The transition state for metal-catalyzed dehalogenation

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Substituent effects have been used to probe the nature of the transition state to catalytic carbon–halogen bond breaking. Kinetics measurements have determined the activation energies (E_{act}) to C–Cl bond breaking on the Pd(111) surface and C–I bond breaking on the Pd(111) and Ag(111) surfaces. These barriers have been measured using alkyl halides with varying degrees of fluorine substitution. The activation energies have been correlated with the inductive or field substituent constants (σ_F) of the fluorinated alkyl groups in order to determine reaction constants ($E_{act} = E_0 + \rho\sigma_F$) for the dehalogenation reactions. In all three cases it has been found that the barriers are insensitive to inductive substituent effects and the reaction constants are all relatively small: $\rho = -0.5 \pm 1.0$ kcal/mol for C–Cl cleavage on Pd(111), $\rho = -0.3 \pm 0.8$ kcal/mol for C–I cleavage on Pd(111), and $\rho = -2.9 \pm 0.4$ kcal/mol for C–I cleavage on Ag(111). This implies that the transition state for dehalogenation is homolytic and occurs early in the reaction coordinate. The implications of this result are discussed for catalytic dehalogenation processes such as hydrodechlorination.

Keywords: palladium, silver, chlorofluorocarbons, dehalogenation, transition state, hydrodechlorination, linear free energy relationships

1. Introduction

The catalytic cleavage of carbon–halogen bonds occurs as an elementary step in a number of important catalytic processes and reactions on metal surfaces. One example is the hydrodechlorination of environmentally hazardous chlorofluorocarbons (CFCs) on supported Pd catalysts to produce benign hydrofluorocarbons (HFCs) [1].

Hydrodechlorination can be used as a general means of conversion of chlorocarbon wastes to valuable hydrocarbons. Another important process is the cleavage of C–I bonds in alkyl iodides which in the field of surface chemistry has been used as an extremely successful and versatile method for producing alkyl groups on metal surfaces [2,3]. As such, reactions involving dehalogenation have been studied on a broad range of different surfaces and catalysts. Most of these important processes involve dehalogenation as a single step in a multistep reaction mechanism. This paper focuses on carbon–halogen bond cleavage on Ag(111) and Pd(111) surfaces and describes the results of an investigation into the nature of the transition state for these dehalogenation reactions.

The study and understanding of kinetics is central to the field of catalysis [4,5]. In a catalytic mechanism consisting of sequences of series and parallel reactions it is the rate constants for the elementary steps that ultimately determine overall activity and selectivity. The most important parameter determining the magnitude of a rate constant is the activation barrier (E_{act}) or the energy difference between the initial state and the transition state for the process. While there has been a great deal of work to study the stable surface species that form the initial state reactants for any given elementary step, comparatively little has been done to characterize the nature of the transition states for surface-catalyzed reactions. An understanding of transition states on surfaces is an important component in the overall understanding of the catalytic reaction kinetics.

The method used in this work to probe the transition state for dehalogenation reactions is based on the use of substituent effects and has its roots in physical organic chemistry [6–8]. The barriers to a given reaction are measured in a series of reactants, which are modified by the addition of various substituent groups. For example, in the current work C–I bond cleavage has been studied in a set of alkyl halides ($R^1R^2R^3C$–I) in which the substituents are various combinations of R = H, F, CH_3, CF_2H, CF_3, CH_3CH_2, CF_3CH_2, and CF_3CF_2. One of the keys to the success of this method on metal surfaces is that the C–F bonds in the substituents are very strong and highly polar. As a result they remain intact during the course of the reaction and influence the activation energy without changing the reaction mechanism. The primary effect on the activation energy occurs through long-range electrostatic field effects, as the dipole moments on the substituent groups interact with charges in the reactant and transition state. These effects have been used successfully to probe the transition states for several surface reactions [9–13].

Given that one knows something about the physical properties of substituent groups and measures the effect of substituents on the activation energy to a reaction, it is possible to infer the characteristics of the changes that occur on going from reactant to transition state. The critical property of the substituents that has been used in this work is their field or inductive character quantified by the empirically derived field substituent constants (σ_F) [7,8].

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A simple linear relationship between these substituent constant and the measured activation barriers serves to define a reaction constant $E_{\text{act}} = E_0 + \rho\sigma_{\text{F}}$. A large value of ρ is of the order of 30–70 kcal/mol and would be typical of a gas-phase deprotonation reaction (R–AH $\rightarrow$ R–A$^-$ + H$^+$) where the substituent can have a strong electrostatic effect on the anionic product [7,14]. Such large values have been measured for the β-hydride elimination reaction in alkoxides on the Cu(111) surface [10]. The current work will show that the reaction constants for C–Cl and C–I bond cleavage on Pd(111) and Ag(111) surfaces are relatively small ($|\rho| < 3$ kcal/mol) indicating that the transition state is homolytic and that there is very little change in charge density during carbon–halogen bond cleavage.

2. Experimental

The experiments described in this letter were performed in an ultra-high-vacuum surface science apparatus. This was equipped with instrumentation for surface cleaning by Ar^+ ion sputtering and surface analysis using low-energy electron diffraction and X-ray photoemission spectroscopy (XPS). A quadrupole mass spectrometer was used for measurements of desorption kinetics. The Pd(111) and Ag(111) samples were purchased commercially and were mounted in the UHV chamber on a manipulator that allowed resistive heating to temperatures over 1300 K and cooling to about 90 K. The alkyl iodides used in this work were purchased commercially from Aldrich Chemical Co. and Lancaster Chemical Co., while the DuPont Corp. supplied the dichloroethanes. The liquids were all purified by cycles of freeze–pump–thawing before use. The purity of gases introduced into the vacuum systems was checked using the mass spectrometer.

The kinetics measurements were made using thermal desorption spectroscopy and XPS. The rate of chlorine uptake during exposure of the Pd(111) surface to the dichloroethanes was measured using XPS. The rate of C–I bond breaking during heating of alkyl iodides adsorbed on the Pd(111) and Ag(111) surfaces was also measured by XPS. Details of the kinetics measurements are described elsewhere [15–18].

3. Results and discussion

The primary goal of the work presented in this letter is to probe the nature of the transition state to dehalogenation on a metal surface. The activation barriers to C–Cl bond breaking and C–I bond breaking have been measured in sets of substituted dichloroethanes and alkyl iodides. These are then correlated with the field substituent parameters (σ_{F}) of the fluorinated substituent groups. The reaction constants (ρ) then serve as probes of the nature of the transition state. Measurement of these reaction constants for both C–I and C–Cl bond cleavage on two metal surfaces indicates the general nature of the results.

3.1. C–Cl cleavage on Pd(111)

The intrinsic activation barrier to C–Cl bond breaking ($E_{\text{C–Cl}}$) was measured using CF_3CFCl_2, CF_3CHCl_2, CFH_2CFCl_2, and CH_3CHCl_2 on the Pd(111) surface [16]. Starting with the reactants in the gas phase, the reaction is assumed to proceed by two steps: adsorption followed by dechlorination.

$$\text{R–Cl}_{(g)} \xrightarrow{k_{\text{ads}}} \text{R–Cl}_{(ad)} \qquad E_{\text{ads}} = -E_{\text{des}}$$

$$\text{R–Cl}_{(ad)} \xrightarrow{k_{\text{C-Cl}}} \text{R}_{(ad)} + \text{Cl}_{(ad)} \qquad E_{\text{ads}} = -E_{\text{C–Cl}}$$

Figure 1 depicts the potential energy diagram for this process and illustrates the fact that the barrier to desorption is lower than the barrier to dechlorination ($E_{\text{des}} < E_{\text{C–Cl}}$) [15,16,19]. As a result, when the dichloroethanes are adsorbed on the Pd(111) surface at low temperature and then heated they desorb into the gas phase rather than dissociate. In order to observe dechlorination, one has to expose the surface at an elevated temperature to the dichloroethane in the gas phase. Under these conditions chlorine is deposited onto the surface. The uptake of chlorine can be measured by following the growth of the Cl 2p peak in an XP spectrum.

The apparent activation energy for chlorine deposition (E_{app}) is a combination of the barrier to desorption and the

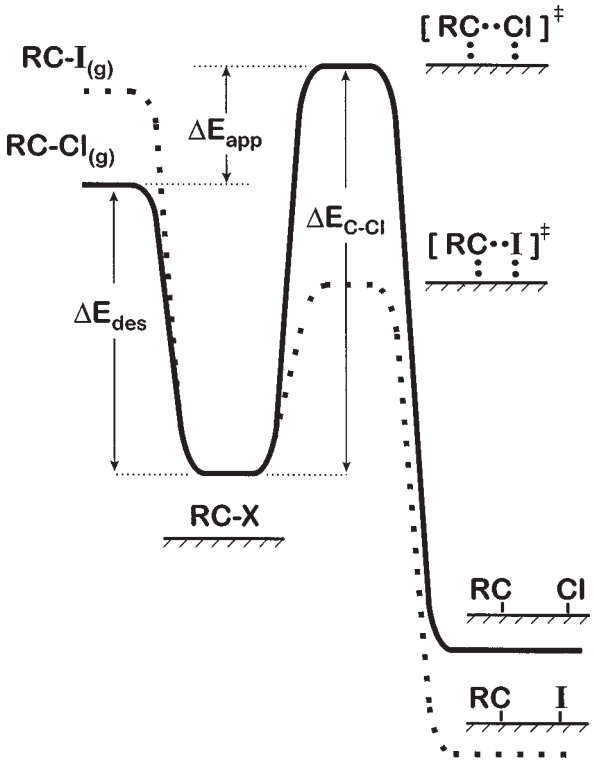

Figure 1. Potential energy diagram for adsorption and dissociation of alkyl iodides and alkyl chlorides. The intrinsic barrier to C–I bond breaking ($E_{\text{C–I}}$) is lower than the desorption energy (E_{des}) and thus C–I bonds in adsorbed alkyl iodides dissociate during heating. The intrinsic barrier to C–Cl bond breaking in alkyl chlorides is higher than the desorption energy and, as a result, adsorbed alkyl chlorides desorb during heating rather than dissociating.

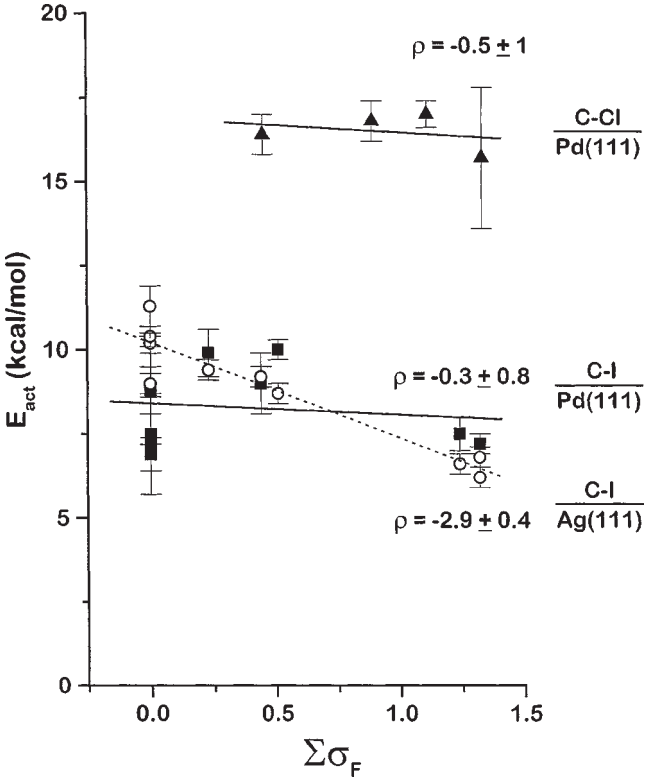

Figure 2. Measured activation energies for C–Cl and C–I bond cleavage on Pd(111) and Ag(111) surface using a set of fluorinated alkyl chlorides and iodides. The activation energies are plotted against the field substituent constants ($\sum \sigma_F$) for the reactant. The reaction constants predicted from these linear free energy relationships are all low or on the order of $\rho \approx 0$, indicating that the transition state for dehalogenation is homolytic.

intrinsic barrier to dechlorination ($E_{app} = E_{C–Cl} - E_{des}$). The desorption energies and the apparent activation energies for dechlorination of the four dichloroethanes were both measured independently on the Pd(111) surface [16]. The desorption energies were estimated from thermal desorption spectra obtained in the limit of low dichloroethane coverage. The desorption process appeared to be first order and the desorption energies were estimated using the peak desorption temperatures and a pre-exponential factor of $\nu = 10^{13}$ s^{-1} in the Redhead equation [20]. The rates of dechlorination were measured by exposing the Pd(111) surface to gas-phase dichloroethanes at temperature in the range 250–350 K. XPS was used to measure the rate of chlorine deposition onto the surface and the apparent activation energy was determined from Arrhenius plots. Finally, the intrinsic barrier to carbon–chlorine bond cleavage was determined as $E_{C–Cl} = E_{app} + E_{des}$ for each of the four dichloroethanes. The results are plotted against the field substituent constants for the dichloroethanes in figure 2. Table 1 lists the substituent constants for each molecule and the desorption and apparent activation energies for dechlorination. It is clear that the E_{des} decreases systematically with increasing fluorination while the E_{app} increases. The two trends cancel and the $E_{C–Cl}$ is estimated at 15–16 kcal/mol for all four dichloroethanes. This number is identical to the number estimated for the barrier to

Table 1
The activation energies for C–Cl bond cleavage ($E_{C–Cl}$) and field substituent constants (σ_F) of the set of 1,1-dichloroethanes used for dechlorination studies on the Pd(111) surface.

Molecule	Field substituents	Field constant σ_F	$\sum \sigma_F$	$E_{C–Cl}$ (kcal/mol)
CH_3CHCl_2	CH_3	0.0	0.45	16.4 ± 0.6
	H	0.0		
	Cl	0.45		
CH_3CFCl_2	CH_3	0.0	0.89	16.8 ± 0.6
	F	0.44		
	Cl	0.45		
CH_2FCFCl_2	CH_2F	0.22	1.11	17.0 ± 0.4
	F	0.44		
	Cl	0.45		
CF_3CFCl_2	CF_3	0.44	1.33	15.7 ± 2.1
	F	0.44		
	Cl	0.45		

C–Cl cleavage in alkyl chlorides on the Cu(100) surface [21,22].

In order to probe the nature of the transition state for C–Cl bond cleavage $E_{C–Cl}$ has been plotted against the field substituent constants for the four dichloroethanes (figure 2). It is immediately apparent that $E_{C–Cl}$ is independent of the degree of fluorine substitution. The slope of the correlation is the reaction constant which is $\rho = -0.5 \pm 1.0$. The implication of this is that the transition state is homolytic in the sense that charge density on the carbon atom is no different from that in the reactant. This suggests that the transition state occurs early in the reaction coordinate for C–Cl bond breaking.

3.2. C–I cleavage on Pd(111)

As an independent check of the observations made for C–Cl bond cleavage on Pd(111) we have performed a similar investigation of C–I bond cleavage reaction on the Pd(111) surface [17]. Both fall into the class of carbon–halogen bond cleavage reactions and thus might be expected to have similar transition states. The primary difference between the two reactions is that the barrier to C–I bond cleavage is lower than the barrier to alkyl iodide desorption ($E_{des} > E_{C–I}$). This is opposite to the case for the alkyl chlorides and is illustrated on the potential energy surface of figure 1. As a consequence, when alkyl iodides are adsorbed on the Pd(111) surface at low temperatures and then heated, they undergo C–I bond cleavage to form an alkyl group coadsorbed with iodine.

$$R–I_{(ad)} \xrightarrow{k_{C–I}} R_{(ad)} + I_{(ad)} \quad E_{act} = E_{C–I}$$

The fact that adsorbed alkyl iodides dissociate during heating means that it is possible to observe and measure directly the kinetics of C–I bond cleavage. This makes it possible to estimate the intrinsic barrier to C–I cleavage ($E_{C–I}$) directly and with less room for error than in the two-step process needed to estimate $E_{C–Cl}$.

Table 2
The activation energies for C–I bond cleavage ($E_{C–I}$) and field substituent constants (σ_F) of the set of alkyl iodides used for deiodination studies on the Pd(111) and Ag(111) surfaces. The activation energies are calculated at approximately half of the saturated monolayer coverage of alkyl iodide.

Molecule	Field substituents	Field constant σ_F	$\sum \sigma_F$	$E_{C–I}$ (kcal/mol)	
				Pd(111)	Ag(111)
CH_3I	H	0.0	0.0	7.2 ± 1.5	11.7 ± 0.5
	H	0.0			
	H	0.0			
CH_3CH_2I	CH_3	0.0	0.0	8.8 ± 0.7	10.2 ± 0.3
	H	0.0			
	H	0.0			
$CH_3CH_2CH_2I$	CH_3CH_2	0.0	0.0	8.8 ± 1.6	10.4 ± 0.3
	H	0.0			
	H	0.0			
$(CH_3)_2CHI$	CH_3	0.0	0.0	7.5 ± 1.1	9.0 ± 0.3
	CH_3	0.0			
	H	0.0			
$(CH_3)_3CI$	CH_3	0.0	0.0	6.9 ± 0.5	–
	CH_3	0.0			
	CH_3	0.0			
$CF_3CH_2CH_2I$	CF_3CH_2	0.23	0.23	9.9 ± 0.7	9.4 ± 0.3
	H	0.0			
	H	0.0			
CF_3CH_2I	CF_3	0.44	0.44	9.0 ± 0.9	9.2 ± 0.3
	H	0.0			
	H	0.0			
$CF_3CF_2CH_2I$	CF_3CF_2	(0.51)	(0.51)	10.0 ± 0.3	8.7 ± 0.3
	H	0.0			
	H	0.0			
CF_2HCF_2I	CF_2H	0.36	1.24	7.5 ± 0.5	6.6 ± 0.3
	F	0.44			
	F	0.44			
CF_3I	F	0.44	1.32	7.2 ± 0.3	6.8 ± 0.3
	F	0.44			
	F	0.44			
CF_3CF_2I	CF_3	0.44	1.32	–	6.2 ± 0.3
	F	0.44			
	F	0.44			

The intrinsic barrier to C–I bond cleavage on the Pd(111) surface has been measured in ten of the alkyl and fluoroalkyl iodides listed in table 2. The kinetics measurements have been made using XPS to differentiate between adsorbed alkyl iodide and iodine atoms adsorbed to the Pd(111) surface. The I $3d_{5/2}$ peak for the alkyl iodide is centered at 620.2 eV, while the I $3d_{5/2}$ peak for adsorbed iodine atoms is positioned at 619.0 eV. As adsorbed alkyl iodides are heated (0.2 K/s) the conversion from alkyl iodide to adsorbed iodine is readily observable and the relative concentrations of the two can be measured as a function of temperature. The temperature at which the maximum reaction rate occurs can be used to estimate $E_{C–I}$ in an analysis similar to the Redhead analysis of desorption spectra for E_{des}.

In order to probe the nature of the transition state for the C–I bond cleavage on Pd(111) the $E_{C–I}$ have been correlated with the field substituent constants of the ten alkyl and fluoroalkyl iodides studied. The barriers have been measured for alkyl iodide coverages corresponding to roughly half of the saturated monolayer. The barriers and substituent constants are listed in table 2 and plotted in figure 2. As in the case of the dechlorination reaction the reaction constant is very small, $\rho = -0.3 \pm 0.8$. The implication is that the transition state for cleavage of the C–I bond is homolytic and not much different from the C–I bond in the reactant alkyl iodide.

3.3. C–I cleavage on Ag(111)

The activation energies for C–I bond cleavage on the Ag(111) surface were measured using the same set of alkyl and fluoroalkyl iodides as were used on the Pd(111) surface [18]. As on the Pd(111) surface the barrier to C–I

bond cleavage is lower than the desorption barrier, so the adsorbed iodides decompose during heating. XPS was used to monitor the relative concentrations of adsorbed iodine and adsorbed alkyl iodide during heating and the temperature of the maximum reaction rate was used to estimate the activation energy to C–I bond cleavage.

By correlating the $E_{\text{C–I}}$ with the field substituent constants it is possible to determine the reaction constant for C–I bond cleavage on the Ag(111) surface. The correlation is illustrated in figure 2 and reveals a reaction constant of $\rho = -2.9 \pm 0.4$. Although this is significantly different from zero, it is nonetheless relatively small when compared to those expected for heterolytic processes or those observed for reactions such as β-hydride elimination [7,9–11,14]. The conclusion is that the transition state for C–I bond breaking on the Ag(111) surface is homolytic, a result that seems to be quite general for catalytic cleavage of carbon–halogen bonds on metal surfaces.

3.4. Implications for catalytic hydrodechlorination

A homolytic transition state for carbon–halogen bond cleavage implies that the transition state is much like the initial state or, in other words, the transition state is early in the reaction coordinate. One of the implications of this is that changes in the nature of the catalytic surface do not have a great effect on $E_{\text{C–Cl}}$ since they would influence the energy of the adsorbed reactant and the transition state in a similar fashion. On the other hand, changes in the catalyst surface can influence E_{app} by influencing E_{des}. Clearly, from examination of figure 1, if E_{des} is increased, then E_{app} will decrease and the net rate of dechlorination will increase accordingly.

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