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Carbon–chlorine bond cleavage in chlorofluoroethanes on Pd(111)

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The kinetics of carbon–chlorine bond cleavage on a Pd(111) surface have been investigated using several dichloroethanes with varying fluorine content (CF_3CFCl_2, CH_3CFCl_2, CH_2FCFCl_2, CH_3CHCl_2, CH_2ClCH_2Cl). Preliminary results show that the dechlorination rates in these molecules exhibit trends that are similar to those observed in catalytic hydrodechlorination over supported Pd catalysts. Fluorination of the 1,1-dichloroethanes decreases the rate constant for dechlorination. The presence of only one chlorine atom on each carbon atom (CH_2ClCH_2Cl vs. CH_3CHCl_2) also reduces the rate constant for dechlorination. A Hammett correlation using field substituent parameters was established for the rate of dechlorination in an attempt to probe the nature of the transition state to carbon–chlorine bond cleavage ($[RC\cdots Cl]^{\ddagger}$). The dechlorination rate constant for 1,1-dichloroethanes is slightly reduced with increasing field effects (increasing fluorination) and the Hammett correlation reveals a reaction constant of $\rho = -1.0 \pm 0.2$. The interpretation of this result is that there is little polarization of the C–Cl bond in the transition state for dechlorination, which is consistent with a transition state that is early in the reaction coordinate.

Keywords: chlorofluoroethanes on Pd(111), carbon–chlorine bond cleavage, catalysis by palladium

1. Introduction

Over the past two decades there has been increasing concern over the detrimental effects of chlorine-containing compounds on the environment. In particular, the depletion of the ozone layer by anthropogenic sources of chlorine has received significant global attention, and chlorofluorocarbons (CFCs) have been identified as major contributors to ozone depletion. In the resulting search for alternatives to CFCs, hydrofluorocarbons (HFCs) have emerged as the best substitutes [1,2]. As an example, CF_3CFH_2 (HFC-134a) has been identified as a replacement for CF_2Cl_2 (CFC-12) used in automobile air-conditioning units.

One method of production of HFCs is the hydrodechlorination of CFCs over a supported Pd catalyst [2]. HFC-134a can be produced from CF_3CFCl_2 (CFC-114a):

$$CF_3CFCl_2 + H_2 \xrightarrow[\text{Pd(111)}]{} CF_3CFH_2 + 2HCl$$

This reaction yields CF_3CFH_2 with a selectivity of greater than 70%, generating as byproducts a mixture of CF_3CH_3, CF_3CH_2F and CF_3CHClF [3–5]. A number of catalytic studies have focused on the hydrodechlorination reaction, and a consistent picture is emerging regarding the relative reactivity of different chlorocarbons. One interesting result is that CF_3CFCl_2 is hydrodechlorinated at a much higher rate than its symmetric isomer CF_2Cl–CF_2Cl [3]. Also, in the hydrodechlorination of various chlorocarbons increasing fluorine content lowers the rate of hydrodechlorination [6]. An understanding of the factors which control activity and selectivity could facilitate improvement in the yield of the desired products.

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 depends predominantly on its activation energy, 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 on Pd surfaces. Such an understanding may help to explain the observed differences in activity and selectivity among reactants and allow prediction of the dechlorination rates of similar CFCs. Knowledge of the critical transition state would aid the development of improved catalysts for HFC production and for disposal of chlorinated industrial waste such as $CCl_2{=}CClH$, $CCl_2{=}CCl_2$, and polychlorinated biphenyls (PCBs).

This investigation has probed the nature of the transition state for C–Cl bond cleavage by measuring the apparent rate constants (k_{app}) for dechlorination of a set of selectively fluorinated chloroethanes on a Pd(111) single-crystal surface. Trends previously found in catalytic hydrodechlorination rates are also observed in the rate constants for dechlorination [3,6]. This suggests that the dechlorination step plays an important part in the overall kinetics for catalytic hydrodechlorination. Furthermore, it was possible to establish a linear free energy relationship (LFER) correlating the dechlorination rate constants with the degree of fluorination of the reactants. LFERs have been applied in physical organic chemistry to probe changes in charge distributions occurring during reactions [7]. For example, if the carbon atom in the transition state is *cationic* with respect to the initial state ($RC^{\delta+}\cdots Cl$), an electronegative substituent (R) such as fluorine would increase the activation barrier by

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destabilizing the electron-deficient transition state. Alternately, if the carbon atom in the transition state is *anionic* with respect to the initial state ($RC^{\delta-}\cdots Cl$), adding an electronegative substituent would lower the barrier by stabilizing the electron-rich transition state. The "electronegativity" of substituent groups such as CF_3 groups is commonly reflected in their field substituent constants (σ_F). The results of this initial study of the dechlorination reaction on a Pd(111) surface show a clear correlation between the rate constant (k_{app}) and the substituent constant (σ_F), but suggest that the change in charge distribution between initial state and the transition state is small.

2. Experimental

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 spotwelding 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 spotwelded 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 XPS (VG Microtech 800 W Al-Kα X-ray source with a CLAM II analyzer), using a pass energy of 140 eV for the Cl[2p] peaks in order to maximize signal and 105 eV for the Pd[3d] peaks. The purity of chemicals used in experimentation was determined using a quadrupole mass spectrometer (Extrel model C50).

The rate of dissociative adsorption of the chloroethanes was measured by exposing the heated crystal (450 K) to a constant pressure (1×10^{-9} Torr, uncorrected for ion-gauge sensitivities) of the chlorofluoroethanes. XP spectra of the surface were obtained periodically during the exposure to measure the chlorine coverage on the surface. Previous thermally programmed desorption (TPD) studies of CF_3CFCl_2 [8] and CH_3CFCl_2 (not reported in this letter) have shown that their desorption from the Pd(111) surface occurs at temperatures below 250 K. As a result, the equilibrium coverage of the chlorofluoroethanes at 450 K is negligible and any chlorine on the Pd(111) surface is adsorbed atomic chlorine. Thus, measurement of the chlorine coverage (θ_{Cl}) versus time provides a measure of the rate of dissociative adsorption.

The calibration of the XPS signal versus 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 $\theta_{Cl} = 0.43$ monolayer (ML) [9]. At $\theta_{Cl} = 0.43$ ML, the ratio of the Cl[2p] 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 Pd(111) surface exposes 1.53×10^{15} atoms/cm^2; thus $\theta_{Cl} = 1$ ML corresponds to 1.53×10^{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 cleavage. The Pd(111) surface was normally exposed to X-rays for roughly half of the total time of exposure to the chloroethanes. Four control experiments were performed, in which the Pd(111) surface at 450 K was exposed to 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 with the X-rays on (for half of the time). In all cases, 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. Apparently, X-ray exposure does not have a significant influence on the measured dechlorination rate constants.

3. Results

The rate constants for dechlorination of CF_3CFCl_2, CH_3CFCl_2, CH_2FCFCl_2, CH_3CHCl_2, and CH_2ClCH_2Cl on the Pd(111) surface were measured at 450 K. Previous thermal desorption experiments using CF_3CFCl_2 have shown that the molecule is molecularly adsorbed on the surface at low temperatures and desorbs during heating at temperatures below 200 K [8]. As a result, to observe dechlorination the heated Pd(111) surface must be continually exposed to the chloroethane. The dissociative adsorption rates were determined by measuring the Cl[2p] signal versus time during exposure to each chloroethane. A typical set of raw data obtained from such an experiment is shown in figure 1. The background signal has been subtracted from these Cl[2p] spectra by fitting a line through ten data points on either sides of the peak. By calculating the area under the Cl[2p] peaks and normalizing to the area under the Pd[3d] peak, θ_{Cl} can be determined. This data has then been plotted as the chlorine uptake curves seen in figure 2. The data points are fitted with a linear regression, and the initial slope is used to determine the initial rate (r) of chlorine deposition. Other work (not shown here) indicates that the deposition rate is first-order in the chloroethane pressure for CH_3CFCl_2, and so, division of the initial rate by the pressure is used to determine the rate constant for chlorine deposition:

$$k_{app} = \frac{r}{2P}.$$

Since the hydrodechlorination of CF_3CFCl_2 and CF_2Cl_2 results in the removal of both chlorine atoms [3–5,10,11], the rate constant for chlorine deposition is taken to be twice the apparent rate constant for molecular dechlorination of CF_3CFCl_2, CH_3CFCl_2, CH_2FCFCl_2 and CH_3CHCl_2. However, since the hydrodechlorination of the CF_2Cl–CF_2Cl results in the removal of only one chlorine atom [3], the rate constant for molecular dechlorination of CH_2Cl–CH_2Cl is taken to be equal to the rate constant for chlorine deposition ($k_{app} = r/P$).

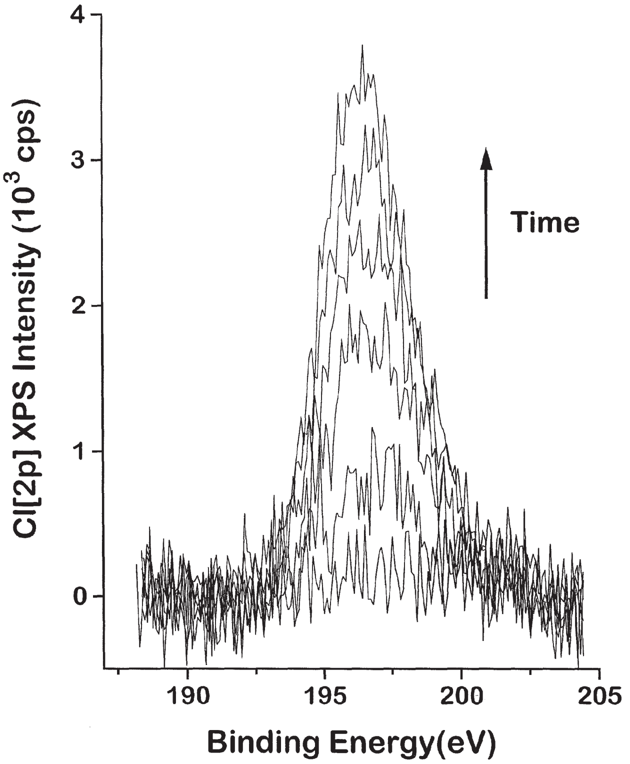

Figure 1. Cl[2p] XPS during exposure of Pd(111) to 1×10^{-9} Torr CH_3CFCl_2 at 450 K. These show the peak area growing monotonically with time during the exposure. The pass energy of the analyzer was 140 eV in order to maximize signal. A straight line fit through ten points on either side of the peak was subtracted as background.

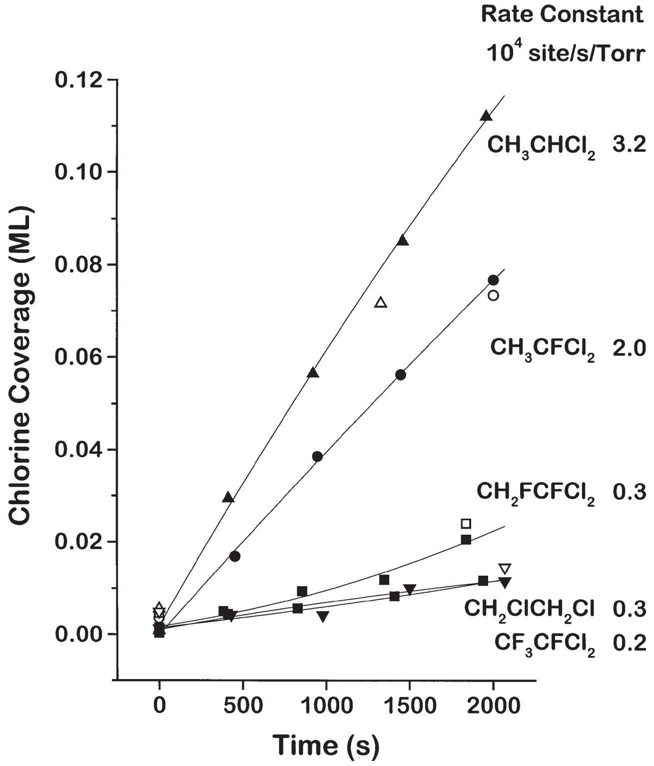

Figure 2. Chlorine coverage on the Pd(111) surface as a function of time during exposure to 1×10^{-9} Torr of chloroethanes at 450 K. The lines through the uptake curves are linear regressions through the points. The rate constants for dechlorination were determined from the slopes of the uptake curves. The open symbols represent control experiments performed in the complete absence of X-rays. In all cases these data points obtained with the X-ray source off were within experimental error of the curves obtained with the X-ray source on. (* The rate constant for CH_2Cl–CH_2Cl is calculated with a factor of 2 difference from those for the 1,1-dichloroethanes, as described in the text.)

The rate constants for dechlorination are shown on figure 2 next to the respective uptake curves in units of molecules/site/s/Torr (site = Pd atom). It is clear that there are differences in the rate constants for dechlorination of the different molecules. Increasing the amount of fluorine in the molecule decreases the rate of dechlorination by a factor of ten. Furthermore, the rate of dechlorination of the CH_3CHCl_2 and the CH_2Cl–CH_2Cl differ by a factor of four. These trends for dechlorination are similar to those for catalytic hydrodechlorination [3,6].

4. Discussion

The rate constants for dechlorination have been determined for five chloroethanes on the Pd(111) surface at a temperature of 450 K. It should be pointed out that, since we are measuring the rate of chlorine uptake on the surface, we do not yet know all details of this reaction. For instance, at this point in time we do not know the ultimate fate of the remainder of the molecule other than to say that the chlorine deposition is accompanied by some carbon deposition but no fluorine deposition. The decomposition of the remaining fragment is the subject of further investigation.

At this point, we interpret the measured rate constants as arising from the early steps of the dechlorination reaction. In the only study to date of CF_3CFCl_2 adsorption on Pd(111) surfaces, Rotondi found that the molecule was reversibly adsorbed [8]. Thus, dechlorination is assumed to proceed via a two-step mechanism; reversible adsorption onto an empty site ($*$) followed by C–Cl bond cleavage:

$$\mathrm{R{-}Cl_{(g)}} + * \overset{K_{\mathrm{eq}}}{\rightleftharpoons} \mathrm{R{-}Cl}\,*$$

$$\mathrm{R{-}Cl}\,* + * \xrightarrow{k_{\mathrm{C-Cl}}} \mathrm{R}\,* + \mathrm{Cl}*$$

At the low $\mathrm{R{-}Cl_{(g)}}$ pressures used in this investigation ($P_{\mathrm{CFC}} = 10^{-9}$ Torr), a Langmuir isotherm predicts that the R–Cl coverage is low and is given by

$$\theta_{\mathrm{R-Cl}} \approx K_{\mathrm{eq}} \cdot P_{\mathrm{R-Cl}}.$$

The C–Cl bond dissociation rate is then given by

$$r = k_{\mathrm{C-Cl}} \cdot \theta_{\mathrm{R-Cl}} \approx k_{\mathrm{C-Cl}} \cdot K_{\mathrm{eq}} \cdot P_{\mathrm{R-Cl}} \approx k_{\mathrm{app}} \cdot P_{\mathrm{R-Cl}}.$$

Consistent with this model, we have observed that the dechlorination rate is indeed first-order in the CH_3CFCl_2 pressure (data not shown). Within the context of this model, for the reaction mechanism we have measured apparent rate constants (k_{app}).

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 catalytic hydrodechlorination reactions which have motivated our investigation. If the slowest or rate-limiting steps in the hydrodechlorination reaction can be modeled by the mechanism described above and all subsequent steps such as hydrogenation and desorption reactions are fast, then the rate constants for the catalytic hydrodechlorination reaction and for the dechlorination reaction on the Pd(111) surface ought to be comparable in the sense that they would both be of the form

$$k_{\text{app}} = k_{\text{C–Cl}} \cdot K_{\text{eq}}.$$

Differences in magnitude would arise due to the fact that the supported Pd catalyst is not composed solely of Pd(111) planes and the reaction temperatures may be different. Clearly, making a direct comparison of reaction rate constants is not possible. However, it is very interesting to note that the basic trends in reactivity of different molecules are the same for catalytic hydrodechlorination and for the dechlorination reaction on the Pd(111) surface. First, putting two chlorine atoms on one carbon atom increases the rate constant for dechlorination. The rate constants for dissociative adsorption of the two isomers CH_3CHCl_2 and $CH_2Cl–CH_2Cl$ differed by a factor of four. Similar results are seen at atmospheric pressures; increasing the number of chlorine atoms on a carbon atom increases the hydrodechlorination rate [3,5,6,12]. Second, increasing the fluorine content of the molecule decreases the dechlorination rate constant. The rate constant for dechlorination of CH_3CHCl_2 is a factor of eight greater than that of CF_3CFCl_2. This trend also matches the trend observed for the hydrodechlorination reaction at atmospheric pressures [6]. The fact that trends for dechlorination rate constants mimic those for catalytic hydrodechlorination is consistent with dechlorination being either the rate-limiting step or, at least, contributing to the overall rate constant for the hydrodechlorination reaction.

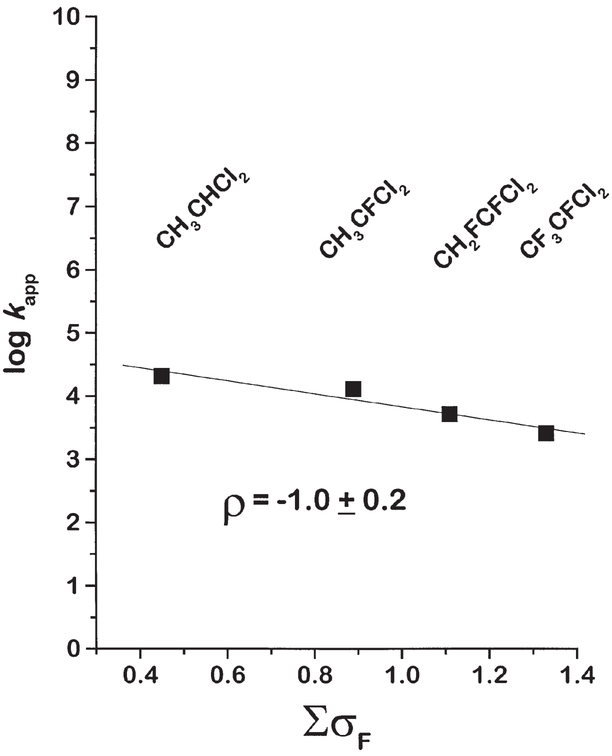

Figure 3. Linear free energy relationship for dechlorination of 1,1-dichloroethanes on Pd(111). The substituent constants are sums of the Hammett field parameters for each substituent on the chlorinated carbon atom. The slope of the relationship gives the reaction constant $\rho = -1.0 \pm 0.2$.

Table 1
List of substituent constants used in LFER [13].

Substituent	σ_F
H	0.0
F	0.44
CH_3	0.0
CH_2F	0.22
CF_3	0.44
Cl	0.45

Table 2
Sum of substituent constants for each molecule in LFER.

Molecule	$\sum \sigma_F$
CF_3CFCl_2	1.33
CH_3CFCl_2	0.89
CH_2FCFCl_2	1.11
CH_3CHCl_2	0.45

One of the primary objectives of these measurements has been to use the effects of substituents to understand the nature of the transition state for the dechlorination reaction. The linear free energy relationship between the dechlorination rate constants and the degree of fluorination in the 1,1-dichloroethanes is shown in figure 3. A LFER is constructed on the basis of the Hammett equation, which describes an empirical relationship between reaction rate constants of a set of selectively substituted compounds:

$$\log(k_{\text{R}}) = \rho \cdot \sigma_{\text{F}} + \log(k_{\text{H}}),$$

where k_R is the rate constant for substituted reactant, k_H the rate constant for unsubstituted reactant, σ_F the field substituent parameter for R, and ρ the reaction constant. The Hammett field parameters for the individual substituents [13] are tabulated in table 1, and the overall substituent constants for the molecules are shown in table 2. It is apparent from figure 3 that the reaction constant is $\rho = -1.0 \pm 0.2$. The magnitude of this number is low by comparison with some such numbers measured on metal surfaces. In the cases of alkyl coupling on the Ag(111) surface and β-hydride elimination in alkoxides on the Cu(111) surface, reaction constants of $\rho = -10$ and $\rho = -22$ have been reported [14–16].

The interpretation of this reaction constant requires some thought about the components of the apparent rate constant ($k_{\text{app}} = k_{\text{C–Cl}} \cdot K_{\text{eq}}$). The apparent rate constants vary by roughly an order of magnitude among the variously substituted dichloroethanes. Unless the adsorption equilibrium constants (K_{eq}) vary greatly among the reactants, this implies that the rate constants for C–Cl bond cleavage also vary by roughly an order of magnitude. Preliminary measurements of the heats of adsorption from TPD spectra suggest that the difference in the heats of adsorption are small, on the order of 1–2 kcal/mol. At 450 K this means that the adsorption equilibrium constants will lie within an order of magnitude of one another. Therefore a plot of $\log(k_{C–Cl})$ versus σ_F would reveal a reaction constant on the order of $\rho_{C–Cl} = 0$ to -2 for the C–Cl bond cleavage reaction. In any reasonable scenario for the values of K_{eq}, the reaction constant $\rho_{C–Cl}$ must be quite small.

The goal of the work is some understanding of the nature of the transition state for the C–Cl bond cleavage reaction during dechlorination and hydrodechlorination. The implication of the relatively low value of $\rho_{C–Cl}$ is that the transition state for the C–Cl bond cleavage is not highly polarized with respect to the initial state. A transition state in which the charge distribution has not changed greatly from that in the initial state would be consistent with a reaction, in which the transition state is early in the reaction coordinate.

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