Dechlorination of Fluorinated 1,1-Dichloroethanes on Pd(111)

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The kinetics of C−Cl bond cleavage have been investigated by studying the dissociative adsorption of four fluorinated 1,1-dichloroethanes (CH_3CHCl_2, CH_3CFCl_2, CH_2FCFCl_2, CF_3CFCl_2) on a Pd(111) surface. The apparent rate constants (k_{app}) and activation energies (E_{app}) for dissociative adsorption on Pd(111) show a systematic trend that depends on the fluorine content of the molecule. Fluorination decreases the rate constant for dissociative adsorption, an effect that is identical to the trend in activity observed for catalytic hydrodechlorination of fluorinated chloromethanes over supported Pd catalysts. Measurement of the desorption energies (E_{des}) of the dichloroethanes on Pd(111) have shown that increasing the amount of fluorine in the molecule decreases the desorption energy. The focus of this investigation has been the determination of the effect of fluorination on the intrinsic activation barrier to C−Cl bond cleavage (E_{C-Cl}). The intrinsic barrier to C−Cl cleavage was determined for each dichloroethane by adding the desorption energy and the apparent activation energy for dissociative adsorption ($E_{C-Cl} = E_{des} + E_{app}$). A linear free energy relationship was established for the rate of dechlorination in an attempt to probe the nature of the transition state to C−Cl bond cleavage ($[RC\cdots Cl]^{\ddagger}$). The intrinsic dechlorination barrier remains unchanged as the degree of fluorination in the molecule is varied. The interpretation of this result is that the electron distribution between the carbon and the chlorine atoms in the transition state for C−Cl bond cleavage is similar to that of the reactant. This is consistent with a homolytic transition state that is early in the reaction coordinate.

1. Introduction

It is believed that stratospheric ozone depletion has been caused largely by the release of chlorofluorocarbons (CFCs) into the environment. CFCs have had extensive commercial application and there is an urgent need to replace them with environmentally benign materials with similar properties. Hydrofluorocarbons (HFCs) are a family of molecules that have emerged as potential substitutes for CFCs in many applications.[1] In particular, CF_3CFH_2 is currently being used to replace CF_2Cl_2 in air-conditioning units.

One route to the production of CF_3CFH_2 is the hydrodechlorination of CF_3CFCl_2 over supported Pd catalysts.

$$CF_3CFCl_2 + 2H_2 \xrightarrow{Pd} CF_3CFH_2 + 2HCl$$
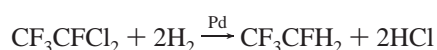
Currently the hydrodechlorination of CF_3CFCl_2 yields CF_3CFH_2 with a selectivity greater than 70%.[2−4] A greater understanding of the mechanism and kinetics of this reaction would aid attempts to improve catalyst activity and selectivity. Previous studies have focused on the hydrodechlorination of several CFCs at atmospheric pressures, and a consistent picture is emerging regarding the mechanism of the reaction and the relative activities of different catalysts and reactivities of different chlorocarbons. One common result is that increasing the number of chlorine atoms attached to a carbon atom increases the rate of hydrodechlorination. For example, on Pd/Al_2O_3 catalysts, CF_3CFCl_2 is hydrodechlorinated at a much higher rate than its symmetric isomer, CF_2Cl-CF_2Cl.[4] Similarly, studies of hydrodechlorination on Pt/Al_2O_3 catalysts have found that increasing the number of chlorine atoms in chloromethanes from CH_3Cl

to CCl_4 increases the rate of hydrodechlorination by a factor of 100 at 120 °C.[5] A comparison of the hydrodechlorination of various chlorofluoromethanes has also revealed that increasing the fluorine content lowers the overall rate of hydrodechlorination on Pd/AlF_3 catalysts.[6] One of the important points to be made in this paper is that these observed trends in CFC reactivity are also observed in the dechlorination of CFCs over Pd(111) surfaces.

Thus far, several mechanisms for the hydrodechlorination reaction have been proposed and some suggestions have been made about the rate-limiting step for hydrodechlorination.[2,3,7−9] Currently, there is no general agreement on the rate-limiting step for the hydrodechlorination of CF_3CFCl_2. Weiss et al. proposed dissociative adsorption as the rate-limiting step in the hydrodechlorination of CCl_4.[5] However, Ribiero et al. propose that the rate-limiting step in the hydrodechlorination of CF_3CFCl_2 is the associative adsorption of the molecule.[3] The focus of the work presented in this paper has been the dechlorination step or cleavage of the C−Cl bond in the adsorbed chlorocarbon, a step which must occur relatively early in the reaction mechanism and certainly appears to influence the overall rate of hydrodechlorination.

Control of activity and selectivity in any catalytic reaction requires a fundamental understanding of the reaction mechanism and the kinetics of each elementary reaction step. The rate of an elementary reaction step is dependent on the activation barrier, the difference between the energies of the reactant and the transition state. The goal of this investigation is to understand the nature of the transition state for the elementary step of C−Cl bond cleavage. Such an understanding will help to explain the observed differences in activity/selectivity among different chlorocarbons and allow prediction of the dechlorination rates of similar CFCs. This knowledge would aid the development

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of catalysts for HFC production and for disposal of other chlorinated industrial wastes.

The method of this investigation has been to use fluorine substitution to probe the nature of the transition state for C−Cl bond cleavage in CFCs on a Pd(111) surface. In a previous study, correlations between the rate constants for dissociative adsorption (dechlorination) of CFCs and their degree of fluorination were shown to match correlations found in catalytic hydrodechlorination rates on supported Pd catalysts.[6,10] This suggests that the dechlorination step plays an important part in the overall hydrodechlorination kinetics. In this paper we report the results of independent measurements of the two steps involved in the dissociative adsorption of CFCs: the reversible adsorption step $[(R−Cl_{(g)} \leftrightarrow R−Cl_{(ad)})]$ and the dechlorination step $[(R−Cl_{(ad)} \rightarrow R_{(ad)} + Cl_{(ad)})]$. Two quantities have been measured: the desorption energy (E_{des}) and the apparent activation energy to dissociative adsorption (E_{app}). The intrinsic activation barrier to C−Cl bond cleavage (E_{C-Cl}) is then calculated as

$$E_{C-Cl} = E_{des} + E_{app}$$

This intrinsic barrier to C−Cl bond cleavage has been determined for four partially fluorinated 1,1-dichloroethanes and can be correlated with the degree of fluorination.

Correlation of reaction rate constants and activation barriers with reactant substitution (in this case fluorination) provides insight into the nature of the transition state of an elementary reaction step. Such correlations are referred to as linear free energy relationships (LFERs) and have been applied in physical organic chemistry extensively as a means of studying organic reactivity.[11-14] These ideas have been applied to surface reactions and catalytic processes in order to gain the same types of insights into surface reactivity. For example, in the transition state for RC−Cl bond cleavage ($[RC \cdots Cl]^{\ddagger}$), if the electron distribution between the carbon and chlorine remains the same on going from the initial state to the transition state, adding an electronegative substituent (R) to the carbon atom would not perturb the activation barrier significantly. However, if the carbon atom in the transition state is *cationic* with respect to the initial state ($[RC^{\delta+} \cdots Cl]^{\ddagger}$), an electronegative substituent such as fluorine would increase the activation barrier by destabilizing the electron-deficient transition state. Alternately, if the carbon atom in the transition is *anionic* with respect to the initial state ($[RC^{\delta-} \cdots Cl]^{\ddagger}$), adding an electronegative substituent would serve to lower the activation barrier by stabilizing the electron-rich transition state. The "electronegativity" of substituent groups such as CF₃ groups is commonly reflected in their inductive or field substituent constants (σ_F). These field constants are empirically derived measures of the electrostatic or field effect of a dipolar group such as CF₃ on nearby charge. For instance, a CF₃ group has a constant of σ_F-(CF₃) = 0.44, while a CH₃ group has a field constant of σ_F-(CH₃) = 0.00.[12] By varying the substituents (degree of fluorination) in the dichloroethanes and measuring the corresponding change in the E_{C-Cl}, we have been able to probe the transition state for C−Cl bond cleavage on Pd(111).

In any study of substituent effects on reaction rates, both the choice of substituent and the placement of the substituent in the reactant are important. Ideally, the substituent should not alter the reaction mechanism, but should stabilize or destabilize the transition state through inductive effects. Substitutions directly at the reaction center (C−Cl bond) may cause steric effects, and the close proximity of an electronegative atom to the reaction center may influence the electron distribution in

the transition state. The introduction of steric and direct electronegative effects can complicate the interpretation of data. In this investigation the CFC of commercial interest is CF₃-CFCl₂. Thus, the choice of reactants used to probe the transition state to C−Cl bond cleavage are variations of this molecule differing in the choice of substituents (CH₃CHCl₂, CH₃CFCl₂, CH₂FCFCl₂, CF₃CFCl₂). Technically these are not all CFCs; however, we shall refer to the set of reactants collectively as CFCs. Fluorine is an ideal choice as a substituent because of its high degree of electronegativity and relatively small size. The high electronegativity of fluorine provides large inductive effects, while its small size minimizes steric effects. Fluorine substitutions have been used successfully in other investigations to probe changes in charge distributions during surface reactions.[15-19] Because of the limited number of CFCs available, substitution had to be done both away from the reaction center and at the reaction center. However, the fact that we have been able to correlate the energetics among reactants suggests that this has not presented problems in this investigation. The results of this study of the dechlorination reaction on Pd(111) surfaces show clear correlations between the substituent constant (σ_F) and three quantities: the apparent activation energy to dissociative adsorption (E_{app}), the desorption energy (E_{des}), and the intrinsic activation barrier to C−Cl bond cleavage (E_{C-Cl}). The net effects of fluorination on the E_{C-Cl} are found to be insignificant and are certainly much smaller than those observed in previous such investigations of other surface reactions such as β-hydride elimination or alkyl coupling.[15-19] These results suggest that there is little change in charge distribution between the initial state and the transition state for cleavage of C−Cl bonds.

2. Experimental Section

All experiments were performed in a stainless steel ultrahigh vacuum (UHV) chamber operated at base pressures below 3×10^{-10} Torr. The Pd(111) crystal was mounted in the chamber by spot-welding between two tantalum wires in mechanical contact with a liquid nitrogen reservoir to provide cooling. The crystal was heated resistively and its temperature was measured by a chromel/alumel thermocouple spot-welded to its edge. The crystal surface was cleaned by multiple cycles of Ar⁺ bombardment followed by periodic annealing to 1200 K. The surface composition was determined by X-ray photoemission spectroscopy (XPS). The XP spectrometer uses a VG Microtech 800W Al Kα X-ray source and a CLAM II analyzer. Spectra were obtained using a pass energy of 140 eV for the Cl 2p peak in order to maximize signal and 105 eV for the Pd 3d peak.

Desorption energies were determined by temperature-programmed desorption (TPD). The Pd(111) surface was exposed to the CFCs through a capillary array attached to a leak valve. The purity of chemicals used in experimentation was determined using a quadrupole mass spectrometer (Extrel Model C50). In a typical TPD experiment, adsorption occurred at a crystal temperature of 90−120 K. The TPD spectrum was obtained by heating the sample at a rate of 3 K/s and using the mass spectrometer to monitor as many as three mass/charge ratios during a single experiment.

The rate of dissociative adsorption of the CFCs was measured by exposing the heated crystal (250−325 K) to a constant background pressure of the CFC and using XPS to monitor the uptake of chlorine on the surface. XP spectra of the surface were obtained periodically during the CFC exposure to measure the chlorine coverage on the surface. TPD studies of CF₃-CFCl₂,[20] CH₃CFCl₂, CH₂FCFCl₂, and CH₃CHCl₂ (reported in
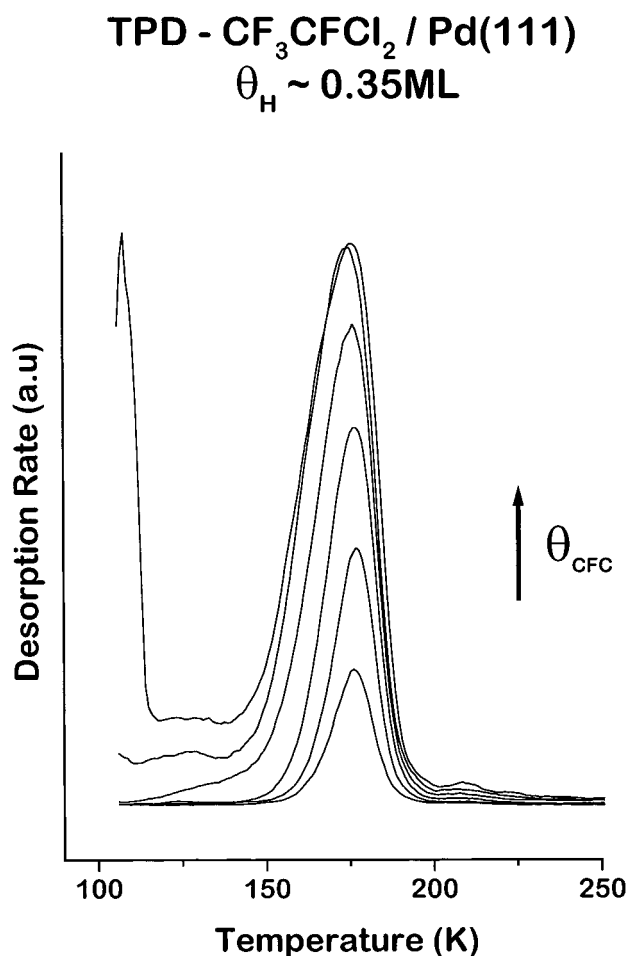
TPD - CF$_3$CFCl$_2$ / Pd(111)
$\theta_H \sim 0.35$ML

Figure 1. TPD spectra for CF$_3$CFCl$_2$ on Pd(111) at varying initial coverages. The initial hydrogen coverage on the surface was ~0.35 ML. The heating rate was 3 K/s. $m/q = 101$.

this paper) have shown that desorption from the Pd(111) surface occurs at temperatures well below 250 K. As a result the equilibrium coverage of the CFCs at temperatures above 250 K can be assumed to be negligible and any chlorine detected on the Pd(111) surface is present in the form of adsorbed atomic chlorine. Thus, measurement of the chlorine coverage versus time provides a measure of the rate of dissociative adsorption.

The calibration of the XPS signal versus chlorine coverage (θ_{Cl}) was achieved by saturating the Pd(111) surface with chlorine by exposure to Cl$_2$ gas at 300 K. This procedure is known to produce an overlayer with a coverage of $\theta_{Cl} = 0.43$ monolayers (ML).[21] At $\theta_{Cl} = 0.43$ ML the ratio of the Cl 2p XPS peak area to the Pd 3d peak area is 0.018. The ratio of the Cl 2p and Pd 3d peak areas is taken to be linear in the chlorine coverage in order to provide a calibration curve. The amount of hydrogen present on the surface was measured by TPD, assuming that a saturated H/Pd(111) surface corresponds to a coverage of $\theta_H = 0.9$ ML.[22] The Pd(111) surface exposes 1.53 $\times$ 10^{15} atoms/cm^2; thus 1 ML of chlorine corresponds to 1.53 $\times$ 10^{15} atoms/cm^2.

One potential problem with the use of XPS to measure chlorine uptake is that the X-rays may influence C−Cl bond cleavage. The Pd(111) surface was normally exposed to X-rays for roughly half of the total time of exposure to the CFCs. Control experiments were performed in which the Pd(111) surface at 450 K was exposed to each of the CFCs in the complete absence of X-rays. At the end of the control experiments, the chlorine coverage was measured and was compared

to the chlorine coverage found following exposures with the X-rays on (for half of the time). For all four CFCs, the chlorine coverage deposited in the absence of X-rays was the same (within our limits of experimental reproducibility) as that deposited with the X-rays on. Control experiments were also performed using CH$_2$FCFCl$_2$ at temperatures of 250, 275 and 300 K. At these lower temperatures, there was no difference in the amount of chlorine deposited either with or without the X-rays. This indicates that the X-ray exposures used did not have a significant influence on the rate constants for dechlorination of the CFCs.

3. Results

3.1. Desorption of the CFCs. Since CFCs are reversibly adsorbed on the Pd(111) surface one of the important parameters in the analysis of the dechlorination rate is the desorption energy. Thermally programmed desorption experiments were performed on Pd(111) to measure the desorption energies of CF$_3$CFCl$_2$, CH$_2$FCFCl$_2$, CH$_3$CFCl$_2$, and CH$_3$CHCl$_2$. For molecular adsorption/desorption, it is assumed that there is no activation barrier to adsorption, and thus, the activation energy to desorption is equal to the desorption energy (E_{des}). The TPD results for CF$_3$-CFCl$_2$ in Figure 1 show that at low initial coverages, the molecule desorbs with a maximum rate at 175 K. As the initial coverage is increased, the peak at 175 K grows until it saturates. This is indicative of the completion of an adsorbed monolayer on the surface. At higher coverages a multilayer desorption peak is seen at 108 K that does not saturate with further increases in coverage. The constant temperature of the monolayer desorption peak is characteristic of first-order desorption. TPD experiments show that the relative intensities of desorption spectra obtained using different m/q ratios are approximately equal to those in the fragmentation pattern of the molecule originally adsorbed on the surface. This indicates that adsorption is reversible. The desorption energy is calculated to be $E_{des} = 45 \pm 1$ kJ/mol, assuming a preexponential factor of $\nu = 10^{13}$ sec^{-1} in the desorption rate constant and a peak temperature measurement accurate to within ± 2 K. It should be noted that the desorption spectra shown in Figure 1 were obtained with hydrogen present on the Pd(111) surface at coverages on the order of 0.35 ML. The hydrogen coverage was determined by monitoring H$_2$ desorption during the TPD experiment. Hydrogen does influence the desorption energy and since it was not possible to completely remove hydrogen from the surface during the dechlorination experiments this effect will be quantified below.

The desorption behavior of the other CFCs is similar to that of CF$_3$CFCl$_2$ in the sense that adsorption is molecular and reversible and occurs at temperatures below 250K. Since the dechlorination experiments are all performed at temperatures >250K the steady state coverage of the CFCs on the Pd(111) surface during dechlorination was very low. As a result it is the low coverage desorption energy that is most important to our analysis of the dechlorination kinetics and this has been measured from TPD spectra for coverages of approximately 0.01 ML of the CFCs (Figure 2). The coverage is determined by comparison of the peak area with that of the complete monolayer. Again, these desorption spectra have been obtained in the presence of roughly 0.35 ML of adsorbed hydrogen. The maximum in the desorption rate of 0.01 ML CH$_2$FCFCl$_2$ occurred at 200 K. This peak temperature corresponds to a desorption energy of 51 ± 1 kJ/mol. TPD experiments for CH$_3$-CFCl$_2$, and CH$_3$CHCl$_2$ performed at initial coverages of 0.01 ML revealed peak desorption temperatures of 212 and 223 K, respectively. These temperatures correspond to desorption energies of 54 ± 1 kJ/mol and 57 ± 1 kJ/mol, respectively.
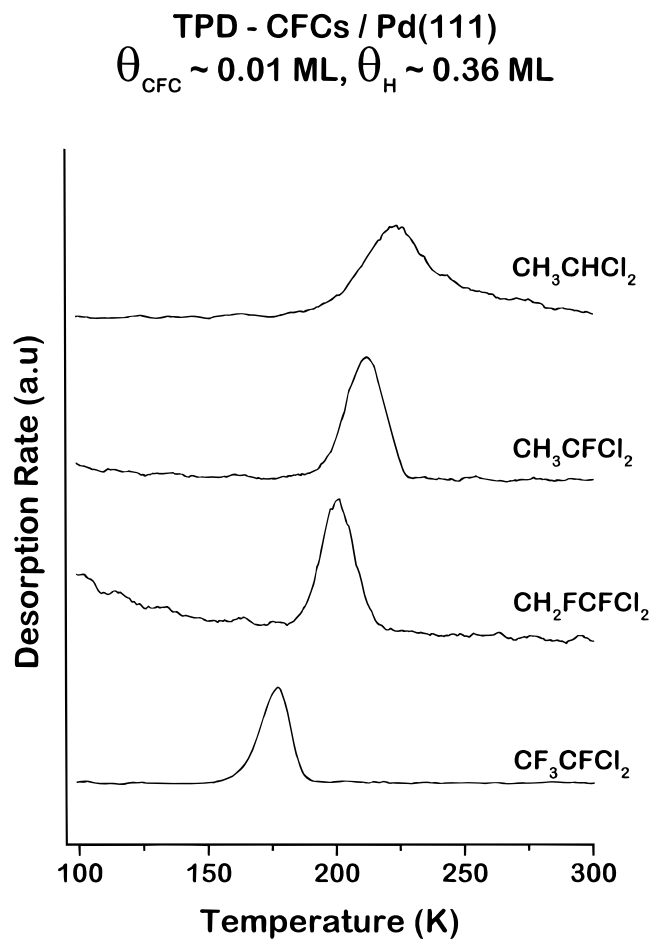
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TPD - CFCs / Pd(111)
$\theta_{CFC} \sim 0.01$ ML, $\theta_H \sim 0.36$ ML

Figure 2. TPD spectra for CH_3CHCl_2, CH_3CFCl_2, CH_2FCFCl_2, and CF_3CFCl_2 at low initial coverages (~0.01 ML) in the presence of ~0.35 ML of adsorbed hydrogen. The heating rate was 3 K/s. $m/q = 63$, 81, 101, and 101, respectively.

E_{des}(CFCs) - θ_H/Pd(111)

Figure 3. Low-coverage ($\theta_{CFC} \approx 0.01$) desorption energies of the CFCs on Pd(111) as a function of the coverage of coadsorbed hydrogen. The hydrogen was adsorbed from the background using H_2 exposure. Fluorination of the CFC systematically decreases the desorption energy. Coadsorbed hydrogen also decreases the desorption energy.

Previous studies of CFCs on the Pd(111) surface have also shown that they are adsorbed molecularly and reversibly. Our TPD results can be compared directly with Rotondi's TPD of CF_3CFCl_2 from Pd(111).[20] Heating rates of 3 K/s were used in both cases and in both cases the results indicate first-order desorption. However, the heat of adsorption of CF_3CFCl_2 calculated using our data is 45 kJ/mol while Rotondi's indicated a desorption energy of 51 kJ/mol. In his investigation, Rotondi addressed the effect of preadsorbed hydrogen on the peak temperature of desorption and found that preadsorbed hydrogen in the amount $\theta_H = 0.5$ ML lowered the desorption energy of CF_3CFCl_2 from 51 kJ/mol to 45 kJ/mol. Monitoring the desorption signal at $m/q = 2$ during our experiments showed that there was hydrogen present on the surface at a coverage of roughly 0.35 ML. Because Pd absorbs hydrogen, the bulk of the crystal can serve as a source of hydrogen at the surface. Although it can be removed by extended heating in UHV it was found that heating the Pd crystal in the presence of the CFCs for extended periods of time always caused the reappearance of hydrogen. Since it was not possible to avoid the presence of hydrogen on the surface during the dechlorination experiments, we have instead quantified the effects of hydrogen on desorption energies and included these effects in our subsequent analysis of the reaction energetics for dechlorination. Figure 3 plots the desorption energies of the fours CFCs (at low coverage) as a function of hydrogen coverage. Hydrogen was coadsorbed with the CFC by exposure of the surface to H_2 gas. As observed previously the desorption energy decreases with increasing
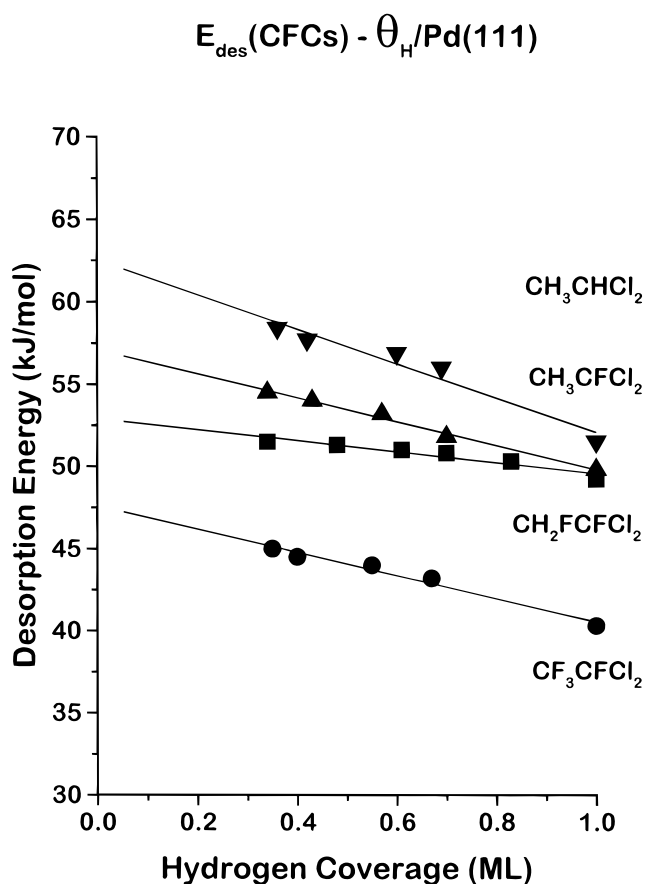
hydrogen coverage. Although the presence of hydrogen lowers the desorption energies of all the CFCs it does not change the relative order of their desorption energies in the range of hydrogen coverages of interest.

3.2. Dissociative Adsorption of Chlorofluoroethanes. Measurement of the kinetics of dissociative adsorption of the CFCs on the Pd(111) surface enables us to determine an apparent activation barrier (E_{app}) to dechlorination which can then be combined with the desorption energy (E_{des}) to calculate the intrinsic barrier to C−Cl bond cleavage ($E_{C−Cl}$). Dissociative adsorption experiments were performed using CF_3CFCl_2, CH_3-$CFCl_2$, CH_2FCFCl_2, and CH_3CHCl_2. The dissociative adsorption rates were determined by exposing the Pd(111) surface to a continuous flux of the CFCs and using the Cl 2p XP spectra to measure the chlorine coverage as a function of the duration of exposure. A typical set of XP spectra obtained from such an experiment is shown in Figure 4. By calculating the area under these curves and normalizing to the area under the Pd 3d peak, the absolute chlorine coverage can be determined from the chlorine coverage calibration curve previously described. These data can then be plotted as the chlorine uptake curve inlaid in Figure 4. The data points are fit using second-order regression. The initial slopes of the uptake curves are used to determine the initial rate (r) of chlorine deposition in units of molecules/site/second. In this case a site is taken to be an exposed Pd atom. These rates can then be used to determine the rate constants for the dechlorination reaction as will be discussed below.

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Chlorine Uptake
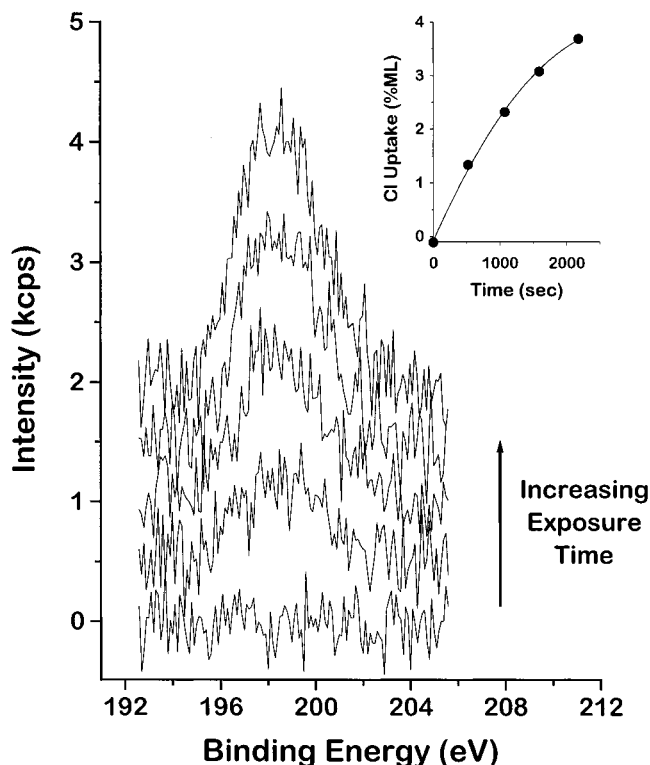**CH_3CHCl_2/Pd(111), $\theta_H \sim 0.6$**

Figure 4. Cl 2p XPS peaks during exposure of Pd(111) to 1×10^{-9} Torr CH_3CHCl_2 at 260 K. The peak grows monotonically with time during the exposure. The pass energy is set at 140 eV to maximize the signal. The inlay shows the chlorine coverage measured using the integrated peak Cl 2p area as a function of time. The initial rate constant for dechlorination (k_{app}) is determined from the initial slope of the fit to the data.

To obtain rate constants for the dechlorination process it is necessary to have an expression relating the rate to the CFC pressure. In this case we believe that the rate law should be of the form

$$r = kP^n_{CFC}$$

where $n = 1$ if the coverage of the CFC is low, as it should be given its low desorption energy. To determine the order of the dechlorination reaction in CFC pressure, dechlorination rates were measured with CFC pressures between 2×10^{-10} and 5×10^{-8} Torr at 300 K and between 1×10^{-8} and 3×10^{-8} Torr at 250 K. The dependence on pressure can be obtained from a plot of $log(r)$ vs $\log(P_{CFC})$. The data in Figure 5 demonstrate that the chlorine deposition rate is of the order $n = 0.84 \pm 0.03$ in the CFC pressure for CH_3CFCl_2 at 300 K and $n = 1.2 \pm 0.3$ at 250 K. We have assumed that the pressure dependence can be approximated as first-order and so, division of the initial rate by the pressure can be used to determine the rate constant for chlorine deposition. Actually, since the hydrodechlorination of CF_3CFCl_2 and CF_2Cl_2 is known to result in the removal of both chlorine atoms[2-4,8], the rate constants for dechlorination of CF_3CFCl_2, CH_3CFCl_2, CH_2FCFCl_2, and CH_3CHCl_2 are taken to be one-half the measured rate constant for chlorine deposition (chlorine uptake).

Dechlorination Rate vs. Pressure
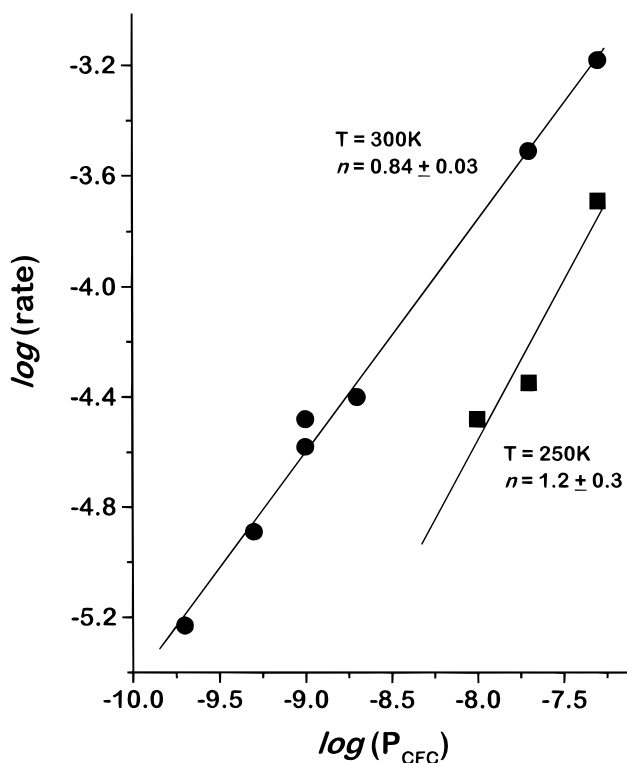**CH_3CFCl_2 / Pd(111), $\theta_H \sim 0.6$**

Figure 5. Order plots for the rate of dechlorination of CH_3CFCl_2 on Pd(111) as a function of pressure at 300 and 250 K. The slope of the plot gives the reaction order, $n = 0.8$ at 300 K and $n = 1.1$ at 250 K. The hydrogen coverage present on the surface prior to dechlorination was $\theta_H \approx 0.6$.

$$k_{app} = \frac{r}{2P_{CFC}}$$

To illustrate the differences in the relative reactivities of the CFCs, chlorine uptake curves obtained at 300 K are illustrated for all four CFCs in Figure 6. The rate constants for dechlorination are shown next to the respective uptake curves in units of molecules/site/second/Torr. It is clear that there are differences in the apparent rate constants for dechlorination of the different CFCs. Increasing the amount of fluorine systematically decreases the rate of dechlorination. This trend is similar to those reported for the catalytic hydrodechlorination of mono- and dichloromethanes on supported Pd catalysts.[6] It should be noted that the pressure of the CFCs is measured by an ionization gauge. Thus, differences in the ion gauge sensitivity to these gases could cause systematic errors in the calculations of the dechlorination rate constants. There are no tabulated ion gauge sensitivities for chloroethanes, however, for CH_2Cl_2 and CF_2Cl_2 the ion gauge sensitivities reportedly differ by only $\sim 10\%$ (Table 1).[23] Thus the expected differences for the chloroethanes are close to the limit of reproducibility of the dechlorination rate constants. Our results indicate that CH_3CHCl_2 is fourteen times more reactive than CF_3CFCl_2, a difference that could not arise from differing ion gauge sensitivities.

To determine an apparent activation energy for dissociative adsorption (E_{app}), chlorine uptake curves were measured using CH_2FCFCl_2 at temperatures in the range 250-450 K and the apparent rate constants for dechlorination were determined using the treatment outlined above. Assuming that the rate constant

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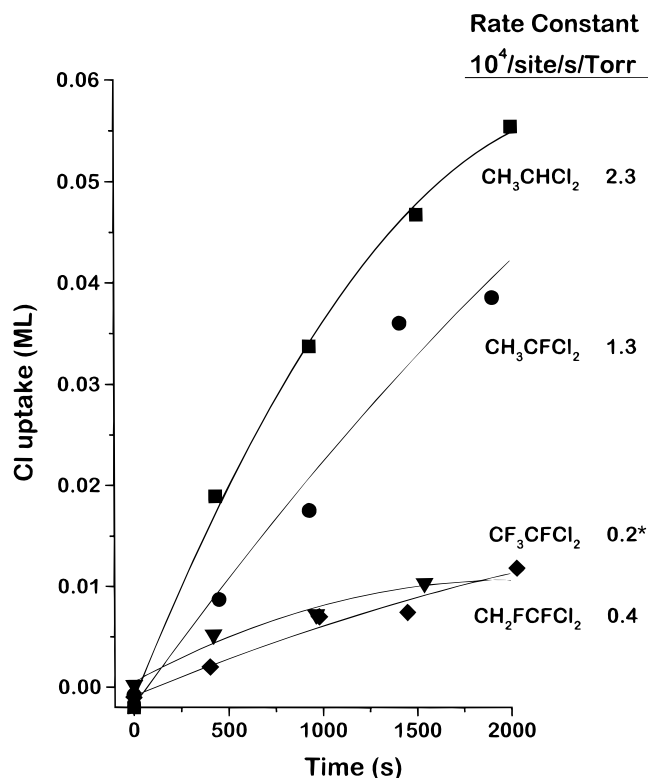## Chlorine Uptake - CFCs / Pd(111)

Figure 6. Chlorine uptake on the Pd(111) surface during exposure at 300 K to 1×10^{-9} Torr of CFC (* dechlorination of CF_3CFCl_2 was measured at 3×10^{-9} Torr). The initial rate constants for dechlorination (k_{app}) are determined from the initial slopes and listed at the right-hand side of the figure.

TABLE 1. Sensitivity of Ionization Gauge to Chloromethanes[23]

molecule	sensitivity S_x/S_{N2}
CH_2Cl_2	3.7
CF_2Cl_2	3.4

is given by an Arrhenius expression of the form

$$k_{app} = A \exp(-E_{app}/RT)$$

it is possible to extract an apparent activation energy for dissociative adsorption from a plot of $\ln(k_{app})$ vs $(1/T)$. For CH_2FCFCl_2, this relationship is not linear over the entire temperature range, as shown in Figure 7. The nonlinearity of the relationship above 350 K indicates that a different mechanism dominates the kinetics of chlorine deposition on the surface at high temperatures. In TPD experiments performed after Cl_2 gas was chemisorbed onto Pd(111), Tysoe et al. found that chlorine started to desorb from the surface in the temperature range 400–500 K at an initial coverage $\theta_{Cl} = 0.12$.[24] They attribute this to atomic chlorine desorbing with some small amount of PdCl. If chlorine were desorbing from the surface during the dissociative adsorption experiment, then the measured chlorine uptake rate would underestimate the rate of chlorine deposition at these high temperatures. This may explain the nonlinearity of the Arrhenius plot at higher temperatures. With this in mind measurements to determine the apparent activation energy for dechlorination were performed at temperatures between 250 and 325 K for all the CFCs. The rate constants for dissociative adsorption of CF_3CFCl_2, CH_3CFCl_2, CH_2FCFCl_2, and CH_3CHCl_2 were measured
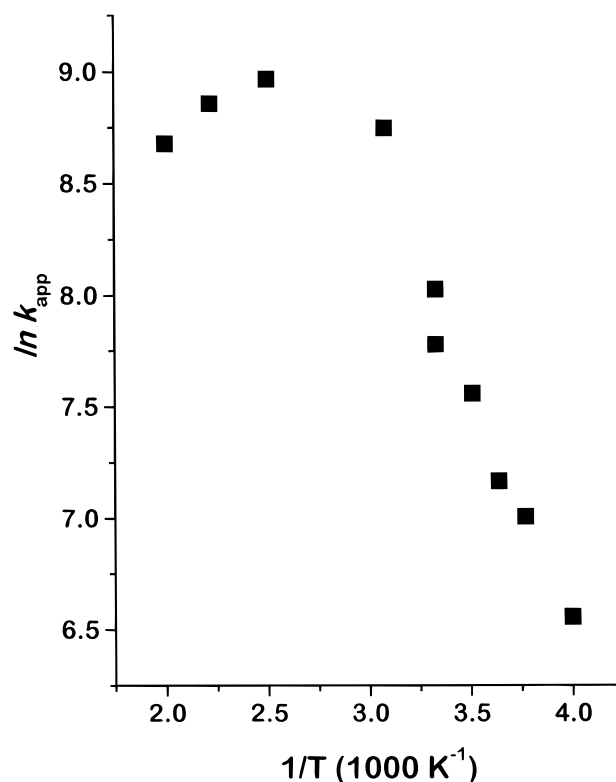
Dechlorination vs. Temperature
CH_2FCFCl_2 / Pd(111), $\theta_H \sim 0.6$

Figure 7. Arrhenius plot for the dechlorination of CH_2FCFCl_2 between 250 and 500 K and $P_{CFC} = 1-1.5 \times 10^{-9}$ Torr. The surface coverage of hydrogen was $\theta_H \approx 0.6$ prior to the measurements of dechlorination rates. The change in slope at high temperatures (>350 K) suggests that a mechanism for chlorine removal from the surface begins to compete with chlorine deposition at high temperatures. This high-temperature effect was also observed for other CFCs.

and the plots of $\ln(k_{app})$ vs $(1/T)$ shown in Figure 8 indicate that at any given temperature, the rate constants for dissociative adsorption decrease with increasing fluorination of the molecule. The apparent activation energies for dissociative adsorption are in the range 8 kJ/mol to approximately 19 kJ/mol for the four different CFCs. The error in the activation barrier to dechlorination of CF_3CFCl_2 is much higher than those of the other molecules due to the fact that the amount of dissociation was low, introducing uncertainty into the measurements of the chlorine surface concentration. Nevertheless the apparent activation energy to dechlorination is clearly influenced by increasing fluorine content.

As mentioned the presence of hydrogen on the Pd(111) surface was unavoidable during these experiments. During extended heating and exposure to the CFCs there appeared to be hydrogen accumulation in the bulk or near-surface of the crystal. This manifested itself in H_2 desorption experiments performed immediately prior to the dechlorination experiments. Under the vacuum conditions of our apparatus the amounts of hydrogen desorbing from the surface could not have adsorbed from the background and must diffuse to the surface from the bulk. The measurements of the E_{app} for dechlorination were made on surfaces with initial hydrogen coverages on the order of $\theta_H \approx 0.6$ ML. This is complicated by the fact that hydrogen desorbs from the surface in the temperature range used for determination of the E_{app} and so this probably represents an
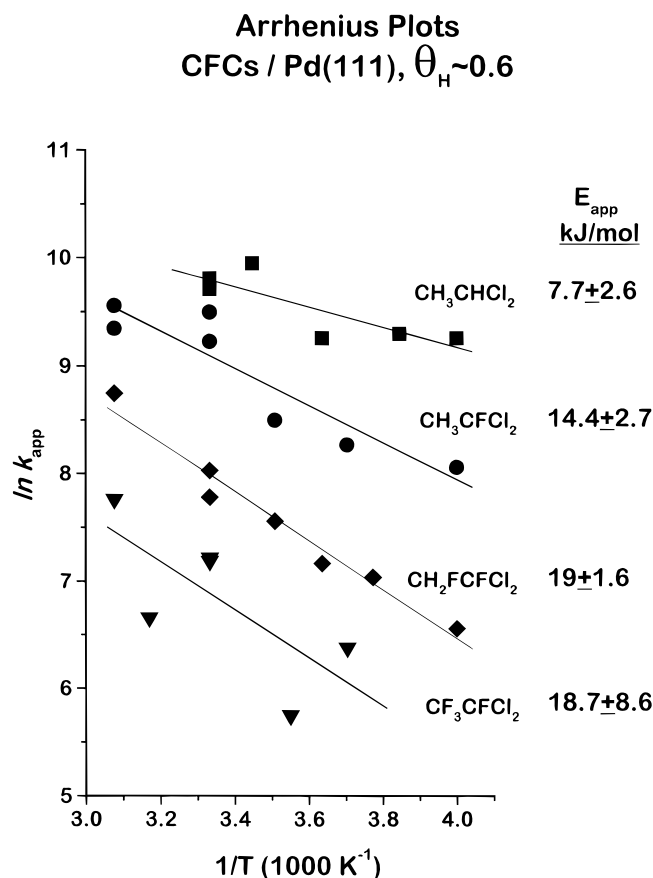
Figure 8. Arrhenius plot for the dechlorination of CFCs. The apparent activation energy (E_{app}) to dechlorination is listed at the right of the figure. Measurements were made with initial hydrogen coverages of $\theta_H \approx 0.6$. Fluorination of the CFC increases the E_{app}.

Figure 9. Correlation of the reaction energetics (E_{app}, E_{des}, and E_{C-Cl}) for CFC dechlorination with the substituent constants of the CFCs. The intrinsic barrier to dechlorination is calculated from $E_{C-Cl} = E_{des} + E_{app}$. The solid lines and symbols refer to measurements made with hydrogen coverages on the order of $\theta_H \approx 0.6$. The dashed lines and open symbols refer to measurements made with initial hydrogen coverages on the order of $\theta_H \approx 0.1$. The key feature of this figure is the slope of the correlation of E_{C-Cl} against $\Sigma\sigma_F$. They are $\rho = 1 \pm 6$ at $\theta_H \approx 0.6$ and $\rho = -2 \pm 4$ at $\theta_H \approx 0.1$.

upper limit on the amount on the surface during dechlorination. By extended high-temperature annealing in UHV the bulk hydrogen concentration was reduced to the point that the surface hydrogen coverages prior to dechlorination were on the order of $\theta_H \approx 0.1$ ML. The E_{app} values for dechlorination of CF_3-$CFCl_2$ and CH_3CHCl_2 (Figure 9) under these conditions were not significantly different from those determined with initial hydrogen coverages of $\theta_H \approx 0.6$ ML. During the course of these measurements, however, the bulk hydrogen content increased and so the absolute surface coverage during the measurements is uncertain. So far as can be ascertained, the effects of hydrogen coverage on either E_{des} or E_{app} are not so great that they influence the final conclusions of this work regarding the nature of the transition state for C−Cl bond cleavage.

4. Discussion

4.1. Mechanism of the Dechlorination Reaction. The experiments reported have determined the E_{des} and the E_{app} for dechlorination of four CFCs on the Pd(111) surface. It should be pointed out that we are simply measuring the rate of chlorine uptake on the surface and do not yet know all mechanistic details of this reaction. However, the presence of chlorine on the surface must be a result of C−Cl bond cleavage. Dissociative adsorption experiments performed at 300 K with CH_3CFCl_2 have shown that there is some carbon but no fluorine-containing species left on the surface. It appears that following C−Cl bond cleavage, at least part of the remaining fragment is removed from the surface by some subsequent process. The loss of alkyl fragments from the Pd surface has been observed in past studies of alkyl halide surface chemistry. Similar results have been reported for
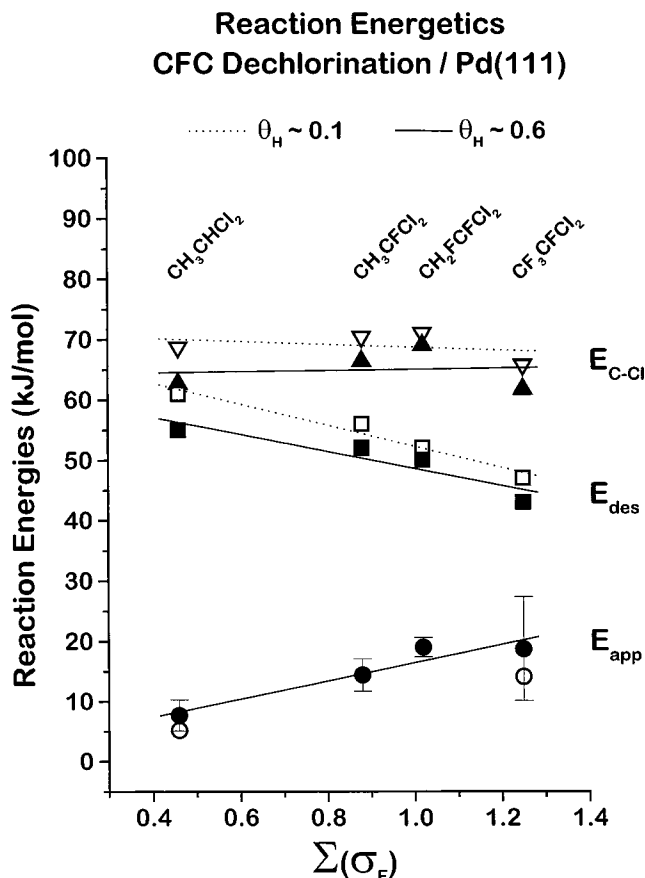
CH_2I_2 on Pd(100) by Solymosi and Kovacs.[25] They found that on a Pd(100) surface CH_2I_2 dissociates to form adsorbed CH_2 and I. The CH_2 groups form CH_4 and C_2H_4, which desorb at temperatures below 250 K. They proposed that some of the C_2H_4 also forms a vinyl species (HC=CH_2) which then forms ethylidyne (CCH_3) on the surface at temperatures between 220 and 230 K. The ethylidyne is hydrogenated to C_2H_4 and desorbs at temperatures above 300 K. Another fraction of the vinyl species decomposes to produce C and gas-phase H_2 at temperatures above 450 K. Although these types of steps may occur with the CFCs, it has not yet been possible to investigate the mechanism by which the fluoroalkyl fragments are lost from the surface.

There have been a number of studies of alkyl halide decomposition on Pt surfaces that indicate that alkyl groups are lost from the surface during heating. Results of this nature have been reported by Lloyd et al. in a study of CH_3CH_2Cl on Pt-(111).[26] In their investigation, Lloyd et al. produced CH_3CH_2 fragments on the Pt(111) surface through the photodissociation of CH_3CH_2Cl. Their high-resolution electron energy loss spectroscopy and TPD results indicate that during heating the CH_3CH_2 fragment first forms C_2H_4 and then CCH_3 on the surface. During the formation of C_2H_4, some C_2H_6 and C_2H_4 desorb from the Pt(111) surface and at approximately 500 K, the CCH_3 species decomposes, releasing H_2. Coupling reactions have also been reported on Pt surfaces as mechanisms by which

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alkyl fragments are removed from the surface. For instance, Zhou and White have showed that photodissociation of CH_3Br on Pt(111) results in the formation of CH_3 fragments on the surface. During TPD, these fragments couple and desorb as C_2H_6 at temperatures below 300 K.[27] Thus there are several plausible mechanisms by which all or part of the dechlorinated fragment of the dissociatively adsorbed CFCs might be removed from the Pd(111) surface. The focus of this investigation has, however, been on the initial steps of the dissociative adsorption process.

To study C−Cl bond cleavage in this work, rate constants for dissociative adsorption were measured by exposing the CFCs to a heated Pd(111) surface. Dechlorination is assumed to proceed through a two step mechanism; reversible adsorption onto an empty surface site (*) followed by C−Cl bond cleavage, requiring a second empty site.

$$R-Cl_{(g)} + * \xrightarrow{K_{eq}} R-Cl *$$

$$R-Cl * + * \xrightarrow{k_{C-Cl}} R * + Cl *$$
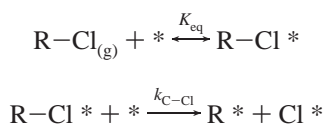
At the low $CFC_{(g)}$ pressures used in this investigation, a Langmuir isotherm predicts that the CFC coverage (θ_{CFC}) is low and is given by

$$\theta_{CFC} \approx K_{eq}P_{CFC}$$

Since we have focused on the initial rates of chlorine uptake, the fraction of empty sites is ∼1 at all times and the empty site requirement for the dechlorination step should not enter into the rate expression. The C−Cl bond dissociation rate is then given by the following expression:

$$r = k_{C-Cl}\theta_{CFC}$$
$$\approx k_{C-Cl}K_{eq}P_{CFC}$$
$$\approx k_{app}P_{CFC}$$

Consistent with this expression we have observed that the rate of chlorine uptake on the Pd(111) surface is indeed roughly first-order in the CH_2FCFCl_2 pressure. Since

$$k_{app} = k_{C-Cl}K_{eq}$$

the intrinsic activation barrier to dechlorination is given by

$$E_{C-Cl} = E_{des} + E_{app}$$

The apparent activation energies (E_{app}) have been extracted from measurements of the rate constants for dissociative adsorption, and the desorption energies (E_{des}) have been extracted from measurements of desorption kinetics.

One of the questions that must be addressed is that of the relationship between the k_{app} that we measure and the kinetics of the Pd-catalyzed hydrodechlorination reactions which have motivated our investigation. If the rate-limiting steps in the hydrodechlorination reaction can be modeled by the mechanism described above and all subsequent hydrogenation and desorption steps are fast, then the rate constants for hydrodechlorination over supported Pd catalysts and the rate constants for the dechlorination reaction on the Pd(111) surface ought to be comparable in the sense that they would both be of the form

$$k = k_{C-Cl}K_{eq}$$

TABLE 2. Field Effect Substituent Constants for CFCs[12]

molecule	field substituents	field constant (σ_F)	$\Sigma\sigma_F$
CH_3CHCl_2	CH_3	0.0	0.45
	H	0.0	
	Cl	0.45	
CH_3CFCl_2	CH_3	0.0	0.89
	F	0.44	
	Cl	0.45	
CH_2FCFCl_2	CH_2F	0.22	1.11
	F	0.44	
	Cl	0.45	
CF_3CFCl_2	CF_3	0.44	1.33
	F	0.44	
	Cl	0.45	

In the case of catalytic hydrodechlorination this expression might also be modified by terms accounting for site blocking by adsorbed hydrogen, CFCs, or intermediate species such as adsorbed Cl. These would all be expected to be present at higher coverages than in our low-pressure experiments. Clearly, making a direct comparison of reaction rate constants is not possible due to the fact that the reaction conditions differ and the catalyst is not composed solely of Pd(111) surfaces. However, it is very interesting to note that the basic trends in CFC reactivity observed during catalytic hydrodechlorination are the same as those observed for dechlorination on the Pd(111) surface. Increasing the fluorine content of the CFC decreases the dechlorination rate constant. The rate constant for dechlorination of CH_3CHCl_2 at 300 K is a factor of 14 greater than that of CF_3CFCl_2 and the apparent activation barrier to dechlorination decreases in the order $CF_3CFCl_2 \sim CH_2FCFCl_2 > CH_3CFCl_2 > CH_3CHCl_2$. This trend matches the trend observed for the hydrodechlorination of chloromethanes over Pd/AlF$_3$ catalysts at atmospheric pressures. In the case of chloromethanes, the rate of CF_2Cl_2 hydrodechlorination is less than 10% of the rate CH_2Cl_2 hydrodechlorination at 440 K.[6] The fact that the trends observed for dechlorination rate constants on the Pd(111) surface mimic those seen for the catalytic hydrodechlorination reaction over Pd/AlF$_3$ catalysts is consistent with dechlorination being either the rate-limiting step or at least contributing significantly to the overall rate constant for the catalytic hydrodechlorination reaction.

4.2. Linear Free Energy Relationship for Dechlorination. The primary objective of this work has been to gain insight into the nature of the transition state to catalytic carbon−chlorine bond cleavage. By varying the amount of fluorine in the CFCs and measuring the corresponding changes in activation energy for an elementary reaction step it is possible to gain such insight. The reaction energetics can be presented in the form of a linear free energy relationship (LFER). LFERs have been widely used in physical organic chemistry to probe changes in the electronic distributions in molecules during reactions.[11−14] The effects of substituents such as fluorine atoms are scaled by using empirically derived substituent constants that are tabulated in the literature. In this case we can correlate E_{C-Cl} with the field substituent constants (σ_F) for each of the CFCs (Table 2). A plot of E_{C-Cl} versus σ_F yields a line with a slope which defines the reaction constant (ρ). The sign (+ or −) and magnitude of the correlation constant or reaction constant provide insight into the change in charge distribution at the reaction center during C−Cl bond cleavage.

The correlations between the substituent constants for the CFCs and E_{des}, E_{app}, and E_{C-Cl} describing dissociative adsorption are shown Figure 9. This shows that increasing the field effect substituent constant (degree of fluorination) of the CFCs increases the E_{app} for dissociative adsorption. The opposite effect

is seen for the E_{des}; increasing the field effect substituent constant of the CFCs causes a decrease in the desorption energy. Given the difficulty in controlling the hydrogen coverage on the surface during the reaction, we have plotted measured energies for initial coverages of $\theta_H \approx 0.1$ (open data points) and $\theta_H \approx 0.6$ (solid data points). The hydrogen coverage was determined from TPD measurements but was not well controlled during the dissociative adsorption experiments. The effect of hydrogen coverage on the desorption energies has been determined quite carefully and is shown in Figure 3. The effects of adsorbed hydrogen on the apparent activation energies for dissociative adsorption were much harder to determine. A coverage of $\theta_H \approx 0.1$ was the minimum that could be easily achieved by annealing the sample prior to the dissociative adsorption experiments. During the dissociative adsorption process the hydrogen content of the Pd bulk would rise and the experiments performed at $\theta_H \approx 0.6$ were performed with hydrogen in the bulk. It should be noted that the coverages of hydrogen are probably not constant across the temperature range used for the measurements of dissociative adsorption kinetics. Although the Pd bulk certainly contained hydrogen which was continuously diffusing to the surface it is also desorbing from the surface in the temperature range 250 to 325 K. As a result it was not possible to determine the effects of hydrogen as carefully as we would have wished. Nonetheless, given the data that we have been able obtain it is unlikely that hydrogen effects would change the basic conclusions of this work.

The intrinsic activation barrier to C−Cl bond cleavage (E_{C-Cl}) is the sum of the apparent barrier to dissociative adsorption (E_{app}) and the desorption energy (E_{des}). This gives 65−70 kJ/mol as an estimate of the intrinsic barrier to C−Cl bond cleavage in all four CFCs. The increase in apparent activation energy is compensated for by the decrease in the desorption energy, thus the overall effect of the substituents on the intrinsic activation barrier is minimal. This is demonstrated by the slope of the LFER being $\rho = -1 \pm 6$ kJ/mol or, in other words, not significantly different from zero. This would imply that the electronic distribution in the transition state to C−Cl bond cleavage is very similar to the initial state. This could be described as a homolytic process and is consistent with a transition state that is "early" in the reaction coordinate. It is important to note that LFERs provide information about the electronic distribution in the transition state relative to those in the initial state, not absolute charge distributions. In absolute terms, the electronic distribution is not equal between the carbon and the chlorine in the initial state (the adsorbed CFC). Because chlorine is more electronegative than carbon, the carbon atom is partially positive and the chlorine atom partially negative. The results presented in this paper imply only that the electronic distribution in the transition state is similar to that in the reactant state.

There are a number of different types of substituent constants that have been tabulated in the literature. A fairly recent review has divided these into field, resonance, polarizability, and electronegativity effects.[12] The magnitudes of these substituent constants have been determined from measurements of reaction energetics for a wide range of gas-phase reactions. Since our data set is limited to four different CFCs we have chosen to limit ourselves to the use of one type of substituent effect, the field effect (denoted by σ_F), to scale the results of our measurements of E_{C-Cl}. The field effect has been successfully in a number of previous studies of substituent effects in surface reactions.[15−19] Resonance effects can be neglected since our reactants have no π-electron systems through which

such effects might be transmitted. Polarizability effects have not been included since the variation among polarizability constants for the CFCs used in this study is much less than that among field effect constants. Probably the most important effect that has been neglected is the possibility of the influence of electronegativity. This is generally regarded to be a short-range effect which can change the electron density on atoms at the reaction center if substitutions are made directly at the reaction center. In our case, having either H or F bonded to the carbon atom of the C−Cl bond can introduce such a complication. Unfortunately, given the limited number of CFCs available for study this was not avoidable. However, neglect of electronegativity effects would not have any impact on the nature of our final observations that there is little change in charge distribution on the carbon atom between the reactant and transition state.

The results of our experiments allow us to estimate the intrinsic activation barrier to C−Cl bond breaking for CFCs adsorbed on the Pd(111) surface at 65−70 kJ/mol. This could not be determined directly from a temperature-programmed reaction spectroscopy (TPRS) experiment since the desorption energies are in the range 45−60 kJ/mol and are lower than the dissociation barriers. As a result, the CFCs adsorbed at low temperatures desorb during heating rather than decomposing. There is one interesting point of comparison in the literature. A series of long-chain alkyl chlorides were used to estimate the barrier to C−Cl bond breaking on the Cu(100) surface.[32] In that set of experiments it was observed that while 1-chlorohexane desorbed from the surface during heating, 1-chloroheptane decomposed. On the basis of this observation and on measurements of the desorption energies of the shorter alkyl chlorides, the barrier to dechlorination was estimated at 65 kJ/mol. This is in exactly the same range as our estimate of E_{C-Cl} on the Pd(111) surface.

To put some perspective on the effects of fluorine substitution on the energetics for C−Cl cleavage on the Pd(111) surface it is instructive to compare the results of this work with the results of other measurements of substituent effects on the barriers to surface reactions. The reaction constant observed for the dechlorination reaction is roughly zero and is much smaller than that observed for other types of surface reactions. In the case of alkyl coupling on Ag(111) surfaces, Paul and Gellman reported a much larger change in activation energy with fluorination.[16] To make a valid comparison, their data has been analyzed using substituent field constants. The LFER obtained from the data has a slope of 108 ± 21 kJ/mol. The conclusion of their study was that in the transition state, the reaction center is electron deficient with respect to the initial state. The β-hydride elimination reaction in alkoxides on the Cu(111) surface has been studied by Gellman and Dai.[17] Again, their data was analyzed using the substituent field constants. If their results are plotted in the same fashion, the LFER would have a slope of 186 ± 20 kJ/mol. The authors interpret this slope as indicating a cationic carbon in the transition state relative to the initial state. Clearly the use of fluorine substitution can result in substantial effects on the barriers to surface reactions.

As a final point of comparison, LFERs have been measured in our laboratory for another dehalogenation reaction: C−I bond breaking on the Ag(111) surface and on the Pd(111) surface. These experiments have used a set of 11 selectively fluorinated alkyl iodides with a broad range of field substituent effects. The results of these measurements have yielded reaction constants of 4.3 ± 0.3 kJ/mol on the Ag(111) surface and 0.2 ± 0.8 kJ/mol on the Pd(111) surface.[33] As in the case of the

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dechlorination reaction these are relatively small by comparison with numbers measured in other processes. They support the conclusion that there is little change in the charge distribution of C−Cl bonds between the initial state and the transition state.

Thus far we have probed the transition state to dechlorination on a Pd(111) surface. This study was motivated by the desire to understand and improve the hydrodechlorination process. The results have shown that the electronic distribution in the transition state is similar to that in the initial state or adsorbed CFC. This implies that stabilizing the initial state on the catalyst surface by increasing its E_{des} would lower the apparent activation barrier to dechlorination and increase overall catalytic activity.

5. Conclusions

In the four partially fluorinated 1,1-dichloroethanes CH_3-$CHCl_2$, CH_3CFCl_2, CH_2FCFCl_2, and CF_3CFCl_2 the intrinsic barriers to dissociation of C−Cl bonds on the Pd(111) surface are insensitive to the effects of fluorination or changes in the substituents attached to the C−Cl bond. The reactivities of the CFCs with respect to dechlorination show trends similar to those observed in the catalytic hydrodechlorination of CFCs on supported Pd/AlF$_3$. This suggests that the rate constant for the dechlorination step is an important contributor to the overall rate law for catalytic hydrodechlorination. The reaction constant obtained from the LFER for dechlorination of the CFCs on Pd(111) is $\rho = 1 \pm 6$ kJ/mol or insignificantly different from zero. This suggests that the transition state for C−Cl bond cleavage is homolytic and occurs early in the reaction coordinate.

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