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The Transition State for Surface-Catalyzed Dehalogenation: C–I Cleavage on Pd(111)

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Substituent effects have been used as a means of probing the nature of the transition state for C–I bond cleavage on the Pd(111) surface. The barriers to C–I cleavage ($\Delta E^{\ddagger}_{\mathbf{C-I}}$) have been measured in a set of 10 different alkyl and fluoroalkyl iodides (CH_3I, CF_3I, CH_3CH_2I, CF_3CH_2I, CF_2HCF_2I, $CH_3CH_2CH_2I$, $CF_3CH_2CH_2I$, $CF_3CF_2CH_2I$, $(CH_3)_2CHI$, and $(CH_3)_3CI$) on Pd(111). These measurements were performed by adsorbing the iodides on the Pd(111) surface at low temperature (90 K) and then heating to 250 K to induce dissociation ($R–I_{(ad)} \rightarrow R_{(ad)} + I_{(ad)}$). X-ray photoemission of the I $3d_{5/2}$ level was used to monitor the extent of reaction during heating. To influence $\Delta E^{\ddagger}_{\mathbf{C-I}}$ the different alkyl and fluoroalkyl groups were chosen to give a wide range of field effect (σ_F) substituent constants. By correlating $\Delta E^{\ddagger}_{\mathbf{C-I}}$ with the field effect through a linear free energy relationship ($\Delta\Delta E^{\ddagger}_{\mathbf{C-I}} = \rho_F \cdot \sigma_F$) it has been possible to compare the activation of C–I bonds on the Pd(111) surface with other dehalogenation reactions (C–Cl cleavage on Pd(111) and C–I cleavage on Ag(111)). In all cases the reaction constants (ρ_F) are very small. For C–I cleavage on the Pd(111) surface $\rho_F = 0$. These results indicate that the transition state to C–I cleavage is homolytic in the sense that it occurs early in the reaction coordinate and the reaction center in the transition state $[C \cdots I]^{\ddagger}$ is not much different from the initial state reactant. This result appears to be generally true of metal catalyzed dehalogenation reactions.

1. INTRODUCTION

Dehalogenation reactions are important elementary steps in a number of catalytic reaction mechanisms and in a number of important processes in surface chemistry. An obvious example is the catalytic hydrodechlorination reaction that involves the cleavage of C–Cl bonds to convert chlorofluorocarbons (CFCs) into hydrofluorocarbons (HFCs) (1–3). Another example is the cleavage of C–I bonds, which is often used in studies of surface chemistry as a route to the formation of stable alkyl groups on metal surfaces (4, 5). The goal of this study is to probe the nature of the transition state to C–I cleavage on Pd(111) surfaces. This is part of a broader effort, which has also included study of the cleavage of C–I bonds on Ag(111) and the cleavage of C–Cl bonds on Pd(111) (6–10).

Since the production of CFCs has been halted as a result of their deleterious effects on the ozone layer, a need has arisen for CFC replacements with similar physical and chemical properties. One such class of chemicals, the HFCs, are not harmful to the ozone layer and are used as alternative compounds in many processes that previously required CFCs. One of the primary routes to the formation of the HFCs is through hydrodechlorination of CFCs using Pd-based catalysts (1–3). These reactions involve the cleavage of C–Cl bonds and subsequent formation of C–H bonds in their place. Needless to say C–Cl cleavage is an important step and there is some evidence that it is either rate limiting or at least influences the overall catalytic reaction rate (6, 7, 11). As such, an understanding of the transition state to C–Cl cleavage and to dehalogenation reactions in general would help to improve our general understanding of catalytic hydrodechlorination and aid the development of new process for catalytic conversion of CFCs into HFCs.

A previous study of the dechlorination of chlorocarbons on the Pd(111) surface made use of a set of four substituted 1,1-dichloroethanes (CF_3CFCl_2, CH_2FCFCl_2, CH_3CFCl_2, and CH_3CHCl_2) (6, 7, 9). In that case the intrinsic barrier to C–Cl cleavage ($\Delta E^{\ddagger}_{\mathrm{C-Cl}}$) was found to be ~60 kJ/mol independent of the degree of fluorine substitution of the molecule. By correlating the values of $\Delta E^{\ddagger}_{\mathrm{C-Cl}}$ with the field substituent constants for the four chlorocarbons, the reaction constant was found to be $\rho_F = 0$. This surprising result suggests that the transition state for C–Cl cleavage is homolytic in the sense that it occurs early in the reaction coordinate and hence looks much like the reactant. This is consistent with the expectation that these dechlorination reactions should be exothermic on a Pd(111) surface and, hence, should be reactant-like in accord with Hammond's postulate (12). The study of C–I cleavage presented in this paper is of another dehalogenation reaction that one might expect to be similar in nature to dechlorination.

The cleavage of C–I bonds has been studied in some depth on the Ag(111) surface (9, 10). That study is very

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similar in nature to the one reported here and also makes use of a set of 10 alkyl and fluoroalkyl iodides to measure the barriers to C–I cleavage ($\Delta E^{\ddagger}_{C-I}$) in a set of molecules with a wide range of substituents on the C–I bond. In that study it was possible to measure both the field and the polarizability reaction constants for C–I cleavage on the Ag(111) surface. These were found to be $\rho_F = -17 \pm 1$ kJ/mol and $\rho_\alpha = -11 \pm 2$ kJ/mol, both of which are significantly different from zero but, nonetheless, relatively low numbers on the scale of reaction constants that can lie in the range of 100–200 kJ/mol for some reactions on surfaces and even higher for ionic gas phase reactions (13, 14). The general conclusion of the study on the Ag(111) surface was that C–I cleavage is homolytic or in other words that the transition state occurs early in the reaction coordinate and is reactant-like. This is consistent with the conclusion for C–Cl cleavage on the Pd(111) surface and is corroborated by the current study of C–I cleavage on the Pd(111) surface.

Although there have been studies of the surface chemistry of CH_3I and CH_3CH_2I on Pd single crystal surface there has been no prior work on the fluoroalkyl iodides. CH_3I adsorbs molecularly on Pd(111) at 90 K and then during heating the C–I bond cleaves at $T < 200$ K to produce $CH_{3,(ad)}$ and $I_{(ad)}$ (15). The $CH_{3,(ad)}$ group is hydrogenated by hydrogen from the Pd bulk and desorbs as CH_4 at $T_p \approx 200$ K. Because of the rapid transfer of hydrogen between the bulk and its surroundings, it is difficult to obtain a hydrogen-free Pd surface when working with hydrocarbons. At high coverages of CH_3I some molecular desorption was observed with a peak desorption temperature at 150 K and the multilayer desorption feature was identified at 135 K. The $I_{(ad)}$ remains on the surface until $T > 850$ K at which point it desorbs leaving a clean surface.

The other published studies of alkyl iodide chemistry on palladium have been performed on the Pd(100) surface using CH_3I and CH_3CH_2I (16–19). The chemistry of CH_3I is reportedly structure dependent (i.e., it differs between Pd(111) and Pd(100)). Unlike Pd(111) where the adsorption is completely molecular at 100 K, on Pd(100) a fraction of the CH_3I dissociates. The remaining $CH_3I_{(ad)}$ undergoes further C–I bond cleavage in the temperature range of 160–190 K with no molecular desorption. On Pd(100) the $CH_{3,(ad)}$ that results from dissociation of $CH_3I_{(ad)}$ primarily hydrogenates to produce CH_4 at 170 K, but a small amount of the coupling product C_2H_6 was also observed (17, 18). The chemistry of CH_3CH_2I is different from CH_3I on Pd(100) (16, 19). Unlike CH_3I, there is no dissociation of the C–I bond in CH_3CH_2I at low temperature (90 K) and the C–I bond of CH_3CH_2I cleaves at $T > 150$ K during heating. The chemistry of the $CH_3CH_{2,(ad)}$ fragment produced by C–I cleavage is complex. A fraction of the $CH_3CH_{2,(ad)}$ is hydrogenated to C_2H_6 at ~180 K and desorbs rapidly. Some $CH_3CH_{2,(ad)}$ dehydrogenates at $T < 180$ K to produce ethylene, C_2H_4, which (unlike C_2H_6) remains on the surface after its formation. Thus C_2H_4 is present on the surface during the C–I bond cleavage of the remaining CH_3CH_2I. The point is that over the temperature range in which C–I cleavage occurs on Pd surfaces there can be concurrent reactions of the product alkyl groups.

The prior results of alkyl iodide studies on the Pd(111) surface illustrate the primary difference between the current study of C–I cleavage on the Pd(111) surface and our previous study on the Ag(111) surface (9, 10). On the Ag(111) surface most of the alkyl groups produced by C–I cleavage are stable until C–I dissociation is complete. On the Pd(111) surface this is not the case and many of the alkyl groups can undergo subsequent reactions over the same temperature range as C–I cleavage. As a result the changing surface composition can influence and complicate the kinetics of the C–I cleavage process.

The study described in this paper has been performed to support our conclusions regarding the nature of the transition states for C–Cl cleavage on Pd(111) and C–I cleavage on Ag(111). We have measured the kinetics of C–I cleavage in a series of ten alkyl and fluoroalkyl iodides on the Pd(111) surface. This has been done by adsorbing the iodides as molecules at low temperature and then using the I $3d_{5/2}$ X-ray photoemission signal to follow the extent of reaction during heating. These kinetics measurements have enabled us to estimate $\Delta E^{\ddagger}_{C-I}$ and then to correlate $\Delta E^{\ddagger}_{C-I}$ with the substituent constants of the groups attached to the C–I bond. This has revealed, as in the case of C–Cl cleavage on the Pd(111) surface (6, 7), that $\Delta E^{\ddagger}_{C-I}$ is insensitive to the nature of the substituents. The implication of this observation will be that the transition state to C–I cleavage occurs early in the reaction coordinate and is reactant-like.

2. EXPERIMENTAL

The experiments described in this paper were performed in an ultra-high vacuum chamber evacuated with a cryopump to a base pressure below 10^{-10} Torr. This apparatus was equipped with instrumentation for surface cleaning by Ar^+ ion sputtering and surface analysis using X-ray photoemission spectroscopy (XPS). In addition a quadrupole mass spectrometer was used for measurements of desorption kinetics and analysis of background gases. Several standard leak valves were mounted on the chamber for introduction of gases and vapors of the alkyl and fluoroalkyl iodides used in the course of this work.

The Pd(111) sample was purchased commercially and mounted in the UHV chamber on a manipulator that allowed resistive heating to temperatures over 1300 K and cooling to about 90 K. Cleaning of the Pd(111) surface was achieved using cycles of Ar^+ ion sputtering and annealing to 1000 K. This was sufficient to produce a clean surface as determined using XPS. The alkyl and

fluoralkyl iodides used in this work were purchased commercially from Aldrich Chemical Co. and Lancaster Chemical Co. The liquids were all purified by cycles of freeze-pump-thawing before use. The purity of gases introduced into the vacuum chamber was checked using the mass spectrometer.

The kinetics of C–I cleavage in iodides adsorbed on the Pd(111) surface were monitored by obtaining a series of I $3d_{5/2}$ X-ray photoemission (XP) spectra during heating of the sample surface from 90 to ~250 K at a heating rate of 0.2 K/s. Monitoring the reaction kinetics is possible because there is a significant difference in the binding energies ($\Delta E_b \approx 1$ eV) of the I $3d_{5/2}$ core level between the alkyl iodides and the atomic iodine deposited onto the Pd(111) surface as a result of C–I bond dissociation. The spectra were obtained with an 800-W Al K_α source and a VG CLAM II hemispherical analyzer operating at a pass energy of 50 eV. A number of criteria went into the choice of the conditions used for the experiments. The resolution of the spectra had to be sufficient to resolve the ~1 eV binding energy difference between the reactant iodides and the product iodine atoms. In addition the total time of the X-ray exposure to the surface had to be kept below the level at which the X rays caused significant damage or dissociation of the iodide. Finally, the time between spectra had to be kept as short as possible to allow sufficient time or temperature resolution over the course of the experiment. The conditions selected allowed collection of I $3d_{5/2}$ spectra in the energy range of 615–625 eV with 0.1 eV/point resolution and 0.2 s dwell time on each point. The total time used to obtain each spectrum was 20 s, which then allowed roughly 50 spectra to be obtained over the temperature range of 90–250 K.

In an experiment in which XPS is used to determine the rate of a surface reaction it is critical to ascertain that the X-rays are not influencing the reaction rate. This was determined by adsorbing a monolayer of CH_3CH_2I onto the Pd(111) surface at 90 K and exposing it to a continuous flux of X-rays. By monitoring the appearance of atomic iodine on the surface it was possible to determine the relative rates of the X-ray induced C–I cleavage versus thermally induced C–I cleavage. Over the period of time normally used for one of our kinetics experiments (800 s) we found that less than 5% of the dissociation of C–I bonds could be attributed to X-ray effects.

The coverages used in this work are all given in terms of the maximum or monolayer coverage of the alkyl and fluoroalkyl iodides that, once adsorbed at low temperature, dissociate during heating to leave $I_{(ad)}$ on the surface. The absolute coverages of the saturated monolayer (ML^{sat}) vary slightly among the alkyl iodides. Using XPS one can calibrate these coverages and all are of the order of 0.2 monolayers with respect to the density of Pd atoms in the Pd(111) surface.

3. RESULTS

To illustrate the experiment, the cleavage of C–I bonds on the Pd(111) surface will be described in detail for the cases of CH_3CH_2I and CH_3I. The description of results will then be generalized to the full set of 10 alkyl iodides used in the course of this investigation.

3.1. C–I Cleavage in CH_3CH_2I on Pd(111)

The extent of C–I dissociation in CH_3CH_2I on the Pd(111) surface was measured by examining the I $3d_{5/2}$ core-level photoemission spectra. The kinetics of dissociation were measured by first adsorbing the CH_3CH_2I at 90 K where the C–I bond remains intact and then heating the surface while obtaining a series of X-ray photoemission spectra to monitor the evolution of the I $3d_{5/2}$ spectrum as the C–I bond breaks. These spectra will be used to determine the coverages of $I_{(ad)}$ and $CH_3CH_2I_{(ad)}$ on the surface and thus the extent of reaction as a function of temperature during constant rate heating.

As on the Pd(100) surface CH_3CH_2I adsorbs molecularly on the Pd(111) surface at 90 K (16, 19). The I $3d_{5/2}$ X-ray photoemission spectrum for $CH_3CH_2I_{(ad)}$ on Pd(111) at 90 K is shown in Fig. 1 and is a single peak centered at 620.0 eV corresponding to photoemission from I in $CH_3CH_2I_{(ad)}$. Figure 1 also shows a series of I $3d_{5/2}$ spectra

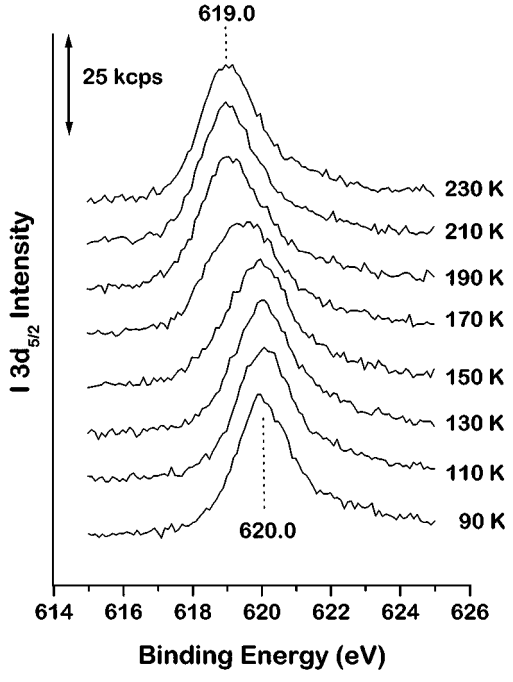

FIG. 1. X-ray photoemission spectra of the I $3d_{5/2}$ peak during heating of $CH_3CH_2I_{(ad)}$ on the Pd(111) surface from $T = 90$ to 230 K at 0.2 K/s. The I $3d_{5/2}$ binding energy for iodine in the $CH_3CH_2I_{(ad)}$ is 620.0 eV and for $I_{(ad)}$ on the Pd(111) surface is 619.0 eV. The continuous conversion from $CH_3CH_2I_{(ad)}$ to $I_{(ad)}$ is apparent.

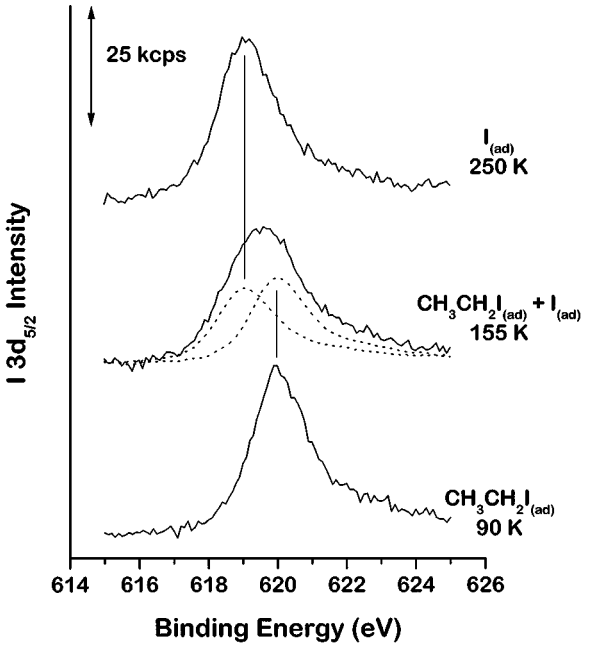

FIG. 2. X-ray photoemission spectra of the I $3d_{5/2}$ region for $CH_3CH_2I_{(ad)}$ on the Pd(111) surface at 90 K and following annealing to 155 and 250 K. The spectrum at 90 K is due to I in $CH_3CH_2I_{(ad)}$, whereas the spectrum at 250 K is due purely to $I_{(ad)}$. The spectrum at 155 K is a due to a combination of both $CH_3CH_2I_{(ad)}$ and $I_{(ad)}$. Dashed lines show the decomposition of the 155 K spectrum into the two components from $I_{(ad)}$ and $CH_3CH_2I_{(ad)}$. The magnitude of the component spectra are determined through the use of factor analysis.

taken at 20 K intervals during heating of the surface from 90 to 230 K at a rate of 0.2 K/s. As the temperature increases the peak broadens and shifts to lower binding energy. The total area under the spectra does not change indicating that there is no net loss of iodine from the surface during the course of heating. At 230 K the peak is narrow again but has shifted to 619.0 eV binding energy and corresponds to photoemission from $I_{(ad)}$ on the Pd(111) surface.

The I $3d_{5/2}$ spectra obtained at temperatures in the range of 90–230 K from $CH_3CH_2I_{(ad)}$ on the Pd(111) surface can be decomposed into two components attributable to $I_{(ad)}$ and $CH_3CH_2I_{(ad)}$. This is illustrated in Fig. 2, which shows the pure $CH_3CH_2I_{(ad)}$ and $I_{(ad)}$ spectra obtained at 90 and 250 K and a decomposition of the spectrum taken at 155 K into these two component spectra. The decomposition was done using factor analysis with the pure $I_{(ad)}$ and $CH_3CH_2I_{(ad)}$ spectra as the basis for decomposition of the spectrum obtained at 155 K. The factor analysis method has been described in detail elsewhere (20). This method has been used to decompose all the spectra taken in the temperature range of 90–280 K and thus to obtain the coverages of $I_{(ad)}$ and $CH_3CH_2I_{(ad)}$ as a function of temperature as shown in Fig. 3. As expected at low temperature the surface is covered purely with $CH_3CH_2I_{(ad)}$, which converts completely into $I_{(ad)}$ by the time the temperature has reached 200 K. The curves illustrated in Fig. 3 give the extent of reaction as a function of temperature and can be used to estimate the value of $\Delta E^{\ddagger}_{C-I}$. By fitting the data with a sigmoidal Boltzmann function as illustrated with the solid curves it is possible to estimate the temperature of maximum rate, T_{max}, from the temperature of the inflection point in $\theta_I(T)$:

$$\theta(T) = \frac{\theta(T_0) - \theta(T_f)}{1 + e^{(T - T_{max})/\Delta T}} + \theta(T_f).$$

The Boltzmann function is a simple sigmoidal function that can reproduce the shape of the $\theta_I(T)$ curves quite well and thus provide a consistent method for determining T_{max}. The important parameters in the function are the initial temperature (T_0), the final temperature (T_f), and the width of the temperature region over which the reaction occurs (ΔT). Using an analysis similar to the Redhead analysis for a first-order desorption process it is possible to relate T_{max} to $\Delta E^{\ddagger}_{C-I}$ through the expression

$$\frac{\Delta E^{\ddagger}_{C-I}}{R \cdot T^2_{max}} = \frac{\nu}{\beta} \cdot e^{-\Delta E^{\ddagger}_{C-I}/R \cdot T_{max}}.$$

The $\theta_I(T)$ curve illustrated in Fig. 3 comes from an initial $CH_3CH_2I_{(ad)}$ coverage of 0.5 ML^{sat} and has a $T_{max} = 151$ K.

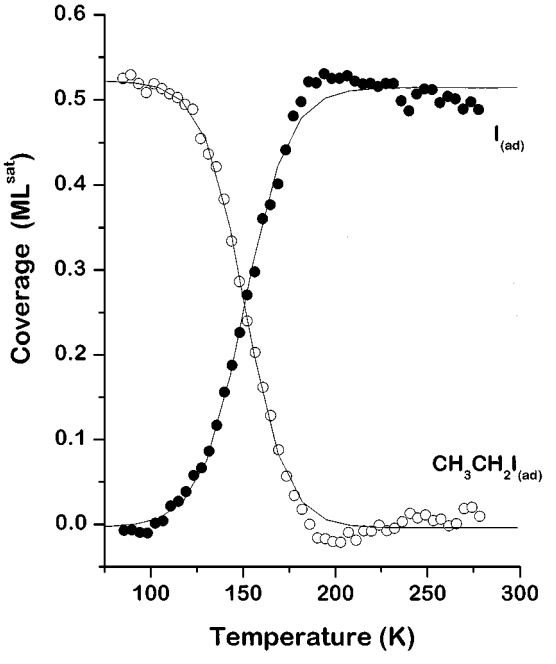

FIG. 3. Coverages of $I_{(ad)}$ (●) and $CH_3CH_2I_{(ad)}$ (○) as a function of temperature during heating of CH_3CH_2I on the Pd(111) surface from 90 to 280 K at 0.2 K/s. Initially all the iodine is present in the form of $CH_3CH_2I_{(ad)}$ with an I $3d_{5/2}$ binding energy of 620.0 eV. During heating the C–I bonds break depositing $I_{(ad)}$ on the Ag(111) surface with an I $3d_{5/2}$ binding energy of 619.0 eV. The total amount of iodine on the surface is conserved. Solid curves represent fits of the data using a Boltzmann function. The inflection points in the fitted curves are used to estimate the temperature (T_{max}) of the maximum C–I bond dissociation rate.

Using the Redhead equation and an assumption of $\nu = 10^{13}$ s^{-1} yields an estimate of $\Delta E^{\ddagger}_{C-I} = 41$ kJ/mol.

One of the points that is immediately clear from the data in Fig. 3 is that the C–I bond is breaking in $CH_3CH_2I_{(ad)}$ and is occurring over quite a broad temperature range. The fit to the Boltzmann function suggests that the width of the decomposition process is $2\Delta T = 22$ K. For a process having a barrier of 41 kJ/mol and a preexponent of 10^{13} s^{-1}, the temperature range over which one might expect the process to occur is $2\Delta T = 6$ K. Fitting the sigmoidal curve by allowing both $\Delta E^{\ddagger}_{C-I}$ and ν to vary yields physically unreasonable values of $\Delta E^{\ddagger}_{C-I} = 9.5$ kJ/mol and $\nu = 10^2$ s^{-1}. An alternate explanation for the width of the temperature range over which the C–I dissociation occurs is that the $\Delta E^{\ddagger}_{C-I}$ depends on the extent of reaction. In our previous study of the dissociation of C–I bonds on the Ag(111) surface, we found that $\Delta E^{\ddagger}_{C-I}$ was independent of the initial coverage of $CH_3CH_2I_{(ad)}$ but did depend on the coverage of $I_{(ad)}$ and thus varied during the course of the reaction. On the Pd(111) surface we have measured the kinetics of C–I bond dissociation during heating using a range of initial coverages of $CH_3CH_2I_{(ad)}$. The $I_{(ad)}$ deposition curves and the fits to the Boltzmann function are shown in Fig. 4 and clearly reveal that T_{max} depends on the initial coverage of $CH_3CH_2I_{(ad)}$. It is interesting to note that this was not the case on the Ag(111) surface. The dependence of T_{max} on the initial coverage of $CH_3CH_2I_{(ad)}$ indicates that $\Delta E^{\ddagger}_{C-I}$ increases with the extent of reaction suggesting that this is the reason for the broad temperature range over which the C–I dissociation occurs. Figure 5 illustrates the dependence of $\Delta E^{\ddagger}_{C-I}$ on the initial coverage of $CH_3CH_2I_{(ad)}$. The coverage dependence of $\Delta E^{\ddagger}_{C-I}$ has been fit to a linear form:

$$\Delta E^{\ddagger}_{C-I} = [1 + \gamma \cdot \theta_{RI}] \cdot (\Delta E^{\ddagger}_{C-I})_0.$$

Using this expression the values of $\Delta E^{\ddagger}_{C-I}$ at coverages of zero and 1/2 ML^{sat} are $(\Delta E^{\ddagger}_{C-I})_0 = 29 \pm 2$ kJ/mol and $(\Delta E^{\ddagger}_{C-I})_{1/2} = 37 \pm 3$ kJ/mol, respectively.

For all the alkyl and fluoroalkyl iodides used in this study we have measured the value of T_{max} over a range of initial coverages. These have been used to estimate the value of $\Delta E^{\ddagger}_{C-I}$ as a function of initial coverage using a physically reasonable preexponent of $\nu = 10^{13}$ s^{-1}. We expect that since we are simply studying one elementary process, C–I cleavage on Pd(111), the values of ν for the different alkyl and fluoroalkyl iodides should be quite similar and, although there may be an error in our estimate of $\nu = 10^{13}$ s^{-1}, it will be systematic. This would introduce some systematic error into our estimates of $\Delta E^{\ddagger}_{C-I}$; however, since we are primarily interested in the relative values of the barriers among these reactants ($\Delta\Delta E^{\ddagger}_{C-I}$), small systematic errors arising from our choice of ν should not be problematic.

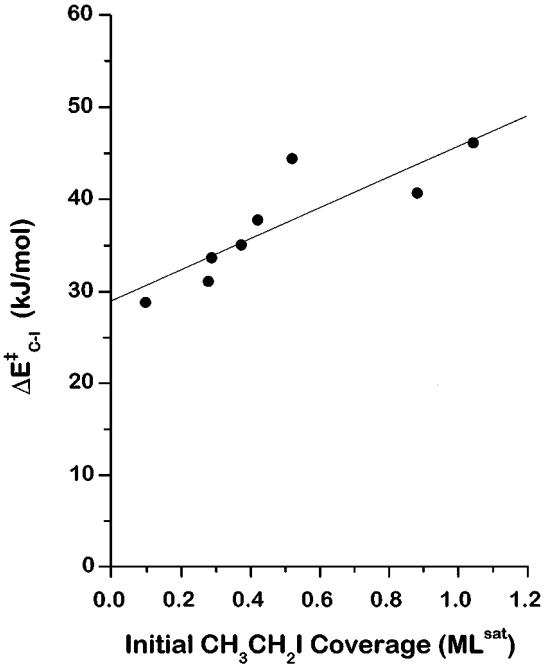

FIG. 5. The values of $\Delta E^{\ddagger}_{C-I}$ determined at different initial coverages of $CH_3CH_2I_{(ad)}$ on the Pd(111) surface. $\Delta E^{\ddagger}_{C-I}$ values were obtained from the Redhead equation using the values of T_{max} from the $\theta_I(T)$ curves obtained at different initial coverages. The coverage dependence of the $\Delta E^{\ddagger}_{C-I}$ has been fit with a straight line.

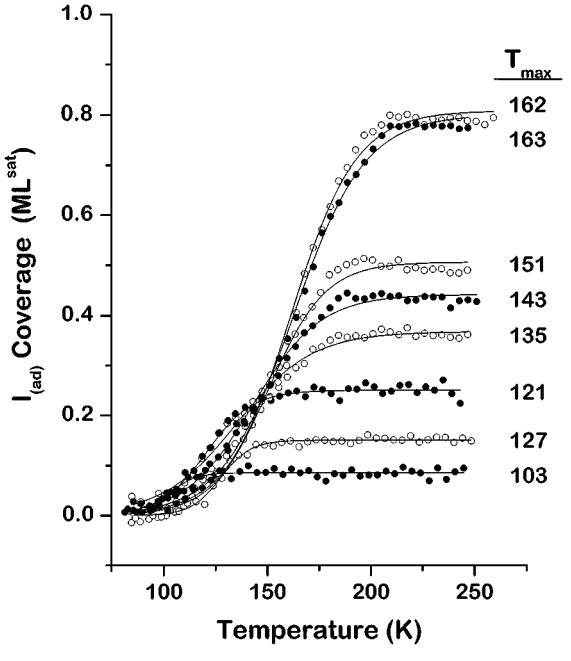

FIG. 4. Coverage of $I_{(ad)}$ as a function of temperature, $\theta_I(T)$, during heating of $CH_3CH_2I_{(ad)}$ on Pd(111) starting with several different initial $CH_3CH_2I_{(ad)}$ coverages. In all cases the $CH_3CH_2I_{(ad)}$ is completely converted to $I_{(ad)}$ during heating from 90 to 250 K. The temperature range and inflection points (T_{max}) of the $\theta_I(T)$ curves are dependent on the initial coverage of $CH_3CH_2I_{(ad)}$. Heating rate = 0.2 K/s.

3.2. C–I Cleavage in CH_3I on Pd(111)

Analysis of the C–I dissociation process on the Pd(111) surface is slightly complicated in some molecules by the fact that some of the C–I bonds are dissociated at the lowest adsorption temperature that can be reached. This is the case for CH_3I in our study. Low-temperature dissociation of the C–I bond was previously reported for CH_3I adsorbed on the Pd(100) surface although in the previous study of its adsorption on the Pd(111) surface dissociation was not reported until the temperature reached 150 K (15–18). Figure 6 illustrates the I $3d_{5/2}$ XP spectra obtained following adsorption of CH_3I on the Pd(111) surface at 90 K and during subsequent heating to 150 K. The four spectra in the temperature range of 90–150 K can all be fit using two peaks: one centered at 620.1 eV due to $CH_3I_{(ad)}$ and the other at 618.8 eV due to $I_{(ad)}$. It is fairly clear that the spectrum obtained at 90 K contains components from both species indicating that some dissociation of the C–I bond has occurred in CH_3I on adsorption. To obtain an XP spectrum of the I $3d_{5/2}$ level in $CH_3I_{(ad)}$ without contributions from $I_{(ad)}$ we have adsorbed a thick multilayer of CH_3I at low temperature and obtained the spectrum shown at the bottom of Fig. 6. This spectrum

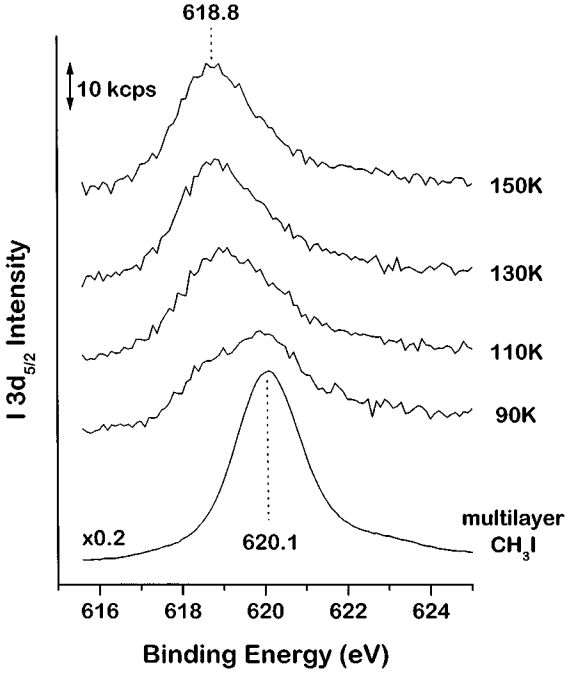

FIG. 6. X-ray photoemission spectra of the I $3d_{5/2}$ peak during heating of CH_3I on the Pd(111) surface from $T = 90$ to 150 K at 0.2 K/s. The peak position for iodine in $CH_3I_{(ad)}$ is at a binding energy of 620.1 eV. For $I_{(ad)}$ on the Pd(111) surface the binding energy is 618.8 eV. The width of the I $3d_{5/2}$ peak at 90 K indicates that some of the $CH_3I_{(ad)}$ has dissociated to produce $I_{(ad)}$ on adsorption. The continuous conversion from $CH_3I_{(ad)}$ to $I_{(ad)}$ is apparent as the surface is heated at a constant rate. The $CH_3I_{(ad)}$ multilayer spectrum shown at the bottom of the figure was used as the basis spectrum for CH_3I in the factor analysis.

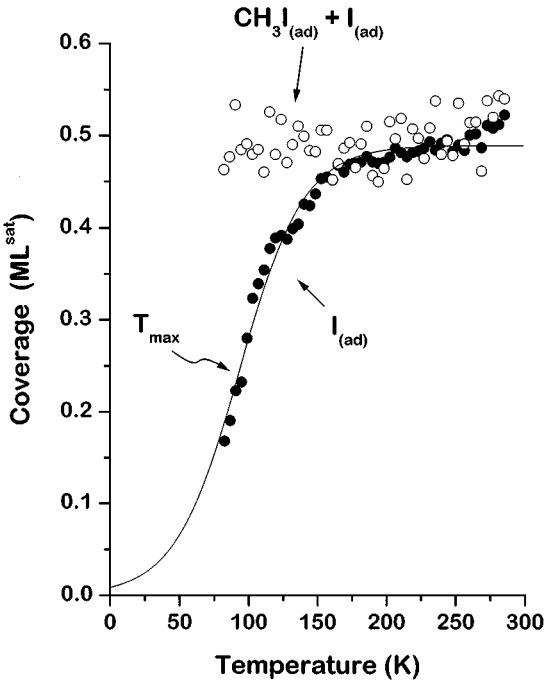

FIG. 7. Coverages of $I_{(ad)}$ (●) and total iodine ($CH_3I_{(ad)} + I_{(ad)}$; ○) as a function of temperature during heating of $CH_3I_{(ad)}$ on the Pd(111) surface from 90 to 280 K at 0.2 K/s. Initially (90 K) most of the iodine is present in the form of $CH_3I_{(ad)}$ (I $3d_{5/2}$ binding energy of 620.1 eV); however, some dissociation has occurred at 90 K. During heating the C–I bonds break depositing $I_{(ad)}$ on the Pd(111) surface (I $3d_{5/2}$ binding energy of 618.8 eV). Total iodine coverage on the surface does not change during heating.

and the spectrum of $I_{(ad)}$ obtained at high temperature can then be used as the basis spectra for the factor analysis decomposition of the spectra at intermediate temperatures to obtain the coverages of $CH_3I_{(ad)}$ and $I_{(ad)}$.

The evolution of the $I_{(ad)}$ coverage during heating of CH_3I adsorbed on the Pd(111) surface can be followed by monitoring the growth of the $I_{(ad)}$ component of the I $3d_{5/2}$ spectra. This is depicted in Fig. 7, which shows the increase in the coverage of $I_{(ad)}$ during heating. Figure 7 also shows the total $CH_3I_{(ad)}$ plus $I_{(ad)}$ coverage on the surface during heating revealing that it remains constant. The data for the coverage of $I_{(ad)}$ has been fit with a sigmoidal Boltzmann curve to estimate the temperature of the maximum dissociation rate. In this case since the coverage at 90 K is nonzero the fit has been obtained by setting $\theta_I = 0$ in the limit of low temperature. This essentially extrapolates the curve to temperatures below 90 K at which the C–I bond would not have dissociated.

3.3. C–I Dissociation in Alkyl and Fluoroalkyl Iodides on Pd(111)

The dissociation of C–I bonds has been studied in a set of 10 substituted alkyl and fluoroalkyl iodides on the Pd(111)

TABLE 1

For All the Alkyl and Fluoroalkyl Iodides on Pd(111)

Molecule	T_{max} (K)	γ $(ML^{sat})^{-1}$	$(\Delta E^{\ddagger}_{C-I})_0$ (kJ/mol)	$(\Delta E^{\ddagger}_{C-I})_{1/2}$ (kJ/mol)
CH_3I	111	1.93	15.3 ± 4.8	30.1 ± 6.3
CH_3CH_2I	134	0.54	29.0 ± 2.3	36.8 ± 2.9
$CH_3CH_2CH_2I$	134	1.52	20.9 ± 5.3	36.8 ± 6.7
$(CH_3)_2CHI$	115	1.43	18.3 ± 3.7	31.4 ± 4.6
$(CH_3)_3CI$	106	1.04	19.0 ± 2.0	28.9 ± 2.1
$CF_3CH_2CH_2I$	151	0.99	27.7 ± 1.8	41.4 ± 2.9
CF_3CH_2I	138	1.17	23.8 ± 2.8	37.7 ± 3.8
$CF_3CF_2CH_2I$	152	0.80	29.9 ± 0.8	41.8 ± 1.3
CF_2HCF_2I	115	1.06	20.5 ± 2.0	31.4 ± 2.1
CF_3I	111	0.87	21.0 ± 1.0	30.1 ± 1.3

Note. T_{max} = the temperature of maximum dissociation rate at 0.5 ML^{sat} coverage, $(\Delta E^{\ddagger}_{C-I})_0$ = the barrier to dissociation in the limit of zero coverage, $(\Delta E^{\ddagger}_{C-I})_{1/2}$ = the barrier to dissociation at 1/2 ML^{sat}, and γ = the coverage dependence of $\Delta E^{\ddagger}_{C-I}$. All the values presented in this table are based on fitting $\Delta E^{\ddagger}_{C-I}$ at several different initial coverages of $R_3Cl_{(ad)}$ (θ_{RI}) to the equation

$$\Delta E^{\ddagger}_{C-I} = [1 + \gamma \cdot \theta_{RI}] \cdot (\Delta E^{\ddagger}_{C-I})_0$$

for each molecule. θ_{RCI} is expressed in terms of fraction of ML^{sat}.

surface. The complete list of iodides and their substituents is given in Tables 1 and 2. The substituents have been chosen to give a wide range of field substituent constants (σ_F). In all cases the dissociation of the C–I bond has been measured by monitoring the I $3d_{5/2}$ spectrum during heating of the iodides on the Pd(111) surface. This has been done using a range of initial alkyl iodide coverages to explore the coverage dependence of the dissociation kinetics. Factor analysis was used to decompose the spectra into their components to obtain the coverages of $I_{(ad)}$ and alkyl iodide as functions of temperature: $\theta_I(T)$ and $\theta_{R-I}(T)$. For the cases in which some of the alkyl iodide dissociated at the adsorption temperature, the pure component XP spectrum was obtained by adsorbing multilayers of the alkyl iodide.

The extent of reaction during alkyl iodide dissociation is depicted for all 10 iodides in Fig. 8. This shows the evolution of $\theta_I(T)$ during heating of the iodides on the Pd(111) surface. In all cases the starting coverage was roughly 1/2 ML^{sat}. To make visualization of the data easier the final coverages have all been normalized to exactly 1/2 ML^{sat}. In all cases the inflection points have been estimated by fitting the $\theta_I(T)$ curves with sigmoidal Boltzmann functions. Clearly the different substituents on the iodides influence the kinetics of C–I cleavage although the range of temperatures over which the inflection points occur is not large. The temperatures of the inflection points (T_{max}) for coverages of 1/2 ML^{sat} have been listed in Table 1 for each of the iodides. T_{max} has been determined at varying initial coverages of the alkyl iodides and the inflection points have then been used to estimate $\Delta E^{\ddagger}_{C-I}$. The values of $\Delta E^{\ddagger}_{C-I}$ as a function of initial iodide coverage are all plotted in Fig. 9 and have been fit with linear expressions to obtain $(\Delta E^{\ddagger}_{C-I})_0$, the barrier in the limit of low coverage, and γ, the coverage dependence of the barrier. These are listed in Table 1 for all of the iodides.

4. DISCUSSION

4.1. The Transition State for C–I Cleavage on Pd(111)

The transition state for cleavage of C–I bonds on the Pd(111) surface can be probed by examining the effects of substituents with know properties on the value of $\Delta E^{\ddagger}_{C-I}$. As illustrated in Fig. 8 the substituents clearly influence $\Delta E^{\ddagger}_{C-I}$. They have been chosen to have a wide range of field effect substituent constants (σ_F) as listed in Table 2. The field effect is an empirical measure of the interaction of the electrostatic field of the substituent with the change in charge that develops at the reaction center in the transition state (14, 21, 22). For example, if the reaction center in the transition state is anionic with respect to the initial state

TABLE 2

The Field Substituent Constants (σ_F) for All the Alkyl and Fluoroalkyl Iodides

Molecule	Substituents	Field constant (σ_F)	$\Sigma\sigma_F$
CH_3I	H	0.0	0.0
	H	0.0	
	H	0.0	
CH_3CH_2I	CH_3	0.0	0.0
	H	0.0	
	H	0.0	
$CH_3CH_2CH_2I$	CH_3CH_2	0.0	0.0
	H	0.0	
	H	0.0	
$(CH_3)_2CHI$	CH_3	0.0	0.0
	CH_3	0.0	
	H	0.0	
$(CH_3)_3CI$	CH_3	0.0	0.0
	CH_3	0.0	
	CH_3	0.0	
$CF_3CH_2CH_2I$	CF_3CH_2	0.23	0.23
	H	0.0	
	H	0.0	
CF_3CH_2I	CF_3	0.44	0.44
	H	0.0	
	H	0.0	
$CF_3CF_2CH_2I$	CF_3CF_2	(0.51)[a]	0.51
	H	0.0	
	H	0.0	
CF_2HCF_2I	CF_2H	0.36	1.24
	F	0.44	
	F	0.44	
CF_3I	F	0.44	1.32
	F	0.44	
	F	0.44	

[a] The value of σ_F for CF_3CF_2 is estimated from the F value reported in Table I of Hansch *et al.* (14) and adding 0.07 to place it on the same scale as σ_F for other similar substituents (CH_2F, CHF_2, CF_3, and CH_2CF_3).

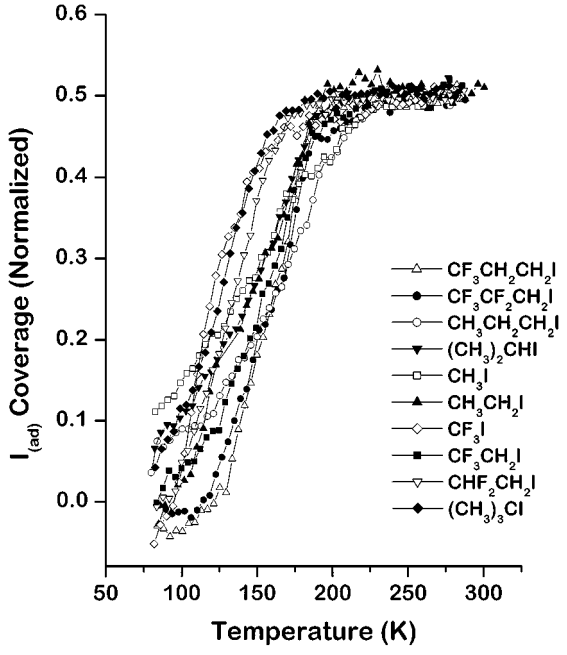

FIG. 8. Coverage of $I_{(ad)}$ versus temperature during dissociation of 10 alkyl and fluoroalkyl iodides on the Pd(111) surface. The initial coverages are all roughly 0.5 ML^{sat}; however, the $I_{(ad)}$ signals have all been normalized to the same value of exactly 0.5 to better visualize the data. Clearly the substitutions of the alkyl groups influence the C–I dissociation kinetics. The barriers to C–I cleavage ($\Delta E^{\ddagger}_{C-I}$) have been estimated by determining the inflection point, T_{max}, in the $\theta_I(T)$ curves. Heating rate = 0.2 K/s.

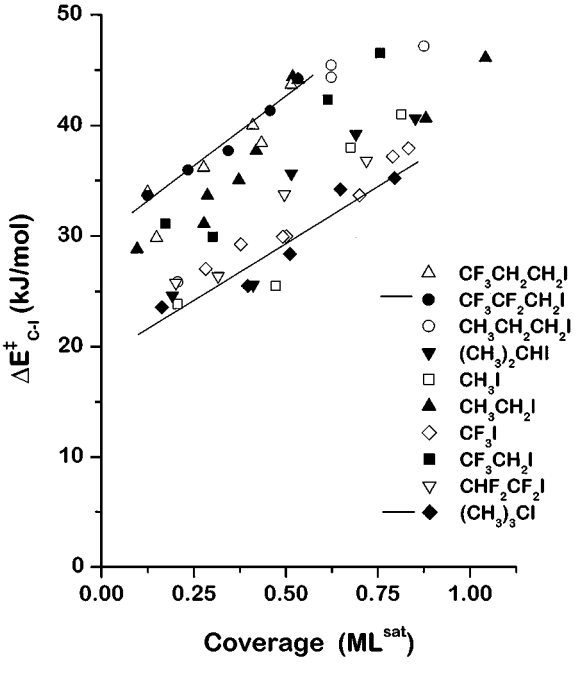

FIG. 9. The activation energy for C–I cleavage ($\Delta E^{\ddagger}_{C-I}$) on the Pd(111) surface for alkyl and fluoroalkyl iodides at various initial coverages. Data for each species have been fit with a line and indicate that the $\Delta E^{\ddagger}_{C-I}$ grows with increasing initial coverage.

(RC–I $\leftrightarrow$ $[RC^{\delta-\cdots}I]^{\ddagger}$) then increasing the field substituent constant will lower the value of $\Delta E^{\ddagger}_{C-I}$. Plotting the values of $\Delta E^{\ddagger}_{C-I}$ against σ_F can yield good correlations, which yield insight into the nature of the transition state for an elementary process.

Since the value of $\Delta E^{\ddagger}_{C-I}$ depends on the initial coverage of the alkyl iodide we have plotted two correlations of the field substituent constants with the alkyl groups. The substituent constants for each of the alkyl iodides are given in Table 2. Figure 10 shows the correlations of $(\Delta E^{\ddagger}_{C-I})_0$ and $(\Delta E^{\ddagger}_{C-I})_{1/2}$ with the substituent constants. The slopes of the correlations indicate that the reaction constant, ρ_F, for C–I cleavage on the Pd(111) surface is not significantly different from zero. This result is identical to that obtained in a previous study of C–Cl cleavage in various 1,1-dichloroethanes on the Pd(111) surface (6, 7). It also corroborates the results of a study of C–I cleavage on the Ag(111) surface. That work yielded a value of $\rho_F = -17 \pm 1$ kJ/mol, which although it is nonzero, is quite small on the scale of values can be observed for reaction constants on surfaces or in the gas phase (13, 14, 21).

On the Ag(111) surface the correlations of reaction barriers and substituent constants were substantially better than

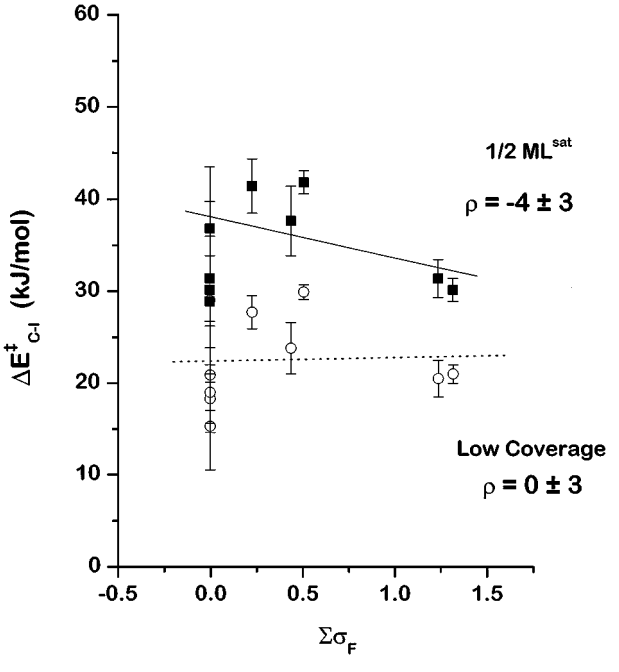

FIG. 10. Correlation of $\Delta E^{\ddagger}_{C-I}$ with the field substituent constants for the alkyl and fluoroalkyl iodides on Pd(111). These are $(\Delta E^{\ddagger}_{C-I})_{1/2}$ measured for initial alkyl iodide coverages of 1/2 ML^{sat} and $(\Delta E^{\ddagger}_{C-I})_0$ measured in the limit of low iniial alkyl iodide coverages. The reaction constant given by the slope of the correlation is $\rho = -4 \pm 3$ kJ/mol at an initial coverage of 1/2 ML^{sat} and $\rho = 0 \pm 3$ kJ/mol in the limit of low initial coverage. The fact that these are $\sim$0 suggests that the transition state for C–I cleavage is homolytic and occurs early in the reaction coordinate.

those observed on the Pd(111) surface. In that case it was possible to correlate $\Delta E^{\ddagger}_{\mathrm{C-I}}$ with both the field (σ_F) and the polarizability (σ_α) substituent constants simultaneously. One of the possible reasons for the superior quality of the data on the Ag(111) surface is that for most of the reactant alkyl iodides the alkyl groups produced by C–I cleavage remained on the surface during the course of the reaction and did not desorb or react until temperatures at which all of the C–I bonds had dissociated. In contrast, the surface chemistry on the Pd(111) surface was more complex and it is certainly the case that some of the alkyl fragments generated on the surface during C–I cleavage reacted by secondary steps in the temperature range over which the C–I cleavage was occurring. These secondary reactions undoubtedly complicated the surface environment in which the C–I cleavage was occurring. Another difference between the reactions on the Ag(111) and Pd(111) surfaces is the fact that on the Pd(111) surface $\Delta E^{\ddagger}_{\mathrm{C-I}}$ appears to depend on the initial coverage of the alkyl iodide. On the Ag(111) surface $\Delta E^{\ddagger}_{\mathrm{C-I}}$ was independent of the initial coverage of alkyl iodide although it did appear to depend on the coverage of $\mathrm{I}_{(\mathrm{ad})}$ which was, of course, increasing during the course of the reaction. Although these differences can certainly account for the differences in the quality of the correlations of $\Delta E^{\ddagger}_{\mathrm{C-I}}$ with σ_F the details are not clear at this point.

The reaction constants for C–I cleavage on the Pd(111) surface and for other metal catalyzed carbon–halogen dissociation reactions are all quite low by comparison with those observed for other reactions on surfaces and in the gas phase. For gas-phase reactions involving ionic species, such as those that occur in proton transfer equilibria, reaction constants can be in the range of $\rho = 100$–200 kJ/mol (14, 21). For reactions such as β-hydrogen elimination that has been studied in some depth on the Cu(111) surface the reaction constant can be as high as 150 kJ/mol (13). These results suggest that reactions involving substantial change in charge at the reaction center can exhibit very large substituent effects. The implication in the case of the dehalogenation reactions on Pd(111) and Ag(111) surfaces is that there is little difference in charge on the reaction center between the alkyl halide reactant and the transition state to carbon–halogen bond cleavage. In this sense the transition state would appear to be reactant-like and hence can be thought of as occurring early in the reaction coordinate. This is depicted in the schematic of Fig. 11, which shows the transition state occurring early in the process of C–I bond cleavage.

The results presented in this work have shown that the substituent effects on C–I cleavage have little or no influence on the energetics of the transition state with respect to the initial state. This is consistent with an early transition state that is reactant-like. Ideally one would demonstrate this by comparing substituent effects on the reaction

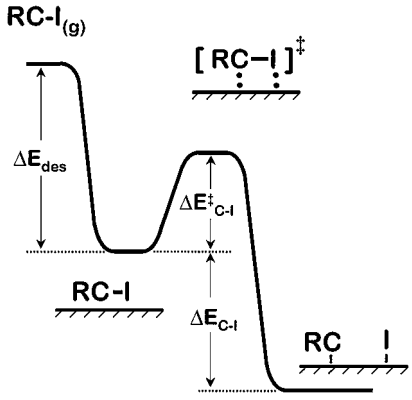

FIG. 11. Potential energy surface for C–I bond cleavage on the Pd(111) surface. The fact that the desorption energy is greater than the barrier to C–I cleavage ($\Delta^{\ddagger}E_{\mathrm{C-I}} > \Delta E_{\mathrm{des}}$) means that the alkyl iodides dissociate during heating rather than desorb. The reaction is exothermic with an early transition state that is homolytic and reactant-like.

barrier, $\Delta E^{\ddagger}_{\mathrm{C-I}}$, with the substituent effects on the overall reaction energy to dissociate the alkyl iodides on the Pd(111) surface. Unfortunately, the reaction energetics are not known. If the alkyl group products of the dissociation are anionic with respect to the alkyl group in the alkyl iodide, then one might expect that fluorine substitution would effect the reaction energetics. If the transition state were late, then $\Delta E^{\ddagger}_{\mathrm{C-I}}$ would also be influenced by fluorine substitution. The fact that this is not observed is consistent with an early transition state and is consistent with the conclusions reached based on Hammond's postulate, as discussed below.

Hammond's postulate suggests that for an exothermic reaction the transition state occurs early in the reaction coordinate (12). To see whether our conclusions regarding the transition state for C–I cleavage on the Pd(111) surface are consistent with this idea it is necessary to determine whether or not C–I cleavage is exothermic. This can be done by using the following Born–Haber cycle:

1)	$\mathrm{CH_3I_{(g)}} \rightarrow \cdot\mathrm{CH_{3,(g)}} + \cdot\mathrm{I_{(g)}}$	234 ± 5 kJ/mol
2)	$\cdot\mathrm{CH_{3,(g)}} \rightarrow \mathrm{CH_{3,(ad)}}$	-138 ± 25 kJ/mol
3)	$\cdot\mathrm{I_{(g)}} \rightarrow \mathrm{I_{(ad)}}$	-228 ± 30 kJ/mol
4)	$\mathrm{CH_3I_{(ad)}} \rightarrow \mathrm{CH_3I_{(g)}}$	39 ± 10 kJ/mol
5)	$\mathrm{CH_3I_{(ad)}} \rightarrow \mathrm{CH_{3,(ad)}} + \mathrm{I_{(ad)}}$	$\Delta E_{\mathrm{C-I}}$ kJ/mol.

Step 1 is the C–I bond energy in $\mathrm{CH_3I}$, which is known to a high degree of accuracy (23). The second step is the C–metal bond strength, which has been measured on the Cu(100) surface but has also been shown to be similar on other metal surfaces (24). The adsorption energy for iodine (step 3) has been estimated from the desorption energy for iodine from the Pd(111) surface. This has been determined from the observed desorption temperature of $T_p = 850$ K

at a heating rate of 2.5 K/s and the assumption that the process is first-order with a preexponent of 10^{13} s^{-1}. The value of the error bars is estimated by assuming that the preexponent might vary by as much as 10^{11} to 10^{15} s^{-1}. Since it is not known whether iodine desorbs in the form of I atoms, I_2, or PdI this value of the desorption energy represents a lower limit on the real value. Finally step 4 represents the desorption of CH_3I from the surface. At high coverages on the Pd(111) surface this has been observed to occur at 150 K (15). Using an estimate that the desorption preexponential factor lies in the range of 10^{11}–10^{15} s^{-1} yields the range of the desorption energy listed previously. Using the cycle presented herein, we estimate that the energy for dissociation of the C–I bond in CH_3I groups on the Pd(111) surface is $\Delta E_{C-I} = -93 \pm 40$ kJ/mol. Thus the fact that the reaction is exothermic, combined with Hammond's postulate suggests that the transition state for C–I cleavage on the Pd(111) surface occurs early in the reaction coordinate. This, of course, is consistent with our conclusion based on the use of substituent effects and the fact that the reaction constant is $\rho = 0$.

4.2. Implications for Dehalogenation Catalysis

The dissociation of C–Cl bonds on the Pd(111) surface was studied using a set of chlorofluorocarbons to determine a reaction constant (6, 7). As in the case of C–I dissociation on the Pd(111) surface the reaction constant was $\rho \sim 0$. There emerges a clear picture of a transition state for the dissociation of carbon–halogen bonds that is homolytic in the sense that it is reactant-like and involves very little charge change. In this sense the transition state probably occurs early in the reaction coordinate as would be predicted on the basis of Hammond's postulate and the fact that dehalogenation reactions on these metal surfaces are exothermic.

One of the consequences of a transition state that is early in the reaction coordinate and thus reactant-like is that changes in the nature of the catalyst will not have large influences on the barrier to that reaction step. For the cases of C–I and C–Cl bond breaking in alkyl iodides and chlorides on the Pd(111) surface the barrier $\Delta E^{\ddagger}_{C-X}$ is not influenced by the changes in the substituent on the reactant. Likewise, minor changes to the catalytic surface are not likely to have much effect on $\Delta E^{\ddagger}_{C-X}$ either. This is not to say that changes in a catalyst should not change the overall rate of a dehalogenation reaction such as hydrodechlorination, merely that the effects are not due to changes in rate for the carbon–halogen bond cleavage step. So, for example, in our previous study of CFC dechlorination on the Pd(111) surface we measured the apparent activation barrier for dechlorination as the difference between the intrinsic barrier to C–Cl cleavage ($\Delta E^{\ddagger}_{C-Cl}$) and the desorption energy (ΔE_{des}),

$$\Delta E^{\ddagger}_{app} = \Delta E^{\ddagger}_{C-Cl} - \Delta E_{des}.$$

Although changing the substituents on the CFC does not influence $\Delta E^{\ddagger}_{C-Cl}$ it does influence ΔE_{des} and thus $\Delta E^{\ddagger}_{app}$ to dechlorination. Similarly, on the basis of the ideas presented here, one might expect that the changes in activity of dechlorination catalysts brought about by changes or modifications to the catalyst surface should be due to changes in the barriers to steps other than the carbon–halogen bond cleavage step.

5. CONCLUSIONS

The measurement of the barriers to C–I bond cleavage in a set of 10 alkyl and fluoroalkyl iodides on the Pd(111) surface has revealed that the field substituent effects on the kinetics of C–I cleavage are negligible as quantified by a field reaction constant of $\rho = 0$. The implication of this observation is that the transition state for the cleavage of C–I bonds on the Pd(111) surface is reactant-like and occurs early in the reaction coordinate.

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