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Turnover rate and kinetic mechanism for the reaction of hydrodechlorination of 1,1-dichlorotetrafluoroethane (CF_3–$CFCl_2$) over a polycrystalline Pd foil

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The kinetics (turnover rate, activation energy, reaction order) of catalytic hydrodechlorination of 1,1-dichlorotetrafluoroethane or CFC 114a (CF_3–$CFCl_2$) were determined on a $\sim 0.5\ cm^2$ palladium polycrystalline foil as a catalyst. The reaction rates were measured in the temperature range of 80–200°C at a total pressure of 770 Torr. Using a reaction cell that was connected to an ultrahigh vacuum surface characterization chamber the composition of the metal surface was monitored before and after reaction. The products formed in a parallel reaction network and the turnover rates at 150°C, 50 Torr CFC 114a, 100 Torr H_2, and 0.1 Torr HCl were $2.1\ s^{-1}$ for CF_3–CFH_2, $3.0 \times 10^{-1}\ s^{-1}$ for CF_3–CFClH, and $6.4 \times 10^{-2}\ s^{-1}$ for CF_3–CH_3. For the two most abundant products, the reaction order is 1 in CF_3–$CFCl_2$, 0.5 in H_2 and -1 in the reaction product HCl. These results suggest that the rate determining step for the reaction is the associative chemisorption of CF_3–$CFCl_2$ on the palladium surface. The palladium surface was free of adsorbates after the reaction with the exception of sulfur impurity that may accumulate during reaction.

Keywords: hydrodechlorination rates and mechanism, Pd model catalysts, 1,1-dichlorotetrafluoroethane, CFC 114a

1. Introduction

Hydrodechlorination is an important catalytic process for several reasons. Although the new ozone friendly hydrofluorocarbon refrigerants contain no chlorine, a practical synthesis for them [1,2] may still use chlorofluorocarbons as intermediates and thus will require a hydrodechlorination step. Chlorine-containing organic molecules are often found in chemical waste and these must be hydrodechlorinated before they can be disposed of by combustion. Despite these and other important applications of hydrodechlorination, basic knowledge of the catalytic chemistry of the reaction is lacking. The turnover rates, reaction orders, and sensitivity of this reaction to the catalyst structure are not available. Several studies of hydrodechlorination have been reported [3–9], but the reactants used in these investigations are different and it is difficult to draw a unified picture of the chemistry involved. The objective of this paper is to present the turnover rates and kinetic mechanism for the hydrodechlorination of a model compound (CFC 114a (CF_3–$CFCl_2$)) on a model catalyst (Pd foil). Other important questions of catalyst structure sensitivity, effect of support, and comparison of model with supported catalysts will be addressed in a forthcoming publication [10]. There are three products formed in the hydrodechlorination of CFC 114a with varying degrees of hydrogenation (CF_3–CH_3, CF_3–CFH_2, and CF_3–CFClH). These products are formed in a parallel mechanism which implies that they are always formed in the same ratio independently of the degree of conversion (< 50%). The absolute rates, however, will be highly dependent on the degree of conversion, as the reaction was found to be inhibited by the reaction product HCl (reaction order -1). The rate determining step for this reaction was found to be the non-dissociative adsorption of CFC 114a.

2. Experimental

The experiments were carried out in a high-pressure (1 atm) batch reactor attached to an ultrahigh vacuum (UHV) chamber with a base pressure of 1.0×10^{-7} Pa (7.5×10^{-10} Torr). The sample was transferred between the UHV chamber and the high-pressure reactor with a welded bellows assembly capable of maintaining an UHV environment during sample transfer. The foil was attached to a sample cart containing two pins for resistive heating and two pins (chromel and alumel) for ther-

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mocouple temperature readings so the sample could be heated and the temperature measured on both stations. The type K thermocouple was spot-welded to the center of the rear of the foil. After reaction, due to desorption of reaction gases, the pressure could not be maintained below 10^{-7} Torr even though a 60 $\ell\ s^{-1}$ turbomolecular pump was connected to the transfer line. After the sample was transferred, the pressure in the main chamber returned to the base pressure in a few minutes.

The batch reactor had a volume of about 700 cm^3. The reactants were circulated with a metal bellows pump (Parker model MB 21) with a flow rate of about 1 $\ell\ min^{-1}$. This flow rate permitted a small conversion per pass. Heat and mass transfer limitations are usually of no concern in this type of experiment since all the active surface area is exposed.

The Pd polycrystalline foil used in this study was 0.1 mm thick, had a total surface area of about 0.5 cm^2 and a purity of 99.99% (Johnson Matthey). Only one side of the foil could be cleaned by Ar sputtering. The foil was cleaned by Ar sputtering at 1000 K and 6.7×10^{-3} Pa (5×10^{-5} Torr), and annealing at 1173 K until no foreign peaks were found by Auger electron spectroscopy (AES). After each reaction, Ar sputtering for 15 min followed by annealing at 1173 K was sufficient, as shown by AES, to clean the surface.

After the sample was transferred into the reactor, about 10 Torr of H_2 was introduced, followed by CFC 114a and the balance of the other gases including H_2. The recirculation pump and the sample heating were then turned on. For the runs with a high pressure of H_2 (500 Torr) the foil (which was spot-welded to two stainless steel posts) was warped after reaction probably by the formation of a palladium hydride. This behavior could be avoided by having the sample heated to about 100°C before H_2 was introduced. The rates did not change significantly by the warping, as confirmed by measuring the rates on a new foil with the gases introduced with the sample hot. However, it was desirable to avoid warping because it would eventually cause the sample-heating pin spot weld to break.

The chlorofluorocarbon was obtained from DuPont Co. and had a purity of 99.99% with only one impurity detected, possibly CF_3–CH_2Cl. This impurity did not change its concentration during the experiments. The CFC was degassed by freeze–pump–thaw cycles and then stored in a glass vial filled with a previously reduced 0.5% Pd on carbon supported catalyst. The other gases were used without further purification and were H_2 (Matheson, prepurified), Ar (Liquid Carbonic, 99.995%) and HCl (Matheson, Semiconductor Grade, 99.995%). The reaction rates were measured in the temperature range of 80–200°C, pressure range of 23–670 Torr in H_2, 21–511 Torr in CF_3–$CFCl_2$ and balance Ar at a total pressure of 770 Torr. The reaction products were analyzed with a gas chromatograph (Hewlett-Packard 5790A) with a flame ionization detector. The products were separated in a 5% Krytox 143AC, 60/80 Carbopack B HT 20′ × 1/8″ column (Supelco). The first analysis was made after 3 min of reaction and subsequent analyses were carried out at intervals of about 20 min.

Blank experiments were run to certify that the background catalytic activity was not significant. Those experiments were run on a stainless steel foil with a feed of 150 Torr of CFC 114a and 630 Torr of H_2. At 150°C, where most of the experiments were run, background reactions could not be detected.

Contamination of the Pd foil by sulfur during reaction was observed. At the end of the reaction, a ratio of Auger intensities S_{152}/Pd_{317} of about 0.25 was determined. The sulfur contamination was not coming from the H_2 or CFC 114a but correlated with the amount of HCl produced. It turns out that H_2/HCl mixtures are good hydrodesulfurization agents . Any residual sulfur compound can be transformed to a chloride and H_2S, which will eventually contaminate the catalyst. The most significant breakthrough in controlling the sulfur poisoning was to remove the rough vacuum oil pump, which was used to briefly pump down the reaction manifold. The use of this pump constantly added sulfur compounds to the reactor by backstreaming. The replacement of this pump with a sorption pump decreased the amount of contamination to a level where initial rates could be measured without the interference of sulfur. The amount of sulfur as a function of reaction time was studied at 150°C, 260 Torr of CFC 114a and 510 Torr H_2. The amount of sulfur on the sample (as determined by AES) increased linearly with time and reached the final saturation value after about 40 min of reaction. The reaction rate did not change significantly up until 25 min of reaction and this data was used for the initial rate calculations.

3. Results

A typical product accumulation versus time plot is shown in figure 1A. The overall conversion at the end of the reaction was lower than 1% in general (0.09% in figure 1A) and for this reason the reaction can be considered pseudo-zero order on H_2 and CFC. The curvature in the plot is due to the inhibition by the reaction product, HCl, which has a reaction order of −1, as will be shown in more detail below. Note that the reaction in figure 1 was carried out at a sufficiently low conversion for the amount of HCl in the gas phase not to cause appreciable sulfur contamination. The inhibition by HCl will cause the turnover rate to depend strongly on the degree of conversion. For this reason, it is best to integrate the rate equation. The resulting integrated equation can be plotted in a linearized form as a function of time and the square of concentration (figure 1B). The rate can then be calculated from the slope of the line,

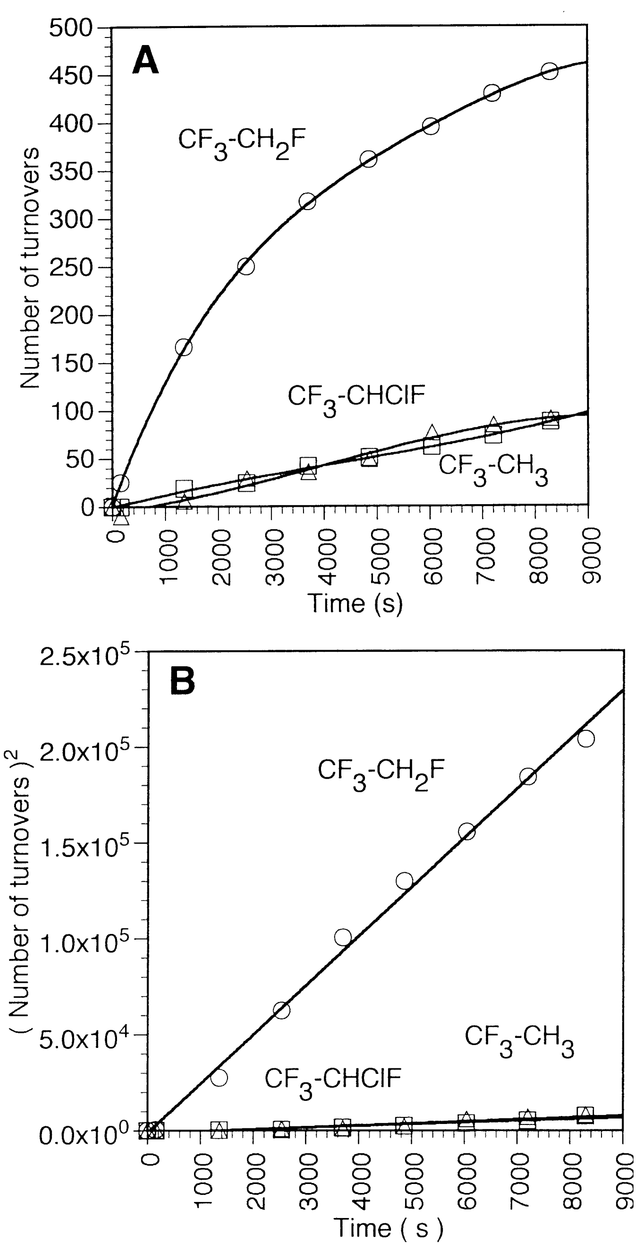

Figure 1. (A) Accumulation plot (number of turnovers versus time) and (B) integrated equation plotted in linear form (effect of HCl accounted for) for the reaction of CFC 114a (CF_3–$CFCl_2$) (260 Torr) and H_2 (508 Torr) at 80°C on a Pd foil. The reaction products were HFC 134a (CF_3–CFH_2) (○), HCFC 124 (CF_3–CFClH) (△) and HFC 143a (CF_3–CH_3) (□).

which will be proportional to the reaction rate constant. The turnover rates for a fixed set of conditions are presented in table 1. In the calculation of turnover rates an atom surface density of 1.0×10^{15} atoms cm^{-2} is assumed and each surface Pd atom considered to be an active site.

The activation energies are also shown in table 1 and were calculated from the Arrhenius plot shown in figure 2. Note that the ordinate of the Arrhenius plot is the slope obtained from the linearized accumulation plots (similar to figure 1B) and that the slope is proportional to the reaction rate constant. The apparent activation energies are close to 100 kJ mol^{-1}.

Table 1
Summary of kinetic data for the reaction of hydrodechlorination of CF_3–$CFCl_2$

	TOR[a] (s^{-1})	E_a (kJ mol^{-1})	Reaction order dependence		
			CFC 114a	H_2	HCl
CF_3–CH_3	6.4×10^{-2}	94 ± 5	0.9	−0.20	−0.7
CF_3–CFH_2	2.1	109 ± 5	0.8	0.44	−1.2
CF_3–CFHCl	3.0×10^{-1}	97 ± 7	0.9	0.52	−0.9

[a] Rates corrected for 50 Torr CF_3–$CFCl_2$, 100 Torr H_2, 0.1 Torr HCl, 150°C.

The plots for the reaction order determination on CFC 114a, H_2, and HCl are shown in figures 3–5. The data are summarized in table 1. The reaction order is close to 1 in CFC 114a, about 0.5 order in H_2 (except for 143a), and about −1 order in HCl.

To study if the three reaction products are formed in series or in parallel, the reactivity data for the first product that would be formed in a series reaction network (HCFC 124), was studied (table 2). A comparison with the rate data for CFC 114a (table 1) shows that HCFC 124 shows a much lower reactivity.

4. Discussion

We could not find any other study in the literature for a direct comparison of rates of hydrodechlorination

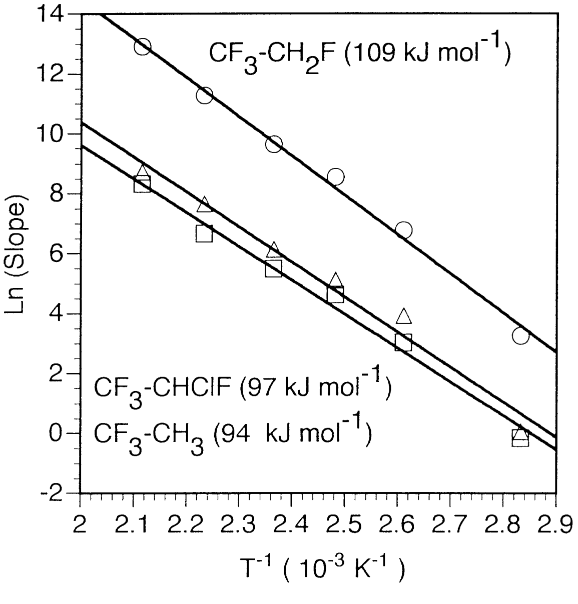

Figure 2. Arrhenius plot for the reaction of CFC 114a (CF_3–$CFCl_2$) (260 Torr) and H_2 (510 Torr) on a Pd foil. The reaction products were HFC 134a (CF_3–CFH_2) (○), HCFC 124 (CF_3–CFClH) (△) and HFC 143a (CF_3–CH_3) (□). Activation energy in parentheses.

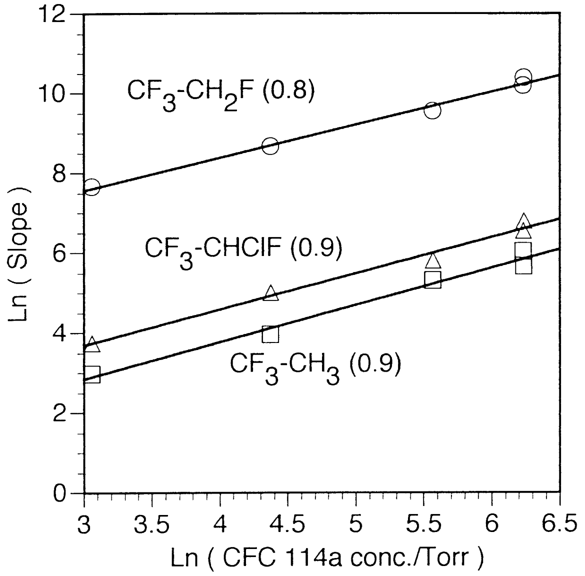

Figure 3. Determination of reaction order in CFC 114a (CF_3–$CFCl_2$). Experiments run at 150°C, 260 Torr H_2, 21–511 Torr CFC 114a. The reaction products were HFC 134a (CF_3–CFH_2) (○), HCFC 124 (CF_3–CFClH) (△) and HFC 143a (CF_3–CH_3) (□). Reaction order in parentheses.

of CFC 114a, although the rates on the foil showed a very good agreement with the rates on supported catalysts [10]. Gervasutti et al. [12] also studied this reaction but these authors did not report a turnover rate, making a comparison of rates very difficult. The rates reported for other feeds cannot be extrapolated for the current case because the rates are highly dependent on the molecular structure of the reactants. The rate of hydrodechlorination depends on the number, type of heteroatoms and the particular carbon atom they are bound to. The more reactive molecules are the ones which have all chlorines in one carbon with the reactivity decreasing sharply as hydrogen or fluorine atoms substitute chlorine in a particular carbon atom [12–15]. For example, a comparison of rates for the very similar feeds CFC 114a (CF_3–$CFCl_2$) (table 1) and HCFC 124 (CF_3–CFClH) (table 2) reveal a difference in the turnover rate of hydrodechlorination by a factor of 250 times.

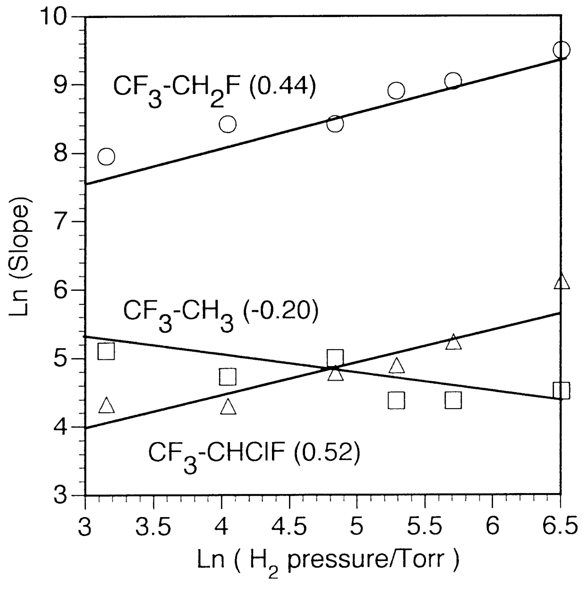

Figure 4. Determination of reaction order in H_2. Experiments run at 150°C, 23–670 Torr H_2, 100 Torr CFC 114a. The reaction products were HFC 134a (CF_3–CFH_2) (○), HCFC 124 (CF_3–CFClH) (△) and HFC 143a (CF_3–CH_3) (□). Reaction order in parentheses.

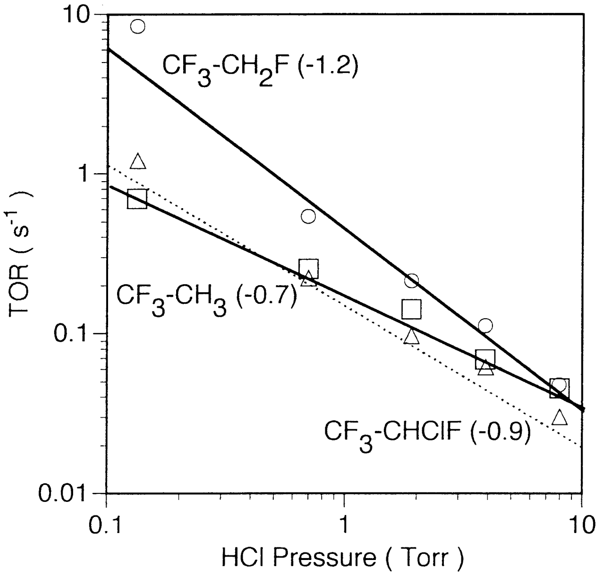

Figure 5. Determination of reaction order in HCl. Experiments run at 150°C, 510 Torr H_2, 260 Torr CFC 114a. The reaction products were HFC 134a (CF_3–CFH_2) (○), HCFC 124 (CF_3–CFClH) (△) and HFC 143a (CF_3–CH_3) (□). Reaction order in parentheses.

Based on the kinetic parameters that were determined by our studies, the following reaction mechanism is proposed for the two main products HCFC 124 (CF_3–CFClH) and HFC 134a (CF_3–CFH_2). The rate determining step is the non-dissociative adsorption of the reactant CFC 114a:

$$CF_3{-}CFCl_2 + * \rightarrow CF_3{-}CFCl_2* \ (\mathrm{RDS}), \quad r = k[\mathrm{CFC}][*] . \qquad (1)$$

(Other steps for the CFC hydrodechlorination are not

Table 2
Summary of kinetic data for the reaction of hydrodechlorination of CF_3–CFClH

	TOR [a] (s^{-1})	E_a (kJ mol^{-1})	Reaction order dependence		
			CFC 124	H_2	HCl [b]
CF_3–CH_3	2×10^{-4}	120 ± 6	0.6	0	n.d.
CF_3–CFH_2	8×10^{-3}	96 ± 5	0.9	0	n.d.

[a] Rates corrected for 50 Torr CF_3–CFClH, 100 Torr H_2, 0.1 Torr HCl (reaction order assumed to be zero), 150°C.

[b] n.d.: not determined.

kinetically significant.) It is also assumed that Cl is the most abundant reaction intermediate

$$[*] + [\mathrm{Cl}*] = [\mathrm{L}] , \qquad (2)$$

where [L] is the total number of sites, and that the surface is equilibrated with H_2 and HCl in the gas phase:

$$\mathrm{H_2} + 2* \rightleftharpoons 2\mathrm{H}* \qquad (3)$$

$$\underline{\mathrm{H}* + \mathrm{Cl}* \rightleftharpoons \mathrm{HCl} + 2* \quad (\times 2)} \qquad (4)$$

$$\mathrm{H_2} + 2\mathrm{Cl}* \rightleftharpoons 2\mathrm{HCl} + 2* \qquad \text{(overall reaction)} \qquad (5)$$

The number of free sites can then be calculated from (2) and (5) and it is equal to $[*] = K\,[\mathrm{H_2}]^{0.5}/[\mathrm{HCl}]$. The final rate will then be

$$r = kK[\mathrm{CFC}][\mathrm{H_2}]^{0.5}/[\mathrm{HCl}] , \qquad (6)$$

which is a good approximation to the experimentally observed rate dependencies for HCFC 124 and HFC 134a (table 1).

The rate dependence on HFC 143a (CF_3–CH_3) does not fit the above mechanism. The above mechanism implies that the almost zero-order dependence on H_2 should also correspond to a zero-order dependence on HCl. Further data are necessary to investigate this matter.

The mechanism above is similar to the one proposed by Sinfelt [9] for the hydrodechlorination of methyl chloride. The order dependence on CFC and HCl was also the same as reported by Campbell and Kemball [16] for the hydrodechlorination of ethyl chloride over Pd films.

Another important feature in this reaction is the reaction selectivity. There are three products formed in this reaction (CF_3–CH_3, CF_3–CFH_2, and CF_3–CFClH) with varying degrees of hydrogenation. Learning how to control their relative rates is of practical importance. One important question in this reaction network is to find out if this reaction is a serial or a parallel hydrogenation. To decide on this question, the rate of reaction of the monohydrogenated product (table 2), which would be the first intermediate in a series reaction, was determined. The rate of hydrodechlorination is 250 times smaller than necessary to explain a serial reaction pathway. The product distribution of HCFC 124 also showed a much smaller selectivity for the formation of HFC 143a (CF_3–CH_3) than shown in the reaction of CFC 114a. Thus, HCFC 124 (CF_3–CFClH) is not an intermediate in the hydrodechlorination of CFC 114a but only one of the products formed in a parallel reaction. A parallel mechanism was also invoked by Wiersma et al. [17] to explain the three products in the hydrodechlorination of CCl_2F_2.

The question of structure sensitivity was not addressed in this contribution but it will be studied by running the reaction over different low Miller index planes of Pd [10]. Fung and Sinfelt [8], based on the small variation of turnover rates (two orders of magnitude) across a period in the periodic table, concluded that this reaction may be structure insensitive on group VIII metals.

5. Conclusions

In the reaction of hydrodechlorination of CFC 114a the products are CF_3–CFH_2 (85%), CF_3–CFClH (12%) and CF_3–CH_3 (3%). The products are formed in parallel reactions. The kinetic mechanism for the two most abundant products appear to involve the non-dissociative adsorption of CFC 114a as the rate determining step, while the surface is covered with Cl that is equilibrated with H_2 and HCl in the gas phase.

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