Carboxylic Acid Deprotonation on the Ag(110) and Ag(111) Surfaces

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The surface chemistry of hydrocarbon carboxylic acids has been compared with that of perfluorinated carboxylic acids on the Ag(110) and Ag(111) surfaces. The hydrocarbon acids adsorb reversibly on the clean silver surfaces. On Ag(110) their desorption energies increase linearly with increasing alkyl chain length (n) and are given by the expression \( \Delta E_{\text{dep}} = 10.6 + 0.9n \) kcal/mol. The surface chemistry of the perfluorinated acids is quite different from that of the hydrocarbon acids in the sense that they deprotonate to form perfluorocarboxylate species on both Ag(110) and Ag(111) surfaces. The perfluorocarboxylates are stable until the surface temperature reaches \( \sim 620 \) K, at which point they decompose yielding desorption of CO\(_2\) and other decomposition fragments. On both Ag surfaces 2,2,2-trifluoroacetate (CF\(_3\)CO\(_2\)) generated by deprotonation of 2,2,2-trifluoroacetic acid (CF\(_3\)CO\(_2\)H) has been identified by its vibrational spectrum. The fact that fluorinated acids deprotonate on the Ag surfaces while the hydrocarbon acids desorb during heating indicates that fluorination lowers the deprotonation barrier, \( \Delta E_{\text{dep}} \), to the point that it is lower than the desorption energy, \( \Delta E_{\text{dep}} \).

1. Introduction

The kinetics of complex chemical reactions are determined by the transition states to elementary chemical reaction steps and the associated reaction barriers, \( \Delta E^\ddagger \). As a result, understanding the nature of the transition state is central to the understanding of chemical reaction kinetics in the gas phase, in solution phase, and on solid surfaces. For catalytic reactions occurring on solid surfaces such understanding will guide manipulation of reaction conditions or reaction pathways in order to increase catalytic activities and improve selectivities. Unfortunately, it is extremely difficult to attempt to detect the transition state for a reaction on a solid surface directly. This paper describes an effort to probe the nature of the transition state to the deprotonation of acids on surfaces through an indirect approach, the use of substituent effects.

The nature of the transition states of several surface reactions has been studied by employing field substituent effects. As an example, \( \beta \)-hydride elimination in hydrocarbon alkoxides on the Cu(111) surface (RCH\(_2\)O-Cu \( \rightarrow \) RCH=O + H-Cu) has been shown to have a transition state in which the \( \beta \)-carbon atom is cationic, \([\text{C}^+\cdots\text{H}]^\ddagger\), with respect to the initial state alkoxide. In that work, fluorinating the substituent (R) of the alkoxides increases its local dipole moment or field effect and destabilizes the \( \beta \)-charge on the \( \beta \)-carbon in the transition state. As a result, fluorination increases the activation barrier to \( \beta \)-hydride elimination, \( \Delta E^\ddagger_{\beta-H} \). If the transition state had been anionic, \([\text{C}^+\cdots\text{H}]^\ddagger\), then \( \Delta E^\ddagger_{\beta-H} \) would have been decreased by fluorination of the substituent. As another example of the use of substituent effects, the transition state for \( \text{C}^\ddagger \) bond breaking in alkyl iodides (R\(_3\)C-\( \rightarrow \)) on Ag(111) and Pd(111) surfaces has been studied via fluorination of the substituent alkyl groups (R). On the Ag(111) surface the transition state for \( \text{C}^\ddagger \) bond breaking has been shown to be slightly anionic with respect to the initial state (R\(_3\)C-\( \rightarrow \) [R\(_3\)C\(^+\cdots\text{I}]^\ddagger\)). In this reaction fluorination of the alkyl substituent groups lowers the activation barrier for \( \text{C}^\ddagger \) cleavage, \( \Delta E^\ddagger_{\text{C}^\ddagger-I} \), by stabilizing the anionic transition state with respect to the initial state. The effect is quite small but clearly significant. On the basis of these and other studies, it appears that fluorine substituent effects are generally useful for probing the nature of the transition states to surface reactions.

The work presented in this paper probes the nature of the transition state for carboxylic acid deprotonation on the Ag(111) and Ag(110) surfaces by comparing the kinetics of deprotonation in hydrocarbon and fluorocarbon acids. Acid deprotonation is a fairly simple reaction which has been studied on a number of metal surfaces and is a reaction which one can imagine occurs by a single elementary step. Previous work has documented the surface chemistry of hydrocarbon acids; however, little has been done to study the fluorinated acids on metal surfaces. By contrast, the kinetics and equilibria for deprotonation in the gas phase or solution phase have been studied extensively in a wide range of hydrocarbon and partially fluorinated acids. As a result, fluorine substituent effects on the gas phase heats of deprotonation...
low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES), leak valves for gas dosing, and Dycor quadrupole mass spectrometers for desorption measurements. The chamber used for the study on the Ag(110) surface is also equipped with a high-resolution electron energy loss (HREEL) spectrometer. The experiments performed on the Ag(111) surface were conducted in a different chamber equipped with a Mg K\textalpha\ X-ray source and a VG CLAM II hemispherical analyser for X-ray photoelectron spectroscopy (XPS). In addition, that chamber was equipped with a Matsumon RS-1FTIR spectrometer with a narrow-banded HgCdTe detector used for Fourier transform infrared reflection—absorption spectroscopy.

The Ag single-crystal samples were purchased from Monocrystals Inc. and were mounted by spot-welding between two Ta wires. The small samples which were then bolted to the ends of the UHV manipulators. The manipulators allowed cooling of the samples to T < 100 K and resistive heating to T > 1000 K. Chromel–alumel thermocouples were spot-welded to the edges of the Ag samples for temperature measurement. The silver samples were cleaned by several cycles of Ar\textsuperscript{±} sputtering followed by annealing to 800 K. Deposits of carbon on the Ag(110) surface resulting from the decomposition of acetates were removed by exposing the crystal to high vacuum at T < 100 K to yield CO\textsubscript{2}, C\textsubscript{H}\textsubscript{4}, and C\textsubscript{H}\textsubscript{2}O\textsubscript{2} which desorbs with a peak maximum at about 480 K. Unreacted oxygen atoms recombine to desorb as O\textsubscript{2} at 550 K. The Ag(110) surface was judged to be free of carbon when no CO\textsubscript{2} was detected by temperature-programmed desorption following oxygen adsorption. Because the Ag(111) surface does not readily adsorb oxygen, it could only be used by using XPS. It was used to monitor the cleanliness of the Ag(111) surface.

The experiments used a series of straight-chain hydrocarbon and fluorocarbon carboxylic acids obtained from Aldrich Chemical Co., Inc. The acids are all liquids and were purified by several cycles of freeze–pump–thawing. The purity of the vapor introduced into the UHV chamber through the leak valves was verified by mass spectrometry. The acids were adsorbed on the clean surfaces at 90 K by backfilling the chamber through a leak valve.

Temperature-programmed desorption (TPD) and temperature-programmed reaction spectroscopy (TPRS) were performed using the Dycar mass spectrometer. After preparation of the adsorbate layers on the Ag surfaces they were positioned in front of the mass spectrometer and heated. The heating rates were 5 and 2 K s\textsuperscript{-1} for Ag(110) and Ag(111) samples, respectively. A variable temperature quartz Crystal Inc. and were mounted by spot-welding between two Ta wires on small sample holders which were then bolted to the ends of the UHV manipulators. The manipulators allowed cooling of the samples to T < 100 K and resistive heating to T > 1000 K. Chromel–alumel thermocouples were spot-welded to the edges of the Ag samples for temperature measurement. The silver samples were cleaned by several cycles of Ar\textsuperscript{±} sputtering followed by annealing to 800 K. Deposits of carbon on the Ag(110) surface resulting from the decomposition of acetates were removed by exposing the crystal to high vacuum at T < 100 K to yield CO\textsubscript{2}, C\textsubscript{H}\textsubscript{4}, and C\textsubscript{H}\textsubscript{2}O\textsubscript{2} which desorbs with a peak maximum at about 480 K. Unreacted oxygen atoms recombine to desorb as O\textsubscript{2} at 550 K. The Ag(110) surface was judged to be free of carbon when no CO\textsubscript{2} was detected by temperature-programmed desorption following oxygen adsorption. Because the Ag(111) surface does not readily adsorb oxygen, it could only be used by using XPS. It was used to monitor the cleanliness of the Ag(111) surface.

The experiments performed on the Ag(110) surface were done in two ultra-high-vacuum (UHV) chambers. Both are equipped with ion guns for cleaning the crystal surface, electron optics for
the surface at a temperature of 90 K. The primary beam energy was 1.3 eV, and the spectra were obtained using multiple scans with a total dwell time of 3.0 s/pt.

3. Results

3.1. Carboxylic Acid on the Clean Silver Surfaces.

CH$_3$CO$_2$H adsorbs and desorbs reversibly on both the clean Ag(110) and Ag(111) surfaces. Figure 1 shows the TPD spectra of CH$_3$CO$_2$H adsorbed on Ag(110) at increasing exposures. The CH$_3$CO$_2$H monolayer desorbs at $T = 195$ K with a coverage-independent peak maximum, indicating first-order desorption kinetics. Following saturation of the monolayer, further adsorption results in formation of a condensed multilayer which desorbs at 162 K and exhibits zero-order desorption kinetics. CH$_3$CO$_2$H adsorption on the clean Ag(111) surface exhibits the same reversible adsorption with the monolayer desorbing at $T = 200$ K. The fact that CH$_3$CO$_2$H desorbs from the Ag(111) surface without decomposition is illustrated by the C 1s and O 1s X-ray photoemission spectra of Figures 2 and 3. The C 1s spectrum taken at 90 K for the adsorbed CH$_3$CO$_2$H monolayer reveals two peaks: one at a binding energy of 288.5 eV from the carbon of the methyl group and the other at 292.5 eV from the carbon of the carboxyl group. This splitting was also observed in a study on the Cu(110) surface which reported binding energies of 286.6 and 290.0 eV for the carbon atoms in the methyl group and carboxyl groups, respectively. The O 1s photoemission spectrum of the adsorbed CH$_3$CO$_2$H monolayer is shown in Figure 3 and shows a single feature with a binding energy of 535.2 eV. Both Figures 2 and 3 reveal that heating the surface to 300 K results in the desorption of the CH$_3$CO$_2$H and leaves the Ag(111) surface clean.

In addition to CH$_3$CO$_2$H the longer, straight-chain carboxylic acids have been studied on the Ag(110) surface. These have included acetic through to hexanoic acid, CH$_3$(CH$_2$)$_n$CO$_2$H. In all cases these are also observed to adsorb and desorb reversibly from the clean Ag(110) surface. Figure 4 shows the desorption of adsorbed monolayers of the straight-chain carboxylic acids from the clean Ag(110) surface. The peak desorption temperature increases by roughly 10–15 K per additional methylene group in the alkyl chain. Using the Redhead equation and estimating that the desorption preexponential factor is $10^{13}$ s$^{-1}$ allows us to estimate the desorption energies, $\Delta E_{\text{des}}$, of the acids. These are plotted in Figure 5 and reveal that the desorption energies increase by ~0.9 kcal/mol of CH$_2$ with the form $\Delta E_{\text{des}} = 10.6 + 0.9n$ kcal/mol, where $n$ is the number of carbon atoms in the alkyl chain.

As observed in previous work, it is only possible to deprotonate CH$_3$CO$_2$H on the Ag(110) and Ag(111) surfaces by first partially oxidizing the surface. The adsorbed oxygen atom acts as a Bronsted base and deprotonates the acid to produce acetate, CH$_3$CO$_2$. During heating the CH$_3$CO$_2$ decomposes to produce CO$_2$, CH$_4$, and other species at temperatures on the order of 600 K. We have also observed that CH$_3$CO$_2$H is deprotonated on the oxidized Ag(110) surface and decomposes to produce CO$_2$ at high temperatures.
3.2. Perfluorinated Carboxylic Acids on Clean Ag Surfaces.

The surface chemistry of the perfluorinated carboxylic acids on the clean Ag(110) and Ag(111) surfaces appears to be quite different from that of the hydrocarbon carboxylic acids. Whereas the hydrocarbon acids are reversibly adsorbed on the clean surface and desorb during heating, the perfluorinated acids all deprotonate to produce perfluorocarboxylates.

The desorption of CF₃CO₂H from the clean Ag(111) surface is shown in Figure 6 as a function of increasing coverage. These TPRS spectra have been obtained by monitoring the signal at \( m/q = 44 \) with the mass spectrometer. At low temperatures these TPR spectra reveal a desorption feature at \( 230 \) K which is probably due to desorption of the CF₃CO₂H monolayer and at the highest coverage a narrow desorption feature at \( 145 \) K that is due to desorption of the CF₃CO₂H multilayer. The most important thing to note is the desorption feature at \( 640 \) K that is not present in the desorption spectra of CH₃CO₂H. Additional ionization fragments observed in the spectrum of the species desorbing at \( 640 \) K that is not present in the desorption spectra of CH₃CO₂H. Additional ionization fragments observed in the spectrum of the species desorbing at \( 630 \) K include m/q = 69, (CF₃)⁺, 50 (CF₂)⁺, and 31 (CF⁺). This feature occurs at a similar temperature to that observed during the decomposition of CH₂CO₂H generated by CH₃CO₂H adsorption on the oxidized Ag(110) surface and suggests that some of the CF₃CO₂H has deprotonated to form trifluoroacetate, CF₃CO₂⁻. The important point is that in the case of CF₃CO₂H this has occurred on the clean Ag(111) surface. The same reaction appears to occur on the clean Ag(110) surface. Figure 7 shows the desorption spectra for perfluoro-acetic, -propionic, and -butanoic acids on the clean Ag(110) surface. These all reveal the same high-temperature desorption feature observed in the case of CF₃CO₂H on the clean Ag(111) surface and suggest that all three are undergoing deprotonation to form perfluorinated carboxylates on the Ag(110) surface.

One interesting point is that we have never been able to determine the fate of the proton that must be lost during the conversion of the fluorinated acids to the fluorinated carboxylates. It does not appear in the desorption spectra as either H₂ or H₂O. While it is possible that it dissolves into the bulk of the Ag samples this seems unlikely. It is possible that it desorbs during the adsorption process. If that is the case, then it implies that deprotonation is occurring at the adsorption temperature of \( 90 \) K.

3.3. CF₃CO₂ on Ag(111) and Ag(110).

The deprotonation of the perfluorinated carboxylic acids on the Ag(110) and Ag(111) surfaces ought to result in the production of perfluorinated carboxylates. In particular, the deprotonation of CF₃CO₂H should result in the production of CF₃CO₂⁻. Evidence for this comes from the XP spectra. Figures 8 and 9 show the C 1s and O 1s XP spectra of a CF₃CO₂H monolayer adsorbed on the Ag(111) surface at \( 90 \) K and after heating to \( 300 \) K. The spectrum of the monolayer at \( 90 \) K reveals poorly resolved features with binding energies of 293.5 eV for the carboxyl group and 295.8 eV for the CF₂CO₂H group. After heating to \( 300 \) K all the CH₃CO₂H has desorbed from the surface.

The XP spectra of the O 1s region for an CH₃CO₂H monolayer adsorbed on the Ag(111) surface at \( 90 \) K and after heating to \( 300 \) K exhibit one broad feature at a binding energy of 535.2 eV for both oxygen atoms in the CO₂H group. After heating to \( 300 \) K all the CH₃CO₂H has desorbed from the surface.

Figure 3. XPS of the O 1s region for an CH₃CO₂H monolayer adsorbed on the Ag(111) surface at \( 90 \) K and after heating to \( 300 \) K. The spectrum exhibits one single broad feature at a binding energy of 535.2 eV for both oxygen atoms in the CO₂H group. After heating to \( 300 \) K all the CH₃CO₂H has desorbed from the surface.

Figure 4. TPD spectra for monolayers of the straight chain carboxylic acids H(CH₂)nCO₂H (n = 1–5) adsorbed on the clean Ag(110) surface at \( 90 \) K. The peak desorption temperatures increase by 10–15 K per CH₂ group in the alkyl chain. The heating rate was \( 5 \) K/s, and the fragment monitored had m/q = 44 amu.

Figure 5. Desorption energies ($\Delta E_{\text{des}}$) of the straight-chain carboxylic acids H(CH$_2$)$_n$CO$_2$H (n = 1–5) adsorbed on the clean Ag(110). The values of $\Delta E_{\text{des}}$ were estimated by using the Redhead equation with the peak desorption temperatures obtained from the monolayer TPD spectra and the assumption that the desorption preexponential was $\nu = 10^{13}$ s$^{-1}$. The $\Delta E_{\text{des}}$ are fit by the line $\Delta E_{\text{des}} = 10.6 + 0.9n$ kcal/mol.

and also loses about 75% of its intensity on heating from 90 to 300 K. Although this is not shown, there is also fluorine left on the surface. It is important to note that the XP spectra shown in Figures 2 and 3 for CH$_3$CO$_2$H on the Ag(111) surface reveal that all the CH$_3$CO$_2$H had desorbed from the surface after heating to 300 K. Further evidence that heating adsorbed CF$_3$CO$_2$H generates adsorbed CF$_3$CO$_2$ comes from the fact that the stoichiometry of the surface species remains F:C:O $\approx$ 3:2:2 on heating from 90 to 500 K.

CF$_3$CO$_2$H and the decomposition intermediate believed to be CF$_3$COH have been studied using HREELS on the Ag(110) surface and FT-IRRAS on the Ag(111) surface. Figure 10 shows the HREEL spectra for a CF$_3$CO$_2$H multilayer on the Ag(110) surface and the species present after annealing to 500 K. Many of the modes observed in the multilayer spectrum can be assigned to vibrational modes observed in gas-phase CF$_3$CO$_2$H.26 These assignments and the mode frequencies are listed in Table 1. The primary feature in the multilayer HREEL spectrum is an unresolved combination of the $\nu_{\text{CF}_3}$, $\nu_{\text{CF}_2}$, $\nu_{\text{CO}}$, and $\delta_{\text{OH}}$ modes at 1210 cm$^{-1}$. Once the surface has been heated to 500 K the spectrum becomes simpler, and the modes can be assigned to those that are observed in an aqueous solution of sodium 2,2,2-trifluoroacetate (CF$_3$CO$_2$Na).26-28 The assignments are listed in Table 2. The modes due to vibrations of the carboxylate group are absent, but the primary feature due to the $\nu_{\text{CF}_3}$ modes is still present.

Figure 6. TPR spectra of CF$_3$CO$_2$H adsorbed on the Ag(111) surface at varying coverages. At the low-coverage regions the spectra of CF$_3$CO$_2$H and CF$_3$CO$_2$ are quite similar, and it would be quite difficult to distinguish between the two on the basis of the frequencies of modes below 1500 cm$^{-1}$. The primary difference which suggests the formation of CF$_3$CO$_2$ from the acid is that the feature due to the $\nu_{\text{CF}_3}$ modes has red-shifted by about 30 cm$^{-1}$. In the reference spectra the $\nu_{\text{CF}_3}$ and $\nu_{\text{CF}_2}$ modes are both red-shifted by about 40 cm$^{-1}$ on going from gas-phase CF$_3$CO$_2$H to aqueous CF$_3$CO$_2$Na.26-28 The other feature which reveals that the low-temperature species is the molecular acid is the loss at 3020 cm$^{-1}$ which is due to the O-H stretch. This feature is not observed in the spectrum of the species thought to be CF$_3$CO$_2$ produced by heating to 500 K. Finally, it is interesting to note that the loss features at 1300–1500 cm$^{-1}$ in the HREEL spectrum of CF$_3$CO$_2$H that are due to the $\nu_{\text{CO}}$ stretch modes are quite weak. This suggests that the CF$_3$CO$_2$H is adsorbed roughly parallel to the surface such that neither of these two modes has significant projections onto the surface normal. The HREEL spectra support the proposal that CF$_3$CO$_2$H deprotonates during heating on the clean Ag(110) surface to produce CF$_3$CO$_2$.

The vibrational spectra of the CF$_3$CO$_2$H monolayer on the Ag(111) surface and the species remaining after heating the monolayer to 300 K have been obtained using FT-IRRAS and are shown in Figure 11. These are much simpler than the HREEL spectra on the Ag(110) surface, and the assignments have also been made by comparison.
with the vibrational spectra of gas-phase CF$_3$CO$_2$H and aqueous CF$_3$CO$_2$H$^+$. The spectrum of the CF$_3$CO$_2$H monolayer reveals features due to both the $\nu$$_{CF_3}$ and $\nu$$_{C-O}$ modes that are resolvable with FT-IRRAS. In addition, the absorption due to the $\nu$$_{C=O}$ mode is visible at 1781 cm$^{-1}$. After heating to 300 K there is only a single absorption that is assigned to the $\nu$$_{CF_3}$ mode. The fact that it is redshifted by 30 cm$^{-1}$ from the spectrum of the CF$_3$CO$_2$H monolayer at 90 K is consistent with the conversion of the adsorbed species into CF$_3$CO$_2$. In addition, the fact that only absorption due to the $\nu$$_{CF_3}$ mode is observed and there are no absorptions due to the $\nu$$_{C=O}$ or the $\nu$$_{CO_2}$ modes is consistent with the formation of a species lying with its plane roughly parallel to the Ag(111) surface. In summary, all the spectroscopic evidence points toward a reaction of CF$_3$CO$_2$H to form CF$_3$CO$_2$ on both the clean Ag(110) and Ag(111) surfaces.

4. Discussion

4.1. Surface Reaction Mechanism of Acids on Ag(110) and Ag(111). The results presented in the previous section provide a clear picture of the reaction mechanism of the hydrocarbon carboxylic acids on the Ag(110) and Ag(111) surfaces that is consistent with previous observations made using formic acid (HCO$_2$H) and CH$_3$CO$_2$H on the Ag(110) surface. CH$_3$CO$_2$H adsorbs and desorbs reversibly on both the Ag(110) and Ag(111) surfaces as illustrated below.

Furthermore, on the Ag(111) surface we observe that all the straight-chain hydrocarbon acids from acetic through to hexanoic acid desorb from the surface during heating without any evidence of deprotonation or decomposition. The only differences among the straight-chain acids are...
that the monolayer desorption energies\(^\textbf{29}\) increase with increasing alkyl chain length. The dependence on the alkyl chain length, \(n\), is given by the expression
\[
\Delta E_{\text{des}} = 10.6 + 0.9n \text{ kcal/mol.}
\]
The value of the desorption energy increment is similar to that for the interaction of straight chain alcohols with the Ag(110) surface for which the desorption energy increment is 1.1 kcal/mol/CH\(_2\)\(^\textbf{30}\) and that for alkyl groups on Cu(111) surfaces for which the desorption energy is incremented by 1.3 kcal/mol/CH\(_2\)\(^\textbf{31}\).

Ultimately, the point of this work has been to probe the nature of the transition state for the deprotonation of the acids. The desorption energy for hexanoic acid is 15.1 kcal/mol and represents a lower limit on the barrier to deprotonation, \(\Delta E^\ddagger_{\text{dep}}\), of the hydrocarbon carboxylic acids.

The fluorinated acids all appear to deprotonate on the Ag(110) and Ag(111) surface during heating. In the case of CF\(_3\)CO\(_2\)H the spectroscopic evidence suggests that, as expected, the deprotonation product is adsorbed CF\(_3\)CO\(_2\).

On the Ag(111) surface there is some desorption of the CF\(_3\)CO\(_2\)H monolayer at \(\sim 225\) K. The deprotonation of CF\(_3\)CO\(_2\)H must occur at lower temperatures to yield CF\(_3\)CO\(_2\).


The fact that it decreases strengthens our argument that the barrier to deprotonation is \( \Delta \epsilon_{\text{dep}} > 15.1 \) kcal/mol. This is due to the fact that fluorination of the methyl group lowers the gas phase heat of deprotonation by at least 1.6 kcal/mol.

The lowering of the \( \Delta \epsilon_{\text{dep}} \) of \( \text{RCO}_2 \text{H} \) on the Ag surfaces by fluorination of the alkyl group is consistent with the effects of fluorination on gas phase and solution phase acidities. Fluorination of the methyl group lowers the gas phase heat of deprotonation of \( \text{CH}_3 \text{CO}_2 \text{H} \) by 25 kcal/mol while in aqueous solution it is lowered by 1.7 kcal/mol.\(^8,32\) This is due to the fact that fluorination of the methyl group stabilizes the carboxylate anion product of the deprotonation reaction.

\[
\text{RCO}_2 \text{H} \rightarrow \text{RCO}_2^- + \text{H}^+
\]

For the acetic acids this effect is a reflection of the fact that the field substituent constant of the CF\(_3\) group, \( \delta_{\text{F}} \) (CF\(_3\)) = 0.44, is much greater than that of the CH\(_3\) group, \( \delta_{\text{F}} \) (CH\(_3\)) = 0.0.\(^3,34\) It is tempting to use this comparison of the effects of fluorine on the gas phase and surface deprotonation energetics to suggest that the deprotonation reaction on the Ag surfaces has a transition state that is anionic with respect to the adsorbed acid.

\[
\text{RCO}_2 \text{H}_{\text{ads}} \rightarrow [\text{RCO}_2^- \cdots \cdots \text{H}^+]^\ddagger
\]

However, it is important to point out that the fluorination also influences the energetics for gas-phase homolytic cleavage of the O–H bond.

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Fluorination of the methyl group lowers the homolytic bond dissociation energy from 105 to 103 kcal/mol. This decrease by 2 kcal/mol falls within the bounds of the effects of fluorination that we have measured on the Ag surfaces. Thus, these measurements do not yet enable us to distinguish between heterolytic and homolytic descriptions of the transition state to acid deprotonation on the Ag surfaces.

Although we know at this point that fluorine substitution of the alkyl groups in carboxylic acids lowers $\Delta E_{\text{dep}}^+$ on the clean Ag surfaces, the magnitude of the effect is still unknown. The value of $\Delta E_{\text{dep}}^+$ for CF$_3$CO$_2$H on the Ag(111) surface is probably of the same order as the $\Delta E_{\text{des}} = 13.5$ kcal/mol. However, for CH$_3$CO$_2$H and the other hydrocarbon carboxylic acids we can estimate only a lower limit on $\Delta E_{\text{dep}}^+$ of 15.1 kcal/mol. In the future, direct measurements of carboxylic acid deprotonation kinetics would be very interesting in order to put a firm value on the difference in $\Delta E_{\text{dep}}^+$ between the hydrocarbon and fluorocarbon acids. This is probably best accomplished by studying the kinetics of the deprotonation process on a surface on which both CH$_3$CO$_2$H and CF$_3$CO$_2$H are known to deprotonate. At that point it would be possible to compare the fluorine substitution effects with those observed in other environments such as the gas phase or solution phase.

5. Conclusion

The $\Delta E_{\text{dep}}^+$ is lower for CF$_3$CO$_2$H than that for CH$_3$CO$_2$H on the Ag(110) and Ag(111) surfaces. As a result, CF$_3$CO$_2$H deprotonates on the clean Ag surfaces under conditions in which the CH$_3$CO$_2$H simply desorbs into the gas phase. The product of the deprotonation of CF$_3$CO$_2$H on the Ag(111) and Ag(110) surfaces has been identified as a CF$_3$CO$_2$H group that appears to be adsorbed with its molecular plane roughly parallel to the surface. The fact that fluorination of the methyl group lowers the $\Delta E_{\text{dep}}^+$ is consistent with its effects on both gas-phase deprotonation and homolytic cleavage of the O–H bonds of acetic acids.

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