermal decomposition ¹¹ of this molecule support this higher activation energy.



 $(1/\omega) \times 10^{7}/s$

FIG. 4.—Variation of $R(C_2H_3F)/R(C_2H_3C)$ with reciprocal collision frequency (ω) for ethyl chloride.

FLUORINE/ETHYLFLUORIDE

This reaction was studied with pressures of fluorine of between 0.007-0.14 Torr and total pressure of 1-0.010 Torr. Only monofluorination occurred under these conditions. Both 1,2-difluoroethane and 1,1-difluoroethane were found as products along with vinyl fluoride.

The reaction scheme parallels that for ethyl chloride

$$CH_3CH_3F + F \rightarrow CH_3CHF + HF$$
 (24)

$$CH_3CH_2F + F \rightarrow CH_2CH_2F + HF$$
 (25)

$$CH_3CHF + F_2 \rightarrow CH_3CHF_2^* + F$$
 (26)

$$CH_2CH_2F + F_2 \rightarrow CH_2FCH_2F^* + F.$$
 (27)

Both 1,2- and 1,1-difluoroethane can eliminate hydrogen fluoride to give vinyl fluoride or be stabilised by collision

$$CH_3CHF_2^* + M \to CH_3CHF_2 + M$$
⁽²⁸⁾

$$CH_3CHF_2^* \rightarrow CH_2 = CHF + HF$$
 (29)

$$CH_2FCH_2F^* + M \rightarrow CH_2FCH_2F + M$$
(30)

$$CH_2FCH_2F^* \rightarrow CH_2 = CHF + HF.$$
 (31)

Most experiments were analysed using a Porapak Q column which did not separate

1,1-difluoroethane from the parent ethyl fluoride. These results were analysed as for ethyl chloride.

From the equations above, analogous expressions to those obtained for ethyl chloride can be derived;

$$\frac{\mathrm{CH}_{2}=\mathrm{CHF}+\mathrm{CH}_{3}\mathrm{CHF}_{2}}{\mathrm{CH}_{2}\mathrm{F}\mathrm{CH}_{2}\mathrm{F}} = \frac{(\mathrm{CH}_{3}\mathrm{CHF}_{2})_{\infty}}{(\mathrm{CH}_{2}\mathrm{F}\mathrm{CH}_{2}\mathrm{F})_{\infty}} + \frac{k_{31}}{f(\mathrm{CH}_{2}\mathrm{F}\mathrm{CH}_{2}\mathrm{F})_{\infty}}\frac{1}{\omega}$$
(32)

$$\frac{\mathrm{CH}_{2}=\mathrm{CHF}+\mathrm{CH}_{2}\mathrm{FCH}_{2}\mathrm{F}}{\mathrm{CH}_{3}\mathrm{CHF}_{2}} = \frac{(\mathrm{CH}_{2}\mathrm{FCH}_{2}\mathrm{F})_{\infty}}{(\mathrm{CH}_{3}\mathrm{CHF}_{2})_{\infty}} + \frac{k_{29}}{f(\mathrm{CH}_{3}\mathrm{CHF}_{2})_{\infty}}\frac{1}{\omega}.$$
 (33)

A graph of $R(CH_2=CHF)/R(CH_2F-CH_2F)$ against $1/\omega$ is shown in fig. 5. This graph neglected contributions from 1,1-diffuoroethane which had almost totally decomposed at these pressures. A later series of experiments using Porapak T did separate the 1,1-diffuoroethane from the ethyl fluoride, and the relative yield of 1,1-C₂H₄F₂ did become very small at low pressures.



 $(1/\omega) \times 10^{7}/s$

FIG. 5.—Fluorination of ethyl fluoride. Variation of $R(CH_2 = CHF)/R(CH_3CHF_2)$ (I), \bullet ; $[R(C_2H_3F) + R(CH_2FCH_2F)]/R(CH_3CHF_2)$ (II), \bullet ; and $R(C_2H_3F)/R(CH_2FCH_2F)$ (III), with reciprocal collision frequency, \bigcirc Porapak Q, \bigcirc Porapak T.

At higher pressures the relative amount of 1,1-difluoroethane increased and the results for this pressure region were analysed on Porapak T, where separation was obtained. The results were plotted using (33) above and are shown in fig. 5. A straight line was obtained, as expected, with an intercept which is the reciprocal of that of fig. 5. To obtain reasonable accuracy in measuring the relative yield of 1,1-difluoroethane the amount of fluorine was increased (0.069-0.0064 Torr) compared with the amount of ethyl fluoride (0.11-0.58 Torr). Local heating was not a serious problem because the actual yields are still low and the real RH/F_2 ratio is still large. However, (33) is much less sensitive to the amount of 1,2-difluoroethane than that of (32) above and k_{29} and k_{30} are more reliable.

From fig. 5 the values for the rate coefficients for elimination from 1,1-difluoroethane and 1,2-difluoroethane can be obtained; $k_{29} = 5.5 \times 10^4 \text{ s}^{-1}$ and $k_{31} = 1.4 \times 10^7 \text{ s}^{-1}$. The small value of k_{29} means that at high pressures the vinyl fluoride is derived almost exclusively from the 1,1-difluoroethane (greater than 95 % in the pressure range above 0.1 Torr). A plot of vinyl fluoride/1,1-difluoroethane against reciprocal collision frequency should approximate to a straight line through the origin at higher pressures. This is also shown in fig. 5 and gives $k_{31} = 1.2 \times 10^7 \text{ s}^{-1}$ agreeing with the value above.

From the limiting high pressure values of 1,1-difluoroethane and 1,2-difluoroethane the ratio of the rate coefficients k_{24}/k_{25} can be obtained from fig. 5 and gives $k_{24}/k_{25} = 1.37$ which is 2.05 on a per hydrogen basis at 295 K.

1,1-DIFLUOROETHANE/FLUORINE

The fluorination of 1,1-difluoroethane was studied by method (ii) in the pressure range 1-0.055 Torr with pressures of fluorine between 0.025-0.009 Torr. The products consisted of 1,1,1-trifluoroethane, 1,1-difluoroethylene and 1,1,2-trifluoroethane. As no *cis*- and *trans*-1,2-difluoroethylenes were observed even at the very lowest pressures, it was fair to assume that all the 1,1-difluoroethylene arose from the decomposition of 1,1,1-trifluoroethane.

The reaction scheme was

 $F + CH_3 CHF_2 \rightarrow CH_3 CF_2 + HF$ (34)

$$F + CH_3 CHF_2 \rightarrow CH_2 CHF_2 + HF$$
(35)

$$CH_3CF_2 + F_2 \rightarrow CH_3CF_3^* + F$$
(36)

$$CH_2CHF_2 + F_2 \rightarrow CH_2FCHF_2^* + F$$
(37)

$$CH_3CF_3^* + M \to CH_3CF_3 + M$$
(38)

$$CH_3CF_3^* \rightarrow CH_2 = CF_2 + HF.$$
 (39)

The rate coefficient for 1,1,1-trifluoroethane elimination can be determined from the slope of fig. 6 where for the simultaneous reactions (38) and (39)

$$\frac{R(CH_2 = CF_2)}{R(CH_3 CF_3)} = \frac{k_{39}}{\omega}$$

assuming again that $\omega = 10^7 \text{ s}^{-1}$ at 1 Torr; $\log (k_{39}/\text{s}^{-1})$ was found to be 6.5.

The linear plot obtained in fig. 6 justifies the neglect of elimination from 1,1,2-trifluoroethane to give 1,1-difluoroethylene although at the lowest pressures used the



FIG. 6.-Fluorination of 1,1,1-trifluoroethane.

P. CADMAN, A. W. KIRK AND A. F. TROTMAN-DICKENSON 1437

upward curvature shown by the $CH_2 = CF_2/CH_3 - CF_3$ ratio may be due to this alternative production of 1,1-diffuoroethylene. From the amount of 1,1,2-triffuoroethane and an estimation of how much *cis*- and *trans*-1,2-diffuoroethylene could have been detected, upper limits can be placed upon the rate coefficients for (40)-(42)

$$CHF_2CH_2F^* \rightarrow cis-CHF = CHF + HF$$
 (40)

$$\rightarrow$$
 trans-CHF=CHF+HF (41)

$$\rightarrow CH_2 = CF_2 + HF \tag{42}$$

of log $(k_{40}/s^{-1}) \leq 3.9$, log (k_{41}/s^{-1}) also ≤ 3.9 and log $(k_{42}/s^{-1}) \leq 3.9$.

From the amount of 1,1-difluoroethylene plus 1,1,1-trifluoroethane to 1,1,2trifluoroethane a ratio of k_{34}/k_{35} of 1.3 ± 0.17 was obtained. Expressed per atom this give a ratio of 3.9 in favour of the C—H on the carbon already containing the fluorine atoms, showing a relatively large difference in the rates of hydrogen abstraction at the one and two positions. The exact same trend was observed in the cases of ethyl chloride and ethyl fluoride.

COMPETITIVE FLUORINATIONS

In the fluorination results above it was found that there was a preference (by a factor of 2-4 times) for the attack on the halogenated methyl hydrogens rather than the unsubstituted ones in ethyl chloride, ethyl fluoride and 1,1-difluoroethane. Competitive fluorination experiments were attempted at 200, 293 and 333 K with ethyl chloride/1,1-difluoroethane mixtures to determine whether the origin of these differences was in the activation energies or in the pre-exponential factors.

Mixtures of 1,1-difluoroethane/ethyl fluoride of ratio 1:1 and 10:7:1 were fluorinated as described above but in the presence of a large excess of nitrogen $(N_2/RH > 10)$. The products found were 1,2-fluorochloroethane, 1,1,1-trifluoroethane and 1,1,2-trifluoroethane (1,1-fluorochloroethane could not be separated as before). Reactions (9), (34) and (35) account for the rate determining steps in the fluorinations and are then followed by (11), (36) and (37) respectively. The average of a number of runs at each temperature were plotted in the Arrhenius form.

The relative Arrhenius parameters obtained on a per atom basis were

$$\log \left(k_{9} / k_{35} \right) = 0.22 - (6\ 690 / 2.3\ RT) \tag{43}$$

where

 $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

and

$$\log \left(k_{34} / k_{35} \right) = 0.16 - (3\ 340 / 2.3\ RT). \tag{44}$$

DISCUSSION

With the fluorination techniques described above it is possible to overcome many of the problems which had arisen in previous fluorination work and to obtain consistent results. The chain fluorination could be limited to monosubstitution and the problem of self heating was not important.

Ethyl fluoride, 1,1-fluorochloroethane, 1,2-fluorochloroethane, 1,1-difluoroethane, 1,2-difluoroethane and 1,1,1-trifluoroethane produced by reactions such as (5) contain energies greater than the critical energies necessary for the elimination of hydrogen halides from them. For 1,1,2-trifluoroethane only upper limits can be placed upon the rate coefficients of the possible elimination reactions, so no conclusions can be drawn as to whether this molecule is also formed with an energy greater than necessary to eliminate hydrogen fluoride.

All the exothermicity of reactions such as (5) need not go into the newly formed fluoride, as some could be partitioned into relative translation.

As $\Delta H^{\circ} = D_{F-F} - D_{R-F} = \Sigma \Delta H_{f}^{\circ}$ (products) $-\Sigma \Delta H_{f}^{\circ}$ (reactants) then to calculate, this exothermicity one must know either the carbon-fluorine bond strength or the ΔH_{f} of the precursor radical involved. The exothermicity of (5) can be calculated quite accurately but for the other reactions this calculation involves a degree of estimation. As the plots in the figures above are linear the strong collison assumption is reasonable in the pressure regions used and at these low excess energies. The energy distribution of the newly formed fluoride must be fairly narrow or these distributions would also produce curvature in the plots against reciprocal frequency.

In the ethyl fluoride case this chemically activated molecule was also made by the other two techniques (a) and (b). From these chemical activation results and the known critical energy for hydrogen fluoride elimination, the calculated RRKM rate coefficient curve and experimental results could be reconciled.¹ The results of the fluorination method above were then fitted to the same calculated curve to obtain the proportion of the exothermicity which is deposited in the fluoride. This was found to be 95 % of the total. It may be that the deposition of closer to 100 % of the available energy into the alkyl fluorides (which would also produce narrow energy distributions) would give rise to the linear reciprocal plots in the figures above. Until more information is available it can only be assumed that the same proportion is deposited for the other molecules studied above. A comparison of the chemical activation results given above for 1,1-fluorochloroethane, 1,2-fluorochloroethane, 1,1-difluoroethane, 1,2-difluoroethane and 1,1,1-trifluoroethane with RRKM calculated curves is given in a separate publication.¹⁰ In this paper the experimental technique, the method of obtaining them and the results themselves are described, not all the products need be measured to obtain the requisite information.

From the relative rate coefficients (on a per hydrogen atom basis) obtained for the attack of fluorine atoms on the C(1) and C(2) carbon atoms it is obvious that attack on the substituted atom is 2-3 times more likely at 293 K than attack on the methyl group. As the pre-exponential factors for the attack on C(2) of ethyl chloride and C(1) and C(2) of 1,1-difluoroethane are similar, it must be the different activation energies which determine the relative rates. Although the activation energies are small and less accurate than desirable, they are of the same order as those of other abstractions and show that $E_{CH_3CH_2C1} < E_{CH_3CHF_2}$ and $E_{CH_3CHF_2} < E_{CH_3CHF_2}$.

APPENDIX

From eqn (8)-(17) at infinite pressure (*i.e.* absence of any elimination) the ratio of $(CH_3CHFCl)/(CH_2FCH_2Cl)$ becomes constant = k_8/k_9 [the rate coefficient ratio for competitive abstraction at C(1) and C(2) positions] at lower pressures in any single run

$$(CH_{3}CHClF) + (CH_{2} = CHF)_{1,1} + (CH_{2} = CHCl)_{1,1} + (CH_{2}FCH_{2}Cl) + CH_{2} = CHF)_{1,2} + (CH_{2} = CHCl)_{1,2} = (CH_{3}CHClF)_{\infty} + (CH_{2}FCH_{2}Cl)_{\infty}$$
(45)

where the subscripts refer to either the origin of that proportion of the total C_2H_3F or C_2H_3Cl , or to very high pressure. The amounts of 1,1- and 1,2-fluorochloroethane shown on the right hand side of (45) are those that would have been obtained in that run at infinite pressure. If f = fraction of a compound found at a pressure p, then at lower pressures where decomposition occurs

$$f(CH_2FCH_2Cl) = \frac{(CH_2FCH_2Cl)}{(CH_3CHFCl)_{\infty} + (CH_2FCH_2Cl)_{\infty}}$$
(46)

and at "infinite ' pressure

$$f(CH_2FCH_2Cl)_{\infty} = \frac{(CH_2FCH_2Cl)_{\infty}}{(CH_3CHFCl)_{\infty} + (CH_2FCH_2Cl)_{\infty}}$$
(47)

$$\frac{f(CH_2FCH_2Cl)_{\infty}}{f(CH_2FCH_2Cl)} = 1 + \frac{(CH_2 = CHF)_{1,2} + (CH_2 = CHCl)_{1,2}}{(CH_2FCH_2Cl)}$$
(48)

$$= 1 + (k_{16} + k_{17})/\omega.$$
⁽⁴⁹⁾

Dividing by $f(CH_2FCH_2Cl)_{\infty}$ and substituting from (46) and (45) above

$$\frac{(\text{total olefin}) + (\text{CH}_{3}\text{CHClF})}{(\text{CH}_{2}\text{FCH}_{2}\text{Cl})} = \frac{1}{f(\text{CH}_{2}\text{FCH}_{2}\text{Cl})_{\infty}} - 1 + \frac{1}{f(\text{CH}_{2}\text{FCH}_{2}\text{Cl})_{\infty}} \frac{(k_{16} + k_{17})}{\omega}.$$
 (50)

This expression is applicable to all runs where the relative amounts of the products at each pressure are known, substituting

$$\frac{1}{f(\mathrm{CH}_{2}\mathrm{FCH}_{2}\mathrm{Cl})_{\infty}} - 1 = \frac{(\mathrm{CH}_{3}\mathrm{CH}\mathrm{ClF})}{(\mathrm{CH}_{2}\mathrm{FCH}_{2}\mathrm{Cl})}$$
(51)

eqn (18) is obtained and a similar expression for the 1,1-isomer can be derived, eqn (19). At higher pressures in a particular run $(CH_2 = CHCl)_{1,2}$ and $(CH_2 = CHF)_{1,2}$ approach zero first so

$$\frac{(\mathrm{CH}_2 = \mathrm{CHF})_{\mathrm{total}}}{(\mathrm{CH}_2 = \mathrm{CHCl})_{\mathrm{total}}} \rightarrow \frac{(\mathrm{CH}_2 = \mathrm{CHF})_{1,1}}{(\mathrm{CH}_2 = \mathrm{CHCl})_{1,1}} = \frac{k_{13}}{k_{14}}.$$
(52)

At much lower pressures

$$\frac{(CH_2 = CHF)_{total}}{(CH_2 = CHCl)_{total}} = \frac{(CH_2 = CHF)_{1,1}}{(CH_2 FCH_2 Cl)} + \frac{(CH_2 = CHF)_{1,2}}{(CH_2 FCH_2 Cl)}$$
(53)

where $(CH_2=CHF)_{1,1}$ is governed by the fraction of CH_3CHFCl which can eliminate HCl *i.e.* k_{13}/k_{14} .

Multiplying the first term of eqn (53) by

$$\frac{(\mathrm{CH}_{2}\mathrm{FCH}_{2}\mathrm{Cl})_{\infty}}{(\mathrm{CH}_{2}\mathrm{FCH}_{2}\mathrm{Cl})_{\infty}}(i.e.\times 1)$$

where

$$(CH_2FCH_2Cl)_{\infty} = (CH_2ClCH_2F) + (CH_2 = CHF)_{1,2} + (CH_2 = CHCl)_{1,2}$$
(54)

and substituting r_1 as the low pressure limiting value of

$$(CH_2 = CHF)_{1,1}/(CH_2FCH_2Cl)_{\infty}$$
,

the following is obtained

$$\frac{(CH_2 = CHF)_{total}}{(CH_2FCH_2Cl)} = r_1 \frac{(CH_2FCH_2Cl) + (CH_2 = CHF)_{1,2} + (CH_2 = CHCl)_{1,2}}{(CH_2FCH_2Cl)} + \frac{(CH_2 = CHF)_{1,2}}{(CH_2FCH_2Cl)}$$
(55)
= $r_1 + [r_2(k_{1,2} + k_{1,2}) + k_{1,2}]1/m$ (55)

$$r_1 + [r_1(k_{16} + k_{17}) + k_{16}] 1/\omega.$$
(56)

Similarly

$$\frac{(CH_2 = CHF)_{total}}{(CH_2 FCH_2 CI)} = r_2 + [r_2(k_{16} + k_{17}) + k_{17}]1/\omega$$
(57)

and r_2 is the low pressure limiting value of $(CH_2 = CHCl)_{1,1}/(CH_2FCH_2Cl)$.

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(PAPER 5/1296)

1440