

## Static and Shock Tube Pyrolyses of Alkyl Fluorides. Part III.† The Thermal Decomposition of 1-Chloro-2-fluoroethane, 1,1-Difluoroethane, and 1,1,1-Trifluoroethane

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The thermal decompositions of 1-chloro-2-fluoroethane, 1,1-difluoroethane, and 1,1,1-trifluoroethane to yield the corresponding alkenes and hydrogen halides have been studied by use of a comparative shock tube technique. 1-Chloro-2-fluoroethane has also been studied in a static system. The rate constants  $\log k/s^{-1}$  obtained were as follows: 1-Chloro-2-fluoroethane (a) by shock tube,  $(13.47 \pm 0.34) - (63,800 \pm 1200)/2.3RT$  (HCl elimination);  $(12.93 \pm 0.32) - (60,800 \pm 1100)/2.3RT$  (HF elimination); (b) static,  $(13.59 \pm 0.32) - (62,250 \pm 1100)/2.3RT$  (HCl elimination, maximum inhibited value);  $(12.95 \pm 0.30) - (60,000 \pm 1000)/2.3RT$  (HF elimination); 1,1-Difluoroethane, by shock tube,  $(13.53 \pm 0.30) - (64,973 \pm 935)/2.3RT$ ; 1,1,1-Trifluoroethane by shock tube,  $(13.80 \pm 0.30) - (73,638 \pm 4138)/2.3RT$ , where  $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$ . The rates of these decompositions are compared with those of similar halogenated compounds and discussed in terms of the ion-pair model.

THE pyrolyses of  $\alpha$ - and  $\beta$ -halogenoethyl halides in the gas phase which have so far been reported<sup>1-7</sup> are listed in Table 1 along with their Arrhenius parameters. Those obtained by Sianesi *et al.*<sup>7</sup> were obtained at only three temperatures over a narrow temperature range in a flow system. The data for 1,2-dichloroethane<sup>5,6</sup> are complicated by the presence of heterogeneous effects and radical sensitised reactions. These effects have been studied in great detail by Holbrook *et al.*<sup>8</sup> Even the earlier results<sup>1,2</sup> for 1,1-dichloroethane appear suspect from the more recent studies of Hartmann *et al.*<sup>3</sup> on 1,1-dichloroethane and Young and Swinbourne<sup>9</sup> for the *gem*-dichlorides of propane and butane.

In addition to these static studies estimates of the activation energies  $\alpha$ - and  $\beta$ -halogenoethanes have been obtained by the chemical activation technique (Table 1). The results shown vary, mainly owing to the assumptions made in the use of unimolecular rate theory, rather than to large experimental discrepancies. The critical energies determined by Kirk<sup>10</sup> using the more exact quantum mechanical approach of Marcus are therefore to be preferred. The largest uncertainty in these values is probably the reliability of the thermochemical data available. The values given are critical energies. Activation energies are *ca.* 1–2 kcal mol<sup>-1</sup> larger than

† Part II, P. Cadman, M. Day, and A. F. Trotman-Dickenson, *J. Chem. Soc. (A)*, 1971, 248.

<sup>1</sup> D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 1949, 165.

<sup>2</sup> K. E. Howlett, *J. Chem. Soc.*, 1952, 3695.

<sup>3</sup> H. Hartmann, H. Heydtmann, and G. Rinck, *Z. phys. Chem.*, 1961, **28**, 71.

<sup>4</sup> D. H. R. Barton and P. F. Onyon, *J. Amer. Chem. Soc.*, 1950, **72**, 988.

<sup>5</sup> D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 1949, 155.

<sup>6</sup> K. E. Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25.

<sup>7</sup> D. Sianesi, G. Nelli, and R. Fontanelli, *Chimica e Industria*, 1968, **50**, 619.

<sup>8</sup> K. A. Holbrook, R. W. Walker, and W. R. Watson, *J. Chem. Soc. (B)*, 1968, 1089.

<sup>9</sup> B. C. Young and E. S. Swinbourne, *J. Chem. Soc. (B)*, 1967, 1181.

<sup>10</sup> A. W. Kirk, Ph.D. Thesis, *University of Wales*, 1968.

these values. In this investigation the comparative shock tube technique<sup>11</sup> described previously has been employed to study the rate of thermal decomposition of 1-chloro-2-fluoroethane, 1,1-difluoroethane, and 1,1,1-trifluoroethane in order to correlate the  $\alpha$ - and  $\beta$ -halogen effects on the ethyl fluorides and for comparison

## RESULTS AND DISCUSSION

The shock tube results were calculated according to the method described previously.<sup>11</sup> The internal standard for all three studies was n-propyl fluoride whose rate constant was given<sup>11</sup> by  $\log k/s^{-1} = 13.26 - 58,300/2.3RT$ . The alkyl chlorides used previously,

TABLE 1  
Arrhenius parameters determined for multihalogenated ethanes

(a) Conventional static, flow, or shock-tube pyrolyses					(b) Determined from chemical activation results	
Halogenated ethane	Temp. range/K	$\log A/s^{-1}$	$E_a/kcal\ mol^{-1}$	Ref.	$E_{critical}/kcal\ mol^{-1}$	Ref.
MeCHCl <sub>2</sub>	629—726	12.08	49.5	1		
	685—722	11.65	48.3	2		
	641—723	13.5	53.5	3		
MeCCl <sub>3</sub>	636—707	14.0	54	4		
CH <sub>3</sub> Cl·CH <sub>2</sub> Cl	657—716	12.76	51.2	5, 6	55	18
MeCHClF (—HCl)	823—883	10.69	44.7	7	56	10
(—HF)	—	—	—	—	59	10
MeCCl <sub>2</sub> F (—HCl)	803—853	11.59	47.0	7	61, 58, 70	a, b, 10
(—HF)	—	—	—	—	—	—
MeCClF <sub>2</sub> (—HCl)	858—903	14.81	60.0	7	61, 58, 70	a, b, 10
(—HF)	—	—	—	—	58, 57, 69	a, b, 10
MeCHF <sub>2</sub>	953—1023	13.31	61.9	7	61	10 *
	1040—1320	13.7	60.8	15		
MeCF <sub>3</sub>	1023—1073	12.14	61.4	7	70	10 *
CH <sub>3</sub> F·CH <sub>2</sub> F	—	—	—	—	62, 62, 60.5, 52, 64	c, d, e, a, 10
CH <sub>3</sub> FCH <sub>2</sub> Cl (—HCl)	—	—	—	—	68	10
(—HF)	—	—	—	—	62	10

\* Recalculated from reference 10 using more recent thermochemical data.

<sup>1</sup> J. A. Kerr, A. W. Kirk, B. V. O'Grady, D. C. Phillips, and A. F. Trotman-Dickenson, *Discuss. Faraday Soc.*, 1967, **44**, 263.  
<sup>2</sup> D. C. Phillips and A. F. Trotman-Dickenson, *J. Chem. Soc. (A)*, 1968, 1667. <sup>3</sup> H. W. Chang and D. W. Setser, *J. Amer. Chem. Soc.*, 1969, **71**, 7648. <sup>4</sup> J. A. Kerr, D. C. Phillips, and A. F. Trotman-Dickenson, *J. Chem. Soc. (A)*, 1968, 1806. <sup>5</sup> S. W. Benson and G. Haugen, *J. Phys. Chem.*, 1965, **69**, 3898.

with values obtained from chemical activation. The static pyrolysis of 1-chloro-2-fluoroethane was also studied.

## EXPERIMENTAL

1-Chloro-2-fluoroethane was prepared by the reaction of anhydrous potassium fluoride with 2-chloroethan-1-ol to give 2-fluoroethan-1-ol.<sup>12</sup> Reaction with thionyl chloride<sup>13</sup> gave 1-chloro-2-fluoroethane. 1,1-Difluoroethane, 1,1,1-trifluoroethane, vinyl chloride, and 1,1-difluoroethylene were obtained from Matheson Ltd. Vinyl fluoride was a K and K product. Olefin impurities from the ethanes were removed either by reaction with bromine and fractional distillation or by passing the ethane through a column of silver nitrate-ethylene glycol on Celite. The purity of reagents was checked by chromatography. The apparatus for the shock tube studies has been described.<sup>11</sup>

The gas chromatographic analyses were done on (1) a Porapak Q column (6 ft  $\times$   $\frac{1}{8}$  in) for 1-chloro-2-fluoroethane and 1,1,1-trifluoroethane; (2) Porapak T (6 ft  $\times$   $\frac{1}{8}$  in) for 1,1-difluoroethane. Both columns were used with temperature programming. The static phase decompositions were carried out in a cylindrical Pyrex vessel of ca. 35 cm<sup>3</sup> volume and surface: volume ratio of 2. A packed vessel was also used with a surface: volume ratio of 10. Both vessels were seasoned before use by decomposing 1-chloro-2-fluoroethane at 723 K for two weeks, during which time 100 fresh additions of the compound were made. No air was allowed to come in contact with the surface during and after this seasoning.

<sup>11</sup> P. Cadman, M. Day, and A. F. Trotman-Dickenson, *J. Chem. Soc. (A)*, 1970, 2498.

which had Arrhenius parameters determined in static studies, were found to be unsuitable owing to the larger rate of decomposition than 1,1-difluoro- and 1,1,1-trifluoro-ethanes. In all cases the test gas mixture employed was less than 1% of the alkyl halides in an excess of argon diluent. Typical mixtures were made up of 3 Torr of n-propyl fluoride and 3 Torr of the compound to be studied in about 800—900 Torr of argon.

**1-Chloro-2-fluoroethane.**—Results were obtained for Mach numbers between 2.34 and 2.72 which correspond to reflected shock temperatures of between 1358 and 1791 K. The decomposition of n-propyl fluoride varied from 1.7 to 79% and that of 1-chloro-2-fluoroethane from 0.8 to 64%. The rate coefficients obtained for both hydrogen chloride and hydrogen fluoride elimination are shown in Figure 1. The best straight line in each case was obtained by the method of least squares where the errors quoted are 90% confidence limits. The Arrhenius equations obtained were  $\log k/s^{-1} = (13.47 \pm 0.34) - (63,800 \pm 1200)/2.3RT$  for elimination of HCl and  $(12.93 \pm 0.32) - (60,600 \pm 1100)/2.3RT$  for elimination of HF, where  $R = 1.987\ cal\ mol^{-1}\ K^{-1}$  throughout this paper.

**1,1-Difluoroethane.**—The results are shown in Figure 2. Shock velocities corresponding to Mach numbers 2.43—2.71 were used. These Mach numbers corresponded to reflected shock temperatures ranging from

<sup>12</sup> F. W. Hoffmann, *J. Amer. Chem. Soc.*, 1948, **70**, 2596.

<sup>13</sup> F. W. Hoffmann, *J. Org. Chem.*, 1950, **15**, 425.

1455 to 1779 K. Decomposition of n-propyl fluoride varied from 15 to 72% while that of 1,1-difluoroethane from 2.8 to 30%. Least-mean-square analysis of the results shown in Figure 1 gave  $\log k/s^{-1} = (13.53 \pm 0.32) - (64,973 \pm 935)/2.3RT$ .

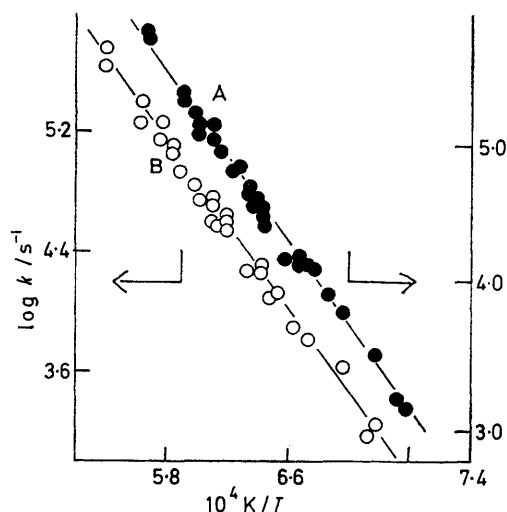


FIGURE 1 Arrhenius plot for 1-chloro-2-fluoroethane; A, elimination of HF; and B, elimination of HCl

**1,1,1-Trifluoroethane.**—The results were obtained over a range of Mach numbers from 2.55 to 2.78 corresponding to reflected shock temperatures of 1590–1865 K. The percentage decompositions varied from 40 to 84 and 2 to 12 for n-propyl fluoride and 1,1,1-trifluoroethane respectively. Least-mean-square analysis of the results shown in Figure 2 gave  $\log k/s^{-1} = (13.80 \pm 0.30) - (73,638 \pm 4138)/2.3RT$ . The error for 1,1,1-trifluoroethane is larger than for the other compounds.

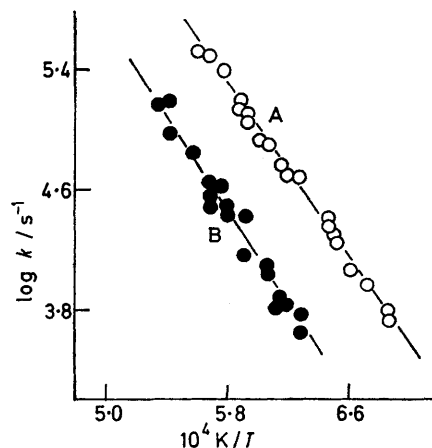


FIGURE 2 Arrhenius plots for A, 1,1-difluoroethane and B, 1,1,1-trifluoroethane

This may be due to the larger difference in rate between this compound and the standard, resulting in larger conversions of the standard at the highest temperature used. Overestimation of temperatures due to non-

ideal shock reflection is probably not important as a temperature 50 K less than the measured temperature changes the activation energy by less than 1 kcal mol<sup>-1</sup>, well within the standard deviation.

The static study of 1-chloro-2-fluoroethane was done in three different ways. (i) Direct studies, in which an unpacked reaction vessel without inhibitor was used; (ii) inhibited studies, in which pyrolyses were carried out in an unpacked vessel but in the presence of but-1-ene, a radical chain inhibitor; and (iii) packed vessel studies, in which a vessel with a five-fold increase in the surface : volume ratio was used.

The effect of change of initial pressure on the first-order rate constants is shown in Figure 3. These results indicate no significant dependence on pressure at 732 K in the range 4–110 Torr for the elimination of hydrogen fluoride. The elimination of hydrogen chloride may be entering its fall-off region below about 30 Torr. The temperature-dependence was studied above 80 Torr

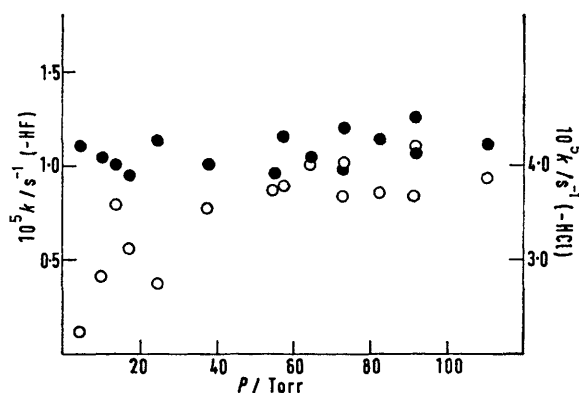


FIGURE 3 Variation of elimination rates of 1-chloro-2-fluoroethane with pressure at 732 K (static pyrolysis); open circles, HCl, closed circles, HF

where there is little pressure-dependence on the rate of elimination.

The variation of the rates of elimination of hydrogen fluoride and chloride with temperature are shown in Figures 4 and 5. The effects of the three sets of experimental conditions show that the elimination of hydrogen fluoride is unaffected by the addition of a radical chain inhibitor or an increase in the surface : volume ratio. The values obtained for the Arrhenius parameters of hydrogen fluoride elimination by the method of least squares are given in Table 2. These results can be

TABLE 2

	$\log A/s^{-1}$	$E_a/\text{kcal mol}^{-1}$
(i) Direct	13.00	60.23
(ii) Inhibited	12.65	59.05
(iii) Packed vessel	13.20	60.78

combined to give the rate of homogeneous unimolecular elimination of hydrogen fluoride from 1-chloro-2-fluoroethane as  $\log k/s^{-1} = (12.95 \pm 0.30) - (60,000 \pm 1000)/2.3RT$ . The results for hydrogen fluoride elimin-

ation obtained in the static pyrolyses are in good agreement with those obtained in the shock tube. The

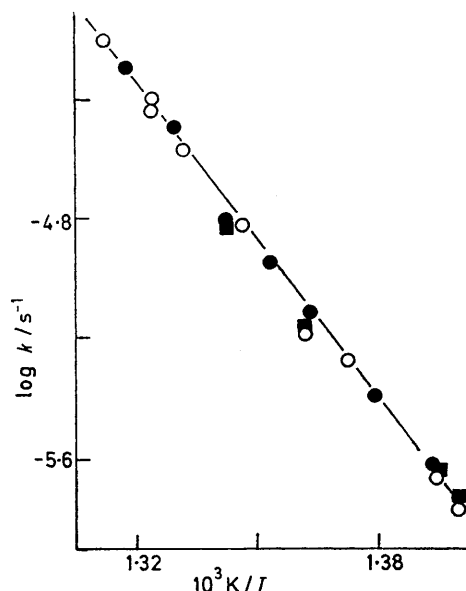


FIGURE 4 Elimination of HF from 1-chloro-2-fluoroethane (static pyrolysis); open circle, direct studies; square, inhibited by but-1-ene; and closed circle, packed vessel

elimination of hydrogen chloride, in contrast to hydrogen fluoride, was found to be retarded by the addition of a

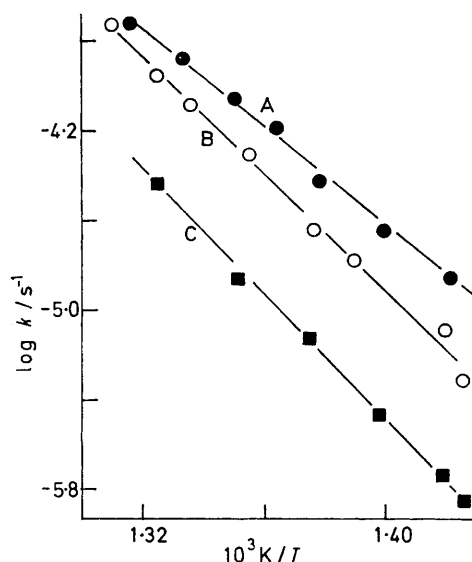


FIGURE 5 Elimination of HCl from 1-chloro-2-fluoroethane (static pyrolysis); A, direct studies; B, packed vessel, and C, inhibited by but-1-ene

chain inhibitor and accelerated by an increase in the surface : volume ratio of the reaction vessel. Arrhenius

parameters corresponding to these three sets of conditions were found to be as in Table 3.

The retardation of the pyrolysis by but-1-ene indicates that a chain radical mechanism contributes to the rate of elimination, in addition to the molecular one. The acceleration in rate observed when the packed vessel is used suggests that the mechanism of this radical chain is heterogeneous, similar to that observed for 1,2-dichloroethane by Barton<sup>1</sup> and Howlett.<sup>2</sup> The maximum inhibited rate gave Arrhenius parameters very similar

TABLE 3

	$\log A/s^{-1}$	$E_a/\text{kcal mol}^{-1}$
(i) Direct	13.23	60.43
(ii) Inhibited	13.59	62.25
(iii) Packed vessel	10.91	50.74

to those obtained in the shock-tube study above and supports this theory, as any heterogeneous effects will be small for the short reaction times obtained in the shock tube.

The results obtained and shown in Figures 1—5 agree reasonably well with those calculated from use of RRKM theory and chemical activation results<sup>10</sup> (Table 1). The results obtained for 1-chloro-2-fluoroethane and 1,1,1-trifluoroethane do not agree with those of Sianesi *et al.*<sup>7</sup> Their Arrhenius parameters for ethyl fluoride are also not in agreement with previously published static and shock tube values.<sup>11,14</sup> The change in pre-exponential parameters on increasing fluorination of the ethanes is also not in accord with theoretical predictions. This discrepancy may be due to the small number of experimental values obtained and the uncertainty in reaction time often associated with flow systems.

The shock-tube pyrolysis of 1,1-difluoroethane has recently been studied by Tschuikow-Roux *et al.*<sup>15</sup> by a slightly different technique. They obtained lower Arrhenius parameters than those reported here. There seems to be no obvious explanation for the differences (a factor of 8 in rate at 1200 K). The present study used higher temperatures and shorter reaction times than those of Tschuikow-Roux *et al.*<sup>15</sup> At the highest temperature used for the study of 1,1-difluoroethane small amounts of acetylene were found in the products. Pyrolysis of the standard, n-propyl fluoride, and 1,1-difluoroethane separately showed that the acetylene came from the propene formed by the n-propyl fluoride decomposition and not from the 1,1-difluoroethane. Acetylene attributed to the further decomposition of vinyl fluoride formed by the pyrolysis of 1,1-difluoroethane has been reported.<sup>15</sup> This is probably due to the much longer reaction times used. Calculations at the highest temperature used in the present study by use of the larger of two published values<sup>16</sup> of the rate of

<sup>14</sup> M. Day and A. F. Trotman-Dickenson, *J. Chem. Soc. (A)*, 1969, 233.

<sup>15</sup> E. Tschuikow-Roux, W. J. Quiring, and J. M. Simmie, *J. Phys. Chem.*, 1970, **74**, 2449.

<sup>16</sup> P. Cadman and W. J. Engelbrecht, *Chem. Comm.*, 1970, 453; J. M. Simmie, E. Tschuikow-Roux, and W. J. Quiring, *J. Phys. Chem.*, 1970, **74**, 992.

decomposition of vinyl fluoride confirmed that production of acetylene was not expected to be important.

Pritchard and his co-workers<sup>17</sup> observed  $\alpha\alpha$ -elimination of HF from 1,1-difluoroethane. While we did not attempt any isotope studies to see if this process was occurring, it is most unlikely to be important. The average energy of the reacting molecules here is much less than in the chemical activation studies.<sup>17</sup> This favours the process with lower activation energy (*i.e.*,  $\alpha\beta$ -elimination). Pritchard and his co-workers estimated<sup>17</sup> the activation energy of the  $\alpha\alpha$ -process to be 10 kcal mol<sup>-1</sup> greater than for the  $\alpha\beta$ -process. The Arrhenius parameters reported here therefore probably refer to the  $\alpha\beta$ -process.

The effect of the  $\alpha$ -fluorination and  $\beta$ -fluorination for the ethyl fluorides are compared in Table 4 which also

TABLE 4

Rate constants ratios for the elimination of HX from  $\alpha$ - and  $\beta$ -halogenoethanes

X Y	Cl Cl	F Cl	Cl F	F F
	Rate ratio (920 K)	Rate ratio (976 K)	Rate ratio (920 K)	Rate ratio (976 K)
CH <sub>3</sub> X·CH <sub>2</sub> Y	1.2 <sup>a</sup>	0.23	0.022	0.155 <sup>f</sup>
CH <sub>3</sub> X·Me	1.0 <sup>b</sup>	1.0 <sup>c</sup>	1.0 <sup>b</sup>	1.0 <sup>c</sup>
CX <sub>2</sub> H·Me	6.0 <sup>c</sup>	0.085		
CX <sub>3</sub> ·Me	14.8 <sup>d</sup>	0.0016		

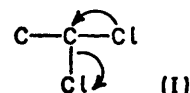
Calculated for a temperature when EtX has a rate coefficient of 1 s<sup>-1</sup>. Values taken from present results and those in Table 1. Values from references 18 and 10 calculated using log *A* = 13.5.

<sup>a</sup> Ref. 18. <sup>b</sup> A. Maccoll and P. J. Thomas, 'Progress in Reaction Kinetics,' vol. 4, Pergamon, Oxford, 1967. <sup>c</sup> Ref. 3. <sup>d</sup> Ref. 4. <sup>e</sup> Ref. 11. <sup>f</sup> Ref. 10.

includes similar data for the ethyl chlorides. The ratios of rates given there are taken for a temperature when the unsubstituted ethyl halide has a rate of 1 s<sup>-1</sup>. The value taken for 1,2-dichloroethane is from the work of Hassler and Setser.<sup>18</sup> This value was chosen because of the uncertainty of the static studies owing to heterogeneous effects.<sup>8</sup>

<sup>17</sup> M. J. Perona, J. T. Bryant, and G. O. Pritchard, *J. Amer. Chem. Soc.*, 1968, **90**, 4782.

In order to explain the observed increase in the rate of elimination on  $\alpha$ -chlorination, Maccoll<sup>19</sup> suggested that the mesomeric release of electrons was larger than the inductive withdrawal at the carbon  $\alpha$  to the chlorine undergoing reaction, as in (I). This was assumed to stabilise the formation of a polar transition state.



In the case of the  $\alpha$ -fluorinated series studied above, a large decrease in the rate of elimination of hydrogen fluoride was observed in proceeding from the mono- to the tri-fluoroethane. A similar trend in rate was observed by Sianesi *et al.*<sup>7</sup> The chemical activation studies of Kirk<sup>10</sup> also predicted this decrease in rate upon  $\alpha$ -fluorination. Fluorine has a larger inductive effect than chlorine but is expected to show smaller mesomeric release of electrons than chlorine. A decrease in rate upon  $\alpha$ -fluorination is consistent with the relative inductive and mesomeric effects in accordance with the experimental trend.

The results for the  $\beta$ -halogenated series indicate that molecules with chlorine in the  $\beta$ -position have a greater rate than with fluorine in this position, both for the elimination of hydrogen fluoride and hydrogen chloride. This can again be explained by fluorine's inductive effect hindering the formation of positive ion formation on the  $\alpha$ -hydrogen being eliminated and on the carbon  $\alpha$  to the halogen. Chlorine's mesomeric effect, being much stronger than for fluorine, helps to counter this inductive effect and hence the reduction in rate is not so marked. Ionic effects can qualitatively explain the relative rates of elimination of hydrogen halide from fluorinated ethanes.

We thank the authors of reference 15 for communicating their results before publication.

[0/1620 Received, September 21st, 1970]

<sup>18</sup> J. C. Hassler and D. W. Setser, *J. Chem. Phys.*, 1966, **45**, 3246.

<sup>19</sup> A. Maccoll, *Adv. Phys. Org. Chem.*, 1966, **3**, 31.