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

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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_3CCl_3, CF_3CFCl_2, CF_3CF_2Cl, and CF_3CHFCl. The desorption energies, ΔE_{des}, of the CFCs were found to increase with increasing number of chlorine atoms in the following order: $CF_3CF_2Cl < CF_3CHFCl < CF_3CFCl_2 < CF_3CCl_3$. The rate constants and apparent barriers to C–Cl cleavage, ΔE_{app}, on the Pd(111) surface were measured using CF_3CFCl_2, CF_3CF_2Cl, and CF_3CHFCl. The trend in ΔE_{app} was found to be opposite that for ΔE_{des}: $CF_3CFCl_2 < CF_3CHFCl < CF_3CF_2Cl$. For CF_3CFCl_2 and CF_3CHFCl the intrinsic activation energy for C–Cl cleavage on the Pd(111) surface, $\Delta E_{C\text{–}Cl}$, was determined by adding the desorption energies and the apparent activation energies for dissociative adsorption, $\Delta E_{C\text{–}Cl} = \Delta E_{app} + \Delta E_{app}$. In contrast with the other compounds, CF_3CCl_3 adsorbed on the Pd(111) surface dechlorinates rather than desorbing during heating, thus allowing direct measurement of $\Delta E_{C\text{–}Cl}$. Comparison of $\Delta E_{C\text{–}Cl}$ and ΔE_{des} among the CFCs suggests that the variations in ΔE_{des} have a greater influence on the dechlorination reactivity than the variations in $\Delta E_{C\text{–}Cl}$.

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_3CFH_2 are used as replacements for their counterpart CFCs such as CF_3CFCl_2. One route to obtain HFCs is the hydrodechlorination of CFCs over supported Pd catalysts [1].

$$CF_3CFCl_2 + 2H_2 \overset{Pd}{\rightarrow} CF_3CFH_2 + 2HCl.$$

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_2O_3 catalysts the rate of hydrodechlorination of CCl_4 is 100 times faster than that of CH_3Cl 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_3CCl_3:CF_3CFCl_2:CF_3CHFCl:CF_3CF_2Cl is 10^7:10^3:3:1

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[5]. 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 $\Delta \mathrm{E}_{\text{C–Cl}}$. 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.

$$\text{R–Cl}_{(g)} \overset{K}{\longleftrightarrow} \text{R–Cl}_{(ad)},$$

$$\text{R–Cl}_{(ad)} \xrightarrow{k_{\text{C–Cl}}} \text{R}_{(ad)} + \text{Cl}_{(ad)}.$$

These two steps are characterized by independent reaction energies, the desorption energy, ΔE_{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

$$r = \frac{k_{\text{C–Cl}}(K P_{\text{CFC}})^n}{(1 + K P_{\text{CFC}})^n}, \tag{1}$$

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_{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 $n = 1$. At low CFC pressures where $K P_{\text{CFC}} \ll 1$, Eq. (1) reduces to

$$r = k_{\text{C–Cl}}(K P_{\text{CFC}})^n. \tag{2}$$

The apparent activation energy for dissociative adsorption, ΔE_{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_3CCl_3, CF_3CFCl_2, CF_3CF_2Cl, and CF_3CHFCl) having varying chlorine content. In the case of CF_3CCl_3 this has been directly measurable because CF_3CCl_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 ΔE_{des} and ΔE_{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 ΔE_{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 ΔE_{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_α 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 $T < 100$ K and resistive heating to $T > 1000$ 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_3CCl_3 (99%, Lancaster Synthesis), CF_3CFCl_2, CF_3CHFCl, and CF_3CF_2Cl. Except for CF_3CCl_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 ~ 3.5 eV). The rates of dissociative adsorption of CF_3CFCl_2, CF_3CF_2Cl, and CF_3CHFCl 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_3CCl_3 were studied with XPS using a pass energy, E_p of 30 eV. The rate of CF_3CCl_3 dechlorination was measured by first exposing the Pd surface to CF_3CCl_3 at low temperature (~ 90 K). XPS was then used to monitor the Cl $2p$ photoemission as the surface was heated at 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 θ_{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, θ_{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 $I_{Cl}/I_{Pd} = 0.018$. The ratio of these peak areas was taken to be linear in the coverage, θ_{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_3CCl_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_3CFCl_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_3CFCl_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 ~ 0.26 L, the multilayer desorption peak appears at $T_p = 109$ K. The desorption energy of CF_3CFCl_2 at low coverages, ΔE_{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, ν, is 10^{13} s^{-1} [12]. The desorption spectra of CF_3CF_2Cl and CF_3CHFCl exhibit the same qualitative dependence on coverage as those of CF_3CFCl_2.

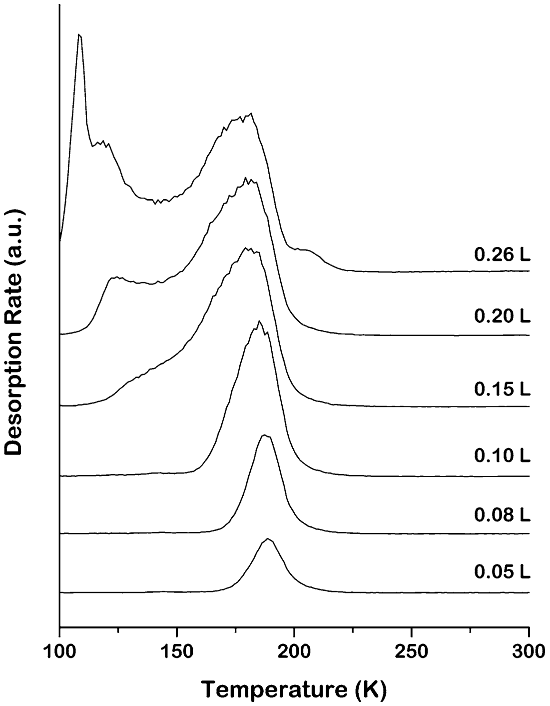

Fig. 1. TPD spectra of CF_3CFCl_2 on Pd(111) at varying initial coverages. Saturation of the monolayer occurs at an exposure of ~ 0.20 L. The heating rate was 2 K/s, and for the ionization fragment monitored, m/q was 69.

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, θ_H, of 0.9 ML [14]. The background hydrogen contamination level on the surface appeared to remain constant at $\theta_H \approx 0.05$ 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 ΔE_{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_3CF_2Cl, CF_3CHFCl, and CF_3CFCl_2 adsorb reversibly on the surface and desorb during heating without dissociation. The estimates of the values of ΔE_{des} for CF_3CF_2Cl, CF_3CHFCl, and CF_3CFCl_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_3CCl_3 desorption spectra are qualitatively different from those of the other three CFCs used in this study. At low coverages, CF_3CCl_3 decomposes on the surface. Molecular desorption of CF_3CCl_3 was not observed until the coverage reached the point that $\theta_{Cl} > 0.3$ 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 $\theta_{Cl} = 0.43$ [11]. At high coverage some fraction of the adsorbed CF_3CCl_3

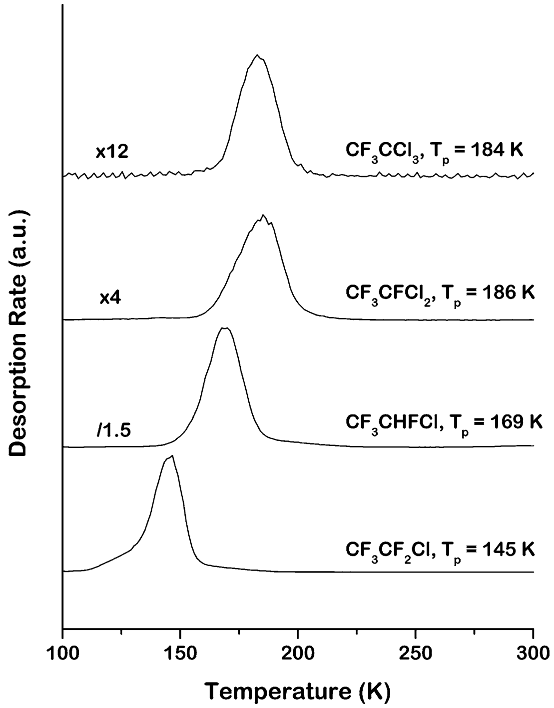

Fig. 2. TPD spectra of CF_3CCl_3, CF_3CFCl_2, CF_3CF_2Cl, and CF_3CHFCl on Pd(111) at low coverages. The heating rate was 2 K/s and m/q was 69.

desorbs at 184 K. 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 CF_3CCl_3 to be higher than that for CF_3CFCl_2; however, this is does not appear to be the case from the data shown in Fig. 2. The reason is that CF_3CCl_3 desorption occurs in the presence of adsorbed chlorine atoms generated by CF_3CCl_3 decomposition and does not occur from the clean Pd(111) surface. As will be shown a fraction of the CF_3CCl_3 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 CF_3CCl_3.

To determine the influence of adsorbed Cl on desorption of the CFCs, CF_3CFCl_2 desorption was studied in the presence of adsorbed Cl atoms. The Pd(111) surface was first exposed to CF_3CCl_3 at 300 K and annealed to 500 K to deposit Cl atoms onto the surface. TPD spectra of CF_3CFCl_2 on the clean surface and the Cl-covered surface are compared in Fig. 3. The peak desorption temperature for CF_3CFCl_2 was found to decrease from $T_p = 186$ to 150 K as a result of the presence of adsorbed Cl. These observations of the effect of adsorbed Cl atoms on CF_3CFCl_2 desorption suggest that Cl atoms generated by dechlorination of CF_3CCl_3 also decrease the peak desorption temperature of CF_3CCl_3. In other words, the peak desorption temperature for CF_3CCl_3 on the clean Pd(111) surface should be $T_p > 184$ K. If one assumes that chlorine has the same effect on the desorption temperature of CF_3CFCl_2 and CF_3CCl_3, then one could estimate that the desorption temperature of CF_3CCl_3 from the clean Pd(111) surface, T_p, would be ≈ 220 K. This would lead to an estimate for the desorption energy for CF_3CCl_3 from clean Pd(111) of $\Delta E_{des} \approx 57$ 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: $CF_3CCl_3 > CF_3CFCl_2 > CF_3CHFCl > CF_3CF_2Cl$.

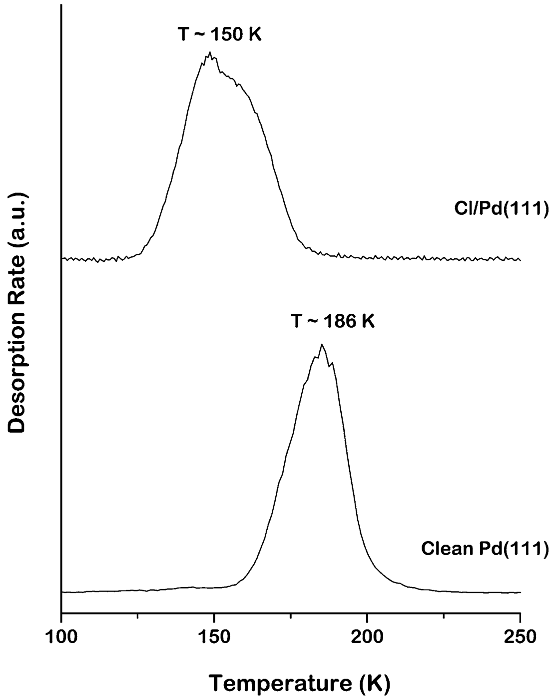

Fig. 3. TPD of CF_3CFCl_2 on both clean and Cl-precovered Pd(111) surfaces. The presence of chlorine on the surface reduces the CF_3CFCl_2 desorption temperature. The heating rate was 2 K/s, and for the ionization fragment monitored, m/q was 69.

3.2. Dissociative adsorption of CFCs on Pd(111)

For the three CFCs that adsorb reversibly on the Pd(111) surface (CF_3CF_2Cl, CF_3CHFCl, and CF_3CFCl_2) 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, $\Delta E_{C\text{–}Cl}$. The rate of dissociative adsorption was measured by exposing the Pd(111) surface to a continuous flux of CFCs and monitoring the Cl $2p$ XP spectra as a function of the exposure time. Fig. 4 shows a set of typical Cl $2p$ XP spectra obtained while the Pd(111) surface was exposed to a back-

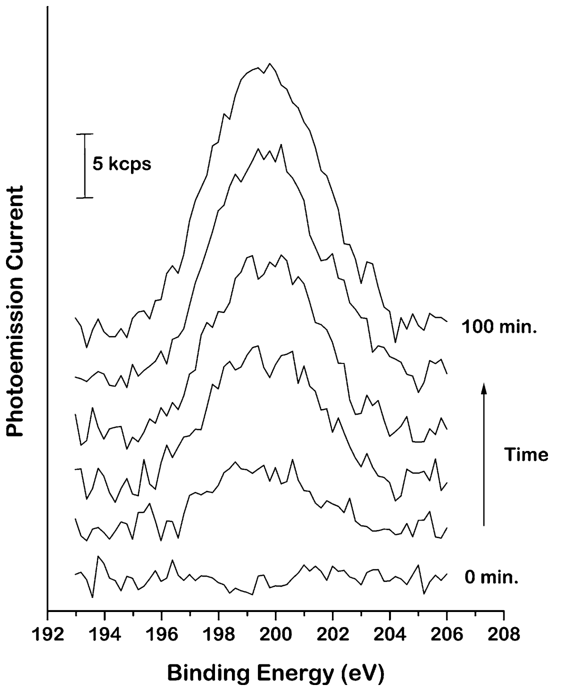

Fig. 4. Cl $2p$ XP peaks during exposure of Pd(111) to 3×10^{-9} Torr of CF_3CFCl_2 at 300 K. The peak grows monotonically with time during exposure. The pass energy, E_p, was 180 eV. The time intervals between obtaining spectra were 20 min.

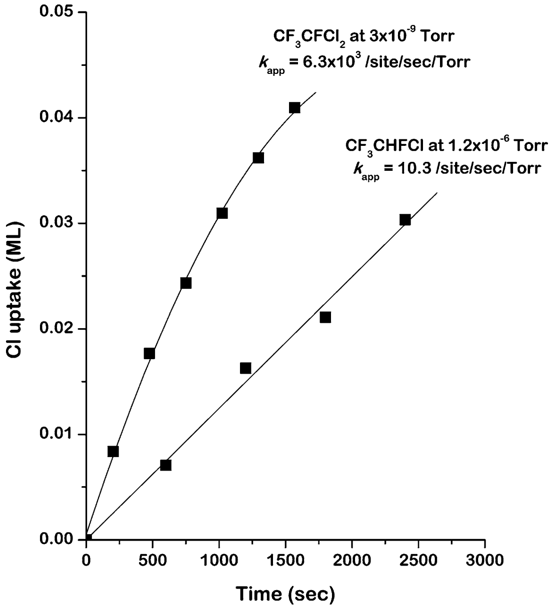

Fig. 5. Cl uptake on Pd(111) during exposure to 3×10^{-9} Torr of CF_3CFCl_2 and 1.2×10^{-6} Torr of CF_3CHFCl at 300 K. The apparent rate constants for dechlorination on the clean Pd(111) surface are determined from the initial slopes of the uptake curves.

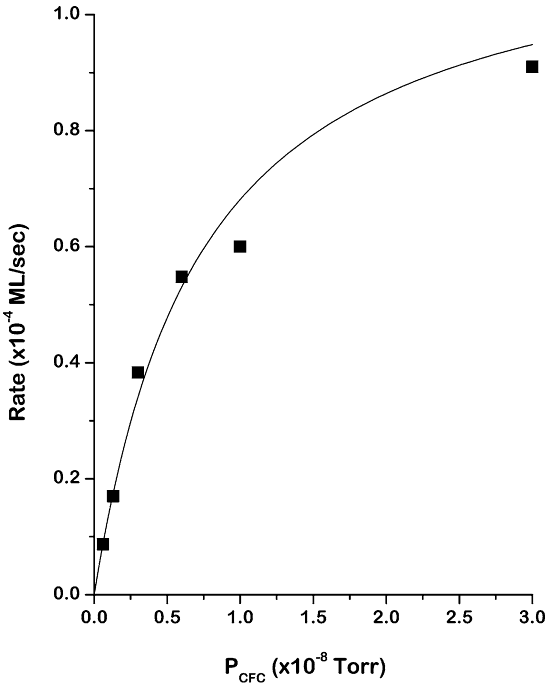

Fig. 6. Rate of CF_3CFCl_2 dechlorination on Pd(111) versus pressure at 300 K. The data have been fit to the functional form for Langmuir kinetics. The plot yields a reaction order, n, of 1.02 ± 0.11.

ground pressure of 3×10^{-9} Torr of CF_3CFCl_2 at 300 K. 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_3CFCl_2 (obtained at a pressure of 3×10^{-9} Torr) and CF_3CHFCl (1.2×10^{-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_3CFCl_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_3CHFCl, 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 $P_{\text{CFC}} \leqslant 10^{-6}$ Torr), dechlorination of CF_3CF_2Cl on the Pd(111) surface was not observable. Presumably either the rate constant for C–Cl bond dissociation or the equilibrium constant for CF_3CF_2Cl 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 CF_3CFCl_2 and that of CF_3CHFCl are first-order processes. As a result the apparent rate constants for dissociative adsorption can be determined from the expression

$$k_{app} = \frac{r}{a P_{CFC}}, \tag{4}$$

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 ΔE_{app}, the apparent barrier to dissociative adsorption of the CFCs on Pd(111).

The relative reactivities of CF_3CFCl_2 and CF_3CHFCl can be compared by reexamining Fig. 5. It is clear from the figure that the apparent rate constant for dissociative adsorption of CF_3CFCl_2 is greater than that for CF_3CHFCl. 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 CF_3CFCl_2 and CF_3CHFCl 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, ΔE_{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 CF_3CFCl_2 and CF_3CHFCl on the Pd(111) surface. These yield ΔE_{app} values of 7.5 ± 1.2 kJ/mol for CF_3CFCl_2 and 12.6 ± 0.7 kJ/mol for CF_3CHFCl. 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 CF_3CF_2Cl, the fact that the apparent rate of dissociative adsorption was not measurable implies that ΔE_{app} for dissociative adsorption of CF_3CF_2Cl is even higher than that of CF_3CHFCl. It should be noted here that the trend of ΔE_{app} is opposite that found for ΔE_{des}. The magnitudes of the ΔE_{app} take the order $CF_3CF_2Cl > CF_3CHFCl > CF_3CFCl_2$.

3.3. Kinetics of CF_3CCl_3 dechlorination on Pd(111)

Rather than desorbing during heating, CF_3CCl_3 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, $\Delta E_{C\text{–}Cl}$. The C–Cl cleavage kinetics can be studied by obtaining Cl $2p$ XP spectra during heating of the CF_3CCl_3 adsorbed on the Pd(111) surface. The Cl $2p$ XP spectra obtained at 90, 163, and 250 K for CF_3CCl_3 on the Pd(111) surface are shown in Fig. 8. Also included in the fig-

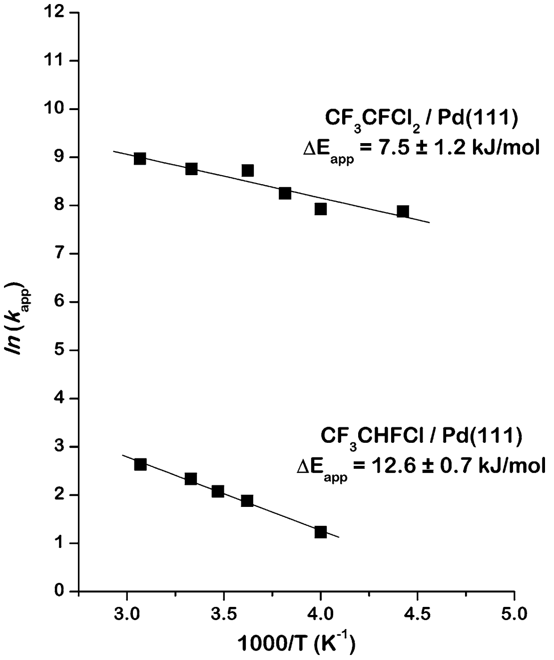

Fig. 7. Arrhenius plots for the dechlorination of CF_3CFCl_2 and CF_3CHFCl on Pd(111). Dechlorination rates were measured in constant pressures of 3×10^{-9} Torr of CF_3CFCl_2 and 1.2×10^{-6} Torr of CF_3CHFCl.

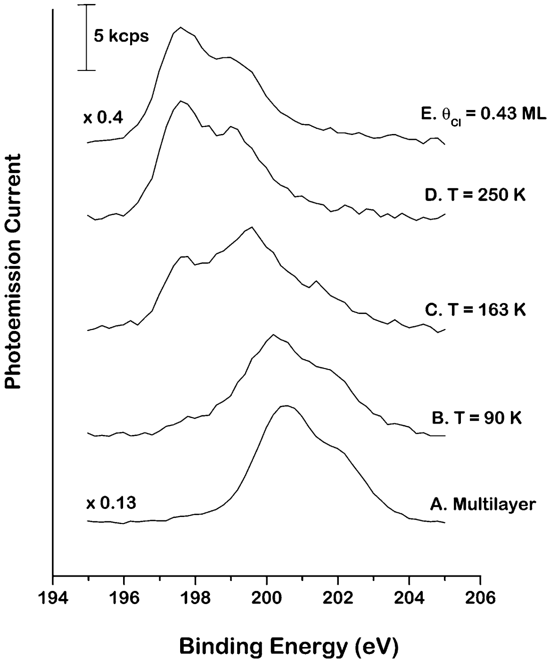

Fig. 8. X-ray photoemission spectra of Cl $2p$ peak in CF_3CCl_3 on Pd(111) during heating at 0.1 K/s. (A) Multilayer CF_3CCl_3 at $T = 95$ K. (B) Monolayer at $T = 90$ K. (C) Monolayer at $T = 163$ K. (D) Monolayer at $T = 250$ K. (E) Spectrum of saturated layer of atomic chlorine on Pd(111).

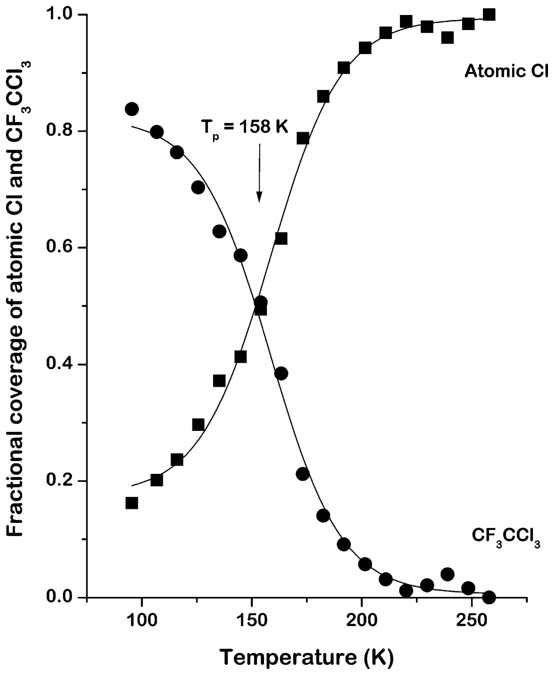

Fig. 9. Fractional coverage of Cl adsorbed as Cl atoms (■) and in CF_3CCl_3 (●) during heating of CF_3CCl_3 on the Pd(111) surface from 95 to 250 K at 0.1 K/s. The solid lines represent fits of the data using a Boltzmann function. The inflection point of the fitted curve is used to determine the temperature of the maximum in the C–Cl bond dissociation rate.

ure are the Cl $2p$ XP spectra of multilayer CF_3CCl_3 and a 0.43 ML coverage of atomic Cl produced by exposure to Cl_2 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 CF_3CCl_3 monolayer is similar to that of the multilayer; however, the shoulder at ~ 198 eV indicates that there has been some low-temperature dissociation of CF_3CCl_3 on the Pd surface. The XP spectrum at 250 K reveals that CF_3CCl_3 has dechlorinated completely to yield atomic Cl on the Pd(111) surface. The XP spectra of multilayer CF_3CCl_3 and saturated Cl monolayer can be used as basis spectra for factor analysis of the spectra at intermediate coverages to determine the coverages of CF_3CCl_3 and atomic Cl on the Pd(111) surface as it is heated.

The kinetics of CF_3CCl_3 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, $\Delta E_{\text{C–Cl}}$. Factor analysis has been used to decompose the Cl $2p$ XP spectra shown in Fig. 8 into components arising from intact CF_3CCl_3 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 CF_3CCl_3 during heating of the Pd(111) surface with a coverage of adsorbed CF_3CCl_3 that ultimately dissociates to generate an atomic Cl coverage, θ_{Cl}, of 0.3 ML. The increase in the coverage of the atomic Cl indicates that CF_3CCl_3 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 $\nu = 10^{13}\ \text{s}^{-1}$, the activation barrier to dechlorination of CF_3CCl_3 on the Pd(111) surface, $\Delta E_{\text{C–Cl}}$ is estimated to be ~ 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):

$$k_{\text{app}} = k_{\text{C–Cl}} K. \tag{5}$$

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:

$$\Delta E_{\text{app}} = \Delta E_{\text{C–Cl}} - \Delta E_{\text{des}}. \tag{6}$$

The TPD spectra of the CFCs from the Pd(111) surface have yielded the desorption energies, ΔE_{des}, while dissociative adsorption measurements have been used to estimate the apparent activation barrier for dechlorination, ΔE_{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 $\Delta E_{\text{C–Cl}}$ for both CF_3CFCl_2 and CF_3CHFCl. $\Delta E_{\text{C–Cl}}$ for CF_3CCl_3 has been obtained directly from measurements of dissociation during heating on the Pd(111) surface.

The values of ΔE_{des}, ΔE_{app}, and $\Delta E_{\text{C–Cl}}$ for the CFCs on Pd(111) are listed in Table 1. ΔE_{des} values decrease in the following order as the number of chlorine atoms is reduced: $CF_3CCl_3 > CF_3CFCl_2 > CF_3CHFCl > CF_3CF_2Cl$. The values of ΔE_{app} exhibit a trend in the direction opposite that of the values of ΔE_{des}: $CF_3CCl_3 < CF_3CFCl_2 < CF_3CHFCl < CF_3CF_2Cl$. This variation in ΔE_{app} matches

Table 1
ΔE_{des}, ΔE_{app}, and $\Delta E_{\text{C–Cl}}$ for CF_3CCl_3, CF_3CFCl_2, CF_3CF_2Cl, and CF_3CHFCl on the Pd(111) surface

CFC	ΔE_{des} (kJ/mol)	ΔE_{app} (kJ/mol)	$\Delta E_{\text{C–Cl}}$ (kJ/mol)
CF_3CCl_3	(57)[a]	< 0	44 ± 2
CF_3CFCl_2	48 ± 2	7.5 ± 1.2	55.5 ± 3
CF_3CHFCl	43.5 ± 2	12.6 ± 0.7	56.1 ± 3
CF_3CF_2Cl	37 ± 2	> 12.6	> 49.6

[a] Estimated from the influence of adsorbed Cl on the ΔE_{des} of CF_3CFCl_2.

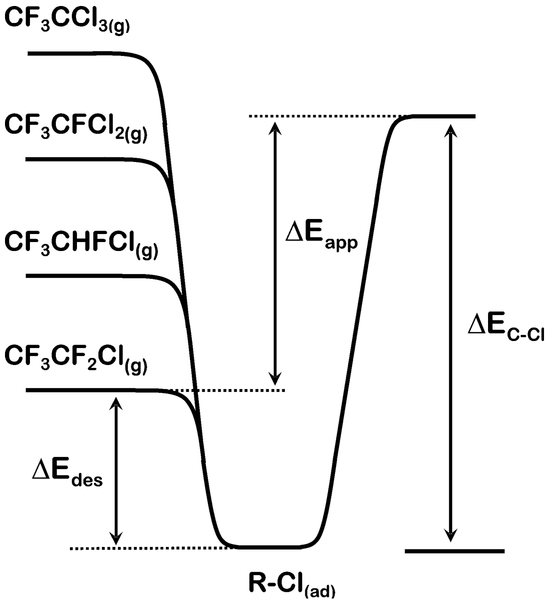

Fig. 10. Potential energy surfaces for C–Cl bond cleavage in CF_3CCl_3, CF_3CFCl_2, CF_3CF_2Cl, and CF_3CHFCl on the Pd(111) surface. The apparent barrier to dechlorination from the gas phase, ΔE_{app}, is equal to the difference between the intrinsic barriers to C–Cl cleavage, $\Delta E_{C\text{–}Cl}$, and the desorption energy, ΔE_{des}. ΔE_{des} increases as the number of chlorine atoms increases. If $\Delta E_{C\text{–}Cl}$ is weakly dependent on the number of chlorine atoms in the molecule, then the variation in ΔE_{app} is due principally to variation in ΔE_{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, $\Delta E_{C\text{–}Cl}$, 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 ΔE_{des} is certainly greater than the variation in $\Delta E_{C\text{–}Cl}$ and thus the influence of ΔE_{des} on ΔE_{app} is greater than that of $\Delta E_{C\text{–}Cl}$. Within this approximation the differences in the observed reactivities or ΔE_{app} arise to the greatest extent from the fact that ΔE_{des} decreases as the number of chlorine atoms in the CFCs decreases. Certainly, this accounts for the differences in reactivity between CF_3CFCl_2 and CF_3CHFCl, as their measured $\Delta E_{C\text{–}Cl}$ values are almost identical and have been measured using the same approach. Our data cannot suggest that the variation in ΔE_{des} is the only source of difference in the reactivities of the CFCs, because in the case of CF_3CCl_3 we have measured an $\Delta E_{C\text{–}Cl}$ value of that is lower than those observed for CF_3CFCl_2 and CF_3CHFCl. It should be noted though that the value for CF_3CCl_3 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 ΔE_{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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