Turnover Rate, Reaction Order, and Elementary Steps for the Hydrodechlorination of Chlorofluorocarbon Compounds on Palladium Catalysts[†]

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The rates of hydrodechlorination catalyzed by Pd supported on carbon for four chlorofluorocarbons spanned a range of 7 orders of magnitude. The rates scaled up to the bond strength of the carbon−chlorine bond for the gas-phase reactant. This finding demonstrates that the rate-determining step involves the scission of the C−Cl bond and suggests, through Polanyi and linear free-energy relationships, that rates for other compounds can be estimated if the C−Cl bond strength is known. The reaction orders for the most abundant products are approximately first-order for the chlorine-containing compound, half-order in H_2, and inverse first-order in HCl. The reaction steps consistent with these orders include a rate-determining step involving the adsorption of the chlorofluorocarbon to a single site (which could be a single surface palladium atom) and equilibrated steps between gas-phase H_2, gas-phase HCl, and adsorbed hydrogen and chlorine atoms. The rates on the supported catalysts are comparable to the ones reported before on a Pd foil, indicating that the support does not play a role in the reaction. The product distribution is independent of conversion, implying that the various products are formed from a single visit of the reactant on the surface and not from readsorption of gas-phase products. The four compounds studied were chloropentafluoroethane ($CF_3−CF_2Cl$), 2-chloro-1,1,1,2-tetrafluoroethane ($CF_3−CFClH$), 1,1-dichlorotetrafluoroethane ($CF_3−CFCl_2$), and 1,1,1-trichloro-2,2,2-trifluoroethane ($CF_3−CCl_3$).

1. Introduction

Hydrodechlorination involves the reaction between H_2 and an organic molecule containing a C−Cl bond to form HCl and a C−H bond. This reaction is quite exothermic and thus with the presence of a catalyst it can be driven to completion. The objective of this contribution is to report on the detailed kinetics of the hydrodechlorination reaction for a family of reactants and to use this information to probe the reaction steps. Knowledge of the kinetics is also important in practice to determine the optimal reaction conditions for the hydrodechlorination reaction.

Hydrodechlorination is an important step in many syntheses that use a chlorine-containing molecule as an intermediate, for example, in the manufacture of $CF_3−CFH_2$ (a widely used refrigerant) from $CF_3−CFCl_2$.[1] Another use of hydrodechlorination is for chlorine removal on a compound that needs to be disposed of. This removal is mandatory before the compounds can be released into the environment due to the adverse effect of chloro-containing molecules on the ozone layer or due to the difficulty to naturally biodegrade these compounds. Another recent application of hydrodechlorination is in the conversion of unwanted chlorinated compounds into useful ones as for example in the conversion of waste 1,2-dichloropropane into propylene.[2] The reaction of hydrodechlorination is thus very important. There are however a number of questions that need to be answered before one can take full advantage of this reaction. These include a tabulation of the rates of hydrodechlorination for any given compound, the reaction kinetic orders,

the reaction steps, and a prediction of product distribution. Some of these issues will be presented here.

There are a growing number of studies on the catalysis of hydrodechlorination reactions in the literature. Palladium is the most active catalyst for this reaction[3] and one of the most studied catalysts. Many studies deal with liquid-phase reactions in the presence of a base but we will discuss only gas-phase reactions. The literature range from studies on model catalysts including evaporated films,[4−7] foils,[8] and single crystals[9] to studies on supported catalysts. These latter studies cover a variety of organic molecules including olefins,[10] aromatic,[11,12] and aliphatic compounds[13−20] with some of the molecules also containing fluorine.

One challenge in designing a hydrodechlorination process is that there is a very large number of chlorofluorocarbons and related compounds and the rates are very dependent on the structure of the reactant. For example, ethane is the only saturated hydrocarbon with two carbons, but more than 40 saturated compounds are possible by the combination of two carbons, hydrogen, chlorine, and fluorine. Since it is not practical to measure the rates for all compounds and the rates are very dependent on the structure of the reactant, a method must be devised to predict the rates. It is going to be shown that the rates of reaction for the family of four compounds $CF_3−CF_2Cl$, $CF_3−CFClH$, $CF_3−CFCl_2$, and $CF_3−CCl_3$ correlate very well with the strength of the C−Cl bond. For this family of compounds, if the rate for one compound is known and the C−Cl bond energies are known for all of them, then the rates for the other compounds can be calculated accurately. In addition, the rates of reaction on the supported catalysts and those on foils and single crystals are similar, which suggests

that the reaction is not sensitive to the structure of the catalyst and that the support does not play an active role in the reaction.

Kinetic data is important in deciding what are the important catalytic reaction steps. The reaction steps proposed for the hydrodechlorination of CF_3-CFCl_2 on palladium foils[8] and single crystals of Pd[9] are

$$CFC + * \rightarrow CFC*$$
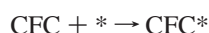
This is the rate-determining step, with all the other steps for the chlorofluorocarbon (CFC) hydrodechlorination not kinetically significant. Here the asterisk represents a catalytic site.

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

$$H_2 + 2* = 2H*$$

$$H* + Cl* = HCl + 2*$$
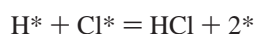
Assuming that Cl* is the most abundant surface intermediate, the final rate will be[8]

$$r = K[CFC][H_2]^{0.5}/[HCl] \tag{1}$$

This is also the kinetic expression for the hydrodechlorination of most of the products for the four compounds tested here over Pd supported on a carbon support. This reaction sequence is also virtually the same as advanced by Sinfelt[21] for the hydrodechlorination of chloromethane, and the rate equation is kinetically similar to the one advanced by Coq et al.[12] for the hydrodechlorination of chlorobenzene. These steps may be applicable in general for hydrodehalogenation reactions on noble metals. However, the rate-determining step as presented above does not show any detail except that it involves one single site. It was proposed before that because only one site is involved, the rate-determining step might involve the nondissociative adsorption of the reactant.[8] This is not a good assumption because in this case the rate should be a weak function of the structure of the reactant, contrary to the findings of this contribution. We will show that the rate-determining step consists of the scission of the carbon—chlorine bond, possibly as an oxidative addition forming a Pd—Cl and a Pd—C bond on the same Pd atom. It is suggested that the active site consists of only one Pd atom, explaining why the reaction is insensitive to the structure of the catalyst. The product distribution also gives a hint to possible reaction intermediates on the surface. We still cannot predict or explain the product distribution and this task would require a description of the reaction steps beyond the rate-determining one.

2. Experimental Methods

2.1. Catalysts. Four catalysts were used in this study. The samples consisted of palladium dispersed on a carbon support. The samples were obtained from Engelhard (0.5% Pd/C-H), DuPont (5% Pd/C-H), or Degussa (5% Pd/C-L) or prepared in house with a support from Cabot Corporation (0.5% Pd/C-L). The designation C-H and C-L on the catalysts stands for high (greater than 1000 m^2 g^{-1}) and low surface area supports (about 100 m^2 g^{-1}). The sample from Engelhard had a metal concentration of 0.5% and was supported on coconut carbon. The sample obtained from DuPont used the same support but had a concentration of Pd of 5%. The support had a total surface area of 1600 m^2 g^{-1} and a pore volume of 0.7–0.8 cm^3 g^{-1}. The pores with a diameter greater than 2 nm accounted for a surface area of 300 m^2 g^{-1} and a pore volume of 0.2 cm^3 g^{-1}. The pores with diameter smaller than 2 nm accounted for the

remaining 1300 m^2 g^{-1} of surface area and 0.5–0.6 cm^3 g^{-1} of pore volume.[22] The average particle size of the Pd particles was about 6.5 nm, which suggests that most of the Pd is in pores greater than 2 nm. A low surface area (29 m^2 g^{-1}) carbon black obtained from Cabot Corporation (Sterling series) was used as a support for a 0.5% Pd/C catalyst. The catalyst was prepared by the incipient wetness method using an aqueous solution of $PdCl_2$ obtained from Aldrich. For the dissolution of $PdCl_2$, 2 mol of HCl were added for every mole of salt with heating applied. From a pore size analysis, the distribution of pore size ranged from 5 to 100 nm with a total pore volume of 0.3 cm^3 g^{-1}. The 5% Pd/C obtained from Degussa was supported on a carbon black with serial number E 9011 XR/W 5% had a BET area of 107 m^2 g^{-1} and a total pore volume of 1.15 cm^3 g^{-1}. These samples were ground with a mortar and pestle and the fraction between 40 and 60 mesh was retained for use in the reactions.

The pore size distribution and pore volume for the Cabot support and Degussa catalysts were measured with a Quantachrom Autosorb-1 volumetric sorption analyzer. The pore volume for the 0.5 and 5% Pd/C-H was measured at the DuPont Experimental Station.[22]

2.2. Reactants. The CFC samples were obtained from the DuPont Experimental Station (CFC 114a—CF_3—$CFCl_2$ and CFC 115—CF_3—CF_2Cl), Lancaster Synthesis (CFC 113a—CF_3—CCl_3), and DuPont Suva Refrigerants (HCFC 124—CF_3—CFClH). The HCl mixture was obtained from Matheson. Three tanks were used during the course of experiments with 18.9%, 15.6%, and 20.7% HCl in He. This mixture was made at Matheson Gas from technical grade HCl and Matheson purity He. A mixture of H_2 and methane, certified as ultrahigh purity, was obtained from Matheson. This mixture contained 1033 ppm methane, used as an internal standard. The hydrogen—methane mixture was passed through a filter containing 5% Pd/C catalyst to react any oxygen in the line into water and trap it on the carbon support. The H_2 (BOC gases) was passed through a Pd membrane (Matheson hydrogen purifier model 8361) before use. Reaction grade helium was obtained from BOC gases and passed through a mass spectrometer gas trap (HP model 5182-3467).

2.3. Reactor Configuration. The delivery of reaction gases was controlled by mass flow controllers (Porter Instrument Co.). CFC 113a (CF_3—CCl_3) is a liquid at room temperature and was added to the reaction mixture by passing helium through the CFC in a saturator. The mass flow controllers were calibrated with bubble flow meters except for the He—HCl mixture. In this case, the flow rates were determined by varying the composition of a mixture of He/HCl and H_2/CH_4, analyzing the mixture by gas chromatography, and observing the change in signal of the methane peak.

Reactions were run in a quartz continuous-stirred tank reactor (CSTR) with the catalyst supported on a fritted quartz disk within the reactor and a thermocouple well in contact with the catalyst to allow for precise measurement of the catalyst temperature. The reaction mixture was mixed with a Senior Flexonics pump model MB-21 at a flow rate of about 1400 sccm. The flow rate into the CSTR circuit from the gas delivery portion of the system and the flow rate out of the CSTR circuit were about 100 sccm. The system was kept at ambient pressure. Reaction products were analyzed with a gas chromatograph (HP 5880) and separated with a 5% Krytox 143AC, 60/80 Carbopack B HT 20' × $^1/_8$" column (Supelco, Inc.). Each of the reactant chlorofluorocarbon and products were calibrated against the methane standard in the hydrogen—methane mixture. Response factors calculated from these calibrations were used to convert

Hydrodechlorination of Chlorofluorocarbon Compounds

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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
0.5% Pd/C-H	1640	7.6	16.7	6.7
5.0% Pd/C-H	1600	85.8	18.0	6.2
0.5% Pd/C-L	29	3.8	8.0	14
5.0% Pd/C-L	107	39.1	8.4	13.3

^{a} Percentage of metal exposed (PME), determined by H_2-O_2 titration at 100 °C. ^{b} Particle size determined from $d = 112/$PME.

the GC signal counts into relative volumetric flow rates. After exiting the system, the gases flowed through a caustic wash (NaOH) to neutralize the HCl in the stream before being vented.

2.4 Data Collection Procedure. Before a new sample of catalyst was used, it was first reduced with a flow of 50 sccm H_2 at 300 °C for 3 h. At the start of each set of reactions, the catalyst (200−500 mg) was reduced with 50 sccm of H_2 at 150 °C for 30−60 min. During the course of the experiments, the changes in concentration and temperature were chosen in a random order so that any variation in the system would not introduce a systematic error. At the end of each experiment, the conditions of the first data point in the series were duplicated and another data point taken. By ensuring that this last point agreed with the first point it could be shown that there was no significant deactivation of the catalyst during the time frame of the experiment.

2.5. Surface Area Measurements. The 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 the procedure of Benson et al.[23] with the reactor temperature held constant at 100 °C. The experimental setup consists of a static system with calibrated volumes where the amount of gas adsorbed on the catalyst can be calculated by a change in pressure measured with a pressure transducer (MKS model 127). The samples were reduced in flowing H_2 (50 cm^3 min^{-1}) for 3 h at 300 °C before the Pd surface area measurements. In subsequent measurements with the same sample, it was reduced in flowing H_2 (50 cm^3 min^{-1}) for 0.5 h at 100 °C. The crystallite size based on chemisorption measurements was estimated from the expression d (nm) = 112/(percentage of metal exposed). This expression assumes spherical particles and a Pd surface atom density equal to an average of the low index planes of 1.27×10^{19} atoms.[24]

2.6. Error Analysis. We have compared the data for the same experiment carried out at identical conditions to calculate the experimental error. The errors in reaction orders are at maximum 10% or maximum 0.1 in 1.0. For the apparent activation energies, the errors were about 10 kJ mol^{-1}. The reproducibility of turnover rate measurements were better than 10%.

3. Results

3.1 Catalyst Properties. Table 1 summarizes the properties of the catalysts used in this study. Four different catalysts with a loading of Pd of 0.5 and 5% and three different carbon supports were used. The high surface area support is designated C-H, and the two low surface area ones are designated C-L. The carbon supports varied in surface area but most importantly in the amount of microporosity. The low surface area supports are nonmicroporous. This property will be important since some of the reactants will condense in the micropores under reaction conditions. The data included in Table 1 are for the catalysts before reaction. Since no deactivation was observed during reaction, except in instances to be discussed below, we do not

TABLE 2: Test for the Presence of Heat and Mass Transfer Gradients

catalyst	PME^a	TOR (s^{-1})^b
0.5% Pd/C-H	16.7%	4.1×10^{-2}
5% Pd/C-H	18.0%	3.9×10^{-2}

^{a} Percentage of metal exposed. ^{b} Turnover rates corrected for 45 Torr of CF_3-CFCl_2, 90 Torr of H_2, 75 Torr of HCl, and 140 °C.

expect any significant change in the properties of the catalyst after reaction.

3.2. Test for Possible Heat and Mass Transfer Limitations. To test for the presence of heat and mass transfer limitations, the Madon−Boudart test[25−27] was employed. The test consists of measuring reaction rates over two catalysts with different metal loading but with similar percentage of metal exposed (PME). The test was performed for the hydrodechlorination of CF_3-CFCl_2 (CFC 114a) and the catalyst with the highest surface area. The results are summarized in Table 2.

3.3. Kinetic Results. The catalytic hydrodechlorination of a family of four compounds was carried out over Pd catalysts supported on carbon. The data used to derive the reaction orders and activation energy will be presented in detail for one of the compounds (CF_3-CFCl_2). For the other three compounds, only the numerical results in tables will be presented. The range where the data was collected will be presented in the text. As will be presented below, the product distribution is given together with the turnovers rates, but it is important to emphasize that it is independent of conversion. Different catalysts were used for the experiments, from low to high total surface area, and thus with different amounts of micropores. Microporosity affected the determination of the order of reaction for the chlorofluorocarbon. Note also that the rates could not be measured at the same conditions for all the compounds since their reactivities span a range of 10^7. The reaction data will be compared at the same conditions at the end of this section. Results from the literature for a Pd foil were also included for direct comparison.

No deactivation of the samples used for kinetic tests was observed for the duration of the tests. The same sample was usually used for a number of days in the determination of kinetic parameters.

3.3.1. CF_3-CFCl_2. The hydrodechlorination reaction of CFC 114a (CF_3-CFCl_2) was carried over a low and a high surface area catalyst and the experimental results are summarized in Table 3. Data from the literature on a Pd foil is also shown for comparison. Three main products are formed corresponding to the hydrodehalogenation on the carbon that contains chlorine. As the number of halogens removed increases, there is a corresponding increase in the apparent activation energy for the reaction. The CFC orders (Figure 1), H_2 orders (Figure 2), and HCl orders (Figure 3) are close to 1, 0.5, and −1, respectively, and were determined by varying the amount of reactant under study and keeping all the other variables constant. In particular, note that because the HCl produced in the reaction inhibits the rates, excess HCl was added in all experiments (except for the HCl order determination) to minimize the number of variables. The conversion of CFC 114a was varied from 0.3% to 15% for the 0.5% Pd/C-H catalysts, with the selectivity remaining constant toward all three products. The selectivity was also constant for the other catalysts. Apparent activation energies were determined from Arrhenius plots as illustrated in Figure 4.

The conditions for the determination of apparent activation energies were 110−140 °C, 170 Torr of CFC, 340 Torr of H_2,

TABLE 3: Kinetic Data for CF₃−CFCl₂ (CFC 114a) Hydrodechlorination

catalyst	product	TOR (s⁻¹)[a]	selectivity[b]	E_a (kJ mol⁻¹)	reaction order dependence		
					CFC 114a	H₂	HCl
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
0.5% Pd/C-H	CF_3-CH_3	1.9×10^{-2}	3.6%	130	0.50	0.20	−1.00
	CF_3-CFH_2	4.8×10^{-1}	88.1%	130	0.45	0.40	−1.00
	$CF_3-CHFCl$	4.5×10^{-2}	8.3%	125	0.40	0.45	−0.70
Pd foil[c]	CF_3-CH_3	1.4×10^{-3}	2.6%	95	0.90	−0.20	−0.70
	CF_3-CFH_2	4.5×10^{-2}	85.5%	110	0.80	0.45	−1.20
	$CF_3-CHFCl$	6.3×10^{-3}	12.0%	100	0.90	0.50	−1.00

[a] Turnover rates corrected for 150 Torr of CF₃−CFCl₂, 200 Torr of H₂, 20 Torr of HCl, and 150 °C. [b] The selectivity is independent of conversion. [c] Data from Ribeiro et al.[8] Reaction orders were assumed to be 1, 0.5, and −1 for CFC 114a, H₂, and HCl, respectively.
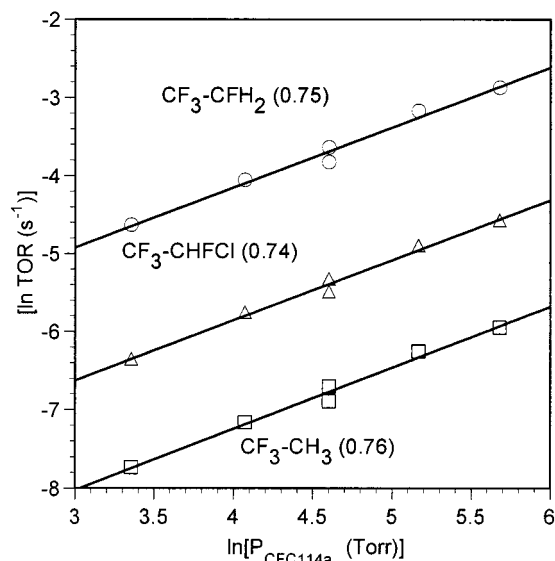

Figure 1. Determination of reaction order in CFC 114a (CF₃−CFCl₂) on 0.5% Pd/C-L. Experiments carried out at 130 °C, 28−300 Torr of CFC 114a, 233 Torr of H₂, 35 Torr of HCl. Turnover rates corrected to 200 Torr of H₂, 20 Torr of HCl.

Figure 2. Determination of reaction order in H₂ for the reaction of CFC 114a (CF₃−CFCl₂) on 0.5% Pd/C-L. Experiments carried out at 130 °C, 110 Torr of CFC 114a, 65−430 Torr of H₂, 42 Torr of HCl. Turnover rates corrected to 150 Torr of CFC 114a, 20 Torr of HCl.

and 50 Torr of HCl. For the CFC order determination, the conditions were 130 °C, 30−300 Torr of CFC, 230 Torr of H₂, and 35 Torr of HCl. For the H₂ order, the conditions were 130 °C, 120 Torr of CFC, 65−430 Torr of H₂, and 40 Torr of HCl. For the HCl order, the conditions were 140 °C, 95 Torr of CFC, 190 Torr of H₂, 10−90 Torr of HCl.

3.3.2. CF₃−CCl₃. The same catalysts used above were also used for the hydrodechlorination (HDCl) of CF₃−CCl₃ (CFC 113a). The kinetic parameters for the hydrodechlorination of CFC 113a are summarized in Table 4. The activation energies increase with the number of chlorine atoms removed. The product distribution is highest for the fully hydrogenated, chlorine-free product, CF₃−CH₃. The selectivity toward the monohydrogenated product, CF₃−CFHCl₂ is significant (~26%) at reaction conditions. The reaction products are much less reactive than the reactant, and the reaction observed is not in series. In fact, the reactant conversion was varied from 0.4 to 4.2% with the selectivity remaining constant toward all three products.

The conditions for the determination of apparent activation energies were 40−65 °C, 56 Torr of CFC, 150 Torr of H₂, and 30 Torr of HCl. For the CFC order determination, the conditions were 45 °C, 15−50 Torr of CFC, 150 Torr of H₂, and 35 Torr of HCl. For the H₂ order, the conditions were 60 °C, 25 Torr of CFC, 35−225 Torr of H₂, and 20 Torr of HCl. For the HCl
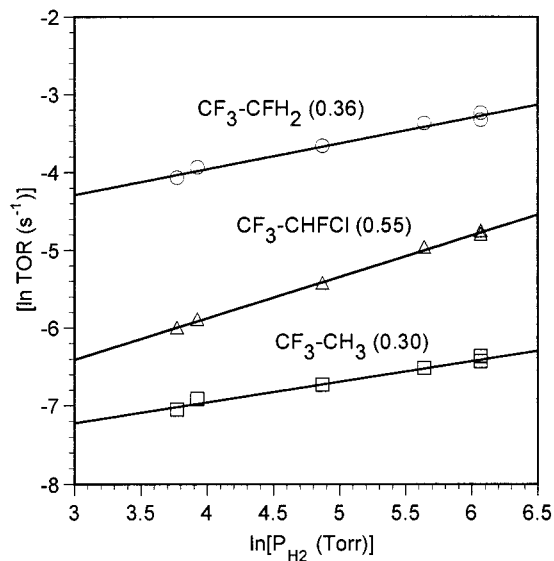
order the conditions were 45 °C, 16 Torr of CFC, 100 Torr of H₂, and 2−100 Torr of HCl.

3.3.3. CF₃−CF₂Cl. The results of the hydrodechlorination (HDCl) of CF₃−CF₂Cl (CFC 115) are summarized in Table 5. The main products formed were CF₃−CHF₂ and CF₃−CH₃ with a selectivity of almost 99% to CF₃−CHF₂. Selectivity to CFC 115 products, CF₃−CH₃ and CF₃−CHF₂, remained constant with varying conversion (1.4−13.6%). Because the amount of the minor product formed is so small, we could not analyze its presence with the mass spectrometer but used the retention time in the gas chromatograph as an identification parameter. It is surprising to find that two C−F bonds are hydrogenated in this case.

The conditions for the determination of apparent activation energies were 220−295 °C, 180 Torr of CFC, 330 Torr of H₂, and 40 Torr of HCl. For the CFC order determination, the conditions were 260 °C, 90−340 Torr of CFC, 200 Torr of H₂, and 25 Torr of HCl. For the H₂ order, the conditions were 260 °C, 180 Torr of CFC, 30−400 Torr of H₂, and 30 Torr of HCl. For the HCl order the conditions were 260 °C, 145 Torr of CFC, 200 Torr of H₂, and 10−65 Torr of HCl.

3.3.4. CF₃−CHFCl. The last compound to be reported in this study was a hydrochlorofluorocarbon, CF₃−CHFCl or HCFC 124. The kinetic results of HCFC 124 are summarized in Table 6. Two products are formed, CF₃−CFH₂ and CF₃−CH₃ with a high selectivity for the formation of the HDCl product, CF₃−
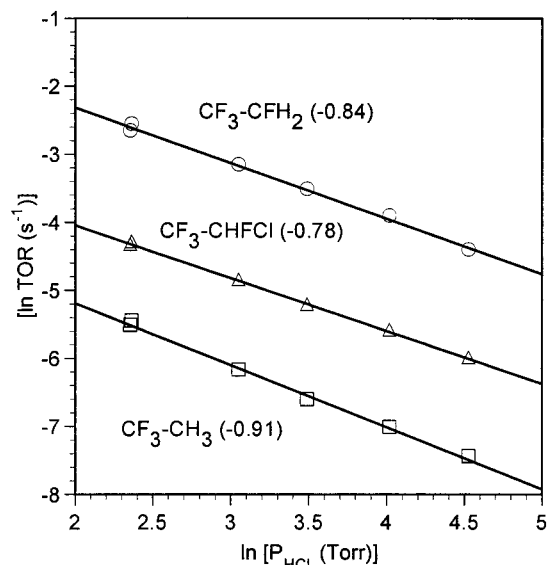
Figure 3. Determination of reaction order in HCl for the reaction of CFC 114a (CF_3-CFCl_2) on 0.5% Pd/C-L. Experiments carried out at 140 °C, 95 Torr of CFC 114a, 192 Torr of H_2, 10–90 Torr of HCl. Turnover rates corrected to 150 Torr of CFC 114a, 200 Torr of H_2
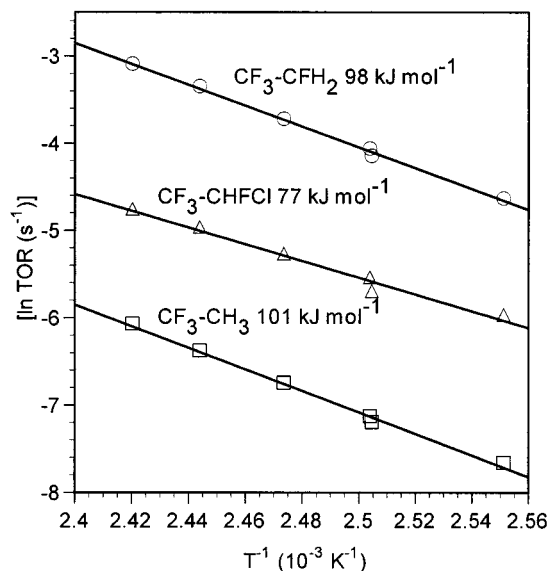

Figure 4. Arrhenius plot for the reaction of CFC 114a (CF_3-CFCl_2) on 0.5% Pd/C-L. Experiments carried out at 110–140 °C, 168 Torr of CFC 114a, 341 Torr of H_2, 49 Torr of HCl. Turnover rates corrected to 150 Torr of CFC 114a, 200 Torr of H_2, 20 Torr of HCl.

CFH_2. The conversion of HCFC 124 was varied from 0.2% to 2.5%, and selectivity values remained constant for both products. There is a higher amount of CF_3-CH_3 formed for the 0.5% Pd/C–H catalyst. Because the reaction temperature is the highest for this compound, deactivation was observed on one of the catalyst samples 0.5% Pd/C-L (not shown in Table 6). This catalyst deactivated and showed a lower selectivity (92%) toward the most abundant product. The reason for this deactivation was believed to be the presence of an impurity in the carbon support.

The conditions for the determination of apparent activation energies were 210–240 °C, 200 Torr of CFC, 320 Torr of H_2, and 40 Torr of HCl. For the CFC order determination, the conditions were 220 °C, 130–300 Torr of CFC, 200 Torr of H_2, and 20 Torr of HCl. For the H_2 order, the conditions were 220 °C, 165 Torr of CFC, 30–400 Torr of H_2, and 30 Torr of

HCl. For the HCl order, the conditions were 225 °C, 130 Torr of CFC, 200 Torr of H_2, and 10–70 Torr of HCl.

3.4. Condensation of CFC in the Pores of the Support. On the Pd catalysts with a carbon support with an area of 1600 m^2 g^{-1} (0.5% Pd/C–H), the reaction order on CF_3-CFCl_2 for the three reaction products is ~0.5 (Table 3), much lower than the order postulated (1.0) from the proposed mechanism discussed in the Introduction (eq 1). An explanation for this effect is that most of the surface area of the support is in the microporous regime (1300 m^2 g^{-1}), which will condense the reactant even if the reaction temperature is above its boiling point (3.6 °C), a known property of microporous solids. In addition, if the reactant is in the liquid state, the reaction order will be zero. The lower than 1.0 reaction order in CFC suggests that a fraction of the carbon support may be filled with liquid at reaction conditions. To determine if the surface is saturated with CFC 114a, adsorption isotherms at 25 °C and 100 °C were obtained. At 25 °C, the adsorption of CFC per gram of catalyst was 0.61 cm^3, a volume that is close to the total pore volume of 0.7–0.8 cm^3 g^{-1} determined with N_2 adsorption. At 100 °C, the amount of CFC 114a adsorbed per gram of catalyst (0.4 cm^3 g^{-1}) is still substantial, suggesting that the CFC may be condensing on the catalyst micropores at reaction temperature (120 °C).

To determine if the low reaction orders were due to the saturation of the Pd pores, a support with a low surface area and virtually no microporosity was prepared. The 0.5% Pd/C-L used a carbon support with a total pore volume of ~0.3 cm^3 g^{-1}, and with no detectable microporosity (Table 1). The reaction order in the three products of the CFC 114a reaction increased from ~0.5 to ~0.75, as shown in Table 3. The reaction orders over the low surface area catalyst are in very good agreement with the reaction orders determined over a Pd foil.

Problems with catalyst pore condensation were more severe with CFC 113a (CF_3-CCl_3) because its boiling point (45.7 °C) is close to the reaction temperature (50 °C). Thus, the reaction order in CFC 113a over the 0.5% Pd/C–H microporous catalyst in the three products range from 0.1 to 0.3 (Table 4), much lower than the proposed order of 1.0. The reaction orders over the nonmicroporous (0.5% Pd/C-L) catalyst increased to the same values found on a foil (Table 4). The reaction orders in CFC 115 (CF_3-CF_2Cl) and HCFC 124 ($CF_3-CHFCl$) were not affected by the change in catalyst support. For both catalysts, the reaction order in CFC was ~1 for the main product and ~0.9 for the minor product. Condensation is unlikely to occur on the catalyst pores for CFC 115 and HCFC 124 due to the much larger difference between boiling point (~−20 °C) and reaction temperature (~240 °C).

3.5. Bond Energy Calculations. The kinetic data above allowed us to calculate the overall rates of hydrodechlorination at any reaction condition for the family of four compounds tested (Table 7). The value for the comparison of rates was chosen based on the conditions necessary for the least amount of extrapolation. Temperature was the variable that changed the rate most significantly and was adjusted to keep reaction rates at a level where they could be precisely measured. The relative turnover rate in Table 7 shows that the rates vary by 7 orders of magnitude, and thus the rate of hydrodechlorination is very dependent on the structure of the molecule. From a practical point of view it is highly desirable to be able to predict, or at least correlate, the rate of hydrodechlorination with an easily measured quantity since there is a large number of chlorofluorocarbon compounds available. We attempted to correlate the rate of hydrodechlorination with the bond dissociation energy

TABLE 4: Kinetic Data for CF$_3$−CCl$_3$ (CFC 113a) Hydrodechlorination

					reaction order dependence		
catalyst	product	TOR (s^{-1})^a	selectivity^b	E_a (kJ mol^{-1})	CFC 113a	H$_2$	HCl
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$_2$Cl	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
0.5% Pd/C-H	CF$_3$−CH$_3$	4.3 × 10^{-1}	85.3%	125	0.30	0.40	−0.90
	CF$_3$−CH$_2$Cl	2.7 × 10^{-3}	1.4%	100	0.15	0.65	−0.85
	CF$_3$−CHCl$_2$	5.0 × 10^{-2}	13.4%	95	0.15	0.40	−0.45
Pd foil^c	CF$_3$−CH$_3$	2.4 × 10^{-1}	67%	100	0.60	0.60	−1
	CF$_3$−CH$_2$Cl	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} Turnover rates corrected for 30 Torr of CF$_3$−CCl$_3$, 120 Torr of H$_2$, 20 Torr of HCl, and 70 °C. ^{b} The selectivity is independent of conversion. ^{c} Data from Ribeiro et al.[32]

TABLE 5: Kinetic Data for CF$_3$−CF$_2$Cl (CFC 115) Hydrodechlorination on the 0.5% Pd/C-H Catalyst

				reaction order dependence		
products	TOR^a (s^{-1})	selectivity^b	E_a (kJ mol^{-1})	CFC 115	H$_2$	HCl
CF$_3$−CH$_3$	5.3 × 10^{-7}	1.4%	130	1.00	0.30	−0.30
CF$_3$−CHF$_2$	3.8 × 10^{-5}	98.6%	120	1.20	0.40	−0.75

^{a} Turnover rates corrected for 150 Torr of CF$_3$−CF$_2$Cl, 200 Torr of H$_2$, 20 Torr of HCl, and 150 °C. ^{b} The selectivity is independent of conversion.

of the C−Cl bond but could not find values in the literature for the bond energy for the four compounds used. The C−Cl bond energy however can be calculated by different methods. We believe that the easiest method is the group additivity method, which is available specifically for chlorofluorocarbons and related compounds.[28] This method may not be very precise but due to its simplicity it can be used to get a preliminary idea about the bond energies. We also used ab initio methods to calculate the C−Cl bond energies. The computer program Gaussian 94 was used to calculate the C−Cl bond dissociation energy by density functional theory (DFT), with the B3PW91/6-311+G(2d,p)//B3PW91/6-311+G(2d,p) model applied (Table 7). We checked for consistency of results by calculating the bond energy difference when the basis set was varied. The values for the bond energies as the largest basis set and theory level were approached did not vary significantly. Note that the bond dissociation is not calculated directly but by a difference of energies following the expression $E(A−B) = E(A) + E(B) − E(AB)$.

Once the bond energies were available, we correlated them with the rates of reaction using known correlations in catalysis as described in detail by Boudart.[29] Starting with the relationship of Polanyi,[27] which states that for a family of similar reactions the difference in activation energy can be related to the difference of reaction enthalpy,

$$\Delta E_a = \alpha \Delta |\Delta H|$$

and from the Arrhenius equation

$$k = k_0\, e^{-E_a/RT}$$

combined with the assumption that k_0 is identical for all the reactions in this group, the relative rates can be established for components in the family

$$\frac{k_1}{k_2} = e^{-\Delta E_a/RT} = e^{-\alpha \Delta |\Delta H|/RT} \quad (2)$$

The $\Delta(\Delta H)$ in eq 2 is for the reaction R−Cl + Pd → R−Pd−Cl, where Pd represents the catalytic site. The enthalpy difference $\Delta(\Delta H)$ between two family members is composed of three terms, corresponding to dissociation of the R−Cl bond (R−Cl → R + Cl, ΔH_{R-Cl}), formation of the R−Pd bond (R + Pd → R−Pd, ΔH_{R-Pd}), and formation of Pd−Cl bond. Note that the enthalpy term for the Pd−Cl bond is common on all members and will cancel out when the difference of enthalpy is calculated. It will be shown next that using a linear free energy formalism, similar to the one in the Hammett relation used in physical−organic chemistry, one needs to calculate only the ΔH_{R-Cl} for the reaction R−Cl → R + Cl to calculate the enthalpy difference ($\Delta(\Delta H)$). Suppose one has the following family of reactions with two corresponding members of each family displayed:

$$\left.\begin{array}{l} R-Pd \rightarrow R + Pd \\ R'-Pd \rightarrow R' + Pd \end{array}\right\}\text{family I} \qquad \left.\begin{array}{l} R-Cl \rightarrow R + Cl \\ R'-Cl \rightarrow R' + Cl \end{array}\right\}\text{family II}$$

Family II is the reference family and family I is the one we would like to find the difference in free energy. The linear relationship between standard free energy for a family of reactions assumes that $(\Delta G^1 - \Delta G_0^1) = \beta(\Delta G^2 - \Delta G_0^2)$, where the superscript refers to the family in question. The constant β depends on the substituent, Pd versus Cl, but will be the same for any two members of the families. If we assume next that entropy factors are the same for the members of the family, then $\Delta(\Delta H^1) = \beta\Delta(\Delta H^2)$. The difference of enthalpy for the reaction of interest will then be $\Delta(\Delta H) = (1 - \beta)\Delta(\Delta H_{R-Cl})$. Substituting the value for $\Delta(\Delta H)$ in eq 2 allows one to calculate the turnover rate of any reaction member in the series as a function of the rate constant of a reference member if the difference in enthalpy of the dissociation reaction in the gas phase (ΔH_{R-Cl}) is known. The experimental value that gives the best fit is one that corresponds to $\alpha(1 - \beta) = 1$. A calculation based on this method is shown in Table 7.

4. Discussion

The objective of this work was to measure the rates of hydrodechlorination and reaction orders for a family of compounds, correlate the magnitude of rates to the bond energy of the C−Cl bond, and to derive information on the reaction steps that are kinetically significant. We will start the discussion by pointing out possible artifacts that may provide incorrect results.

4.1. Possible Artifacts: Heat and Mass Transport, Condensation of CFC on Pores, Inhibition by HCl. Our first task was to show that the rates could be measured without the interference of heat and mass transport gradients, since this reaction is quite exothermic. For that purpose we used the

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TABLE 6: Kinetic Data for $CF_3-CHFCl$ (HCFC 124) Hydrodechlorination

					reaction order dependence		
catalyst	product	TOR $(s^{-1})^a$	selectivity[b]	E_a (kJ mol^{-1})	HCFC 124	H_2	HCl
0.5%Pd/C-H	CF_3-CH_3	8.4×10^{-4}	2.9%	145	0.85	0.20	−0.20
	CF_3-CFH_2	2.8×10^{-2}	97.1%	130	1.00	0.35	−0.85
5%Pd/C-L	CF_3-CH_3	7.6×10^{-5}	0.4%	130	0.95	0.30	−0.30
	CF_3-CFH_2	2.0×10^{-2}	99.6%	105	1.10	0.45	−0.80
Pd foil[c]	CF_3-CH_3	1.6×10^{-4}	0.8%	120	0.60	0	−1
	CF_3-CFH_2	1.9×10^{-2}	99.2%	100	0.90	0	−1

[a] Turnover rates corrected for 250 Torr of $CF_3-CHFCl$, 250 Torr of H_2, 25 Torr of HCl, and 230 °C. [b] The selectivity is independent of conversion. [c] Data from Ribeiro et al.[8]

TABLE 7: Comparison of Measured Turnover Rates to Predicted Values

				relative TOR calculated by		
reactant	TOR $(s^{-1})^a$	relative TOR	C−Cl bond energy (kJ mol^{-1})[b]	GAM[c]	enthalpy[d]	bond energy[e]
CF_3-CF_2Cl	4×10^{-5}	1	325	1	1	1
$CF_3-CHFCl$	1×10^{-4}	3	323	1	1.4	1.4
CF_3-CFCl_2	3×10^{-1}	7×10^3	294	18	1.5×10^3	5×10^3
CF_3-CCl_3	5×10^2	1×10^7	261	2×10^6	2×10^7	7×10^7

[a] Turnover rates corrected for 150 Torr of CF_3-CFCl_2, 200 Torr of H_2, 20 Torr of HCl, and 150 °C. [b] Gaussian DFT method B3PW91/6-311+G(2d,p)// B3PW91/6-311+G(2d,p). [c] group additivity method (GAM), Zhang and Pollard.[28] [d] Gaussian DFT method B3PW91/6-311+G(2d,p)// B3PW91/6-311+G(2d,p). [e] Gaussian DFT method B3PW91/6-311+G(2d,p)// B3PW91/6-311+G(2d,p).

Madon−Boudart test.[25] This test consists of measuring the rates in catalysts with the same percentage of metal exposed (same particle size) but different loading. Table 2 shows that the rates for the two catalysts are not affected by the loading, which indicates that the kinetic data is free of transport limitations for the measurement of CFC 114a (CF_3-CFCl_2). We did not apply the Madon−Boudart test for the other catalysts or for the other compounds. The catalyst tested in Table 2 is the one with the support with the highest surface area and microporosity and thus the one where transport limitations would be most severe. It is also reasonable to assume that for the other compounds the measurements will be free of transport limitations since the turnover rates were kept in the same range of values (10^{-2} s^{-1}) by adjusting the temperature.

From the data presented on section 3.4, we can conclude that the lower reaction order on CFC for the support with significant microporosity was caused by condensation of CFC in the micropores. The measured value, without pore condensation, is closer to 1.0 (Table 3). Thus, the data on the microporous supports have to be interpreted carefully. Note that these data are show here only for purposes of comparison. The kinetic parameters are taken from the catalysts where no condensation were observed.

The last artifact to be discussed, and the most pervasive, is the strong inhibiting effect of HCl as observed by a reaction order of close to −1 for the four halogen-containing compounds used in this study. This effect was reported in other studies by Campbell and Kemball[4] and Coq et al.[12] Note that inhibition is distinct from poisoning since it is reversible and caused simply by competition of sites between HCl and the reactant (see mechanism discussed in the Introduction). Thus, the amount of HCl present (or conversion) should be specified when rates are reported. For example, the rate would increase by about 10 times if the concentration of HCl was decreased by 10 times. Another effect of not considering the inhibition by HCl, to be discussed below, is an "apparent activation energy" 2 times lower than the correct one. It is thus critical to establish and correct the effect of HCl for hydrodechlorination reactions. Note that a more complex interaction of HCl with a Pt particle was discussed by Zhang and Beard.[30] The authors suggested that on small particles

of Pt (about 0.5 nm) HCl can bind irreversibly decreasing the rate for hydrodechlorination of CCl$_4$ but on larger particles (about 6 nm) the effect is not present.

4.2. Reaction Orders. The reaction orders were measured for all reaction products. There are at least two products formed when the reactants are hydrogenated, and in some cases three. The reason for the multiple products is that all halogens (including fluorine) can be substituted by a hydrogen in the carbon that contains chlorine. It is important to state again that the reaction orders in CFC on the high surface area catalyst 0.5% Pd/C−H are lower than expected due to condensation in the pores of the support. The results for the CFC order will be discussed for the catalysts where no condensation is observed.

As discussed in the Introduction, the reaction order proposed before for hydrodechlorination is first order in CFC, half order in H_2, and inverse first order in HCl. For the first chlorine removed, the results are close to the proposed values with the following observations. (1) The orders for the CFCs are quite similar to the values found for a foil and are slightly lower than 1.0. (2) The orders for H_2 and HCl are quite close to the expected value of half and inverse first order. It is important to note that the discrepancies are not a result of an error in the measurements. The cause for these discrepancies may be related to the shortcomings of our proposed kinetic mechanism, where a multistep process is being simplified by a unique rate-determining step.

For two of the compounds tested (CF_3-CFCl_2 and CF_3-CCl_3), a second chlorine is also removed. The kinetic orders again conform to the expected rates. When a third halogen is removed to form CF_3-CH_3, the reaction order in H_2 and HCl however is much lower. In three of the compounds, one fluorine atom was removed, and in the fourth compound (CF_3-CCl_3) another chlorine atom was removed. Whatever the case, the reaction order in H_2 is lower than the expected value of 0.5 while the reaction order is also low for HCl on $CF_3-CFHCl$ and CF_3-CF_2Cl. One explanation is that this is a reaction network and the assumed rate-determining step may not be a good approximation for the reaction mechanism where two very strong bonds are broken. The lower order dependence in H_2 for this reactant was reported before for a foil[8] and two single

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crystals[31] and can be seen in Tables 3 and 6 for the foil data. The hydrogen orders for CF_3-CCl_3 on the foil (Table 4) may be due to absorption of hydrogen in the Pd foil at the low reaction temperatures for that experiment.[32]

4.3. Reaction Selectivity. An important feature of all four of the hydrodechlorination reactions studied is the reaction selectivity. The number of reaction products with varying degrees of hydrogenation were two or three depending on the reactant molecule. Experiments were conducted to determine the effect of conversion on the selectivity for each reactant. The selectivity toward the products remained constant as the conversion was varied in all catalysts tested and for all four reactants. This fact implies that the products are formed in a parallel reaction network on the surface. In other words, once the reactant adsorbs, it desorbs as a product that does not return to the surface again. This fact is supported by the observation that the reaction products are much less reactive than the reactant, and once they leave the surface of the catalyst they do not compete for adsorption with the reactant. The addition of hydrogen makes the remaining C−Cl bonds stronger. For example, as can be verified in Table 7, for the reaction of CF_3-CFCl_2 the monohydrogenated product ($CF_3-CFHCl$) is about 3000 times less active than the reactant.

Although the selectivity for a given catalyst does not change during an experiment, the selectivity of the reaction for different catalysts may change. This change in selectivity is usually associated with a deactivation. One explanation, based on the results of Table 6, is that impurities on the carbon play a role in the reaction. The catalyst 0.5% Pd/C−H (Table 6) based on a coconut support shows a lower selectivity toward the main product than a sample supported on a high purity carbon (5% Pd/C-L). It is possible that due to the higher temperature used in the hydrodechlorination of $CF_3-CFHCl$ (about 250 °C), impurities on the carbon support are migrating and interacting with Pd and changing its selectivity. An even bigger change in selectivity was observed for the 0.5% Pd/C-L sample (not shown in Table 6) where the initial selectivity to CF_3-CFH_2 decreased to 92% with the sample also deactivating as a function of time. The Pd surface area decreased by a factor of 4 after reaction. This is a carbon black not purified for catalysis applications and impurities may be migrating to the Pd particles. Another example on the role of impurities on the carbon support is described by van de Sandt et al.[33] on the performance of hydrodechlorination catalysts. A more indirect effect is the interaction between the support and Pd as proposed by Coq et al.[34] to explain a large change in the selectivity for the reaction of CF_2Cl_2 hydrodechlorination over different supports. Another possibility is that the reaction is sensitive to the structure of the catalyst and structural changes on the Pd particles are induced by the support. However, this does not seem to be the case, as different single crystal structures of Pd did not change substantially the selectivity, but the addition of an impurity (sulfur) changed the selectivity drastically.[9] In addition to selectivity changes, Krishnankutty and Vannice[35] have proposed that the carbon support modifies the properties of the Pd catalyst for some reactions by providing interstitial and surface atoms to Pd.

4.4. Apparent Activation Energy. The apparent activation energy for the various reactions varied from 80 to 145 kJ mol^{-1}. There is a small but definite trend of a higher apparent activation energy as more halogens are removed. This trend does not support the existence of a common rate-determining step for all reaction products since an unique rate-determining step for all of them also implies an unique activation energy value. The

fact that the activation energy increases as more halogens are removed is an indication that a more complex reaction network than the one we are proposing for this reaction is necessary, in other words, that the rate-determining step assumption is only an approximation.

The activation energy is quite similar between the low surface area support catalyst (0.5% Pd/C-L) and the Pd foil. However, the activation energy was always higher on the high surface area support catalyst (0.5% Pd/C-H). As discussed above, one difference with this catalyst is the microporous support which causes condensation of the CFC on the pores at reaction temperature. As will be discussed next, this condensation cannot explain a higher activation energy. We measured the "enthalpy of interaction" for CF_3-CFCl_2 between 25 and 100 °C using the Clausius−Clapeyron relation. The experimental procedure consisted of collecting adsorption isotherms at four different temperatures using the gas adsorption system described in section 2.5. At a coverage that corresponds to about 20% of a monolayer on the carbon support, the enthalpy of interaction was 40 kJ mol^{-1} on the microporous support of the catalyst 0.5% Pd/C-H and 14 kJ mol^{-1} on the nonmicroporous support of the catalyst 0.5% Pd/C-L. We interpret the difference in enthalpy of interaction between the two samples as an indication of the different microporous nature of the samples since the microporous structure will cause a different interaction of the molecules being adsorbed. This fact has been discussed in the literature, for example by Vernov et al.,[36] who described how the heat of adsorption and condensation is significantly higher on microporous solids. Even though the adsorption on the support should not interfere with the apparent activation energy step, in the case of the microporous support, the temperature will influence the amount of pore condensation, which in turn will influence the fraction of reaction that is occurring in the liquid versus gas phase. If the rates are dependent on the phase of the reactant, and if the rate is higher when there is condensation (note in Tables 3, 4, and 6 that the overall rates are 1.5−2.5 higher on the microporous solid Pd/C−H), then the apparent activation energy will be lower due to pore condensation, which is the opposite of the effect observed. Another possibility is an effect of the carbon support on the Pd. Krishnankutty and Vannice studied adsorption, absorption,[37] and reaction properties[35] on Pd/C catalysts and found that the turnover rates and activation energies for CO and benzene hydrogenation could be affected by the carbon support when compared with catalysts supported on other materials. For hydrodechlorination, this explanation does not seem to carry over, as the rates, apparent activation energies, and reaction orders are similar for a foil (unsupported) and a Pd/C sample.

It is important to note that the activation energies will be calculated incorrectly if the inhibiting effect of HCl is not accounted for. The activation energy is usually measured by increasing the temperature for a fixed amount of catalyst which implies that the conversion level will increase with the reaction temperature. If excess HCl is not added to the feed, as the temperature is increased the rate will not increase as fast as expected because more HCl is also being produced. It is easy to calculate that if excess HCl is not added and the rates not corrected for its effect, the "apparent activation energy" will be one-half of the actual value. Apparent activation energy results of Karpinski et al.[38] for the hydrodechlorination of CFC 114a (CF_3-CFCl_2) are approximately a factor of 2 lower than those calculated in this study. This factor may be due to the effect of HCl, although some of their data suggests that the reaction order in HCl is zero order.

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4.5. Comparison of Rates with the Ones in the Literature. We have attempted to compare the measured rates in this study with others in the literature. We made a direct comparison with the hydrodechlorination rates on a Pd foil[9,32] for CFC 113a (CF_3-CCl_3), HCFC 124 ($CF_3-CFClH$), and CFC 114a (CF_3-CFCl_2) as summarized in Tables 3, 4, and 6. The rates show a factor of 2−6 difference between the foil and Pd supported on carbon. The selectivity is similar for supported and unsupported catalysts. This agreement is excellent when one takes into consideration the uncertainties in measuring rates on catalysts with vastly different metal surface area. This agreement also confirms that the reaction is structure insensitive since the rates are also similar to the ones on Pd(110) and Pd(111).[9] We can also conclude that the carbon support does not play a significant role on the hydrodechlorination chemistry (except when impurities in the carbon are present, as discussed above).

Numerous studies of hydrodechlorination reactions have been conducted, but many did not report a turnover rate[15] or did not quantify the effect of HCl. Comparison of rates with the ones in the literature was thus not possible. In some other cases, the turnover rate was reported but the reaction order on HCl was different from ours, indicating a different reaction mechanism possibly by reaction of chlorine with the support.[38,20]

Another difficulty in comparing rates in catalytic reactions in general is deactivation. Although we did not observe deactivation for the catalyst in our studies, Early et al.[20] observed deactivation for the reaction of CF_3-CFCl_2 on non-carbon supported samples. Interestingly, the same catalysts are stable for the hydrodechlorination of CF_2Cl_2.[39,20] Oxide supports may react with chlorine and fluorine produced in the reaction if the conditions of reaction are appropriate. The newly formed halogenated support may have a lower total surface area causing the metal particles to sinter.[40] For the catalysts supported on carbon, however, Wiersma et al.[19] reported that the Pd surface area actually increases with time on stream for the reaction with CF_2Cl_2. These catalysts still deactivated due to strong adsorption of deposits on the surface.

**4.6 Correlating C−Cl Bond Energy with Reaction Rates.** As suggested in Table 7, the rate of reaction increases as the bond energy decreases. A quantitative comparison was made using the relationship of Polanyi as discussed above. The results of the comparison were shown in Table 7. The rates calculated using the bond strength estimated from the Group Additivity Method could not predict the rates for CF_3-CFCl_2 very well. The reason for the discrepancy is that it is an approximate method. For the comparison of bond strength with the ones in the literature, we could find the C−Cl bond energy only for CF_3-CF_2Cl from the work of Coomber and Whittle[41] with a value of 346.0 ± 7.1 kJ mol^{-1}, a difference of 21 kJ mol^{-1} or 6% from the value calculated in Table 7. Note that the values listed in Table 7 are calculated at 0 K but the one in the literature is at 298 K. Making the necessary temperature corrections using Gaussian provides a value for the bond strength at 298 K of 324.6 kJ mol^{-1}, an even larger difference. The temperature corrections from 0 to 298 K were 5−10 kJ mol^{-1} and did not affect the relative comparisons. We kept the values at 0 K because they are easier to calculate. The comparison with the experimental rate results using the values from the ab initio calculations showed excellent matching. Note that the values calculated using the bond strength do not differ from the ones calculated using the enthalpy of reaction and that the reaction temperature chosen for the comparison in Table 7 (150 °C) was picked in the middle of the temperature range used in the experiments to minimize errors by extrapolation. Note, however,

that using other reaction temperatures for the comparison in the range 50−200 °C produced similar but not identical results as the apparent activation energies are not the same.

This agreement for the rates is important in practice because it allows one to predict the rate of dechlorination for a series of compounds. It also gives important insight for the reaction steps. It strongly suggests that the rate-determining step involves the scission of the C−Cl bond. If this is the case, the relative difference in activation energies should be the same as the relative difference in bond energies. The values for the activation energies, however, show the right trend but do not provide good qualitative prediction. For example, the difference in bond energy between the extremes of the comparison, CF_3-CF_2Cl and CF_3-CCl_3, is 63 kJ mol^{-1}, but the difference in the apparent activation energies for the hydrodechlorination of the first chlorine is only 22 kJ mol^{-1}.

The correlation between rate of dehalogenation and bond strength was also observed for the rate of hydrodefluorination. The rate of hydrogenation is higher for compounds with a lower number of fluorine atoms (lower bond strength) attached to the carbon.[42] Note that linear free energy relationships, in the form of the Hammett equation of physical−organic chemistry, have been used before for hydrodechlorination. The rates for the hydrodechlorination of substituted chlorobenzene[43] varied by a factor of 10 and followed the Hammett relation as different substituents on the benzene ring were added. A similar Hammett relation for dehalogenation was described for aliphatic compounds by Buelow et al.[44] who found that the rate constant for dissociative adsorption decreased as more fluorine atoms were added.

4.7 Reaction Steps. From the reaction kinetics, it was proposed that the rate-determining step involves the scission of the C−Cl bond, the active site may consist of one Pd atom, and that H_2 and HCl are in equilibrium with adsorbed H and Cl. We also know from the rate measurements that the product distribution is independent of conversion, which implies that the reactant adsorbs on the surface and reacts in a sequential manner. In other words, there is no readsorption of products for further reaction. We propose that the rate-determining step (RDS) for a generic R−Cl reactant is the oxidative addition

$$R-Cl + Pd \rightarrow R-Pd-Cl$$
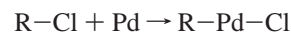
with Pd making a σ-bond with the carbon atom in the R fragment. This type of addition can be found in the organotransition metal chemistry literature. The oxidative addition of an alkyl halide R−X on a Pd(0) species to produce a σ-alkyl metal halide complex has been reported,[45] although examples are more common when R is aryl or vinyl.[46] The latter groups are apparently more reactive. This higher reactivity has been observed on a Pt/Al_2O_3 catalyst where vinyl chloride was found to be much more reactive than ethyl chloride[10] for hydrodechlorination. Note again that we have no direct evidence for this step, except for the analogy with organometallic chemistry. Once the R−Pd−Cl compound is formed, hydrogen atoms on the surface may attack it forming R−H and Pd−Cl or R−Pd and HCl. In the first case, a monohydrogenated compound is formed, and in the second case, another chlorine (or fluorine) may be extracted from R forming R=Pd−Cl. We also have no information on the nature of the carbene-like species formed, and the fragment R could be bound to two Pd atoms on the surface. This complex may be attacked by a hydrogen again forming a hydrogenated species, or it may lose another halogen. The product distribution will depend on the relative rates of hydrogenation versus dehalogenation. Note that the reasoning

about these reaction steps is based exclusively on the fact that the product distribution is independent of conversion and thus there must be a sequential reaction (dehalogenation/hydrogenation) on the surface. Examples of proposed sequential reactions are the hydrodechlorination of CCl_4,[14] CCl_2F_2,[18,47] and CF_3-CFCl_2.[38,8] This property is due to the fact that the products are less reactive than the reactants: as the molecule undergoes sequential hydrodechlorination, the remaining C−Cl bonds on the hydrogenated carbon become stronger.

There are other studies in the literature about the reaction steps for hydrodechlorination. Campbell and Kemball[4] studied the hydrodechlorination of CH_3-CH_2Cl on Pd films. The reaction order in HCl and ethyl chloride were determined and were the same as reported here. Through reaction with D_2, they found that the reaction mechanism must involve the formation of a carbene-like species since the product (ethane) was substantially enriched in CH_3-CHD_2. Zhou et al.[48] found that the dehalogenation step (the RDS in our case) is homolytic, as also proposed here. The studies by Coq et al.[12] for the hydrodechlorination of chlorobenzene on Pd proposes a rate equation that is kinetically indistinguishable from the one presented here, and thus the rate data for chlorobenzene supports the reaction steps proposed here. Note however that the reaction steps proposed by Coq et al.[12] for hydrodechlorination of chlorobenzene differ from the ones presented here. As is well-known, different reaction steps can be constructed that will produce the same rate equation. Some of the kinetic parameters for the hydrodechlorination of CF_2Cl_2 have also been discussed. The inhibition by HCl is confirmed by Coq et al.[12] and van de Sandt et al.[47] but not observed by Ahn et al.[17] The reaction steps and overall rate proposed by Coq et al.[18] and Ahn et al.[17] are quite different than the ones reported here. The reaction steps may be different for this compound.

A direct experiment to verify the nature of the adsorbed intermediates is not available. Deshmukh and d'Itri[49] attempted to trap fluorocarbene species formed on the reaction of hydrodechlorination of CCl_2F_2 by reaction with ethylene but could not observe any fluorinated addition product. As discussed by the authors, the concentration of the fluorocarbene may be very small, which is to be expected if the rate-determining step is the first dechlorination as proposed here. Evidence that a carbene species is formed can be derived by observing the product distribution for the reaction of CF_3-CFCl_2 (Table 3) and $CF_3-CFHCl$ (Table 6). The ratio of products CF_3-CFH_2 to CF_3-CH_3 is about 20 for the first compound and about 250 for the second compound. The reason for this difference is that for CF_3-CFCl_2 a carbene-like species can be formed by dechlorination but in the case of $CF_3-CFHCl$ a C−H or a C−F bond, much stronger bonds than C−Cl, need to be broken for the carbene to form.

There are still a few issues that the reaction steps proposed cannot explain. One that does not seem intuitive is the tendency of hydrogenating C−F bonds on chlorofluorocarbons. These bonds are much stronger than the C−Cl bonds and should not be broken at the conditions where the C−Cl bonds are broken. For example, the C−F bond in CF_3-CFCl_2 is 100 kJ mol^{-1} stronger than the C−Cl bond, and yet the C−F bond is broken in about 5% of the products. Another example is for CF_3-CF_2Cl where CF_3-CF_2H is the main product with CF_3-CH_3 as the minor product but CF_3-CFH_2 was not detected. A similar example in the literature is the hydrodefluorination of CH_3-CF_2H which forms ethane almost exclusively but no CH_3-CFH_2.[42] Explaining the selectivity is still not possible and a

complete reaction network with additional steps to the ones proposed here is necessary.

4. Summary and Conclusion

The turnover rates and reaction orders were determined for a family of four chlorofluorocarbons. The rates of hydrodechlorination span a range of 7 orders of magnitude, which shows that the rates are very dependent on the structure of the chlorofluorocarbons. Fortunately, we found out that the rates correlate very well with the strength of the C−Cl bond. Rates can be predicted within a factor of 7 in a range of 10^7 for the four compounds tested provided that the rate for one of the members of the family is known.

The reaction steps for the reaction of hydrodechlorination were proposed based on the orders of reaction. The rate-determining step involves the C−Cl scission bond since the rates correlate with the strength of the C−Cl bond. By analogy to organometallic chemistry, we propose that this step is the oxidative addition of the reagent in one Pd atom. Surface H and Cl are in equilibrium with H_2 and HCl in the gas phase and the most abundant surface intermediate is chlorine. This kinetic scheme explains the strong inhibition of HCl in hydrodechlorination reactions. It is clear that these products are formed in a sequential step on the surface and not from a sequential readsorption of products from the gas phase. The reaction order in H_2 is particularly low for the product where all the halogens have undergone hydrodehalogenation (formation of CF_3-CH_3). We suggested that only one Pd atom is involved in the rate-determining step which explains why the overall rate does not change with the Pd structure. The rates for supported catalysts are comparable to the ones on a foil or a single crystal indicating that the carbon support does not play a role in the hydrodechlorination chemistry (except for impurities on the carbon). To explain the reaction selectivity remains a challenge.

There are some artifacts that need to be avoided when studying this chemistry. Microporosity is common in many carbon supports and because the boiling point of chlorofluorocarbons are close to the reaction temperature, there is the possibility for condensation on the pores of the carbon. This condensation may affect the reaction orders. Hydrogen chloride inhibits the reaction by competing for sites with the reactant. Its concentration must be specified when reporting rates and its effect accounted for when calculating the apparent activation energy.

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