Chlorofluorocarbon Dechlorination on Pd(111): Effect of Chlorine Stoichiometry

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Chlorofluorocarbon dechlorination on Pd(111): effect of chlorine stoichiometry

Boonchuan Immaraporn, PingPing Ye, and Andrew J. Gellman

Abstract

The kinetics of C–Cl bond cleavage on the Pd(111) surface have been measured using four chlorofluorocarbons (CFCs) containing different numbers of chlorine atoms on the primary carbon: CF$_3$CCl$_3$, CF$_3$CFCl$_2$, CF$_3$CF$_2$Cl, and CF$_3$CHFCl. The desorption energies, $\Delta E_{\text{des}}$, of the CFCs were found to increase with increasing number of chlorine atoms in the following order: CF$_3$CF$_2$Cl $<$ CF$_3$CHFCl $<$ CF$_3$CFCl$_2$ $<$ CF$_3$CCl$_3$. The rate constants and apparent barriers to C–Cl cleavage, $\Delta E_{\text{app}}$, on the Pd(111) surface were measured using CF$_3$CFCl$_2$, CF$_3$CF$_2$Cl, and CF$_3$CHFCl. The trend in $\Delta E_{\text{app}}$ was found to be opposite that for $\Delta E_{\text{des}}$: CF$_3$CFCl$_2$ $<$ CF$_3$CHFCl $<$ CF$_3$CF$_2$Cl. For CF$_3$CFCl$_2$ and CF$_3$CHFCl the intrinsic activation energy for C–Cl cleavage on the Pd(111) surface, $\Delta E_{\text{C–Cl}}$, was determined by adding the desorption energies and the apparent activation energies for dissociative adsorption, $\Delta E_{\text{C–Cl}} = \Delta E_{\text{app}} + \Delta E_{\text{app}}$. In contrast with the other compounds, CF$_3$CCl$_3$ adsorbed on the Pd(111) surface dechlorinates rather than desorbing during heating, thus allowing direct measurement of $\Delta E_{\text{C–Cl}}$. Comparison of $\Delta E_{\text{C–Cl}}$ and $\Delta E_{\text{des}}$ among the CFCs suggests that the variations in $\Delta E_{\text{des}}$ have a greater influence on the dechlorination reactivity than the variations in $\Delta E_{\text{C–Cl}}$.

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Keywords: Dechlorination; Hydrodechlorination; Chlorofluorocarbons; Palladium

1. Introduction

Chlorofluorocarbons (CFCs) are believed to harm the environment by depleting the stratospheric ozone layer. As a result they are no longer produced for commercial use and alternative compounds have been developed with similar physicochemical properties but less potential for destruction of the ozone layer. One such class of compounds are the hydrofluorocarbons (HFCs), which can be produced by hydrodechlorination of CFCs [1–3]. Currently a number of HFCs such as CF$_3$CFH$_2$ are used as replacements for their counterpart CFCs such as CF$_3$CFCl$_2$. One route to obtain HFCs is the hydrodechlorination of CFCs over supported Pd catalysts [1].

CF$_3$CFCl$_2$ + 2H$_2$ $\xrightarrow{\text{Pd}}$ CF$_3$CFH$_2$ + 2HCl.

Several mechanisms and rate-determining steps have been proposed for the catalytic hydrodechlorination reaction shown above. A recent study suggested that the rate-determining step involves C–Cl bond cleavage possibly via oxidative addition [4,5]. Although there is not complete agreement on the rate-determining step, previous studies have shown that rates of CFC dechlorination on the Pd(111) surface correlate quite well with rates of hydrodechlorination on Pd catalysts [6,7]. The agreement in the trend between rates of dechlorination and rates of catalytic hydrodechlorination implies that C–Cl cleavage must be kinetically significant in the hydrodechlorination reaction.

Previous studies of the hydrodechlorination of CFCs over several catalysts have revealed that as the number of chlorine atoms attached to a carbon atom increases, the rate of hydrodechlorination also increases [4,5,7,8]. For instance, on Pt/Al$_2$O$_3$ catalysts the rate of hydrodechlorination of CCl$_4$ is 100 times faster than that of CH$_3$Cl under identical conditions [8]. On supported Pd catalysts, a systematic study of the hydrodechlorination of four different CFCs reported by Thompson et al. revealed that the ratio of the turnover rates for hydrodechlorination of CF$_3$CCl$_3$:CF$_3$CFCl$_2$:CF$_3$CHFCl:CF$_3$CF$_2$Cl is $10^7$:363:1.
In that work a correlation was established between the C–Cl bond strengths of the four CFCs and the turnover rate. This correlation was the basis for the proposal that the C–Cl cleavage step is rate limiting in the overall hydrodechlorination reaction. This article explores the kinetics of CFC dechlorination on the Pd(111) surface by focusing on the intrinsic barrier to C–Cl cleavage, \( \Delta E_{\text{C-Cl}} \). The goal is to understand the origin of the variations in the hydrodechlorination activity of CFCs having varying numbers of chlorine atoms on the primary carbon.

Prior work has investigated the influence of fluorination on the barrier to C–Cl cleavage in a set of substituted 1,1-dichloroethanes with varying fluorine content [9]. A linear free energy relationship between the substituent field constants and \( \Delta E_{\text{C-Cl}} \) showed that fluorination has little effect on \( \Delta E_{\text{C-Cl}} \). In other words the values of \( \Delta E_{\text{C-Cl}} \) were very similar among the four compounds studied. The implication of that observation is that the transition state to cleavage of the C–Cl bond is homolytic in the sense that it is reactant-like.

Dechlorination of chlorocarbons is a two-step process comprising of reversible molecular adsorption followed by C–Cl dissociation.

\[
R-\text{Cl}_{(g)} \xrightarrow{K} R-\text{Cl}_{(ad)}, \\
R-\text{Cl}_{(ad)} \xrightarrow{k_{\text{C-Cl}}} R_{(ad)} + \text{Cl}_{(ad)}.
\]

These two steps are characterized by independent reaction energies, the desorption energy, \( \Delta E_{\text{des}} \), and the intrinsic barrier to C–Cl cleavage, \( \Delta E_{\text{C-Cl}} \). This mechanism leads to a kinetic rate law of the type used previously to interpret the dissociative adsorption kinetics of 1,1-dichloroethanes on the Pd(111) surface [9]. Assuming a Langmuir-type isotherm for CFC adsorption, the rate of dissociative adsorption can be expressed as a function of CFC pressure as

\[
r = \frac{k_{\text{C-Cl}} (KP_{\text{CFC}})^n}{(1 + KP_{\text{CFC}})^n},
\]

where \( r \) is the rate, \( k_{\text{C-Cl}} \) is the rate constant for C–Cl cleavage, \( K \) is the equilibrium constant for CFC adsorption, \( P_{\text{CFC}} \) is the CFC pressure, and \( n \) is the reaction order in CFC coverage on the surface. One would expect that the reaction order for dissociation should be \( n \approx 1 \). At low CFC pressures where \( KP_{\text{CFC}} \ll 1 \), Eq. (1) reduces to

\[
r = k_{\text{C-Cl}} (KP_{\text{CFC}})^n. \tag{2}
\]

The apparent activation energy for dissociative adsorption, \( \Delta E_{\text{app}} \), that one would measure during exposure of a surface to CFCs in the gas phase would be the difference between the energetics for the elementary reaction steps:

\[
\Delta E_{\text{app}} = \Delta E_{\text{C-Cl}} - n \cdot \Delta E_{\text{des}}. \tag{3}
\]

This investigation has measured the intrinsic barrier to C–Cl cleavage for four CFCs (CF\(_3\)CCl\(_3\), CF\(_3\)CFCl\(_2\), CF\(_3\)CF\(_2\)Cl, and CF\(_3\)CHFCl) having varying chlorine content. In the case of CF\(_3\)CCl\(_3\) this has been directly measurable because CF\(_3\)CCl\(_3\) dissociates by C–Cl bond cleavage during heating on the surface. The other three CFCs, however, desorb molecularly during heating, and thus it has been necessary to measure \( \Delta E_{\text{des}} \) and \( \Delta E_{\text{app}} \) independently to determine \( \Delta E_{\text{C-Cl}} \). The results of these measurements of CFC dechlorination kinetics on the Pd(111) surface show that increasing the number of chlorine atoms attached to the primary carbon atom increases the value of \( \Delta E_{\text{des}} \) but has less influence on the values of \( \Delta E_{\text{C-Cl}} \). As a consequence increasing the number of chlorine atoms in the CFC decreases the value of \( \Delta E_{\text{app}} \) and results in an increase in the net rate for dechlorination.

2. Experimental

All the experiments were performed in an UHV chamber equipped with an ion gun for cleaning the Pd(111) surface, leak valves for gas dosing, and a Dycor quadrupole mass spectrometer for temperature-programmed desorption (TPD) measurements. X-Ray photoemission spectroscopy (XPS) was performed using an Al-K\(_\alpha\) X-ray source and SPECS Phobios 150 MCD-9 concentric hemispherical electron energy analyzer.

The Pd(111) single-crystal sample was purchased from Monocrystals Inc. and was mounted by spotwelding between two Ta wires on a small sample holder, which was then bolted to the end of the UHV manipulator. The manipulator allows cooling of the samples to \( T < 100 \text{ K} \) and resistive heating to \( T > 1000 \text{ K} \). A chromel–alumel thermocouple was spotwelded to the edge of the Pd sample for temperature measurement. The Pd sample was cleaned by several cycles of Ar\(^+\) sputtering followed by annealing to 1000 K. XPS was used to monitor the cleanliness of the Pd(111) surface. Deposits of carbon on the Pd(111) surface resulting from decomposition of the CFCs were removed by exposing the crystal to 10\(^{-7}\) Torr of O\(_2\) for 10 min while it was heated to 1000 K. Adsorbed oxygen atoms react with carbon to produce CO or CO\(_2\), both of which desorb rapidly at 1000 K. The Pd(111) surface was judged to be free of carbon when only O\(_2\) desorption (no CO or CO\(_2\)) was detected during TPD measurements obtained following oxygen adsorption at 90 K.

The chlorofluorocarbons were generously provided by Professor Fabio Ribero: CF\(_3\)CCl\(_3\) (99%, Lancaster Synthesis), CF\(_3\)CFCI, CF\(_3\)CFCHCl, and CF\(_3\)CF\(_2\)Cl. Except for CF\(_3\)CCl\(_3\) the CFC samples were gaseous or in the form of pressurized liquids. Before use liquid samples were transferred at room temperature into glass vials with PTFE stopcocks. Before their vapor was introduced into the chamber via a leak valve, they were purified by several cycles of freeze–pump–thawing to remove any high-vapor-pressure impurities. The purity of the vapor introduced into the UHV chamber was verified by mass spectrometry.

TPD experiments were performed by first adsorbing the CFCs on the Pd(111) surface at 90 K. The surface was then
heated at 2 K/s while using the Dycor mass spectrometer to measure the desorption rate. During dissociative adsorption experiments XPS was performed with an X-ray source power of 480 W and an analyzer pass energy of $E_p = 180$ eV (resolution $\sim 3.5$ eV). The rates of dissociative adsorption of CF$_3$CFCl$_2$, CF$_2$CF$_2$Cl, and CF$_2$CHFCl were measured by using XPS to monitor Cl uptake during exposure of the Pd(111) surface to a constant pressure of the CFCs with the surface at temperatures in the range 225–325 K. The kinetics of C–Cl bond cleavage in adsorbed CF$_3$CCl$_3$ were studied with XPS using a pass energy, $E_p$ of 30 eV. The rate of CF$_3$CCl$_3$ dechlorination was measured by first exposing the Pd surface to CF$_3$CCl$_3$ at low temperature ($\sim 90$ K). XPS was then used to monitor the Cl 2p photomission as the surface was heated to 0.1 K/s. Eighteen Cl 2p spectra were obtained at temperatures between 95 and 250 K to monitor the dissociation of the C–Cl bond in this temperature range.

Calibration of the Cl 2p XPS signal versus $\theta_{\text{Cl}}$ was achieved by saturating the Pd(111) surface with chlorine by exposure to Cl$_2$ gas at 300 K. Under these conditions the exposure has been shown to give a saturation chlorine coverage, $\theta_{\text{Cl}}$, of 0.43 [10]. Exposures to chlorine at higher temperatures, however, can give rise to higher coverages [11]. At this coverage the ratio of the Cl 2p peak area to the Pd 3d peak area was $I_{\text{Cl}}/I_{\text{Pd}} = 0.018$. The ratio of these peak areas was taken to be linear in the coverage, $\theta_{\text{Cl}}$.

### 3. Results

#### 3.1. Desorption of CFCs from Pd(111)

The initial study of CFC adsorption on the Pd(111) surface has focused on their desorption kinetics. With the exception of CF$_3$CCl$_3$, all the CFCs adsorb reversibly on the Pd(111) surface and desorb from the surface during heating. Fig. 1 shows the desorption spectra for different initial coverages of CF$_3$CFCl$_2$ on Pd(111) obtained by monitoring the ionization fragment at $m/q = 69$ during heating at a rate of 2 K/s. Ionization fragments at $m/q = 31$, 47, and 85 were also monitored and indicated that CF$_3$CFCl$_2$ desorbs molecularly without dissociation. At exposures below 0.10 L, molecular desorption occurs with a peak desorption temperature, $T_p$, of 186 K that is independent of coverage. As the coverage is increased further the desorption peak broadens to lower temperatures, and once the exposure is increased to $\sim 0.26$ L, the multilayer desorption peak appears at $T_p = 109$ K. The desorption energy of CF$_3$CFCl$_2$ at low coverages, $\Delta E_{\text{des}}$, is calculated to be 48 kJ/mol using Redhead’s equation and the assumptions that the desorption kinetics are first-order and that the desorption preexponential factor, $\nu$, is $10^{13}$ s$^{-1}$ [12]. The desorption spectra of CF$_3$CF$_2$Cl and CF$_2$CHFCl exhibit the same qualitative dependence on coverage as those of CF$_3$CFCl$_2$.

Previous studies have found that the presence of hydrogen on the surface can influence the kinetics of CFC desorption [9,13]. Hydrogen desorption from the Pd(111) surface was monitored periodically throughout this study. The hydrogen desorption signal at $m/q = 2$ was calibrated with respect to the desorption signal for a hydrogen-saturated Pd(111) surface with a coverage, $\theta_{\text{H}}$, of 0.9 ML [14]. The background hydrogen contamination level on the surface appeared to remain constant at $\theta_{\text{H}} \approx 0.05$ ML throughout the course of this work. At this level its effect on the desorption energetics of the CFCs is not significant.

TPD spectra of the four CFCs on the Pd(111) surface were used to estimate their $\Delta E_{\text{des}}$ values. Fig. 2 compares the desorption spectra obtained by monitoring the signal at $m/q = 69$ during TPD of all four CFCs at low coverages. CF$_3$CFCl$_2$, CF$_2$CHFCl, and CF$_3$CFCl$_2$ adsorb reversibly on the surface and desorb during heating without dissociation. The estimates of the values of $\Delta E_{\text{des}}$ for CF$_3$CF$_2$Cl, CF$_3$CHFCl, and CF$_3$CFCl$_2$ are 37, 43.5, and 48 kJ/mol, respectively. In other words as the fluorine content of the CFC decreases, the desorption energy increases.

The CF$_3$CCl$_3$ desorption spectra are qualitatively different from those of the other three CFCs used in this study. At low coverages, CF$_3$CCl$_3$ decomposes on the surface. Molecular desorption of CF$_3$CCl$_3$ was not observed until the coverage reached the point that $\theta_{\text{Cl}} > 0.3$ ML. Chlorine coverage was determined by calibrating the area under the Cl 2p X-ray photoemission (XP) peak with respect to that of the Cl-saturated Pd surface having $\theta_{\text{Cl}} = 0.43$ [11]. At high coverage some fraction of the adsorbed CF$_3$CCl$_3$
Fig. 2. TPD spectra of CF₃CCl₃, CF₃CFCl₂, CF₃CF₂Cl, and CF₃CHFCl on Pd(111) at low coverages. The heating rate was 2 K/s and m/q was 69.

Fig. 3. TPD of CF₃CFCl₂ on both clean and Cl-covered Pd(111) surfaces. The presence of chlorine on the surface reduces the CF₃CFCl₂ desorption temperature. The heating rate was 2 K/s, and for the ionization fragment monitored, m/q was 69.

The desorption energy that one would estimate from this peak, ΔE_{des}, is 47.5 kJ/mol; however, this is not necessarily the intrinsic desorption energy that one would get from the clean Pd(111) surface. On the basis of the trend established for the desorption temperatures of the other CFCs on the Pd(111) surface one would expect the ΔE_{des} for CF₃CCl₃ to be higher than that for CF₃CFCl₂; however, this is does not appear to be the case from the data shown in Fig. 2. The reason is that CF₃CCl₃ desorption occurs in the presence of adsorbed chlorine atoms generated by CF₃CCl₃ decomposition and does not occur from the clean Pd(111) surface. As will be shown a fraction of the CF₃CCl₃ undergoes dechlorination on the Pd(111) surface at temperatures below 250 K. Dechlorination yields adsorbed Cl atoms on the Pd(111) surface which could influence the desorption kinetics of the remaining molecularly adsorbed CF₃CCl₃.

To determine the influence of adsorbed Cl on desorption of the CFCs, CF₃CFCl₂ desorption was studied in the presence of adsorbed Cl atoms. The Pd(111) surface was first exposed to CF₃CCl₃ at 300 K and annealed to 500 K to deposit Cl atoms onto the surface. TPD spectra of CF₃CFCl₂ on the clean surface and the Cl-covered surface are compared in Fig. 3. The peak desorption temperature for CF₃CFCl₂ was found to decrease from Tₚ = 186 to 150 K as a result of the presence of adsorbed Cl. These observations of the effect of adsorbed Cl atoms on CF₃CFCl₂ desorption suggest that Cl atoms generated by dechlorination of CF₃CCl₃ also decrease the peak desorption temperature of CF₃CCl₃. In other words, the peak desorption temperature for CF₃CCl₃ on the clean Pd(111) surface should be Tₚ > 184 K. If one assumes that chlorine has the same effect on the desorption temperature of CF₃CFCl₂ and CF₃CCl₁, then one could estimate that the desorption temperature of CF₃CCl₃ from the clean Pd(111) surface, Tₚ, would be ≈ 220 K. This would lead to an estimate for the desorption energy for CF₃CCl₃ from clean Pd(111) of ΔE_{des} ≈ 57 kJ/mol. In summary, the TPD results for CFC desorption from the Pd(111) surface reveal that the ΔE_{des} values of all four CFCs decrease as the number of fluorine atoms increases or as the number of chlorine atoms decreases: CF₃CCl₃ > CF₃CFCl₂ > CF₃CHFCI > CF₃CF₂Cl.

3.2. Dissociative adsorption of CFCs on Pd(111)

For the three CFCs that adsorb reversibly on the Pd(111) surface (CF₃CFCl₂, CF₃CHFCl, and CF₃CFCl₂) direct kinetic measurement of C–Cl bond cleavage on the Pd(111) surface is impossible. Instead, measurement of the dissociative adsorption kinetics was performed by exposure of the Pd(111) surface at elevated temperatures to the CFC in the gas phase. The apparent activation barrier to dissociative adsorption, ΔE_{app}, was obtained from these measurements and combined with the desorption energy, ΔE_{des}, to yield the intrinsic activation barrier to C–Cl bond cleavage, ΔE_{C-Cl}. The rate of dissociative adsorption was measured by exposing the Pd(111) surface to a continuous flux of CFCs and monitoring the Cl₂ XP spectra as a function of the exposure time. Fig. 4 shows a set of typical Cl₂ XP spectra obtained while the Pd(111) surface was exposed to a back-
Fig. 4. Cl 2p XP peaks during exposure of Pd(111) to $3 \times 10^{-9}$ Torr of CF$_3$CFCl$_2$ at 300 K. The peak grows monotonically with time during exposure. The pass energy, $E_p$, was 180 eV. The time intervals between obtaining spectra were 20 min.

Fig. 5. Cl uptake on Pd(111) during exposure to $3 \times 10^{-9}$ Torr of CF$_3$CFCl$_2$ and $1.2 \times 10^{-6}$ Torr of CF$_3$CHFCl at 300 K. The apparent rate constants for dechlorination on the clean Pd(111) surface are determined from the initial slopes of the uptake curves. Chlorine coverage was determined based on the area under the Cl 2p peaks and used to construct a plot of atomic Cl uptake versus exposure time. Fig. 5 displays the uptake curves for CF$_3$CFCl$_2$ (obtained at a pressure of $3 \times 10^{-9}$ Torr) and CF$_3$CHFCl ($1.2 \times 10^{-6}$ Torr) obtained at 300 K. The uptake curve can be fit to a quadratic function and the slope at $t = 0$ is a measure of the initial rate of chlorine deposition in units of Cl atoms per site per second and ultimately the apparent rate constant for dissociative adsorption, $k_{app}$, in units of Cl atoms per site per second per Torr.

Before the Cl uptake curves can be analyzed to determine the rate constants for C–Cl cleavage the order of the reaction, $n$, in the gas pressure must be determined. Fig. 6 shows the rate of chlorine uptake versus pressure during CF$_3$CFCl$_2$ exposure to the Pd(111) surface at 300 K. This has been fit to the expression in Eq. (1) for the rate, assuming that the adsorption process is first order but that the reaction order in adsorbate coverage is of unknown order, $n$. The fit to the data in Fig. 6 yields a reaction order, $n$, of 1.02 ± 0.11. A similar analysis yields a reaction order for dissociative adsorption of CF$_3$CHFCl, $n$, of 1.1 ± 0.1. It appears from the results of these experiments that the dissociative adsorption of the CFCs on the Pd(111) surface can be considered to be a first-order process.

The rates of dissociative adsorption of the CFCs on the Pd(111) surface are dependent on the nature of the CFC. Under the experimental conditions accessible in this study ($T = 200–350$ K and $P_{CFC} \leq 10^{-6}$ Torr), dechlorination of CF$_3$CF$_2$Cl on the Pd(111) surface was not observable. Presumably either the rate constant for C–Cl bond dissociation or the equilibrium constant for CF$_3$CF$_2$Cl adsorption is so low that prohibitively high pressures would be needed to observe chlorine deposition at a measurable rate.
As shown, both the dissociative adsorption of CF₃CFCl₂ and that of CF₃CHFCl are first-order processes. As a result the apparent rate constants for dissociative adsorption can be determined from the expression

$$k_{\text{app}} = \frac{r}{aP_{\text{CFC}}},$$  \hspace{1cm} (4)

where \(a\) is the number of chlorine atoms in the CFC molecule. This expression yields good measures of the rate constants for dissociative adsorption over the pressure range in which the adsorption isotherm is linear. Ultimately, values of the rate constant obtained at varying temperatures will be used to determine \(\Delta E_{\text{app}}\), the apparent barrier to dissociative adsorption of the CFCs on Pd(111).

The relative reactivities of CF₃CFCl₂ and CF₃CHFCl can be compared by reexamining Fig. 5. It is clear from the figure that the apparent rate constant for dissociative adsorption of CF₃CFCl₂ is greater than that for CF₃CHFCl. Increasing the number of chlorine atoms increases the apparent reactivity. This is consistent with the observations reported by Thompson et al. for the hydrodechlorination reaction of CF₃CFCl₂ and CF₃CHFCl on Pd catalysts [5]. Under conditions of catalytic hydrodechlorination the rates differ by a factor of \(\sim 300\), whereas under our conditions for dechlorination on the Pd(111) surface the rates differ by a factor of \(\sim 60\).

The apparent activation energy for the dissociative adsorption of CFCs on the Pd(111) surface, \(\Delta E_{\text{app}}\), can be found from the temperature dependence of the rate constants for dissociative adsorption. A series of chlorine uptake curves were measured at temperatures in the range 225 to 325 K and the apparent rate constants were determined using the procedure described above. Note that the temperature range used is well above the desorption temperature of the CFCs. Hence, the coverage of molecular CFCs on the Pd(111) surface during the dissociative adsorption experiment is not significant. Fig. 7 shows Arrhenius plots for the dissociative adsorption of both CF₃CFCl₂ and CF₃CHFCl on the Pd(111) surface. These yield \(\Delta E_{\text{app}}\) values of 7.5 \(\pm\) 1.2 kJ/mol for CF₃CFCl₂ and 12.6 \(\pm\) 0.7 kJ/mol for CF₃CHFCl. It is evident that the apparent activation energy for C–Cl bond cleavage increases by decreasing the number of chlorine atoms in the CFC. For CF₃CFCl₂, the fact that the apparent rate of dissociative adsorption was not measurable implies that \(\Delta E_{\text{app}}\) for dissociative adsorption of CF₃CF₂Cl is even higher than that of CF₃CHFCl. It should be noted here that the trend of \(\Delta E_{\text{app}}\) is opposite that found for \(\Delta E_{\text{des}}\). The magnitudes of the \(\Delta E_{\text{app}}\) take the order CF₃CF₂Cl > CF₃CHFCl > CF₃CFCl₂.

3.3. Kinetics of CF₃CCl₃ dechlorination on Pd(111)

Rather than desorbing during heating, CF₃CCl₃ undergoes dechlorination on the Pd(111) surface. This enables us to make a direct measurement of the rate of C–Cl bond cleavage and thus a direct measurement of the intrinsic barrier to dechlorination, \(\Delta E_{\text{C–Cl}}\). The C–Cl cleavage kinetics can be studied by obtaining Cl 2p XP spectra during heating of the CF₃CCl₃ adsorbed on the Pd(111) surface. The Cl 2p XP spectra obtained at 90, 163, and 250 K for CF₃CCl₃ on the Pd(111) surface are shown in Fig. 8. Also included in the fig-

![Fig. 7. Arrhenius plots for the dechlorination of CF₃CFCl₂ and CF₃CHFCl on Pd(111). Dechlorination rates were measured in constant pressures of 3 \(\times\) 10⁻⁹ Torr of CF₃CFCl₂ and 1.2 \(\times\) 10⁻⁶ Torr of CF₃CHFCl.](image)

![Fig. 8. X-ray photoemission spectra of Cl 2p peak in CF₃CCl₃ on Pd(111) during heating at 0.1 K/s. (A) Multilayer CF₃CCl₃ at \(T = 95\) K. (B) Monolayer at \(T = 90\) K. (C) Monolayer at \(T = 163\) K. (D) Monolayer at \(T = 250\) K. (E) Spectrum of saturated layer of atomic chlorine on Pd(111).](image)
ure are the Cl 2p XP spectra of multilayer CF3CCl3 and a 0.43 ML coverage of atomic Cl produced by exposure to Cl2 gas [11]. The figure clearly shows the evolution of the Cl 2p XP peak position and linewidth as the temperature increases from 90 to 250 K. At 90 K the XP spectrum of the CF3CCl3 monolayer is similar to that of the multilayer; however, the shoulder at $\sim 198$ eV indicates that there has been some low-temperature dissociation of CF3CCl3 on the Pd surface. The XP spectrum at 250 K reveals that CF3CCl3 has dechlorinated completely to yield atomic Cl on the Pd(111) surface. The XP spectra of multilayer CF3CCl3 and saturated Cl monolayer can be used as basis spectra for factor analysis of the spectra at intermediate coverages to determine the coverages of CF3CCl3 and atomic Cl on the Pd(111) surface as it is heated.

The kinetics of CF3CCl3 dechlorination on the Pd(111) surface have been studied by using the Cl 2p XP peak to measure the extent of the dechlorination reaction during heating. The measurements have obtained the Cl uptake curve which can be analyzed to give an estimate of the barrier to dechlorination, $\Delta E_{C-Cl}$. Factor analysis has been used to decompose the Cl 2p XP spectra shown in Fig. 8 into components arising from intact CF3CCl3 and atomic Cl [15]. A similar approach was used to study the dissociation of C–I bonds in alkyl iodides adsorbed on Pd(111) and Ag(111) surfaces [16,17]. Fig. 9 plots the fractions of atomic Cl and Cl present in CF3CCl3 during heating of the Pd(111) surface with a coverage of adsorbed CF3CCl3 that ultimately dissociates to generate an atomic Cl coverage, $\theta_{Cl}$, of 0.3 ML. The increase in the coverage of the atomic Cl indicates that CF3CCl3 undergoes dechlorination at temperatures as low as 90 K. The data have been fit with Boltzmann curves to determine the temperature of the peak dissociation rate, $T_p = 158$ K. Using Redhead’s equation and assuming that the preexponent in the rate constant for C–Cl cleavage is $\nu = 10^{13}$ s$^{-1}$, the activation barrier to dechlorination of CF3CCl3 on the Pd(111) surface, $\Delta E_{C-Cl}$ is estimated to be $\sim 44$ kJ/mol [12].

4. Discussion

4.1. Kinetic analysis of CFC dechlorination

The cleavage of C–Cl bonds in CFCs is a two-step process: adsorption of CFCs onto the surface followed by C–Cl bond cleavage. At low CFC pressures, the apparent rate constant for C–Cl bond cleavage for a first-order process ($n = 1$) comes from Eq. (2):

$$k_{app} = k_{C-Cl}K.$$  

From this the apparent barrier to C–Cl bond cleavage can be seen to come from two components: the intrinsic barrier to C–Cl cleavage and the energy of desorption of CFC from the surface:

$$\Delta E_{app} = \Delta E_{C-Cl} - \Delta E_{des}.$$  

The TPD spectra of the CFCs from the Pd(111) surface have yielded the desorption energies, $\Delta E_{des}$, while dissociative adsorption measurements have been used to estimate the apparent activation barrier for dechlorination, $\Delta E_{app}$. As in previous work studying the dechlorination of 1,1-dichloroethanes on the Pd(111) surface, this approach has been used in this work to obtain estimates of $\Delta E_{C-Cl}$ for both CF3CCl2 and CF3CHFCl. $\Delta E_{C-Cl}$ for CF3CCl3 has been obtained directly from measurements of dissociation during heating on the Pd(111) surface.

The values of $\Delta E_{des}$, $\Delta E_{app}$, and $\Delta E_{C-Cl}$ for the CFCs on Pd(111) are listed in Table 1. $\Delta E_{des}$ values decrease in the following order as the number of chlorine atoms is reduced: CF3CCl3 > CF3CFCl2 > CF3CHFCl > CF3CF2Cl. The values of $\Delta E_{app}$ exhibit a trend in the direction opposite that of the values of $\Delta E_{des}$: CF3CCl3 < CF3CFCl2 < CF3CHFCl < CF3CF2Cl. This variation in $\Delta E_{app}$ matches

Table 1

<table>
<thead>
<tr>
<th>CFC</th>
<th>$\Delta E_{des}$ (kJ/mol)</th>
<th>$\Delta E_{app}$ (kJ/mol)</th>
<th>$\Delta E_{C-Cl}$ (kJ/mol)</th>
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<tr>
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<td>$55.5 \pm 3$</td>
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<tr>
<td>CF3CHFCl</td>
<td>$43.5 \pm 2$</td>
<td>$12.6 \pm 0.7$</td>
<td>$56.1 \pm 3$</td>
</tr>
<tr>
<td>CF3CF2Cl</td>
<td>$37 \pm 2$</td>
<td>$&gt; 12.6$</td>
<td>$49.6$</td>
</tr>
</tbody>
</table>

$^a$ Estimated from the influence of adsorbed Cl on the $\Delta E_{des}$ of CF3CFCl2.
Fig. 10. Potential energy surfaces for C–Cl bond cleavage in CF₃CCl₃, CF₃CFCl₂, CF₃CF₂Cl, and CF₃CHFCl on the Pd(111) surface. The apparent barrier to dechlorination from the gas phase, $\Delta E_{\text{app}}$, is equal to the difference between the intrinsic barriers to C–Cl cleavage, $\Delta E_{\text{C–Cl}}$, and the desorption energy, $\Delta E_{\text{des}}$. $\Delta E_{\text{des}}$ increases as the number of chlorine atoms increases. If $\Delta E_{\text{C–Cl}}$ is weakly dependent on the number of chlorine atoms in the molecule, then the variation in $\Delta E_{\text{app}}$ is due principally to variation in $\Delta E_{\text{des}}$.

the relative reactivities of these compounds observed in hydrodechlorination catalysis [5]. To a first approximation the differences in reactivity can be explained using the potential energy diagram illustrated in Fig. 10. This shows the intrinsic barrier to C–Cl cleavage, $\Delta E_{\text{C–Cl}}$, as being independent of molecular structure. This was observed for our previous study of the dechlorination of 1,1-dichloroethanes on Pd(111) [9]. Although this is a very rough approximation of the results that we observe, the variation in $\Delta E_{\text{des}}$ is certainly greater than the variation in $\Delta E_{\text{C–Cl}}$ and thus the influence of $\Delta E_{\text{des}}$ on $\Delta E_{\text{app}}$ is greater than that of $\Delta E_{\text{C–Cl}}$. Within this approximation the differences in the observed reactivities or $\Delta E_{\text{app}}$ arise to the greatest extent from the fact that $\Delta E_{\text{des}}$ decreases as the number of chlorine atoms in the CFCs decreases. Certainly, this accounts for the differences in reactivity between CF₃CFCl₂ and CF₃CHFCl, as their measured $\Delta E_{\text{C–Cl}}$ values are almost identical and have been measured using the same approach. Our data cannot suggest that the variation in $\Delta E_{\text{des}}$ is the only source of difference in the reactivities of the CFCs, because in the case of CF₃CCl₃ we have measured an $\Delta E_{\text{C–Cl}}$ value of that is lower than those observed for CF₃CFCl₂ and CF₃CHFCl. It should be noted though that the value for CF₃CCl₃ has been estimated using a different method and the assumption that the preexponent for C–Cl cleavage is $\nu = 10^{13}$ s⁻¹. If there is any systematic difference between the results produced by the two methods, this could account for some of the difference. Nonetheless, the basic conclusion of our work is that the differences in the reactivities of the CFCs containing different number of Cl atoms must be in part due to the differences in their energies of desorption from the surface.

5. Conclusion

Measurements of the energetics of the different steps involved in the dechlorination of CFCs on the Pd(111) surface have provided some insight into the differences in reactivities of the CFCs under conditions of catalytic hydrodechlorination. A decrease in $\Delta E_{\text{des}}$ as a result of decreasing number of chlorine atoms in the CFC results in a net increase in the apparent barrier to dechlorination and, thus, a decrease in the overall reactivity.

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References