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Hydrodechlorination of chlorofluorocarbons CF_3–$CFCl_2$ and CF_3–CCl_3 over Pd/carbon and Pd black catalysts

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Abstract

The reaction of hydrodechlorination for the chlorofluorocarbons (CFCs) CF_3–$CFCl_2$ and CF_3–CCl_3 was studied over Pd supported on carbon and Pd black catalysts. The rates and selectivity were similar on all samples although Pd black samples had a higher selectivity for the more hydrogenated products. The difference in selectivity and rate for Pd black is attributed to the presence of an impurity on the surface. The reaction orders are about first order in CFC, half-order in H_2, and inverse first-order in HCl. These results indicate that the irreversible adsorption of CFC is the rate-determining step and that H_2 and HCl are equilibrated with hydrogen and chlorine on the surface. Experiments with D_2 on CF_3–CFHCl confirm that the adsorption step is irreversible. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodechlorination; Chlorofluorocarbons; Pd/carbon catalyst; Pd black catalyst

1. Introduction

In the 1980s, halogenated chlorofluorocarbons (CFCs) were scientifically linked to the depletion of the ozone layer [1]. The stable and inert nature of CFCs is advantageous in many applications but it also enables them to escape from the lower atmosphere without decomposition, and contribute to stratospheric ozone depletion. Hydrofluorocarbons (HFCs) are much less harmful to the environment and have some of the useful properties of CFCs and may thus serve as a replacement for CFCs [2]. One of the routes to produce HFCs is the reaction between CFC and H_2 catalyzed by a noble metal. This reaction may also be used to transform the large amounts of CFCs that exist today into the more environmentally benign HFCs [1,3]. The transformation of CFCs into HFCs requires a knowledge of catalytic hydrodechlorination, the subject of this contribution.

Hydrodechlorination reactions have been studied over a number of metals, such as Pd [4–9], Pt [10–12], and Rh [10,12–14], with Pd usually the most selective catalyst for this reaction. The role of the support has been studied on carbon [15,16], alumina [4] and fluorinated alumina [5]. While some authors have suggested that the support play a role in the reaction [17], we have previously reported that the support (carbon) does not influence reaction kinetics beyond condensation of CFC reactant on microporous supports [16]. While most contributions report on supported catalysts, hydrodechlorination literature does include studies on evaporated films [18–20], foils [7,8,21], and single crystals [8]. A limited number of studies have been reported on bulk metal powders [22,23]. In this publication, we will extend our previous reports on CF_3–$CFCl_2$ and CF_3–CCl_3 hydrodechlorination kinetics on supported Pd catalysts [16] by reporting the results on Pd black.

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Turnover rates, selectivity and reaction orders have been presented for only a limited number of compounds [4,5,7–9,17,21]. Even less has been published about possible reaction steps [13,14,24,25]. Thompson et al. [16] suggested that the rate-determining step is the adsorption of the CFC on only one catalytic site. The rate-determining step consists of the scission of the carbon–chlorine bond, possibly as an oxidative addition, forming a Pd–Cl and Pd–C–R bond on the same catalytic site [16]. This proposed rate-determining step was deduced from the kinetics and from the fact that there is a correlation between gas-phase C–Cl bond strength and reactivity. Weiss et al. [26] also proposed dissociative adsorption of the CFC as the rate-determining step for CCl_4 hydrodechlorination. The reaction steps proposed are a simplification and cannot predict, for example, the reaction selectivity, which is a key property of the catalyst. It is thus necessary to learn the details of steps beyond the rate-determining one. Isotopic tracing may help to understand the hydrodechlorination reaction steps. A limited number of studies of hydrodechlorination have been conducted with isotopes. Campbell and Kemball [18] found through reaction of CH_3–CH_2Cl on Pd films with D_2 that the reaction steps must proceed through a carbene like intermediate since the product (ethane) was significantly enriched with the doubly deuterated product CH_3–CHD_2. However, we will report that in the reaction of CF_3–CFHCl with deuterium on Pd/C, the most abundant product (98%) is the mono-deuterated product CF_3–CFHD. The absence of deuterium in the reactant during reaction also suggests that adsorption of CFC is irreversible.

2. Experimental methods

2.1. Catalysts

Two palladium catalysts supported on carbon and an unsupported palladium black catalyst were used in this study. The supported catalysts differed in the total surface area or the type of carbon used. The denomination for the support, C-L, is to point out that these supports have a low surface area. A 5% Pd catalyst supported on carbon (5% Pd/C-L) was obtained from Degussa. The second carbon supported catalyst (0.5% Pd/C-L) was prepared in house via an incipient wetness procedure on a carbon support manufactured by the Cabot (Sterling Series). The incipient wetness method utilized an aqueous solution of $PdCl_2$ (Aldrich, 99.99%) with the addition of 2 mol of HCl per mole of precursor with additional heating to aid in the dissolution of $PdCl_2$. Additional information on the supported catalyst can be found elsewhere [16]. The supported samples were ground with a mortar and pestle and 40/60 mesh particles were retained for use in catalytic studies. The Pd black (Alfa Aesar, 99.9%) was used as received.

2.2. Reactants

The CFC 114a (CF_3–$CFCl_2$) samples were obtained from DuPont, CFC 113a (CF_3–CCl_3) from Lancaster Synthesis, and HCFC 124 (CF_3–CFHCl) from DuPont Suva Refrigerants. The 15–20% HCl/He mixtures (three used in this study) were prepared by Matheson with technical grade HCl and Matheson purity He. The hydrogen source contained 1033 ppm of CH_4, which was used as an internal standard and for calibration of the gas chromatograph. The hydrogen–methane mixture was passed through a packed bed containing a 5% Pd/C catalyst to eliminate any oxygen from the H_2 mixture. Hydrogen was obtained from BOC gases and certified as CGA Grade D. The pure H_2 gas was passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. The deuterium was obtained from Cambridge Isotope Laboratories. It contained 99.6% D_2 and 0.4% HD, and before use it was passed through a Pd membrane (Matheson hydrogen purifier model 8361).

2.3. Reactor configuration

The gas manifold was constructed of $\frac{1}{8}$ in. diameter stainless steel tubing and flowrates were controlled with mass flow controllers (Porter Instrument). For CFC 113a (CF_3–CCl_3), a liquid at room temperature, addition to the reaction mixture was made by passing helium through the CFC in a saturator. The reaction portion of the flow system was made of Pyrex and could be manipulated to operate in continuous or in batch mode. The reactor was made out of quartz with the catalyst held on a fritted disk. Most reaction rates were measured while operating in continuous stirred tank reactor (CSTR) mode with a thermocouple extending into the reactor so that the thermocouple was well in contact with the catalyst bed. The CSTR was equipped with a gas pump (Senior Flexonics model MB-21) for circulating the gases at a rate of about 1400 $cm^3 min^{-1}$ which allowed differential operation and minimized heat and transport effects. Inlet and effluent flow rates were 100 $cm^3 min^{-1}$.

Reactions of CFC 114a (CF_3–$CFCl_2$) over Pd black showed a much higher selectivity to HFC 143a (CF_3–CH_3) causing a higher concentration of HF in the reactor and simultaneous deposition of an unidentified fine white powder on the glass portion of the reactor. For this reason, CFC 114a experiments over Pd black were then conducted in a stainless steel plug flow reactor (PFR). Hydrogen chloride was added to the feed to allow the reactor to operate in a differential mode, since HCl is a reaction product, which inhibits the reaction. Blank experiments were run with the stainless steel reactor to ensure that the reactor walls did not catalyze hydrodechlorination.

The exiting gas stream was sent to a gas chromatograph (GC) for analysis. The column used in the GC was a 5% Krytox™ 143AC, 60/80 Carbopack B HT $20' \times \frac{1}{8}$ in. column from Supelco. Each of the reactant CFC and products were calibrated against the methane standard in the hydrogen–methane mixture. Response factors were then determined for each compound. The distribution of deuterium in the reaction products was monitored with a Hewlett Packard mass spectrometer (MS) 5970. The MS was connected to the existing GC to allow a portion of the gases eluting the column to be directed to the MS (through a capillary tube) before entering the FID detector. In this way, signals were obtained simultaneously from the MS and the GC. After exiting the system, the gases flowed through a NaOH solution to neutralize the HCl present in the effluent stream.

2.4. Data collection procedure

Two to five hundred milligrams of fresh catalyst was initially loaded into the reactor and reduced for 3 h at 300°C with 50 $cm^3 min^{-1}$ H_2. At the start of each experiment, the catalyst was reduced for 0.5–1 h at 150°C with 50 $cm^3 min^{-1}$ H_2. For a particular set of conditions, the reaction was run for 30–60 min before a data point was taken. Temperature and concentration parameters for activation energy determination and reaction orders were varied in a random fashion so that any variation in the system would not introduce a systematic error. In order to ensure that deactivation had not occurred during the duration of the experiment, the first point in the series was duplicated at the end of the experiment.

In general, reaction orders were determined by varying the partial pressure of the compound under study and maintaining all other variables (partial pressures and temperature) constant. The difficulty of delivering CFC 113a prevented the use of the standard reaction order experimental procedure. Instead of keeping each of the gas flow rates constant except CFC and helium, the CFC flow rate was held constant and the other flow rates were adjusted. By varying the total flow rate in this manner, the CFC 113a concentration is changed. The flow rate of each of the other gases was adjusted so that the same concentration of the gas was maintained in the reaction mixture.

2.5. Surface area measurements

Total surface area was measured using the BET method with N_2. The Pd metal surface area was measured by the hydrogen–oxygen titration method according to Benson et al. [27]. The experimental system consisted of a volumetric system constructed in Pyrex and pumped by a diffusion pump with a liquid nitrogen cooled trap. The amount of gas adsorbed was determined by measuring pressure change in the calibrated volume of the system with a pressure transducer (MKS model 127).

Both the BET method and H_2–O_2 titration method were used to determine the metal surface area of the Pd black since it is an unsupported metal. A Pd atom density, equal to an average of the low index planes, of 1.27×10^{19} atoms m^{-2} was assumed [28].

The samples were initially reduced in flowing H_2 (50 $cm^3 min^{-1}$) for 3 h at 300°C before the Pd surface area measurements. After the initial reduction of 3 h, subsequent reduction was conducted at 100°C for 0.5 h. The crystallite size based on chemisorption measurements was estimated from the expression, $d\,(\mathrm{nm}) = 112/(\text{percentage of metal exposed})$. This expression is valid under the assumption of spherical particles and a Pd atom density of 1.27×10^{19} atoms m^{-2}.

X-ray diffraction (Rigaku Geigerflex diffractometer) of reduced catalysts was also conducted. Samples for XRD analysis were reduced in a manner identical to those previously described, and then passivated with 60 Torr of O_2. Particle size was determined from the width of the diffraction peak using X-ray line broadening technique. The Scherrer equation was used to calculate Pd particle size with appropriate correction for instrumental line broadening.

2.6. Error analysis

We have compared the data for the same experiment carried out at identical conditions to calculate experimental errors. The errors in reaction orders are at a maximum 10% and errors in the apparent activation energies were 10 kJ mol^{-1}. Turnover rate reproducibility was better than 90%.

3. Results and discussion

3.1. Catalyst properties

The properties of the catalysts used in this study are presented in Table 1. The supported catalysts had a Pd loading of 0.5 or 5% and two different carbon supports were used. It has been shown that the carbon support plays no role in the hydrodechlorination reaction [16].

The low surface area supports (designated C-L) were non-microporous. A number of analyses were conducted on Pd black to follow the sintering behavior. The BET surface area of Pd black before reduction was 27 m^2 g^{-1}. Upon reduction for 1 h at 100°C the surface area decreased to 7.9 m^2 g^{-1}, and further reduction at 300°C for 1 h decreased the area to 1.5 m^2 g^{-1}. A comparison of surface area determined by BET and H_2–O_2 titration was conducted to verify whether the entire surface area of the Pd black powder consisted of palladium. Differences in surface areas determined by the two techniques would suggest that impurities (such as other metals) were present on the surface. According to the certificate of analysis, some impurities in Pd black are silicon, silver, iron, rhodium and platinum. Surface areas determined by BET and H_2–O_2 titration (assuming a Pd atom density of 1.27×10^{19} atoms m^{-2}) were 1.5 and 1.2 m^2 g^{-1}, respectively. This result indicates that the surface may have some impurities (within the limits of the assumption of Pd atom density). Note that, however, this test will not rule out the presence of another substance on the surface that has an oxygen stoichiometry identical to Pd (e.g., another noble metal).

Particle sizes determined by XRD line broadening are also shown in Table 1. There is a good agreement between chemisorption and XRD particle sizes for the 0.5% Pd/C-L sample. On the other hand, the Pd particle size measured by XRD for the 5% Pd/C-L is about three times smaller than that determined by chemisorption, suggesting that the particles are formed by a number of smaller agglomerates.

The data presented in Table 1 is representative of catalyst properties before reaction. Since no deactivation occurred during reaction, changes in catalyst properties were expected to be minor after the reaction. The stability of catalyst properties under reaction condition is supported by data for Pd black. When examined after the hydrodechlorination of CFC 113a, the PME value before reaction (after reduction) was 0.49%, while after reaction the PME value was 0.43%, a smaller value but within our experimental error.

The presence of heat and mass transfer limitations was tested using the Madon–Boudart test [29,30]. From results presented in previous work [16], heat

Table 1
Catalyst properties

Catalyst	BET surface area (m^2 g^{-1})	Amount of surface Pd (μmol g^{-1})	PME[a]	Particle diameter (nm)	
				Chemisorption[b]	XRD
Pd black	1.5	30.1	0.32	350	>100
0.5% Pd/C-L	29	3.8	8.0	14	14
5% Pd/C-L	107	39.5	8.4	13	5

[a] Percentage of metal exposed, determined by H_2–O_2 titration at 100°C.

[b] Particle size determined from $d = 112/\mathrm{PME}$.

and mass transfer limitations were non-existent with the highest surface area catalyst, where transport limitations would be most severe.

3.2. Kinetic measurements

Kinetic data on an unsupported Pd powder will be presented and compared to the data on Pd/carbon and a foil for two CFCs (CF_3–$CFCl_2$ and CF_3–CCl_3). We would like to propose that the reaction steps to be presented also apply to other chlorine-containing compounds. If this generalization is true, it will be an important achievement as the number of organic compounds that contain chlorine is large and their properties are very dependent on molecular structure. Results on deuterium isotope substitution will also be presented to illustrate possible reaction steps.

3.2.1. Structure sensitivity and selectivity

In previous studies, the reaction of hydrodechlorination was studied for four compounds (CF_3–CF_2Cl, CF_3–CFClH, CF_3–$CFCl_2$ and CF_3–CCl_3) on palladium foils [7,8,21], single crystals of Pd [8], and Pd supported on carbon [16]. The turnover rates for hydrodechlorination are independent of the catalyst type, suggesting the structure insensitivity of this reaction. Table 2 contains the kinetic data for Pd black, 0.5% Pd/C-L, and Pd foil. The rates for the major product, CF_3–CFH_2 are at most a factor of 6 different when the catalysts are compared. This is remarkable since there are large differences in specific surface area between the foil and the supported catalysts. These results confirm previous findings [8] that the reaction is structure insensitive for CF_3–$CFCl_2$ on Pd.

There was no deactivation or change in selectivity throughout the duration of the experiment. The selectivity for the most abundant hydrodechlorination product, CF_3–CFH_2, is about 85% for the 0.5% Pd/C-L catalyst and foil, while the selectivity on the Pd black is about 75%. A lower selectivity on Pd black during a hydrodechlorination reaction has been documented before. van de Sandt et al. [22] reported selectivity to CH_2F_2 from CF_2Cl_2 of 85% for a 1 wt.% Pd/C catalyst, while the selectivity to CH_2F_2 was only 75% on Pd black. Our interpretation of the data is that an impurity is responsible for the lower selectivity since supported catalysts, foils and single crystals do not show appreciable variation in selectivity. From the certificate of analysis, this particular sample may have Si, Pt, Ru, Rh, and Fe at levels of about 10 ppm for each compound. Because this is a bulk sample, if these impurities migrate to the surface a substantial enrichment may be achieved.

The kinetic data for CFC 113a (CF_3–CCl_3) hydrodechlorination is summarized in Table 3. The same three catalysts used for CF_3–$CFCl_2$ hydrodechlorination were used for CF_3–CCl_3 hydrodechlorination. The turnover rate for the main product, CF_3–CH_3, is about $10^{-1}\,s^{-1}$ for all three catalysts. The hydrodechlorination of CFC 113a also seems to be a

Table 2
Kinetic data for CF_3–$CFCl_2$ hydrodechlorination

Catalyst	Product	TOR[a] (s^{-1})	Selectivity[b] (%)	E_a ($kJ\,mol^{-1}$)	Reaction order dependence		
					CFC 114a	H_2	HCl
Pd black	CF_3–CH_3	1.5×10^{-2}	16	120	1.10	0.01	−0.80
	CF_3–CFH_2	7.4×10^{-2}	76	110	1.00	0.20	−0.80
	CF_3–CHFCl	7.9×10^{-3}	8	85	1.00	0.50	−0.70
0.5% Pd/C-L	CF_3–CH_3	1.2×10^{-2}	4	100	0.75	0.30	−0.90
	CF_3–CFH_2	2.7×10^{-1}	84	100	0.75	0.35	−0.85
	CF_3–CHFCl	4.0×10^{-2}	12	75	0.75	0.55	−0.80
Pd foil[c]	CF_3–CH_3	1.4×10^{-3}	2.7	95	0.90	−0.20	−0.70
	CF_3–CFH_2	4.5×10^{-2}	85.3	110	0.80	0.45	−1.20
	CF_3–CHFCl	6.3×10^{-3}	12.0	100	0.90	0.50	−1.00

[a] Rates corrected for 150 Torr CF_3–$CFCl_2$, 200 Torr H_2, 20 Torr HCl, at 150°C.

[b] The selectivity is independent of conversion.

[c] Data from Ribeiro et al. [7]. Reaction orders were assumed to be 1, 0.5, and −1 for CFC 114a, H_2, and HCl, respectively.

Table 3
Kinetic data for CF_3–CCl_3 hydrodechlorination

Catalyst	Product	TOR[a] (s^{-1})	Selectivity[b] (%)	E_a ($kJ\,mol^{-1}$)	Reaction order dependence		
					CFC 113a	H_2	HCl
Pd black	CF_3–CH_3	9.6×10^{-2}	85.9	140	0.70	0.25	−0.90
	CF_3–CH_2Cl	3×10^{-3}	2.7	120	0.70	0.65	−1.00
	CF_3–$CHCl_2$	1.3×10^{-2}	11.5	120	0.60	0.40	−0.80
0.5% Pd/C-L	CF_3–CH_3	1.6×10^{-1}	78.3	100	0.60	0.25	−0.75
	CF_3–CH_2Cl	5.1×10^{-3}	2.6	85	0.50	0.45	−0.70
	CF_3–$CHCl_2$	3.8×10^{-2}	19.1	80	0.60	0.50	−0.75
Pd foil[c]	CF_3–CH_3	2.4×10^{-1}	67	100	0.60	0.60	−1
	CF_3–CH_2Cl	1.9×10^{-2}	6	80	0.80	1.00	−1
	CF_3–$CHCl_2$	9.6×10^{-2}	27	80	0.60	1.20	−1

[a] Rates corrected for 30 Torr CF_3–CCl_3, 120 Torr H_2, 20 Torr HCl, at 70°C.
[b] The selectivity is independent of conversion.
[c] Data from Ribeiro and Somorjai [21].

structure insensitive reaction, although the average particle size is too large for a definite conclusion. Note that no kinetic data is available on single crystal surfaces for CFC 113a hydrodechlorination, as was the case for CFC 114a discussed above, or for a series of supported catalysts with particle sizes in the critical size range (1–10 nm). Thus, a definite conclusion on structure sensitivity for CFC 113a cannot be made. The selectivity on Pd black is also higher for the most hydrogenated product, CF_3–CH_3, than on the other catalysts, also suggesting that a surface impurity is playing a role.

3.2.2. Reaction orders

The reaction steps were proposed based on measured reaction orders. The reaction orders and activation energies for the hydrodechlorination reaction are summarized in Tables 2 and 3 for CF_3–$CFCl_2$ and CF_3–CCl_3, respectively. The three main products formed are all derived from the sequential dehalogenation of the carbon bonded to chlorine. The CFC, H_2, and HCl reaction orders for the products of CF_3–$CFCl_2$ hydrodechlorination over Pd black are presented in Figs. 1–3, respectively.

The reaction steps proposed before for the hydrodechlorination reaction and based on kinetic data are

$$\mathrm{CFC} + * \rightarrow \cdots \tag{1}$$

The above step is the rate-determining step, with all the following steps for the CFC hydrodechlorination not kinetically significant. The symbol $*$ represents a catalytic site.

The surface is also equilibrated with H_2 and HCl in the gas phase:

$$H_2 + 2* = 2H* \tag{2}$$

$$H* + Cl* = HCl + 2* \tag{3}$$

Making the assumption that Cl$*$ is the most abundant

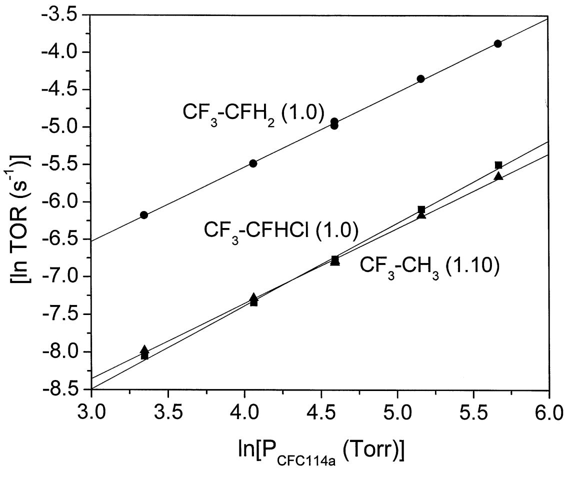


Fig. 1. Determination of reaction order in CFC 114a (CF_3–$CFCl_2$) on Pd black. Experiments were carried out at 125°C, 30–300 Torr CFC, 230 Torr H_2, and 30 Torr HCl. Turnover rates corrected to 200 Torr of H_2, 20 Torr of HCl.

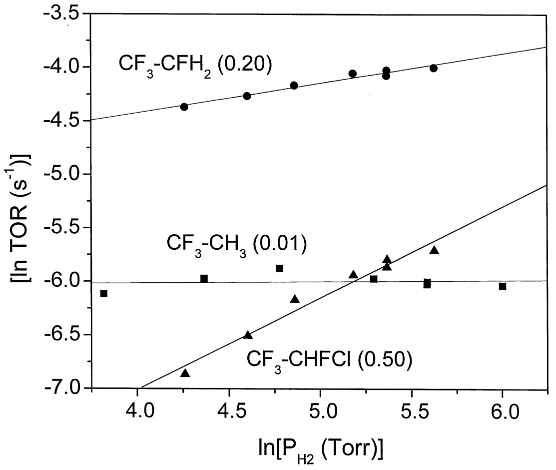


Fig. 2. Determination of reaction order in H_2 for the reaction of CFC 114a (CF_3–$CFCl_2$) on Pd black. Experiments were carried out at 130°C, 160 Torr CFC, 50–400 Torr H_2, and 30 Torr HCl. Turnover rates corrected to 150 Torr of CFC 114a, 20 Torr of HCl.

surface intermediate, the final rate will be [7]:

$$r = \frac{k[\mathrm{CFC}][\mathrm{H_2}]^{0.5}}{[\mathrm{HCl}]} \qquad (4)$$

This expression is accurate for the most abundant product formed but it is not correct for some of the products. For example, the reaction order in H_2 for CF_3–CH_3 is zero when CF_3–$CFCl_2$ is the reactant, much lower than the expected value of 0.5. Similar to Pd foil [7] and the single crystals [8,9] results, the reaction order in H_2 for this product is significantly lower than the expected value, while the CFC and HCl orders are in good agreement with the expected orders. The explanation for the zero-order dependence in H_2 on single crystals was attributed to H_2 storage in the bulk of Pd [9]. The authors were able to show that hydrodechlorination of CF_3–$CFCl_2$ occurred in the absence of gas-phase H_2 when solid-state hydrogen was available. A change in selectivity was noted as hydrogen was obtained from the gas phase or the solid state. Similar to the Pd black case, an increase in selectivity of CF_3–CH_3 occurred, but at the expense of the under-hydrogenated product (CF_3–CFHCl) rather than the hydrodechlorination product, CF_3–CFH_2.

The strong inhibition effect of HCl is apparent by the approximately inverse first-order dependence. The inhibiting effect of HCl has been accounted for in determining the apparent activation energy by reporting all the rates at the same HCl concentration (Fig. 4). This is an important consideration since the rates are a strong function of the amount of HCl (conversion).

To construct a kinetic reaction sequence from the reaction orders, we must ensure that the measured kinetic parameters are intrinsic and have not been

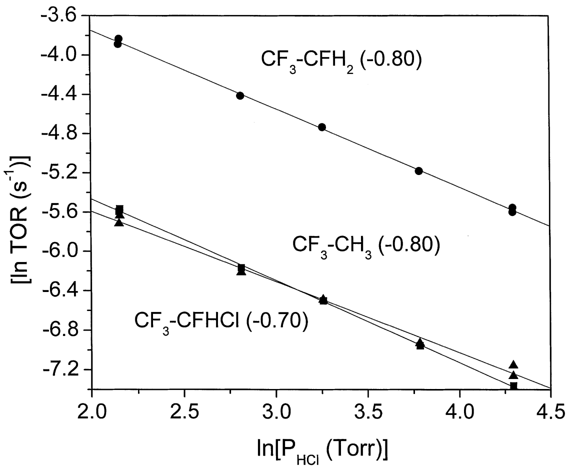


Fig. 3. Determination of reaction order in HCl for the reaction of CFC 114a (CF_3–$CFCl_2$) on Pd black. Experiments were carried out at 125°C, 110 Torr CFC, 190 Torr H_2, and 10–70 Torr HCl. Turnover rates corrected to 150 Torr of CFC 114a, 200 Torr of H_2.

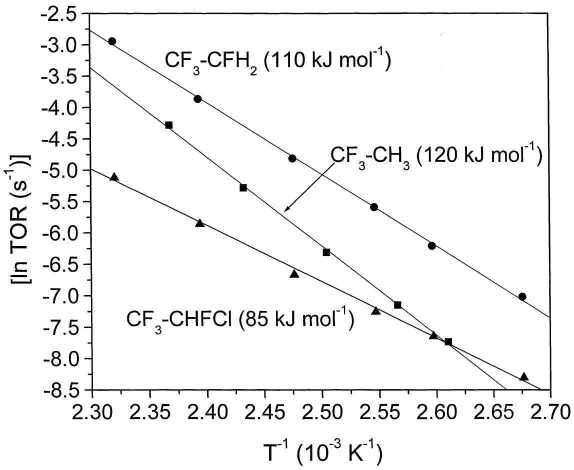


Fig. 4. Arrhenius plot for the reaction of CFC 114a (CF_3–$CFCl_2$) on Pd black. Experiments were carried out at 100–150°C, 170 Torr CFC, 340 Torr H_2, and 40 Torr HCl. Turnover rates corrected to 150 Torr of CFC 114a, 200 Torr of H_2 and 20 Torr HCl.

subjected to possible artifacts. Condensation of the CFC in the pores of microporous supports has caused reaction orders in CFC to be lower than expected [16]. On Pd black, there seems to be no apparent effect of CFC condensation, evidenced by the reaction orders of 1.0 and ∼0.7 for CF_3–$CFCl_2$ and CF_3–CCl_3, respectively. CFC orders on Pd black are in very good agreement with Pd foil data, suggesting that condensation of CF_3–CCl_3 is minimal on Pd black.

The conclusion is that the previously proposed reaction steps are also valid on Pd black. The higher selectivity for the more hydrogenated product on Pd black may be due to a surface impurity.

3.2.3. *Rate-determining step*

The rate-determining step, Eq. (1), does not specify how the CFC binds to the surface. Because only one catalytic site is involved, Ribeiro et al. [7] proposed that this step was the non-dissociative adsorption of the CFC. A non-dissociative step would indicate a weak dependence of rates on the molecular structure. However, a study of a series of four CFC compounds showed that the turnover rate varied by a factor of 10^7 [16] and correlated with the gas-phase C–Cl bond strength, which indicated that the rate-determining step involved the scission of the C–Cl bond. Even if only one site is available, it is in fact plausible that the scission of the C–Cl bond occurs on a single Pd atom by analogy with the oxidative addition step found in organometallic chemistry [31,32]. If only one atom is needed, it explains why this reaction appears to be insensitive to the palladium structure. As a direct analogy from organometallic chemistry, the oxidative addition of an alkyl halide satisfies C–Cl bond scission on one Pd atom. We have proposed, by analogy from organometallic chemistry, that the rate-determining step for a generic R–Cl reactant is the oxidative addition

$$\text{R–Cl} + \text{Pd}^0 \rightarrow \text{R–Pd–Cl}$$

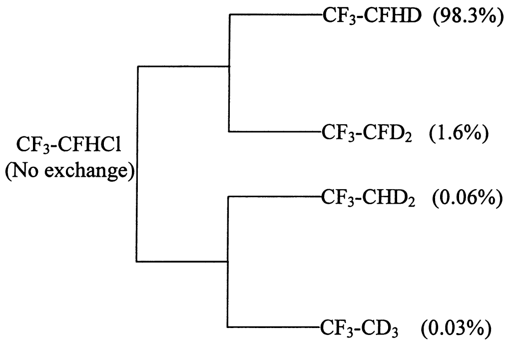
Once the R–Pd–Cl compound is formed, surface hydrogen atoms can react with the R fragment forming R–H and Pd–Cl. The R–H represents a monohydrogenated product, such as CF_3–CFHCl or CF_3–$CHCl_2$.

Information on reaction intermediates was also inferred from the fact that the reaction selectivity is independent of conversion. This observation translates into the fact that once the reactant is adsorbed it follows a reaction pathway on the surface until it desorbs, never returning to the surface again. This fact is also consistent with the finding that as chlorine atoms are substituted by hydrogen atoms, the bond strength of the remaining chlorine atoms become stronger and the molecule once in the gas phase becomes much less reactive than the reactant. For example, the reactivity of CF_3–CFHCl is 3000 times lower than CF_3–$CFCl_2$ [16].

3.2.4. *Reaction steps beyond the rate-determining step*

We still cannot predict or even explain the product distribution of the hydrodechlorination reaction. Although the product distribution suggests possible reaction intermediates on the surface, prediction of product distribution can only be accomplished with a description of the reaction steps beyond the rate-determining one.

Deuterium substitution reactions were conducted to determine more details about hydrodechlorination chemistry. Learning more about the chemistry of HCFC 124 (CF_3–CFHCl) hydrodechlorination is possible with D_2 substitution. The experiments were performed by starting the reaction in a continuous-stirred tank reactor mode, with the objective to reach a steady-state value, and then switching to a batch mode, to reach a high value of conversion. The experimental procedure consisted of carrying out the reaction until the conversion reached a constant value at 16% in the continuous mode and then switching to a batch operation by turning off the inlet and outlet valves from the reactor. The conversion of HCFC 124 at time zero on the batch reactor was thus 16% and the reaction was continued to a final conversion of 54%. The selectivity for exchange on all products was independent of conversion. Note that the carbon containing the chlorine also contains a hydrogen atom. From gas-phase calculations using the Gaussian 98^{TM} software package, the C–H bond is $100\,kJ\,mol^{-1}$ stronger than the C–Cl bond. Considering only the bond strength as a variable, it is expected that C–H bonds should not break at conditions where C–Cl bonds are broken. In fact, an isotope distribution (Scheme 1) verifies that in more than 98% of the products, the C–H bond remains intact. Also, because in 1.6% of the 134a (CF_3–CFD_2) product the hydrogen bond is also



Scheme 1. Deuterium distribution in HCFC 124 (CF_3–CFHCl) hydrodechlorination reaction. (Selectivity independent of conversion from 16% to a final HCFC conversion of 54%. Reaction performed at 240°C, 516 Torr CF_3–CFHCl, 147 Torr D_2. The catalyst was 5% Pd/C-L.) Selectivity in parenthesis.

broken, it is reasonable to assume that if the adsorption step were reversible, some of the hydrogens in the reactant would have been exchanged for deuterium (CF_3–CFDCl would have been detected). The exchange in the reactant was never observed, even at 54% conversion, which indicates that the adsorption step as indicated in step (1) above is irreversible.

The most abundant CFC reaction intermediate on the Pd surface is possibly CF_3–CFH–Pd, representative of a mono-hydrogenated intermediate. Less than 2% of the FC 134a (CF_3–CFH_2) that is formed loses the hydrogen bound to the carbon. The formation of the minor product FC 143a is split between CF_3–CHD_2 and CF_3–CD_3.

To illustrate the complexity and the difficulty of generalizing results with hydrodechlorination reactions, it is instructive to examine the reaction of D_2 exchange with chloroethane (CH_3–CH_2Cl). Campbell and Kemball [18] found that for a Pd film the most abundant deuterated ethane was CH_3–CHD_2, a result that we have reproduced on 5% Pd/C-L. This finding indicates that a carbene intermediate is formed on the surface in contrast with the reaction on CF_3–CFHCl described above where 98% of the time only one deuterium is exchanged, and thus almost no carbene species seem to be forming.

It is evident that explaining selectivity is still not possible. In order to explain reaction selectivity, a complete reaction network with additional steps to those proposed here are necessary.

4. Summary

The reaction steps for the reaction of hydrodechlorination were reviewed and deuterium isotope data was used to elucidate further details of the reaction steps. We have suggested that the rate-determining step is an oxidative addition of an alkyl halide on one Pd atom. Surface H and Cl are in equilibrium with H_2 and HCl in the gas phase and chlorine is the most abundant surface intermediate. Kinetic data on Pd black suggests that the proposed reaction steps are also valid on this bulk sample. The deuterium substitution experiments yielded some insight on hydrodechlorination chemistry. In the hydrodechlorination of HCFC 124 (CF_3–CFHCl), the adsorption is confirmed as irreversible, the C–Cl bond is broken most frequently, although a small percentage of time C–H and C–F bonds are broken. Explaining selectivity is still not possible, and a more complete reaction sequence must be assembled before selectivity can be estimated.

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