

The behaviour of chlorofluoroethanes on β -aluminium(III) fluoride: a [^{36}Cl] radiotracer study

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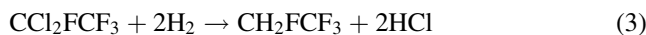
Abstract

A [^{36}Cl] radiotracer study of the behaviour of 1,1,2-trichlorotrifluoroethane on β -aluminium(III) fluoride at elevated temperature indicates that the isomerisation of $\text{CCl}_2\text{FCClF}_2$ to CCl_3CF_3 occurs by an intramolecular process. Isomerisation is followed by dismutation of CCl_3CF_3 to give CCl_2FCF_3 and $\text{CCl}_3\text{CClF}_2$. In neither reaction, surface Al–Cl groups are formed. The compound $\text{CCl}_3\text{CClF}_2$ undergoes further reaction, readily, apparently also via dismutation processes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The conversion of unwanted stocks of 1,1,2-trichlorotrifluoroethane, which prior to the Montreal Protocol was used widely as a degreasing solvent, to the CFC-alternative refrigerant, 1,1,1,2-tetrafluoroethane, HFC-134a, could be a more attractive option for its disposal than by combustion. We have been investigating a possible route for the conversion of $\text{CCl}_2\text{FCClF}_2$ to CH_2FCF_3 that does not require the use of anhydrous hydrogen fluoride (HF) and have demonstrated [1,2] that on a laboratory scale, this can be achieved by an heterogeneously catalysed process. Formally, the process can be described in three steps (Eqs. (1)–(3)).



β -Aluminium(III) fluoride, which has the hexagonal tungsten bronze structure [3], is a good catalyst for the conversion of $\text{CCl}_2\text{FCClF}_2$ to CCl_3CF_3 at 633 K and has reasonable selectivity for the desired product, CCl_2FCF_3 [1]. Experiments under flow conditions using the related catalyst, γ -alumina

pre-fluorinated with dichlorodifluoromethane, and very short catalyst contact times have confirmed that CCl_2FCF_3 is formed via the intermediate (CCl_3CF_3) and imply that the conversion of CCl_3CF_3 to CCl_2FCF_3 proceeds by a dismutation reaction rather than by a simple fluorination [2].

Additional evidence for these findings is now presented from the results of a [^{36}Cl] radiotracer study in which events that occur at the surface of β - AlF_3 during its exposure to $\text{CCl}_2\text{FCClF}_2$ or other members of the chlorofluoroethane series, $\text{C}_2\text{Cl}_{6-n}\text{F}_n$, were examined using a Geiger–Müller direct monitoring method. This technique was developed in Glasgow for [^{14}C] adsorption measurements relevant to hydrocarbon catalysis by supported metals [4] and has been used subsequently with the radiotracers [^{36}Cl] and [^{35}S] for a variety of applications. It has been particularly useful in probing Lewis acid–base interactions at fluorinated surfaces [5–7] and in monitoring the progress under static conditions of catalytic reactions involving fluorine-containing compounds, for example the CsF catalysed chlorofluorination of sulfur tetrafluoride [8,9].

2. Results and discussion

A study of the catalytic behaviour of β -aluminium(III) fluoride towards 1,1,2-trichlorotrifluoroethane under static conditions was carried out to aid the interpretation of the

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Table 1
Reaction of $\text{CCl}_2\text{FCClF}_2$ with $\beta\text{-AlF}_3$ and fluorinated γ -alumina

Catalyst	Reaction conditions			Conversion (%) ^a						Retention (%) ^b
	Temperature (K)	Time (h)	$\text{CCl}_2\text{FCClF}_2$ (mmol)	112 a	113	113 a	114	114 a	115	
$\beta\text{-AlF}_3$	613	24	3.68	2.4	4.0	18.7	3.0	52.6	0.8	18.5
F- γ -alumina	643	24	4.10	1.7	0	43.1	2.2	38.6	1.1	13.3

^a Determined by ^{19}F NMR spectroscopy; defined as: mmol products/mmol reactant 113. Key for compounds: 115, CClF_2CF_3 ; 114, $\text{CClF}_2\text{CClF}_2$; 114a, CCl_2FCF_3 ; 113, $\text{CCl}_2\text{FCClF}_2$; 113a, CCl_3CF_3 ; 112a, $\text{CCl}_3\text{CClF}_2$.

^b Defined as: (mmol identified products – mmol reactant 113)/reactant 113. Shown by GC–MS and ^{19}F NMR to contain $\text{CCl}_3\text{CClF}_2$, C_2Cl_6 and C_2Cl_4 .

radiotracer experiments, since radiotracer experiments per se do not provide chemical identification of the reaction products. Therefore, it was necessary to establish the detailed chemistry under conditions that would be similar to those used in the radiotracer experiments to be described in the following paragraphs. The behaviour of γ -alumina, previously fluorinated with sulfur tetrafluoride, was also examined, since previous work under flow conditions has shown that the behaviour of both the materials is very similar [1].

Under static conditions, 1,1,2-trichlorotrifluoroethane was converted to a mixture of other members of the series, $\text{C}_2\text{Cl}_{6-n}\text{F}_n$, by contact with $\beta\text{-AlF}_3$ or γ -alumina, which had been fluorinated with SF_4 , also under static conditions. Conversion was essentially complete at 613–643 K within 24 h (Table 1). The product distributions were similar to those reported from catalytic reactions under flow conditions [1] in that both catalysts favoured the formation of the asymmetric isomers, CCl_3CF_3 and CCl_2FCF_3 . The major products formed in the presence of fluorinated γ -alumina were CCl_3CF_3 followed by CCl_2FCF_3 , with the reverse order being found over $\beta\text{-AlF}_3$ (Table 1). In neither case were substantial quantities of the more highly fluorinated product (CClF_2CF_3) observed but a mixture of compounds, $\text{C}_2\text{Cl}_{6-n}\text{F}_n$ with $n < 3$ was apparent. They were not removed completely from the reaction vessel by vacuum distillation at ambient temperature (Table 1) but could be removed by distillation above room temperature under dynamic vacuum.

Repetition of the reactions, up to six times, using the same sample of $\beta\text{-AlF}_3$ or fluorinated γ -alumina in each case, did

not change the observed behaviour to any great extent. Although there was a build-up of less volatile products, identified as a mixture of $\text{CCl}_3\text{CClF}_2$, C_2Cl_6 and C_2Cl_4 , in the metal vessel over the course of each series of reactions, this did not appear to inhibit the catalytic activity. Product distributions obtained using fluorinated γ -alumina were relatively constant over a series of multiple additions. Typical product composition data, obtained from GC analysis, were $\text{C}_2\text{Cl}_3\text{F}_3$ isomers 38–56%, $\text{C}_2\text{Cl}_2\text{F}_4$ isomers 60–41% and CClF_2CF_3 2–3%. The organic material retained, quantified by mass balance and expressed as a fraction of the mass of the reactant $\text{CCl}_2\text{FCClF}_2$, rose from 8.3% after the first addition to an approximately constant value of 25% in subsequent experiments of the series. The corresponding results obtained using $\beta\text{-AlF}_3$ were more variable. However, apart from one experiment, the fraction of organic material retained was always in the range of 13–47%. With neither catalyst, however, was there any discernible relationship between the product distribution and the quantity of material retained. Therefore, it was concluded that the variability in the behaviour was due to physical rather than chemical reasons.

A sample of $\beta\text{-AlF}_3$ was exposed to a [^{36}Cl]-labelled mixture of $\text{CCl}_2\text{FCClF}_2$, CCl_3CF_3 , $\text{CClF}_2\text{CClF}_2$ and CCl_2FCF_3 (molar ratio 40:24:18:18) under comparable conditions in a silica, in situ Geiger–Müller counting vessel. [^{36}Cl] Surface count rates (due to self-absorption of the [^{36}Cl] β^- emission, radiation from the bulk solid is not detected in this type of experiment) obtained at various points during the exposure are summarised in Table 2.

Table 2
Variation of the [^{36}Cl] count rate during the exposure of a [^{36}Cl]-labelled chlorofluoroethane mixture (22.7 kPa) to $\beta\text{-AlF}_3$ (5.95 mmol) at 523–73 K

Experimental step	[^{36}Cl] Surface count rate (count min^{-1})	Vapour phase observation
CFC mixture added ^a	409	
Heating for 20 h then cool to room temperature	1350	
Volatile material removed	321	Proportions of CCl_3CF_3 and CCl_2FCF_3 increased ^b
Second aliquot of CFC added ^c	815	
Heating for 20 h then cool to room temperature	2648	Colourless liquid apparent on vessel walls
Volatile material removed		CCl_3CF_3 and CCl_2FCF_3 ^b
Pump		
After 5 min	1408	
After 2 h	1003	
After 6 h	Background	

^a 22.7 kPa, count rate 6081 count min^{-1} .

^b Observation using FTIR.

^c 8.9 kPa.

Addition of the [^{36}Cl]-labelled mixture led to the immediate detection of [^{36}Cl] activity on the surface and the count rate increased significantly after heating at 523–573 K for 20 h. However, the surface count rate decreased markedly when the volatile material was removed at room temperature under static vacuum. Although the composition of the volatile material was not determined quantitatively, FTIR examination suggested that the proportions of CCl_3CF_3 and CCl_2FCF_3 had increased in the vapour. The addition of a second aliquot of the [^{36}Cl]-labelled mixture resulted in a similar behaviour; however, additionally, a colourless liquid condensed on the surface of the vessel after heating. The [^{36}Cl] count rate from the surface decreased slowly as the cell was pumped under dynamic vacuum and a background count was recorded after pumping for 6 h (Table 2).

By analogy with the observations made using unlabelled compounds, it is considered that the [^{36}Cl] activity detected on the surface as the reaction proceeded, originated from [^{36}Cl]- $\text{CCl}_3\text{CClF}_2$ and other relatively involatile members of the series, $\text{C}_2\text{Cl}_{6-n}\text{F}_n$. Formation of Al–Cl bonds did not occur, since the [^{36}Cl] count rate determined from the surface returned to background at the conclusion of the experiment (Table 2).

These observations indicate that the isomerisation of $\text{CCl}_2\text{FCClF}_2$ to CCl_3CF_3 occurs by an intramolecular process, a situation that has also been found for isomerisation on fluorinated chromia [10] and on partially fluorinated aluminium(III) chloride [11,12]. By analogy with isomerisation on fluorinated chromia [10], it is concluded that, although $\text{CCl}_2\text{FCClF}_2$ may be dissociatively adsorbed via C–F bond fission, the surface F that is formed does not become equivalent to surface Al–F species. The [^{36}Cl] results are also consistent with the formation of $\text{CCl}_3\text{CClF}_2$ and CCl_2FCF_3 directly from CCl_3CF_3 , by a process in which halogen exchange involving the replacement of F on the $\beta\text{-AlF}_3$ surface by Cl is not involved. This is consistent with the dynamic behaviour of $\text{CCl}_2\text{FCClF}_2$ over CCl_2F_2 -fluorinated γ -alumina under flow conditions using very short contact times [2]. Unfortunately, an analogous [^{36}Cl] experiment using SF_4 -fluorinated γ -alumina proved impossible to perform due to contamination of the counters, presumably by trace HF that is evolved from this material during heating. However, the very similar product distributions obtained using the two catalysts (Table 1) imply that the reaction pathway is identical. It appears that the behaviour shown by these surfaces towards $\text{CCl}_2\text{FCClF}_2$ is the result of Lewis acid sites that are strong enough, both to isomerise $\text{CCl}_2\text{FCIF}_2$ and activate the CF_3 group of CCl_3CF_3 , enabling a subsequent dismutation reaction to occur.

Since these findings were of key importance, additional experiments were carried out. The behaviour of the three compounds, $\text{CCl}_2\text{FCClF}_2$, CCl_3CF_3 and CCl_2FCF_3 , each individually labelled with [^{36}Cl], towards $\beta\text{-AlF}_3$ was examined at 643 K, a temperature at which isomerisation/dismutation behaviour should be readily observed (Table 1). As a preliminary to these experiments, the behaviour of

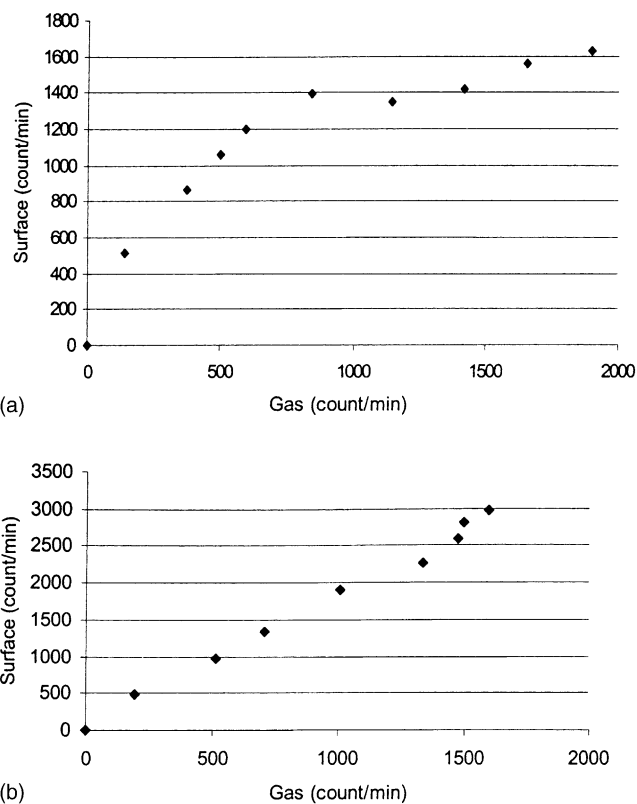


Fig. 1. Room temperature adsorption isotherm of (a) [^{36}Cl]- CCl_2FCF_3 and (b) [^{36}Cl]- $\text{CCl}_2\text{FCClF}_2$ on $\beta\text{-AlF}_3$.

[^{36}Cl]-labelled CCl_2FCF_3 , $\text{CCl}_2\text{FCClF}_2$ and CCl_3CF_3 towards $\beta\text{-AlF}_3$ was examined at room temperature. The Geiger–Müller direct monitoring technique enables adsorption isotherms to be determined by derivation of the [^{36}Cl] surface count rate over a range of pressure, the latter being reflected by the [^{36}Cl] count from the vapour above the surface.

The room temperature adsorption isotherm of [^{36}Cl]- CCl_2FCF_3 on $\beta\text{-AlF}_3$ (Fig. 1a) was indicative of physical adsorption. Since the surface area of $\beta\text{-AlF}_3$ is relatively small, $26.3 \text{ m}^2 \text{ g}^{-1}$ [1], the adsorption isotherm was not particularly well defined and long counting times were required to minimise the counting errors. There was no evidence for a chemical reaction, although when volatile material was removed under static vacuum, the [^{36}Cl] surface count took several hours to decrease to the background value (Table 3).

Table 3
Variation in the [^{36}Cl] surface count rate during the exposure of [^{36}Cl]-labelled 1,1-dichlorotetrafluoroethane (0.4 mmol) to $\beta\text{-AlF}_3$ (5.95 mmol) at 295 K^a

Time (h)	[^{36}Cl] Surface count rate (count min^{-1})	Vapour phase observation
1 h	1140	
Vapour removed	804	CCl_2FCF_3 ^b
After ca. 6 h	Background	

^a Initial count rate: 595 count min^{-1} .

^b By FTIR.

Table 4

Variation of the [^{36}Cl] surface count rate during the exposure of [^{36}Cl]-labelled 1,1,2-trichlorotrifluoroethane (0.35 mmol) to $\beta\text{-AlF}_3$ (5.95 mmol) at 295 K^a

Time (h)	[^{36}Cl] Surface count rate (count min ⁻¹)	Vapour phase observation
1	1391	
Vapour removed	831	$\text{CCl}_2\text{FCClF}_2$ ^b
2	170	
3	74	
24	Background	

^a Initial count rate: 511 count min⁻¹.

^b By FTIR.

This observation and the results reported in the following paragraphs, indicate that the adsorbate–adsorbent interaction was stronger than might have been expected on the basis of physical adsorption alone. It is concluded that some of the CCl_2FCF_3 is strongly adsorbed. Exposure of [^{36}Cl]- $\text{CCl}_2\text{FCClF}_2$ to $\beta\text{-AlF}_3$ under comparable conditions (pressure in the range 0–6700 Pa) did not result in the observation of a saturation [^{36}Cl] surface count rate (Fig. 1b), unlike the behaviour of [^{36}Cl]-labelled CCl_2FCF_3 (Fig. 1a). The adsorption isotherm determined for [^{36}Cl]- CCl_3CF_3 was very similar to that for [^{36}Cl]- $\text{CCl}_2\text{FCClF}_2$ and in both cases, adsorbed material was removed relatively slowly from the surface (Tables 4 and 5). However, in neither case was there any evidence for the formation of permanently retained species or reaction products on $\beta\text{-AlF}_3$ after exposure. For example, the effect of successive exposures of [^{36}Cl]- $\text{CCl}_2\text{FCClF}_2$ aliquots to the same sample of $\beta\text{-AlF}_3$ is shown in Fig. 2. Had even a small proportion of the adsorbed species been permanently retained, the [^{36}Cl] count rate from the surface would have increased over the series of additions. However, as in the case of CCl_2FCF_3 , it is concluded that some $\text{CCl}_2\text{FCClF}_2$ and CCl_3CF_3 is strongly adsorbed.

[^{36}Cl] Surface count rates and changes in the composition of the vapour phase that were observed when [^{36}Cl]-labelled CCl_2FCF_3 , $\text{CCl}_2\text{FCClF}_2$ or CCl_3CF_3 were exposed to $\beta\text{-AlF}_3$ at 643 K are contained in Tables 6–8. In each case, a significant [^{36}Cl] surface count was observed after heating a sample of a [^{36}Cl]-labelled chlorofluoroethane in the presence of $\beta\text{-AlF}_3$. This was reduced to the background count rate on pumping. The IR spectra of the vapour phase after

Table 5

Variation in the [^{36}Cl] surface count rate during the exposure of [^{36}Cl]-labelled 1,1,1-trichlorotrifluoroethane (0.5 mmol) to $\beta\text{-AlF}_3$ (5.95 mmol) at 295 K^a

Time (h)	[^{36}Cl] Surface count rate (count min ⁻¹)	Vapour phase observation
1	1117	
Vapour removed	1054	CCl_3CF_3 ^b
2	651	
3.5	Background	

^a Initial count rate: 781 count min⁻¹.

^b By FTIR.

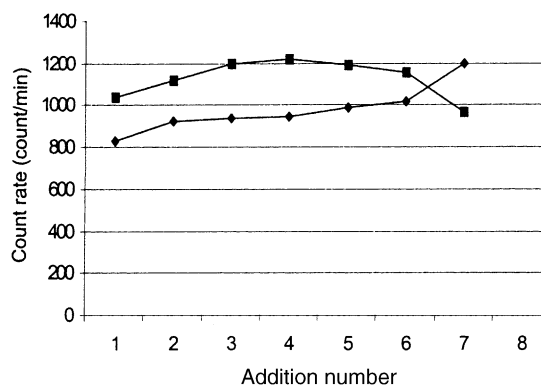


Fig. 2. Variation of surface (■) and gas (◆) [^{36}Cl] count rates with multiple additions of [^{36}Cl]- $\text{CCl}_2\text{FCClF}_2$ aliquots to $\beta\text{-AlF}_3$.

heating indicated, qualitatively, that transformations to other members of the series, $\text{C}_2\text{Cl}_{6-n}\text{F}_n$ had occurred. This was particularly apparent in reactions that involved [^{36}Cl]- $\text{CCl}_2\text{FCClF}_2$ or [^{36}Cl]- CCl_3CF_3 (Tables 7 and 8). During the reaction of CCl_3CF_3 , a relatively involatile, colourless liquid formed on the surface of the counting vessel (Table 8), reminiscent of the observation made (Table 2) during the reaction of a [^{36}Cl]-chlorofluoroethane mixture.

These experiments have provided important confirmatory evidence to support our previous kinetic studies [2]. The results indicate that the behaviour of $\text{CCl}_2\text{FCClF}_2$ on $\beta\text{-AlF}_3$ involves isomerisation to CCl_3CF_3 (Eq. (1)) followed by dismutation of the latter to give CCl_2FCF_3 and $\text{CCl}_3\text{CClF}_2$ (Eq. (2)). The formation of these directly from CCl_3CF_3 , without the intervention of other species, is indicated by the behaviour of CCl_3CF_3 itself as a reactant under identical conditions.

Estimates of the free energy change for Eq. (2) indicate that the reaction is favourable thermodynamically but it does pose a mechanistic difficulty, since the CF_3 group is a very stable entity. As we have pointed out elsewhere [2], there are numerous precedents in the literature for activation of a C–F bond, although the great majority of cases are not particularly good analogies for the reaction studied here. However,

Table 6

Variation in the [^{36}Cl] surface count rate during the exposure of [^{36}Cl]-labelled 1,1-dichlorotetrafluoroethane (0.3 mmol) to $\beta\text{-AlF}_3$ (5.95 mmol) at 643 K^a

Experimental step	[^{36}Cl] Surface count rate (count min ⁻¹)	Vapour phase observation
CCl_2FCF_3 addition		
Heating for 22 h then cool	1329	
Volatile material removed		Major component: CCl_2FCF_3 ^b Trace: CCl_3CF_3 , $\text{CCl}_3\text{CClF}_2$ ^b
Immediately	695	
After 1 h	660	
After ca. 6 h	Background	

^a Count rate: 489 count min⁻¹ at 295 K.

^b By FTIR.

Table 7

Variation of the [³⁶Cl] surface count rate during the exposure of [³⁶Cl]-labelled 1,1,2-trichlorotrifluoroethane (0.4 mmol) to β-AlF₃ (5.95 mmol) at 643 K^a

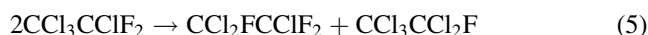
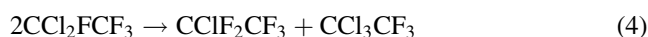
Experimental step	[³⁶ Cl] Surface count rate (count min ⁻¹)	Vapour phase observation
CCl ₂ FCClF ₂ addition		
Heating for 22 h then cool	2133	
Volatile material removed		Major components: CCl ₂ FCClF ₂ , CCl ₃ CF ₃ , CCl ₂ FCF ₃ ^b Minor components: CClF ₂ CClF ₂ , CClF ₂ CF ₃ , CCl ₃ CClF ₂ , CCl ₂ FCCl ₂ F ^b
Immediately	982	
After 1 h	780	
After 3 h	633	
After ca. 6 h	306	
After pumping	Background	

^a Count rate: 635 count min⁻¹ at 295 K.^b By FTIR.

it is plausible to propose that the adsorbed state of CF₃CCl₃ on β-AlF₃ is Cl₃CC^{δ+}F₂ ··· F ··· Al^{δ-}. Dismutation requires adsorption of two CCl₃CF₃ molecules at the neighbouring sites followed by a concerted interchange of F from the αC of one molecule to the βC of the other and Cl from βC to αC in the reverse sense. From an operational point of view, it is considered that the Lewis acidity of the surface site on β-AlF₃ at which CCl₃CF₃ is adsorbed must be comparable with that of a molecular strong Lewis acid such as antimony pentafluoride. For example, in a very recent report describing the SbF₅-catalysed alkylation of polyfluoroolefins by hydrofluorocarbons, it has been proposed that the first step in the reaction involves the formation of an activated complex, for example, FC^{δ+}H₂ ··· F ··· Sb^{δ-}F₅. It is further proposed that this reacts with the olefin to generate a carbocation, fluoroantimonate intermediate [13]. Interestingly, CF₃X, X = H, Br, Cl or I, apparently cannot be activated using SbF₅ but activation is possible using solid aluminium(III) chlorofluoride, AlCl_{0.2–0.1}F_{2.8–2.9}, as a catalyst [14]. A comparative study of solid aluminium(III) fluoride Lewis acids with SbF₅ is an area that would repay further study, particularly since a theoretical basis for comparisons among molecular Lewis acid fluorides has been established by Christie et al. [15].

Further dismutations on β-AlF₃ are possible. Dismutation of CCl₂FCF₃ (Eq. (4)), although apparently less facile than dismutation of CCl₃CF₃, does appear to occur, based on the

FTIR results obtained (Tables 7 and 8). Further reaction of CCl₃CClF₂ is also evident and a dismutation appears to be an appropriate description in this case (Eq. (5)).



Further reaction of CCl₃CCl₂F would lead to C₂Cl₆, either via dismutation or by chlorination with other highly chlorinated chlorofluoroethanes, and C₂Cl₄ is formed from C₂Cl₆ by thermal decomposition.

The use of the term “dismutation”, which we define here as a concerted ligand exchange reaction between two identical species without change in the oxidation state of the central atoms involved, to describe the inter-conversions that are characteristic of catalysed reactions involving chlorofluoroethanes, has a long history. Although the term “disproportionation” has often been used as a synonym, we prefer to restrict its use to situations where changes in oxidation states occur.

Catalytic halogen inter-conversions among chlorofluoroethanes were apparently first proposed by Tatlow and co-workers in 1974 to rationalise product distributions that were the result of the fluorination of C₂Cl₆ by HF in the presence of an aluminium fluoride catalyst [16]. Subsequently, Kolditz et al. proposed dismutation reactions combined with isomerisation, to account for product

Table 8

Variation in the [³⁶Cl] surface count rate during exposure of [³⁶Cl]-labelled 1,1,1-trichlorotrifluoroethane (0.7 mmol) to β-AlF₃ (5.95 mmol) at 643 K^a

Experimental step	[³⁶ Cl] Surface count rate (count min ⁻¹)	Vapour phase observation
CCl ₃ CF ₃ addition		
Heating for 22 h then cool	4058	
Volatile material removed		Major component: CCl ₂ FCF ₃ ^b Minor component: CCl ₃ CF ₃ ^b Trace: CClF ₂ CF ₃ ^b Liquid formed on the counting cell surface
Immediately	2034	
After 1 h	1075	
After ca. 6 h	Background	

^a Count rate: 1123 count min⁻¹ at 295 K.^b By FTIR.

distributions within the $C_2Cl_{6-n}F_n$, $n = 1-5$, series that were observed over aluminium fluoride or chromia catalysts [17,18]. Marangoni et al. followed a similar approach to account for the transformations of $C_2Cl_2F_4$ isomers on fluorinated chromia [19,20]. The behaviour of $C_2Cl_3F_3$ isomers on a variety of supported chromia catalysts and on AlF_3 has been discussed also by Blanchard and co-workers [21–23] in terms of isomerisation and dismutation. They concluded that the acidity of the catalyst active site is an important factor in determining the reaction pathway followed [23]. However, dismutation reactions are not appropriate in every case. The distributions of the isotopes, $[^{36}Cl]$ and $[^{18}F]$, in the individual components of chlorofluoroethane mixtures obtained by flow of CCl_2FCClF_2 or $CClF_2CClF_2$ over $[^{36}Cl]$ - or $[^{18}F]$ -labelled fluorinated chromia catalysts are inconsistent with the occurrence of concerted dismutation processes. In this instance, non-concerted halogen exchange, F for Cl and Cl for F, reactions that involve catalyst surface halide, are more appropriate descriptions [10,24].

3. Conclusions

The reaction of CCl_2FCClF_2 on the surface of $\beta-AlF_3$ occurs via an intramolecular isomerisation process to give CCl_3CF_3 . Further reaction of CCl_3CF_3 occurs via dismutation rather than by halogen exchange. This appears to be a characteristic feature of $\beta-AlF_3$ and presumably also of fluorinated alumina catalysts. The activation of the CF_3 group CCl_3CF_3 that is required for dismutation implies that the $\beta-AlF_3$ surface has very strong Lewis acid sites.

4. Experimental

4.1. Experiments with chlorine-36

The behaviour of β -aluminium(III) fluoride towards $[^{36}Cl]$ -labelled chlorofluoroethanes was examined using a Geiger–Müller direct monitoring method, developed in Glasgow for $[^{14}C]$ adsorption measurements [4] and subsequently used to study heterogeneous systems involving fluorides where the β^- emitting isotopes, $[^{36}Cl]$ and $[^{35}S]$, were employed as probes [5–9]. An evacuable Pyrex counting vessel with a gas handling facility was used for measurements at ambient temperature. Two Geiger–Müller counters were positioned within the vessel to enable $[^{36}Cl]$ activity from the vapour phase and from the vapour plus surface (due to self-absorption of the β^- emitter $[^{36}Cl]$, activity from the bulk solid was not detected) to be monitored concurrently. The counting tubes were inter-calibrated using $H^{36}Cl$ at several pressures, counts being recorded simultaneously on two scalars. These enabled $[^{36}Cl]$ counts from the surface of a solid placed below one of the counters to be determined by subtraction of

the gas phase counts after correction for background. Solid samples (0.5 g) were introduced into the vessel contained in a Pyrex boat connected to a Pyrex rod containing a soft iron bar. The arrangement enabled the boat to be moved with the aid of a magnet within the vessel after evacuation. Samples were spread as thinly as possible in order to approach the required criterion of an infinitely thin solid layer. Cell and solids were thoroughly degassed before a measured pressure of $[^{36}Cl]-C_2Cl_{6-n}F_n$, was added via a calibrated gas-handling manifold. The system was allowed to equilibrate and counts from the two Geiger–Müller tubes recorded simultaneously. Counting times were chosen to enable substantial counts (normally 10^4 to minimise the counting errors) to be accumulated. Volatile material was removed under static vacuum and the process repeated using a different pressure. Pressures of volatile components were in the range of 1300–6700 Pa. At the conclusion of the determination of an adsorption isotherm or of a reaction sequence, volatile material was removed by distillation under static or dynamic vacuum as appropriate and the count from $[^{36}Cl]$ material retained on the solid determined.

The behaviour of $[^{36}Cl]$ -labelled chlorofluoroethanes towards $\beta-AlF_3$ at elevated temperatures was studied in a similar fashion using a silica counting vessel equipped with a heated zone remote from the counters, the solid being moved into or out of the heated zone using a magnet. All counts were recorded at ambient temperature.

4.2. Preparation of $[^{36}Cl]$ -labelled compounds

The conventional route to members of the chlorofluoroethane series by reaction between C_2Cl_6 , or a mixture of $C_2Cl_4 + Cl_2$, and anhydrous HF, catalysed by fluorinated chromia under flow conditions [25], was modified for use under static conditions in order to facilitate the use of isotopically labelled reagents.

All operations were carried out using a Monel vacuum system or an N_2 -filled glove box. The reaction vessel was a Monel pressure vessel (90 cm³). A sample of commercial, amorphous chromia (1.0 g), previously calcined at 523 K in vacuo for 24 h, was pre-fluorinated with three aliquots (8.4 mmol) of anhydrous HF (Fluorochem, 99%) at 523 K for 24 h, unused HF being removed before admission of the next aliquot. The vessel containing the catalyst was charged with C_2Cl_6 (1.0 g; 4.27 mmol) in the glove box and then, after connection to the vacuum line, with sufficient HF to give the required molar ratio. This was varied in different experiments using $C_2Cl_6:HF$ molar ratios in the range 1:2 to 1:4. The mixture was allowed to react using temperatures in the range 423–573 K. Reaction times were in the range 4–72 h. At the end of the reaction period, the vessel was allowed to cool to room temperature and the volatile contents distilled onto NaF, contained in a Monel or stainless steel vessel. The mixture was allowed to contact NaF for sufficient time for unchanged HF to be sorbed, then the volatile material was transferred to an evacuated Pyrex

ampoule for analysis by FTIR spectroscopy, ^{19}F NMR spectroscopy and GC.

The composition of the product depended on the reaction variables in a complex fashion. For example, with an $\text{HF}:\text{C}_2\text{Cl}_6$ molar ratio of 4:1 at 673 K, the product mixture contained predominantly difluorinated species. Similar results were obtained with a 3:1 molar ratio at 573 K for 5 h or at 423 K for 27 h. The most useful reaction conditions were $\text{HF}:\text{C}_2\text{Cl}_6 = 3:1$, temperature 548–573 K and time 48 h. The major components of product mixtures were $\text{CCl}_2\text{FCClF}_2$, CCl_3CF_3 , $\text{CClF}_2\text{CClF}_2$ and CCl_2FCF_3 . Reactions using $\text{C}_2\text{Cl}_4:\text{Cl}_2$ (1:1 molar ratio) gave similar mixtures. Although the proportions of each component varied somewhat from reaction to reaction, the ranges, $\text{CCl}_2\text{FCClF}_2$ (19–40 mol%), CCl_3CF_3 (11–35 mol%), $\text{CClF}_2\text{CClF}_2$ (18–30 mol%) and CCl_2FCF_3 (8–27 mol%) were defined sufficiently for the experiments in which they were used. Minor components containing two or less F atoms were readily removed by distillation in vacuo.

Mixtures labelled with chlorine-36 were prepared in an identical fashion from $^{36}\text{ClCl}$, which was prepared by the oxidation of $[\text{Cl}^{36}]^-$ anion (Amersham International, 9250 kBq diluted with concentrated aqueous HCl), by $[\text{MnO}_4]^-$ in aqueous acidic conditions [26,27]. Trace HCl and H_2O were removed by trap to trap distillation over solid KMnO_4 then P_2O_5 and the product, contained in a stainless steel vessel, was stored over P_2O_5 in vacuo.

Individually labelled chlorofluoroethanes were prepared according to the previously reported method [27] by photochemical (medium pressure Hg lamp) irradiation at room temperature. Mixtures of the appropriate hydrofluoroethane or hydrochlorofluoroethane precursor and $^{36}\text{ClCl}$ were irradiated for 24 h in a silica ampoule fitted with a Pyrex/PTFE stopcock (J. Young). The conditions required for complete reaction were established using inactive Cl_2 ; no impurities were detected using FTIR or ^{19}F NMR spectroscopy after fractionation of the product mixtures in vacuo. Reaction stoichiometries were for $\text{CCl}_2\text{FCClF}_2:\text{CH}_2\text{FCHF}_2:\text{Cl}_2$ (1:3); for $\text{CCl}_3\text{CF}_3:\text{CHCl}_2\text{CF}_3:\text{Cl}_2$ (1:1); for $\text{CCl}_2\text{FCF}_3:\text{CH}_2\text{FCF}_3:\text{Cl}_2$ (1:2).

4.3. Reactions between 1,1,2-trichlorotrifluoroethane and $\beta\text{-AlF}_3$ or fluorinated γ -alumina under static conditions

1,1,2-Trichlorotrifluoroethane (ca. 0.5 g), previously degassed and dried by storage over 4 Å molecular sieves, was added to $\beta\text{-AlF}_3$ or fluorinated γ -alumina (0.5 g in each case) contained in a stainless steel pressure vessel (75 cm³, Hoke) and attached to a Pyrex vacuum line. Mixtures were heated at 613–643 K for 24–72 h. Volatile products were removed by distillation in vacuo at room temperature, weighed, and analysed by FTIR (Nicolet Impact 410), GC (Varian 3400, FID, Chrompak 30 m capillary column) and ^{19}F NMR spectroscopy (Bruker WP200 SY). The latter was particularly useful for quantitative analyses when iso-

meric mixtures were present, since, using GC, base line separation of $\text{C}_2\text{Cl}_3\text{F}_3$ and $\text{C}_2\text{Cl}_2\text{F}_4$ isomers was difficult to achieve. Less volatile organic products were removed by heating the reaction vessel while pumping through a cooled U-trap. The components present were identified by ^{19}F NMR and GC-MS (HP 5971, quadrupole detector interfaced with an HP 5890 series II chromatograph).

The effect of successive additions (up to six) of $\text{CCl}_2\text{FCClF}_2$ to a sample of $\beta\text{-AlF}_3$ or fluorinated γ -alumina was examined in a similar fashion, volatile products being analysed by GC. In these experiments, the less volatile material was not removed between each addition but was examined at the end of a reaction sequence.

4.4. Catalyst preparation

γ -Aluminium(III) fluoride was prepared by the temperature programmed dehydration [3] of $\text{AlF}_3\cdot 3\text{H}_2\text{O}$ (5.0 g, Aldrich, purity 97%) under He (30 cm³ min⁻¹), heating from room temperature to 493 K at 5 K min⁻¹, held at 493 K for 1 h, heating to 723 K at 10 K min⁻¹, held at 723 K for 2 h, finally allowed to cool to room temperature under He flow. The $\beta\text{-AlF}_3$ so formed was transferred in a sealed vessel to a N_2 glove box (H_2O ca. 1 ppm) where subsequent manipulations were performed. Its identity was confirmed by XRD. Samples prepared in Berlin or Glasgow showed identical behaviour. Its BET area was 26.3 m² g⁻¹.

Fluorinated γ -alumina was prepared under static conditions in a Monel metal pressure vessel (Hoke, 90 cm³) attached to a Monel vacuum line [28,29]. Typically, γ -alumina (Degussa, BET area = 110 m² g⁻¹, 1.5 g) previously caked, sieved to produce 500–1000 μm particles and calcined in vacuo for 8 h at 523 K, was allowed to react with SF_4 (9.0 mmol, 99%, Fluorochem) for 2 h, nominally at room temperature. Volatile products, a mixture of OSF_2 and SO_2 , whose components were identified by FTIR spectroscopy, were removed by distillation and the process repeated twice. The product, an off-white solid, was transferred to and handled subsequently in a glove box. It could be stored for short periods in FEP; storage in Pyrex led to etching, indicating that HF was lost slowly from the solid. For this reason, smaller quantities (0.5 g) were prepared for use in situ, with the appropriate adjustment of the quantity of SF_4 . Single point determinations of BET area (Coulter SA 3100 instrument) gave values in the range 80–90 m² g⁻¹. The imprecision was possibly a result of the corrosive nature of the material. Fluorine content was not determined directly but a value of ca. 22% was inferred from a previous [^{18}F] study of the fluorination carried out under very similar conditions [28].

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References

- [1] H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, J.M. Winfield, *J. Fluorine Chem.* 107 (2001) 45–52.
- [2] H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, J.M. Winfield, *J. Fluorine Chem.* 110 (2001) 181–189.
- [3] A. Le Bail, C. Jacoboni, M. Leblanc, R. De Pape, H. Duroy, J.L. Fourquet, *J. Solid State Chem.* 77 (1988) 96–101.
- [4] A.S. Al-Ammar, G. Webb, *J. Chem. Soc., Faraday Trans.* 174 (1978) 195–205.
- [5] K.W. Dixon, J.M. Winfield, *J. Chem. Soc., Dalton Trans.* (1989) 937–942.
- [6] T. Baird, A. Bendada, G. Webb, J.M. Winfield, *J. Mater. Chem.* 1 (1991) 1071–1077.
- [7] T. Baird, A. Bendada, G. Webb, J.M. Winfield, *J. Fluorine Chem.* 66 (1994) 117–122.
- [8] G.A. Kolta, G. Webb, J.M. Winfield, *Appl. Catal.* 2 (1982) 257–268.
- [9] T. Baird, A. Bendada, M. Selougha, G. Webb, J.M. Winfield, *J. Fluorine Chem.* 69 (1994) 109–113.
- [10] L. Rowley, J. Thomson, G. Webb, J.M. Winfield, A. McCulloch, *Appl. Catal. A: Gen.* 79 (1991) 89–103.
- [11] W.T. Miller Jr, E.W. Fager, P.H. Griswald, *J. Am. Chem. Soc.* 72 (1950) 705–707.
- [12] D.G. McBeth, M.M. McGeough, G. Webb, J.M. Winfield, A. McCulloch, N. Winterton, *Green Chem.* 2 (2000) 15–20.
- [13] G.G. Belen'kii, V.A. Petrov, P.R. Resnick, *J. Fluorine Chem.* 108 (2001) 15–20.
- [14] V.A. Petrov, C.G. Krespan, *J. Fluorine Chem.* 102 (2000) 199–204.
- [15] K.O. Christe, D.A. Dixon, D. McLemore, W.W. Wilson, J.A. Sheehy, J.A. Boatz, *J. Fluorine Chem.* 101 (2000) 151–153.
- [16] M. Vecchio, G. Gropelli, J.C. Tatlow, *J. Fluorine Chem.* 4 (1974) 117–139.
- [17] L. Kolditz, G. Kauschka, W. Schmidt, *Z. Anorg. Allg. Chem.* 434 (1977) 41–54.
- [18] L. Kolditz, U. Calov, G. Kauschka, W. Schmidt, *Z. Anorg. Allg. Chem.* 434 (1977) 55–62.
- [19] L. Marangoni, C. Gervasutti, L. Conte, *J. Fluorine Chem.* 19 (1981/82) 21–34.
- [20] L. Marangoni, D. Carmello, R. Passerini, *Chim. Ind. (Milan)* 67 (1985) 467–480.
- [21] D. Bechadegue, M. Blanchard, P. Canesson, *Appl. Catal.* 20 (1986) 179–187.
- [22] D. Bechadegue, M. Blanchard, P. Canesson, in: *Heterogeneous Catalysis and Fine Chemicals*, in: M. Guisnet, et al. (Eds.), Elsevier, Amsterdam, 1988, pp. 257–264.
- [23] M. Blanchard, L. Wendlinger, P. Canesson, *Appl. Catal.* 59 (1990) 123–128.
- [24] L. Rowley, G. Webb, J.M. Winfield, A. McCulloch, *Appl. Catal.* 52 (1989) 69–80.
- [25] B. Kemnitz, J.M. Winfield, in: *Advanced Inorganic Fluorides*, in: T. Nakajima, B. Žemva, A. Tressaud (Eds.), Elsevier, Amsterdam, 2000, pp. 367–401 (Chapter 12).
- [26] G. Brauer, *Handbook of Preparative Inorganic Chemistry*, 2nd Edition, Vol. 1, Academic Press, New York, 1965, pp. 272–274.
- [27] L. Rowley, G. Webb, J.M. Winfield, *J. Fluorine Chem.* 38 (1988) 115–117.
- [28] A. Bendada, G. Webb, J.M. Winfield, *Eur. J. Solid State Inorg. Chem.* 33 (1996) 907–916.
- [29] J. Thomson, G. Webb, J.M. Winfield, D. Bonniface, C. Shortman, N. Winterton, *Appl. Catal. A: Gen.* 97 (1993) 67–76.