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Mechanistic aspects of the isomerization reactions of 1,1,2,2-tetrafluoroethane on a CFC-conditioned chromia catalyst

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Abstract

The mechanism of the isomerization reactions of 1,1,2,2-tetrafluoroethane on a CFC-conditioned chromia catalyst was investigated. The desired 1,1,1,2-tetrafluoroethane can be obtained from its symmetric isomer in the presence of a chromia catalyst conditioned exclusively with chlorine-free fluorocarbons. In the presence of chlorofluorocarbons, hydrogen chloride is formed as a result of the decomposition reactions of the haloalkane used and is strongly adsorbed on to the surface. This HCl causes a very complex system of side-reactions. In addition, a second kind of chlorine, inactive chloride bonded to chromium, is formed which can only be removed as the result of a very slow solid–gas reaction.

Mechanistic information was obtained by examining the effects of substituting DCl for HCl as the chlorine source for the reaction with consecutive isomerization products of 1,1,2,2-tetrafluoroethane. Thus, it is most probable that dehydrohalogenation/hydrohalogenation processes (elimination/addition mechanism) are mainly responsible for the formation of the halo-olefins and halocarbons observed on chromia.

As the HCl/DCl adsorbed on the surface is very quickly removed by the reactions with the halocarbons and halo-olefins, it is advantageous to employ pulse techniques to evaluate this reaction system.

Keywords: Isomerization; 1,1,2,2-Tetrafluoroethane; Chromia catalyst; Mechanism; Reaction pathways

1. Introduction

CH_2FCF_3 (HFC-134a) is one of the most important substitutes for the ozone-depleting chlorofluorocarbons (CFC's) [1,2]. There are several ways to synthesize HFC-134a. The most important reaction processes are (**i**) starting from perchloroethylene (PCE) as a combination of hydrofluorination/chlorination reactions followed by a combination of consecutive chlorine/fluorine exchanges and dehydrochlorination reactions, or (**ii**) starting from trichloroethylene with a hydrofluorination reaction step, followed by consecutive chlorine solidus fluorine exchange reactions. The latter process proved to be a more complex reaction, characterized mainly by a combination of dehydrochlorination/hydrofluorination (elimination/addition) reactions and Cl/F exchange reactions [3,4].

On starting from PCE, different isomers of $C_2Cl_{6-x}F_x$ compounds are possible. The desired product however is CH_2FCF_3. It is therefore desirable to obtain CFC-114a as the intermediate compound in order to ensure that HFC-134a is obtained after drastic dehydrochlorinations. Consequently, it is still important to investigate the isomerization reactions in the so-called CFC-110 series [5–7]. What should be mentioned here is that the conditioning of solid catalysts with CFCs generally produces mainly fluorinated, but also partially chlorinated, active surfaces. The halogenation process of chromia catalysts with different halocarbons has recently been investigated with XPS spectroscopy [8]. It was shown that the overall halogen content is virtually unaffected by the CFC or HCFC gas used, but that certain changes in the F/Cl ratio are observable. These changes are mainly the result of differences in the thermodynamic forces depending on the gas phase used.

Winfield et al. [9,10] employed tracer techniques to differentiate the exchange activity of the halogen deposited on to γ-alumina as a result of conditioning. They found two kinds of chloride on the surface, (i) a mobile chloride which was very active towards exchange and which could be transferred into the gas molecule and (ii) an inert chloride which

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was so strongly bound in the solid that it was incapable of undergoing any exchange reaction.

Different isomers with the same chemical composition also exist in the corresponding HFC system, but in contrast to the CFC system the isomerization reactions of the latter have not been investigated to any extent until now. The patent literature only deals briefly with the catalysts for these isomerization reactions [11–14]. For all these various reasons, we commenced to an investigation of the isomerization of HFC-134 (CHF_2CHF_2) to HFC-134a (CH_2FCF_3) on a CHF_2CHF_2-conditioned chromia catalyst [15]. Our results showed that there are fundamental differences in the reactions which occur, which are strongly dependent on the conditioning gases used. If the chromia is conditioned exclusively with HFC-134 so that no chlorine comes into contact with the catalyst, a clear distinguishing reaction pattern is observed. In contrast, if the gases employed for the conditioning process contain chlorine, e.g., HCFC-133 numerous new products suddenly appear.

The results of kinetic investigations on conditioned, chlorine-free chromia catalysts are summarized in Ref. [15] and demonstrate that an isomerization equilibrium, i.e.

$$CHF_2\text{-}CHF_2 \rightleftarrows CHF{=}CF_2 + HF \rightleftarrows CH_2F-CF_3 \qquad (1)$$

occurs. This equilibrium tends to the right in accordance with thermodynamic calculations.

Our interest has also focused on the catalytic behaviour of chlorine-containing conditioned chromia catalysts and their influence on the product distribution. The present paper therefore deals with the type and function of chlorine being deposited on the solid as a result of conditioning with CFC's and the evaluation of the reaction processes occuring.

2. Experimental details

The reactor (Ø 5.1 mm) and associated equipment (nickel, copper construction) have already been illustrated and described in Ref. [15]. A pulse technique was used exclusively for all experiments in order to follow the reactions occurring between the gaseous phase and the reactive intermediate compounds adsorbed on to the catalyst surface.

Sample injection was effected via a gas sample valve to ensure accurate and consistent injection volumes. A second six-port valve, situated behind the pulse reactor, was equipped with an external heat-conducting detector, which indicated the presence of the product gas and enabled its extremely accurate injection into the GC. Quantitative analysis of the product gas was performed using a capillary gas chromatograph GC-14A from Shimadzu (column Poraplot U, 25 m). All gas lines were heated in order to prevent any condensation of the organic products.

Investigations of the isomerization reactions of HFC-134 were performed using chromia which was synthesized by the volcano reaction of ammonium dichromate. X-Ray measurements revealed that the crystalline phase was exclusively α-(Cr_2O_3) beside amorphous components which were identified from the broadening of the X-ray patterns. The powder obtained was pressed into pellets, cut and subdivided into fractions of 300–500 μm thickness. The surface area of the catalyst used was 54 $m^2\ g^{-1}$ and the bulk density 0.98 g ml^{-1}. All experiments were carried out using the same amount of catalyst, i.e. 600 mg. Before starting the reaction, the chromia catalyst was activated. Only a brief description of the conditioning process with HFC-134 will be given here. A continuous N_2 stream was used as the inert carrier gas. The gaseous HFC-134 was delivered in pulses (volume = 1 ml_{STP}) to this carrier gas. Since the flow rate of the nitrogen was known, the contact time of the organic gas pulse could be determined assuming an ideal laminar gas flow. Conditioning with HFC-134 was undertaken out using ca. 30 pulses (contact time, 16.8 s; reactor temperature, 400 °C) of the halocarbon, this being sufficient to allow the catalyst to reach its highest isomerization activity.

In contrast to the procedure described above, conditioning of chromia with CFC-12 was always carried out using a continuous halocarbon gas flow for a period of 1 h (contact time, 5.3 s; reactor temperature, 400 °C).

The DCl used was synthesized by hydrolyzing PCl_5 (Merck) with D_2O (Merck). The HFC-134 employed was a product of Fluorochem Ltd., the CFC-12 was from Hoechst AG and HCl from Merck.

Chloride analyses were performed semi-quantitatively in an area scan mode using an electron microscope (SEMQ) from ARL (USA). The chlorine was detected over an area of 30 μm^2 up to a depth of 2–4 μm. The maximum deviation of the measurement was 10%. The MS measurements were carried out using a GC–MS coupling, i.e. a GC 17A/QP-5000 instrument from Shimadzu and an MS unit, QMG-4211, from Balzers, respectively.

3. Results and discussion

3.1. The state of chlorine on the chromia surface

As has already been shown in Ref. [15], a definite number of HFC pulses (ca. 30) are needed to activate the chromia catalyst for isomerization reactions. In parallel to this, coke-formation processes also have to be considered since these result in a slow but permanent decrease of activity with reaction time. It was shown that the use of both CH_2Cl–CCl_2F (HCFC-131a) and CCl_2F_2 (CFC-12) as conditioning halocarbons results in the same Cl/F composition and analogous surface structures for the chromia catalyst [8], but with a decreased tendency to coke formation in the case of CFC-12. In order to suppress such coke formation as for as possible, we subsequently used CFC-12 as the conditioning gas phase in our investigations.

Thus, chromia was conditioned with CFC-12 at 400 °C using a constant gas flow. The catalyst was then maintained under these conditions until no organic compounds or hydro-

Table 1
Product distribution (%) in relation to pulse number of HFC-134 employed [a]

Products	Pulse number				
	1	2	4	8	16
CHF_2–CHF_2		0.05	8	18	36
CH_2F-CF_3	0.1	13	79	78	62
CH_2Cl-CF_3	0.04	62	13	3	0.7
$CHCl_2$-CHF_2 + CH_2Cl-$CClF_2$		0.1			
$CHF{=}CF_2$		0.08	0.5	0.5	0.5
$CHCl{=}CF_2$	0.4	0.7	0.05	0.04	0.05
$CHCl{=}CFCl$ + $CHF{=}CCl_2$	0.8	3	0.07		
$CHCl{=}CCl_2$	99	21	0.07		

[a] Catalyst: Chlorine conditioned with CCl_2F_2.

gen halides could be detected in the carrier gas. The conditioned chromia catalyst was then pulsed with HFC-134. Whereas in the case of the exclusively fluorinated catalyst (HFC-134 conditioned) only HFC-134 and 134a and the intermediate compounds $CHF{=}CF_2$ and HF were observed, on CFC-12 conditioned chromia a wide range of additional new products suddenly appeared. Table 1 lists the main products which could be clearly identified by GC–MS methods. Because not all of these were accessible, the necessary correction coefficients could not be determined precisely, thus making a quantitative determination impossible. Consequently, only the changes in the relative peak areas of all compounds are listed, indicating the general development with every new pulse of HFC-134 semi-quantitatively.

The general conclusion to be drawn from the development of the relative concentrations shown in Table 1 is that there is obviously a certain amount of very exchange-active chlorine on the surface, causing the formation of several chlorinated products. Consequently, chlorinated products are major components of the reaction mixture during the first few pulses but these products decrease rapidly with increasing pulses of HFC-134. Obviously, the mobile, exchange-active chlorine on the surface results in a different product distribution due to the formation of chlorinated products. On removing this mobile chlorine from the solid, the pure isomerization reaction becomes more and more dominant, as can be seen from the strong increase in the HFC-134, HFC-134a and TCE concentrations. After about 20 pulses of HFC-134 all the mobile chlorine had clearly been removed; this was demonstrated by the complete disappearance of all chlorinated products.

As will be discussed later, the products listed in Table 1 are components of a complex chlorination/fluorination exchange process. Additionally, a series of other compounds were also formed, mostly in trace quantities only, which disappeared after the first pulse used: these were CF_4, CHF_3, CH_2F_2, $CHCl_2F$, C_2HF_5, C_2ClF_5, $C_2HCl_2F_3$, C_2HCl_3, cycle-C_4F_8, HCOOH and CH_3COOH. These compounds do not belong to the general exchange processes. They are either oxidation products of certain major products due to the possible presence of chromium in higher oxidation states as reported by Brunet et al. [16], or indicators of some minor radical reactions. In all cases, these minor products were only detectable during the first or second HFC-134 pulse.

In order to obtain more information about the kind of exchange-active chlorine on the surface, electron microscopy measurements were performed. Fig. 1 depicts typical backscattering electron micrographs, showing part of an α-Cr_2O_3 surface conditioned with CFC-12 [Fig. 1(a)]. The same section of surface is shown in Fig. 1(b) which indicates the distribution of chlorine on the surface. The white areas represent the chlorine distribution due to emitted Cl Kα radiation. Apparently, the chlorine is not incorporated continuously but accumulates on to the probably inhomogeneously distributed acid sites on the surface; the chlorine content in the white areas is about double that in the other parts.

In order to distinguish between organic chlorine (in halocarbons) found in case of Winfield's *deep purple room temperature catalyst* [9,10,17] and inorganic chlorine (metal chlorides or hydrogen chloride), the concentration of the

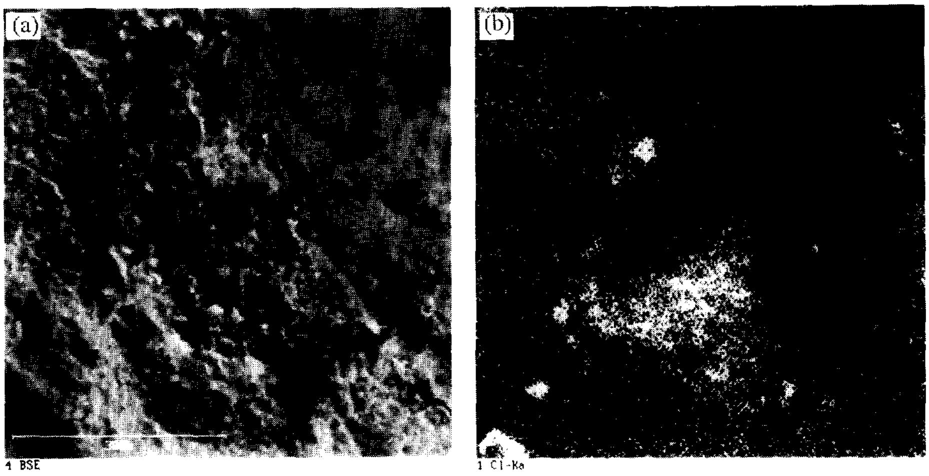


Fig. 1. Back-scattering electron micrograph of a chromia surface (a) activated with CFC-12 and (b) showing the Cl distribution on the surface (white areas originated due to Cl Kα radiation).

overall chlorine content and the carbon content of the treated chromia catalyst were measured. Three different samples were selected representing the general conditions on the surface of the conditioned chromia (cf. Figs. 2 and 3). Sample 1 represents chromia conditioned with CFC-12; sample 2 represents chromia initially conditioned with HFC-134 but then followed by treatment with CFC-12; and sample 3 is the same as sample 1 but immediately pulsed with HFC-134 according to the procedure described previously, where a reaction between the solid surface and HFC-134 clearly occurs. In all cases the samples were held in the pulse reactor at 400 °C in a continuous nitrogen gas flow (absence of haloalkanes) until no desorption of any previous reaction gases could be observed. The corresponding chlorine and carbon concentrations, respectively, are depicted as (a). These samples were then evacuated at 400 °C until the Cl and C contents, respectively, remained constant indicating removal of volatile compounds such as HCl or halocarbons [shown as (b)]. The last columns [marked as (c)] represent the Cl or C contents, respectively, after the catalyst surfaces had been treated with pulses of oxygen in order to remove any coke which might be deposited on the surface.

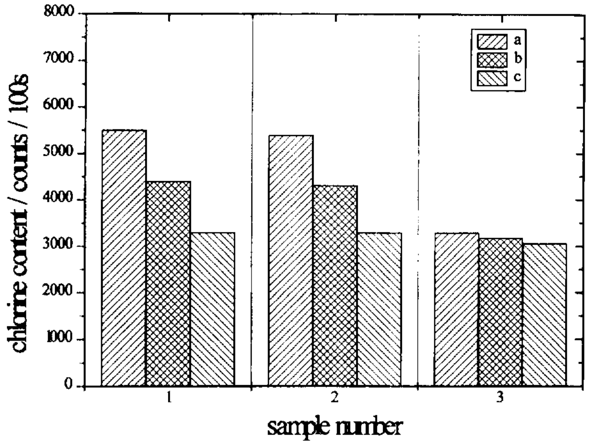


Fig. 2. Chlorine content on the chromia surface under different conditions. Sample 1: chromia conditioned with CFC-12; sample 2: chromia initially conditioned with HFC-134 and then treated with CFC-12; sample 3: chromia conditioned with CFC-12 and then treated with HFC-134. The histograms correspond to (a) the original samples; (b) samples a following evacuation at 400 °C; and (c) samples a following treatment with O_2.

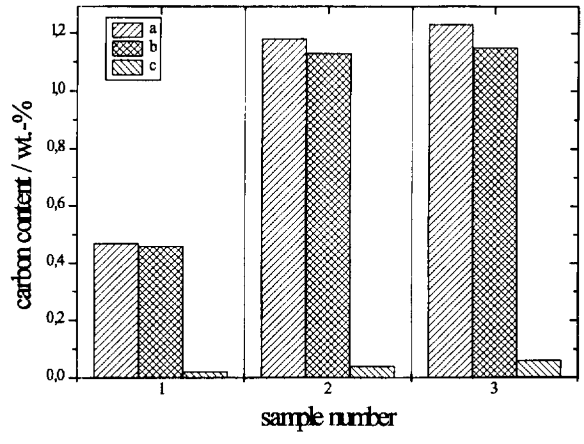


Fig. 3. Carbon content on the chromia surface under different conditions. Sample 1: chromia conditioned with CFC-12; sample 2: chromia conditioned with HFC-134 and then treated with CFC-12; sample 3: chromia conditioned with CFC-12 and then treated with HFC-134. The histograms correspond to (a) original samples; (b) samples a following evacuation at 400 °C; and (c) samples a following treatment with O_2.

As can be seen from Fig. 2, regardless of whether CFC-12 or HFC-134 followed by treatment with CFC-12 was used for the conditioning process, exactly the same chlorine content occurred on the surface of both samples. This can be regarded as further proof that the same halide content and nearly the same surface conditions can be produced by employing different halocarbons for conditioning. On evacuating both these samples at 400 °C, a clear reduction of the chlorine content on the chromia surface can be observed. Only a very small amount of chlorine could not be removed under these conditions. In order to distinguish between organic and inorganic chlorine, the changes in carbon content must be observed under the same conditions (cf. Fig. 3). As is to be expected, in the case of the CFC-12 conditioned chromia there was much less carbon deposited on the surface than in the case of the HFC-134 conditioned chromia, probably due to the higher tendency of HFC-134 towards coke formation. However, in both cases, there was some release of carbon when the samples were evacuated at 400 °C. If these results are compared with the release of chlorine, it seems clear that most of the chlorine liberated was of inorganic nature (adsorbed HCl). If sample 3 is now included in these considerations, only very small decreases in both the chlorine and carbon contents are found. But it can be clearly seen from Fig. 2 that the chloride content was nearly constant in all three cases regardless of the treatment employed and was exactly on the same absolute level as both the other samples are after the mobile chlorine had been removed from the surface.

The explanation is that, in terms of the reactions of HFC-134 with the conditioned chromia catalyst as briefly discussed previously, the whole mobile, exchange-active chlorine undergoes halogen-exchange reaction to leave a residue of deposited, inactive chlorine. A further characteristic of the nature of this inactive chlorine, whether derived from a metal chloride or chlorine of a kind associated with oligomeric organic material (pre-stage of coke), becomes apparent when oxygen post-treatment is used (cf. Figs. 2 and 3, values depicted as c). It is known that oxygen can remove coke from a solid surface at a certain temperature. In all cases, nearly the whole carbon content was removed from the surface up to the level of the untreated chromia, whereas the chlorine content appeared to be unaffected by oxygen post-treatment. This means the rest of the non-reactive chlorine deposited on the chromia catalyst apparently mainly consists of non-volatile inorganic chloride, a type of chromium chloride which is not detectable by XRD due to its very small amount or amorphous nature. However, this chloride can also be removed as result of the normal solid–gas reaction when the latter is conducted over lengthy time periods.

Consequently, we must conclude that in the case of sample 3 both the other post-treatments (evacuation or oxygen pulsing) have no influence on the chloride content because all mobile chlorine has already been removed chemically by reaction with HFC-134. The fact that the carbon contents of sample 3 and sample 2 are equal and remain constant even after evacuating can also be explained in a similar manner.

The conclusions, which can be drawn from these results are:

(i) there is a certain amount of mobile chlorine, strongly adsorbed or exchangeable, deposited on the solid surface and (ii) the mobile chlorine is mainly of an inorganic nature (adsorbed HCl and/or active Cr–Cl type).

In order to obtain direct evidence about the chemical composition of the mobile chlorine on the surface, chromia catalysts conditioned with CFC-12 were adjusted to 400 °C and left in a continuous nitrogen flow until no desorption products could be detected. These samples were then evacuated at the same temperature and the liberated gas phase was transferred directly into a mass spectrometer. In all cases only H_2O, HF, HCl and CO_2 were found as desorbed compounds. Although, the rate of fluorination was higher in the case of alumina, this is mainly in accord with the results of Winfield et al. [9,10], who also found two kinds of surface chlorine using ^{36}Cl tracer experiments on γ-alumina conditioned with CCl_4: chlorine produced as a result of the direct chlorination of the solid by CCl_4 and $COCl_2$, and chlorine which was exchange-active and which they concluded was, in fact, hydrogen chloride (originating as a byproduct from the same reaction). Since we employed CCl_2F_2 in our work, we did not find chloro- or fluoro-phosgene but it seems clear that similar relations occur in the system investigated here.

As shown previously, only oxygen post-treatment of the catalysts effects complete removal of the carbon and mobile chlorine deposited on the surface. For this reason the compounds liberated as a result of oxygen treatment were also detected using GC–MS coupling. Again a CFC-12 conditioned catalyst was treated with one pulse of oxygen (2 ml_{stp}) at 400 °C and the gas flow was then separated and identified by GC–MS methods. In addition to hydrogen halides, the gases detected were CO_2 (reaction product of coke and O_2) and the dismutation products of CFC-12 (CCl_4, CCl_3F, CCl_2F_2, $CClF_3$). At the second oxygen pulse, only mere traces of the latter were detectable and these disappeared completely with the third pulse, indicating that in fact only traces, but still detectable amounts, of these halocarbons were adsorbed. However, to the best of our knowledge, this is the first time that the adsorption of halocarbons under such extreme conditions ($T = 400$ °C) has been demonstrated unambiguously because of the use of a very sensitive technique. Even after evacuating a conditioned chromia catalyst, traces of desorbed halocarbons could be found as a result of oxygen treatment during the first pulse.

3.2. Halogen exchange between the gas phase and the mobile chlorine on the chromia surface

In order to evaluate the reactions occurring between the gas phase components and the mobile chlorine on the chromia surface, an active chromia catalyst, conditioned with HFC-134 and catalyzing exclusively the pure isomerization reaction of HFC-134, was treated with one pulse of HCl (2 ml). Then, HFC-134 was again pulsed over the now HCl-loaded catalyst. The resulting ion chromatogram is presented in Fig. 4(b). A comparison with the ion chromatogram obtained from passing a pulse of HFC-134 over chromia firstly conditioned with CFC-12 [Fig. 4(a)], reveals an identical product distribution for both. Apparently the manner in which the chromia catalyst is treated with chlorine/fluorine compounds is not significant. Ultimately, the conditioning process results in the same active state. This provides additional proof that in all cases conditioning with chlorofluorocarbons results in HCl being formed which is strongly adsorbed on the surface and which plays the role of the mobile chlorinating agent. Clearly, the adsorbed HCl is capable of undergoing catalyzed halogen-exchange reactions with a series of different aliphatic and olefinic fluorocarbons.

Our main goal was to establish the reaction processes in this complex reaction system. In principle, two possible reaction mechanisms could result in the observed product spectrum. In Scheme 1, after the first dehydrofluorination step which occurs during the ordinary isomerization reaction of HFC-134 to HFC-134a [15], starting from the three reactants CHF_2-CHF_2, $CHF{=}CF_2$ and CH_2F-CF_3, the chlorinated products observed in the reaction mixture may be mainly explained by consecutive substitution reactions (fluorine/chlorine exchange) with HCl. However, as can be seen in Scheme 1, not all the possible products could be detected. Either they were not formed or they were very reactive intermediates which reacted immediately to form more stable products. What is unsatisfactory is that the formation of $CHF{=}CCl_2$ determined in the product mixture cannot be explained by just discussing such a substitution reaction process.

In Scheme 2, the compounds given are those to be expected if only dehydrohalogenation/hydrohalogenation reactions (elimination/addition mechanism) are considered. If both hydrohalogenation according to the Markovnikov rule as well as hydrohalogenation according to the anti-Markovnikov rule are considered, the same compounds can be expected but also some additional isomers, as in Scheme 1. Again not all the possible products of such an elimination/addition mechanism could be detected, but the formation of the isomer $CHCl{=}CClF$ can now be explained.

However, the formation of all products detected in the experiment can be more or less explained according to two different mechanistic pathways. In principle, it should be possible to differentiate between both reaction pathways by employing deuterium chloride (DCl) as the chlorinating agent. A D-for-H exchange occurs to a very small extent on

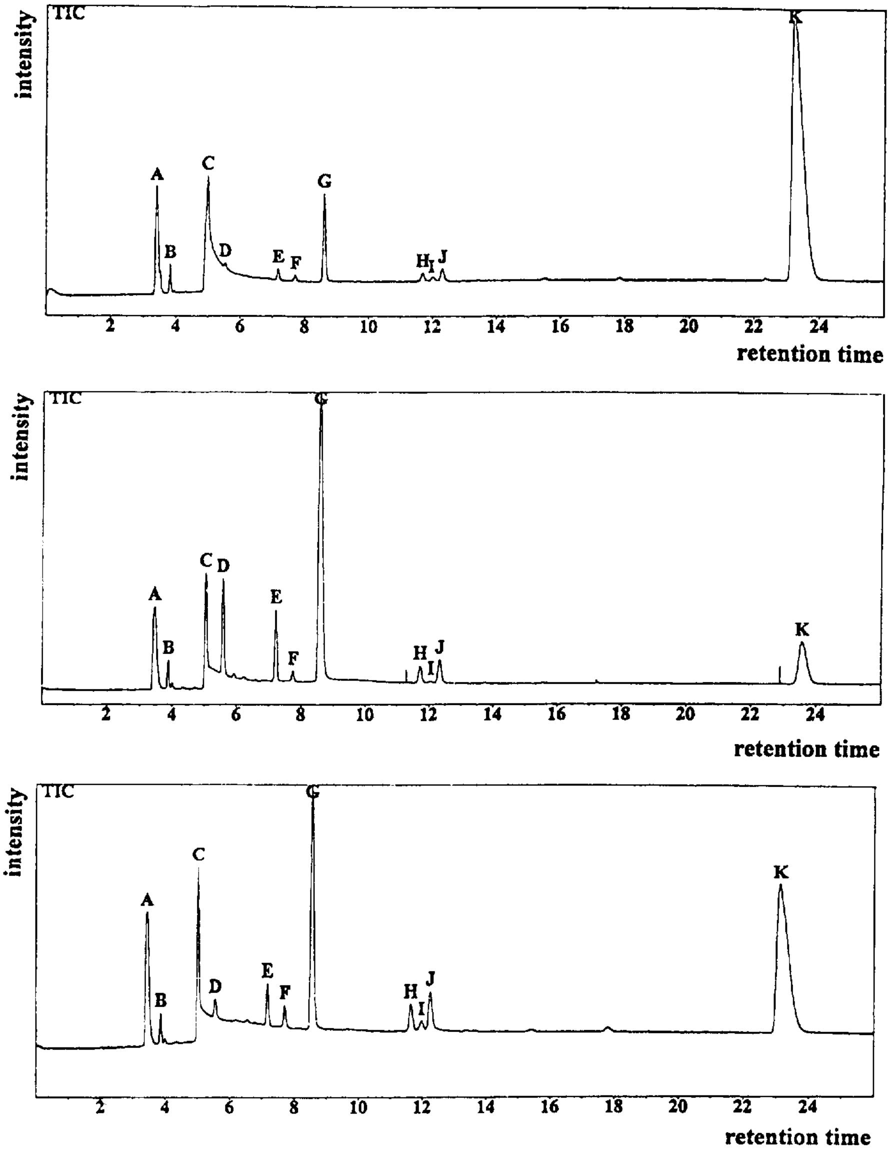
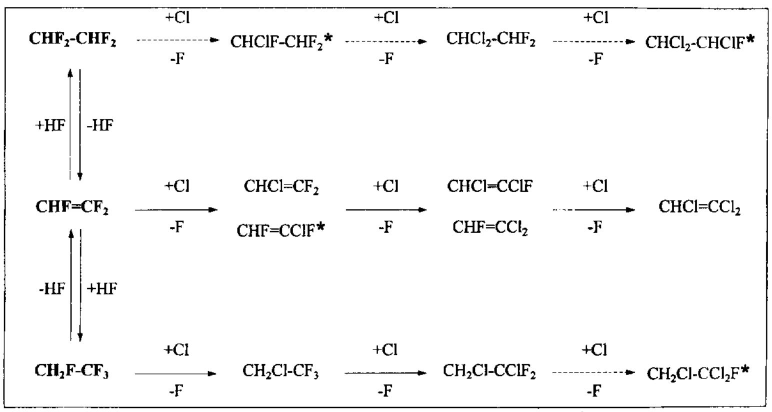
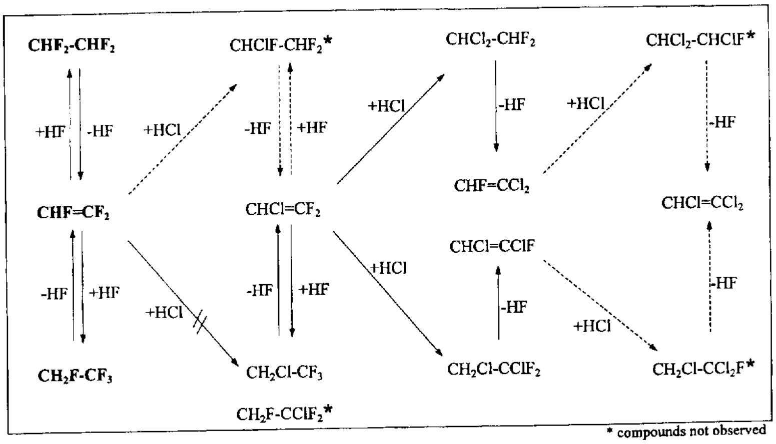


Fig. 4. Ion chromatogram of desorbed products resulting from a pulse of HFC-134. Top: a pulse of HFC-134 over chromia conditioned with CFC-12; middle: a pulse of HFC-134 over chromia conditioned with HFC-134 and then loaded with one pulse of HCl; bottom: same procedure as for the middle diagram, but DCl used instead of HCl. The products identified are indicated as follows: **A**, N_2; **B**, CO_2; **C**, $H_2O/CHF_2{-}CF_3$; **D**, $CH_2F{-}CF_3$; **E**, $CHCl{=}CF_2/CDCl{=}CF_2$; **F**, $CHCl_2F/CDCl_2F$; **G**, $CH_2Cl{-}CF_3/CDHl{-}CF_3/CD_2Cl{-}CF_3$; **H**, C_2HCl_2F/C_2DCl_2F; **I**, $CHCl_2{-}CF_3/CDCl_2{-}CF_3$; **J**, C_2HCl_2F/C_2DCl_2F; and **K**, $CHCl{=}CCl_2/CDCl{=}CCl_2$.



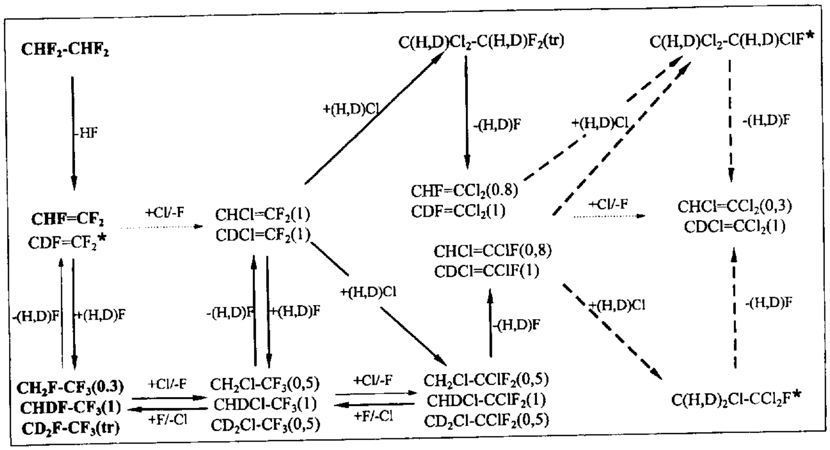
* compounds not observed

Scheme 1. Direct fluorine/chlorine exchange mechanism over chromia catalyst containing adsorbed HCl (broken lines: unresolved reaction pathways).



* compounds not observed

Scheme 2. Elimination/addition mechanism over chromia catalyst containing adsorbed HCl (broken lines: unresolved reaction pathways).



* compounds not observed

Scheme 3. Reaction pathways for the isomerization of HFC-134 and consecutive side-reactions with adsorbed deuterium chloride over chromia catalyst {reaction pathways: proven (solid line); probable, but unresolved (broken line); less probable (dotted line)}.

fresh chromia surfaces via surface hydroxy groups but becomes unimportant after a certain extent of fluorination of the chromia surface due to the removal of these hydroxy groups as demonstrated by Kijowski et al. [18]. Hence, a D-for-H exchange can most probably be excluded under the conditions used, which is also in agreement with the results of Kavanagh et al. [3] who employed deuterohalides for mechanistic investigations of the synthesis of HCFC-133a starting with trichloroethylene. Therefore, the experimental results only lead to the conclusion of halogen-exchange reactions. If only these halogen-exchange reactions occur, all the compounds generated should only contain hydrogen rather than deuterium; if elimination/addition reactions are dominant, deuterium should also be incorporated into the organic compounds.

For this reason, we repeated the procedure mentioned above, but replaced HCl by DCl. The resulting ion chromatogram is given in Fig. 4(c) and clearly shows the same product distribution as obtained in the case of Fig. 4(a) and 4(b). However, the advantage now is the appearance of a wide range of deuterated products. Recognizing the qualitative and especially quantitative (H-to-D ratio) distribution of these deuterated products, it is now possible to obtain a deeper understanding of the real processes occurring in this complex reaction system. In Scheme 3, those reaction pathways are given which we now believe to be responsible for the formation of all the products observed. In this scheme we differentiate between three levels of probability: those reactions which we are sure will occur (unbroken line); those which will probably occur (broken lines); and those which are unlikely to occur (dotted lines). Special attention is paid to the H-to-D ratio in the compounds as this sometimes allows a prediction of the different routes possible for the formation of a given product. Thus, for all compounds the content of deuterium or hydrogen is given in brackets as values relative to the content of the major product being expressed as unity. This information can also be taken from the ion chromatograms.

As can be seen in Scheme 3, the initial reaction is the dehydrofluorination of HFC-134, to form TCE and HF as intermediates as has already been described in Ref. [15]. HF can react with TCE according the Markovnikov rule, forming

HFC-134a. Most probably and parallel to this, HF undergoes a halogen exchange with DCl forming DF and HCl. Consequently, the following hydrogen halides must be considered in the reaction system: HF, DF, HCl and DCl. The use of HFC-134 allows HF to be eliminated but no other kind of halogen exchange occurs (mono-chlorinated products are missing). The formation of deuterated representatives of HFC-134a can be explained either by the deuterofluorination of TFE (addition of DF) or by the fluorination (Cl/F exchange) of $C(H,D)_2Cl–CF_3$, which is itself formed by the deuterofluorination of $C(H,D)Cl{=}CF_2$. The latter olefin can be formed by the chlorination of TFE. In principle, however, this reaction cycle can proceed in the opposite direction. Even the D/H ratio does not allow a clear distinction to be drawn between both processes. But from former investigations of the catalyzed synthesis of HFC-134 [4] there is clear evidence that the fluorine/chlorine exchange reaction of TFE [forming $C(H,D)Cl{=}CF_2$] is a minor reaction. An additional argument is that deuterated TFE was never observed. Since a very higher reactivity for $CDF{=}CF_2$ may be assumed in comparison to $CHF{=}CF_2$, the presence of virtually equal amounts of $CHCl{=}CF_2$ and $CDCl{=}CF_2$ can only be explained through their formation via HFC-133a.

It is conspicuous that the asymmetric isomers of HCFC-132 are major components. This can be explained both by the (H,D)Cl addition mechanism according to the Markovnikov rule [starting from $C(H,D)Cl{=}CF_2$] and also by a fluorine/chlorine exchange reaction starting from HCFC-133a. However, the hydrogen/deuterium ratio observed in HFC-132a can originate in both cases from the starting compounds, making a definite decision between both impossible. Moreover, in terms of the concentrations of the isomers of HCFC-132 observed in practice, one would conclude that reaction according to the Markovnikov rule is dominant for the (H,D)F addition of $C(H,D)Cl{=}CF_2$ or the exchange reaction of HCFC-133a, respectively. However, as the concentrations of the possible isomers of the olefin $C_2(H,D)Cl_2F$ are of the same concentration, both reaction processes, i.e. Markovnikov and anti-Markovnikov, have to be accorded the same significance. Morever, it is somewhat surprising that the H/D ratio decreases from 1 in all isomers of HCFC-132 to 0.8 in the case of both isomers of dichloromonofluoroethylene. In an ordinary F/Cl exchange between $C(H,D)Cl{=}CF_2$ and (H,D)Cl, this ratio would remain constant as well as in the elimination reactions of HCFC-132. However, in the latter case it is possible that HF elimination dominates slightly over DF elimination due to the kinetic isotope effect. Consequently, the formation of the stable end-product of this reaction scheme, TCE, cannot arise from an ordinary fluorine/chlorine exchange because of the further remarkable change in the H/D ratio. As this ratio decreases from 0.8 in the case of dichloromonofluoroethylene to 0.3 in the case of TCE, again the only plausible explanation is (H,D)Cl addition to the olefin to form HCFC-131. The latter is known to be extremely unstable in the presence of a suitable catalyst [4] and cannot therefore be detected in the product mixture. Consequently, the unstable intermediate undergoes a very fast (H,D)F elimination forming the stable end-product, TCE. Again, the only explanation for the decrease in the H/D ratio is the kinetic isotope effect favouring the elimination of HF.

4. Conclusions

The industrially desirable HFC-134a can be obtained from the symmetric isomer HFC-134 in the presence of a chromia catalyst conditioned exclusively with chlorine-free fluorocarbons. In the presence of chlorofluorocarbons hydrogen, chloride as well as hydrogen fluoride (not of direct interest in the present) would be formed and strongly adsorbed on to the surface. In contrast to hydrogen fluoride, HCl seems to give rise to a very complex system of side-reactions. However, in all cases, trihalogeno–ethylenes and tetrahalogeno–ethanes, respectively, were found exclusivelly, i.e. the same general product distribution as in pure HFC-134 isomerization. Probably, HF acts in a similar manner as found for HCl, the advantage by employing HCl or DCl, respectively, being at least that different chlorinated derivatives are detectable. In case of exclusively fluorinated compounds this differentiation is impossible unless ^{18}F-labelled HF is used.

By employing pulse techniques in combination with deuterium isotopes, it is possible to readily resolve this complex reaction pattern of side-reactions. As the HCl adsorbed on the surface is very quickly removed via these reactions, it is advantageous to use pulse techniques to evaluate the reaction processes which take place. These processes occur during the first few seconds of reaction and cannot therefore be recorded using an ordinary continuous gas flow regime. As mentioned at the very beginning, it is desirable to produce HFC-134a by dehydrohalogenating CFC-113a. In principle, it is also possible to start from CFC-113 and isomerize the hydrogenated product, HFC-134, later. As our results reveal, in this case chlorine-free catalysts have to be used in order to avoid all the side-reactions discussed in this paper.

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References

[1] L.E. Manzer and V.N.M. Rao, *Adv. Catal., 39* (1993) 329.
[2] V.N.M. Rao, in R.E. Banks et al. (eds.), *Organofluorine Chemistry: Principles and Commercial Applications*, Plenum Press, New York, 1994, p. 159.

[3] D.M.C. Kavanagh, T.A. Ryan and B. Myle, *J. Fluorine Chem., 64* (1993) 167.
[4] A. Kohne and E. Kemnitz, *J. Fluorine Chem., 75* (1995) 103.
[5] D. Bechadergue, M. Blanchard and P. Canesson, *Appl. Catal., 20* (1986) 179.
[6] M. Blanchard, L. Wendlinger and P. Canesson, *Appl. Catal., 59* (1990) 123.
[7] L. Rowley, J. Thomson, G. Webb, J.M. Winfield and A. McCulloch, *Appl. Catal., 79* (1991) 89.
[8] E. Kemnitz, A. Kohne, I. Grohmann, A. Lippitz and W.E.S. Unger, *J. Catal., 159* (1966) 270.
[9] J. Thomson, G. Webb and J.M. Winfield, *J. Mol. Catal., 67* (1991) 117.
[10] J. Thomson, G. Webb and J.M. Winfield, *J. Mol. Catal., 68* (1991) 347.
[11] L.E. Manzer and V.N.M. Rao, US Pat. 4 902 838, 1990.
[12] G.J. Moore and H.M. Massey, Eur. Pat. 365 296, 1990.
[13] G.P. Khara, US Pat. 5 039 639, 1991.
[14] S. Okazaki, M. Ogura and Y. Mochizuki, Eur. Pat. 450 467, 1991.
[15] E. Kemnitz and K.-U. Niedersen, *J. Catal., 155* (1995) 283.
[16] S. Brunet, B. Requieme, E. Matouba, J. Barrault and M. Blanchard, *J. Catal., 152* (1995) 70.
[17] F. McMonagle, R. Marshall and J.M. Winfield, *11th. Eur. Symp. Fluorine Chem.*, Bled/Slovenia, Sept. 1995, Abs. p. 88.
[18] J. Kijowski, G. Webb and J.M. Winfield, *Appl. Catal., 27* (1986) 181.