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# Catalytic fluorination of trichloroethene by anhydrous hydrogen fluoride in the presence of fluorinated chromia under static conditions. Synthesis of [$^{18}$F]-labelled $CF_3CH_2F$ and [$^{36}$Cl]-labelled $CF_3CH_2Cl$. Catalytic dehydrofluorination of $CF_3CH_2F$ and $CF_3CH_2Cl$

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Dedicated to Professor Paul Tarrant on the occasion of his 85th birthday

**Abstract**

Catalytic fluorination of trichloroethene by anhydrous hydrogen fluoride at 653 K in the presence of fluorinated amorphous chromia under static conditions leads to a mixture of products in which partially halogenated olefins predominate. These are converted to mixtures containing $CF_3CH_2F$ and $CF_3CH_2Cl$ by a second fluorination using fresh catalyst. The results of product analyses from reactions carried out under various conditions have been used to design a synthesis of [$^{18}$F]-$CF_3CH_2F$ from $CCl_2{=}CHCl$. It is proposed that [$^{18}$F] labelling occurs via direct [$^{18}$F]- for [$^{19}$F] exchange rather than by a dehydrofluorination/hydrofluorination route. [$^{36}$Cl]-labelled $CF_3CH_2Cl$ is readily prepared from $CF_3CH_2F$ and $H^{36}Cl$ in the presence of chromia catalysts. Enthalpies of dehydrofluorination of $CF_3CH_2F$ and $CF_3CH_2Cl$ in the vapour phase have been computed.[1] © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Catalytic fluorination; Fluorine-18; Chlorine-36; Fluorinated chromia; *ab initio* computation

## 1. Introduction

1,1,1,2-Tetrafluoroethane is firmly established as an important CFC-alternative refrigerant and, as a result, fundamental aspects of its catalytic synthesis from trichloroethene and anhydrous hydrogen fluoride under heterogeneous flow conditions have been widely reported. Chromia is the most widely-used catalyst precursor [1–5] but other materials that have been investigated include alumina-based aerogels [6] and fluorides containing aluminium, chromium(III), magnesium and mixtures thereof [7–12]. We have recently reported the behaviour of heavily fluorinated chromia doped with zinc or nickel(II) in the catalytic fluorination of $CF_3CH_2Cl$ to $CF_3CH_2F$ [13]. The reactions involved in the multi-step catalytic fluorination of $CCl_2{=}CHCl$ are complex and under flow conditions olefinic biproducts are normally observed due to the propensity of $CF_3CH_2F$, $CF_3CH_2Cl$ and intermediates formed in earlier fluorination steps to undergo dehydrofluorination. In principle, conversion of $CCl_2FCH_2Cl$, formed from $CCl_2CHCl + HF$, to $CF_3CH_2F$ could occur by dehydrochlorination then hydrofluorination pathways rather than by direct F-for-Cl halogen exchange but the available evidence [e.g. [1,4] suggests that the latter is preferred.

We now report the results of a study of the catalytic fluorination of $CCl_2{=}CHCl$ carried out under static conditions in the presence of fluorinated chromia. This was undertaken with the objective of preparing $CF_3CH_2F$ and $CF_3CH_2Cl$ labelled with the radioisotopes [$^{18}$F] and [$^{36}$Cl], respectively. Although the synthesis of [$^{18}$F]-labelled

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[1] Non-SI units employed: $\text{Å} = 10^{-10}$ m; a.u. $\approx 4.36 \times 10^{-18}$ J $\approx 6.27089 \times 10^{2}$ kcal mol$^{-1}$.

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$CF_3CH_2F$ has been reported via the reactions of $CF_3CH_2F$ or $CF_3CH_2OTs$ with $[K(crypt)]^{18}F$ [14], a synthesis based on $CCl_2{=}CHCl$ would have the advantage of being applicable also to a $[^{14}C]$-labelled product. The target compounds have been prepared and much useful information obtained concerning the dehydrofluorination behaviour of $CF_3CH_2F$ and its precursors. The results can be compared with the distribution of products obtained from catalytic fluorination of $CCl_2{=}CHCl$ under flow conditions [4].

## 2. Results and discussion

### 2.1. Product distribution studies

The distribution of products obtained from the fluorination of trichloroethene by anhydrous hydrogen fluoride, mole ratio $HF{:}CCl_2CHCl \geq 4:1$, at four different temperatures in the range 373–653 K in the presence of lightly fluorinated amorphous chromia and under static conditions, is shown diagrammatically in Fig. 1. Conversion of $CCl_2CHCl$ increased with temperature and was essentially complete at 653 K after 18 h. However, the major components of the organic product mixture were partially fluorinated olefins and chloro-olefins, the ethanes, $CF_3CH_2Cl$ and $CF_3CH_2F$ being $\leq 15\%$ of the total organic fraction. The distributions of saturated and olefinic $C_2$ compounds are compared in Fig. 1(a, b); the major product was $CF_2{=}CHCl$ and minor products were $CF_3CH_2Cl$, $CF_3CH_2F$ and $CF_2{=}CHF$. The observed behaviour can be rationalised by assuming that the dominant processes are catalytic fluorination of $CCl_2{=}CHCl$ to give $CF_3CH_2Cl$ and dehydrofluorination of $CF_3CH_2Cl$ giving $CF_2{=}CHCl$ (Scheme 1). This is in harmony with previous work under flow conditions (e.g. [1,4,6]). Very active catalysts are required for the fluorination of $CF_3CH_2Cl$ to $CF_3CH_2F$, a step which is thermodynamically limited [2–4,8,10,13]. The origin of the 'other olefins' in Fig. 1(b) was not investigated but results from a study under flow conditions suggest that this component may have been $CClF{=}CHCl$, formed from dehydrochlorination of $CCl_2FCH_2Cl$ or dehydrofluorination of $CClF_2CH_2Cl$ [4]. Crucially, deactivation of the catalyst was rapid and was accompanied by the apparent formation of a black coating, possibly the result of oligomerization of olefinic products [cf. [15].

The results of a further HF treatment of the organic product mixture in the presence of fresh fluorinated chromia are illustrated in Fig. 1(c). This stage was characterised by a marked reduction in $CF_2{=}CHCl$ and an increase in $CF_3CH_2F$. The rationalisation is given in Scheme 2. The olefinic components, mainly $CF_2{=}CHF$ and $CF_2{=}CHCl$, could be removed by KOH treatment, giving an organic product comprising $CF_3CH_2F$ and $CF_3CH_2Cl$ in the mole ratio 3 : 1 as determined by G.C. This two-step process, though somewhat laborious, gave reproductible results.

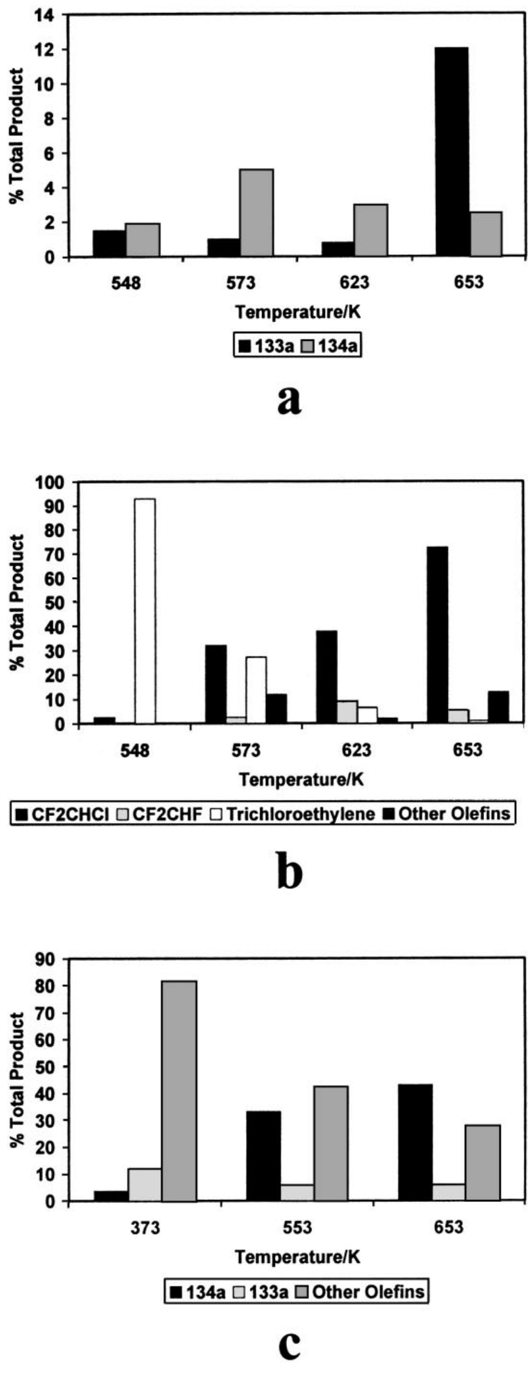

Fig. 1. Distribution of organic products, determined by G.C., from catalytic fluorination of $CCl_2{=}CHCl$ under static conditions; (a) $CF_3CH_2Cl$ (133*a*) and $CF_3CH_2F$ (134a) from a one step reaction; (b) olefinic products from a one step reaction; (c) $CF_3CH_2Cl$ (133*a*) and $CF_3CH_2F$ (134a) after a second step using fresh catalyst.

### 2.2. Preparation of $[^{18}F]$-labelled $CF_3CH_2F$ and $[^{36}Cl]$-labelled $CF_3CH_2Cl$

Following the observations reported above, the behaviour of $[^{18}F]$-labelled anhydrous hydrogen fluoride towards a mixture of $CF_3CH_2F$ and $CF_3CH_2Cl$ (3 : 1 mole ratio and prepared as described) was examined under static condi-

**Dominant reactions**

$CCl_2{=}CHCl + 3HF \rightarrow CCl_2FCH_2Cl \rightarrow CClF_2CH_2Cl \rightarrow CF_3CH_2Cl$

$CF_3CH_2Cl \rightarrow CF_2{=}CHCl + HF$

**Minor reactions**

$CF_3CH_2Cl + HF \rightarrow CF_3CH_2F + HCl$

$CF_3CH_2F \rightarrow CF_2{=}CHF + HF$

Scheme 1

Table 1
[18]F] Activity expected in organic product depending on the pathway; $CF_3CH_2Cl/CF_3CH_2F(1:3) + 5[^{18}F]$-HF

| Reactant | Pathway | Expected $[^{18}F]$-activity in organic fraction/% |
|---|---|---|
| $CF_3CH_2F$ | $^{18}F$-for-F exchange | 13 |
| $CF_3CH_2F$ | $-HF/+H^{18}F$ | 31 |
| $CF_3CH_2Cl$ | $-HF/+H^{18}F$ | 13 |
| $CF_3CH_2F+$<br>$CF_3CH_2Cl$ | $-HF/+H^{18}F$ | 37 |
| $CF_3CH_2F+$<br>$CF_3CH_2Cl$ | $-HF/+H^{18}F$<br>and $^{18}F$-for-F exchange | 43 |

tions at 653 K in the presence of fresh fluorinated chromia. The contact time was 2 h, being determined by the short half-life (110 min) of $[^{18}F]$; under these conditions there were no observable chemical reactions as indicated by G.C. analyses before and after $H^{18}F$ treatment.

Under these conditions ca. 13% of the $[^{18}F]$ activity originally present in $H^{18}F$ was detected in the organic fraction while ca. 3%, equivalent to an uptake of $H^{18}F$ by the fluorinated chromia catalyst of 2 mmol HF $g^{-1}$, was detected from the catalyst. The level to which $[^{18}F]$ was incorporated in the organic enables an inference to be made about the nature of the incorporation route. Some of the possibilities are summarised in Table 1. Comparisons between the data in Table 1 and the experimental value of 13% suggest that under these conditions, labelling of $CF_3CH_2F$ via a dehydrofluorination then hydrofluorination pathway is unlikely, since higher levels of $[^{18}F]$ incorporation would have been expected. Because of the reaction stoichiometry used, this route cannot be definitively excluded for $CF_3CH_2Cl$. However, it is considered far more likely that the $[^{18}F]$ incorporation observed in the organic fraction is due predominantly to a direct $^{18}F$-for-F exchange reaction on $CF_3CH_2F$. It is believed that dehydrofluorination/hydrofluorination pathways at the fluorinated chromia surface are inhibited by the large excess of HF present on the surface as indicated by the incorporation of $[^{18}F]$ by the catalyst (see above).

This view is consistent with our recent $[^{18}F]$ measurements on fluorinated chromia and metal(II) promoted chromias under flow conditions [13]. It is consistent also with previous studies of catalytic fluorination under flow conditions, where partially fluorinated olefinic products are observed if HF levels are insufficiently high [4] or as a catalyst looses its activity [2]. A dehydrofluorination-hydrofluorination pathway is feasible however, in the absence of added HF which is the case in the previous synthesis of $[^{18}F]$-$CF_3CH_2F$ [14] and in the related catalytic isomerisation of $CHF_2CHF_2$ to $CF_3CH_2F$ [16–18].

The synthesis of $[^{36}Cl]$-labelled $CF_3CH_2Cl$ was achieved in a straightforward manner from a reaction between equimolar quantities of $CF_3CH_2F$ and anhydrous $H^{36}Cl$ in the presence of unfluorinated amorphous chromia at 673 K under static conditions, conversions of $CF_3CH_2F$ being 95% with minimal olefin formation, after 1 h. However, a more detailed examination of the reaction in the temperature range 653–693 K in the presence of fluorinated or unfluorinated chromias of varying degrees of crystallinity, in some cases doped with zinc(II) [13], indicated a more complex situation. Monitoring these reactions by G.C. at various times led to a maximum in the concentration of $CF_3CH_2Cl$ being observed after 60–90 min. Thereafter, the proportion of $CF_3CH_2Cl$ in a reaction mixture decreased at the expense of $CF_3CH_2F$. In some cases the process was followed over a 3 h period during which $CF_3CH_2F$ first decreased, then increased, then decreased again. However, the proportion of $CF_3CH_2Cl$ never reached that observed after the first stage. Small quantities of olefins were formed during these reactions but were never greater than 4% of the total organic mixture. They, together with any hydrogen halide present, were readily removed by treatment with moist NaOH pellets and by careful adjustment of the time of reaction, pure

**Dominant reactions**

$CF_2{=}CHCl + HF \rightarrow CF_3CH_2Cl$

$CF_3CH_2Cl + HF \rightarrow CF_3CH_2F + HCl$

**Minor reactions**

$CF_3CH_2F \rightarrow CF_2{=}CHF$

and/or: $CF_2{=}CHCl + HF \rightarrow CF_2{=}CHF + HCl$

Scheme 2

Table 2
Computational results

| | $CF_3CH_2F$, 134a | $CF_3CH_2Cl$, 133a | $CF_2{=}CHF$ | $CF_2{=}CHCl$ | HF |
|---|---|---|---|---|---|
| Symmetry | $C_s$ | $C_s$ | $C_s$ | $C_s$ | $C_{\infty v}$ |
| State | ${}^1A'$ | ${}^1A'$ | ${}^1A'$ | ${}^1A'$ | ${}^1\Sigma$ |
| RHF/6-311G(d,p) | | | | | |
| $-E$/a.u. | 474.790272 | 834.837651 | 374.676325 | 734.729259 | 100.046904 |
| *NIMAG* | 0 | 0 | 0 | 0 | 0 |
| *zpe*/kcal mol$^{-1}$ | 31.0 | 29.86 | 20.14 | 19.14 | 6.45 |
| RMP2/6-311G(d,p) | | | | | |
| $-E$/a.u. | 475.878679 | 835.865285 | 375.549497 | 735.540873 | 100.267216 |
| *NIMAG* | 0 | 0 | 0 | 0 | 0 |
| *zpe*/kcal mol$^{-1}$ | 29.18 | 28.22 | 18.66 | 17.82 | 6.08 |
| RMP4(SDQ)/6 311G(d,p)// RMP2/6-311G(d,p) | | | | | |
| $-E$/a.u. | 475.898373 | 835.894161 | 375.565673 | 735.565499 | 100.286106 |

$CF_3CH_2Cl$ or $CF_3CH_2{}^{36}Cl$ could be obtained. The behaviour observed here is consistent with our previous observations of labile, catalytically active fluoride on fluorinated chromia surfaces [13,19]. This led to the development of an halogen exchange model for the behaviour of chlorofluoroethanes on fluorinated chromia [20] and it appears that a similar model is applicable to the $CF_3CH_2Cl$, $CF_3CH_2F$ system.

### 2.3. *Ab initio computations of the dehydrofluorination reactions of $CF_3CH_2F$ and $CF_3CH_2Cl$*

In order to obtain a greater understanding of the relationships between $CF_3CH_2X$, X = F or Cl, and their dehydrofluorinated products, the structures and vibrational frequencies of $CF_3CH_2F$, $CF_3CH_2Cl$, $CF_2{=}CH_2$ and $CF_2{=}CHCl$ were computed quantum chemically at the HF and electron correlated MP2 level of theory at a 6-311G(d,p) basis. In addition, single point calculations were performed for all species at the MP4(SDQ) level of theory employing again a 6-311G(d,p) basis. Details are given in Table 2.

The calculated total energies (Table 3) can be used to predict theoretically the enthalpies for the HF elimination reactions. The HF elimination energies of $CF_3CH_2Cl$ and $CF_3CH_2F$ were calculated, which, after correction [21–23] for zero-point energies (*zpe*, Table 2), differences in rotational ($\Delta U^{\mathrm{rot}} = +\,\mathrm{RT}$) and translational ($\Delta U^{\mathrm{tr}} = +\,3/2\,\mathrm{RT}$) degrees of freedom, and the work term ($p\Delta V = +\,\mathrm{RT}$), were converted into the gas phase HF elimination enthalpy values at room temperature. At all levels of theory applied, the dehydrofluorination of $CF_3CH_2F$ is slightly more favourable than that of $CF_3CH_2Cl$ with the difference, $\Delta[\Delta H^{\circ}_{298}] = 3.34$ kcal mol$^{-1}$ (HF), 2.84 kcal mol$^{-1}$ (MP2) and 2.40 kcal mol$^{-1}$ (MP4). However, in real situations, the small difference between the enthalpies for the HF elimination reactions is insignificant, for example it is comparable to what might be expected from the effects of intermolecular interactions that would be present in condensed phases. It is considered that the data that result from calculations at the MP2 or MP4//MP2 levels (Table 3) are far more reliable than those from HF or semiempirical methods. For example, the generally poor agreement between experimental data and those from HF calculations for fluorine containing molecules, demonstrates the great importance of electron correlation for accurate predictions in non metal fluorides. A previous computational study, using the semi-empirical AM1 method, of fluorination and dehydrohalogenation reactions in the $CCl_2{=}CHCl$, $CF_3CH_2Cl$, $CF_3CH_2F$ system [4] should be regarded, therefore, as a useful guide rather than being definitive. Notwithstanding, where overlap exists the agreement is reasonable.

Table 3
Reaction energies for the dehydrofluorination reactions

| | Dehydrofluorination of $CF_3CH_2Cl$ | Dehydrofluorination of $CF_3CH_2F$ |
|---|---|---|
| $\Delta E^{\mathrm{el}}$ (HF)/kcal mol$^{-1}$[a] | 42.05 | 38.57 |
| $\Delta H^{\circ}_{298}$(HF)/kcal mol$^{-1}$[a] | 39.71 | 36.37 |
| $\Delta E^{\mathrm{el}}$ (MP2)/kcal mol$^{-1}$[a] | 38.86 | 35.90 |
| $\Delta H^{\circ}_{298}$(MP2)/kcal mol$^{-1}$[a] | 36.49 | 33.65 |
| $\Delta E^{\mathrm{el}}$(MP4)/kcal mol$^{-1}$[b] | 29.22 | 26.70 |
| $\Delta H^{\circ}_{298}$(MP4)/kcal mol$^{-1}$[b] | 26.85 | 24.45 |

[a] MP2/6-311G(d,p)//MP2/6-311G(d,p).

[b] MP4(SDQ)/6-311G(d,p)//MP2/6-311G(d,p); *zpe* values taken from the MP2 calculation (Table 2).

## 3. Experimental

### 3.1. *Catalytic fluorination*

The chromia used in all the experiments, except when noted below, was produced by the decomposition of ammonium dichromate and then calcined for 3 h at 523 K under dynamic vacuum. The chromia was fluorinated immediately before use by opening the vessel to successive aliquots of

HF vapour at room temperature with degassing between aliquot addition. All fluorinations and reactions were performed in stainless steel or Monel metal reaction vessels attached to a Monel metal vacuum line.

A series of nine experiments was undertaken; some experiments employed a single batch of catalyst, others were performed in two stages, using a fresh batch of fluorinated chromia and more HF for the second stage. The products were analysed, after removal of any HF present, using a Varian 3400 gas chromatograph with a SilicaPLOT 30 m capillary column. Product identities were established by comparison with standards and relative sensitivities were established for $CF_3CH_2Cl$ and $CF_3CH_2F$ from experimentally determined calibration curves.

Step 1. Calcined (523 K) volcano chromia (0.2 g) which had been fluorinated at room temperature with four successive aliquots (ca. 2 mmol each) of HF, was used; 2.2 mmol of trichloroethene were reacted with 11 mmol HF over the catalyst at 548 K for 3 h.

Step 2. The catalyst was prepared in a manner identical to Step 1; 2 mmol of $CCl_2{=}CHCl$ were reacted with 8 mmol of HF over the catalyst at 623 K overnight.

Step 3. As in Step 2 but heated to 573 K overnight.

Step 4. The product mixture from Step 3 was heated to 623 K overnight over a fresh sample of the same catalyst.

Step 5. The catalyst and reagents were exactly as in Step 2, but heated to 653 K overnight.

Step 6. Repeat Step 5.

Step 7. The products from Step 6 were condensed onto fresh fluorinated chromia, prepared as before, and the mixture heated to 523 K overnight.

Step 8. The product mixture from Step 7 was heated to 653 K, over the same catalyst, for 1 h.

Step 9. Trichloroethene (3.0 mmol), HF (10.0 mmol) and of chromia (0.2 g prepared as before) were allowed to react overnight at 653 K. The product mixture was condensed onto fresh fluorinated chromia and reacted at 653 K for 1 h. The product mixture from this second stage was then condensed onto NaOH pellets before CG analysis.

### 3.2. Preparation of labelled compounds

#### 3.2.1. [$^{18}$F]-labelling

Fluorine-18 was supplied by the John Mallard Scottish PET Centre, Grampian University Hospitals Trust, Aberdeen as an effectively 'no carrier added' aqueous solution (activities supplied were in the range 50–450 MBq). After transfer to Glasgow, an [$^{18}$F] solution was added to aqueous CsOH (1.0 g, in 5–10 cm$^3$) and the mixture carefully neutralised with aqueous HF (40%). Usually ca. 2 cm$^3$ were required. Solid $Cs^{18}F$ was obtained by evaporation and drying, then transferred to a Monel metal vessel attached to a Monel vacuum line and evacuated. Anhydrous HF (up to 15 mmol) was labelled with [$^{18}$F] by exchange with $Cs^{18}F$ at 523 K for 0.5 h. Specific count rates of each sample of $H^{18}F$ prepared were determined using a well scintillation counter by condensing a measured quantity (normally 0.5 mmol) onto dry CsF contained in an FEP counting tube, and were in the range 600–5600 count s$^{-1}$ mmol$^{-1}$. Background and decay corrections were applied in all cases. The initial [$^{18}$F] activities supplied enabled the isotope to be used over several half-lives.

1,1,1,2-Tetrafluoroethane labelled with [$^{18}$F] was prepared from $CCl_2{=}CHCl$ by the following procedure, the quantities given being typical of those used. To a Monel metal pressure vessel containing chromia (0.2 g), previously fluorinated at room temperature with four successive aliquots (2.0 mmol) of anhydrous HF, was added $CCl_2{=}CHCl$ (8.0 mmol) then anhydrous HF (20.0 mmol). The mixture was allowed to react at 653 K overnight. Volatile material was condensed onto KOH pellets contained in a stainless steel vessel and stored at room temperature for 2 h. The organic material isolated (3.0 mmol) was a mixture of $CF_3CH_2F$ and $CF_3CH_2Cl$ (3 : 1) as determined by GC, and was added by distillation to a second Monel metal pressure vessel containing fluorinated chromia followed by $H^{18}F$ (15.0 mmol). The contents were heated to 653 K for 2 h then, after cooling, treated with KOH for 0.5 h at room temperature. The organic fraction (1.78 mmol) was transferred to a Pyrex counting vessel; its specific count rate, determined in the frozen state, was 378 count s$^{-1}$ mmol$^{-1}$. For comparison, the initial specific count rate of $H^{18}F$ in this experiment was 563 count s$^{-1}$ mmol$^{-1}$ and that of the fluorinated chromia catalyst after reaction was 1143 count s$^{-1}$ g$^{-1}$. Analysis of the organic fraction by GC after complete decay of [$^{18}$F] indicated that its chemical composition was unchanged by the $H^{18}F$ treatment.

#### 3.2.2. [$^{36}$Cl]-labelling

2-Chloro-1,1,1-trifluoroethane, labelled with [$^{36}$Cl] was prepared from the reaction of $CF_3CH_2F$ with anhydrous $H^{36}Cl$ in the presence of unfluorinated amorphous chromia at 673 K. Anhydrous $H^{36}Cl$ was prepared by a modified literature procedure [24] from conc. $H_2SO_4$ and aqueous [$^{36}$Cl]-chloride ion using a Pyrex reaction vessel fitted with a pressure-equilibrated dropping funnel and a series of traps containing $P_4O_{10}$ and cooled in $CO_2/CH_2Cl_2$ and liq. $N_2$/isopentane baths. The collection trap was fitted with PTFE/Pyrex stop-cocks enabling it to be transferred to a Pyrex vacuum line for subsequent storage (in a Monel metal vessel over $P_4O_{10}$).

Aqueous [$^{36}$Cl] sodium chloride (6750 MBq, 1.0 cm$^3$; Amersham International) was diluted with conc. HCl (9.0 cm$^3$) and aliquots of this solution were added dropwise to $H_2SO_4$ contained in the reaction vessel. Typical [$^{36}$Cl] count rates of $H^{36}Cl$ prepared by this procedure, measured using a Pyrex Geiger Müller direct monitoring cell [25], were ca. 1000 count min$^{-1}$.

To a Monel metal pressure vessel containing amorphous unfluorinated chromia (2.0 g), previously calcined at 523 K in vacuo, was added a mixture of $CF_3CH_2F$ (6.1 mmol) and $H^{36}Cl$ (6.0 mmol) by vacuum distillation. The mixture was allowed to react at 673 K for 1 h. After cooling to room temperature, the volatile material was condensed onto moist NaOH pellets, the process being repeated until there was no evidence for either HCl or HF in the IR spectrum of the fraction. Analysis by GC indicated that the ratio $CF_3CH_2Cl$:$CF_3CH_2F$ was $\geq 95 : 5$. Longer reaction times led to product mixtures containing higher proportions of $CF_3CH_2F$.

Other catalysts, partially crystalline chromias both unfluorinated and fluorinated and zinc(II)-doped fluorinated chromias [13], were evaluated for use in this reaction. Generally they were less active, although pre-fluorination was beneficial for the partially crystalline materials as was Zn(II) doping. The [$^{36}Cl$]- count rates of $CF_3CH_2{}^{36}Cl$ prepared in this way were ca. 4000 count $min^{-1}$ as determined by the Geiger Müller direct monitoring method [25] at 100 Torr pressure.

### 3.3. Computational studies

Preliminary geometries for all compounds, $CF_3CH_2F$, $CF_3CH_2Cl$, $CF_2$=$CH_2$, $CF_2$=CHCl and HF, were calculated semiempirically (PM3) [26] in $C_1$ symmetry with the program package HyperChem [27] and were optimized to $C_S$ ($CF_3CH_2F$, $CF_3CH_2Cl$, $CF_2$=$CH_2$, $CF_2$=CHCl) or $C_{\infty v}$ (HF) symmetry, respectively. The structures, vibrational frequencies and zero point energies (*zpe*) for all molecules were then optimized within $C_s$ or $C_{\infty v}$ symmetry with the *ab initio* method at the RHF level of theory at the 6-311G(d,p) basis with the program package Gaussian 98 (Revision A.3) [28]. Electron correlation was taken into consideration (structure optimization, vibrational frequencies and *zpe* values at the 6-311G(d,p) basis) by applying perturbation theory according to Møller-Plesset (MP) which takes higher excitations into account by using a perturbation operator and using Rayleigh-Schrödinger perturbation theory to obtain a better wave function and energies (second order, notation MP2) [29–32]. In addition, single point calculations were performed for all species at the MP4(SDQ) level of theory which accounts for single, double and quadruple substitutions [33] employing a 6-311G(d,p) basis.

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