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Isomerization Reactions of 1,1,2,2-Tetrafluoroethane: A Kinetic and Mechanistic Study

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Kinetic and mechanistic studies of the isomerization reactions of 1,1,2,2-tetrafluoroethane to 1,1,1,2-tetrafluoroethane on conditioned chromia were carried out. In contact with the surface of the solid 1,1,2,2-tetrafluoroethane undergoes a separation of HF, forming noticeable amounts of the olefin trifluoroethylene. Due to rearrangement of the adsorbed gas molecules in the surface, HF is re-added, forming 1,1,1,2-tetrafluoroethane according to the Markovnikov rule.

$$CHF_2—CHF_2 \rightleftharpoons CHF{=}CF_2 + HF$$
$$CHF{=}CF_2 + HF \rightleftharpoons CH_2F—CF_3$$

A mathematical adjustment was carried out in order to describe the reaction mechanism. Modelling of the isomerization reaction suggests that the best agreement between the experimental and the calculated data can be achieved when the decomposition of CHF_2–CHF_2 to HF and $CHF{=}CF_2$ is considered to be reversible. The experimentally determined values of rate constants indicate a significant influence of the adsorption equilibria on these reactions. © 1995 Academic Press, Inc.

INTRODUCTION

The enormous ozone depletion potential (ODP) of chlorofluorocarbons (CFCs), in addition to their global warming potential (GWP), has led to very strict regulations regarding their replacement. As alternatives, two different compound classes have been discussed: these are hydrochlorofluorocarbons (HCFCs), which have only low ODP/GWP values and hydrofluorocarbons (HFCs) which have no ODP and only low GWP values due to the absence of chlorine and the presence of hydrogen in the molecule. In the long term only the HFCs are of principal interest and technical importance. The synthesis of all these compounds results from a heterogeneous catalyzed fluorine/chlorine exchange between chlorinated hydrocarbons and gaseous HF. Oxides and fluorides of aluminium and chromium, respectively, are mainly used as catalysts (1–5). The fluorination reactions with HF are accompanied by other halogen exchange reactions caused by the same catalyst, namely, dismutation reactions, isomerization reactions, and dehydrohalogenation reactions. Depending on the reaction conditions, these different reactions can occur as competitive processes which may greatly influence the selectivity. Though these phenomena have been well known for many years (6–8), knowledge about the processes and their dependence on the reaction conditions is unsatisfactory. However, it seems to be clear that dismutation, isomerization, and dehydrohalogenation processes take place particularly in the absence of HF.

Most work regarding isomerization reactions has been carried out in the $C_2Cl_{6-n}F_n$ series, with $n = 0$ to 6. The first results were published by Kolditz *et al.* (9) and Paleta *et al.* (10). They found correlations between thermodynamic data and observed isomerization equations depending on the different catalysts employed. According to the mechanism proposed by Kolditz *et al.*, isomerization takes place as an intramolecular chlorine/fluorine exchange in a CFC molecule adsorbed on the catalyst surface. Bechadergue *et al.* carried out kinetic measurements in the same CFC series (11), as well as investigations regarding the isomerization activity of several solid catalysts (12).

In the last few years Webb, Winfield, and co-workers (13–15) have made important contributions to the isomerization mechanisms of the $C_2Cl_{6-n}F_n$ series by employing radio-tracer techniques. Thus, they found that fluorination reactions with HF and isomerization reactions take place at different sites on the surface of the catalyst. Furthermore, it seems that isomerization proceeds according to a concerted intramolecular mechanism (15).

One of the most important CFC alternatives is HFC 134a (CH_2FCF_3), which can be considered part of the $C_2H_2Cl_{4-n}F_n$ series (with n = 0–4). The synthesis of HFC 134a results from the hydrofluorination of trichloroethylene and the dehydrochlorination of CFC 114a, respectively, in the presence of suitable hydrogenation catalysts. As has already been shown in the $C_2Cl_{6-n}F_n$ series, in the $C_2H_2Cl_{4-n}F_n$ series HFC 134a can also be pro-

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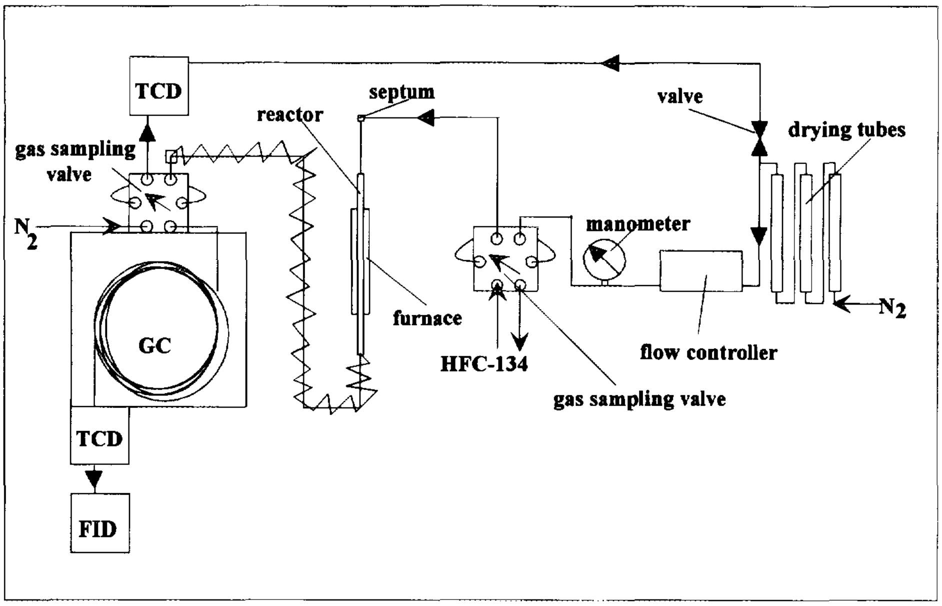

FIG. 1. Scheme of apparatus used for the pulse method.

duced through the isomerization of HFC 134 (CHF_2–CHF_2).

In contrast to the perhalogenated compounds of the $C_2Cl_{6-n}F_n$ series the HFCs are subject to dehydrohalogenation reactions which complicate the reaction process.

Due to the technical importance of HFC 134a as well as the hitherto uninvestigated isomerization reactions in this system, we have focused our interest on this problem. The first results of kinetic and mechanistic investigations will be reported in this paper.

EXPERIMENTAL

The kinetic investigations of isomerization reactions were carried out by employing a special pulse technique. The main features of the apparatus are shown in Fig. 1. The nitrogen used as carrier gas can be adjusted as necessary by a flow controller. By employing a six-port valve with variable column volume, the amount of HFC 134 can be very precisely measured. An adjusted HFC/N_2 pulse passes through the reactor which contains the catalyst. The reactor is heated using an adjustable furnace. The products thereby formed are transferred to a second six-port valve via heated gas lines. This six-port valve is equipped with an external heat conducting detector, which indicates the presence of the product gas and enables its extremely accurate injection into the GC. The 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 made of copper, while the reactor was made of nickel.

Chromia employed as model catalyst was synthesized by heating ammonium dichromate. The powder obtained was pressed into pellets, cut, and subdivided into grain fractions of 300 to 500 μm. The surface area of the catalyst was 48 m^2/g and the bulk density 1.24 g/ml. All experiments were carried out using the same amount of catalyst, namely, 760 mg. The surface area of the catalysts used varied during reaction from 48 to 39 m^2/g depending on the conditions (chemical modification of the surface).

The conditioning of the chromia catalyst used was carried out in all cases with pulses of HFC 134; the temperature was 693 K, the contact time was 16.8 s.

The HFC 134 employed was a product of Heräus. For comparative measurements the following compounds were used: HFC 134a (Hoechst), trifluoroethylene (TFE) synthesized by the debromination of 1,2 dibromo-1,1,2-trifluoroethane (Hoechst), and HF (Merck). Gas product analysis was carried out by employing capillary gas chromatography as well as GC/MS coupling and GC/FTIR technique.

The RD of the kinetic measurements were within the range of ±3%, in all cases.

RESULTS

The Conditioning of Chromia by Reaction with CHF_2–CHF_2

It is known from the investigations of other authors (10–15) that CFCs halogenate with chromia in a first reaction step and that chlorides and fluorides of chromium are formed. This so-called conditioning leads to a catalyst surface with a nearly constant halogen content and catalytic activity. Our own investigations reveal that during the conditioning reactions with representatives of the $C_2H_2Cl_{4-n}F_n$ series a catalytic phase is formed in the surface which can be considered to be very similar to β-CrF_3 (16). This has been concluded from XPS measurements (17, 18) combined with catalytic characterization on Cr_2O_3, CrF_2OH, β-CrF_3, and α-CrF_3 which clearly show that β-CrF_3 is the only phase immediately active. Chromia as well as chromium hydroxyfluoride undergoes a fluorination in the surface resulting finally in a catalytically active phase, whereas α-CrF_3 is in all cases catalytically inactive. Additionally, there are always small amounts of chloride in the surface. This chloride is extremely mobile and reactive, causing chlorinating reactions of the gas phase in addition to the isomerization reactions of HFC 134, if such a conditioned catalyst is employed. For this reason the conditioning was exclusively carried out using HFC 134 under the same conditions as the isomerization reaction. Figure 2 shows the typical dependence of the conversion degree of HFC 134 to HFC 134a on the given pulse number. In the first stage the catalytic activity increases with increasing pulse number due to the conditioning of the surface area. After maintaining a stable maximum, the catalytic activity decreases again.

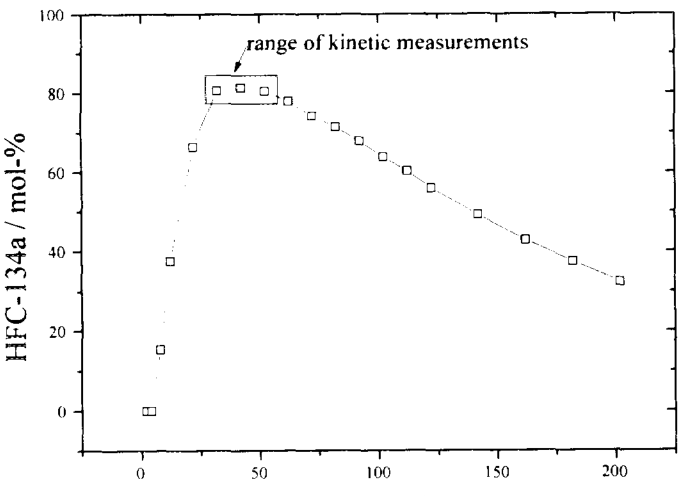

FIG. 2. Concentration of HFC 134a in the organic gas phase depending on the pulse number (temperature, 693 K; educt, HFC 134; pulse volume, 0.5 ml/stp., contact time, 16.8 s).

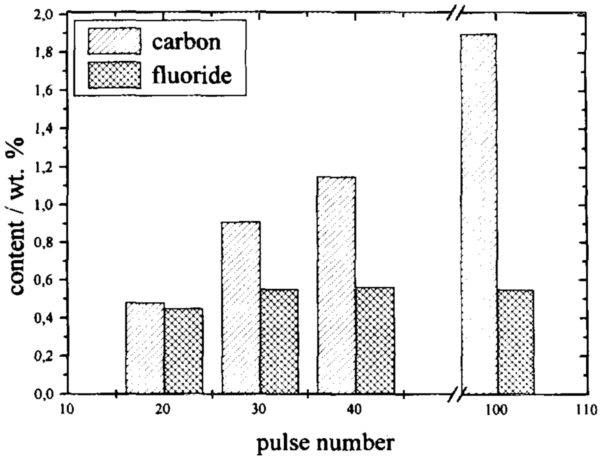

FIG. 3. Carbon and fluoride content in the solid phase depending on the pulse number (temperature, 693 K; educt, HFC 134; pulse volume, 0.5 ml/stp; contact time, 16.8 s).

This behaviour is caused by different processes. At first, as a result of the heterogeneous reaction between the oxide and the haloalkane, chromium fluoride is formed, shown by the increasing fluoride content of the solid (cf. Fig. 3). At the same time gaseous by-products such as CO, CO_2, and HF can be observed. These reactions occur relatively fast, leading to the stage of highest activity of the catalyst used. Obviously the active sites in the surface not only catalyze isomerization reactions but also cause the partial destruction of HFC 134, forming coke (increasing carbon content in Fig. 3). These reactions probably occur on sites which are responsible for isomerization: the formation of coke covers these sites and therefore the isomerization activity decreases (cf. Fig. 2).

As can be seen from Fig. 2, after about 30 pulses the stage of highest activity is reached. This is accompanied by a stable amount of fluoride in the solid as the heterogeneous reaction between the gas phase and the solid is nearly finished. All the kinetic measurements described in the following were carried out for this reason in the plateau stage of the conversion/pulse number diagram of Fig. 2. After 50 pulses at the most, the measurements were stopped and a new catalyst was employed and conditioned before starting the measurements again.

The Isomerization of HFC 134 on Conditioned Chromia

The isomerization equilibrium between HFC 134 and HFC 134a is shown by

$$CHF_2{-}CHF_2 \rightleftharpoons CH_2F{-}CF_3, \quad \Delta_R G^0 = -9.8 \text{ kJ mol}^{-1}. \qquad [1]$$

(The calculation of the free molar standard formation enthalpies was carried out semiempirically according to the Austin Model 1 AM1 *method* [17]).

Due to the formation of a CF_3 group, the formation of the asymmetric isomer is thermodynamically assisted, but depends kinetically on suitable catalysts.

The isomerization reactions of HFC on activated chromia produced the following experimentally determined products:

$CH_2F{-}CF_3$ (HFC 134a); $CHF{=}CF_2$(TFE) and HF.

(The quantity of HF formed was simply equalised to the amount of TFE gas-chromatographically detected because our own results show clearly, in agreement with Kohne (17), *that the conditioned catalyst keeps an unchangeable fluoride content in the surface. That means no further reaction with the gas phase occurs.)*

This suggests for the reaction pathway of the isomerization a dehydrofluorination of the TFE produced, followed by a hydrofluorination according to the Markovnikov rule. Thus, with TFE and HF as educts, the formation of HFC 134a as major product was clearly proved by experiment. On the other hand, independent on variation of the reaction conditions starting again with TFE and HF as educts, HFC 134 was always only detected in small amounts (Eq. [3]):

$$CHF{=}CF_2 + HF \rightleftharpoons CH_2F{-}CF_3 \qquad [2]$$

$$CHF{=}CF_2 + HF \rightleftharpoons CHF_2{-}CHF_2. \qquad [3]$$

However, the formation of considerable amounts of TFE (up to 38%) and HF from HFC 134a in the presence of a suitable catalyst was clearly proved. For this reason Eq. [2] must be considered, in fact, as a reversible reaction. The production of HFC 134 was also proved analytically, although the amount in all cases was in the region of a few tenths of a percent. Under the concrete reaction conditions, the reaction is therefore pushed very strongly in the direction of the olefin TFE and HF.

In Fig. 4 the kinetic curves of the isomerization reactions of HFC 134 to HFC 134a are presented for different temperatures.

The symbols in the graphs represent the experimentally measured values.

DISCUSSION

According to the experimental results represented by Eqs. [2] and [3], the following model for the reaction pathway for the isomerization of HFC 134 to HFC 134a can be established. In a first reaction step the dehydrofluorination process of HFC 134 occurs, forming TFE as well as HF. The reaction is irreversible and tends completely to the side of the products.

The second step, namely, the formation of HFC 134a according to the Markovnikov rule and dehydrofluorina-

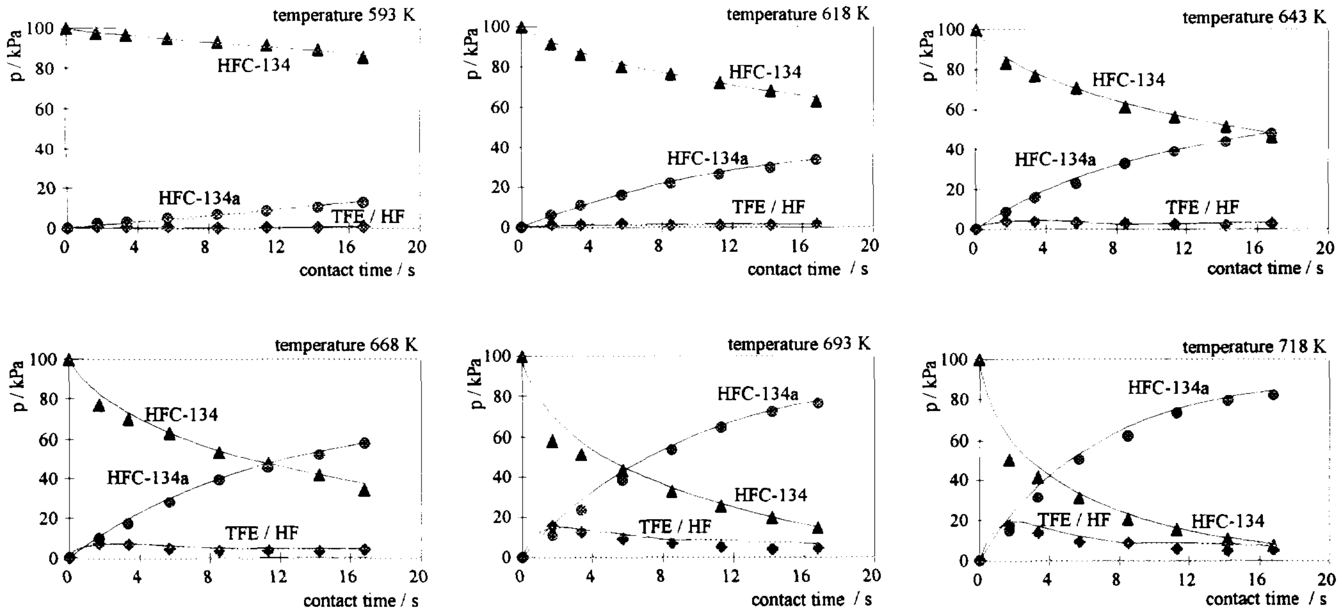

FIG. 4. Product distribution/contact time curves: points, experimental data; lines, fitted, using model 2 (educt, HFC 134; pulse volume, 0.5 ml/stp.).

tion accompanied by the formation of TFE and HF, is a reversible reaction.
Model 1:

$$CHF_2—CHF_2 \rightarrow CHF{=}CF_2 + HF \quad [4]$$

$$CHF{=}CF_2 + HF \rightleftharpoons CH_2F—CF_3. \quad [5]$$

The appearance of the intermediates TFE and HF in notable quantities according to Eq. [4] is clearly to be seen from Fig. 4. The form of the concentration/time curves (maximum of the curves) is also characteristic of the formation of the intermediates.

Through a numeric integration procedure, a differential equation system, such as in model 1, was adjusted to the experimentally determined partial pressure/contact time curves.

The kinetic investigations in the heterogeneous system under consideration are based on the assumption that the adsorption/desorption processes in the catalyst surface have already been established and that the chemical surface reaction determines the rate of reaction. For an irreversible surface reaction of the first order for a compound A one can find

$$A_{ad} \xrightarrow{k_{sr}} B_{ad} \quad [6]$$

$$dp_A/dt = -k_{sr} \cdot a_A, \quad [7]$$

where k_{sr} is the rate constant and a_A is the surface concentration of the gaseous compound A.

Our own investigations prove that the adsorption isotherms of the participating fluorocarbons as well as the hydrogen halides are of the Langmuir type. The measurements were carried out in the starting region of these isotherms, in the so-called Henry law region, which is characterized by low partial pressures as well as high temperatures. For this reason the isotherm equation can be simplified as

$$a_A = a_{max} \cdot K_A \cdot p_a, \quad [8]$$

where a_{max} is the maximum surface concentration of the gaseous compound A and K_A is the equilibrium constant of adsorption.
From Eqs. [7] and [8] it follows that

$$\begin{aligned} dp_A/dt &= -k_{sr} \cdot K_A \cdot a_{max} \cdot p_A \\ &= -k_{exp} \cdot p_A. \end{aligned} \quad [9]$$

The experimentally attainable reaction constant k_{exp} is consequently made up of three different constants.

In Fig. 5 the results of adjustment according to model 1 are given for a temperature of 643 K as an example.

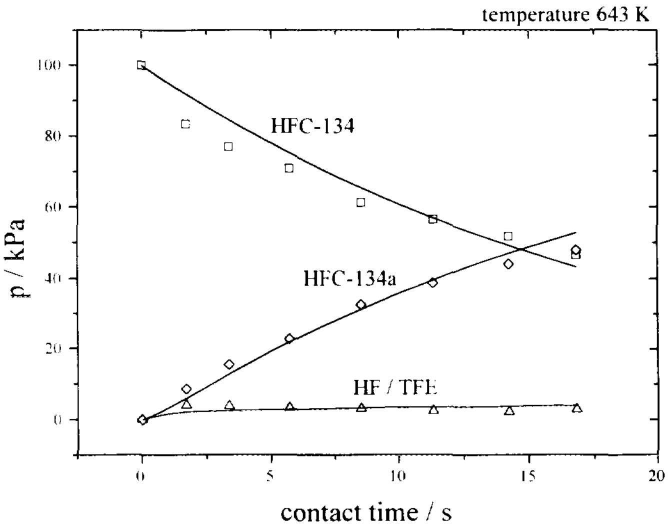

FIG. 5. Product distribution/contact time curves fitted, using model 1 (educt, HFC 134; pulse volume, 0.5 ml/stp.).

The disparity of the experimentally determined data and the curves adjusted according to model 1 is conspicuous throughout the whole reaction range. Consequently, an additional reaction model was drafted into the mathematical adjustment. This model considers the experimentally ambiguous reverse reaction of TFE, forming the symmetric HFC 134 according to Eq. [3].
Model 2:

$$CHF_2—CHF_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CHF{=}CF_2 + HF \quad [10]$$

$$CHF{=}CF_2 + HF \underset{k_4}{\overset{k_3}{\rightleftharpoons}} CH_2F—CF_3. \quad [11]$$

The results of the numeric adjustment according to model 2 have already been represented in Fig. 4 by the solid curves and are in quite better line with the experimentally obtained data. Thus, the course of isomerization of HFC 134 according to model 2 is clearly to be favoured.

The reaction order determined using model 2 as well as the molecularity with regard to HFC equals one.

The numeric integration procedure used contains a parameter to be given as a raster proportional to the residence time. Successive adapted values for k_1 are obtained as a result of the refinement of this raster to infinity, whereas the ratio k_1/k_2 remains constant. The equilibrium according to Eq. [10] is consequently to be considered a momentary one, which is reached very quickly. This means that the consecutive reaction of the intermediates TFE and HF represent the actual rate controlling step. This corresponds to the values determined, since k_3 is one to two powers smaller than k_1. Since k_4 is in turn much smaller than k_3, very high concentrations of HFC 134a are observable. This corresponds completely to the experimental data.

Finally, the rate constants k_1, k_3, and k_4 are consistent with the experimentally obtained concentration/time curves.

Not consistent are the relatively large values of k_2 (same scale as k_1). The k_2 value determines the reformation of symmetric HFC 134 from TFE and HF. Accordingly, considerable amounts of HFC 134 should be produced, whereas very low concentrations of HFC 134 were experimentally determined.

A possible explanation can be given in consideration of the fact that the experimentally observed reaction constant is composed of several partial constants. In accordance with this, the reversible reaction (Eq. [10]) consists of two different equations:

$$\mathrm{CHF_2{-}CHF_2} \rightleftharpoons \{\mathrm{CHF_2{-}CHF_2}\}_{\mathrm{ads}} \qquad [12]$$

$$\{\mathrm{CHF_2{-}CHF_2}\}_{\mathrm{ads}} \rightleftharpoons \{\mathrm{CHF{=}CF_2}\}_{\mathrm{ads}} + \{\mathrm{HF}\}_{\mathrm{ads}}. \qquad [13]$$

Even if only one of these partial reactions is reversible, the integral reaction in Eq. [10] appears to be reversible. This means the reversibility deduced from model 2 could be caused on the one hand by the desorption of unreacted HFC 134 as described in Eq. [12]. On the other hand, a partial reverse reaction corresponding to Eq. [13] cannot be completely excluded: TFE and HF, formed by the dissociation of HFC 134, are situated on the surface *in statu nascendi* in such a way that a recombination is possible if this recombination reaction is fast enough in comparison to consecutive processes. The adsorption of TFE and HF from the gas phase, however, must not necessarily lead to the same surface complex of both molecules. Different positions of TFE and HF are probably formed as a result of the direct adsorption from the gas phase favouring the formation of the asymmetric product. This could explain the only very small amount of symmetric HFC 134 found in the reaction of TFE with HF on the catalyst surface.

In Fig. 6, a hypothetical model based on the experimental data as well as on the mathematical adjustment is given for the mechanism of the isomerization of HFC 134 to HFC 134a.

The adsorptive coupling of a HFC molecule on the surface of the solid polarises the carbon–fluorine bond. The abstraction of the H atom at the second C atom results in the separation of HF and the formation of di- or π-adsorbed TFE, both of which are in a dynamic sorption equilibrium. This is followed by an electrophilic attack by the H atom on the olefin double bond and by the F atom on the CF_2 unit, leading to the agglomeration of HF according to the Markovnikov rule. The supply of HFC 134 finally effects the desorption of HFC 134a.

The Action of the Conditioned Surface

In this paper the actual surface state of the conditioned chromia has not been extensively investigated. However, from the comprehensive XPS spectroscopic investigations (18) it is known that, independent of the conditioning gas used (CFC, HCFC, HFC), a catalytically active phase is always formed in the surface which seems to be chemically and topologically very similar to β-CrF_3. It has already been stated above that the chromia surface becomes fluorinated during conditioning and that from all the chromium fluorides investigated only β-CrF_3 is catalytically active from the very beginning. In addition, no remarkable differences in the catalytic activity of the conditioned solids were found when different conditioning gases were used.

In the case of isomerization reactions, we found that the reaction pattern appears quite different depending on whether chlorine-containing halocarbons or a chlorine-free compound was used. In agreement with the results in Refs. (17) and (18), we found very small but unambiguous amounts of chloride in the surface when using derivatives of the 130 series containing chlorine. In this case, in addition to the expected isomerization products TFE, HF, and HFC 134a, several chlorethylenes as well as chlorinated derivatives of the 130 series were also found. The formation of the chlorinated compounds gradually de-

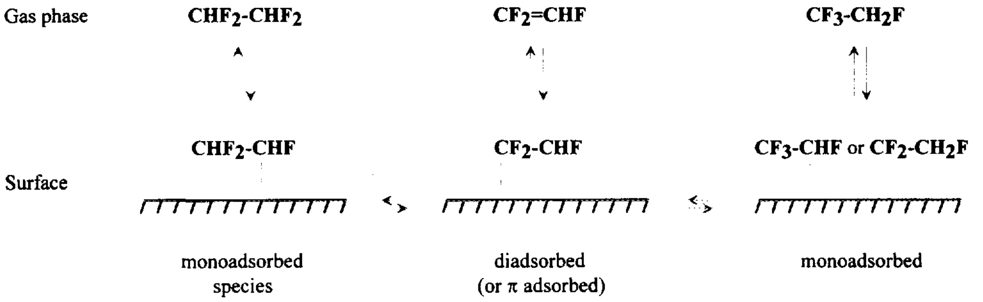

FIG. 6. Mechanistic model proposed for the isomerization reactions of HFC 134 to HFC 134a.

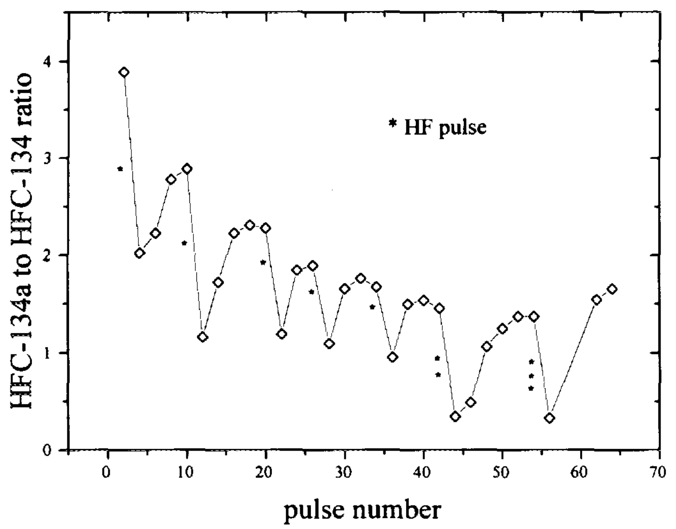

FIG. 7. Variation of the ratio HFC 134a to HFC 134 depending on the number of loaded HF pulses (educt, HFC 134; pulse volume, 1 ml/stp; temperature, 693 K; HF pulse volume, 2 ml/stp.).

creases, until after a while their formation disappears completely. Only traces of chloride are detectable after this period. It has thereby been proved that at least a certain amount of the solidified halogen content in the surface area is very exchange active and takes part directly in the halogen exchange reaction. This is only detectable when small pulses of the olefin are used. In a continuous gas flow the cleavage of the active surface halogenide would probably disappear. Similar conclusions are drawn by Rowley *et al.* (15) for the isomerization reactions of $C_2Cl_3F_3$ and its derivatives. The mobility of halogenides in the surface of the solid can also be found when HFC 134 is used exclusively for conditioning: in contact with trichlorethylene during the initial stage such a catalyst yields fluorinated ethylenes as well as traces of HFC 132 ($C_2H_2CL_2F_2$) and HFC 133 ($C_2H_2C1F_3$). This proves that at least two reaction pathways occur: these are chlorine/fluorine exchange as well as dehydrofluorination reactions of fluorinated ethylenes, followed by hydrofluorination reactions of unchanged ethylenes. This is the only explanation for the appearance of fluorinated representatives of the 130 series. The dehydrofluorination of ethylenes (forming unstable acetylenes) might be the initial pathway to coke formation and the reason for the observed deactivation of the catalyst in this reaction system.

During the isomerization of HFC 134 hydrogen fluoride is released throughout in considerable amounts and combines with TFE, forming HFC 134a. For this reason the influence of free HF was tested by loading certain pulses of pure HF gas onto the catalyst followed by further HFC pulses (cf. Fig. 7). HF is clearly so strongly adsorbed on catalytically active surface sites that the organic molecules cannot enter these centres with the result that finally the isomerization reactions decrease significantly. With every new HFC pulse the adsorbed HF becomes more and more desorbed so that the isomerization activity increases again. As can be seen from Fig. 7, these cycles can be repeated over and over. Irreversibly adsorbed HF, as well as increasing coke formation on the surface, might be responsible for the observed overall decrease in catalyst activity during these cycles.

Adsorption experiments in the system Cr_2O_3/(HFC134; HFC 134a; TFE, HF), which are currently being carried out, as well as isotopic exchange experiments may give more detailed information about these problems.

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