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Deuterium isotope studies of the hydrofluorination of chloroethenes over chromia catalysts

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Abstract

The mechanism of the catalytic fluorination of chloroalkenes over a chromia catalyst has been investigated by examining the effects of substituting DF for HF as the fluorine source for reaction with tetrachloroethene and trichloroethene. At a temperature of 250 °C and a HF(DF)/alkene molar ratio of 4.2:1, the rate of conversion of tetrachloroethene is increased by using DF and there is a concomitant increase in the selectivity to some chlorofluoroalkanes and a decrease in the selectivity to chlorofluoroalkenes. The opposite behaviour observed for the halogenated alkenes and alkanes indicates that the alkenes are not important intermediates in the production of the alkanes by a series of hydrofluorination and dehydrochlorination reactions. For tetrachloroethene, the main reaction pathway to the alkanes is a direct chlorine/fluorine exchange over a heavily fluorinated chromia surface with minimal C—H/C—D cleavage of intermediates. Substitution of DF for HF causes no change in the product selectivities from reaction with trichloroethene over chromia catalysts. However, the presence of dideutero — and monodeutero — products shows that both chlorine/fluorine exchange and HF addition/HCl elimination pathways are occurring for the less-substituted alkene.

Introduction

Because of the problems of ozone depletion in the stratosphere via its reaction with chlorine atoms, suggested by Rowland and Molina [1] from the photolysis of chlorofluorocarbons (CFCs), alternatives are now being sought for use as refrigerants, aerosols and foaming agents [2–5]. Two possible replacement compounds are CF_3CHCl_2 (HCFC-123) and CF_3CH_2F (HFC-134a) which can be produced by the hydrofluorination of tetrachloroethene (Per) and trichloroethene (Tri), respectively, over chromia catalysts. In the case of HFC-134a, the compound CF_3CH_2Cl (HCFC-133a) is produced as an intermediate. These replacement compounds could be formed by two mechanisms, either by a direct chlorine/fluorine exchange or

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by a sequence of hydrofluorination and dehydrochlorination reactions culminating in these products. One possible way of distinguishing between these two mechanisms is to substitute DF for HF and to search for isotope effects on the rates of reaction and on the product selectivities. The direct exchange mechanism would show no isotope effects because no C—H (D) bonds are broken, but the hydrofluorination/dehydrochlorination mechanism should show significant isotope effects since the dehydrochlorination could involve cleavage of C—D/C—H bonds which differ in zero point energy by ~5 kJ mol^{-1}. Kinetic isotope effects have been widely used in the study of elimination reactions [6] and particularly of dehydrochlorination reactions over acidic and basic solids. The dehydrochlorination of 1,2-dichloroethane over magnesium phosphate at 320 °C or magnesium sulphate at 160 °C show large isotope effects of 1.7 and 3.0 close to those expected theoretically, 2.6 and 3.6 [7]. Recent studies of the dehydrochlorination of 1,2-dichloroethane over copper(II) chloride/alumina catalysts also show a kinetic isotope effect indicating considerable C—D/C—H cleavage in the rate-determining step [8]. Here, we report the results of our studies of the hydrofluorination of tetrachloroethene and trichloroethene using DF and HF.

Experimental

Design and construction of equipment

The reactor and associated equipment (stainless steel construction) are illustrated schematically in Fig. 1. HF or DF were fed into the reactor in a stream of nitrogen using a sparging method known to be suitable for the

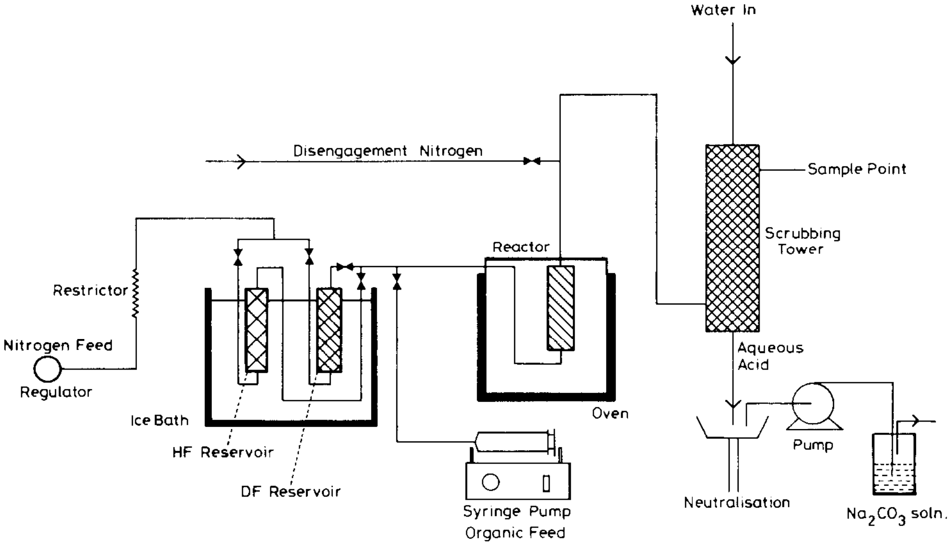


Fig. 1. Schematic illustration of hydrofluorination reactor.

feeding of low flows of hydrogen fluoride. Thus, a low flow of nitrogen is passed through HF or DF reservoirs, cooled at 0 °C in a bath of melting ice, resulting in a partial pressure of HF or DF in the nitrogen corresponding to its respective vapour pressure at that temperature. In order to calibrate these flows accurately, the nitrogen-containing HF or DF was bubbled into a known quantity of standard sodium hydroxide aqueous solution (0.1 M) containing phenolphthalein and the time for neutralisation noted.

Liquid Per or Tri were fed, simultaneously with the HF or DF, into the reactor using an automatic syringe pump (B. Braun Perfusor model VI). This instrument was calibrated by feeding either of the organic liquids at a given setting on the pump into an empty reactor whilst diluting the off-gas from the reactor with an accurately measured flow rate of disengagement nitrogen. Knowing the flow rate of the nitrogen, analysis of the organic material, using the calibrated GC, enabled the vapour flow rate to be calculated.

Trace heating of the pipework was used to ensure that the liquids were vaporised prior to entry to the reactor which was enclosed in a temperature-controlled oven. A thermocouple positioned at the base of the reactor bed was used to monitor reaction temperatures.

Unreacted HF, and any HCl generated from the reaction, was continuously removed by scrubbing with water (≈ 10 cm^3 min^{-1}) over a polypropylene packing contained in the scrubbing tower. The effluent from the scrubber was neutralised with aqueous sodium carbonate solution (0.7 M) which was continuously pumped from the storage vessel via a peristaltic pump before being sent to drain.

Disengagement nitrogen (400–500 cm^3 min^{-1}) was used to prevent the condensation of any heavy organic material and to reduce the solubilities of the organic components in water. Samples of the scrubbed reactor off-gases were taken with a glass syringe at the sample point indicated in Fig. 1 and injected into the GC or GC/MS unit.

Analysis was carried out using a calibrated Varian 3500 gas chromatograph fitted with an FID detector. Sample injection was made via a gas sample valve to ensure accurate and consistent injection volumes. The chromatographic column employed was a CPsil 19 CB column, 50 m in length, with an internal diameter of 0.32 mm. The column inlet pressure was 1.84×10^5 N m^{-2} and the carrier gas employed was helium (dried over molecular sieves) operated at a flow rate of 1.7 cm^3 min^{-1}. A series of programmed temperature increases up to 225 °C were used, with the detector temperature set at 225 °C.

The peak area counts generated by this instrument were imputed into a computer Symphony spreadsheet which permitted the rapid calculation of yields, selectivities of products, conversion of starting materials, contact time, space time yield and superficial linear velocities. This method was quantitative as indicated by the mass and element balances computed.

For HF/DF experiments, chromia pellets (33 g, 30 cm^3) were charged into the reactor and heated overnight in a stream of air at 400 °C. The reactor was then cooled to 240 °C, the air flow replaced with HF, and the crystalline catalyst prefluorinated for 2 h. After this time, Per was introduced so as to obtain a molar flow ratio of 4.2:1. During the first 4.5 h of operation, the catalyst undergoes a 'bedding-in' phase in which the high surface concentration of Cr^{VI} is reduced to Cr^{III} and fluorination of the chromia surface occurs.

When the catalyst had settled, the temperature was held steady at approximately 250 °C and the reaction selectivities accurately measured. Once steady conditions had been achieved, the HF was replaced with an equimolar flow of DF and the reaction selectivities re-measured under steady-state conditions.

On completion of the experiments described above, the reactant flows were replaced with those of trichloroethene and HF, fed simultaneously to the catalyst bed in the molar ratio of about 1:4.2, respectively. The temperature of the reactor was controlled at 276 °C. When the catalyst had settled to these new conditions, the reaction off-gases were accurately analysed and the HF flow replaced with an equimolar flow of DF. The effect of deuterium substitution was then monitored with respect to the selectivities and isotope distribution of the reaction products.

Mass spectrometry

Qualitative analyses were performed using a Hewlett Packard 5971A bench top GC/MS fitted with a CPsil 19 CB column (50 m, 0.32 mm i.d.) which was temperature-programmed. Mass spectra were normalised to 100 relative to the parent ion.

Results and discussion

Hydrofluorination of tetrachloroethene

A typical product spectrum obtained from the reaction of tetrachloroethene with hydrogen fluoride over chromia is given in Table 1, together with the overall rates of formation (expressed in mol min^{-1}) and product selectivities. These results were obtained using 250 cm^3 of catalyst at a mean bed temperature of 242 °C after about 8 h of operation, and are based on a feed of 43.8 $cm^3\ min^{-1}$ (1.82×10^{-3} mol min^{-1}) of gaseous perchloroethene and an HF/Per molar ratio of 6.85:1.

The desired HCFC-123, CF_3CHCl_2, is the major product (58.7% yield) with FC-122, $CF_2ClCHCl_2$, as the main secondary product. The alkenes FC-1111, $CFCl{=}CCl_2$, and FC-1112a, $CF_2{=}CCl_2$, were also produced in significant yields. As previously mentioned, two possible reaction mechanisms could result in this observed product spectrum.

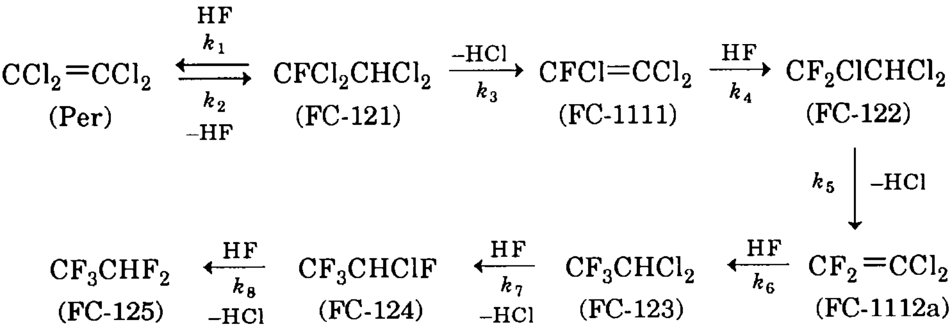
In Scheme 1, the first hydrofluorination step to produce FC-121 is followed by a series of dehydrochlorination and rehydrofluorination steps in sequence, finally culminating in HCFC-123 which is unable to undergo direct dehydrochlorination because there are no C—H and C—Cl bonds β to each other. The formation of FC-123a, $CF_2ClCHClF$, could occur either by iso-

TABLE 1

Hydrofluorination of tetrachloroethene: product spectrum and rates of formation

Compound	Formula	Rate of formation (10^{-3} mol min^{-1})	Selectivity (%)
FC-121	$CFCl_2CHCl_2$	0.00092	0.10
FC-1111	$CFCl{=}CCl_2$	0.065	7.15
FC-122	$CF_2ClCHCl_2$	0.173	19.15
FC-1112a	$CF_2{=}CCl_2$	0.00196	0.22
FC-123	CF_3CHCl_2	0.532	58.74
FC-123a	$CF_2ClCHClF$	0.0927	5.25
FC-124	CF_3CHClF	0.0201	1.14
FC-125	CF_3CHF_2	0.0000[a]	0.00[a]
FC-114a	CF_3CFCl_2	0.0071	0.40
FC-133a	CF_3CH_2Cl	0.0127	0.72

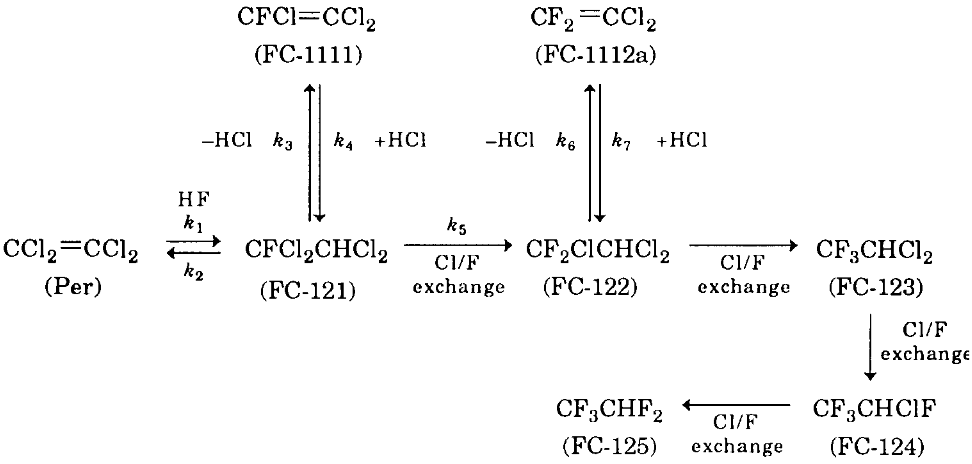
[a] Frequently detected, especially at higher temperatures.



Scheme 1. Dehydrochlorination/hydrofluorination mechanism over chromia catalysts.

merisation of HCFC-123 or by an anti-Markovnikov addition of HF to FC-1111, $CFCl{=}CCl_2$, followed by dehydrochlorination of the resultant $CFCl_2CHClF$ and subsequent hydrofluorination of FC-1112, $CFCl{=}CFCl$, to give FC-123a. The very minor products FC-124, CF_3CHClF, and FC-125, CF_3CHF_2, also require isomerisation reactions followed by dehydrochlorination and rehydrofluorination. The most important aspect of this mechanism in the present context is that the chlorofluoroalkenes, FC-1111 and FC-1112a, are major intermediates in the reaction pathway. Since their formation involves dehydrochlorination which has been found to exhibit a marked deuterium isotope effect [7, 8], the substitution of DF for HF should result in a diminution in the production of these alkenes and the saturated alkanes formed from them by subsequent HF and DF addition.

In Scheme 2, after the first hydrofluorination step the saturated products FC-122, FC-123, FC-124 and FC-125 result from direct chlorine exchange with fluoride moieties on the surface of the chromia catalyst, which had been preconditioned by treatment with the reactant streams for several hours



Scheme 2. Direct chlorine/fluorine exchange mechanism over chromia catalyst.

TABLE 2

Effects of DF substitution for HF on the selectivities of products from the fluorination of perchloroethene at 250 °C

Hydrogen fluoride		Deuterium fluoride	
Compound	Selectivity (std)[a] (mol%)	Compound	Selectivity (std)[a] (mol%)
CCl_2FCHCl_2	0 (0)	CCl_2FCDCl_2	0 (0)
$CClF=CCl_2$	9.0 (0.5)	$CClF=CCl_2$	4.7 (0.6)
$CClF_2CHCl_2$	12.4 (1.6)	$CClF_2CDCl_2$	4.4 (1.3)
$CF_2=CCl_2$	0.2 (0.1)	$CF_2=CCl_2$	0 (0.05)
CF_3CHCl_2	42.2 (0.7)	CF_3CDCl_2	46.5 (2.6)
$CF_2ClCHClF$	10.5 (1.4)	$CF_2ClCDClF$	3.2 (1.8)
CF_3CHClF	22.0 (3.0)	CF_3CDClF	32.1 (1.4)
CF_3CHF_2	1.5 (0.6)	CF_3CDF_2	7.7 (1.8)
CF_3CH_2Cl	0.5 (0.1)	CF_3CD_2Cl	0.9 (0.2)
CF_3CCl_2F	1.8 (0.06)	CF_3CCl_2F	0.5 (0.3)

[a] std = standard deviation.

under the reaction conditions. The most important difference between Schemes 1 and 2 is that the chlorofluoroalkenes, FC-1111 and FC-1112a, are not primary intermediates on the reaction pathways but merely the products of side-reactions. Scheme 2 predicts different deuterium isotope effects on the yields of the major saturated products FC-122, FC-123, FC-124 and FC-125 compared with those on the side-product alkenes.

The effects of DF substitution on product selectivities are shown in Table 2. The overall rate of conversion of Per was also increased by replacing HF with DF. The most significant result of using DF on selectivities was the reduction in the relative yields of the two alkenes FC-1111 ($CFCl=CCl_2$) and FC-1112a ($CF_2=CCl_2$) and a growth in the fluorochloroalkanes FC-123

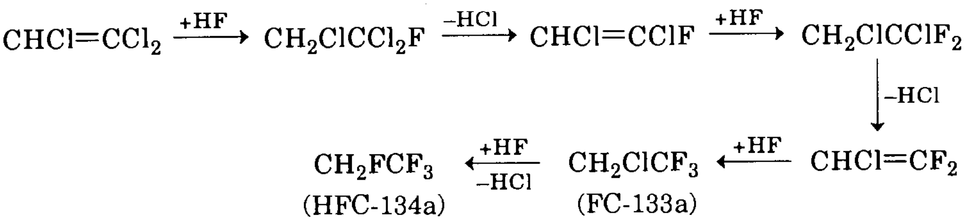
(CF_3CHCl_2), FC-124 (CF_3CHClF) and FC-125 (CF_3CHF_2). The opposite behaviour of the alkenes and the major alkane products is a clear indication that the latter products cannot be produced solely via the alkenes as intermediates (Scheme 1). The decrease in the alkene yield occurs because of the reduced rate of dedeuterochlorination (k_3 and k_6) reactions involving some degree of C—D bond cleavage in the rate-determining step. The rate constant of the back-reaction, k_2, is also reduced by using DF, so that the overall rate of conversion of Per is increased as found experimentally. By the same token, the reduced rate of the back-reaction will also cause an increase in the rates of formation of the saturated chlorofluoroalkanes by direct chlorine fluorine/exchange (Scheme 2) as is also observed experimentally. Their yields will also be increased because of the reduced loss of intermediates to produce the side-product alkenes. The decrease in the yield of FC-122, $CF_2ClCHCl_2$, by DF substitution is anomalous. It may be significant that Cl/F exchange at the fluorinated carbon in $CFCl_2CHCl_2$ and $CF_2ClCHCl_2$ is much more rapid than that at the protonated carbon in CF_3CHCl_2 and CF_3CHClF, as is evidenced by the net formation of the midway intermediate CF_3CHCl_2 in highest yield and the complete absence of the first intermediate $CFCl_2CHCl_2$. There may be some degree of bridging in a carbonium ion intermediate which could result in a secondary deuterium isotope effect as the hybridisation at the β-carbon changes on bridging. It is clear from the results of substituting HF by DF that the major reaction pathway for the fluorination of perchloroethene is direct chlorine/fluorine exchange on the highly fluorinated chromia catalyst surface (Scheme 2).

Hydrofluorination of trichloroethene

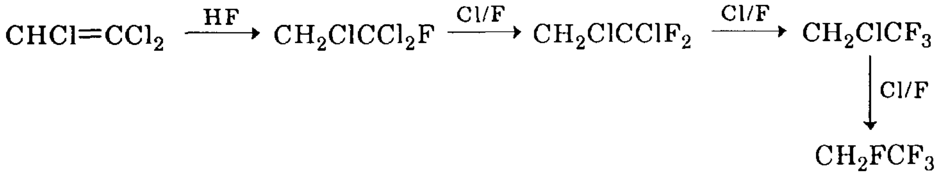
The products from the reaction of Tri with HF over the chromia catalyst consist of CH_2ClCF_3 (FC-133a, typically 90%) and CH_2FCF_3 (HFC-134a, typically 10%). Switching the feed from HF to DF had no detectable effect (other than that arising from isotopic substitution) on the product selectivities under the reaction conditions employed.

By analogy with the fluorination of tetrachloroethene, two possible reaction pathways account for the observed products. The addition/elimination mechanism is illustrated in Scheme 3, whilst the chlorine/fluorine exchange mechanism is illustrated in Scheme 4.

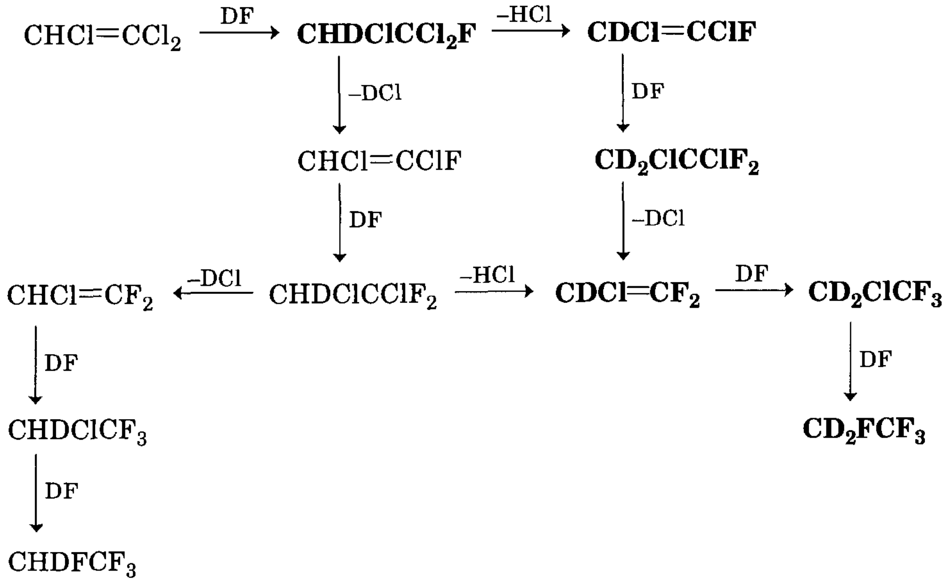
To distinguish between the two schemes outlined above, it is necessary to examine the isotope distribution of the reaction products as a consequence



Scheme 3. Hydrofluorination of trichloroethene — addition/elimination mechanism.



Scheme 4. Hydrofluorination of trichloroethene — chlorine/fluorine exchange mechanism.



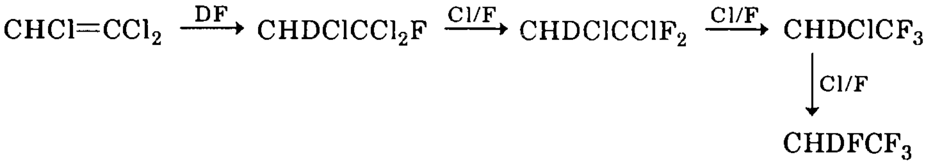
Scheme 5. Deuterofluorination of trichloroethene — addition/elimination mechanism.

of deuterium substitution. Since Tri contains hydrogen in its formation, the presence or absence of H or D in the products can be used diagnostically in the elucidation of the reaction pathway.

In the addition/elimination mechanism, the substitution of DF for HF in the reaction with Tri should result predominantly in doubly-deuterated FC-133a-d_2 (CF_3CD_2Cl), as shown emboldened in Scheme 5. Singly-deuterated FC-133a-d_1 (CF_3CHDCl) would be expected to be present as a minor component owing to (a) the statistical predominance of CF_3CD_2Cl and (b) the influence of the kinetic isotope effect in favouring the elimination of HCl over DCl.

In contrast, the chlorine/fluorine exchange mechanism would result in final products containing only one deuterium atom per molecule, Scheme 6.

The mass spectrum of the GC-separated FC-133a component from the Tri/DF reaction is recorded in Table 3. The presence of both singly- and doubly-deuterated species is clearly in evidence, demonstrating that the Cl/F exchange mechanism cannot be invoked exclusively. However, the proportion



$$\begin{tikzcd}
CHCl{=}CCl_2 \arrow[r, "DF"] & CHDClCCl_2F \arrow[r, "Cl/F"] & CHDClCClF_2 \arrow[r, "Cl/F"] & CHDClCF_3 \arrow[d, "Cl/F"] \\
 & & & CHDFCF_3
\end{tikzcd}$$

Scheme 6. Deuterofluorination of trichloroethene — chlorine/fluorine exchange mechanism.

TABLE 3

Mass spectrum of the FC-133a component from the reaction of Tri with deuterium fluoride

Ion	*m/z*	Abundance (%)
$[CD_2ClCF_3]^+$	119.9	69.2
$[CHDClCF_3]^+$	118.9	100
$[CD_2CF_3]^+$	85.05	28.7
$[CHDCF_3]^+$	84.05	48.0
$[CF_3]^+$	68.95	14.3
$[CD_2Cl]^+$	51.05	8.27
$[CHDCl]^+$	50.05	11.8

of singly-deuterated CF_3CHDCl species is far in excess of the quantity expected for a purely addition/elimination mechanism. The ratio of 0.7:1.0 from the parent molecular ions $[CF_3CD_2Cl]^+$ and $[CF_3CHDCl]^+$ indicates that both reaction pathways are operative for the chromia-catalysed hydrofluorination of Tri. The loss of the dehydrochlorination route in the case of Per shows that hydrogen substitution by chlorine markedly reduces the rate of this process. Such effects are well documented for HCl elimination in both the gas and solution phases [9].

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