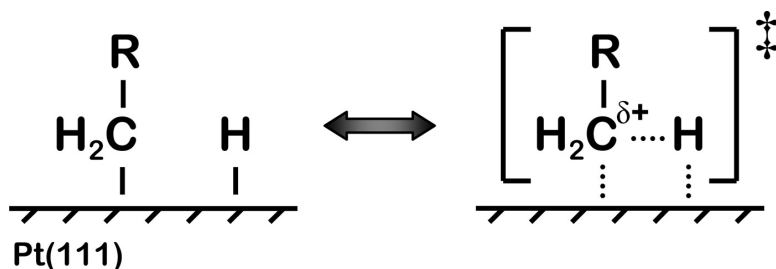


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Transition State for Alkyl Group Hydrogenation on Pt(111)

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Abstract: Substituent effects have been used to probe the characteristics of the transition state to hydrogenation of alkyl groups on the Pt(111) surface. Eight different alkyl and fluoroalkyl groups have been formed on the Pt(111) surface by dissociative adsorption of their respective alkyl and fluoroalkyl iodides. Coadsorption of hydrogen and alkyl groups, followed by heating of the surface, results in hydrogenation of the alkyl groups to form alkanes, which then desorb into the gas phase. Temperature-programmed reaction spectroscopy was used to measure the barriers to hydrogenation, $\Delta E_{\ddagger}^{\ddagger}$, which are dependent on the size of the alkyl group (polarizability) and the degree of fluorination (field effect). This example is one of only two surface reactions for which the influence of the substituents on $\Delta E_{\ddagger}^{\ddagger}$ has been correlated with both the field and the polarizability substituent constants of the alkyl groups in the form of a linear free energy relationship. Increasing both the field and the polarizability constants of the alkyl groups increases the value of $\Delta E_{\ddagger}^{\ddagger}$. The substituent effects are quantified by a field reaction constant of $\rho_{\alpha} = 27 \pm 4$ kJ/mol and a polarizability reaction constant of $\rho_{\alpha} = 19 \pm 3$ kJ/mol. These suggest that the transition state for hydrogenation is slightly cationic with respect to the alkyl group on the Pt(111) surface, $\text{RC} + \text{H} \leftrightarrow \{\text{RC}^{\delta+} \cdots \text{H}\}^{\ddagger}$.

1. Introduction

Heterogeneous catalysis is fundamentally a kinetic phenomenon. A deep understanding of this phenomenon requires a combined understanding of both catalytic reaction mechanisms and the influence of catalysts on elementary surface-reaction kinetics. The latter implies that it is important to understand the nature of the transition states to elementary catalytic surface reactions.¹ Unfortunately, there are very few experimental studies of the transition states to elementary catalytic reaction steps because of the lack of experimental methods for characterizing transition states on surfaces. The use of substituent effects is one successful approach that can be used for experimental study of the transition states for a number of elementary surface reactions.^{2,3} One example is a study of the β -hydride elimination of alkoxides on the Cu(111) surface, which has shown that the transition state is cationic with respect to the alkoxy reactant, $\{\text{RC}^{\delta+} \cdots \text{H}\}^{\ddagger}$.⁴ Another example is carboxylic acid deprotonation on Cu(100).⁵ Substituent effects revealed that the transition state for deprotonation is anionic with respect to the initial-state acid, $\{\text{RCO}_2^{\delta-} \cdots \text{H}\}^{\ddagger}$ and occurs early in the reaction coordinate. A third example is dehalogenation of alkyl halides

on Pd(111) and Ag(111) surfaces.^{6–9} Studies of the deiodination of a series of alkyl iodides and the dechlorination of dichloroethanes have shown that the transition states for both C–I and C–Cl bond cleavage are homolytic and that substituents have almost no effect on the relative energies of the transition state and the initial state. The use of substituent effects offers a unique approach to probing the transition states for heterogeneous catalytic reactions and, ultimately, understanding the influence of catalysts on the kinetics of each elementary step.¹

Hydrogenation of alkyl groups is one of the most common reduction reactions occurring on transition metal surfaces. For example, methane formation from methyl moieties has been observed and studied on single crystals of Pt(111), Ni(100), Pd(100), Ru(001), Cu(110), and Cu(111) and on films of iron, nickel, palladium, lead, gold, and copper.¹⁰ Alkyl group hydrogenation can be studied on metal surfaces by first generating isolated alkyl groups from alkyl iodides. It is well-known that propyl groups can be formed on the Pt(111) surface by adsorption of propyl iodide at low temperature, followed by heating to dissociate the C–I bond and generate adsorbed propyl groups and iodine atoms. During heating in the presence of preadsorbed hydrogen, propyl groups on the Pt(111) surface can be hydrogenated to form propane, which desorbs at about

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250 K.^{11,12} The rate limiting step in the appearance of the propane is the hydrogenation of the propyl groups.¹²

Thermal decomposition of alkyl iodides on the Pt(111) surface can also lead to the formation of alkanes in the absence of preadsorbed hydrogen. This must occur via a mechanism that uses some source of hydrogen other than adsorption from the gas phase. Immediately following cleavage of the C–I bond in ethyl iodide, the resulting ethyl groups dehydrogenate at temperatures as low as 170 K to yield ethylene. During heating, the chemisorbed ethylene is then hydrogenated at a higher temperatures to reform ethyl groups, which can then be hydrogenated to form ethane.¹³ In this mechanism, the rate-limiting step in the appearance of ethane in the gas phase is the hydrogenation of the adsorbed ethylene rather than the hydrogenation of the ethyl groups.

The hydrogenation of olefins such as ethylene and propylene has been studied on the Pt(111) surface with and without preadsorbed hydrogen.^{11,12,14,15} On Pt(111), ethylene undergoes self-hydrogenation via an initial C–H bond breaking step to generate adsorbed hydrogen atoms which are consumed by subsequent hydrogenation of the remaining ethylene. The C–H bond breaking in ethylene is the rate-limiting step for self-hydrogenation of ethylene on Pt(111). Co-adsorption of hydrogen with ethylene increases the ethane yield and lowers the apparent activation energy for the hydrogenation reaction. Ethylene hydrogenation occurs by a stepwise mechanism in which ethyl groups are formed as intermediates. The ethyl groups can either acquire a second hydrogen atom at the α -carbon to form ethane, which desorbs, or lose a β -hydrogen atom by β -hydride elimination to form ethylene.¹⁴ Propylene is hydrogenated by a similar mechanism in which hydrogenation to a propyl group is rate-limiting and is followed by fast hydrogenation of the propyl group to form propane, which desorbs.¹⁵

In this work, the activation barrier to the hydrogenation of alkyl groups, $\Delta E_{\text{H}}^{\ddagger}$, has been measured by using a set of substituted alkyl and fluoroalkyl groups coadsorbed on Pt(111) with an excess of H atoms. The alkyl and fluoroalkyl groups were prepared by thermal dissociation of the corresponding iodides. The alkyl and fluoroalkyl substituent groups were bonded to the α -C and influenced the value of $\Delta E_{\text{H}}^{\ddagger}$. One important feature of this work has been the fact that it has used substituents varying in both their field and their polarizability substituent constants and has used enough different substituents to be able to correlate the impact of both field and polarizability effects on the nature of the transition state. This provides insight into the character of charge distribution both in the initial state and in the transition state, rather than just the change in charge distribution between the two states. The only other such study of both field and polarizability effects in an elementary surface reaction step has been a study of C–I bond cleavage on the Ag(111) surface.⁶ In the case of alkyl group hydrogenation on Pt(111) studied in this report, the correlation of the substituents' field and polarizability constants, σ_{F} and σ_{p} , with $\Delta E_{\text{H}}^{\ddagger}$ suggests that the initial-state alkyl groups are slightly anionic with respect to the transition state for hydrogenation, $\text{RC} + \text{H} \leftrightarrow \{\text{RC}^{\delta-} \cdots \text{H}\}^{\ddagger}$.

2. Experimental Section

All experiments were performed in an ultrahigh-vacuum chamber evacuated with a cryopump to a base pressure of 2×10^{-10} Torr. This chamber is equipped with a quadrupole mass spectrometer. It is also equipped with an Ar^+ ion gun for cleaning the surface and several leak valves for introduction of gases and vapors of the alkyl and fluoroalkyl iodides used in this study. In addition, X-ray photoelectron spectroscopy (XPS) was used to monitor the cleanliness of the surface and to measure the initial coverage of iodides.

The Pt(111) sample purchased from Monocrystals Co. was mounted by spot-welding it between two Ta wires connecting it to a manipulator, which allowed translation in the x , y , and z directions and rotation about the z -axis by 360° . The Pt(111) sample could be cooled to temperatures less than 90 K and resistively heated to temperatures greater than 1200 K. The temperature was measured by a chromel–alumel thermocouple spot-welded to the Pt(111) sample. The surface was first cleaned by cycles of Ar^+ sputtering, followed by annealing to 1000 K. Surface cleanliness was determined by using XPS. Between experiments, the surface was cleaned by annealing at 1000 K to desorb iodine and by annealing at 1000 K in 2×10^{-7} Torr of O_2 to remove any residual carbon from the sample surface.

The temperature-programmed reaction (TPR) spectra were obtained by using a Dycor M200M quadrupole mass spectrometer. The adsorption of alkyl iodides was performed with the Pt(111) surface cooled to 95 K. Exposures of the hydrogen and the alkyl iodides to the Pt(111) surface were recorded in units of Langmuirs ($1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$), with the pressure measured by an ion gauge and left uncorrected for ion-gauge sensitivity. After adsorption of the alkyl iodides, the sample was positioned in front of the aperture to the mass spectrometer. The Pt(111) sample was then heated at a rate of $\beta = 2 \text{ K/s}$ while using the mass spectrometer to monitor signals of desorbing species at up to five *mlq* ratios.

The relative initial coverages of the alkyl iodides and hydrogen reported in this paper were determined as follows. Atomic iodine was deposited onto the Pt(111) surface by adsorbing ethyl iodide onto a clean surface at approximately 95 K and annealing at 700 K for 60 s. This left atomic iodine on the surface without significant amounts of carbon. Higher total iodine coverages were achieved by repeated cycles of exposing the surface to 2 L of ethyl iodide and then heating to 700 K. The cumulative iodine coverage on the surface following each ethyl iodide adsorption and thermal decomposition cycle was measured by using XPS and is shown in Figure 1. It can be seen from Figure 1 that a cumulative ethyl iodide exposure of about 4 L saturated the Pt(111) surface with iodine. An ethyl iodide exposure of 1 L produced $\sim 30\%$ of the saturation coverage of iodine. Because one ethyl iodide molecule produces one iodine atom on the surface after annealing to 700 K, the iodine coverage can be used as a measure of the coverage of ethyl groups generated by ethyl iodide exposure. Except when indicated, the alkyl iodide exposures used in this work were controlled to give alkyl group coverages that corresponded to $\sim 30\%$ of the saturation coverage of iodine on the Pt(111) surface.

Hydrogen atoms were deposited onto the Pt(111) surface by exposing the clean surface at a temperature of 120 K to H_2 . The exposures of H_2 used in this study were 0, 1, 3, and 10 L. The coverage of hydrogen was determined by temperature-programmed desorption (TPD) measurements in which the Pt(111) surface was heated at a rate of 2 K/s while monitoring the desorption of hydrogen by using the mass spectrometer. A saturation coverage of atomic hydrogen was achieved after a 10 L exposure of the Pt(111) surface to H_2 . Exposures of 1 and 3 L produced hydrogen coverages of 40 and 70% of saturation, respectively.

The alkyl and fluoroalkyl iodides were purchased commercially from Aldrich Chemical Co. and SynQuest Laboratories, Inc., respectively. They were purified by cycles of freeze–pump–thawing before use. The purity of the gases and vapors introduced into the vacuum chamber were verified by using the mass spectrometer.

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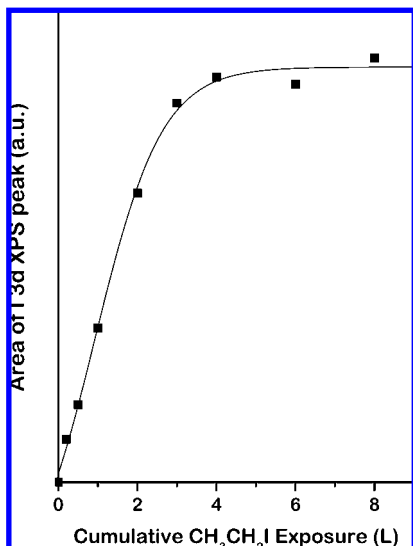


Figure 1. I 3d XPS signal on the Pt(111) surface during repeated exposures to ethyl iodide at 95 K, followed by thermal decomposition by heating to 700 K. Saturation of the Pt(111) surface with iodine occurs after a cumulative exposure of ~ 4 L.

3. Results

In this study, the hydrogenation kinetics of eight different alkyl and fluoroalkyl groups (Table 1) were measured on the Pt(111) surface. The alkyl and fluoroalkyl groups were prepared from the corresponding alkyl iodides by thermal dissociation of their C–I bonds on the Pt(111) surface. In the presence of preadsorbed hydrogen, heating resulted in hydrogenation of the alkyl groups to alkanes. This section is divided into three subsections describing the thermal decomposition of alkyl iodides, the hydrogenation of alkyl groups, and the hydrogenation of fluoroalkyl groups.

3.1. Formation of Alkyl and Fluoroalkyl Groups on Pt(111).

Thermal decomposition of alkyl iodides adsorbed on single-crystal metal surfaces is a well-established method for producing alkyl groups. In many studies, it has been shown that low-temperature adsorption of alkyl iodides, followed by heating, results in the dissociation of the C–I bond.^{16,17} Provided that the coverage of the atomic iodine coadsorbed with the alkyl groups does not approach saturation, the iodine acts as a passive spectator to subsequent reactions of the alkyl groups. On the Pt(111) surface, C–I bond cleavage in 1-iodopropane occurs at temperatures between 160 and 220 K and results in the formation of adsorbed *n*-propyl groups, CH₃CH₂CH₂–, and atomic iodine. On Pt(111) and Cu(111) surfaces, C–I bonds in ethyl iodide dissociate when heated to approximately 170 K.^{6,18} As in the cases of alkyl iodides, C–I bonds in fluoroalkyl iodides have been shown to cleave at temperatures below 200 K on Ag(111) and Pd(111) surfaces to produce adsorbed fluoroalkyl groups.^{6,7}

In this study, the C–I bonds in alkyl and fluoroalkyl iodides have been observed to break at temperatures below 200 K on the Pt(111) surface. C–I bond cleavage in CF₃CH₂CH₂I on Pt(111) is revealed by the I 3d_{5/2} XP spectra shown in Figure 2. CF₃CH₂CH₂I was adsorbed molecularly at 95 K on the Pt(111) surface with the C–I bond intact (note the I 3d_{5/2} peak

binding energy of $E_B = 620.8$ eV). The I 3d_{5/2} binding energy remained unchanged after annealing to a temperature of 160 K. Upon heating the sample to 200 K, however, the I 3d_{5/2} binding energy decreased by 0.7 eV to $E_B = 620.1$ eV. This shift to a lower binding energy is indicative of dissociation of the C–I bond and the deposition of the iodine atom on the Pt(111) surface and, as a consequence, the formation of an adsorbed CF₃CH₂CH₂– group. The I 3d_{5/2} peak areas in the XP spectra shown in Figure 2 remained constant until the sample temperature reached approximately 800 K, indicating that adsorbed iodine atoms are stable on the Pt(111) surface up to this temperature. In conclusion, CF₃CH₂CH₂I decomposes on the Pt(111) surface at temperatures below 200 K, leaving CF₃CH₂CH₂– and iodine on the surface.

On the Pt(111) surface, C–I bonds in other fluoroalkyl iodides are expected to break at temperatures below 200 K, the temperature by which CF₃CH₂CH₂I has decomposed to form CF₃CH₂CH₂– and iodine on the surface. It has been reported that the transition state for dehalogenation is homolytic on Ag(111) and Pd(111) surfaces and that the energy barriers to the cleavage of C–I bonds in different fluorine-substituted alkyl iodides on the Ag(111) and Pd(111) surfaces are relatively insensitive to the fluorination of the alkyl group.^{6,7} It has been reported also that the barriers to dehalogenation are relatively insensitive to the nature of the surface and that the range of these barriers is relatively small.¹ Accordingly, we expect that the barriers to C–I bond cleavage of all the alkyl and fluoroalkyl iodides that we have studied on the Pt(111) surface should be similar to that of CF₃CH₂CH₂I and that the C–I bonds are cleaved in all these species by annealing to ~ 200 K.

3.2. Hydrogenation of Alkyl Groups on Pt(111).

Heating of the alkyl and fluoroalkyl groups generated by alkyl iodide dissociation on the clean Pt(111) surface results in thermal decomposition in the temperature range 300–500 K. Figure 3 shows the TPR spectra obtained after exposure of the Pt(111) surface at 95 K to 1.5 L of 1-iodopropane. This exposure resulted in a coverage of 1-iodopropane that was $\sim 30\%$ of the saturation coverage of iodine on the Pt(111) surface. The desorption traces shown in Figure 3 were obtained by monitoring the signal of ionization fragments at $m/q = 2$ (hydrogen), 27 (propylene and propane), 29 (propane), and 127 (1-iodopropane). Heating this low coverage of 1-iodopropane leads to C–I bond cleavage but not to the desorption of the alkyl iodide or propane (the hydrogenation product). Although Zeera et al. did observe some formation of propane during the decomposition of propyl iodide on the clean Pt(111) surface, their experiment was performed with the propyl iodide at close to saturation coverage, whereas this experiment was performed at roughly one-third of the saturation coverage.¹¹ This coverage dependence of the self-hydrogenation is also consistent with the observations of White et al.¹² In our work, we observe that at low temperature, some propylene desorbs with a peak desorption temperature of approximately 150 K. This low-temperature feature indicates that there is some C–I bond cleavage on the surface at these temperatures. However, rather than indicating a low-temperature β -hydride elimination step leading to propylene desorption, it is quite possible that the signal at $m/q = 27$ is due to the direct desorption of a propyl group and its subsequent fragmentation in the ionizer of the mass spectrometer. This low-temperature formation of alkyl radicals during C–I cleavage has been observed before on Ni(100) and Cu(111) surfaces.^{19,20} Molecular

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Table 1. Field Substituent Constants ($\Sigma\sigma_F$), Polarizability Substituent Constants ($\Sigma\sigma_a$), Temperatures of Maximum Hydrogenation Rate (T_{max}), and Barriers to Hydrogenation (ΔE_{H}^\ddagger) of the Alkyl and Fluoroalkyl Groups Studied on the Pt(111) Surface

alkyl group	substituents	field constants	$\Sigma\sigma_F$	polarizability constants	$\Sigma\sigma_a$	T_{max}	ΔE_{H}^\ddagger (kJ/mol)
CH ₃ CH ₂ –	CH ₃	0	0	–0.35	–0.35	234	60.8
CH ₃ CH ₂ CH ₂ –	CH ₃ CH ₂	0	0	–0.49	–0.49	232	60.3
(CH ₃) ₂ C(H)–	H	0	0	0	–0.70	211	54.6
(CH ₃) ₃ C–	CH ₃	0	0	–0.35	–1.05	189	48.8
	CH ₃	0		–0.35			
	CH ₃	0		–0.35			
	CH ₃	0		–0.35			
CF ₃ CH ₂ CH ₂ CH ₂ –	CF ₃ CH ₂ CH ₂	0.12	0.12	–0.55	–0.55	245	63.7
CF ₃ CH ₂ CH ₂ –	CF ₃ CH ₂	0.23	0.23	–0.46	–0.46	258	67.2
CF ₃ CF ₂ CH ₂ CH ₂ –	CF ₃ CF ₂ CH ₂	0.24	0.24	–0.53 ^a	–0.53	258	67.2
(CF ₃) ₂ CHCH ₂ –	(CF ₃) ₂ CH	0.44	0.44	–0.57	–0.57	263	68.6

^a Estimated on the basis of substituent-group additivity and a fall-off factor of 2.3 with the number of carbon atoms from reaction center.^{26,27}

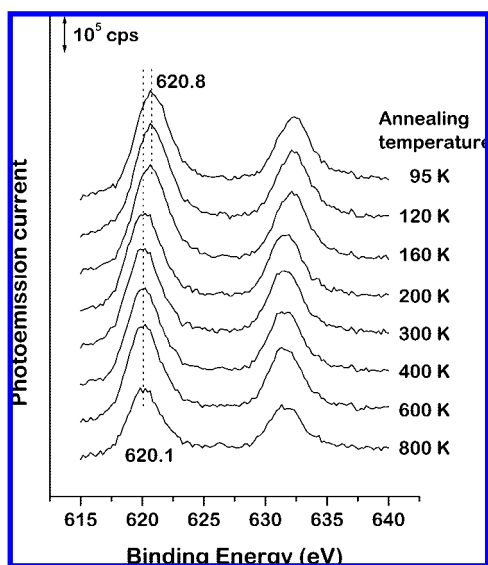


Figure 2. I 3d XPS of the Pt(111) surface after exposure to 2 L of CF₃CH₂CH₂I at 95 K and subsequent annealing to the temperatures indicated on the right. The I 3d_{5/2} binding energies are 620.8 eV for iodine in the adsorbed CF₃CH₂CH₂I and 620.1 eV for iodine atoms on the Pt(111) surface.

hydrogen desorption occurred with two peaks centered at approximately 315 and 415 K. These results are similar to those reported by White et al.¹² This behavior is typical of *n*-propyl groups on transition-metal surfaces where they undergo β -hydride elimination to form di- σ -bonded propylene.¹² Subsequently, the di- σ -bonded propylene dehydrogenates to form propylidyne, CH₃CH₂C≡Pt, which decomposes to graphitic carbon and atomic hydrogen at temperatures above 400 K. The hydrogen desorption peak at 315 K is attributed to the recombination of hydrogen atoms released by the β -hydride elimination of propyl groups and the decomposition of the di- σ -bonded propylene to propylidyne. The hydrogen desorption peak at 415 K is due to the decomposition of propylidyne.¹¹ The assignment of the peak at 315 K to recombination of hydrogen atoms on the Pt(111) surface is supported by the fact that the peak desorption temperature of hydrogen from the clean Pt(111) surface is observed in the range 270–320 K. The broad hydrogen desorption peaks at higher temperatures arise from the decomposition of hydrocarbon fragments remaining on the surface. The important observation from the point of view of this work is that there is no propane formed during decomposition of propyl groups on the clean Pt(111) surface.

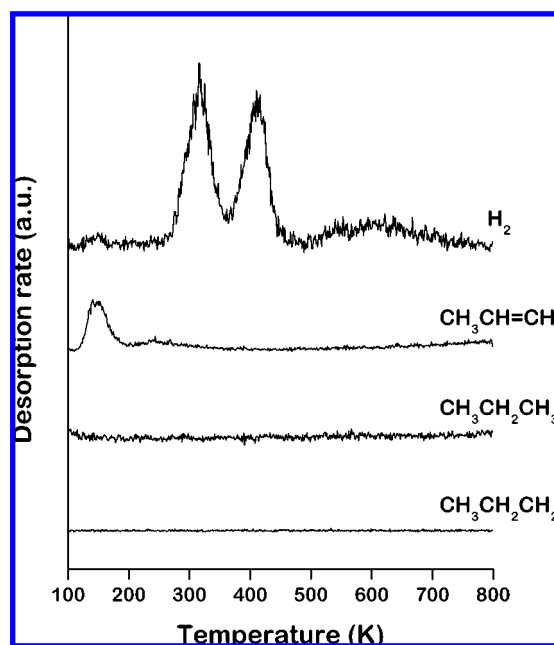


Figure 3. TPR spectra of 1.5 L CH₃CH₂CH₂I on clean Pt(111). The surface was exposed to CH₃CH₂CH₂I at 95 K. The heating rate was 2 K/s. Signals were monitored at $m/q = 2, 27, 29,$ and 127. No production of propane is observed.

TPR spectra of coadsorbed hydrogen and propyl groups on the Pt(111) surface reveal the formation and desorption of propane. Figure 4 shows the TPR spectra obtained from the Pt(111) surface by using hydrogen pre-exposures of 0, 1, 3, and 10 L at 120 K followed by exposures of 1.5 L of 1-iodopropane at 95 K. An exposure of 10 L of H₂ produced a monolayer (saturation coverage) of hydrogen atoms on the Pt(111) surface, whereas exposures of 1 and 3 L of H₂ produced approximately 0.4 and 0.7 ML of hydrogen, respectively. Figure 4 clearly reveals the reaction between adsorbed hydrogen atoms and propyl groups, resulting in the formation and desorption of propane at approximately 235 K. Figure 4 also reveals that the propane desorption-peak temperature is independent of the adsorbed hydrogen coverage.

The coadsorption of hydrogen and other alkyl iodides on the Pt(111) results in the formation of alkanes during subsequent heating. In TPR of propyl groups coadsorbed with high hydrogen coverages, no propylene desorption is observed. TPR spectra of iodoethane, 2-iodopropane, and 2-iodo-2-methyl propane coadsorbed with hydrogen atoms on Pt(111) surfaces

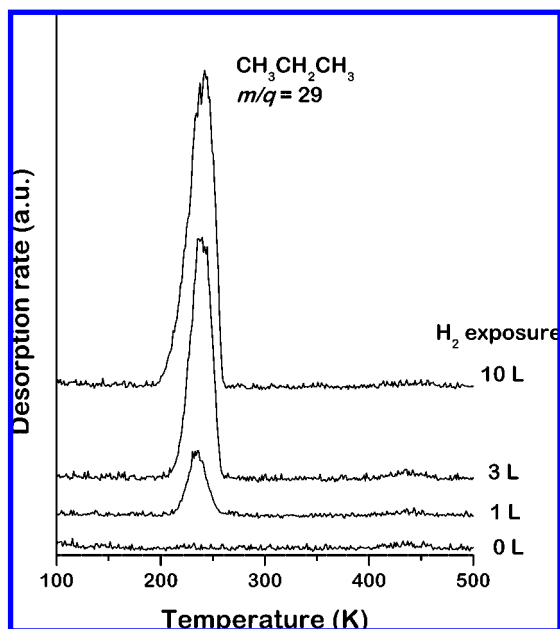


Figure 4. TPR spectra of 1.5 L $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ on Pt(111) with different pre-exposures to H_2 . The surface was first exposed to H_2 at 120 K and then to 1.5 L of $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ at 95 K. The heating rate was 2 K/s. The desorption of propane was monitored by collecting the signal at $m/q = 29$ and is observed to occur once hydrogen has been preadsorbed on the surface.

that were first exposed to 0, 1, 3, and 10 L of H_2 are similar to those obtained by using 1-iodopropane. In the absence of preadsorbed hydrogen, there is no alkane formation. As shown in Table 1, the alkanes produced by the hydrogenation of the alkyl groups by preadsorbed hydrogen all form at different temperatures. For the alkyl iodides studied in this work, the alkane desorption temperature is independent of the hydrogen coverage on the Pt(111) surface.

In order to prove that the evolution of alkanes from the Pt(111) surface during alkyl hydrogenation is not rate-limited by desorption of the alkane product, TPD spectra of butane on the Pt(111) surface were obtained (data not shown). During heating, submonolayer coverages of butane desorbed at approximately 175 K, and it is reasonable to expect that submonolayer coverages of ethane, propane, and iso-butane would desorb at even lower temperatures. The peak temperatures for alkane desorption during alkyl hydrogenation are all higher than 175 K, indicating that the evolution of the alkanes from the Pt(111) surface is rate-limited by the hydrogenation step rather than by the desorption of the alkane product. Thus, the peak temperatures for alkane desorption during TPRS of coadsorbed hydrogen and alkyl groups can be used to estimate the activation barriers for hydrogenation, $\Delta E_{\text{H}}^{\ddagger}$.

In order to confirm that the alkanes formed during TPR of coadsorbed hydrogen and alkyl groups were the product of alkyl hydrogenation rather than olefin hydrogenation, TPR experiments were performed by using hydrogen and propylene coadsorbed on a Pt(111) surface. TPR spectra were obtained from the Pt(111) surface exposed to 1 L of H_2 followed by 0.35 L of propylene. XPS of the C 1s level showed that the coverage of propylene was approximately the same as the coverage of propyl groups used in the TPR experiments described above. On the Pt(111) surface prepared with coadsorbed hydrogen and propyl groups, propane desorption occurred at approximately 235 K (Figure 3), whereas with propylene as the precursor,

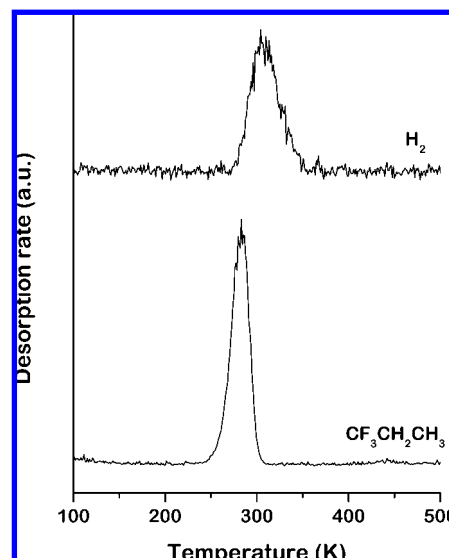


Figure 5. TPR spectra of 2 L of $\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$ on clean Pt(111). The surface was exposed to $\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$ at 95 K. The heating rate was 2 K/s. Signals were monitored at $m/q = 2$ and 29. Heating of adsorbed $\text{CF}_3\text{CH}_2\text{CH}_2-$ does lead to the formation and desorption of trifluoropropane.

propane desorption occurred at 270 K. These results indicate that hydrogenation of the alkyl groups is kinetically favored over hydrogenation of the olefin. Furthermore, a previous study of the TPR of propyl groups coadsorbed with deuterium has shown that the product is dominated by d_1 -propane, again suggesting that there is little contribution from an olefin intermediate.¹¹ Thus, during TPR of coadsorbed alkyl iodides and hydrogen on the Pt(111) surface, alkane desorption is rate-limited by alkyl group hydrogenation rather than olefin hydrogenation.

3.3. Hydrogenation of Fluoroalkyl Groups on Pt(111). Adsorption of fluoroalkyl iodides on the Pt(111) surface leads to the formation and desorption of fluoroalkanes during heating. Figure 5 shows the TPR spectra obtained after a 2 L exposure of $\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$ to the clean Pt(111) surface at 95 K. As in the case of $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$, this exposure resulted in a coverage of $\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$ that was equal to $\sim 30\%$ of the saturation coverage of iodine on the Pt(111) surface. In contrast to the TPR spectra obtained from the alkyl iodides on the clean Pt(111) surface, which showed no alkane production, a peak attributed to desorption of trifluoropropane was observed at 285 K during heating of adsorbed $\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$. The desorption of trifluoropropane was confirmed by monitoring the signals of ionization fragments at $m/q = 29$ (CH_2CH_3^+), 59 (CFCHCH_3^+), 69 (CF_3^+), and 79 ($\text{CF}_2\text{CH}_2\text{CH}_3^+$). The source of hydrogen for this self-hydrogenation must be the decomposition of $\text{CF}_3\text{CH}_2\text{CH}_2-$ groups. One of the most likely mechanisms of hydrogen release is β -hydride elimination by the $\text{CF}_3\text{CH}_2\text{CH}_2-$ groups on the Pt(111) surface.²¹ Hydrogen then reacts with the remaining $\text{CF}_3\text{CH}_2\text{CH}_2-$ groups to produce $\text{CF}_3\text{CH}_2\text{CH}_3$. As has been shown in previous work, fluorination of the propyl group increases the barrier to β -hydride elimination.^{21,22} As a result, β -hydride elimination occurs at a higher temperature in $\text{CF}_3\text{CH}_2\text{CH}_2-$ than in $\text{CH}_3\text{CH}_2\text{CH}_2-$. At a higher temperature, the rate constant for hydrogenation is higher, and thus, the

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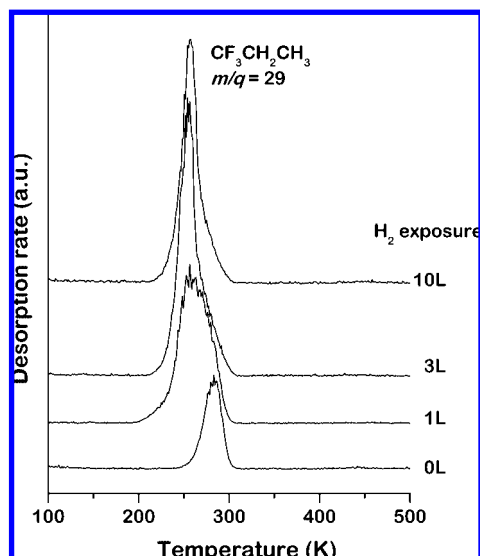


Figure 6. TPR spectra of 2 L of $\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$ on Pt(111) with different pre-exposures to H_2 . The surface was first exposed to H_2 at 120 K and then to 2 L of $\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$ at 95 K. The heating rate was 2 K/s. The desorption of trifluoropropane was monitored by collecting the signal at $m/q = 29$. In the presence of preadsorbed hydrogen, the peak temperature for trifluoropropane desorption decreases, indicating that the rate of hydrogenation by preadsorbed hydrogen is faster than that by self-hydrogenation.

$\text{CF}_3\text{CH}_2\text{CH}_2-$ groups self-hydrogenate, whereas the $\text{CH}_3\text{CH}_2\text{CH}_2-$ groups do not. Figure 5 also shows that hydrogen desorption occurs over the temperature range from 275 to 350 K, with a peak centered at approximately 310 K. Hydrogen is clearly being released onto the Pt(111) surface at the temperatures at which trifluoropropane is desorbing into the gas phase. In the absence of preadsorbed hydrogen, the desorption of trifluoropropane during $\text{CF}_3\text{CH}_2\text{CH}_2-$ decomposition is probably rate-limited by the kinetics of β -hydride elimination rather than hydrogenation.

In the presence of preadsorbed hydrogen on the Pt(111) surface, fluoroalkyl groups undergo hydrogenation without prior β -hydride elimination. TPR spectra of $\text{CF}_3\text{CH}_2\text{CH}_2-$ groups (Figure 6) reveal that the $\text{CF}_3\text{CH}_2\text{CH}_3$ desorption temperature decreases as the hydrogen pre-exposure increases from 0 to 3 L and then remains constant at 258 K as the hydrogen pre-exposure increases from 3 to 10 L. This temperature is significantly lower than the temperature of 285 K observed for $\text{CF}_3\text{CH}_2\text{CH}_3$ desorption during $\text{CF}_3\text{CH}_2\text{CH}_2-$ decomposition on Pt(111) in the absence of preadsorbed hydrogen. This shift in the peak hydrogenation temperature suggests that the rate-limiting step for hydrogenation switches from the β -hydride elimination step, in the absence of preadsorbed hydrogen, to the C–H bond formation step, in the presence of preadsorbed hydrogen. The peak temperature of 258 K was used to estimate the activation barrier for hydrogenation of $\text{CF}_3\text{CH}_2\text{CH}_2-$ groups on the Pt(111) surface.

The hydrogenation kinetics of three other fluoroalkyl groups ($\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2-$, $\text{CF}_3\text{CH}_2\text{CH}_2-$, and $(\text{CF}_3)_2\text{CHCH}_2-$) on the Pt(111) surface are similar to those of $\text{CF}_3\text{CH}_2\text{CH}_2-$. The TPR spectra of these four fluoroalkyl iodides coadsorbed with hydrogen on the Pt(111) surface are shown in Figure 7. The hydrogenation temperatures for $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2-$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2-$, and $\text{CF}_3\text{CH}_2\text{CH}_2-$ were approximately 245, 258, and 258 K, respectively. As the extent of fluorination increases, the $\Delta E_{\text{H}}^\ddagger$ increases, and thus, the observed hydrogenation temper-

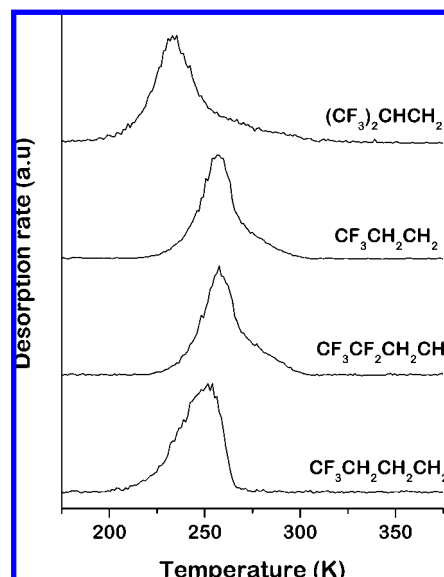


Figure 7. TPR spectra of fluoroalkyl iodides coadsorbed with hydrogen on Pt(111). The surface was first exposed to 10 L of H_2 at 120 K and then to fluoroalkyl iodides at 95 K. The exposure to fluoroalkyl iodides was controlled to give a coverage roughly equal to 30% of the saturation coverage of iodine on the Pt(111) surface. The heating rate was 2 K/s.

ature increases. On the basis of this trend for the hydrogenation of fluoroalkyl groups, one would expect that the hydrogenation temperature of $(\text{CF}_3)_2\text{CHCH}_2-$, the most highly fluorinated of the reactants used, would be the highest among those of these four fluoroalkyl groups; however, Figure 7 shows that $(\text{CF}_3)_2\text{CHCH}_2-$ seems to behave anomalously. The hydrogenation temperature of $(\text{CF}_3)_2\text{CHCH}_2-$ was the lowest among those of the four fluoroalkyl groups. This anomaly might arise from steric effects of $(\text{CF}_3)_2\text{CHCH}_2-$, which differ from those of the other straight-chain fluoroalkyl groups because $(\text{CF}_3)_2\text{CHCH}_2$ is branched. To demonstrate the impact of steric effects on the hydrogenation of $(\text{CF}_3)_2\text{CHCH}_2-$, Figure 8 shows a comparison of TPR spectra obtained by exposing the Pt(111) surface to 10 L of H_2 , followed by 2.4 and 0.5 L exposures to $(\text{CF}_3)_2\text{CHCH}_2\text{I}$. The hydrogenation temperature for $(\text{CF}_3)_2\text{CHCH}_2$ was observed to increase from 235 to 263 K as a result of decreasing the exposure of $(\text{CF}_3)_2\text{CHCH}_2\text{I}$. At the lower exposure (0.5 L), the surface is not crowded with $(\text{CF}_3)_2\text{CHCH}_2-$, and the interactions between $(\text{CF}_3)_2\text{CHCH}_2-$ molecules are negligible. The peak hydrogenation temperature of 263 K observed after the 0.5 L exposure to $(\text{CF}_3)_2\text{CHCH}_2\text{I}$ was the highest among those of the four fluoroalkyl groups used in this study. The possible role of steric effects on the hydrogenation kinetics of the straight-chain fluoroalkyl groups were explored by using $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, the longest of the straight-chain fluoroalkanes. TPR spectra were obtained from Pt(111) surfaces pre-exposure to 10 L H_2 and then exposure to 0.5 and 2.3 L of $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ (data not shown). The hydrogenation temperatures were the same for the two exposure conditions, suggesting that exposures to the straight-chain fluoroalkyl iodides of ≤ 2.3 L were low enough to limit steric effects.

As in the case of the hydrogenation of alkyl groups, it is also important to demonstrate that evolution of fluoroalkanes from the Pt(111) surface is rate-limited by hydrogenation and not by the desorption of fluoroalkanes. Not all the fluoroalkanes produced are commercially available; hence, it was not possible to experimentally measure the molecular desorption kinetics of

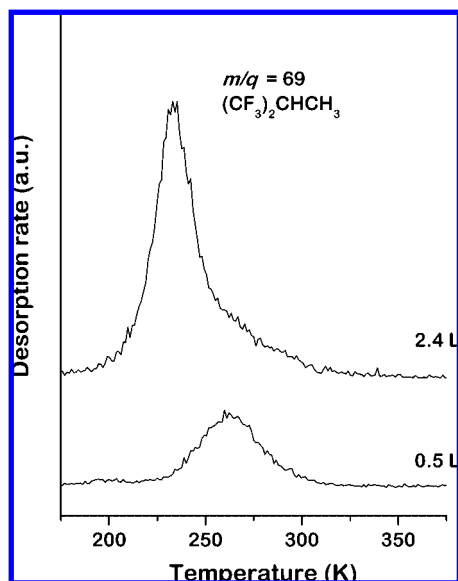


Figure 8. TPR spectra of $(\text{CF}_3)_2\text{CHCH}_2\text{I}$ coadsorbed with hydrogen on Pt(111). The surface was first exposed to 10 L of H_2 at 120 K and then to $(\text{CF}_3)_2\text{CHCH}_2\text{I}$ at 95 K (2.4 or 0.5 L). The heating rate was 2 K/s. The desorption of $(\text{CF}_3)_2\text{CHCH}_3$ was monitored by collecting the signal at $m/q = 69$. Decreasing the exposure to $(\text{CF}_3)_2\text{CHCH}_2\text{I}$ increases the hydrogenation temperature.

all four fluoroalkane products. Instead, however, it is sufficient to consider the previously mentioned results for the kinetics of butane desorption from the clean Pt(111) surface. The peak desorption temperature of submonolayer butane coverages on the Pt(111) surface was approximately 175 K, well below the fluoroalkane desorption temperatures observed after hydrogenation of the fluoroalkyl groups. The desorption energy and thus the desorption-peak temperature of fluorinated alkyl ethers have been found to be lower than those of their hydrocarbon ether counterparts on the Cu(111), Al(110), and Pt(111) surfaces.^{23–25} It is reasonable to assume that the desorption energies and desorption-peak temperatures of fluorinated alkanes will also be lower than those of their hydrocarbon counterparts. TPD showed that desorption of butane from the Pt(111) surface occurs at approximately 175 K, suggesting that $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_3$, $\text{CF}_3\text{CH}_2\text{CH}_3$, and $(\text{CF}_3)_2\text{CHCH}_3$ should desorb at even lower temperatures. The fact that the peak temperatures for fluoroalkane desorption following hydrogenation of the four fluoroalkyl groups are all >200 K indicates that the appearance of the fluoroalkane products in the gas phase is rate-limited by hydrogenation rather than by desorption. Thus, the peak temperatures for fluoroalkane desorption observed in TPR spectra of fluoroalkyl groups and hydrogen coadsorbed on the Pt(111) surface can be used to estimate the activation barriers, $\Delta E_{\text{H}}^\ddagger$, for hydrogenation of the fluoroalkyl groups.

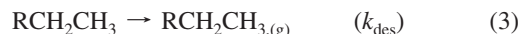
4. Discussion

4.1. Analysis of Alkyl Hydrogenation Kinetics on Pt(111).

The TPR spectra of alkyl groups and hydrogen coadsorbed on the Pt(111) surface have been obtained in order to measure the

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barriers to hydrogenation of a set of alkyl and fluoroalkyl groups with varying degrees of fluorine substitution and alkyl group size. On the hydrogen saturated Pt(111) surface, the hydrogenation mechanism is assumed to occur via the elementary steps shown below.



Here, $\text{RCH}_2\text{CH}_2\text{-I}$ is chosen to represent the alkyl iodides with different substituents, R. Prior to the reaction, H_2 is adsorbed dissociatively to produce hydrogen atoms, and the alkyl iodide is adsorbed at low temperature. During heating, the C–I bond of the alkyl iodide dissociates at temperatures below 200 K to produce an alkyl group and an iodine atom. Cleavage of the C–I bond is facile and occurs at lower temperatures than the subsequent reaction steps. The second reaction step is the hydrogenation of the alkyl group by preadsorbed hydrogen to form an adsorbed alkane. Preadsorption of deuterium rather than hydrogen results predominantly in the formation of d_1 -propane in the case of propyl groups on Pt(111).¹¹ The final reaction step is the desorption of the alkane. Our independent measurements of the alkane desorption kinetics show that the rate constant for desorption of the alkane is much higher than the rate constant for hydrogenation of the alkyl group, $k_{\text{des}} > k_{\text{H}}$. Therefore, the hydrogenation of the alkyl group is the rate-limiting step in the production and desorption of the alkane.

Dehydrogenation (β -hydride elimination) of the alkyl group on the Pt(111) surface must be considered as a possible source of hydrogen for hydrogenation of alkyl groups to alkanes. The alkyl group could lose a hydrogen atom by β -hydride elimination to form an olefin. The olefin could then either desorb from the surface or react further to form an alkylidyne.^{11,12} Previous study of the thermal activation of propyl (isopropyl and *n*-propyl) groups on the Pt(111) surface has demonstrated that the presence of preadsorbed hydrogen greatly increases the propane yield at the expense of propene production; in the case of *n*-propyl groups, no propene desorption was detected in the absence of preadsorbed hydrogen.¹¹ Under our experimental conditions, with a monolayer coverage of preadsorbed hydrogen, it is reasonable to assume that hydrogenation by adsorbed hydrogen atoms is the predominant reaction path leading to the formation of alkanes. Thus, the alkane desorption kinetics can be used to measure the kinetics of the hydrogenation of alkyl groups.

Analysis of the kinetics for the formation of alkanes by hydrogenation of alkyl groups are discussed in the Supporting Information. Because the measurement is performed with an excess of hydrogen initially adsorbed on the surface, the overall hydrogenation and alkane desorption kinetics are pseudo-first-order in the alkyl group coverage, and the desorption kinetics can be analyzed by using the first-order Redhead equation and an estimated pre-exponential factor of $\nu = 10^{13} \text{ s}^{-1}$ to obtain estimates of the barriers to hydrogenation, $\Delta E_{\text{H}}^\ddagger$. This is consistent with the analysis by Zaera et al. of the kinetics of ethyl group hydrogenation to ethane on the Pt(111) surface.¹³ There have been no careful measurements of the pre-exponential factors for this type of two-component second-order surface reaction. It should be pointed out that a systematic error in the value of the pre-exponent used in this work would change the estimated barriers to hydrogenation, $\Delta E_{\text{H}}^\ddagger$, systematically. It would not change the trend observed for the substituent effects

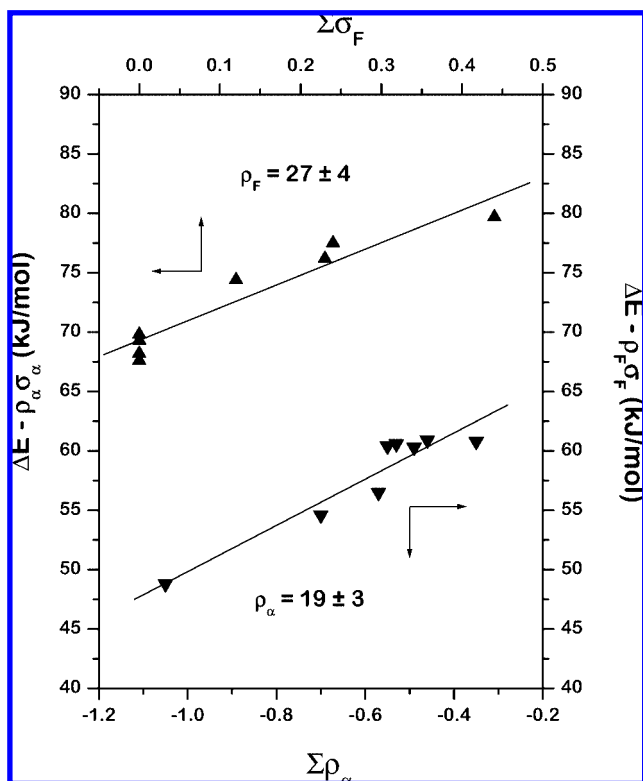


Figure 9. Linear free energy relationship for the barriers to hydrogenation, $\Delta E_{\text{H}}^{\ddagger}$, of alkyl and fluoroalkyl groups on Pt(111) by using a two-variable linear fit to the field (σ_{F}) and polarizability (σ_{α}) substituent constants. The field effect is plotted by using the top- and left-hand axes. The polarizability effect is plotted by using the bottom- and right-hand axes. The reaction constants are $\rho_{\text{F}} = 27 \pm 4$ kJ/mol and $\rho_{\alpha} = 19 \pm 3$ kJ/mol.

or the qualitative insights into the nature of the transition states obtained from our ultimate interpretation of these trends.

4.2. Transition state for Hydrogenation of Alkyl Groups. The goal of this study has been to probe the nature of the transition state for alkyl group hydrogenation by hydrogen atoms on the Pt(111) surface by measuring the activation barriers for hydrogenation, $\Delta E_{\text{H}}^{\ddagger}$, of a set of different alkyl and fluoroalkyl groups. The alkyl and fluoroalkyl groups used in this study have substituents, R, with a range of field substituent constants, $\sigma_{\text{F}}^{\text{R}}$, and polarizability substituent constants, $\sigma_{\alpha}^{\text{R}}$, found in the literature.^{26,27} As can be seen from Table 1, the values of $\Delta E_{\text{H}}^{\ddagger}$ are influenced by the substituents on the alkyl groups. The values of $\Delta E_{\text{H}}^{\ddagger}$ can be correlated with the field and polarizability substituent constants by using a simple linear free energy relationship.

$$\Delta E_{\text{H}}^{\ddagger}(\text{R}) = \rho_{\alpha}\sigma_{\alpha}^{\text{R}} + \rho_{\text{F}}\sigma_{\text{F}}^{\text{R}} + \Delta E_{\text{H}}^{\ddagger}(\text{H}) \quad (4)$$

The reaction constants, ρ_{F} and ρ_{α} , are measures of the sensitivity of the barrier to the field and polarizability effects of the substituents, respectively. The quantity $\Delta E_{\text{H}}^{\ddagger}(\text{H})$ is the barrier to hydrogenation of an alkyl group with hydrogen as a substituent, which in this study would be the case for an adsorbed methyl group, $\text{H}_3\text{C}-$. The values of ρ_{F} and ρ_{α} have been determined by fitting eq 4 to the data in Table 1, and the results are illustrated in Figure 9. The field effect has been isolated by plotting $\Delta E_{\text{H}}^{\ddagger}(\text{R}) - \rho_{\alpha}\sigma_{\alpha}^{\text{R}}$ versus $\sigma_{\text{F}}^{\text{R}}$ by using the top- and the left-hand axes, whereas the polarizability effect has been isolated by plotting $\Delta E_{\text{H}}^{\ddagger}(\text{R}) - \rho_{\text{F}}\sigma_{\text{F}}^{\text{R}}$ versus $\sigma_{\alpha}^{\text{R}}$ by using the bottom- and the right-hand axes. The value of the field

reaction constant is $\rho_{\text{F}} = 27 \pm 4$ kJ/mol, and the value of the polarizability reaction constant is $\rho_{\alpha} = 19 \pm 3$ kJ/mol.

The reaction constants provide some insight into the nature of the transition state for alkyl group hydrogenation on the Pt(111) surface. The field effect substituent constant is an empirical measure of the dipole moment of the substituent. The field substituent constant increases with increasing fluorination, which generates a dipole with its positive end oriented close to the hydrogenation reaction center. The fact that ρ_{F} is positive indicates that increasing the dipole moment of the substituent increases the reaction barrier or, in other words, destabilizes the transition state with respect to the initial state. This is consistent with a reaction in which the reaction center, the α -carbon atom, is more electropositive in the transition state than in the initial state alkyl group. To put the magnitude of $\rho_{\text{F}} = 27 \pm 4$ kJ/mol into perspective, it can be compared to the values of ρ_{F} for other surface reactions. An example of a heterolytic process is the β -hydride elimination reaction of alkoxides to form aldehydes on the Cu(111) surface. In that reaction, the value of the field reaction constant is $\rho_{\text{F}} \approx 150$ kJ/mol, and the β -carbon atom is cationic or electropositive in the transition state with respect to the initial state, $\{\text{RC}^{\delta+} \cdots \text{H}\}^{\ddagger}$.⁵ An example of a homolytic process is the C–I cleavage in the alkyl and fluoroalkyl iodides on the Ag(111) surface, where the reaction constant has a value of $\rho_{\text{F}} = -17$ kJ/mol. Because the reaction constant for C–I cleavage is quite small, the transition state can be described as homolytic, although the fact that $\rho_{\text{F}} < 0$ indicates that there is a slight increase in electron density in the transition state relative to the initial state.⁶ The value of ρ_{F} for hydrogenation of alkyl groups on the Pt(111) surface is higher than that for C–I cleavage on the Ag(111) surface but with the opposite sign. The positive but relatively low value of ρ_{F} indicates that the transition state for hydrogenation of alkyl groups is slightly cationic with respect to the initial state or, in other words, that there is a slight decrease in electron density at the reaction center in the transition state leading to the formation of the C–H bond, $\{\text{RC}^{\delta+} \cdots \text{H}\}^{\ddagger}$.

The value of the polarizability reaction constant for alkyl group hydrogenation on the Pt(111) surface is $\rho_{\alpha} = 19 \pm 3$ kJ/mol. Polarizability always stabilizes nearby charges by screening. If the charge density (positive or negative) is greater in the transition state than in the reactant, highly polarizable substituents will stabilize the energy of the transition state and thus lower the reaction barrier. If the charge density (positive or negative) is higher in the reactant than in the transition state, highly polarizable substituents will stabilize the energy of the reactant and thus increase the reaction barrier. Note that the convention used for polarizability constants is that σ_{α} takes on increasingly negative values as the polarizability of the substituent group increases.^{26,27} Thus, a substituent with greater polarizability (more negative value of σ_{α}) energetically stabilizes (lowers) the energy of nearby charges. The value of $\rho_{\alpha} = 19 \pm 3$ kJ/mol for hydrogenation of alkyl groups on the Pt(111) surface indicates that the polarizability of the substituent is stabilizing the transition state with respect to the initial state. Thus, the charge density on the α -carbon must be slightly greater in the transition state than in the reactant. Our final picture of the transition state for alkyl group hydrogenation on the Pt(111) surface is shown in Figure 10.

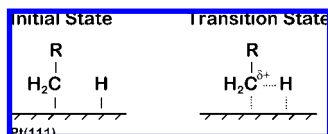


Figure 10. Transition state for alkyl group hydrogenation on the Pt(111) surface. The substituent effects reveal that the transition state is relatively cationic with respect to the initial state and that the transition state holds a higher charge density.

5. Conclusion

The activation barriers to hydrogenation, $\Delta E_{\text{H}}^{\ddagger}$, of substituted alkyl groups adsorbed on the Pt(111) surface have been shown to be influenced by the field effects and polarizability of the substituents. One important feature of this work has been the fact that it has used substituents varying in both their field and polarizability substituent constants and has used enough different substituents to be able to correlate the impact of both field and polarizability effects on the nature of the transition state. This provides insight into the character of charge distribution in both the initial state and in the transition state, rather than just the

change in charge distribution between the two states. The only other such study of both field and polarizability effects in a surface reaction has been a study of C–I bond cleavage on the Ag(111) surface.⁶ In the case of alkyl group hydrogenation on Pt(111), both the field effect, $\rho_{\text{F}} = 27 \pm 4$ kJ/mol, and the polarizability effect, $\rho_{\alpha} = 19 \pm 3$ kJ/mol, cause the barrier to hydrogenation to increase. The magnitude of the reaction constants is small but suggests that the α -carbon in the transition state for hydrogenation of alkyl groups on Pt(111) is slightly cationic with respect to the α -carbon atom in an adsorbed alkyl group and that the charge density on the α -carbon in the transition state is slightly higher than in the reactant.

Acknowledgment. This work has been funded by NSF grant number CBET-0651182.

Supporting Information Available: Details of the kinetic analysis of the TPD spectra to yield estimates of the activation energies for alkyl group hydrogenation, $\Delta E_{\text{H}}^{\ddagger}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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