Transition State for *β*-Hydride Elimination in Alkyl Groups on Pt(111)

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The transition state for *β*-hydride elimination in alkyl groups on the Pt(111) surface has been probed by studying the effects of fluorine substitution on the barriers to *β*-hydride elimination, $\Delta E^{\ddagger}_{\beta H}$. Four different fluoroalkyl groups have been formed on the Pt(111) surface by dissociative adsorption of four fluoroalkyl iodides: RCH_2CH_2-I (R = CF_3, CF_3CH_2, and CF_3CF_2) and $(CF_3)_2CHCH_2-I$. In the absence of preadsorbed hydrogen, fluoroalkyl groups on the Pt(111) surface dehydrogenate via *β*-hydride elimination to form unsaturated fluorocarbons and deposit hydrogen atoms onto the surface. Those hydrogen atoms then hydrogenate the remaining fluoroalkyl groups to produce fluoroalkanes that desorb rapidly from the surface. The kinetics of hydrogenation and fluoroalkane desorption are rate limited by the *β*-hydride elimination step and thus serve as measures of the kinetics of *β*-hydride elimination. The field effects of the fluorinated substituents increase the barriers to *β*-hydride elimination with a reaction constant of $\rho_F = 19 \pm 2$ kJ/mol. The interpretation of this effect is that the *β*-carbon atom in the transition state is cationic, $[RC^{\delta+}\cdots H]^{\ddagger}$, with respect to the reactant. The field effect of the fluorinated substituent energetically destabilizes the electron deficient *β*-carbon atom in the transition state. This is consistent with observations made on the Cu(111) surface; however, the substituent effect is significantly smaller on the Pt(111) surface. On the Pt(111) surface, the transition state for *β*-hydride elimination is less polarized with respect to the initial state alkyl group than on the Cu(111) surface.

1. Introduction

The *β*-hydride elimination reaction is an important elementary reaction step in the surface chemistry and organometallic chemistry of alkyl and alkoxy groups. These species can be formed on many metal surfaces by the dissociative adsorption of alcohols or alkyl iodides, and under reaction conditions, *β*-hydride elimination is the most favored dehydrogenation pathway.[1−6] As an example, during temperature programmed reaction studies, ethoxy groups, CH_3CH_2O-, on Ag and Cu surfaces decompose by cleavage of a *β*-CH bond to produce acetaldehyde which desorbs rapidly into the gas phase.[7] Ethyl groups, CH_3CH_2-, on Cu(110) decompose via *β*-hydride elimination at 225 K to produce ethylene, which desorbs rapidly.[3] *β*-Hydride elimination in CH_3CH_2- and CD_3CD_2- groups leads to the formation of $CH_2=CH_2$ and $CD_2=CD_2$, respectively . These products desorb with kinetics that reveal a deuterium isotope effect indicating that the evolution of ethylene into the gas phase is rate-limited by *β*-hydride elimination.[3] *β*-Hydride elimination is also a common elementary reaction step of adsorbed alkyl and alkoxy groups in heterogeneous catalytic reactions; therefore, understanding the nature of the transition state to *β*-hydride elimination can provide insight into the function of catalytic surfaces in a number of important catalytic processes.

Over the past 15 years, the nature of the transition states for *β*-hydride elimination and other surface reactions have been investigated using substituent effects.[8−10] The general application of fluorine substituent effects to probe the transition states for surface reactions has been reviewed elsewhere.[10] The first of such studies focused on *β*-hydride elimination in substituted ethoxy groups on Cu(111).[7] In that study, fluorine substituent effects were used to perturb the activation barriers to *β*-hydride elimination, $\Delta E^{\ddagger}_{\beta H}$, in adsorbed ethoxy groups ($R-CH_2O-Cu$, R = CH_3, CFH_2, CF_2H, and CF_3). Fluorination of the methyl group in ethoxy groups on Cu(111) systematically increased the value of $\Delta E^{\ddagger}_{\beta H}$ from 121 ± 4 kJ/mol in ethoxy to 176 ± 6 kJ/mol in trifluoroethoxy. The conclusion drawn from that study was that the formation of the transition state for the *β*-hydride elimination in ethoxy groups involves charge separation that leaves the *β*-carbon atom in the transition state cationic, $[RC^{\delta+}\cdots H]^{\ddagger}$, with respect to the initial state. Fluorination of the methyl group energetically destabilizes the cationic transition state with respect to the initial state, thus raising the barrier to *β*-hydride elimination. A similar investigation studied the transition state for *β*-hydride elimination in alkyl groups on Cu-(111).[11] In that investigation, the $\Delta E^{\ddagger}_{\beta H}$ for trifluoropropyl groups, $CF_3CH_2CH_2-$, was found to be higher than that for propyl groups, $CH_3CH_2CH_2-$. Both of these studies on the Cu-(111) surface indicate that the transition state for *β*-hydride elimination is cationic, $[RC^{\delta+}\cdots H]^{\ddagger}$, with respect to the initial state and occurs late in the reaction coordinate. Density functional theory (DFT) calculations of the overall reaction energies for the conversion of ethoxy groups to acetaldehydes, $\Delta E_{\beta H}$, and of the energies and structures of the transition states for *β*-hydride elimination in ethoxy groups on Cu(111) support the suggestion that the transition state occurs late in the reaction coordinate.[12,13] Thus, our understanding of the nature of the transition state to *β*-hydride elimination on Cu surfaces is now supported by both theory and experiment.

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β-Hydride Elimination in Alkyl Groups on Pt(111)

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Although β-hydride elimination has been observed in alkyl groups on Pt(111),[1,14] those studies have not reported values of $\Delta E^{\ddagger}_{\beta H}$ and none have attempted to probe the nature of the transition state. As on Cu surfaces, alkyl groups are generated on Pt(111) by the adsorption of alkyl iodides and subsequent dissociation of C−I bonds. The kinetics of alkyl iodide and alkyl group decomposition on Pt(111) are, however, much more complicated than those on Cu(111). On Pt(111), ethyl iodide decomposition generates ethyl groups that react by β-hydride elimination to produce adsorbed ethylene.[14,15] It has been proposed that the rate constant for C−I bond breaking to form ethyl groups on Pt(111) is lower than the rate constant for β-hydride elimination of those ethyl groups to form ethylene. During heating, some ethylene desorbs at 170 K immediately after C−I bond cleavage; however, rather than desorbing, most of the ethylene remains on the surface to form ethylidyne at higher temperatures. Thus, the low-temperature ethylene thermal desorption peak is rate limited by C−I bond cleavage and cannot be used to measure $\Delta E^{\ddagger}_{\beta H}$. At high ethyl iodide coverages on Pt(111), an additional high-temperature ethylene desorption peak is observed at ~300 K due to the high-temperature formation of ethylene by β-hydride elimination. This desorption temperature is, however, close to the peak desorption temperature observed for adsorbed ethylene desorbing from Pt(111). Thus, the appearance of ethylene in the gas phase may be rate limited by ethylene desorption rather than β-hydride elimination and its kinetics cannot be used to measure $\Delta E^{\ddagger}_{\beta H}$. During heating, propyl iodide decomposition on Pt(111) yields propylene desorption in two temperature regimes: one from 130 to 170 K and the other from 250 to 270 K.[1,16] As in the case of the ethyl groups, the lower temperature peak may be rate-limited by C−I bond breaking while the higher temperature peak is close to that of the desorption of molecularly adsorbed propylene. Thus, the adsorption and decomposition of alkyl groups on the Pt(111) surface does not provide insight into the kinetics of β-hydride elimination.

Although the decomposition of alkyl groups on the Pt(111) surface cannot be used to probe the nature of the transition state for β-hydride elimination on the Pt(111) surface, the decomposition kinetics of *fluoro*alkyl groups can. This is made possible by the fact that fluorination of the alkyl groups increases $\Delta E^{\ddagger}_{\beta H}$ to the point that the rate constant for β-hydride elimination is lower than that of fluoroalkyl group hydrogenation. As a result, the hydrogen atoms generated by β-hydride elimination can hydrogenate the remaining fluoroalkyl groups to produce fluoroalkanes that desorb rapidly from the Pt(111) surface. Thus, fluoroalkane desorption can be used to probe the kinetics of β-hydride elimination.

In this work, the transition state for β-hydride elimination on Pt(111) was investigated by measuring the $\Delta E^{\ddagger}_{\beta H}$ for four fluoroalkyl groups: RCH_2CH_2- (R = CF_3, CF_3CH_2, and CF_3-CF_2) and $(CF_3)_2CHCH_2-$. Correlation of the values of $\Delta E^{\ddagger}_{\beta H}$ with the field substituent constants, σ_F, of the fluoroalkyl groups yields a linear free energy relationship that indicates that the transition state for β-hydride elimination is cationic with respect to the initial state, $[RC^{\delta+}\cdots H]^{\ddagger}$. This is similar to the transition states proposed for β-hydride elimination in adsorbed alkyl groups and alkoxides on Cu(111). The substituent effect is, however, significantly smaller on the Pt(111) surface than on the Cu(111) surface indicating that on the Pt(111) surface the transition state is less polarized with respect to the initial state of the alkyl groups, than on the Cu(111) surface.

2. Experimental Section

All the 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 used for temperature programmed desorption (TPD) and temperature programmed reaction spectroscopy (TPRS). This chamber is also equipped with an Ar^+ ion gun for cleaning the surface and several leak valves for the introduction of gases and hydrocarbon vapors into the chamber. Low-energy electron diffraction optics were used to judge the order of the surface. 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 was purchased from Monocrystals Co. and was mounted by spot-welding between two Ta wires on a manipulator, which allows 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 below 90 K and resistively heated to temperatures higher 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 using XPS. Between TPD experiments, the surface was cleaned by annealing at 1000 K in 2×10^{-7} Torr of O_2 to desorb iodine and remove any residual carbon.

The temperature programmed reaction spectra were obtained using a Dycor M200M quadrupole mass spectrometer. Fluoroalkyl iodides were adsorbed by exposure of their vapor to the Pt(111) surface at 95 K. The exposures were recorded in units of Langmuirs (1 L = 10^{-6} Torr s) measured using the ion gauge without correction for ion gauge sensitivity. During TPRS measurements, the Pt(111) surface was heated at a rate of 2 K/s while the mass spectrometer was used to monitor signals at up to five *m/q* ratios simultaneously.

The fluoroalkyl iodide exposures were controlled to give coverages that correspond to ~30% of the saturation coverage of iodine on the Pt(111) surface. Saturation of iodine on the Pt(111) surface was achieved by repeated cycles of exposing the Pt(111) surface to 2 L or less of ethyl iodide at 95 K and then heating to 700 K. The exposures of hydrogen used in this work were 1, 3, and 10 L, which yielded hydrogen coverages of 40%, 75%, and 100% of the saturation hydrogen coverage.

The alkyl and fluoroalkyl iodides were purchased from SynQuest Laboratories, Inc. They were purified by cycles of freeze−pump−thawing before use. The purity of the gases and vapors introduced into the vacuum chamber was checked using the mass spectrometer.

3. Results

3.1. Formation of Alkyl and Fluoroalkyl Groups on Pt-(111). Thermal decomposition of alkyl iodides adsorbed on single-crystal surfaces is a well-established method for producing alkyl moieties on metal surfaces. In many studies, it has been shown that low-temperature adsorption of alkyl iodides followed by heating results in the dissociation of C−I bonds.[6,17] This C−I bond dissociation occurs below 200 K and leaves stable alkyl groups on the surface. During heating, these alkyl groups can hydrogenate to form alkanes, β-hydride eliminate to form alkenes, react by C−C coupling to form longer alkanes, or undergo complete decomposition by hydrogenolysis. As in the case of alkyl iodides, the C−I bonds in fluoroalkyl iodides have been shown to break at temperatures below 200 K to produce adsorbed fluoroalkyl groups on Ag(111) and on Pd-(111) surfaces.[18−20] Our work has made use of this methodology
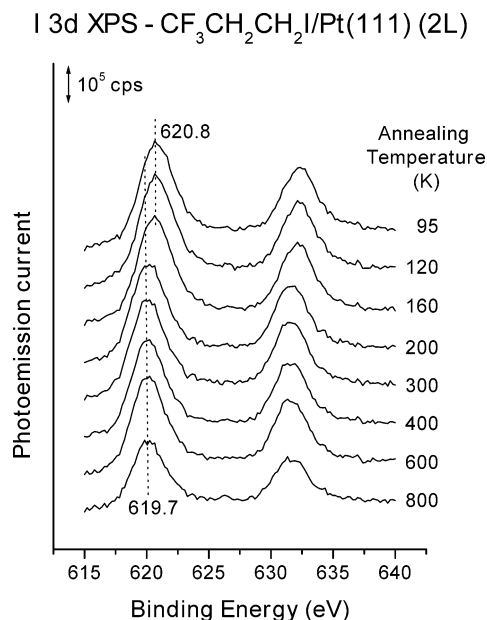
I 3d XPS - CF₃CH₂CH₂I/Pt(111) (2L)

Figure 1. I 3d XPS of the Pt(111) surface following exposure to 2 L of CF$_3$CH$_2$CH$_2$I at 95 K. Spectra were obtained after annealing the sample to the temperatures indicated on the right. The I 3d$_{5/2}$ binding energies are 620.8 eV for iodine in the adsorbed CF$_3$CH$_2$CH$_2$I and 619.8 eV for iodine atoms on the Pt(111) surface.

TPRS - CF₃CH₂CH₂I/Pt(111) (2L)

Figure 2. TPRS of 2 L of CF$_3$CH$_2$CH$_2$I adsorbed on the Pt(111) surface at 95 K. The heating rate is 2 K/s. Signals were monitored at $m/q = 2$, 27, and 29. Trifluoropropane produced by self-hydrogenation of adsorbed trifluoropropyl groups desorbs in a peak at 283 K.

to deposit various coverages of fluoroalkyl groups on the Pt-(111) surface.

In this study, the C−I bonds in fluoroalkyl iodides have been observed to break at temperatures below 200 K on Pt(111). The kinetics of C−I bond cleavage in 3,3,3-trifluoropropyl iodide, CF$_3$CH$_2$CH$_2$I, on Pt(111) have been examined by obtaining the I 3d$_{5/2}$ XP spectra shown in Figure 1. At 95 K, trifluoropropyl iodide is adsorbed molecularly on Pt(111) with the C−I bond intact and the I 3d$_{5/2}$ peak has a binding energy of 620.8 eV. The I 3d$_{5/2}$ binding energy remains constant following annealing to temperatures up to 160 K. After the surface has been annealed at 200 K, however, the I 3d$_{5/2}$ binding energy shifts by −1.1 eV to 619.7 eV. The shift to lower binding energy is indicative of the dissociation of the C−I bond and the formation of an I atom on the Pt(111) surface and, as a consequence, the formation of an adsorbed trifluoropropyl group, CF$_3$CH$_2$CH$_2$−. The I 3d$_{5/2}$ peak area remains constant until the annealing temperature reaches 800 K. It has been reported that the diffusion of iodine into the Pt(111) crystal bulk takes place at ∼800 K[14] and that iodine desorbs from Pt(111) at ∼825 K.[16] In conclusion, fluoroalkyl iodides undergo C−I cleavage on the Pt(111) surface at temperatures below 200 K leaving fluoroalkyl groups and I atoms on the surface. The I atoms are stable on Pt(111) to temperatures as high as 800 K.

3.2. β-Hydride Elimination in Fluoroalkyl Groups on Pt-(111). While there have been many studies of the surface chemistry of alkyl iodides on the Pt(111) surface, there have been comparatively few studies of *fluoro*alkyl iodides on the Pt(111) surface. Figure 2 shows the TPR spectra obtained following exposure of 2 L of trifluoropropyl iodide to the Pt-(111) surface at 95 K. This exposure leads to a coverage of trifluoropropyl iodide that is roughly 30% of the saturation coverage of iodine that can be adsorbed on Pt(111) by repeated adsorption and decomposition of ethyl iodide. Heating the adsorbed trifluoropropyl iodide leads to C−I bond breaking without molecular desorption. The desorption traces shown in Figure 2 are those for $m/q = 2$ (H$_2$), 27 (C$_2$H$_3$$^+$ with contributions from both trifluoropropylene, CF$_3$CH=CH$_2$, and

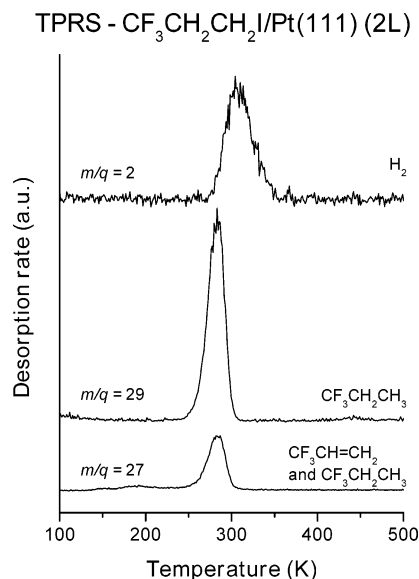trifluoropropane, CF$_3$CH$_2$CH$_3$) and 29 (C$_2$H$_5$$^+$ from trifluoropropane, CF$_3$CH$_2$CH$_3$). From these spectra, it is clear that trifluoropropane is produced and desorbs at 283 K. The source of hydrogen for this self-hydrogenation must be the decomposition of trifluoropropyl groups by β-hydride elimination. The hydrogen deposited on the surface reacts with the remaining trifluoropropyl groups to produce trifluoropropane which then desorbs rapidly. Figure 2 also shows hydrogen desorption occurring with a peak centered at about 308 K. This peak arises from the recombination of hydrogen atoms released by the decomposition of trifluoropropyl groups at lower temperatures. Also note that, for $m/q = 27$, there is a small peak at ∼180 K, which may arise from trifluoropropylene produced by a low-temperature β-hydride elimination mechanism that might coincide with the C−I bond cleavage process. This peak is much smaller than the peak at 283 K. The F 1s XP spectra of trifluoropropyl iodide on Pt(111) obtained after heating to increasing temperatures show that the fluorine coverage does not change significantly below 200 K, indicating that the amount of trifluoropropylene desorbing at low temperatures comes from less than 2% of the adsorbed trifluoropropyl groups. The kinetics of trifluoropropane desorption have been used to measure the $\Delta E_{\beta H}^{\ddagger}$ in trifluoropropyl groups on Pt(111).

To demonstrate that the kinetics of trifluoropropyl hydrogenation to trifluoropropane are rate limited by the β-hydride elimination step rather than the hydrogenation step, hydrogenation of the trifluoropropyl groups in the presence of preadsorbed hydrogen was studied on the Pt(111) surface. Figure 3 shows the TPR spectra obtained by exposure of the Pt(111) surface at 95 K to 0, 1, 3, and 10 L of H$_2$ followed by 2 L of trifluoropropyl iodide and subsequent heating at 2 K/s. Note that the preadsorbed hydrogen does not significantly affect the coverage of trifluoropropyl iodide on Pt(111). The I 3d$_{5/2}$ XPS peak intensity varied by less than 10% as the preexposure of hydrogen was increased from 0 to 10 L. The TPR spectra in Figure 3 show that the hydrogenation temperature shifts from 283 K down to 258 K as the preexposure to H$_2$ increases from 0 to 10 L. This shift in the peak hydrogenation temperature indicates that the rate-limiting step for hydrogenation switches from β-hydride elimination in the absence of preadsorbed
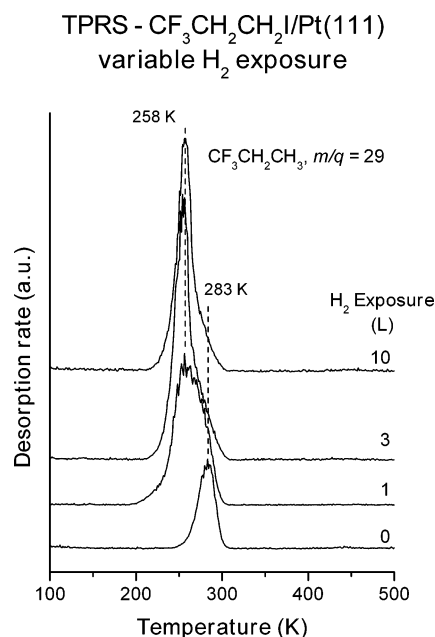
β-Hydride Elimination in Alkyl Groups on Pt(111)

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TPRS - CF$_3$CH$_2$CH$_2$I/Pt(111)
variable H$_2$ exposure

Figure 3. TPRS of 2 L of CF$_3$CH$_2$CH$_2$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 CF$_3$CH$_2$CH$_2$I at 95 K. The heating rate was 2 K/s, while monitoring the desorption of trifluoropropane by monitoring the signal at $m/q = 29$.

hydrogen to hydrogenation in the presence of preadsorbed hydrogen. The most important point is that self-hydrogenation on the clean Pt(111) surface is rate limited by the supply of hydrogen atoms created via β-hydride elimination in the adsorbed trifluoropropyl groups. Similar results were observed in a study of propyl groups on Pt(111):[1] in the presence of coadsorbed hydrogen, the hydrogenation steps are typically faster than β-hydride elimination; in the absence of coadsorbed hydrogen atoms, the rate-limiting step for olefin and alkyl hydrogenation is β-hydride elimination. As a consequence, the self-hydrogenation kinetics of the fluoroalkyl groups can be used to measure the kinetics of β-hydride elimination.

The chemistry of three other fluoroalkyl groups (CF$_3$CF$_2$-CH$_2$CH$_2$−, CF$_3$CH$_2$CH$_2$CH$_2$−, and (CF$_3$)$_2$CHCH$_2$−) on the Pt-(111) surface is similar to that of CF$_3$CH$_2$CH$_2$−. Fluoroalkanes desorb from the surface following adsorption of the fluoroalkyl iodide on the clean Pt(111) surface. The TPR spectra of all four fluoroalkyl groups on the clean Pt(111) surface without preexposure to H$_2$ are presented in Figure 4. The desorption spectra shown in Figure 4 are those of the fluoroalkanes generated by hydrogenation of the corresponding fluoroalkyl groups. The peak self-hydrogenation temperatures for CF$_3$CH$_2$CH$_2$CH$_2$−, CF$_3$-CF$_2$CH$_2$CH$_2$−, CF$_3$CH$_2$CH$_2$−, and (CF$_3$)$_2$CHCH$_2$− are $T_p = $ 263, 283, 283, and 310 K, respectively, and are shown in Table 1. In all four cases, the kinetics of hydrogenation by preadsorbed hydrogen are faster than the self-hydrogenation kinetics observed on the clean Pt(111) surface. Because the self-hydrogenation reaction on the clean Pt(111) surface is rate-limited by the supply of hydrogen released by β-hydride elimination in the fluoroalkyl group, the results shown in Figure 4 indicate that as the extent of alkyl group fluorination increases, the barrier to β-hydride elimination increases.

It is important to demonstrate that the appearance of the fluoroalkanes in the gas phase is rate limited by β-hydride elimination and not by the kinetics of fluoroalkane desorption. Not all the fluoroalkanes produced are commercially available, and so, it is not possible to measure the molecular desorption kinetics of all four fluoroalkanes experimentally. Instead, we

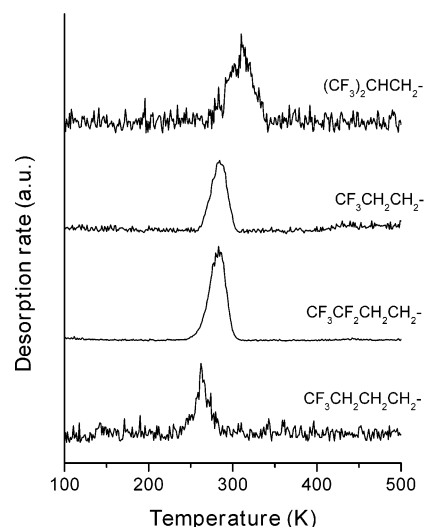TPRS - fluoroalkyl iodides / Pt(111)

Figure 4. TPRS of fluoroalkyl iodides on Pt(111) without pre-exposure to H$_2$. The heating rate was 2 K/s, and the spectra monitor the desorption of the fluoroalkane produced by the hydrogenation of the fluoroalkyl group indicated on the right.

TABLE 1: Fluoroalkyl Iodides Studied on Pt(111), Substituents on the β-Carbon, Substituent Field Constants (σ_F),[24] the Temperature of the Maximum β-Hydride Elimination Rate (T_{max}), and the Barrier to β-Hydride Elimination ($\Delta E^{\ddagger}_{\beta H}$)
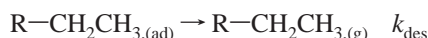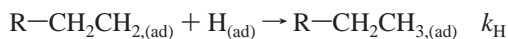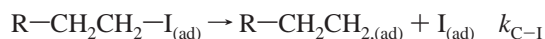
molecule	substituent	field constant	$\Sigma\sigma_F$	T_{max}	$\Delta E^{\ddagger}_{\beta H}$ (kJ/mol)
CF$_3$CH$_2$CH$_2$CH$_2$I	H, CF$_3$CH$_2$	0, 0.23	0.23	263	69
CF$_3$CH$_2$CH$_2$I	H, CF$_3$	0, 0.44	0.44	283	74
CF$_3$CF$_2$CH$_2$CH$_2$I	H, CF$_3$CF$_2$	0, 0.51	0.51	283	74
(CF$_3$)$_2$CH−CH$_2$I	CF$_3$, CF$_3$	0.44, 0.44	0.88	310	81

have measured the kinetics of butane, CH$_3$CH$_2$CH$_2$CH$_3$, desorption from the clean Pt(111) surface. The peak desorption temperature at submonolayer coverages is 175 K, well below the fluoroalkane desorption temperatures observed during self-hydrogenation of the fluoroalkyl groups. The reactions studied in this work produce fluoroalkanes, and fluorination tends to reduce the desorption energy of most hydrocarbons. Fluorination of alkyl ethers decreases their desorption energies on the Cu-(111), Al(110), and Pt(111) surfaces.[21−23] It is reasonable to assume that fluorination of the alkanes will also result in lower desorption energies and lower desorption temperatures. Our TPD measurements of butane on Pt(111) showed that desorption of submonolayer coverages of butane occurs at approximately 175 K. On the basis of the discussion above, it is reasonable to expect that CF$_3$CH$_2$CH$_2$CH$_3$, CF$_3$CF$_2$CH$_2$CH$_3$, CF$_3$CH$_2$CH$_3$, and (CF$_3$)$_2$-CHCH$_3$ would desorb at even lower temperatures. The fact that self-hydrogenation of the four fluoroalkyl groups results in fluoroalkane desorption at temperatures above 200 K indicates that appearance of the fluoroalkane products in the gas phase is rate limited by self-hydrogenation rather than desorption. Thus, the peak fluoroalkane desorption temperatures observed during fluoroalkyl decomposition on Pt(111) can be used to estimate the activation barriers for β-hydride elimination, $\Delta E^{\ddagger}_{\beta H}$, in the four fluoroalkyl groups.

4. Discussion

4.1 Analysis of the β-Hydride Elimination Kinetics on Pt-(111). The TPR spectra of fluoroalkyl groups on the Pt(111) surface have been obtained in order to estimate the kinetic

parameters for β-hydride elimination. These TPR spectra measure the kinetics of β-hydride elimination indirectly through self-hydrogenation kinetics. The self-hydrogenation mechanism is assumed to occur via the elementary steps shown below. Here, $R-CH_2CH_2-I$ is chosen to represent alkyl iodides with different substituents, R.

$$R-CH_2CH_2-I_{(ad)} \rightarrow R-CH_2CH_{2,(ad)} + I_{(ad)} \quad k_{C-I}$$

$$R-CH_2CH_{2,(ad)} \rightarrow R-CH=CH_{2,(ad)} + H_{(ad)} \quad k_{\beta H}$$

$$R-CH_2CH_{2,(ad)} + H_{(ad)} \rightarrow R-CH_2CH_{3,(ad)} \quad k_H$$

$$R-CH_2CH_{3,(ad)} \rightarrow R-CH_2CH_{3,(g)} \quad k_{des}$$

The first step, C−I bond cleavage in the adsorbed iodide, occurs at lower temperatures (<200 K) than the other reaction steps. The second step is β-hydride elimination to produce hydrogen atoms and an olefin, $R-CH=CH_2$, adsorbed on the surface. The olefin can desorb from the surface (not shown) or react further to form an alkylidyne (not shown). The third step is the hydrogenation of the remaining alkyl groups by hydrogen atoms released by the β-hydride elimination step. The final step is the rapid desorption of the alkane with a rate constant k_{des}. As discussed in the Results section, the overall self-hydrogenation of the alkyl group is rate limited by the β-hydride elimination of the alkyl group; $k_{\beta H} < k_H < k_{des}$. As a consequence, alkane desorption kinetics can be used as an indirect measure of the kinetics of β-hydride elimination.

The details of the analysis of the TPR spectra to estimate the kinetics of β-hydride elimination are described in Appendix A. The relationship between the peak temperature, T_p, and activation barrier for the β-hydride elimination, $\Delta E_{\beta H}^{\ddagger}$, can be expressed as

$$\frac{\Delta E_{\beta H}^{\ddagger}}{RT_p{}^2} = \frac{\nu}{\beta} \exp\left(\frac{-\Delta E_{\beta H}^{\ddagger}}{RT_p}\right) \tag{1}$$

Here, β is the heating rate and ν is the pre-exponential factor for β-hydride elimination. The pre-exponent has been estimated at $\nu = 10^{13}$ s^{-1}. It is important to point out that in this study we are less interested in the absolute value of $\Delta E_{\beta H}^{\ddagger}$ than in its change as a result of fluorine substitution. Thus, because errors in ν enter systematically into the calculation of $\Delta E_{\beta H}^{\ddagger}$, they still allow analysis of the trends in $\Delta E_{\beta H}^{\ddagger}$ through a linear free energy relationship with the field substituent constants, σ_F, of the fluoroalkyl groups.

4.2. Transition State for β-Hydride Elimination of Alkyl Groups on Pt(111). The primary goal of this work has been to probe the characteristics of the transition state for β-hydride elimination of alkyl groups on Pt(111) by measuring $\Delta E_{\beta H}^{\ddagger}$ in several fluorinated alkyl groups. Figure 4 demonstrates quite clearly that β-hydride elimination occurs at different temperatures for alkyl groups with different substituents; thus, the nature of the substituent does influence the value of $\Delta E_{\beta H}^{\ddagger}$. The effects of fluorine substitution on the values of $\Delta E_{\beta H}^{\ddagger}$ can be quantified through correlations with the substituents' field constants, σ_F. The field substituent constants have been determined empirically through studies of the substituent effects on a number of reactions and are tabulated in the physical organic chemistry literature.[24,25] The increase in σ_F with increasing fluorination on going from $CF_3CH_2CH_2CH_2-$ to $(CF_3)_2$-$CHCH_2-$ destabilizes the transition state with respect to initial state alkyl group, thus increasing $\Delta E_{\beta H}^{\ddagger}$. The linear free

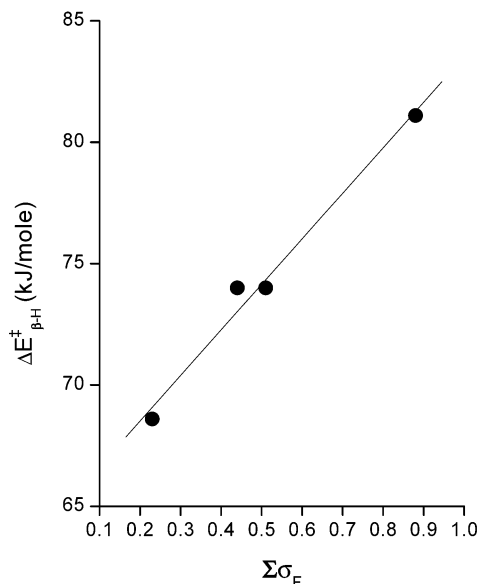## LFER for β-hydride elimination in fluoroalkyl groups on Pt(111)

Figure 5. Linear free energy relationship for the barriers to β-hydride elimination, $\Delta E_{\beta H}^{\ddagger}$, of fluoroalkyl groups on Pt(111). The reaction constant is $\rho_F = 19 \pm 2$ kJ/mol.

energy relationship (LFER)[24] shown in Figure 5 has been used to correlate the values of $\Delta E_{\beta H}^{\ddagger}$ with the field substituent constants to obtain the reaction constant, $\rho_F = 19 \pm 2$ kJ/mol.

The nature of the transition state for β-hydride elimination in alkyl groups on Pt(111) can be inferred from the reaction constant, ρ_F, obtained from the slope of the LFER in Figure 5. The sign of the reaction constant for β-hydride elimination in alkyl groups on the Pt(111) surface is positive, suggesting that the transition state is cationic with respect to the initial state, $[RC^{\delta+\cdots}H]^{\ddagger}$, as is believed to be the case on the Cu(111) surface.[11] The field effect of the fluorinated substituent energetically destabilizes the electron deficient β-carbon atom. A similar transition state was described by molecular orbital calculations of β-hydride elimination in alkyl groups on Al surfaces. Those calculations predicted a four-center transition state with a cationic β-carbon atom.[26]

It is important to note that the substituent effect measurements on the Pt(111) surface suggest that distinct differences exist between the charge distributions on the transition states for β-hydride elimination of alkyl groups on the Cu(111) and the Pt(111) surfaces. To put the value of $\rho_F = 19 \pm 2$ kJ/mol into perspective, it can be compared to the value of the reaction constant for β-hydride elimination in alkyl and alkoxy groups on the Cu(111) surface.[7,11] For the β-hydride elimination of alkoxides to aldehydes and ketones on Cu(111), it was found that $\rho_F = 150$ kJ/mol. The transition state for β-hydride elimination has also been probed using propyl and trifluoropropyl groups adsorbed on Cu(111).[11] In that reaction, fluorination increased the barrier to β-hydride elimination by $\Delta\Delta E_{\beta H}^{\ddagger} = 35$ kJ/mol corresponding to a reaction constant of $\rho_F = 80$ kJ/mol which is also significantly higher than the value observed on the Pt(111) surface. The change in charge density on the β-carbon atom during β-hydride elimination appears to be greater on the Cu(111) surface than on the Pt(111) surface, leading to a higher reaction constant.

The origin of difference in the nature of the transition state for β-hydride elimination on the Pt(111) and Cu(111) surfaces is interesting. For methoxy decomposition by β-hydride elimi-

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nation, it has been shown that the transition state occurs later on the Cu(111) surface than on the Pt(111) surface consistent with the fact that the reaction is exothermic on Pt(111) but endothermic on Cu(111).[27,28] The same is probably true for the transition states for *β*-hydride elimination of alkyl groups on Pt (111) and Cu(111). One way of looking at this is that the differences in the charge distributions between the initial state and the transition state are sensitive to the position of the transition state along the reaction coordinate for *β*-hydride elimination. If the transition state on Cu(111) can be described as occurring later in the reaction coordinate than on Pt(111), then one would expect the transition state to be more cationic with respect to the reactant on Cu(111) than on Pt(111). A thorough analysis of this problem would require a study of the electronic structures of the transition states on the two surfaces.
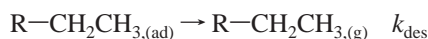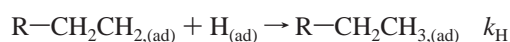
Finally, it is worthwhile discussing the reaction that we believe has been studied in this work. In this paper, we propose that adsorbed fluoroalkyl iodides on Pt(111) decompose to fluoroalkyl groups and iodine at temperatures below 200 K and that the fluoroalkyl groups decompose by *β*-hydride elimination to produce adsorbed olefins and hydrogen. This *β*-hydride elimination step is the rate-limiting step for self-hydrogenation of the fluoroalkyl groups. Therefore, self-hydrogenation can be used to probe the kinetics of *β*-hydride elimination. It is necessary to point out that different reaction mechanisms have been suggested in studies of ethyl and propyl group decomposition on Pt(111).[1,15] The authors of those studies suggest that self-hydrogenation is rate limited by the insertion of the hydrogen into ethylene or propylene (as opposed to ethyl or propyl). If this is also the case for the fluoroalkyl groups, then what we have studied is the microscopic reverse of *β*-hydride elimination, insertion of a hydrogen atom into an olefin. The transition state for this reverse of *β*-hydride elimination can be described as having a carbon atom that is electron deficient with respect to the olefin. Unfortunately, by using only TRPS and monitoring the reaction products only, we cannot be absolutely certain what reactions occur on the surface. At this point, we believe that the observed reaction is rate limited by *β*-hydride elimination.

5. Conclusions

We have demonstrated that fluorination of alkyl groups on the Pt(111) surface exerts an influence on the kinetics of their decomposition by *β*-hydride elimination. The activation barrier to *β*-hydride elimination, $\Delta E^{\ddagger}_{\beta H}$, increases as the extent of fluorination increases. The transition state can be described as one in which the *β*-carbon atom is cationic with respect to the alkyl group, $[RC^{\delta+}\cdots H]^{\ddagger}$. The electronic structure of this transition state is similar to those proposed for the *β*-hydride elimination of alkoxy and alkyl groups on the Cu(111) surface although the magnitude of charge buildup in the transition state is smaller on the Pt(111) surface than on the Cu(111) surface.

Appendix A: Analysis of TPRS Kinetics for *β*-Hydride Elimination, Hydrogenation, and Desorption in Fluoroalkyl Groups on the Pt(111) Surface

The mechanism of alkyl group decomposition to yield alkanes is described by the following three elementary steps, each of which has its associated rate constant and activation barrier.

$$R-CH_2CH_{2,(ad)} \rightarrow R-CH{=}CH_{2,(ad)} + H_{(ad)} \quad k_{\beta H}$$

$$R-CH_2CH_{2,(ad)} + H_{(ad)} \rightarrow R-CH_2CH_{3,(ad)} \quad k_H$$

$$R-CH_2CH_{3,(ad)} \rightarrow R-CH_2CH_{3,(g)} \quad k_{des}$$

The rate constants for hydrogenation, k_H, and for desorption, k_{des}, are both greater than the rate constant for *β*-hydride elimination. The rate of alkane desorption is given by

$$r_{des} = k_{des}\theta_{RCH2CH3}$$

At steady state, the coverage of adsorbed alkanes is given by

$$\frac{d\theta_{RCH2CH3}}{dt} = 0 = k_H\theta_{RCH2CH2}\theta_H - k_{des}\theta_{RCH2CH3}$$

so the rate of alkane desorption is given by

$$r_{des} = k_H\theta_{RCH2CH2}\theta_H$$

At steady state, the coverage of adsorbed hydrogen is given by

$$\frac{d\theta_H}{dt} = 0 = k_{\beta H}\theta_{RCH2CH2} - k_H\theta_{RCH2CH2}\theta_H$$

and so the expression for the desorption rate becomes

$$r_{des} = k_{\beta H}\theta_{RCH2CH2}$$

Thus, the rate of alkane desorption is simply described as a first-order process in the concentration of adsorbed alkyl groups and the analysis of the desorption kinetics is identical to the Redhead analysis used for a first-order desorption process. The relationship between the peak desorption temperature and the barrier to *β*-hydride elimination is simply given by the Redhead equation,

$$\frac{\Delta E^{\ddagger}_{\beta H}}{RT_p^2} = \frac{\nu}{\beta}\exp\left(\frac{-\Delta E^{\ddagger}_{\beta H}}{RT_p}\right)$$

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