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STUDIES ON A VAPOUR-PHASE PROCESS FOR THE MANUFACTURE OF CHLOROFLUOROETHANES

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SUMMARY

Fluorination of hexachloroethane or of tetrachloroethylene + chlorine by hydrogen fluoride at *ca.* 400 °C in the presence of an aluminium fluoride catalyst gives the unsymmetrical isomers of dichlorotetrafluoroethane and of trichlorotrifluoroethane as the major products. Under similar conditions but using a catalyst of aluminium fluoride containing small amounts of iron, chromium and nickel, symmetrical trichlorotrifluoroethane is the major product. Analogous fluorinations of various intermediates over these catalyst systems have been studied and detailed information about the reaction pathways obtained. Under suitable conditions, s-trichlorotrifluoroethane or s-dichlorotetrafluoroethane can be prepared in a high state of purity.

INTRODUCTION

Notwithstanding the profound advances made in fluorocarbon chemistry in recent years, chlorofluoro-methanes and -ethanes remain by far the most important commercial organic fluorochemicals. Introduced first[1] in the early 1930s, they are still manufactured[2] in essentially the same way by the reaction of hydrogen fluoride with the corresponding chlorocarbon, or mixture of chlorine and hydrocarbon. This reaction may be carried out either in the liquid phase[2] using an antimony halide catalyst at comparatively low temperatures and elevated pressures, or in the vapour phase running at high temperatures and using a solid catalyst[2–7]. Many different catalysts have been proposed, including aluminium fluoride[4]. Both processes are highly efficient but are still being improved. Thus, for the chlorofluoromethanes, a recently-patented vapour-phase process[5] operates in a recirculatory system using a heterogeneous catalyst such as aluminium fluoride in a fluidised bed.

Fluorination of hexachloroethane in the liquid phase with hydrogen fluoride in the presence of an antimony halide catalyst proceeds according to equation (1) and gives[2] the symmetrical isomers (III), (IV) and (V) as by far the principal products with the following molecular formulae:

$$\underset{(I)}{C_2Cl_6} \rightarrow \underset{(II)}{CCl_3CCl_2F} \rightarrow \underset{(III)}{CCl_2FCCl_2F} \rightarrow \underset{(IV)}{CCl_2FCClF_2} \rightarrow \underset{(V)}{CClF_2CClF_2} \quad (1)$$

In the vapour phase in the presence of most solid catalysts[6, 8], including aluminium fluoride[7], only small proportions of (III), (IV) and (V) are formed. The reaction usually proceeds with the formation of the unsymmetrical isomers (VI), (VII) and (VIII) as the major products [equation(2)].

$$\underset{(I)}{C_2Cl_6} \rightarrow \underset{(II)}{CCl_3CCl_2F} \rightarrow \underset{(VI)}{CCl_3CClF_2} \rightarrow \underset{(VII)}{CCl_3CF_3} \rightarrow \underset{(VIII)}{CCl_2FCF_3} \rightarrow \underset{(IX)}{CClF_2CF_3} \quad (2)$$

Such isomers are the more stable ones from a thermodynamic point of view, but are less stable towards hydrolysis[8]. Hence, the symmetrical isomers (IV) and (V) are much preferred for industrial uses as solvents and propellants. Separation of mixed isomers is very difficult (Table 1). For making chlorofluoroethanes, therefore, the liquid-phase process has held the advantage hitherto. Recently, however, a specially selective catalyst has been developed[7] consisting of aluminium fluoride containing small amounts of iron, chromium and nickel, and use of this in the vapour-phase process leads to the formation of symmetrical isomers, *e.g.* (IV) and (V), as the major products. The scope of this convenient process is therefore extended significantly with the introduction of these modified catalysts.

TABLE 1

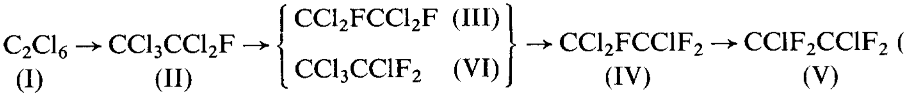
BOILING POINTS AND MELTING POINTS OF CHLOROFLUOROETHANES

Formula		B.p./°C	M.p./°C
CCl_3CCl_3	(I)	(sublimes)	184.5
CCl_3CCl_2F	(II)	136.8	100.0
CCl_2FCCl_2F	(III)	92.8	24.6–26
CCl_3CClF_2	(VI)	91.5	40.6
CCl_2FCClF_2	(IV)	47.6	—35
CCl_3CF_3	(VII)	45.9	14.2
$CClF_2CClF_2$	(V)	3.8	—94
CCl_2FCF_3	(VIII)	3.6	—56.6
$CClF_2CF_3$	(IX)	—38.7	—106

The purpose of the present work was to study in more detail the reactions leading to the formation of the different isomers, and to establish further the catalytic activity of the new systems in which the behaviour of aluminium fluoride has been modified.

RESULTS AND DISCUSSION

Fluorination in the vapour phase of hexachloroethane or mixtures of tetrachloroethylene and chlorine that correspond to hexachloroethane and using hydrogen fluoride/aluminium fluoride, may be carried out readily in the temperature range 300–500 °C. Below 300 °C the reaction proceeds very slowly, whilst above 500 °C pyrolytic phenomena occur. For our experiments, a temperature o 400 °C was chosen because at this temperature it is easiest to make comparisons between catalysts of varying selectivities such as aluminium fluoride alone (type AlMN3 Montedison was used) and the same aluminium fluoride conditioned with the halides of iron, chromium and nickel[7]. The results of runs 1 and 2 reported below (Table 2) show that the reaction involving AlF_3 alone proceeds predominantly according to equation (2), whereas with AlF_3–Fe/Cr/Ni the course of the reaction follows equation (3).



$$\underset{(I)}{C_2Cl_6} \rightarrow \underset{(II)}{CCl_3CCl_2F} \rightarrow \left\{\begin{array}{ll} CCl_2FCCl_2F & (III) \\ CCl_3CClF_2 & (VI) \end{array}\right\} \rightarrow \underset{(IV)}{CCl_2FCClF_2} \rightarrow \underset{(V)}{CClF_2CClF_2} \quad (3)$$

TABLE 2

CHLOROFLUORINATION OF C_2Cl_4[a]

Run No.	1	2
Catalyst	AlF_3	AlF_3–Fe/Cr/Ni[b]
Molar ratio $HF/Cl_2/C_2Cl_4$	3.5/1.34/1	3.3/1.3/1
Catalyst volume/cm^3	280	280
Duration of run/h	2.5	2.5
Collected products/mol %		
$CClF_2CF_3$ (IX)	9.8	0.2
CCl_2CClF_2 (V)	8.4	2.5
CCl_2FCF_3 (VIII)	41.0	0.5
CCl_2FCClF_2 (IV)	5.5	44.0
CCl_3CF_3 (VII)	19.6	0.4
CCl_2FCCl_2F (III)	0.6	21.1
CCl_3CClF_2 (VI)	2.9	10.4
CCl_3CCl_2F (II)	0.8	7.5
CCl_2CCl_2	10.9	12.5
CCl_3CCl_3 (I)	0.5	0.9
$CClF_2CClF_2$: $C_2Cl_2F_4$ (%)	17	83
CCl_2FCClF_2: $C_2Cl_3F_3$ (%)	22	99
CCl_2FCCl_2F: $C_2Cl_4F_2$ (%)	18	67
Conversion HF (%)	77	68
Organic recovery (%)	98	97

[a] Reaction temperature 400 °C; contact time 3 s.

[b] The catalyst contained 0.98 % Fe, 0.90 % Cr and 1.93 % Ni.

These results confirm that the composition of the products depends on the nature of the catalyst which must profoundly influence the reaction mechanism. No hydrogen-containing products were found from either system.

The fluorination of hexachloroethane is more complicated than it appears. From the literature, it has long been believed that the overall process can involve three different types of general reaction, all contributing to the final product mixtures. The first and foremost reaction is clearly halogen exchange promoted by the catalyst between hydrogen fluoride and chlorine present in an organic molecule, *e.g.*:

$$HF + C_2Cl_3F_3 \xrightarrow{[AlF_3]} HCl + C_2Cl_2F_4 \tag{4}$$

Secondly, disproportionations of chlorofluorocarbons are well known[9–11] and catalysis of them by aluminium fluoride has been demonstrated[10], *e.g.*:

$$2C_2Cl_3F_3 \xrightarrow{[AlF_3]} C_2Cl_4F_2 + C_2Cl_2F_4 \tag{5}$$

Thirdly, direct isomerisation reactions have been described[11], *e.g.*:

$$\underset{\text{(IV)}}{CCl_2FCClF_2} \xrightarrow{[AlF_3]} \underset{\text{(VII)}}{CCl_3CF_3} \tag{6}$$

We have studied the activities of the two different catalyst systems to try to establish whether these three types of process are in fact proceeding in each case. The experiments were carried out in a laboratory-scale flow system with the catalyst in a fluid bed. Analysis of products was by gas–liquid chromatography and infrared spectroscopy.

Catalysis by aluminium fluoride alone

Experiments carried out with AlF_3 alone are summarised in Table 3 and show clearly that this catalyst promotes all three processes, fluorination, disproportionation and isomerisation. The fluorinating activity of these catalysts is obvious, and halogen exchange using hydrogen fluoride alone is usually slow[2]. Disproportionation is clearly demonstrated by runs 4 and 5 of Table 3 involving s-trichlorotrifluoroethane, (IV). In these runs hydrogen fluoride was absent, and more than 50 mol % of the products contained amounts of fluorine different from that present in the starting material, divided roughly equally between gain and loss. Run 3, where some hydrogen fluoride was present, is noteworthy. Even here, products with contents of fluorine lower than that of trichlorotrifluoroethane were formed, though only in small amounts, fluorination and disproportionation occurring at the same time.

TABLE 3

REACTIVITY OF $C_2Cl_3F_3$ AND $C_2Cl_2F_4$ OVER AlF_3 CATALYST[a]

Run No.	3	4	5	6	7	8
Feed and molar ratio	1 CCl_2FCClF_2 (IV) + 1 HF	1 CCl_2FCClF_2 (IV) + 1 N_2	CCl_2FCClF_2 (IV)	0.95 $CClF_2CClF_2$ (V) + 0.05 CCl_2FCF_3 (VIII) + 1 N_2	0.95 $CClF_2CClF_2$ (V) + 0.05 CCl_2FCF_3 (VIII) + 9 N_2	0.95 $CClF_2CClF_2$ (V) + 0.05 CCl_2FCF_3 (VIII) + 1 N_2
Catalyst volume/cm^3	280	280	280	280	280	94
Duration of run/h	2	1	1	1	1	2
Contact time/s	3	3	3	3	3	1
Collected products/mol %						
$CClF_2CF_3$ (IX)	10.3	6.8	8.1	22.0	24.5	9.8
$CClF_2CClF_2$ (V)	7.6	4.8	3.7	20.8	22.7	44.5
CCl_2FCF_3 (VIII)	51.4	23.8	16.1	32.4	30.2	35.7
CCl_2FCClF_2 (IV)	9.4	5.2	5.2	2.8	4.5	1.6
CCl_3CF_3 (VII)	18.2	38.5	42.2	20.3	18.1	8.4
CCl_2FCCl_2F (III)	0.4	1.5	1.6	0.1	—	—
CCl_3CClF_2 (VI)	2.1	7.3	8.7	0.6	—	—
CCl_3CCl_2F (II)	—	2.9	3.9	0.1	—	—
CCl_3CCl_3 (I)	—	1.6	3.2	—	—	—
CCl_2CCl_2	0.6	7.6	7.3	0.9	—	—
$CClF_2CClF_2$: $C_2Cl_2F_4$ (%)	13	17	18	39	43	55
CCl_2FCClF_2: $C_2Cl_3F_3$ (%)	34	12	11	12	20	16
CCl_2FCCl_2F: $C_2Cl_4F_2$ (%)	17	17	16	—	—	—
Conversion (%)						
$C_2Cl_2F_4$	—	—	—	47	48	21
$C_2Cl_3F_3$	72	57	53	—	—	—
HF	72	—	—	—	—	—
Organic recovery (%)	99	94	96	99	94	95

[a] Reaction temperature 400 °C.

The isomerising activity of the catalyst is shown by runs 6–8 in which s-dichlorotetrafluoroethane (V) was passed over AlF_3 in the presence of different quantities of nitrogen. In the products of these reactions, large quantities (*ca.* 35 mol %) of unsymmetrical dichlorotetrafluoroethane (VIII) were found, the presence of which could not be explained by disproportionation reactions of other products according to schemes such as the following:

$$\underset{\text{(IX)}}{2CClF_2CF_3} \rightarrow \underset{\text{(VIII)}}{CCl_2FCF_3} + \underset{\text{(X)}}{C_2F_6} \qquad (7)$$

$$\underset{\text{(IV) and (VII)}}{2C_2Cl_3F_3} \rightarrow \underset{\text{(III) and (VI)}}{C_2Cl_4F_2} + \underset{\text{(VIII)}}{CCl_2FCF_3} \qquad (8)$$

The reaction products did not in fact include C_2F_6 (X) or $C_2Cl_4F_2$ [(III) and (VI)] or species of lower fluorine content. Though disproportionation did give rise to 10–25 mol % each of C_2ClF_5 (IX) and $C_2Cl_3F_3$ [(IV) and (VII)], the formation of CCl_2FCF_3 (VIII) cannot be explained in this way and it must arise by a direct isomerisation process [equation (9)]. It appears also that CCl_3CF_3 (VII) does not disproportionate readily.

$$\underset{\text{(V)}}{CClF_2CClF_2} \rightarrow \underset{\text{(VIII)}}{CCl_2FCF_3} \qquad (9)$$

An isomerisation reaction of this type carried out over aluminium chloride has been reported by Miller and colleagues[11] and found to proceed by a mechanism involving intramolecular rearrangements of the halogen atoms. Runs 6 and 7 of Table 3 indicate that varying the concentration of s-dichlorotetrafluoroethane (V) by five times gave rise to little variation in the composition of the products and hence of the reaction rate. Our opinion, therefore, is that this isomerisation proceeds by a mechanism similar to that postulated by Miller[11], which does not require the direct collision at a surface, and hence exchange of halogen, by two organic molecules of the same species. It is most likely to be an intramolecular process occurring on the catalyst surface. Other evidence for direct isomerisation is provided by runs 4 and 5 of Table 3. The amounts of unsymmetrical trichlorotrifluoroethane (VII) formed are so high with respect to those of other compounds such as C_2ClF_5 (IX), C_2Cl_5F (II) and C_2Cl_4/C_2Cl_6 (I), that it is unlikely that it can all be produced from disproportionation reactions. Consequently, a large part of the unsymmetrical trichlorotrifluoroethane (VII) must arise from isomerisation [equation (6)]. In runs 4 and 5 it is shown that dilution with nitrogen also has little effect on this isomerisation, suggesting again that this process proceeds by a unimolecular mechanism.

This type of argument may be developed further and conclusions drawn about what has hitherto been called the disproportionation process. Comparisons of runs 4 and 5 and of runs 6 and 7 of Table 3 show that variations in the concentrations of the starting chlorofluoroethanes do not greatly influence the proportions of the products that arise from disproportionations as well as from isomerisations. We can, therefore, conclude that these transformations also proceed by processes which do not involve the direct collision of two or more molecules of the chlorofluoroethanes. Therefore, it seems that the disproportionation reactions must also proceed by mechanisms involving collision between a molecule of an organic halogen compound and an active centre of the catalyst according to equations such as the following:

$$C_2Cl_3F_3 + [AlF_3] \rightarrow C_2Cl_2F_4 + [AlClF_2] \tag{10}$$

$$C_2Cl_3F_3 + [AlClF_2] \rightarrow C_2Cl_4F_2 + [AlF_3] \tag{11}$$

$[AlClF_2]$ is used to represent catalyst containing chlorine; we do not know its constitution.)

To confirm the possibility of such processes, involving exchange between the catalyst and the organic reagents, we carried out experiments typified by runs 23 and 24 (Table 4). These demonstrated that passage of chloroethanes over AlF_3 in the absence of hydrogen fluoride gave small quantities of chlorofluoroethanes, and that some chlorine was fixed on the catalyst [equation (12)].

TABLE 4

HALOGEN EXCHANGE BETWEEN HALOCARBONS AND AlF_3 CATALYST [a]

Run No.	23	24
Feed/% wt.	12 % C_2Cl_6 + 88 % C_2Cl_4	CCl_2FCClF_2 (IV)
Catalyst	AlF_3	AlF_3 recovered after run 23
Catalyst volume/cm^3	280	140
Chlorine in the catalyst/% wt.		
before the run	0.0	0.57
after 4 h	—	0.04
after 9 h	0.51	—
after 14 h	0.57	—
Contact time/s	3	1.5
Duration/h	14	4
Organic reaction products		
after 15 min	small quantities of C_2Cl_5F, $C_2Cl_4F_2$, $C_2Cl_3F_3$	—
after 1.5 h	*ca.* 0.1 % C_2Cl_5F	—
after 3 h	*ca.* 0.1 % C_2Cl_5F	—
after 4 h		C_2ClF_5, $C_2Cl_2F_4$, CCl_3CF_3, $C_2Cl_4F_2$, C_2Cl_5F, C_2Cl_6, C_2Cl_4
after 9 h	*ca.* 0.1 % C_2Cl_5F	—
after 14 h	*ca.* 0.1 % C_2Cl_3F	—

[a] Reaction temperature 400 °C.

TABLE 5

REACTIVITY OF $C_2Cl_3F_3$, $C_2Cl_2F_4$ OVER AlF_3-Fe/Cr/Ni[a]

Run No.		36	10	11	12	13	37
Feed and molar ratio		1 CCl_2FCClF_2 (IV) + 1 HF	0.50 CCl_2FCClF_2 (IV) + 0.50 CCl_3CF_3 (VII) + 1 HF	CCl_2FCClF_2 (IV)	1 CCl_2FCClF_2 (IV) + 1 N_2	1 CCl_2FCClF_2 (IV) + 2 N_2	0.96 $CClF_2CClF_2$ (V) + 0.04 CCl_2FCF_3 (VIII) + 1 N_2
Catalyst volume/cm^3		280	280	280	280	280	275
Duration of run/h		2	2	1	1	2	1
Catalyst composition							
before the run	Fe (%)	0.78	0.79	0.79	0.78	0.78	0.91
	Cr (%)	0.75	0.75	0.75	0.75	0.74	0.87
	Ni (%)	1.48	1.48	1.48	1.48	1.45	1.76
	Cl (%)	0.05	0.05	0.05	0.05	—	0.05
after the run	Fe (%)	0.75	0.76	0.78	0.78	0.75	0.90
	Cr (%)	0.74	0.74	0.74	0.74	0.73	0.87
	Ni (%)	1.40	1.45	1.45	1.45	1.43	1.75
	Cl (%)	0.76	—	—	2.02	2.04	—
Collected products/mol %							
$CClF_2CF_3$	(IX)	1.0	2.9	—	—	—	0.3
$CClF_2CClF_2$	(V)	38.2	11.1	9.4	9.4	8.0	95.5
CCl_2FCF_3	(VIII)	3.9	44.4	1.7	1.8	1.7	3.0
CCl_2FCClF_2	(IV)	53.5	29.5	79.0	80.0	79.0	1.2
CCl_3CF_3	(VII)	0.4	9.3	0.5	0.5	0.6	
CCl_2FCCl_2F	(III)	0.4	0.4	1.3	1.2	9.2	—
CCl_3CClF_2	(VI)	2.6	2.4	7.6	6.8		—
CCl_3CCl_2F	(II)	—	—	—	—	—	—
CCl_3CCl_3	(I)	—	—	—	—	—	—
CCl_2CCl_2		—	—	0.5	0.3	1.5	—
$CClF_2CClF_2$: $C_2Cl_2F_4$ (%)		91	20	85	84	83	97

CCl_2FCClF_2: $C_2Cl_3F_3$ (%)	99.3	76	99.3	99.4	99.3	—
CCl_2FCCl_2F: $C_2Cl_4F_2$ (%)	13	15	15	15	—	—
Conversion (%)						
$C_2Cl_3F_3$	46	62	20	20	20	—
$C_2Cl_2F_4$	—	—	—	—	—	1.5
HF	43	56	—	—	—	—
Organic recovery (%)	99	94	99	97	99	99

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[a] Reaction temperature 400 °C; contact time 3 s.

$$C_2Cl_6 + [AlF_3] \rightarrow C_2Cl_5F + [AlClF_2] \tag{12}$$

A sample of catalyst obtained from such an experiment was then treated with s-trichlorotrifluoroethane (IV). The catalyst lost its chlorine and reverted to aluminium fluoride, and the organic product contained all the halogenoethanes from C_2ClF_5 to C_2Cl_6/C_2Cl_4 with a small overall up-take of chlorine [equation (11)].

The demonstration of these direct exchanges of halogen between the catalyst and the halogenoethanes suggested that in the presence of hydrogen chloride it would be possible to obtain chlorination of a chlorofluorocarbon according to equation (13), *i.e.* the reverse of the process usually desired:

$$C_2Cl_3F_3 + HCl \rightarrow C_2Cl_4F_2 + HF \tag{13}$$

Such reactions occurred but will not be detailed. The effect is well demonstrated by runs 25, 27, 33 and 43 (Table 7) which were carried out over the AlF_3–Fe/Cr/Ni catalyst to be described later. Evidently, therefore, all these processes are equilibria and it seems that they all proceed by mechanisms involving exchange of halogen between hydrogen halide and the catalyst, and between catalyst and the organic reagents, according to schemes such as equations (14) and (15):

$$HF + [AlClF_2] \rightleftharpoons HCl + [AlF_3] \tag{14}$$

$$C_2Cl_3F_3 + [AlF_3] \rightleftharpoons C_2Cl_2F_4 + [AlClF_2] \tag{15}$$

It will be noted that equation (15) is essentially the same as those already postulated for the "disproportionation" reaction—see equations (10) and (11). Successful fluorinations proceed therefore by the use of sufficiently high local concentrations of hydrogen fluoride to drive equilibria (14) and (15) in the desired direction. Furthermore, the "disproportionation" reaction is not a specific entity, but arises from a series of equilibria between the organic and inorganic chlorofluorides [*cf.* equations (10), (11) and (15)]. In the absence of added hydrogen halide, these can lead to a given chlorofluoroethane being converted into most of its fellows.

Catalysis by aluminium fluoride modified with iron, chromium and nickel

By the use[7] of an aluminium fluoride catalyst containing appropriate quantities of iron, chromium and nickel halides, and choosing the optimum reaction conditions, it is possible to obtain trichlorotrifluoroethane containing the symmetrical isomer (IV) in proportions as high as 99.8%, and dichlorotetrafluoroethane containing better than 98% of the symmetrical isomer (V). These proportions are as good as those obtained from the best liquid-phase processes and can be approached in large-scale operation.

We repeated the types of experiment just reported for catalysis by AlF_3 to try to segregate the basic processes occurring over the modified catalysts, and the runs are recorded in Table 5. It is obvious from Table 2 that under comparable conditions AlF_3–Fe/Cr/Ni gives a lower overall degree of fluorination than AlF_3 alone, and this has been confirmed. It was further shown that fluorination and "disproportionation" occur as before, though in the absence of hydrogen fluoride smaller quantities of products ascribable to "disproportionation" are present than when AlF_3 alone is used. Runs 11–13 suggest nevertheless that the unimolecular mechanism discussed above still applies.

However, there is one characteristic feature in which the catalytic activity of these modified systems differs from that of AlF_3 alone. In the steps of the process leading to the formation of trichlorotrifluoroethane and dichlorotetrafluoroethane, the direct isomerisation reactions [*i.e.* equations (6) and (9)] do not appear to occur to any extent. All the runs in Table 5 into which unsymmetrical isomers of $C_2Cl_3F_3$ (VII) and $C_2Cl_2F_4$ (VIII) were not actually introduced are noteworthy for the very low amounts of these products formed, compared to the corresponding runs of Table 3. It seems logical to conclude therefore that the modifying activity of iron, chromium and nickel (particularly of iron) consists in rendering inactive those centres of the aluminium fluoride catalyst which promote isomerisation.

The experiments to be described in detail later (Table 7) showed that with AlF_3–Fe/Cr/Ni it is possible to chlorinate a chlorofluorocarbon with hydrogen chloride [equation (13)]. In accordance with the argument developed for catalysis by AlF_3 alone, it therefore seems reasonable to conclude that with AlF_3–Fe/Cr/Ni also the reactions proceed by similar mechanisms involving halogen exchange between hydrogen halides and the catalyst, and between the catalyst and chlorofluorocarbons [equations (14) and (15)], and that the activity of this catalyst differs only in the suppression of isomerisation.

If this is so, one apparent anomaly needs to be resolved: in the chlorofluorination of perchloroethylene with AlF_3–Fe/Cr/Ni (run 2, Table 2), the tetrachlorodifluoroethane formed contains a significant proportion of the unsymmetric isomer (VI), and the effect was confirmed in the runs of Table 5. We therefore carried out a series of experiments involving the formation and further reactions of tetrachlorodifluoroethane (Table 6). It would have been useful to start by studying the fluorination of pentachlorofluoroethane (II), but under our experimental conditions, even by reducing reaction times and HF concentrations to a minimum, it was not possible to stop the process at this stage. The principal product was in fact trichlorotrifluoroethane. We therefore passed samples of tetrachlorodifluoroethane with varying isomer ratios (runs 20–22) over the AlF_3–Fe/Cr/Ni catalyst in the absence of HF. These experiments showed that, of the two isomers, the symmetrical one (III) reacts rather more readily. Also relevant at this point are the chlorinations of fluorinated derivatives referred to earlier, the results of which are given in Table 7. It was found that the symmetrical isomer (III) reacts more easily with hydrogen chloride and the same catalyst system (run 33). Run 27 is specially significant also, showing that in the chlorination of s-trichlorotrifluoro-

TABLE 6

REACTIVITY OF $C_2Cl_4F_2$ OVER AlF_3-Fe/Cr/Ni [a]

Run No.		19	20	21	22
Feed and molar ratio		0.50 CCl_2FCCl_2F (III) + 0.50 CCl_3CClF_2 (VI) + 1.3 HF	0.82 CCl_2FCCl_2F (III) + 0.18 CCl_3CClF_2 (VI) + 1 N_2	0.50 CCl_2FCCl_2F (III) + 0.50 CCl_3CClF_2 (VI) + 1 N_2	0.20 CCl_2FCCl_2F (III) + 0.80 CCl_3CClF_2 (VI) + 1 N_2
Catalyst volume/cm^3		280	280	280	280
Duration of run/h		1	1	1	1
Catalyst composition					
before the run	Fe (%)	0.78	0.78	0.78	0.78
	Cr (%)	0.75	0.75	0.75	0.75
	Ni (%)	1.48	1.48	1.48	1.48
	Cl (%)	0.05	0.05	0.05	0.05
after the run	Fe (%)	0.75	0.75	0.75	0.75
	Cr (%)	0.74	0.71	0.71	0.72
	Ni (%)	1.45	1.42	1.43	1.45
	Cl (%)	2.06	2.06	2.11	2.10
Collected products/mol %					
$CClF_2CClF_2$	(V)	12.1	0.6	0.7	0.4
CCl_2FCF_3	(VIII)	2.5			
CCl_2FCClF_2	(IV)	58.2	27.9	29.0	27.7
CCl_3CF_3	(VII)	0.6	0.3	0.3	0.3
CCl_2FCCl_2F	(III)	10.1	28.6	19.3	6.2
CCl_3CClF_2	(VI)	12.8	20.6	35.8	55.8
CCl_3CCl_2F	(II)	1.9	13.0	7.5	—
CCl_3CCl_3	(I)	0.2	1.5	1.2	1.1
CCl_2CCl_2		1.6	7.5	6.2	8.5
$CClF_2CClF_2$: $C_2Cl_2F_4$ (%)		83	—	—	—

CCl_2FCClF_2: $C_2Cl_3F_3$ (%)	98.9	99.0	98.9	98.8
CCl_2FCCl_2F: $C_2Cl_4F_2$ (%)	44	58	35	10
Conversion (%)				
$C_2Cl_4F_2$	77	51	45	38
HF	66	—	—	—
Organic recovery (%)	96	98	97	98

---

[a] Reaction temperature 400 °C; contact time 3 s.

TABLE 7

REACTION OF $C_2Cl_2F_4$, $C_2Cl_3F_3$ AND $C_2Cl_4F_2$ WITH HCl AND AlF_3–Fe/Cr/Ni[a]

Run No.		25	27	43	33
Feed and molar ratio		0.95 $CClF_2CClF_2$ (V) + 0.05 CCl_2FCF_3 (VIII) + 1 HCl	1 CCl_2FCClF_2 (IV) + 1 HCl	0.51 CCl_2FCClF_2 (IV) + 0.49 CCl_3CF_3 (VII) + 1 HCl	0.56 CCl_2FCCl_2F (III) + 0.44 CCl_3CClF_2 (VI) + 1 HCl
Catalyst volume/cm^3		280	280	280	280
Duration of run/h		2	2	2	1.5
Catalyst composition					
before the run	Fe (%)	0.98	0.98	0.92	0.98
	Cr (%)	0.90	0.90	0.90	0.90
	Ni (%)	1.93	1.93	1.85	1.93
	Cl (%)	2.30	2.30	n.d.	2.30
after the run	Fe (%)	0.75	0.85	0.80	0.80
	Cr (%)	0.91	0.91	0.90	0.93
	Ni (%)	1.78	1.78	1.80	1.78
	Cl (%)	2.96	2.90	3.06	2.90
Collected products/mol %					
$CClF_2CClF_2$	(V)	91.0	0.8	0.3	0.2
CCl_2FCF_3	(VIII)	3.8	0.2	11.1	
CCl_2FCClF_2	(IV)	0.5	79.7	31.2	19.3
CCl_3CF_3	(VII)	3.8	0.5	39.8	0.2
CCl_2FCCl_2F	(III)	0.5	1.6	0.5	21.5
CCl_3CClF_2	(VI)		15.3	12.6	38.3
C_2Cl_5F	(II)	—	0.5	0.8	9.2
C_2Cl_6	(I)	—	—	—	1.8
C_2Cl_4		0.4	1.4	3.7	9.5
$CClF_2CClF_2$: $C_2Cl_2F_4$ (%)		96	77	3	—

CCl_2FCClF_2: $C_2Cl_3F_3$ (%)	12	99.4	44	99.1
CCl_2FCCl_2F: $C_2Cl_4F_2$ (%)	—	10	4	36
Conversion (%)				
$CClF_2CClF_2$	4	—	—	—
$C_2Cl_3F_3$	—	20	29	—
$C_2Cl_4F_2$	—	—	—	40
HCl	—	18	12	11
Organic recovery (%)	98	99	97	93

[a] Reaction temperature 400 °C; contact time 3 s.

ethane (IV) the tetrachlorodifluoroethane obtained was very largely the unsymmetrical isomer (VI).

In our opinion, the results indicate that the amounts of unsymmetrical tetrachlorodifluoroethane (VI) found in the products formed using the AlF_3–Fe/Cr/Ni system can be explained without the need to invoke an isomerisation process of the type promoted by the AlF_3 catalyst. Isomer (VI) is formed preferentially by chlorination of the symmetrical trichloride (IV) and once formed is removed more slowly than its symmetrical isomer (III) by both fluorination and chlorination.

Returning now to the chlorinations of Table 7, it is noteworthy that in these experiments, and in others listed in Tables 5 and 6 where no hydrogen chloride was added, the chlorine content of the catalyst increased. Run 43 is of interest. It appears that chlorination is occurring preferentially with the symmetrical isomer (IV) (*cf.* run 27), but that even under these conditions the unsymmetric isomer (VII) is undergoing fluorination to give unsymmetric tetrafluoride (VIII). In run 10, when hydrogen fluoride was present it had been shown that isomer (VII) fluorinates more readily than (IV). Run 25 indicates that the symmetrical tetrafluoride (V) is chlorinated relatively slowly.

The various reactions involved with the HF–AlF_3–Fe/Cr/Ni system are collected together in Figure 1 and, if the proportions of the individual products from the experiments are compared, conclusions about the reaction rates may be drawn as given in the right-hand column. For conversion A, no direct results could be obtained but it seems likely that fluorination to the s-$C_2Cl_4F_2$ (III) predominates. These results suggest that the selectivity shown in the overall process arises from two factors: (a) fluorination proceeds to give the symmetrical compounds preferentially, *i.e.* reactivities are in the order $-CCl_3 > -CCl_2F > -CClF_2$ (as has been generally accepted[2] for fluorinations of this type from the time of the original reports[12]) and (b) chlorination proceeds preferentially at $-CCl_2F$ groups rather than at $-CClF_2$ (which would be expected). Very little direct isomerisation occurs.

It was of interest to test one aspect of these conclusions by studying the fluorination of the isomers of $C_2Cl_2F_4$ [(V) and (VIII)] over the modified catalyst (see Table 8). The symmetrical isomer (V) reacted very slowly, but the unsymmetric isomer (VIII) was partly converted to the pentafluoride (IX). Conclusion (a) above is not in accord with the observation that CCl_2FCCl_2F (III) fluorinates faster than CCl_3CClF_2 (VI). Compound (III) presumably reacts faster because it has two $-CCl_2F$ groups, each with reactivity only a little below that of the $-CCl_3$ group of (VI).

All these considerations suggest that the significant stages in this overall fluorination process may be best represented as in Figure 2. Compounds or reactions not represented have only very minor roles in the process.

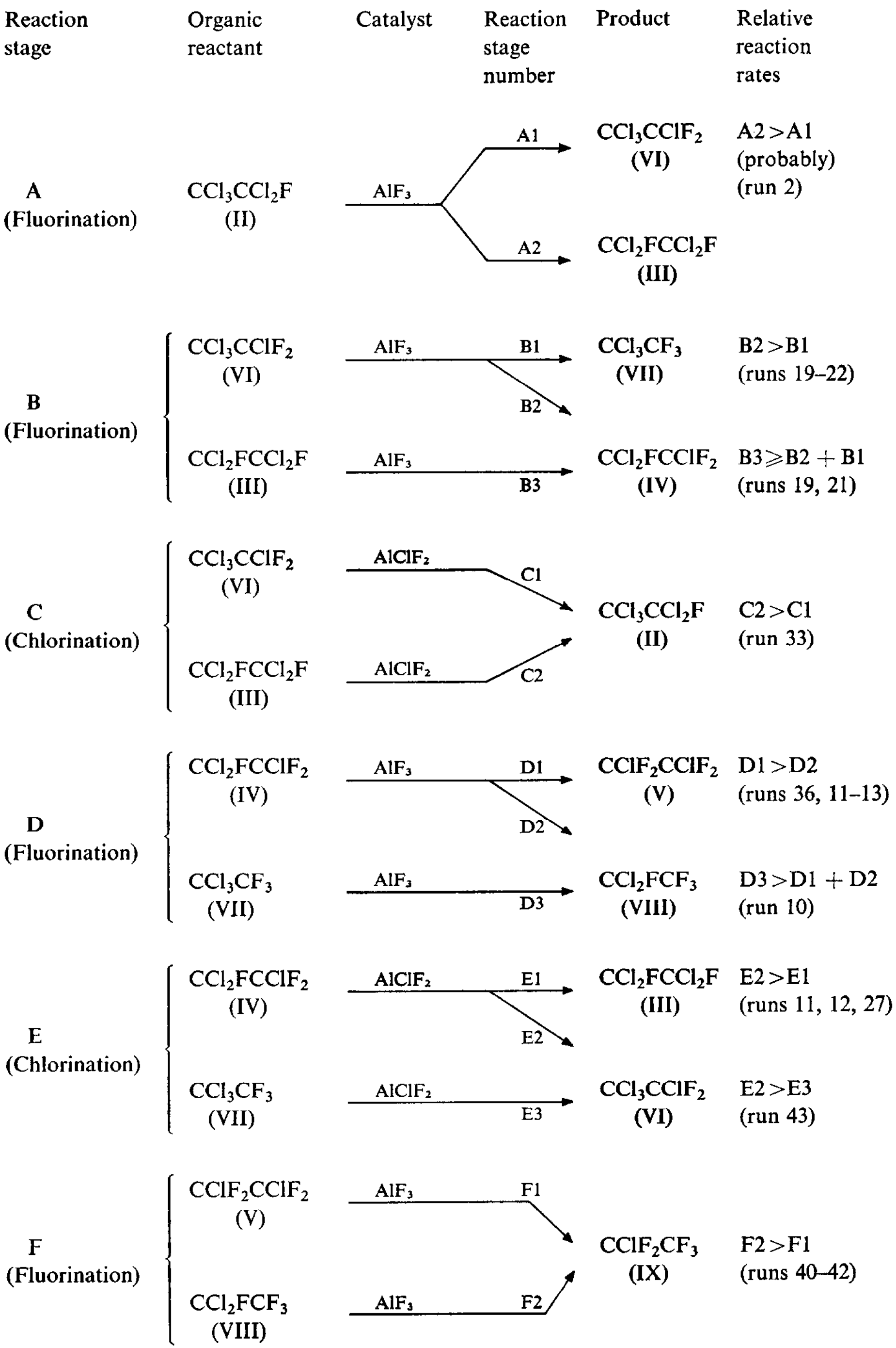


Fig. 1. Interconversions of chlorofluoroethanes over AlF_3–Fe/Cr/Ni catalysts.

TABLE 8

FLUORINATION OF $C_2Cl_2F_4$ OVER AlF_3–Fe/Cr/Ni [a]

Run No.	40	41	42
Feed and molar ratio	0.96 $CClF_2CClF_2$ (V) + 0.04 CCl_2FCF_3 (VIII) + 1 HF	0.44 $CClF_2CClF_2$ (V) + 0.56 CCl_2FCF_3 (VIII) + 1 HF	0.15 $CClF_2CClF_2$ (V) + 0.85 CCl_2FCF_3 (VIII) + 1 HF
Catalyst volume/cm^3	280	280	280
Duration of run/h	1	1	1
Collected products/mole %			
$CClF_2CF_3$ (IX)	9.5	27.6	38.5
$CClF_2CClF_2$ (V)	88.2	41.5	12.5
CCl_2FCF_3 (VIII)	1.8	30.0	47.1
$C_2Cl_3F_3$	0.5	0.9	1.9
$CClF_2CClF_2$: $C_2Cl_2F_4$ (%)	98	58	21
Conversion (%)			
$C_2Cl_2F_4$	10	29	41
HF	10	28	37
Organic recovery (%)	99	97	97

[a] Reaction temperature 450 °C; contact time 3 s; catalyst AlF_3 containing 0.5 % Fe, 0.5 % Cr and 0.5 % Ni.

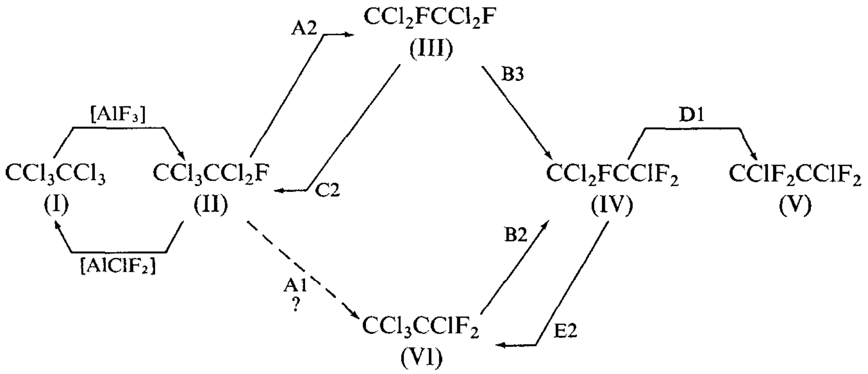
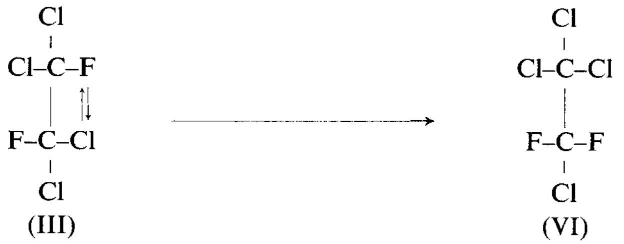


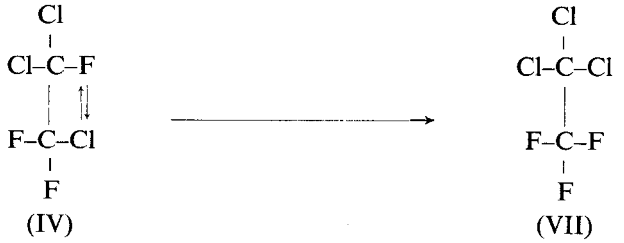
Fig. 2. Sequence of fluorination of C_2Cl_6 by HF and AlF_3–Fe/Cr/Ni catalyst.
Reaction stages A2, (A1), B2, B3 and D1 are the fluorinations occurring preferentially (Fig. 1).
Reaction stages C2 and E2 are the chlorinations occurring preferentially (Fig. 1).

Isomerisation in catalysis by aluminium fluoride

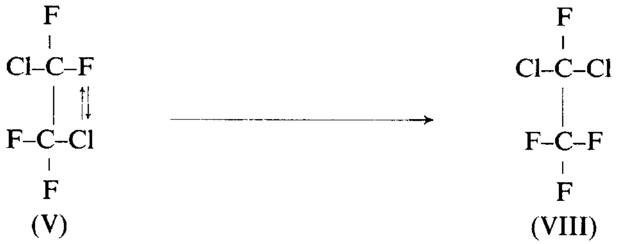
Returning to catalysis by AlF_3 alone, from the results reported above it appears that iron, chromium and nickel do block the centres of activity responsible for isomerisation reactions but that they do not greatly interfere with the centres responsible for halogen exchange in either direction. This supports the conclusion that isomerisations observed with AlF_3 do not proceed through a halogen-exchange mechanism and, by exclusion, must utilise an intramolecular mechanism of the type suggested by Miller[11]. Naturally, the transformations of symmetrical to unsymmetrical isomers according to equations (16)–(18) are favoured by the greater thermodynamic stabilities of the latter ($\geqslant$C–F bonds increase in strength as the number of fluorine atoms carried on that carbon increase[13]). For fluorinations with HF and AlF_3–Fe/Cr/Ni, although s-$C_2Cl_4F_2$ (III) reacts somewhat faster than unsymmetrical $C_2Cl_4F_2$ (VI), the unsymmetrical $C_2Cl_3F_3$ (VII) is fluorinated faster than the symmetrical isomer (IV), and the unsymmetrical $C_2Cl_2F_4$ (VIII) also fluorinates faster than the symmetrical isomer (V). Almost certainly the same applies to catalysis by AlF_3 alone (this is difficult to test because of isomerisation, but the last case is true for other catalyst systems[8]). It is thus easy to see why AlF_3 alone appears to be the more active catalyst. The reaction pathway involves initial fluorination to give the symmetrical isomers preferentially [first stages of equation (1)] followed by rapid intramolecular isomerisations to give the unsymmetrical isomers [equations (16)–(18)]. These are then fluorinated further fairly readily.



(III) (VI) (16)



(IV) (VII) (17)



(V) (VIII) (18)

The reactions involved make up a scheme represented in Figure 3. Again, only significant stages are included.

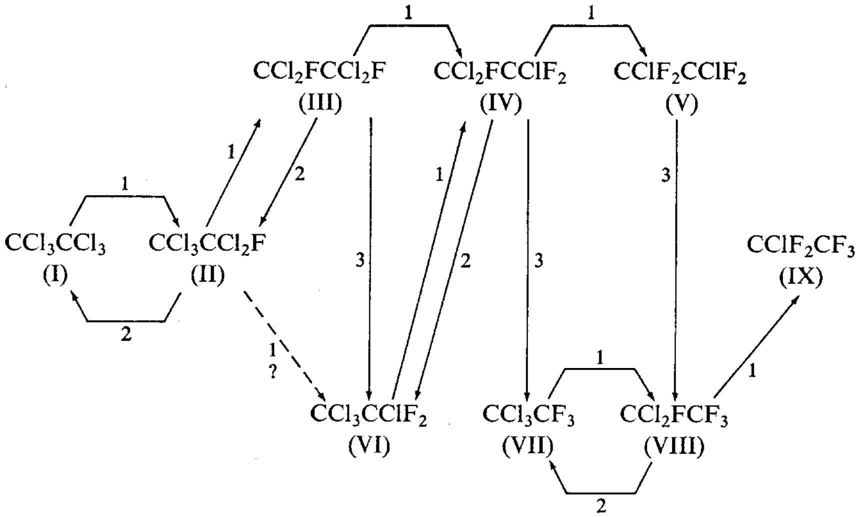


Fig. 3. Sequence for fluorination of C_2Cl_6 by HF and AlF_3 catalyst. (1) Fluorine uptake; (2) chlorine uptake; and (3) isomerisation.

GENERAL CONCLUSIONS

All these results involving fluorinations by hydrogen fluoride and aluminium fluoride are apparently explained if it is assumed firstly that hydrogen halides and aluminium halides form an equilibrium system [equation (14)], and that aluminium halides and chlorofluorocarbons give equilibria of a second type [*e.g.* equation (15)]. A sufficient excess of hydrogen fluoride will ensure overall fluorination. Then, although $-CCl_3$ groups are fluorinated readily, the derived $-CCl_2F$ groups are not very stable. They may be fluorinated almost as readily as $-CCl_3$, but will also revert back easily to $-CCl_3$ with chlorine-containing centres in the catalyst [arising as in equation (12)]. The products of the next stage of fluorination ($-CClF_2$ groups) are much more stable than $-CCl_2F$. Under normal operating conditions, they cannot be fluorinated further with HF/AlF_3 at all readily, and the same applies to back-exchange to $-CCl_2F$ with chlorine-containing catalyst. These processes completely explain the reaction products obtained from HF and AlF_3–Fe/Cr/Ni catalysts.

With AlF_3 alone as catalyst they still hold, but are interspersed with those of another type, *i.e.* isomerisations of products with chlorine on each carbon in either $-CCl_2F$ or $-CClF_2$ groups to give maximum unsymmetry. Isomerisations are inhibited if iron, chromium and nickel are present in the catalyst, but occur readily with AlF_3 alone. Because of this, and the ready fluorination of $-CCl_3$ and $-CCl_2F$ groups, it is possible to obtain C_2ClF_5 with HF/AlF_3.

EXPERIMENTAL

Interconversions of chlorofluoroethanes

The runs were carried out (Fig. 4) in an Inconel tube (R) (diameter 5 cm, length 100 cm) externally heated by an electrical furnace (F). A set of thermocouples, in an Inconel well, made it possible to read the temperatures (T_1, T_2, T_3) at three different heights along the reactor: there was no gradient between T_1, T_2 and T_3. The catalyst was held in place by an Inconel sintered disc; the reactions were carried out under fluid bed conditions (linear velocity 5 cm s^{-1}).

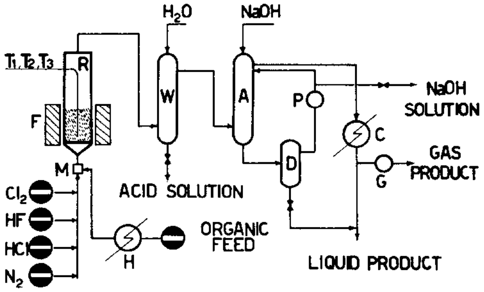


Fig. 4. Diagram of the apparatus employed for the interconversion of chlorofluoroethanes.

Organic compounds other than $C_2Cl_2F_4$ were metered in the liquid phase by a pump and vaporised; $C_2Cl_2F_4$ was measured in the gas phase by a flow meter. The whole organic feed was heated to 200 °C (in H) and introduced into a gas mixer (M) where it was blended with Cl_2, HF, HCl or N_2; the latter gases were also measured by flow meters.

The reactions were all carried out at constant temperature (generally 400 °C) and constant pressure (slightly over atmospheric pressure, *i.e.* 780 mmHg).

The reaction products were washed with water at 50 °C in a polytetrafluoroethylene bottle (W) and then with a 10% NaOH solution at room temperature in a glass column (A). The organic products eventually condensed in A were separated from NaOH in a decanter (D); the NaOH was recycled into A by a pump (P). The gas leaving A was cooled to 0 °C in a condenser (C) and the liquid obtained was combined with that collected in D. The remaining gas was measured in a gas meter (G) and collected in a PVC balloon. The gas and liquid were analysed separately, first by GLC and then by IR spectroscopy.

Organic feeds were *ca.* 600 g h^{-1} for all runs reported except 7 (135 g h^{-1}), 1 and 2 (175 g h^{-1}), 13 (400 g h^{-1}) and 5 and 11 (1200 g h^{-1}).

Catalysts

Two catalysts were used: an aluminium fluoride of the type referred to previously (ref. 7, example 2; the particular batch used was Montedison AlMN3) and the same containing iron, chromium and nickel. In order to prepare the latter, a solution of $NiCl_2{\bullet}6H_2O$ (60–78 g), $CrCl_3{\bullet}6H_2O$ (38–46 g) and $FeCl_3$ (22–28 g) in sufficient water to give a final volume of 150 cm^3 (corresponding to the total volume of the pores of the aluminium fluoride to be impregnated) was poured on to 1000 g of AlMN3 Montedison under continuous-stirring conditions. The mixture was dried and heated at 400 °C with anhydrous HF.

The catalyst had the following particle size distribution:

Over 120	mesh	(ASTM	sieve)	5%
120–140	”	”	”	15%
140–170	”	”	”	13%
170–200	”	”	”	16%
200–230	”	”	”	19%
230–270	”	”	”	13%
270–325	”	”	”	13%
Under 325	”	”	”	6%

Analysis of products

Analytical GLC work was carried out using a 6 m copper column (diameter 4 mm) packed with 25% (w/w) silicone oil DC 550 on Chromosorb P, 60/80 mesh, and with a thermal conductivity detector [carrier gas; He, 30 cm^3 min^{-1} at about 2 atm: temperature (a) column; programmed temperature 5 °C min^{-1} increase, initial 50 °C, final 150 °C; (b) introduction 120 °C; (c) detector 120 °C].

The isomer ratio of $C_2Cl_4F_2$ was determined by GLC using a similar column packed with 25% (w/w) Kel-F 3 on celite, 60/80 mesh [carrier gas; He, 45 cm^3 min^{-1}: temperature (a) column; 50 °C (constant); (b) introduction 120 °C; (c) detector 120 °C]. Known mixtures were calibrated by NMR spectroscopy.

The isomer ratio of $C_2Cl_3F_3$ and of $C_2Cl_2F_4$ was determined by GLC analysis and IR spectroscopy, GLC conditions being the same as for $C_2Cl_4F_2$. A GLC fraction of $C_2Cl_3F_3$ or $C_2Cl_2F_4$ was then introduced into the infrared cell and a vapour-phase spectrum measured using a Perkin–Elmer Model 137 instrument and a gas cell of 10 cm optical path with NaCl windows. Analytical bands used were as follows:

(a) Determination of CCl_2FCClF_2 : $C_2Cl_3F_3$ (%) less than 98.5; for CCl_2FCClF_2, 1109 cm^{-1}; for CCl_3CF_3, 1255 cm^{-1}.

(b) Determination of CCl_2FCClF_2 : $C_2Cl_3F_3$ (%) between 98.5 and 99.8; for CCl_2FCClF_2, 1414, 1377, 1342 cm^{-1}; for CCl_3CF_3, 1255 cm^{-1}.

(c) Determination of $CClF_2CClF_2$: $C_2Cl_2F_4$ (%); for $CClF_2CClF_2$, 1140 cm^{-1}; for CCl_2FCF_3, 1295 cm^{-1}.

The isomer ratios were derived from calibration curves of known mixtures of $C_2Cl_3F_3$ or $C_2Cl_2F_4$ analysed both by NMR and IR spectroscopy. Many results were confirmed directly by NMR analysis. The accuracy obtained was ±2% when the quantity of symmetrical isomer of $C_2Cl_2F_4$, $C_2Cl_3F_3$ and $C_2Cl_4F_2$ was less than 15%.

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