Journal of Catalysis **194,** 233–239 (2000)
doi:10.1006/jcat.2000.2948, available online at http://www.idealibrary.com on IDEAL®

Carbon–Chlorine Bond Dissociation on the Pd(111) Surface

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Received December 9, 1999; revised May 5, 2000; accepted June 7, 2000

Dissociation of the C–Cl bonds in straight chain alkyl chlorides ($CH_3(CH_2)_nCl$, $n = 0$–5) adsorbed on the Pd(111) surface has been investigated using temperature programmed desorption (TPD) and X-ray photoemission spectroscopy (XPS). Short chain alkyl chlorides adsorbed on the Pd(111) surface at low temperatures desorb during heating because the intrinsic activation energy for C–Cl bond cleavage (ΔE_{C-Cl}) is greater than the desorption energy (ΔE_{des}). Systematically increasing the alkyl chain length increases ΔE_{des} until it is greater than ΔE_{C-Cl}. The value of ΔE_{C-Cl} was estimated by determining ΔE_{des} of the smallest alkyl chloride to dissociate during heating, i.e., the smallest alkyl chloride with $\Delta E_{C-Cl} \leq \Delta E_{des}$. The TPD and XPS studies showed that while adsorbed $CH_3(CH_2)_2Cl$ desorbs from the Pd(111) surface during heating, $CH_3(CH_2)_3Cl$ is the shortest alkyl chloride to dissociate. This implies that $\Delta E_{C-Cl} > \Delta E_{des}$ for $CH_3(CH_2)_2Cl$ and $\Delta E_{C-Cl} < \Delta E_{des}$ for $CH_3(CH_2)_3Cl$. The estimated range for the value of ΔE_{C-Cl} is 60–64 kJ/mol and is consistent with the value of ΔE_{C-Cl} estimated from previous studies of the dechlorination of fluorinated 1,1-dichloroethanes on the Pd(111) surface. © 2000 Academic Press

1. INTRODUCTION

Chlorofluorocarbons (CFCs) are an important contributor to stratospheric ozone depletion (1, 2). CFCs are chemically inert, and once released into the atmosphere ultimately diffuse upward into the stratosphere. In the stratosphere, high energy UV radiation causes photodissociation of the CFCs to produce chlorine atoms that then participate in a chain reaction in which ozone is destroyed. CFCs have had widespread commercial applications as refrigerants, foam-blowing agents, aerosol propellants, industrial solvents, and cleaning agents (3–5). Finding safe ways to dispose of CFCs and replace them is an urgent technological and ecological priority. Suitable replacements for CFCs must have physical properties that closely match those of the CFCs. One class of alternatives to CFCs are hydrofluorocarbons (HFCs), which do not contain chlorine and have low ozone depleting potential (6). For example, CF_3CFH_2 is currently being used to replace CF_2Cl_2 in some automobile air-conditioning applications.

Catalytic hydrodechlorination is one of the routes used to convert environmentally hazardous CFCs into environmentally benign HFCs (7–10). Currently, the selectivity and activity for the hydrodechlorination of most CFCs is still relatively low and could be improved by a greater understanding of the kinetics and mechanism of the catalytic reaction (11–13). The catalytic cleavage of carbon–chlorine bonds is one of the elementary steps of hydrodechlorination on metal catalysts. A greater understanding of the energetics of carbon–chlorine bond dissociation on catalytic surfaces would aid attempts to improve catalyst activity and selectivity.

In previous studies of CFC dechlorination, four fluorinated 1,1-dichloroethanes (CH_3CHCl_2, CH_3CFCl_2, CH_2FCFCl_2, CF_3CFCl_2) were used to study the kinetics of C–Cl bond cleavage on the Pd(111) surface (14–16). The apparent rate constants and activation energies for dissociative adsorption on the Pd(111) surface show a systematic trend that depends on the fluorine content of the molecule. Fluorination decreases the rate constant for dissociative adsorption by increasing the apparent activation barrier for dissociative adsorption (ΔE_{app}). This can be understood in terms of the energetics for adsorption and dissociation shown in Fig. 1. Dissociative adsorption is a two step process involving molecular adsorption followed by dissociation by cleavage of the C–Cl bond. The apparent activation energy for these two combined steps is given by

$$\Delta E_{app} = \Delta E_{C\text{–}Cl} - \Delta E_{des},$$

where ΔE_{C-Cl} is the intrinsic activation barrier to cleavage of the C–Cl bond and ΔE_{des} is the desorption energy. The desorption energy has been measured by thermally programmed desorption and tends to decrease as the fluorine content of the molecule increases. The net result of these measurements of ΔE_{app} and ΔE_{des} is that the intrinsic activation barrier (ΔE_{C-Cl}) for C–Cl bond cleavage shown in Fig. 1 remains unchanged as the fluorination of the molecule is increased. The value of ΔE_{C-Cl} for C–Cl bond cleavage determined by this two step measurement method is about 65 kJ/mol. The purpose of this paper is to describe the results of an independent measurement of ΔE_{C-Cl}.

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0021-9517/00 $35.00

Direct measurement of the C–Cl dissociation kinetics for small alkyl chlorides adsorbed on the Pd(111) surface at low temperatures is difficult because ΔE_{des} is less than $\Delta E_{\mathrm{C-Cl}}$. As a result, during heating they tend to desorb before dissociation can occur. For alkyl halides, lengthening the alkyl chain does not change the gas phase carbon–halogen bond energy (17); however, it can certainly increase the alkyl halide desorption energy from a surface. As a result one can imagine increasing the alkyl chain length to the point that ΔE_{des} is greater than $\Delta E_{\mathrm{C-Cl}}$. Figure 2 illustrates this relationship between ΔE_{des} and $\Delta E_{\mathrm{C-Cl}}$ for a set of alkyl chlorides of increasing chain length. This combination of effects on the alkyl halide dissociation/desorption has been demonstrated on aluminum and copper surfaces (18, 19). In those cases, ΔE_{des} increases roughly linearly with chain length. If one makes the assumption that $\Delta E_{\mathrm{C-Cl}}$ is independent of chain length, then one can estimate $\Delta E_{\mathrm{C-Cl}}$ by measuring the value of ΔE_{des} in a series of alkyl chlorides of increasing chain length. The assumption that $\Delta E_{\mathrm{C-Cl}}$ is independent of chain length is supported by the fact that the C–Cl bond strength is independent of chain length and by our previous observation that $\Delta E_{\mathrm{C-Cl}}$ is independent of substitutions on the alkyl group (14–17). An estimate of $\Delta E_{\mathrm{C-Cl}}$ comes from identifying the shortest alkyl chloride that dissociates during heating. In this case, $\Delta E_{\mathrm{C-Cl}}$ lies between ΔE_{des} for the longest alkyl chloride that desorbs from the surface and ΔE_{des} for the shortest alkyl that dissociates.

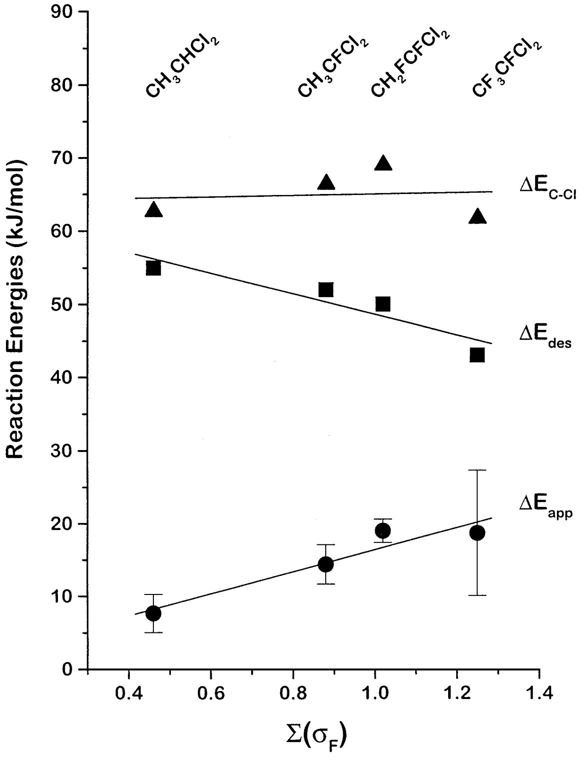

FIG. 1. Correlation of the reaction energetics (ΔE_{app}, ΔE_{des}, and $\Delta E_{\mathrm{C-Cl}}$) for CFC dechlorination on Pd(111) with the substituent constants of the CFCs (14–16). The intrinsic barrier to dechlorination is calculated from $\Delta E_{\mathrm{C-Cl}} = \Delta E_{\mathrm{app}} + \Delta E_{\mathrm{des}}$. The key feature of this figure is the fact that $\Delta E_{\mathrm{C-Cl}}$ is almost independent of the degree of fluorine substitution in the CFC as quantified by the substituent constants $\sum(\sigma_F)$.

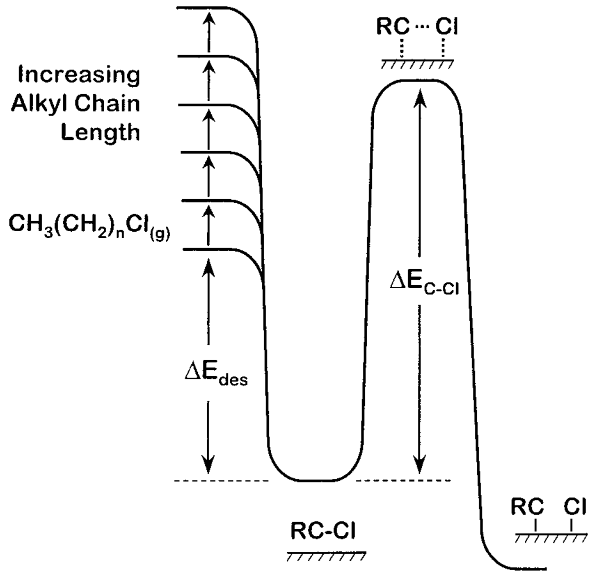

FIG. 2. Potential energy diagram for adsorption and dissociation of alkyl chlorides on a surface. The desorption energies (ΔE_{des}) for alkyl chlorides increase roughly linearly with alkyl chain length. The intrinsic barrier to C–Cl cleavage ($\Delta E_{\mathrm{C-Cl}}$) is assumed to be independent of the chain length. The longer chain alkyl chlorides with $\Delta E_{\mathrm{des}} > \Delta E_{\mathrm{C-Cl}}$ dissociate during heating while the shorter chain alkyl chlorides with $\Delta E_{\mathrm{des}} < \Delta E_{\mathrm{C-Cl}}$ can desorb from the surface.

In this paper, six straight chain alkyl chlorides ($CH_3(CH_2)_nCl$, $n = 0$–5) were used to determine $\Delta E_{\mathrm{C-Cl}}$ for C–Cl bond cleavage on the Pd(111) surface. The ΔE_{des} for each alkyl chloride was obtained from temperature programmed desorption (TPD) experiments. Dissociation of the C–Cl bond was observed by using X-ray photoemission spectroscopy (XPS) to monitor the presence of chlorine on the Pd(111) surface after heating. The TPD and XPS studies presented in this paper suggest that $CH_3(CH_2)_3Cl$ is the smallest alkyl chloride that dissociates with $\Delta E_{\mathrm{des}} = 49$–64 kJ/mol. $CH_3(CH_2)_2Cl$ is the largest molecularly adsorbed alkyl chloride which completely desorbs during heating with $\Delta E_{\mathrm{des}} = 44$–60 kJ/mol. The range of $\Delta E_{\mathrm{C-Cl}}$ on the Pd(111) surface is estimated to be 60–64 kJ/mol. This result is consistent with our estimate based on measurements of dechlorination kinetics for the CFCs on the Pd(111) surface.

2. EXPERIMENTAL

Experiments were conducted in a stainless-steel ultrahigh vacuum (UHV) chamber with a base pressure of 1–2×10^{-10} Torr. UHV was achieved by use of an ion pump. The Pd(111) crystal (99.999% purity, 1.0 cm^2 area, 2 mm thick) was mounted on a manipulator allowing controlled *x*, *y*, *z* translation and rotational motion. The crystal was spot-welded between two tantalum wires in mechanical contact with a liquid nitrogen reservoir to provide cooling. The crystal was heated resistively and the temperature was measured by a chromel–alumel thermocouple spot-welded to the bottom edge of the crystal. The crystal surface was cleaned by Ar^+ ion sputtering using a differentially pumped ion gun (Perkin–Elmer, model 04-303) and by periodic annealing to 1200 K. The surface composition was analyzed using X-ray photoemission spectroscopy (XPS). The XP spectrometer used a VG Microtech 800W Al $K\alpha$ X-ray source and a hemispherical electron energy analyzer. The Pd(111) crystal surface structure was determined by low energy electron diffraction.

All of the alkyl chlorides (purity 99.0+%) were obtained from Aldrich Chemicals. Prior to introduction into the vacuum system, they were purified and degassed by several freeze–pump–thaw cycles with liquid nitrogen. The compounds were stored in glass vials and shielded from light. The purity of the compounds used in experiments was verified using a quadrupole mass spectrometer. Exposure of the Pd(111) surface to alkyl chlorides was achieved by backfilling the chamber through a capillary array attached to a leak valve. The Pd(111) crystal was positioned in front of the capillary array during exposure in order to saturate the Pd(111) surface but keep a low exposure pressure. Different exposures were achieved by varying the distance between the capillary array and the Pd(111) crystal surface.

The desorption energies of the alkyl chlorides were determined by temperature programmed desorption spectra obtained with varying initial coverages. For TPD experiments the clean Pd(111) surface was exposed to the alkyl chlorides and adsorption was carried out at a crystal temperature of 85–100 K. The Pd(111) crystal was then positioned in front of the mass spectrometer at a distance of 5 mm from the aperture to the ionizer and heated at a rate of 3 K/s. Three masses were monitored by the mass spectrometer during a single TPD experiment. The peak temperature for monolayer adsorption was used to calculate the desorption energy for each alkyl chloride.

Dissociation of the C–Cl bond in the alkyl chlorides was determined by monitoring the presence of chlorine on the Pd(111) surface using X-ray photoemission spectroscopy. Straight chain alkyl chlorides were adsorbed on the Pd(111) crystal surface at 85–100 K. The Pd(111) crystal was heated at a rate of 2 K/s to 450 K and then held at that temperature while the XPS measurements were performed. This temperature was high enough to ensure that no alkyl chloride from the background adsorbed on the surface during the course of the XPS measurement. At the same time it is too low for any desorption of chlorine that might be left on the surface as a result of C–Cl bond cleavage during heating to 450 K. The XP spectrum for the Cl $2p_{3/2}$ peak was obtained by monitoring photoemission of electrons with binding energies in the range from 193 to 203 eV.

3. RESULTS

3.1. *Temperature Programmed Desorption of Alkyl Chlorides*

The desorption kinetics of six straight chain alkyl chlorides ($CH_3(CH_2)_nCl$, $n = 0$–5) were measured by TPD experiments. The TPD results for increasing coverages of $CH_3(CH_2)_2Cl$ on the Pd(111) surface are shown in Fig. 3 and reveal that the peak desorption temperature shifts from 250 K at low coverage to about 173 K at monolayer coverage. At higher coverages a multilayer desorption peak is observed at 120 K that does not saturate with further increases in coverage. The TPD experiments also show that the relative intensities of the desorption spectra obtained by monitoring several m/q ratios with the mass spectrometer are approximately equal to those in the fragmentation pattern of $CH_3(CH_2)_2Cl$ obtained during background dosing. This indicates that the adsorption of $CH_3(CH_2)_2Cl$

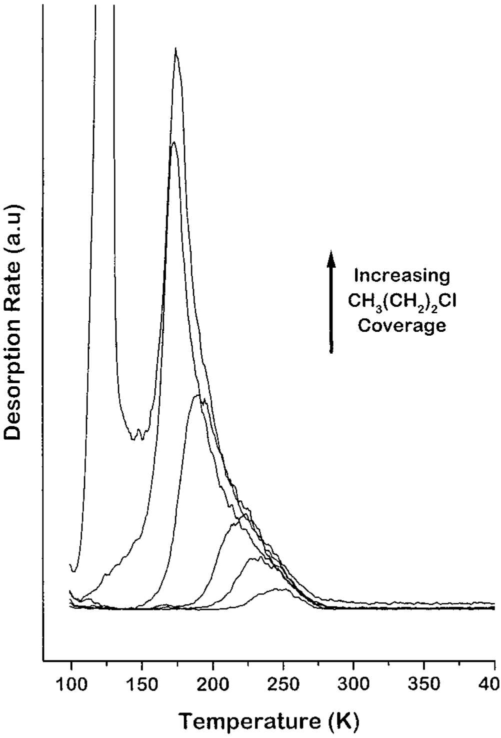

FIG. 3. TPD spectra for $CH_3CH_2CH_2Cl$ adsorbed on the Pd(111) surface at varying initial coverages. At low initial coverage, the molecule desorbs with a maximum rate at about 250 K. As the initial coverage is increased, the monolayer desorption peak grows until it is saturated and the peak temperature is shifted to 173 K. At higher coverages a multilayer desorption peak can be seen at about 120 K that does not saturate with further increase in coverage. The heating rate was 3 K/s. The fragment monitored in the mass spectrometer had $m/q = 49$.

is reversible and molecular. For molecular adsorption/desorption, it is assumed that there is no activation barrier to adsorption, and thus, the measured barrier to desorption for $CH_3(CH_2)_2Cl$ is equal to its desorption energy. The coverage dependence of the desorption peak temperature in the TPD spectra indicates that the process cannot be thought of as a simple first-order process with a coverage independent desorption rate constant. The shift to lower temperatures might be due to a second-order process or to a first-order process in which the desorption energy is decreasing with increasing coverage. The latter seems more likely since there is no reason to believe that simple molecular desorption should be a second-order process. It seems most likely that interactions between adsorbed molecules could easily account for the decrease in the desorption energy with increasing coverage.

The coverage dependence of the desorption spectra for all the alkyl chlorides adsorbed on the Pd(111) surface is similar to that observed for $CH_3(CH_2)_2Cl$. Rather than illustrate the full coverage dependence of the TPD spectra for each of the six alkyl chlorides used in this work we have reported those obtained at low and at high coverages. Figures 4 and 5 show the desorption spectra obtained with coverages on the order of 0.10 monolayers (ML) and 1.0 ML, respectively. The monolayer coverage was defined as the coverage at which the onset of the multilayer desorption feature was observed. Coverages for other TPD spectra of a given molecule were determined by comparing the peak areas with those of the monolayer spectra. The spectra at monolayer coverage are quite complicated in the sense that they have multiple peaks and suggest that ΔE_{des} may be a somewhat complicated function of coverage. The general feature that is quite easily observed is that the desorption peak temperatures increase with increasing alkyl chain length. This is consistent with the simple picture of ΔE_{des} increasing with chain length as depicted in the potential energy surface of Fig. 2.

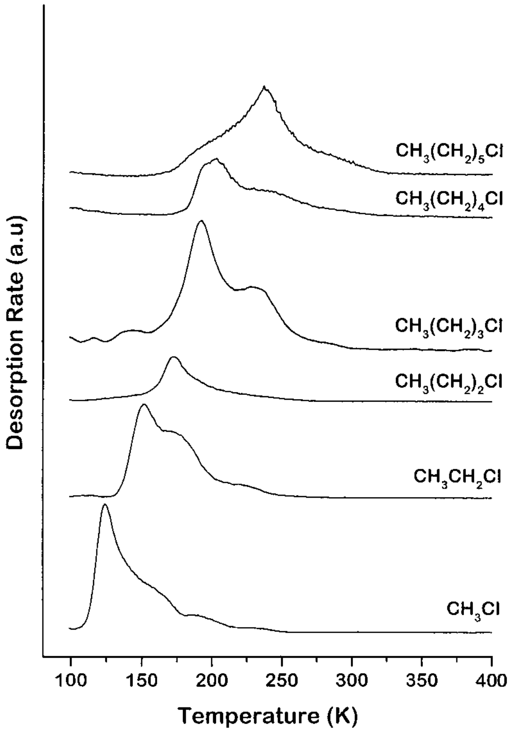

FIG. 5. TPD spectra for $CH_3(CH_2)_nCl$ ($n = 0$–5) at saturated monolayer coverage. The heating rate was 3 K/s and the fragments monitored in the mass spectrometer had $m/q = 50, 64, 49, 56, 55, 55$, respectively. The maximum desorption rates for different alkyl chlorides are positioned at 125, 152, 173, 193, 203, and 237 K.

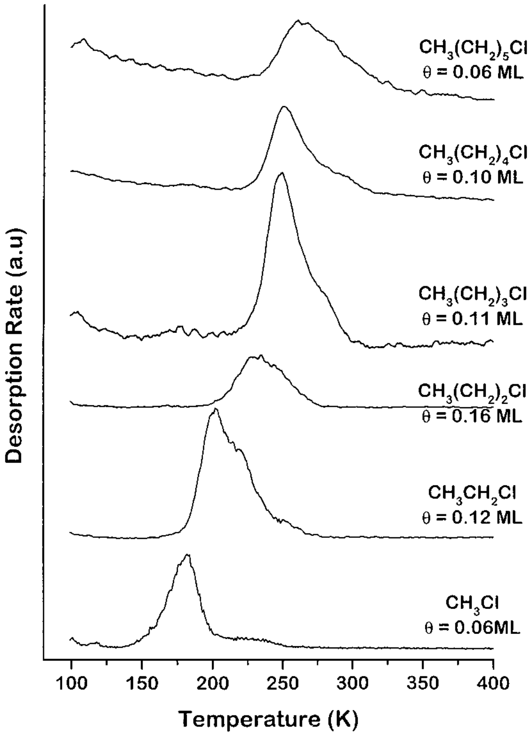

FIG. 4. TPD spectra for $CH_3(CH_2)_nCl$ ($n = 0$–5) at low initial coverage ($\theta \sim 0.10$ ML). The heating rate was 3 K/s and the fragments monitored in the mass spectrometer had $m/q = 50, 64, 49, 56, 55, 55$, respectively. The maximum desorption rates for different alkyl chlorides occur at $T_p = 184$, 201, 235, 248, 251, and 262 K.

The TPD results for CH_3Cl and CH_3CH_2Cl both show that the desorption peaks are coverage dependent. At low initial coverage (~0.1 ML), the desorption peaks for CH_3Cl and CH_3CH_2Cl shown in Fig. 4 are positioned at about 184 and 201 K, respectively. As the CH_3Cl and CH_3CH_2Cl coverages on the Pd(111) surface are raised, the monolayer desorption peaks for both CH_3Cl and CH_3CH_2Cl enlarge until they are saturated . The desorption peak temperature for CH_3Cl shifts from 184 to 125 K and the desorption peak temperature for CH_3CH_2Cl shifts from 201 to 152 K as their initial coverages increase. For both CH_3Cl and CH_3CH_2Cl the relative intensities of desorption spectra obtained using different m/q ratios are approximately equal to those in the fragmentation pattern obtained by background dosing. This indicates that the adsorption of both CH_3Cl and CH_3CH_2Cl can be described as reversible and molecular.

The TPD spectra for $CH_3(CH_2)_3Cl$, $CH_3(CH_2)_4Cl$, and $CH_3(CH_2)_5Cl$ are complicated. As in the cases of the shorter chain alkyl chlorides the peak desorption temperatures decrease with increasing coverage and at high coverages reveal several features. More importantly, the fragmentation patterns of the desorbing species do not exactly match those of the adsorbed molecule. This suggests that at least some fraction of the adsorbed alkyl chloride reacts to form other desorption products. Since only three m/q ratio were monitored for each species no detailed attempt has been made to identify the reaction products.

Previous studies of four fluorinated 1,1-dichloroethanes (CH_3CHCl_2, CH_3CFCl_2, CH_2FCFCl_2, CF_3CFCl_2), on the Pd(111) surface have shown that adsorbed hydrogen affects their desorption energies and it is not possible to completely remove hydrogen from the surface. The hydrogen coverage was determined by monitoring H_2 desorption during TPD experiments. By extended high-temperature annealing in UHV, the surface hydrogen coverage was reduced to ~0.1 ML. This is the same range used for the studies of fluorinated 1,1-dichloroethanes. All of the TPD experiments were performed at this hydrogen coverage to ascertain that the ΔE_{des} estimated for the alkyl chlorides are comparable.

3.2. *X-Ray Photoemission Spectroscopy of Alkyl Chlorides*

Dissociation of the alkyl chlorides deposits chlorine atoms on the Pd(111) surface that can be observed by obtaining Cl $2p_{3/2}$ XP spectra. Figure 6 illustrates the Cl $2p_{3/2}$ XP spectra of the surface following adsorption of $CH_3(CH_2)_2Cl$, $CH_3(CH_2)_3Cl$, $CH_3(CH_2)_4Cl$, $CH_3(CH_2)_5Cl$ at $T < 100$ K and heating of the Pd(111) crystal to 450 K. It is quite clear that the adsorption and desorption of $CH_3(CH_2)_2Cl$ does not leave chlorine on surface. The temperature of 450 K to which the crystal was heated during XPS experiments was selected to be sufficiently high that all molecular species have desorbed and yet below the temperature needed to induce chlorine desorption. Similar XPS experiments using CH_3Cl, CH_3CH_2Cl also show that chlorine is not detected on the surface after their adsorption and desorption. These results demonstrate that the adsorption and desorption of CH_3Cl, CH_3CH_2Cl, and $CH_3(CH_2)_2Cl$ on the Pd(111) surface are reversible and not dissociative. Figure 6 also shows quite clearly that chlorine was found on the Pd(111) surface after the adsorption and desorption of $CH_3(CH_2)_3Cl$, $CH_3(CH_2)_4Cl$, and $CH_3(CH_2)_5Cl$. Of the chlorine in the initially adsorbed monolayers of the alkyl chlorides about half is left on the surface as a result of heating and dissociation. While some of fraction of the adsorbed monolayer dissociates the remainder presumably desorbs as indicated by the desorption spectra.

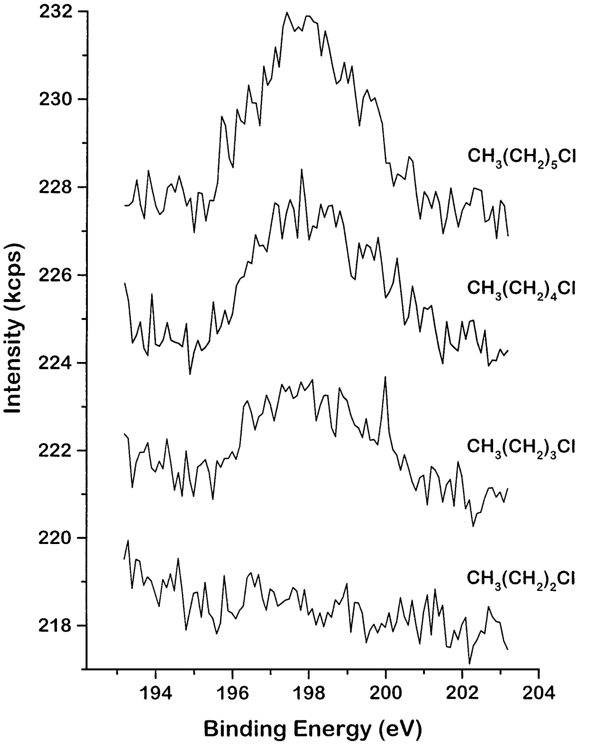

FIG. 6. Cl $2p_{3/2}$ XP spectra for $CH_3(CH_2)_nCl$ ($n = 2$–5) adsorbed on the Pd(111) surface at $T < 100$ K and then heated to 450 K. The exposure to each of the alkyl chlorides was ~0.5 L. The XP spectra reveal that adsorption and heating of the $CH_3(CH_2)_2Cl$ results in desorption from the surface and no dissociation. Some fraction of the longer chain alkyl chlorides dissociate during heating to leave atomic chlorine on the surface. The XP spectra were obtained with the sample temperature held at 450 K.

A sequential set of $CH_3(CH_2)_5Cl$ exposures each followed by heating and XPS measurements was conducted to understand the effect of adsorbed chlorine on alkyl chloride dissociation. The first 0.5 L exposure of the surface to $CH_3(CH_2)_5Cl$ was performed with the crystal temperature at 220 K at which only one monolayer of $CH_3(CH_2)_5Cl$ adsorbed on surface. The Pd(111) crystal was then heated to 450 K and held at that temperature while XPS was used to detect the amount of chlorine deposited on the surface (Fig. 7). Further exposures to 0.5 and 1.0 L of $CH_3(CH_2)_5Cl$ followed by heating and XPS did not result in the deposition of further amounts of chlorine onto the surface. Although the surface is not nearly saturated with chlorine, the further dissociation of alkyl chlorides appears to be inhibited by the presence of some chlorine on the surface.

The absolute amount of chlorine deposited on the surface can be calibrate against the known coverage produced by exposure of the Pd(111) surface to Cl_2 gas. Erley (21) and Tysoe (22) observed that the saturation chlorine coverage generated by Cl_2 exposure at 300 K is about $\theta_{Cl} = 0.43$ monolayer. The desorption temperature for chlorine atoms is above 800 K at coverages below 0.33 ML on the Pd(111) surface. The chlorine coverage generated by

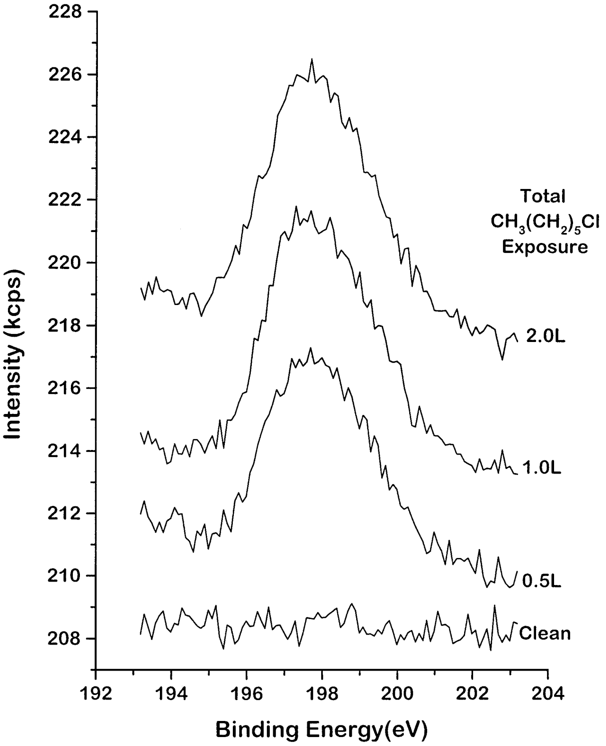

FIG. 7. Cl $2p_{3/2}$ XP spectra following sequential exposures of the Pd(111) surface to $CH_3(CH_2)_5Cl$ at 220 K followed by heating to 450 K. Each $CH_3(CH_2)_5Cl$ exposure is ~0.5 L. The exposure listed by each spectrum indicates the total exposure. Chlorine is left on the surface following the first exposure and heating cycle. Subsequent exposure and heating does not result in the deposition of additional chlorine. The implication is that atomic chlorine on the Pd(111) surface inhibits the further dissociation of alkyl chlorides.

three sequential $CH_3(CH_2)_5Cl$ exposures on the Pd(111) surface is calibrated to be $\theta_{Cl} = 0.03$ ML, which is far less than the saturation coverage produced by Cl_2 gas.

4. DISCUSSION

The XPS studies indicate that as one increases the chain length of the alkyl chlorides, $CH_3(CH_2)_3Cl$ is the first to dissociate on the Pd(111) surface during adsorption at $T < 100$ K followed by heating to 450 K. By estimating the desorption energies of the alkyl chlorides it should be possible to estimate the value of ΔE_{C-Cl}, the barrier to C–Cl bond cleavage. This is slightly complicated by the observed coverage dependence of the peak desorption temperatures of the TPD spectra which suggests that ΔE_{des} is coverage dependent. We have used Redhead's equation (20) and the peak desorption temperature of the spectra shown in Figs. 4 and 5 to estimate the range of ΔE_{des} for each of the alkyl chlorides.

$$\frac{\Delta E_{des}}{R \cdot T_p^2} = \frac{\nu}{\beta} \cdot e^{-\Delta E_{des}/R \cdot T_p}.$$

In this expression T_p is the peak desorption temperatures, R is the gas constant, and β is the heating rate. The quantity ν is the preexponent in the rate constant for desorption and is taken to be $10^{13}\,s^{-1}$. This provides estimates of the desorption energies for the alkyl chlorides at coverages of one monolayer and more importantly at low coverages of ~0.10 ML. Both are plotted in Fig. 8 and give a range for the desorption energies of each molecule. For the short chain alkyl chloride, ΔE_{des} increases linearly with chain length and then appears to reach some saturation value. This is consistent with the fact that for the longer chain alkyl chlorides, dissociation is observed and the temperature at which desorption occurs is presumably limited by the dissociation process. For high coverages the majority of the initially adsorbed alkyl chloride desorbs and ΔE_{des} increases linearly with chain length.

The barrier to C–Cl bond cleavage can be estimated from the low coverage values of ΔE_{des} for the longest chain alkyl chloride to desorb completely and the shortest chain alkyl chloride for which dissociation is observed. The ΔE_{C-Cl} is estimated to lie between these limits. The basic assumption is that there is a competition between desorption and

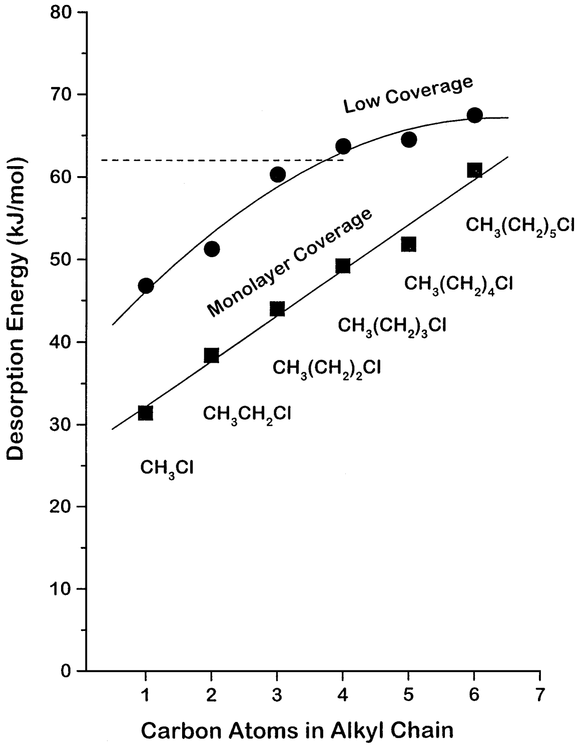

FIG. 8. The desorption energies for $CH_3(CH_2)_nCl$ ($n = 0$–5) at low (~0.1 ML) and high (~1 ML) coverages on the Pd(111) surface. The desorption energies were calculated by assuming no activation barrier to adsorption and a preexponential factor of $\nu = 10^{13}\,s^{-1}$ in the desorption rate constant. The onset of C–Cl bond dissociation appears between $n = 2$ and 3. This places the estimate of the barrier to C–Cl bond cleavage at $\Delta E_{C-Cl} = 60$–64 kJ/mol, between the low coverage desorption energies of $CH_3(CH_2)_2Cl$ and $CH_3(CH_2)_3Cl$.

dissociation and that once ΔE_{des} is increased to a point that it is $>\Delta E_{\mathrm{C-Cl}}$ dissociation begins to dominate. One of the underlying assumptions is that the rate constants for desorption and dissociation are both for first-order processes and have preexponents of similar magnitude. Since both processes are unimolecular this can be justified. The $CH_3(CH_2)_2Cl$ desorbs completely with a range of $\Delta E_{\mathrm{des}} = 44–60$ kJ/mol. For $CH_3(CH_2)_3Cl$, which is the shortest alkyl chloride to dissociate, the range of ΔE_{des} is 49–64 k/mol. This suggests that $\Delta E_{\mathrm{C-Cl}}$ lies in the range 60–64 kJ/mol.

The primary goal of this paper has been to provide an estimate for $\Delta E_{\mathrm{C-Cl}}$ on the Pd(111) surface for comparison with the value estimated from the two step method used during the study of CFC dechlorination on this surface (14–16). The estimate of $\Delta E_{\mathrm{C-Cl}} = 60–64$ kJ/mol obtained in this work is consistent with the value obtained from the study of the dechlorination of fluorinated 1,1-dichloroethanes (CH_3CHCl_2, CH_3CFCl_2, CH_2FCFCl_2, CF_3CFCl_2) on the Pd(111) surface. It is also very close to the result obtained from an investigation of carbon–halogen dissociation on the Cu(111) surface. In that study Lin and Bent used the same approach as has been used here to estimate $\Delta E_{\mathrm{C-Cl}} \sim 65$ kJ/mol on the Cu(111) surface (14).

Several observations suggest that the dissociation of C–Cl bonds on the Pd(111) surface is influenced by the presence of adsorbed chlorine itself. The first is that the amount of chlorine on the surface following the adsorption and heating of $CH_3(CH_2)_3Cl$, $CH_3(CH_2)_4Cl$, and $CH_3(CH_2)_5Cl$ is roughly the same for all three as indicated by the XPS results in Fig. 6. One would expect that as ΔE_{des} increases with increasing chain length, an increasing fraction of the adsorbed alkyl chloride remains on the surface to temperatures at which it can dissociate. This is not observed and instead only about half of the adsorbed alkyl chloride dissociates. Second, Fig. 7 shows that the sequential or repeated adsorption of $CH_3(CH_2)_5Cl$ followed by heating does not result in the deposition of increasing amounts of chlorine on the surface. Most of the chlorine on the surface was contributed by the first $CH_3(CH_2)_5Cl$ exposure. Atomic chlorine on the Pd(111) surface apparently inhibits further alkyl chloride dissociation. In essence, this means that although a small fraction of the alkyl chlorides dissociate during heating, the deposition of chlorine onto the surface then causes $\Delta E_{\mathrm{C-Cl}}$ to increase and thus exceed ΔE_{des} so that the remainder of the alkyl chloride desorbs. The implication is that our estimate of $\Delta E_{\mathrm{C-Cl}} = 60–64$ kJ/mol holds for the clean Pd(111) surface or only at low chlorine coverages. The measurements of $\Delta E_{\mathrm{C-Cl}}$ in the CFCs on the Pd(111) surface were made under conditions of low coverage and give comparable values to the value measured in the alkyl chlorides.

5. CONCLUSIONS

The intrinsic barrier to carbon–chlorine bond cleavage ($\Delta E_{\mathrm{C-Cl}}$) in alkyl chlorides adsorbed on the Pd(111) surface has been estimated to lie in the range 60–64 kJ/mole. This value is consistent with the value of $\Delta E_{\mathrm{C-Cl}}$ determined previously using a set of fluorinated 1,1,-dichloroethanes (14–16). The work reported in this paper validates the method used in that work, in which $\Delta E_{\mathrm{C-Cl}}$ was determined from the sum of the apparent barrier to dechlorination and the desorption energy ($\Delta E_{\mathrm{C-Cl}} = \Delta E_{\mathrm{app}} + \Delta E_{\mathrm{des}}$). The net result is to supply further support for the conclusion of that work that the transition state to dechlorination occurs early in the reaction coordinate for C–Cl bond cleavage.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant CTS 9509850. The authors thank Prof. J. L. d'Itri and her students for their advice and suggestions.

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