Radiotracers in fluorine chemistry. Part 18 [1]. Sulphur tetrafluoride chlorofluorination catalysed by Group 1 fluorides supported on fluorinated γ-alumina. A comparison with unsupported fluorides

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Abstract

Caesium or potassium fluorides supported on γ-alumina and then exhaustively fluorinated with SF_4, F_2SO or anhydrous HF (in the latter case after SO_2 pretreatment) are effective catalysts for the room-temperature chlorofluorination of SF_4 by ClF to give SF_5Cl. Kinetic studies using chlorine-36 and sulphur-35 radiotracers indicate that the maximum catalytic activity corresponds to a metal fluoride loading of 5.5 mmol g^{-1}, consistent with previous radiotracer adsorption studies. At this loading, the behaviour of supported CsF is comparable to that of unsupported CsF which has been activated by treatment with $(CF_3)_2CO$. Activated commercial mercury(II) fluoride is a less active catalyst.

1. Introduction

Although caesium and potassium fluorides supported on γ-alumina are strongly basic materials that have catalytic value [2], they cannot be used successfully in situations where anhydrous conditions are required because of their hydroxylated and hydrated surfaces. We have demonstrated recently, however, that this deficiency can be overcome by exhaustive fluorination of the surface using sulphur tetrafluoride, thionyl fluoride or anhydrous HF after pretreatment with sulphur dioxide [1]. Although fluorination results in a decrease in surface area, it has no material effect on the MF (M = Cs or K) surface particles; the maximum surface concentration of F^- corresponds to a metal fluoride loading of 5.5 mmol g^{-1} for both fluorinated [1] and unfluorinated [3] supports.

In order to test the catalytic properties of CsF and KF supported on fluorinated γ-alumina, we have determined the kinetics of the model reaction (Eq. (1))

$$SF_4 + ClF \longrightarrow SF_5Cl \qquad (1)$$

This reaction is catalysed by unsupported CsF at room temperature [4] and the results of a radiotracer study [5], employing chlorine-36 and sulphur-35, are consistent with the surface reaction (Eq. (2)) moderated by two poisoning processes (Eqs. (3) and (4)).

$$CsF\cdot ClF(ads.) + CsF\cdot SF_4(ads.) \longrightarrow SF_5Cl(g) + 2CsF(s) \qquad (2)$$

$$CsF\cdot SF_4(ads.) \rightleftharpoons Cs^+[SF_5]^-(s) \qquad (3)$$

$$CsF\cdot ClF(ads.) \longrightarrow Cs^+[ClF_2]^-(s) \qquad (4)$$

Using a radiotracer approach similar to that employed earlier [5], we have been able to compare the catalytic behaviour of supported CsF and KF, unsupported CsF and unsupported mercury(II) fluoride. The latter was chosen since it can behave similarly to CsF in synthetic and catalytic situations [6–8], and in an early [^{18}F]-exchange study, it was shown that $SF_3{}^{18}F$ underwent exchange with HgF_2 under heterogeneous conditions to a greater extent than with other difluorides [9]. In addition, the high yield synthesis of ClF from ClF_3 and $HgCl_2$ with HgF_2 being the co-product [10] suggests that the interaction between ClF and HgF_2 is minimal at room temperature; hence, the poisoning effect of ClF in the preparation of SF_5Cl (Eq. (4)) might be expected to be reduced. A preliminary account of part of this work has been given [11].

2. Experimental

2.1. Instrumentation and radiochemical methods

Vacuum line (Pyrex or Monel as appropriate) and glove-box techniques were used throughout this work.

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Details of the instrumentation used have been given elsewhere [3]. Labelled $^{35}SF_4$ [12] and ^{36}ClF [1] were prepared by established procedures and measurements involving these compounds were made using the Glasgow-developed, Geiger–Müller direct radiochemical monitoring technique [13,14].

2.2. Catalyst preparation

Caesium and potassium fluorides (BDH Optran grade) were supported on γ-alumina (Degussa C) by an aqueous or non-aqueous $MeCN/(CF_3)_2CO$ route, using methods described previously [3], loadings being in the range of 0.6–20.0 mmol g^{-1}. Samples were fluorinated using SF_4 or F_2SO or SO_2 (following pretreatment with anhydrous HF), as these reagents have been shown to be equally effective for the removal of both surface hydroxyl groups and bound water [1].

Mercury(II) fluoride was a commercial product, yellow in colour and stated to be anhydrous. Its BET surface area, as determined by [^{85}Kr] adsorption [15], was 0.70–1.32 $m^2\ g^{-1}$ (95% confidence limits from replicate determinations on three different samples). The solid (12.0 mmol) was treated with SF_4 (6.0 mmol) in a stainless-steel pressure vessel at room temperature for 16 h. Volatile material was shown to be a mixture of F_2SO, SiF_4 and unchanged SF_4 by IR spectroscopy. The solid was colourless and its BET area was 1.72–2.40 $m^2\ g^{-1}$. Mercury(II) fluoride was also activated by the $(CF_3)_2CO/MeCN$ route used previously for CsF [16]. A mixture of commercial HgF_2 (16.8 mmol), MeCN (7 cm^3) and $(CF_3)_2CO$ (34.0 mmol) was allowed to react at room temperature overnight. Thermal decomposition (353 K, 12 h in vacuo) of the solid isolated after removal of material volatile at room temperature gave a yellow solid whose BET area, as determined by N_2 adsorption, was 16.3–20.9 $m^2\ g^{-1}$. Mass balance data from the decomposition and IR spectroscopy were consistent with the formation and subsequent decomposition of the adduct $HgF_2 \cdot 2(CF_3)_2CO$.

2.3. Catalysed chlorofluorination of SF_4

Reactions between SF_4 and ClF in the presence of a supported metal fluoride or HgF_2 catalyst were carried out in a Monel metal pressure vessel (95 cm^3) attached to a calibrated, ClF_3-passivated, Monel metal vacuum system containing a Heise Bourdon gauge (±1.0 Torr). Reactant stoichiometries were determined by pressure measurements and reaction times were normally 1 h. Products volatile at room temperature were separated by fractional distillation and were identified by their IR spectra, molecular weight determinations or vapour pressure measurement as appropriate. Sulphur chloride pentafluoride labelled with [^{35}S] or [^{36}Cl] was prepared from $^{35}SF_4$ or ^{36}ClF using a 1:1 reaction stoichiometry.

Reactions involving radiolabelled mixtures, $^{35}SF_4$ + ClF or $SF_4 + {}^{36}ClF$, were carried out in a Pyrex Geiger–Müller counting cell. A predetermined gas mixture was admitted to the cell, counted and then the catalyst sample (normally 2.0 g) added in vacuo by dropping it directly into a movable boat. This was positioned under one of the Geiger–Müller counters and the [^{35}S] or [^{36}Cl] count rate from the surface of the catalyst was determined at regular intervals. In most cases, the decreases in [^{35}S] or [^{36}Cl] surface activities could be following with time and they exhibited a second-order dependence.

3. Results and discussion

The reaction between SF_4 and ClF to give SF_5Cl is a good model system for comparing the catalytic activities of fluoride anion materials, since reaction occurs rapidly at room temperature and is not complicated by side processes. The degree of conversion to SF_5Cl is highly dependent on the ClF/SF_4 mole ratio, however, and a systematic examination was carried out to determine the optimum conditions for the catalysis. Using a 1:1 mole ratio (4.0 mmol of each gaseous reactant) and a CsF loading of 4.4 mmol g^{-1} supported on γ-alumina and fluorinated with SF_4 (2.0 g catalyst sample), the yield of SF_5Cl was 80% after 1 h at room temperature under static conditions. As the quantity of ClF was decreased keeping SF_4 constant, the yield of SF_5Cl based on ClF fell to c. 40% at $ClF/SF_4 = 1:6.7$. Under these conditions, c. 20% of the reactant mixture was retained by the catalyst. Supported KF (loading 4.4 mmol g^{-1}) and pretreated HgF_2 catalysts showed related behaviour, although the degrees of conversion to SF_5Cl and the fractions of the reactants retained by the solids were both lower than for supported CsF. Similar behaviour was observed for all catalysts when ClF was held constant and SF_4 reduced.

The results mirror those found previously when using unsupported CsF [5] and a 1:1 mole ratio was used in all kinetic experiments.

3.1. Caesium fluoride and potassium fluoride supported on fluorinated γ-alumina

The effects of six different catalysts on the yield of SF_5Cl obtained under otherwise identical reaction conditions are compared in Table 1. Neither the impregnation method (aqueous or non-aqueous) nor the reagents used for fluorination of the γ-alumina surface had any marked effect, but supported CsF was consistently more active than supported KF, SF_5Cl yields being c. 80% compared with 60%–65%. There was no evidence for a loss in catalytic activity over a series of six experiments with a given catalyst sample, providing the mole ratio ClF/SF_4 was 1:1.

TABLE 1. Yields of SF_5Cl from sequential reactions SF_4+ClF (1:1 mole ratio) in the presence of a Group 1 fluoride catalyst supported on fluorinated γ-alumina (loading 4.4 mmol g^{-1})

Run No.	SF_4+ClF[a] (mmol)	Yield of SF_5Cl (mmol)[b]					
		Aqueous impregnation: Fluorination with			Non-aqueous impregnation: Fluorination with		
		SF_4	F_2SO	SO_2/HF	SF_4	F_2SO	SO_2/HF
(*a*) *Using supported CsF*							
1	12.0	4.9	4.8	4.5	4.8	4.9	4.6
2	6.0	2.5	2.6	2.4	2.4	2.4	2.55
3	8.0	3.4	3.4	3.3	3.5	3.3	3.3
4	20.0	8.1	7.9	8.0	8.2	7.8	8.0
5	14.0	5.7	5.5	5.7	5.5	5.6	5.6
6	10.0	4.1	4.2	3.9	3.9	4.1	4.2
(*b*) *Using supported KF*							
1	10.0	3.15	3.0	3.3	3.1	3.2	3.2
2	14.0	4.5	4.3	4.3	4.4	4.3	4.5
3	8.0	2.5	2.6	2.3	2.4	2.4	2.5
4	6.0	2.0	1.9	2.0	1.8	1.9	1.8
5	20.0	6.0	6.1	5.7	5.9	5.9	6.1
6	8.0	2.4	2.5	2.2	2.4	2.5	2.3

[a] Total reactants.
[b] Error, ±0.1 mmol.

For both supported CsF and KF, maximum catalytic activity was observed at a loading of 5.5 mmol g^{-1}. In each case the yields of SF_5Cl increased markedly over the loading range 0.6–5.5 mmol g^{-1}, to 96% and 73% respectively, and decreased steadily in the range 5.5–15.0 mmol g^{-1}. Above this composition the solids showed no catalytic ability. This volcano relationship (see Fig. 2 of ref. [11]) is almost identical to the relationships found for the adsorption of ^{36}ClF on these materials [1], and confirms the hypothesis that the catalytically active sites are metal fluoride particles.

Reactions of $^{36}ClF+SF_4$ or $ClF+{}^{35}SF_4$, using 1:1 mole ratio mixtures in the presence of supported CsF or KF at room temperature, resulted in the detection of [^{36}Cl] or [^{35}S] radioactivity from the solids, in all cases within the time of mixing. Since the radioisotopes are both β^- emitters and therefore subject to self-absorption, detection of radiation was essentially limited to the surface of a solid and the changes in [^{36}Cl] or [^{35}S] surface count rates during a reaction provided a sensitive method for comparing different catalysts. Representative data from both [^{36}Cl] and [^{35}S] experiments using supported CsF are contained in Fig. 1. In traces 1–3 inclusive, both build-up and decay of the surface activity were observed, the order of catalytic activity implied for the supported CsF catalysts being $8.8<1.1<4.4$ mmol g^{-1}. For traces 4 and 5, the build-up of surface activity was complete within the time of mixing and only its decay was observed. Overall, the data are consistent with maximum catalytic activity at a loading of 5.5 mmol g^{-1}. In all cases, the final [^{36}Cl] and [^{35}S] surface count rates corresponded to background and the decreases in count rates obeyed a second-order relationship. Experiments using [^{36}Cl]- and [^{35}S]-labelled SF_5Cl established that its adsorption on the supported metal fluoride was very weak; hence, the decay in surface count rate was a direct measure of the rate of the reaction depicted in Eq. (2). This is identical to the situation found for unsupported CsF [5]. Second-order rate constants so determined are contained in Table 2. They indicate that, at a given loading, supported CsF was more active catalytically than supported KF and that maximum activity occurred at a 5.5 mmol g^{-1} loading.

There was no evidence for catalyst poisoning [Eqs. (3) or (4)] when the reactant ClF/SF_4 mole ratio was 1:1 or 1:2. However, using a mole ratio $^{36}ClF/SF_4=2{:}1$, the [^{36}Cl] surface count rate did not reach background, indicating that a strongly bound species was formed. Removal of all volatile material and the addition of further SF_4 led to a small reduction in the surface count rate and the formation of some $SF_5{}^{36}Cl$ in the vapour phase. This suggests that $Cs^+[ClF_2]^-$ formed under these circumstances (Eq. (4)) reacts with SF_4 to some extent to give SF_5Cl, but that the reaction is very slow.

Surface fluorinations with HF alone or with F_2CO did not produce effective catalysts. The former reagent led to catalysts with very low activity and the latter resulted in SF_5Cl contaminated by hydrolysis products because fluorination of the surface hydroxyl groups had been incomplete. Both outcomes were not unexpected

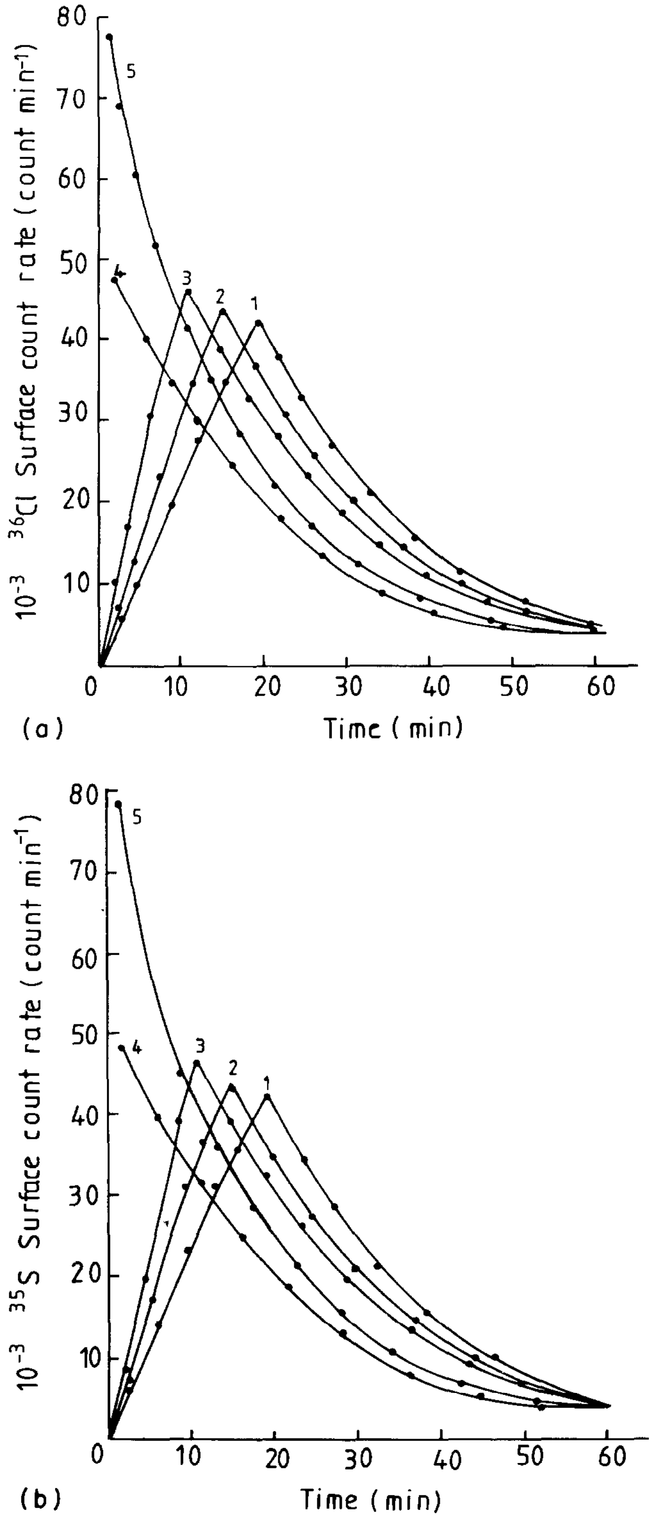

Fig. 1. Variation of (a) [^{36}Cl] surface count rate (b) [^{35}S] surface count rate with time in catalysed $ClF + SF_4$ (1:1 mole ratio) reactions at room temperature. Catalyst details: curves 1, 2 and 3, supported CsF (loading 8.8, 1.1 and 2.0 mmol g^{-1}), aqueous impregnation, fluorination with SF_4; curve 4, supported CsF (loading 4.4 mmol g^{-1}), non-aqueous impregnation, fluorination with F_2SO; curve 5, supported CsF (loading 5.5 mmol g^{-1}), aqueous impregnation, fluorination with SO_2 then HF.

TABLE 2. Variation of second-order rate constant for $SF_4 + ClF \rightarrow SF_5Cl$ with catalyst composition[a]

Metal fluoride loading (mmol g^{-1})	Second-order rate constant/(count^{-1} min) min^{-1} $\times 10^6$ in the presence of supported			
	CsF[b]	CsF[b]	KF[b]	KF[b]
0.6	3.3(1)[c]	3.4(1)		
1.1	3.9(2)	3.8(2)		
2.0	4.5(5)	4.6(6)	3.0(2)[c]	2.8(2)
4.4	6.6(2)	6.5(2)	4.3(2)	4.4(2)
5.0	7.3(4)	7.4(5)	5.2(4)	5.1(5)
5.5	7.9(5)	7.8(4)	6.0(5)	5.9(7)
6.0	6.8(4)	6.7(4)	4.9(5)	5.1(5)
7.5	4.4(3)	4.3(4)	3.6(4)	3.5(4)
8.8	3.3(4)	3.4(3)	2.2(3)	2.3(3)
15.5	1.2(2)	1.3(3)	1.2(2)	

[a] Reaction conditions: room temperature, $SF_4/ClF = 1:1$, catalyst wt. = 2.0 g. The methods used for impregnation and surface fluorination had no effect on the data obtained.

[b] Data in the first column derived from [^{36}Cl] measurements and data in the second column from [^{35}S] measurements.

[c] ( ) = uncertainty in the second figure.

on the basis of the behaviour of these reagents in the study of surface fluorination [1]. Otherwise, there was no evidence for the involvement of the fluorinated γ-alumina support in the catalysis at room temperature. In contrast, reactions between SF_4 and ClF in the presence of supported CsF or KF (loading 4.4 mmol g^{-1}) carried out at 373 K for 0.5 h did not produce SF_5Cl but a mixture of sulphuryl halides, F_2SO_2 Cl_2SO_2 and $FClSO_2$, which were identified by their IR spectra [17]. This reaction resulted in complete deactivation of the catalyst. Physical examination of the solids by transmission electron microscopy, IR spectroscopy and powder XRD indicated that tetrafluoroaluminate phases, $MAlF_4$ (M = Cs or K [18]), had been formed, presumably via a reaction related to that which results in M_3AlF_6 formation during impregnation of γ-alumina with MF [2,3]. There was no evidence for the presence of MF particles in the solids after these reactions.

3.2. Mercury(II) fluoride

It was necessary to pretreat mercury(II) fluoride chemically in order to study its catalytic behaviour. Two methods were adopted, fluorination of the surface with SF_4 at room temperature or treatment with $(CF_3)_2CO$ in the presence of MeCN followed by thermal decomposition in vacuo of the adduct formed. The latter method has been used to activate CsF for catalytic purposes [5,16] and was the more successful of the two pretreatments, one reason being that the surface area of the resulting material was significantly greater. Yields of SF_5Cl from three series, each of three reactions, between ClF and SF_4, 1:1 mole ratio, at room temperature for 1 h, were 75% when $(CF_3)_2CO$-pretreated HgF_2 was used. Corresponding experiments using HgF_2 pretreated with SF_4 and reaction times of 4 h led to yields of 45%. In both cases, the optimum yield of SF_5Cl was obtained using a 1:1 ClF/SF_4 mole ratio.

Adsorption experiments involving ^{36}ClF or $^{35}SF_4$ indicated that ^{36}ClF was strongly adsorbed on both materials. Adsorption of $^{35}SF_4$ was weaker, being barely detectable on HgF_2 that had been pretreated with SF_4. Desorption of ^{36}ClF from $(CF_3)_2CO$-activated HgF_2 at room temperature was very slow. Radiotracer and manometric experiments both indicated that the interaction probably involved bulk material, since the combining ratio HgF_2/ClF was 1.0:0.7. This solid did not react with SF_4 to give SF_5Cl. In contrast, $^{35}SF_4$ adsorbed on $(CF_3)_2CO$-pretreated HgF_2 did react with ClF to give $^{35}SF_5Cl$.

Admission of 1:1 mole ratio mixtures of $^{36}ClF + SF_4$ or $ClF + ^{35}SF_4$ to HgF_2 activated by $(CF_3)_2CO$ resulted in behaviour very similar to that described for the supported Group 1 fluorides. [^{36}Cl] or [^{35}S] surface activities were detected within the time of mixing and decreased via a second-order process.

3.3 *Comparisons among supported and unsupported metal fluorides*

The behaviour of fluorinated γ-alumina-supported CsF, KF and HgF_2, activated by the $(CF_3)_2CO$ route, in the reaction between ClF and SF_4 was very comparable to the behaviour of $(CF_3)_2CO$-activated CsF [5]. It is reasonable to suppose that, in all the cases examined here, chlorofluorination of SF_4 occurred via the surface reaction (Eq. (2)) in which ClF and SF_4 are both adsorbed on to surface F^- anion. The catalytic activity of $(CF_3)_2CO$-activated HgF_2 was significantly less than that of unsupported CsF activated by the same route and, based on the yields of SF_5Cl obtained, was comparable to that of supported KF at a loading of 5.5 mmol g^{-1}. The catalytic activities of unsupported, $(CF_3)_2CO$-activated CsF and the supported material (loading 5.5 mmol g^{-1}) were comparable. On economic grounds, therefore, CsF supported on γ-alumina, pretreated with SO_2 and fluorinated with HF offers a distinct advantage.

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