The Transition State for Metal-Catalyzed Dehalogenation: C−I Bond Cleavage on Ag(111)

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Abstract: The kinetics of C−I bond cleavage on the Ag(111) surface have been measured in a set of 10 alkyl and fluoroalkyl iodides. All the iodides adsorb molecularly on the Ag(111) surface at low temperatures and then dissociate during heating at temperatures below 200 K. X-ray photoemission spectroscopy was used to monitor the rate of C−I cleavage during heating. Estimation of the barrier to C−I cleavage ($\Delta E^{\ddagger}_{C-I}$) indicates that it is sensitive to the nature of the alkyl or fluoroalkyl substituent groups bonded to the α-carbon atom. The barriers can be correlated to the field and polarizability substituent constants (σ_F and σ_α) of the alkyl groups and reveal that the reaction constants for C−I cleavage are quite low ($\rho_F = -17 \pm 1$ kJ/mol and $\rho_\alpha = -11 \pm 2$ kJ/mol). This suggests that the transition state for C−I cleavage is slightly anionic with respect to the adsorbed iodide ($RC-I \rightarrow [RC^{\delta-}\cdots I]^{\ddagger}$) or, in other words, that the electron density on the carbon atom of the C−I bond is slightly greater in the transition state than in the reactant iodide. The magnitudes of the reaction constants, however, are relatively low. The implication is that the transition state to C−I cleavage is fairly homolytic in the sense that it occurs early in the reaction coordinate and is like the initial state iodide.

1. Introduction

Cleavage of carbon−halogen bonds on metal surfaces is an important elementary step in a number of chemical processes. One process which is of current interest and which has motivated this work is the catalytic hydrodechlorination of chlorofluorocarbons (CFCs).[1,2] A second is the dissociation of carbon−iodine bonds which is used to create stable alkyl groups on many metal surfaces.[3,4] The experiments described in this paper have been designed to reveal the characteristics of the transition state to C−I cleavage on the Ag(111) surface. They are part of a larger study which has provided a consistent picture of the nature of the transition state for carbon−iodine and carbon−chlorine bond cleavage on both Ag(111) and Pd(111) surfaces.[5−8]

Catalytic hydrodechlorination is used to convert chlorofluorocarbons (CFCs) into hydrofluorocarbons (HFCs).[1,2] The most commonly studied catalyst for hydrodechlorination of CFCs is Pd supported on C, Al_2O_3, or SiO_2. Although the mechanism is far from clearly understood, dechlorination or cleavage of C−Cl bonds must be an important elementary step in the process. There is some evidence that it is either rate limiting, or at least influences the overall reaction kinetics.[5,6,9−11] As such, an understanding of the nature of the transition state for the C−Cl cleavage step can provide valuable insight into catalytic hydrodechlorination kinetics that could be used to suggest directions for improvement of existing catalysts. Prior study of the cleavage of C−I bonds on the Pd(111) surface suggests that the transition state is homolytic in the sense that the electron distribution at the reaction center is not much different from that in the reactant.[5,6] In other words, the transition state probably occurs early in the reaction coordinate for C−Cl cleavage. To provide corroborating evidence for the nature of the transition state in C−Cl cleavage, we have performed similar studies of the intrinsic barrier to another dehalogenation reaction, the cleavage of C−I bonds in alkyl and fluoroalkyl iodides adsorbed on the Ag(111) and Pd(111) surfaces.

The cleavage of C−I bonds on metal surfaces is an important reaction in its own right since it has been used to produce stable hydrocarbon fragments on many metal surfaces.[3,4] In many investigations on metal surfaces, it has been observed that low-temperature adsorption of alkyl iodides followed by heating results in the dissociation of the C−I bond. Most studies report that this occurs at temperatures in the range 100−200 K to leave stable alkyl groups on the surface. For the most part, it is the hydrocarbon fragments that are the object of investigation. Although there have been many studies of alkyl iodides, the number of studies of fluoroalkyl iodides is very limited. In the work reported in this paper, it is the cleavage of the C−I bonds that is of interest since it falls into the general class of dehalogenation reactions. Unlike the previous studies of alkyl iodides on metal surfaces, this study has been focused on determination of the reaction energetics for the C−I cleavage step.

The Ag(111) surface is particularly good for our study of the kinetics of C−I cleavage because the chemistry of the product alkyl groups on Ag(111) surfaces is well documented.[12−20]

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In all cases, the C−I bond breaks at temperatures below 200 K. This produces alkyl and fluoroalkyl groups which react by coupling to form alkanes and fluoroalkanes which desorb from the surface. With the exception of ethyl and isopropyl coupling reactions which occur at ∼185 K, the alkyl coupling occurs at $T > 200$ K and thus does not influence the kinetics of the C−I cleavage reaction. The only species which do not couple on the Ag(111) surface are the fluoroalkyl groups with fluorine atoms in the β-position with respect to the surface. Those react by β-fluoride elimination at $T > 200$ K to form olefins.[19] The important point is that all reaction steps of the alkyl or fluoroalkyl fragments occur at temperatures above that of C−I cleavage so the kinetics of the C−I cleavage are not influenced by concurrent surface reactions.

In this work, the barrier to C−I cleavage ($\Delta E^{\ddagger}_{\mathrm{C-I}}$) has been measured in a set of 10 substituted alkyl and fluoroalkyl iodides. The substituents are the groups bonded to the α-C (H, F, CH_3, CF_3, etc.) and are not involved directly in the C−I cleavage reaction. The barriers to C−I cleavage have been correlated to the field and polarizability constants (σ_F and σ_α) of the substituents as defined in the literature,[21,22]

$$\Delta E^{\ddagger}_{\mathrm{C-I}} = \rho_F\sigma_F + \rho_\alpha\sigma_\alpha + \Delta E^{\ddagger}_{\mathrm{H_3C-I}} \tag{1}$$

Methyl iodide, CH_3I (in which all substituents are H atoms), is the reference compound for the correlation. Hydrogen is the reference substituent for both the field and polarizability substituent constants ($\sigma_F(\mathrm{H}) = 0$ and $\sigma_\alpha(\mathrm{H}) = 0$). The results will show that the reaction constants, ρ_F and ρ_α, are low. This has also been observed for C−I and C−Cl cleavage on Pd(111) surfaces and supports the general conclusion that the transition state occurs early in the reaction coordinate.[5−8]

2. Experimental Section

The experiments were performed in an ultrahigh-vacuum (UHV) surface science apparatus 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. 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 Ag(111) sample was purchased commercially and was 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 Ag(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 X-ray photoemission spectroscopy. 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 thermally programmed reaction spectra (TPRS) were obtained using a Dycor M200M quadrupole mass spectrometer. The sample was initially cooled to 90 K, following which adsorption was performed by positioning the Ag(111) surface roughly 1 cm from a capillary array doser attached to one of the leak valves. Exposures of the sample surface to the iodides were recorded in units of Langmuirs (10^{-6} Torr•s) measured using the ion gauge. These were not corrected for ion gauge sensitivity. The sample was heated at a rate of 2 K/s while monitoring the desorption of up to three m/q ratios with the mass spectrometer.

The kinetics of the C−I cleavage reaction in iodides adsorbed on the Ag(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 ($\Delta E_b \approx 2$ eV) of the I $3d_{5/2}$ core level between the alkyl iodides and the adsorbed atomic iodine deposited onto the Ag(111) surface as a result of C−I bond dissociation. The spectra were obtained with an 800 W Al Kα 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 2 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 615−625 eV with 0.1 eV/point resolution and 0.2 s dwell time per 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 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 Ag(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 iodine coverages reported in this paper were determined absolutely. Exposure of the Ag(111) surface to CH_3CH_2I at 300 K produces a saturated overlayer of iodine in a $(\sqrt{3} \times \sqrt{3})$R30° lattice at a coverage of one-third of a monolayer with respect to the Ag atoms in the Ag(111) surface. The ratio of the I $3d_{5/2}$ XPS signals for this overlayer to the Ag $3d_{5/2}$ signal for the clean Ag(111) surface was used to calibrate the coverage of iodine in all other experiments.

3. Results

During the course of this work, we have measured the kinetics of C−I bond cleavage in 10 different alkyl and fluoroalkyl iodides. The molecules studied are listed in Table 1. The following three sections provide detailed descriptions of the data obtained for three molecules (CH_3CH_2I, CH_3I, and CF_3I) before summarizing the results for the entire set.

3.1. C−I Bond Cleavage in CH_3CH_2I. The chemistry and reaction kinetics of CH_3CH_2I on the Ag(111) surface are typical of most of the molecules used in this investigation and will be described in some detail in this section. The kinetics of C−I bond cleavage in CH_3CH_2I were measured by first adsorbing CH_3CH_2I on the Ag(111) surface at 90 K and then obtaining I $3d_{5/2}$ XP spectra as a function of temperature during heating at a constant rate. At low temperature, CH_3CH_2I is adsorbed molecularly with the C−I bond intact, and the I $3d_{5/2}$ peak has a binding energy of 620.3 eV. Once the surface has been heated to 220 K, all C−I bonds are broken, and the iodine is adsorbed to the Ag(111) surface as atoms. As a result, the I $3d_{5/2}$ binding

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Table 1. List of the Alkyl and Fluoroalkyl Iodides Studied on Ag(111), Including the Field Substituent Constants ($\Sigma\sigma_F$), the Polarizability Substituent Constants ($\Sigma\sigma_\alpha$), the Temperature of Maximum Dissociation Rate (T_{max}), and the Barrier to Dissociation ($\Delta E^{\ddagger}_{C-I}$)

molecule	substituents	field constant (σ_F)	$\Sigma\sigma_F$	polarizability constant (σ_α)	$\Sigma\sigma_\alpha$	T_{max} (K)	$\Delta E^{\ddagger}_{C-I}$ (kJ/mol), Ag(111)
CH_3I	H	0.0	0.0	0.0	0.0	178	49 ± 3
	H	0.0		0.0			
	H	0.0		0.0			
CH_3CH_2I	CH_3	0.0	0.0	0.35	0.35	155	43 ± 2
	H	0.0		0.0			
	H	0.0		0.0			
$CH_3CH_2CH_2I$	CH_3CH_2	0.0	0.0	0.49	0.49	158	44 ± 2
	H	0.0		0.0			
	H	0.0		0.0			
$(CH_3)_2CHI$	CH_3	0.0	0.0	0.35	0.70	138	38 ± 2
	CH_3	0.0		0.35			
	H	0.0		0.0			
$CF_3CH_2CH_2I$	CF_3CH_2	0.23	0.23	0.23	0.23	143	39 ± 2
	H	0.0		0.0			
	H	0.0		0.0			
CF_3CH_2I	CF_3	0.44	0.44	0.25	0.25	140	38 ± 2
	H	0.0		0.0			
	H	0.0		0.0			
$CF_3CF_2CH_2I$	CF_3CF_2	(0.51)	0.51	0.38	0.38	133	36 ± 2
	H	0.0		0.0			
	H	0.0		0.0			
CF_2HCF_2I	CF_2H	0.36	1.24	0.27	0.01	102	28 ± 2
	F	0.44		0.13			
	F	0.44		0.13			
CF_3I	F	0.44	1.32	0.13	0.39	105	28 ± 2
	F	0.44		0.13			
	F	0.44		0.13			
CF_3CF_2I	CF_3	0.44	1.32	0.25	0.01	96	26 ± 2
	F	0.44		0.13			
	F	0.44		0.13			

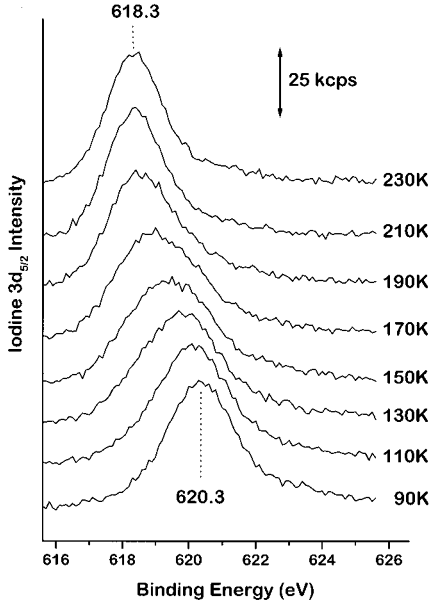

Figure 1. X-ray photoemission spectra of the I $3d_{5/2}$ peak during heating of 0.24 ML CH_3CH_2I on the Ag(111) surface from $T = 90$ to 230 K. The I $3d_{5/2}$ binding energies are 620.3 eV for iodine in the adsorbed molecule and 618.3 eV for iodine on the Ag(111) surface. The continuous conversion from $CH_3CH_2I_{(ad)}$ to $I_{(ad)}$ is apparent as the surface is heated at a constant rate of 0.2 K/s.

energy shifts by 2.0 eV to 618.3 eV. These values of the I $3d_{5/2}$ binding energies are consistent with those reported in the literature for CH_3I and CH_3CH_2I on Ag(111). This shift of the I $3d_{5/2}$ binding energy during CH_3CH_2I dissociation is illustrated quite clearly in Figure 1, which shows a series of spectra obtained at equally spaced temperatures in the range 90−230 K. The continuous loss in intensity of the peak at 620.3 eV ($CH_3CH_2I_{(ad)}$) is accompanied by a continuous increase in the intensity of the peak at 618.3 eV ($I_{(ad)}$).

The chemistry of many of the alkyl iodides on the Ag(111) surface is documented, and the fates of the alkyl groups and the iodine atoms are known.[13−18] During heating, the $CH_3CH_{2(ad)}$ fragments remain on the surface and do not react until the temperature reaches 185 K, at which point they couple and desorb as butane. This butane desorption temperature is consistent with that measured by other researchers.[14,16] The important point is that the reaction of the ethyl fragment occurs after the majority of the C−I bonds have dissociated. The $I_{(ad)}$ remains on the surface during the C−I cleavage and does not desorb until ~830 K. It is believed that $I_{(ad)}$ desorbs as I atoms from Ag(111).[13]

The dissociation of the C−I bond in adsorbed CH_3CH_2I was monitored by obtaining a set of 50 I $3d_{5/2}$ XP spectra during heating from 90 to 290 K at a rate of 0.2 K/s. The spectra can be decomposed into contributions from two adsorbed species ($CH_3CH_2I_{(ad)}$ and $I_{(ad)}$) through the use of the factor analysis or principal component analysis method.[23,24] This method uses the I $3d_{5/2}$ spectra of a pure $CH_3CH_2I_{(ad)}$ monolayer and a pure $I_{(ad)}$ layer as the basis spectra for linear decomposition of the mixed composition spectra. The principal component basis spectrum for $CH_3CH_2I_{(ad)}$ is simply the low-temperature (90 K) I $3d_{5/2}$ XP spectrum centered at 620.3 eV, and the basis spectrum for $I_{(ad)}$ is the high-temperature (250 K) spectrum centered at 618.3 eV. The coverages of $CH_3CH_2I_{(ad)}$ (θ_{RI}) and $I_{(ad)}$ (θ_I) are obtained by least-squares fitting of those principal component spectra to all 50 raw spectra simultaneously. The factor analysis technique has been described in detail.[23,24] Figure 2 shows a plot of the

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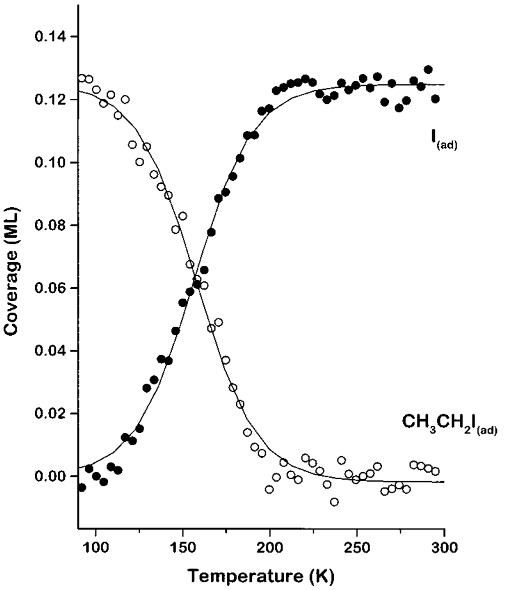

Figure 2. Coverages of $I_{(ad)}$ and $CH_3CH_2I_{(ad)}$ as a function of temperature during heating of $CH_3CH_2I_{(ad)}$ on the Ag(111) surface. Initially (90 K), all the iodine is present in the form of adsorbed $CH_3CH_2I_{(ad)}$ (I $3d_{5/2}$ binding energy of 620.3 eV). During heating, the C−I bonds break, depositing $I_{(ad)}$ on the Ag(111) surface (I $3d_{5/2}$ binding energy of 618.3 eV). Heating rate = 0.2 K/s.

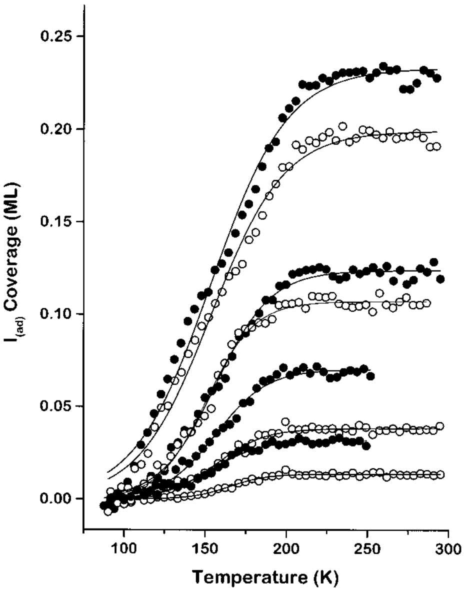

Figure 3. Coverage of $I_{(ad)}$ as a function of temperature for several initial coverages of $CH_3CH_2I_{(ad)}$. In all cases, the $CH_3CH_2I_{(ad)}$ is completely converted to $I_{(ad)}$ during heating. The temperature range and inflection points of the $I_{(ad)}$ vs T curves are independent of the initial coverage of $CH_3CH_2I_{(ad)}$. Heating rate = 0.2 K/s.

coverages of $I_{(ad)}$ and $CH_3CH_2I_{(ad)}$ (θ_I and θ_{RI}) during heating. These show the continuous conversion from one species into the other. Plotting the sum of the two coverages reveals that there is no loss of iodine atoms from the surface during the heating. Fitting a Boltzmann function to the $\theta_I(T)$ curve allows one to identify an inflection point (T_{max}) which is the maximum in the rate of C−I bond breaking.

$$\theta(T) = \frac{\theta(T_0) - \theta(T_f)}{1 + e^{(T-T_{max})/\Delta T}} + \theta(T_f) \qquad (2)$$

($\theta(T_0)$ is the initial $I_{(ad)}$ coverage, $\theta(T_f)$ is the final $I_{(ad)}$ coverage, and ΔT is the width of the curve). It should be noted that the Boltzmann curve is a symmetric S-shaped curve with enough degrees of freedom to adequately represent the data. It does not represent an analytical solution to a kinetic model that ought to represent the data. The curves used to fit the data for $\theta_I(T)$ and $\theta_{RI}(T)$ are shown in Figure 2 as the solid lines. The most important quantities to be extracted from these data are the temperatures of maximum reaction rate (T_{max}) since these are to be used to estimated the barriers to C−I bond cleavage.

One of the features of the $\theta_I(T)$ curve observed in Figure 2 is that the dissociation of CH_3CH_2I on the Ag(111) surface occurs over a fairly broad temperature range. The maximum dissociation rate occurs at $T_{max} = 160$ K, and the width of the temperature range is $\Delta T = 65$ K. This is too broad a range for a simple first-order process with a rate constant having a physically reasonable pre-exponent (ν) and a single value of the activation barrier ($\Delta E^{\ddagger}_{C-I}$). Analysis of the dissociation kinetics for a first-order process with a physically reasonable pre-exponent of $\nu = 10^{13}$ s^{-1} and a barrier of 43 kJ/mol (the value estimated for CH_3CH_2I dissociation) suggests that the reaction ought to occur with a value of $T_{max} = 155$ K but over a much narrower temperature range $\Delta T = 15$ K. The most likely explanation for the large value of ΔT is that $\Delta E^{\ddagger}_{C-I}$ is dependent on the extent of reaction (ζ). This seems quite plausible since both reaction products ($I_{(ad)}$ and $CH_3CH_{2(ad)}$) remain on the surface during the course of the reaction, thus continuously changing the reaction environment. The dissociation reaction must require free sites for adsorption of the $I_{(ad)}$ and the alkyl group, and as the reaction proceeds these become blocked. Coverage dependence of surface reaction barriers is commonly observed and could easily account for the large temperature range over which C−I bond cleavage is observed.

To explore the possibility that the barrier to C−I cleavage depends on adsorbate coverage, the kinetics of C−I cleavage in CH_3CH_2I were measured as a function of initial reactant coverage ($\theta_{CH_3CH_2I}{}^0$). The result is the set of curves shown in Figure 3, illustrating $\theta_I(T)$ for increasing $\theta_{CH_3CH_2I}{}^0$. For all of these experiments, the surface was initially clean. The fact is that the peak dissociation temperature does not appear to depend on $\theta_{CH_3CH_2I}{}^0$. A plausible explanation for this is that the CH_3CH_2I can diffuse on the Ag(111) surface to coalesce into islands. In such a scenario, the local coverage of CH_3CH_2I within these islands would be independent of the total amount on the surface. This is consistent with the observation that the kinetics of C−I cleavage do not depend on $\theta_{CH_3CH_2I}{}^0$. The origin of the width of the temperature range over which C−I bond cleavage cannot be changes in the coverage of $CH_3CH_2I_{(ad)}$ during the course of the reaction.

Another plausible reason for the apparently large temperature range for C−I bond cleavage is that one of the products is inhibiting the reaction and that as the extent of reaction increases, $\Delta E^{\ddagger}_{C-I}$ is increasing. The coverage of $I_{(ad)}$ certainly changes throughout the course of the C−I cleavage reaction and might plausibly influence $\Delta E^{\ddagger}_{C-I}$. It has been possible to make an independent determination of the effects of iodine coverage on the kinetics of C−I cleavage. Several $\theta_I(T)$ curves were obtained with differing initial coverages of adsorbed iodine, $\theta_I{}^0$, and are shown in Figure 4. The initial coverage of CH_3CH_2I was $\theta_{CH_3CH_2I}{}^0 \approx 0.13$ for all three experiments. It is quite apparent from these curves that increasing the amount of $I_{(ad)}$ on the surface increases T_{max} for C−I cleavage. The form of the curves in Figure 4 suggests that the apparent breadth in the temperature range for C−I cleavage in adsorbed CH_3CH_2I can be attributed to inhibition of the reaction by iodine deposited onto the Ag(111) surface during the course of the reaction. The

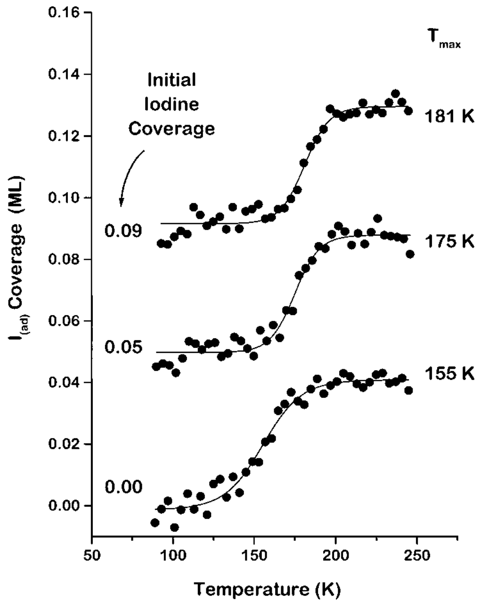

Figure 4. Coverage of $I_{(ad)}$ as a function of temperature during the decomposition of $CH_3CH_2I_{(ad)}$ at several initial coverages of $I_{(ad)}$. The temperature range and inflection points of the $I_{(ad)}$ vs T curves are dependent on the initial coverage of $I_{(ad)}$. These suggest that, during the decomposition of $CH_3CH_2I_{(ad)}$, the increasing coverage of $I_{(ad)}$ causes an increase in $\Delta E^{\ddagger}_{C-I}$. Heating rate = 0.2 K/s.

inhibition by $I_{(ad)}$ as measured by the width of the reaction temperature range (ΔT) seems to decrease as θ_I^0 increases. This is observable in the narrowing width of the curve at increasing θ_I^0. This complicates the kinetics because it implies that $\Delta E^{\ddagger}_{C-I}$ is changing throughout the course of the reaction. Given the complexity of the reaction kinetics, the analysis of data will be limited to estimation of $\Delta E^{\ddagger}_{C-I}$ by use of the temperature of the peak dissociation rate, T_{max}, which occurs at an extent of reaction of roughly $\zeta = 1/2$ for all initial coverages of CH_3CH_2I.

3.2. C−I Bond Cleavage in CH_3I. The chemistry of CH_3I on the Ag(111) surface is somewhat more complicated than that of CH_3CH_2I and the other alkyl iodides due to the fact that some of the CH_3I desorbs during heating. Of the 10 iodides studied during the course of this work, CH_3I is the only one for which any molecular desorption is observed. During heating, a fraction of the CH_3I desorbs at 195 K (heating rate of $\beta = 2$ K/s). Some, of course, decomposes, and CH_3I desorption is followed by the desorption of C_2H_6 at $T_p = 215$ K. C_2H_6 is formed by coupling of the methyl groups produced by C−I cleavage in the fraction of CH_3I that dissociated. Measurements of the I $3d_{5/2}$ XPS spectrum before and after heating to 275 K indicated that 30−50% of the CH_3I desorbed, depending on the initial coverage of CH_3I. Of all the iodides studied in this work, CH_3I has the highest barrier to dissociation ($T_{max} = 175$ K) and probably the lowest barrier to desorption. As a result, a temperature is reached during heating at which the CH_3I that remains on the surface desorbs.

The concurrent decomposition and desorption of CH_3I can be monitored using XPS. Figure 5 shows the evolution of θ_I and $\theta_{CH_3I} + \theta_I$ on the surface during heating. At 100 K, all the iodine on the surface is present in the form of $CH_3I_{(ad)}$. During heating, $CH_3I_{(ad)}$ begins to dissociate to produce $CH_{3(ad)}$ and $I_{(ad)}$ ($CH_3I_{(ad)} \rightarrow CH_{3(ad)} + I_{(ad)}$). This process continues until the temperature reaches ~180 K. At that point there is a sudden drop in the total iodine concentration ($\theta_I + \theta_{CH_3I}$) as the remaining CH_3I desorbs. It is clear in Figure 5 that the total amount of iodine on the surface decreases by ~40%. Although 180 K is slightly below the T_p from the TPR spectrum (which was collected at $\beta = 0.2$ K/s), it is a temperature where the desorption rate is significant. The very sharp decrease in total iodine concentration is consistent with and is typical of a first-order desorption process with a constant barrier and a physically reasonable pre-exponential factor. It is clear from both the XPS and TPRS experiments that the C−I bond cleavage in CH_3I does not reach completion.

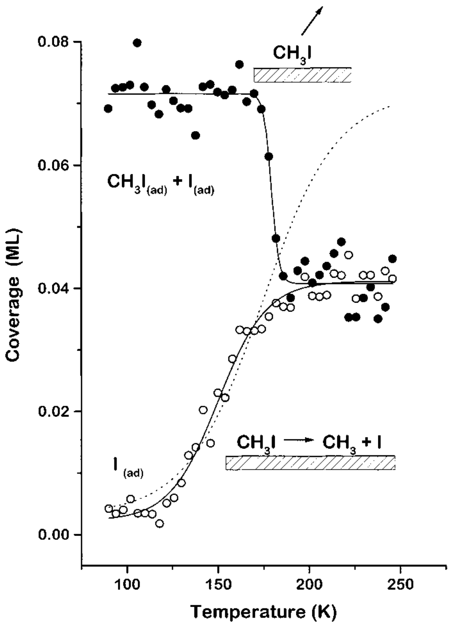

Figure 5. Coverage of $I_{(ad)}$ and the total I coverage ($CH_3I_{(ad)} + I_{(ad)}$) as a function of temperature during heating of CH_3I on the Ag(111) surface. The $CH_3I_{(ad)}$ dissociates during heating until 180 K, at which point the remaining $CH_3I_{(ad)}$ desorbs into the gas phase. At that point, the total I coverage on the surface drops. The solid curves are fits of Boltzmann functions to the data. The dashed curve is a fit of a Boltzmann function to the data for $\theta_I(T)$, assuming that all of the $CH_3I_{(ad)}$ dissociates. Heating rate = 0.2 K/s.

The analysis of the $\theta_I(T)$ curve to yield an estimate of $\Delta E^{\ddagger}_{C-I}$ is complicated by the fact that some of the CH_3I desorbs. In the case of CH_3I, a Boltzmann curve has been used to fit data in the temperature range of 90−180 K; however, the high-temperature limit is chosen as though all the CH_3I had dissociated on the surface. This is illustrated by the dashed line in Figure 5. In essence, this curve for $\theta_I(T)$ is extended to high temperature to simulate the case in which there is no desorption of CH_3I and C−I cleavage reaches completion as it does for all the other iodides.

3.3. C−I Bond Cleavage in CF_3I. The highly fluorinated iodides have low $\Delta E^{\ddagger}_{C-I}$, and as a result, some fraction of an adsorbed layer dissociates on the Ag(111) surface at temperatures below the 90 K limit of our apparatus. This complicates the analysis of the reaction kinetics. The compounds that decomposed at low temperature had at least two fluorine atoms bound to the reaction center (CF_3I, CF_2HCF_2I, and CF_3CF_2I). Several XP spectra of 0.08 ML of CF_3I at different temperatures are plotted in Figure 6. The partial dissociation at low temperature is illustrated by the spectrum of CF_3I adsorbed at 90 K. From the width and shape of the curve, it is obvious that even at 90 K, some CF_3I has dissociated. The partial dissociation at 90 K (before heating) posed a problem for the choice of the XP spectra of the pure fluoroalkyl iodides to be used as basis spectra for the factor analysis. This problem was solved by using the XP spectrum from a multilayer coverage of the fluoroalkyl iodide. The multilayer (~1 ML of I atoms) was formed by

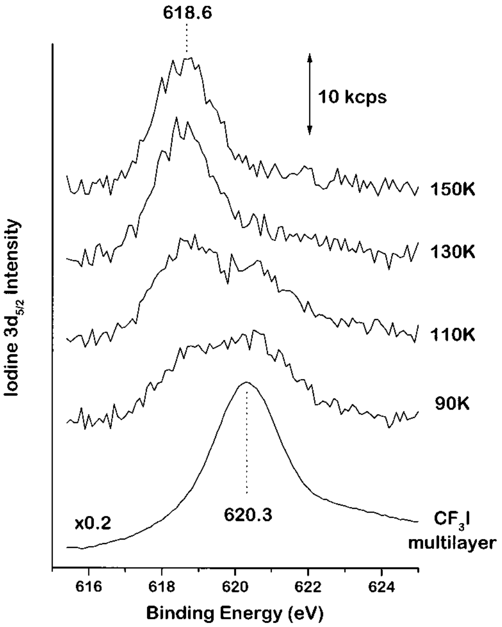

Figure 6. X-ray photoemission spectra of the I $3d_{5/2}$ peak during heating of 0.08 ML of $CF_3I_{(ad)}$ on the Ag(111) surface from $T = 90$ to 150 K. CF_3I is partially dissociated at 90 K. The continuous conversion from $CF_3I_{(ad)}$ (I $3d_{5/2}$ binding energy of 620.3 eV) to $I_{(ad)}$ (I $3d_{5/2}$ binding energy of 618.6 eV) is apparent as the surface is heated at a constant rate of 0.2 K/s.

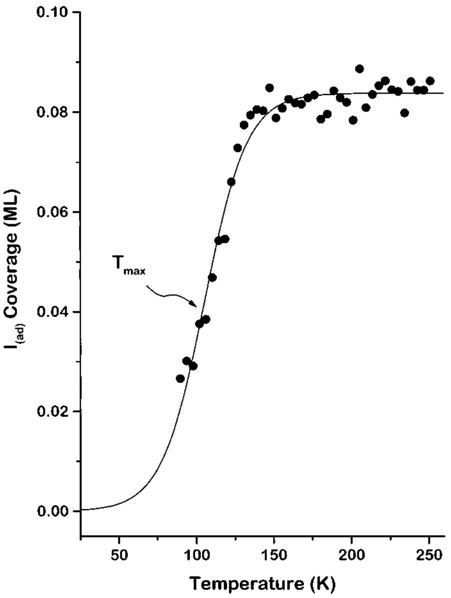

Figure 7. Coverage of $I_{(ad)}$ as a function of temperature during heating of $CF_3I_{(ad)}$ on the Ag(111) surface. Initially (90 K), ~70% of the iodine is present in the form of $CF_3I_{(ad)}$ (I $3d_{5/2}$ at 620.3 eV). During heating, the C−I bonds break depositing $I_{(ad)}$ on the Ag(111) surface (I $3d_{5/2}$ at 618.6 eV). The Boltzmann fit is extended to zero $I_{(ad)}$ coverage at low temperature as if no initial dissociation occurred. Heating rate = 0.2 K/s.

exposing the surface to a large flux of the CF_3I and then taking an XP spectrum, as shown in Figure 6. The $\theta_I(T)$ curve is plotted in Figure 7 and has been fit by a Boltzmann curve with the initial low-temperature value of θ_I fixed equal to zero. In essence, these curves simulate the data that would be expected if the sample could be cooled to <90 K. The XP spectra and the $\theta_I(T)$ curves for CF_2HCF_2I and CF_3CF_2I had features similar to those of CF_3I in the sense that some fraction dissociated at $T < 90$ K, and the $\theta_I(T)$ curves were analyzed in the same manner as for CF_3I.

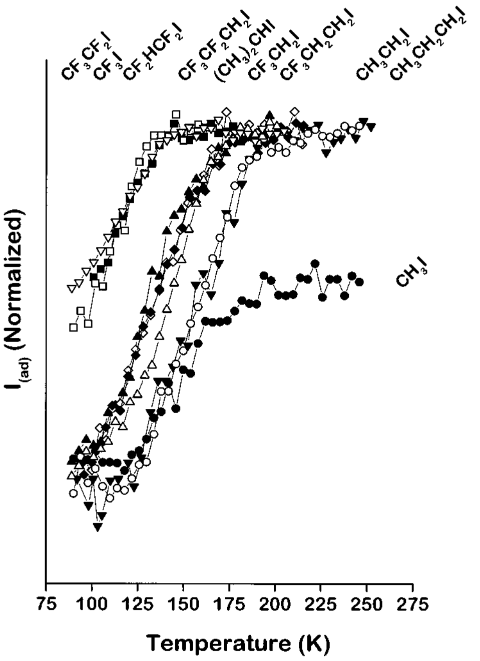

Figure 8. Coverage of $I_{(ad)}$ versus temperature during dissociation of alkyl and fluoroalkyl iodides on the Ag(111) surface. The coverages are all roughly 0.16 ML; however, the high-temperature $I_{(ad)}$ signals have all been normalized to the same value in order to aid visual comparison of the curves. Since the dissociation kinetics are independent of coverage, this does not affect the position of the inflection points. Clearly, the substitutions of the alkyl groups influence the C−I dissociation kinetics. Heating rate = 0.2 K/s.

3.4. C−I Bond Cleavage in Alkyl and Fluoroalkyl Iodides.

X-ray photoemission spectra have been collected to measure the dissociation kinetics of a series of alkyl and fluoroalkyl iodides ($R_3C{-}I_{(ad)} \rightarrow R_3C_{(ad)} + I_{(ad)}$, where R = H, F, CH_3, CF_3, CH_3CH_2, CF_3CH_2, CF_2HCF_2, CF_3CF_2, $CH_3CH_2CH_2$, $CF_3CH_2CH_2$, $CF_3CF_2CH_2$, or $(CH_3)_2CH$) on Ag(111). (In this notation, R is not necessarily the same for all three substituents of $R_3C{-}I$). The molecules that were studied are listed in Table 1. These iodides were chosen specifically to be a statistically reasonable set of molecules that undergo the same reaction (C−I cleavage) and have substituents (R) with a broad range of field and polarizability substituent constants. Starting at 90 K with an initial coverage of the alkyl iodide of $\theta_{R_3CI}{}^0 \approx 0.16$ ML (roughly half of the saturation I coverage), a series of XP spectra of the I $3d_{5/2}$ region were collected as the surface was heated at a rate of 0.2 K/s. To obtain the $\theta_I(T)$ curves, these spectra were analyzed in the same fashion as described above for $CH_3CH_2I_{(ad)}$ by using factor analysis decomposition to obtain the coverages of $I_{(ad)}$ and $R_3CI_{(ad)}$ as a function of temperature. The inflection points of the $\theta_I(T)$ curves were used to estimate the values of the $\Delta E^{\ddagger}{}_{C-I}$ at an extent of reaction of $\zeta = 1/2$. The fact that all the curves run roughly parallel to one another suggests that the dependence of the rate on θ_I is the same for all molecules and that the dependence on the substituents is similar at all extents of the C−I cleavage reaction.

The $\theta_I(T)$ dissociation curves for all of the molecules studied are shown in Figure 8. Since the initial coverage of alkyl iodide does not affect the dissociation kinetics, normalizing the curves to the same final coverage will not affect the position of their inflection points. The one exception, of course, is CH_3I, some of which desorbs before all of the C−I bonds cleave. Boltzmann functions were used to fit the $\theta_I(T)$ curves in order to determine the inflection points or the temperatures of maximum dissociation rate, T_{max}. It is important to point out that several approaches including simple visual inspection were used to determine $T_{\max}$, and the results of this work are insensitive to the method. The values of $T_{\max}$ from the $\theta_{\mathrm{I}}(T)$ curves provide the basis for the estimation of the activation barriers for C−I cleavage, $\Delta E^{\ddagger}_{\mathrm{C-I}}$. The details of the analysis are described in the Discussion section, and the results for the entire set of iodides are presented in Table 1. Not surprisingly, the substituent groups on the alkyl and fluoroalkyl iodides do have an influence on the $\Delta E^{\ddagger}_{\mathrm{C-I}}$.

4. Discussion

4.1. Analysis of C−I Dissociation Kinetics. The XPS experiments performed in this work generated the $\theta_{\mathrm{I}}(T)$ curves of Figure 8, which are measures of the kinetics of C−I cleavage in all the alkyl iodides studied. Although the reaction itself should be quite simple, there are obvious complexities that are introduced into the kinetics by the dependence of the reaction rate on the coverage of adsorbed iodine, θ_{I}. As a result, the analysis of the kinetics will be limited to use of the temperature of maximum reaction rate ($T_{\max}$) for estimation of the barrier to C−I cleavage. In essence, this is an estimate of $\Delta E^{\ddagger}_{\mathrm{C-I}}$ at an extent of reaction of $\zeta = 1/2$. In much the same way as the peak desorption temperature, T_{p}, is used to determine desorption energies, ΔE_{des}, in the analysis of thermal desorption spectra, the peak dissociation temperature, $T_{\max}$, has been used to estimate $\Delta E^{\ddagger}_{\mathrm{C-I}}$.[25] The elementary reaction step,

$$\mathrm{CH_3CH_2I_{(ad)}} \rightarrow \mathrm{CH_3CH_{2,(ad)}} + \mathrm{I_{(ad)}}$$

will be modeled with an Arrhenius rate expression assuming first-order kinetics,

$$\begin{aligned}\frac{\mathrm{d}\theta_{\mathrm{I}}}{\mathrm{d}t} &= k_{\mathrm{C-I}}(\theta_{\mathrm{CH_3CH_2I}}{}^{0} - \theta_{\mathrm{I}}) \\ &= \nu\, \mathrm{e}^{-\Delta E^{\ddagger}_{\mathrm{C\text{-}I}}/RT}(\theta_{\mathrm{CH_3CH_2I}}{}^{0} - \theta_{\mathrm{I}})\end{aligned}$$

Since the total amount of iodine does not change during heating, the coverages of $\mathrm{I_{(ad)}}$ and $\mathrm{CH_3CH_2I_{(ad)}}$ are related to the initial alkyl iodide coverage ($\theta_{\mathrm{CH_3CH_2I}}{}^{0}$) by the following expression,

$$\theta_{\mathrm{I}} + \theta_{\mathrm{CH_3CH_2I}} = \theta_{\mathrm{CH_3CH_2I}}{}^{0}$$

$T_{\max}$ is the inflection point of the $\theta_{\mathrm{I}}(T)$ curve and satisfies the condition

$$\left.\frac{\mathrm{d}^2\theta_{\mathrm{I}}}{\mathrm{d}t^2}\right|_{T_{max}} = 0$$

Thus, if we assume first-order kinetics, the Redhead equation[25] applies,

$$\frac{\Delta E^{\ddagger}_{\mathrm{C-I}}}{RT^2_{\max}} = \frac{\nu}{\beta}\, \mathrm{e}^{-\Delta E^{\ddagger}_{\mathrm{C\text{-}I}}/RT_{max}} \tag{3}$$

The quantity β is the heating rate, and with a value for the pre-exponent ν this equation can be used to estimate the value of $\Delta E^{\ddagger}_{\mathrm{C-I}}$. The value chosen for the pre-exponent is $\nu = 10^{13}\ \mathrm{s}^{-1}$, which should be a reasonable estimate for what ought to be a simple unimolecular dissociation with adsorbed reactant and products. It is important to note that, in this investigation, we are most interested in the relative values of $\Delta E^{\ddagger}_{\mathrm{C-I}}$ among a large set of iodides. Given that we are studying the same reaction in each reactant, the pre-exponent for each should be quite similar. Thus, although an error in the choice of $\nu = 10^{13}\ \mathrm{s}^{-1}$ may introduce a systematic error into the estimated values of $\Delta E^{\ddagger}_{\mathrm{C-I}}$, the estimate of the relative values should be quite good. The values of $\Delta E^{\ddagger}_{\mathrm{C-I}}$ are listed in Table 1 and range from 26 kJ/mol for $\mathrm{CF_3CF_2I}$ up to 49 kJ/mol for $\mathrm{CH_3I}$. The effects of the substituents on the $\Delta E^{\ddagger}_{\mathrm{C-I}}$ can be used to infer the characteristics of the transition state to C−I cleavage.

4.2. Transition State for C−I Cleavage. The aim of our measurements of the kinetics of C−I cleavage on the Ag(111) surface has been to determine the nature of the transition state for this important dehalogenation reaction. Linear free energy relationships (LFERs) serve as a very effective tool for scaling measured activation energies and correlating them to properties of the substituents. A glance at Figure 8 shows that the $\theta_{\mathrm{I}}(T)$ curves for each of the iodides do not coincide in temperature; thus, the nature of the substitution does have some influence on the C−I dissociation kinetics. The range of the maximum dissociation temperatures for this set of iodides is ∼80 K. The reactants were carefully chosen to have substituents that span a wide range of field (σ_{F}) and polarizability (σ_{α}) substituent constants. The field effect results from the electrostatic interaction of a local dipole moment on the substituent with a change in charge density (Δq) at the reaction center on going from reactant to transition state.[21,22] Naturally, if there is no change in charge density at the reaction center, there will be no field effect interaction with the substituents. Polarizability is a measure of the dipole moment that is induced in a substituent by a nearby charge (in either the reactant or the transition state) and is roughly correlated to the size of the substituent. Again, if there is no change in charge density at the reaction center, then there is no change in induced dipole in the substituent, and there will be no substituent polarizability effect. These two effects can be correlated simultaneously with a multivariable linear fit using eq 1. A good correlation will result if these effects are sufficient to adequately describe the changes in activation energy induced by the various substituents on the reactants. The linear free energy relationship for C−I cleavage on Ag(111) is plotted in Figure 9. To make this two-dimensional plot, eq 1 was rewritten in two forms, one to demonstrate the field effect and one for the polarizability effect:

$$\text{(field)}\qquad \Delta E^{\ddagger}_{\mathrm{C-I}} - \rho_{\alpha}\sigma_{\alpha} = \rho_{\mathrm{F}}\sigma_{\mathrm{F}} + \Delta E^{\ddagger}_{\mathrm{H_3C-I}} \tag{4}$$

$$\text{(polarizability)}\qquad \Delta E^{\ddagger}_{\mathrm{C-I}} - \rho_{\mathrm{F}}\sigma_{\mathrm{F}} = \rho_{\alpha}\sigma_{\alpha} + \Delta E^{\ddagger}_{\mathrm{H_3C-I}} \tag{5}$$

Clearly, a good correlation results for both of these effects with $\rho_{\mathrm{F}} = -17 \pm 1$ kJ/mol ($r^2 = 0.98$) and $\rho_{\alpha} = -11 \pm 2$ kJ/mol ($r^2 = 0.83$). The quality of these fits indicates that these two effects are sufficient to adequately describe the electronic substituent effects on $\Delta E^{\ddagger}_{\mathrm{C-I}}$.

The value of LFERs in determining the nature of transition states has been demonstrated in previous measurements of surface reactions such as β-hydride elimination in alkoxides on Cu(111).[26−28] Those experiments showed that, for heterolytic processes, the values of ρ_{F} are on the order of 100−200 kJ/mol. As an additional point of comparison, gas-phase proton-transfer equilibria ($\mathrm{RH_{(g)}} \leftrightarrow \mathrm{R^-_{(g)}} + \mathrm{H^+_{(g)}}$) also have large values of $\rho_{\mathrm{F}} \approx 200−300$ kJ/mol.[21,22] By these standards, the values of ρ_{F} and ρ_{α} for C−I cleavage on Ag(111) are very low. The good correlation and negative value of the inductive reaction constant

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[25] Redhead, P. A. *Vacuum* **1962**, *12*, 203.

[26] Gellman, A. J.; Dai, Q. *J. Am. Chem. Soc.* **1993**, *115*, 714.

[27] Forbes, J. G.; Gellman, A. J. *J. Am. Chem. Soc.* **1993**, *115*, 6277.

[28] Gellman, A. J. *Acc. Chem. Res.* **2000**, 33, 19.

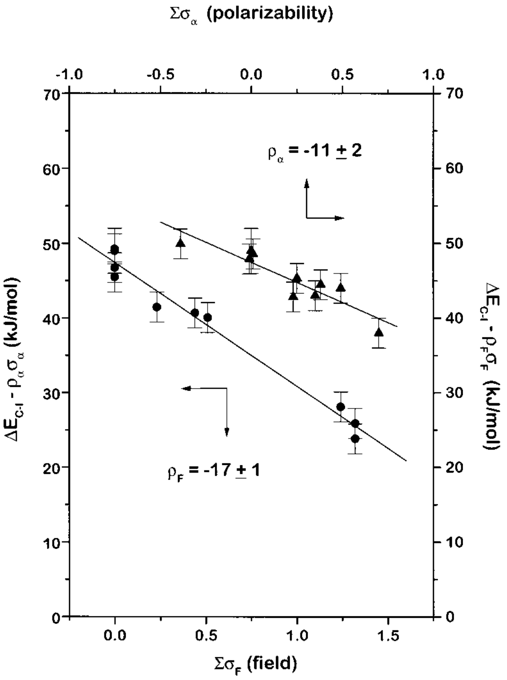

Figure 9. Linear free energy relationship for the barriers to C−I cleavage ($\Delta E^{\ddagger}_{C-I}$) in alkyl and fluoroalkyl iodides on Ag(111) using a two-variable linear fit to the field (σ_F) and polarizibility (σ_α) substituent constants. The field effect uses the left and bottom axes. The polarizibility effect uses the right and top axes.

(ρ_F) indicate that, relative to the initial state, there is, in fact, an increase in electron density at the reaction center in the transition state (RC−I → $[RC^{\delta-}\cdots I]^{\ddagger}$). The low value of ρ_F indicates that the change in charge density is small compared to that of a truly ionic process such as gas-phase deprotonation. As such, the transition state is best described as one which looks like the initial state alkyl iodide. In other words, the transition state for C−I cleavage on Ag(111) can be described as homolytic in the sense that it probably occurs early in the reaction coordinate.

Correlation of reaction energies with only the field substituent constants (σ_F) can provide information on the charge density change (Δq) between the initial state and the transition state of a reaction. This study of C−I cleavage on Ag(111) has provided an unusual opportunity through the use of polarizability constants to determine whether the absolute charge is present in the initial state or the transition state.[21,22] Inclusion of the polarizability constants (σ_α) in a multivariable linear correlation often does not significantly improve the fit because of the lack of sufficient data. As can be seen in Figure 9, a very good correlation of $\Delta E^{\ddagger}_{C-I}$ versus $\Sigma\sigma_\alpha$ is obtained in this case for C−I cleavage on Ag(111). The important feature of polarizability substituents is that they lower the potential energies of charged reactants and transition states regardless of whether the charge is positive or negative. The interaction between a polarizible object and a static charge, q, is proportional to $|q|^2$. This fact results in a *decrease* in activation energy with an increase in substituent polarizability if the magnitude of the charge is greater in the transition state than in the reactant. Alternatively, it results in an *increase* in the activation energy if the magnitude of the charge is greater in the reactant than in the transition state. The negative value of ρ_α observed in the C−I cleavage on the Ag(111) surface indicates that in the transition state for C−I cleavage, the reaction center has more electron density than the initial adsorbed iodide.

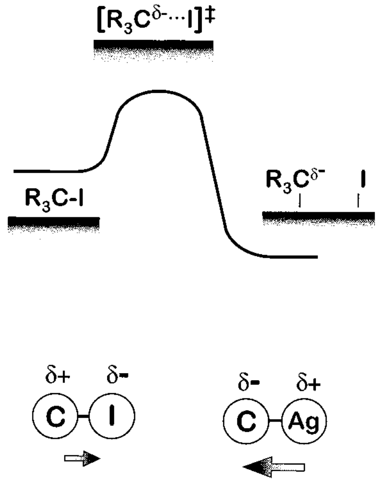

Figure 10. Potential energy surface for C−I bond cleavage on the Ag(111) surface. The reaction is exothermic with an early transition state. The process involves a transition state which is homolytic in the sense that it is reactant-like. The substituent effects reveal that there is some slight increase in the charge density on the α-carbon atom in the transition state.

The results of the linear free energy correlation suggest that the transition state for C−I cleavage is electron rich relative to the initial state alkyl iodide. A schematic illustration of the proposed transition state is provided in Figure 10. This makes some sense if one considers the electronegativities of the atoms involved in the bond-breaking and bond formation processes. Considering the electronegativities of C (2.55), I (2.66), and Ag (1.93), the C−I bond of the reactant is likely to be less polar than the C−Ag bond of the product.[29] Furthermore, the direction of polarity reverses since the order of electronegativity is I > C > Ag. The direction of bond polarity change is such that the C atom forming the Ag−C bond in the product alkyl group is likely to be more electron rich than in the alkyl iodide with the C−I bond. Theoretical calculations of methyl radical adsorption on several metal surfaces have indicated that there is a transfer of electron density from the metal to the methyl group upon adsorption.[30] Further evidence of electron-rich alkyl groups comes from the observation of C−H vibrational mode softening in alkyl groups on the Cu(111) surface.[31] This vibrational mode softening is explained by transfer of d-band electrons of the Cu into antibonding σ_{CH}* orbitals in the α-position of the adsorbed alkyl group. The sign of ρ_α in our LFER is consistent with a transition state $[RC^{\delta-}\cdots I]^{\ddagger}$ that has some of the characteristics of this anionic alkyl group. It should be noted that, although an increase in electron density in the transition state for C−I cleavage on Ag(111) has been identified, the magnitudes of ρ_α and ρ_F are quite low, and thus the magnitude of charge density increase is quite small.

4.3. Thermochemistry of C−I Cleavage. Hammond's postulate is often cited when transition states are described as being product-like (late) or reactant-like (early). Hammond's postulate states that, for exothermic reactions, the energy of the transition state is closer to that of the reactants than the products.[32] Therefore, if a reaction is exothermic, the structure of the transition state is similar to that of the initial state. Application of Hammond's postulate obviously requires knowl-

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(29) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(30) Zheng, C.; Apeloig, Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 749.

(31) Lin, J.-L.; Bent, B. E. *Chem. Phys. Lett.* **1992**, *194*, 208.

(32) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

edge of the thermochemistry of the process. Thermochemical information is not readily available for surface reactions in which metal−adsorbate bond strengths are needed. One can nevertheless estimate the thermochemistry of C−I cleavage from the following reaction scheme:

(1)	$CH_3I_{(g)}$	→	$\bullet CH_{3,(g)} + \bullet I_{(g)}$	234 kJ/mol
(2)	$\bullet CH_{3,(g)}$	→	$CH_{3,(ad)}$	-138 kJ/mol
(3)	$\bullet I_{(g)}$	→	$I_{(ad)}$	-234 kJ/mol
(4)	$CH_3I_{(ad)}$	→	$CH_3I_{(g)}$	54 kJ/mol
(5)	$CH_3I_{(ad)}$	→	$CH_{3,(ad)} + I_{(ad)}$	$\Delta H_{C\text{-}I} = -84$ kJ/mol

Step 1 is simply the gas-phase homolytic bond strength which is easily obtained from the literature and is known with a relatively high degree of accuracy.[33] The heat of methyl group adsorption on the Cu(100) surface has been estimated in the literature but has been shown to be similar on other metal surfaces.[34] We have chosen to use the same number for methyl group adsorption on the Ag(111) surface (step 2). Step 3, the heat of adsorption of $I_{(ad)}$, is equated with the desorption energy as estimated from the peak desorption temperature in a TPD experiment.[13] Evidence in the literature suggests that the $I_{(ad)}$ desorbs as atoms from the Ag(111) surface. The heat of CH_3I desorption from the Ag(111) surface (step 4) is estimated from the monolayer desorption peak temperature T_p of 185 K. It is clear that despite the uncertainty in the estimates of the thermochemistry of each of these steps, C−I bond cleavage on the Ag(111) surface is certainly exothermic, $\Delta H_{C-I} = -84$ kJ/mol. Thus, the conclusion that the transition state is reactant-like is in complete agreement with the prediction of Hammond's postulate.

A potential energy diagram for C−I bond cleavage with a picture of the transition state is shown in Figure 10. The substituent effects clearly indicate that there is an increase in electron density in the transition state for C−I cleavage on the Ag(111) surface, but Hammond's postulate and comparison to truly heterolytic reactions such as deprotonation of alcohols indicate that the transition state occurs early in the reaction coordinate and that the increased electron density is, in fact, very small.

4.4. Implications for Hydrodechlorination Catalysis. The C−I dissociation kinetics measured on the Ag(111) surface can be compared with those measured for similar reactions on other surfaces. The $\Delta E^{\ddagger}_{C-I}$ have been measured on the Pd(111) surface using the same set of alkyl and fluoroalkyl iodides used in this work.[7,8] The kinetics for C−I cleavage on the Pd(111) surface are a bit more complex on the Pd(111) surface than on the Ag(111) surface due to the fact that, for many of the reactants, the alkyl and fluoroalkyl products desorb from the surface during the course of the C−I bond cleavage reaction. Nonetheless, the results of these two sets of experiments provide a consistent picture of the nature of the transition state for deiodination. On the Pd(111) surface, the substituent effects are smaller than those observed on the Ag(111) surface, and the value of the field effect reaction constant is $\rho_F = -1.4 \pm 3.3$ kJ/mol. In other words, $\Delta E^{\ddagger}_{C-I}$ is insensitive to the fluorine substituent effects. The correlation to the field effect constants suggests that the transition state for C−I cleavage on the Pd(111) surface is very much like the initial state reactant and occurs early in the reaction coordinate with little change in charge density distribution.

The picture of the transition state for deiodination on the Ag(111) and Pd(111) surfaces is consistent with that developed for an analogous dehalogenation reaction: the cleavage of C−Cl bonds on the Pd(111) surface.[5−7] This is an important reaction since it is one of the elementary steps that must occur in the catalytic hydrodechlorination of CFCs on supported Pd catalysts. Dechlorination kinetics were measured in a set of four chlorocarbons on the Pd(111) surface: CF_3CFCl_2, CFH_2CFCl_2, CH_3CFCl_2, and CH_3CHCl_2. The activation barriers to C−Cl cleavage, $\Delta E^{\ddagger}_{C-Cl}$, were correlated to the field substituent constants of these molecules and revealed a reaction constant of $\rho_F = -2 \pm 4$ kJ/mol. As with C−I cleavage on the Pd(111) surface, this is not significantly different from zero. These results suggest that the transition state to the dechlorination step of catalytic hydrodechlorination is reactant-like and occurs early in the reaction coordinate.

It is interesting to consider the implication of an early transition state on surface-catalyzed dehalogenation reactions. The basic observation of the work described above has been that the barrier to dehalogenation is insensitive to the substituents used on either the alkyl iodides or the chlorides used as reactants. By extension, then, one might speculate that the barriers would be insensitive to the nature of the metal surface on which the reaction is occurring. In the case of deiodination, this suggestion has some support from the many studies of alkyl iodides on metal surfaces. Although few of these studies have focused on the careful measurement of C−I bond cleavage kinetics, the majority report that dissociation occurs over a fairly narrow window of temperatures in the range 100−200 K. This has been observed on many metal surfaces and suggests that the kinetics for dehalogenation reactions are only weakly influenced by the nature of the surface on which they occur.

5. Conclusions

The barrier to the cleavage of C−I bonds in fluorine-substituted alkyl iodides on the Ag(111) surface is reduced by both the field and the polarizibility effects of the substituted alkyl groups. The magnitude of this effect is small, suggesting that the transition state to C−I cleavage is very much like the initial state or reactant. In other words, the transition state occurs early in the reaction coordinate. The correlation of the barriers with the field substituent constants suggests that, in the transition state, the α-carbon atom is slightly anionic with respect to the initial state. The correlation with the polarizibility constants suggests that the excess absolute charge exists in the transition state.

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