J. Am. Chem. Soc. 1993, 115, 6277–6283 6277

The β-Hydride Elimination Mechanism in Adsorbed Alkyl Groups

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Received August 5, 1992. Revised Manuscript Received December 16, 1992

Abstract: We have examined the kinetics of the β-hydride elimination reaction in propyl ($CH_3CH_2CH_2$-Cu) and trifluoropropyl ($CF_3CH_2CH_2$-Cu) groups on the Cu(111) surface. These species are formed at low temperatures ($T < 120$ K) by adsorption of propyl iodide (1-iodopropane, $CH_3CH_2CH_2I$) and trifluoropropyl iodide (1,1,1-trifluoro-3-iodopropane, $CF_3CH_2CH_2I$) and have been identified by their vibrational spectra. The adsorbed propyl groups decompose by β-hydride elimination to give propylene ($CH_3CH{=}CH_2$) and trifluoropropylene ($CF_3CH{=}CH_2$). Fluorination of the terminal methyl group increases the barrier to β-hydride elimination from 12.6 kcal/mol in adsorbed propyl to 21.0 kcal/mol in adsorbed trifluoropropyl. This dramatic influence of fluorine on the barrier indicates that charge separation in the transition state is of the form $C_\beta^{\delta+}\cdots H^{\delta-}$. Substitution of fluorine into the methyl group increases the reaction barrier by energetically destabilizing the cationic β-carbon in the transition state.

1. Introduction

The β-hydride elimination reaction and its microscopic reverse, olefin insertion into a metal–hydrogen bond, occur in numerous organometallic systems and have been studied for some time.[1,2] This reaction is of enormous importance in many heterogeneous catalytic reactions, including hydrocarbon conversion, olefin hydrogenation, the partial oxidation of alcohols, and in the chemical vapor deposition of metals.[3–6] Fairly recently β-hydride elimination has been shown to be the mechanism for dehydrogenation of alkyl groups generated from alkyl iodide adsorption on metal surfaces. The first observation of this process resulted from the adsorption of ethyl iodide on the Pt(111) surface to form ethyl groups (CH_3CH_2-Pt) which then decomposed to ethylene.[7] Selective deuteration clearly demonstrated that the reaction forming ethylene was β-hydride elimination. β-Hydride elimination has also been observed in alkyl groups adsorbed to Cu surfaces and leads to the formation of alkenes.[8–10] In this investigation we have used propyl iodide (1-iodopropane, $CH_3CH_2CH_2I$) to generate propyl groups on the Cu(111) surface ($CH_3CH_2CH_2$-Cu) which decompose by β-hydride elimination to yield propylene ($CH_3CH{=}CH_2$).[8] By also using trifluoropropyl iodide (1,1,1-trifluoro-3-iodopropane, $CF_3CH_2CH_2I$) we are able to compare the kinetics of β-hydride elimination in adsorbed propyl and trifluoropropyl ($CF_3CH_2CH_2$-Cu) on the Cu(111) surface. Fluorine substitution has an enormous influence on the β-hydride elimination rate, and we have taken advantage of this to understand the nature of charge separation in the transition state.

The reactions of alkyl iodides on Cu surfaces have been studied in some depth as a means to observe the formation of adsorbed alkyl groups and the various reactions in which they participate. These reactions include hydrogenation, complete dehydrogenation, β-hydride elimination to yield olefins, and even alkyl coupling to yield long-chain alkyl groups.[8–10] Again, selective deuteration demonstrated that the formation of olefins occurred by β-hydride elimination. We are specifically concerned with adsorbed propyl groups which can be generated on the Cu(111) surface and have been identified using HREELS.[11] At low coverages the propyl groups react on the surface by β-hydride elimination to give propylene which desorbs into the gas phase and has been identified using mass spectrometry.[9] Propylene desorption following β-hydride elimination is very rapid and can be used as a measure of the β-hydride elimination kinetics. At high coverages the reaction rate actually decreases. The reaction kinetics at high coverages are more complex and can only be understood by including site blocking effects which result in net reduction of the reaction rate. This effect has been observed during decomposition of butyl groups on the Cu(110) surface and has been studied in some detail.[12]

The results described here are part of a larger body of work in which fluorine has been used as a substituent in several surface species to influence reaction kinetics and provide a probe of transition state energetics. In a detailed study paralleling this one we have been able to study the energetics of the β-hydride elimination reaction in ethoxide and monofluoro-, difluoro-, and trifluoroethoxide ($F_nCH_{3-n}CH_2O$-Cu, $n = 0$–3) on the Cu(111) surface.[13] Fluorination of the methyl group increases the barrier to β-hydride elimination by destabilizing a transition state of the form $C_\beta^{\delta+}\cdots H^{\delta-}$. Fluorine has the opposite effect on deprotonation rates, lowering the barrier to acetic acid deprotonation on the Ag(110) surface by stabilizing the anionic transition state.[14,15] In a third example, the propyl coupling reactions observed on the Ag(111) surface, fluorination of the terminal methyl group has

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0002-7863/93/1515-6277$04.00/0

very little influence on the reaction kinetics.[16,17] This is consistent with the idea that there is very little charge separation in the transition state for these reactions. In many respects we are finding that fluorine is an ideal substituent for use in surface chemistry. Its high electronegativity results in strong influences on the energetics of reactions involving charged transition states. At the same time its relatively small size means that the steric differences between methyl and trifluoromethyl groups are minimal.

2. Experimental Section

The experiments were all performed in two ion pumped UHV chambers equipped with Ar^+ ion sputter guns, retarding field analyzers for Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), and quadrupole mass spectrometers for desorption measurements. One chamber also contained the high resolution electron energy loss spectrometer. A capillary array gas doser attached to a leak valve was used for introduction of gases into the chambers. The exposures to adsorbates are reported in Langmuirs ($1\ L = 1 \times 10^{-6}$ Torr·s) and are not corrected for differences in ion gauge sensitivity.

The sample was a Cu crystal cut and polished to expose the (111) surface. It was attached to a sample holder by spotwelding between two Ta wires. The sample holder was then mounted in contact with two liquid nitrogen reservoirs at the end of a manipulator. In the UHV chamber the sample could be cooled to <100 K or resistively heated to >1000 K with the temperature measurement made using a thermocouple attached to the side of the crystal. The sample temperature during heating was controlled by a computer. The surface was cleaned by cycles of Ar^+ ion sputtering followed by annealing to 900 K in vacuum.

Reaction/desorption experiments were performed with a shrouded quadrupole mass spectrometer. The sample was positioned within 2–3 mm of the aperture to the ionizer and then heated at variable rates with the temperature ramp controlled by computer. The mass spectrometer was capable of recording signals for up to five m/q ratios simultaneously.

The vibrational spectra were obtained using an LK-2000-10 HREEL spectrometer. Spectra were collected in multiple scans with collection times of 1 s/pt and incident beam energies of 0.77 eV for the propyl groups and 2.0 eV for the trifluoropropyl species. The sample was held at ~120 K while the spectra were being collected.

Trifluoropropyl iodide and propyl iodide were obtained from Lancaster Synthesis. The propyl iodide was filtered through a column of basic alumina to remove iodine and HI and was then distilled at reduced pressure. The trifluoropropyl iodide was used as received. The compounds were then stored in small glass vials containing a piece of etched copper wire and were protected from exposure to light. A small column of basic alumina was placed between the liquid sample and the leak valve to trap trace quantities of HI during the study. Both samples were degassed by several cycles of freezing, pumping, and thawing before introduction into the vacuum system.

3. Results

1. Vibrational Spectra of Adsorbed Propyl Groups. Figure 1A shows the HREEL vibrational spectrum of multilayers of propyl iodide adsorbed on the Cu(111) surface at 120 K. The modes and their assignments are given in Table I. The spectrum contains many of the modes expected based on comparison with the IR spectrum of liquid phase propyl iodide.[18] The observation of the ν_{CI} stretch modes at both 510 and 590 cm⁻¹ indicates the presence of both *trans* and *gauche* conformers in the multilayer.

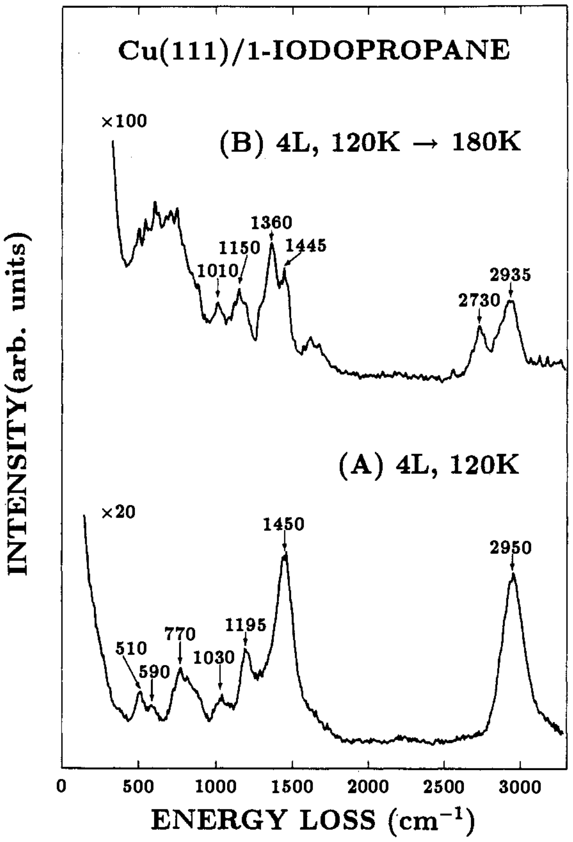

Figure 1. (A) HREEL spectrum for multilayers of propyl iodide adsorbed on the Cu(111) surface at 120 K ($I_{el} = 1.4 \times 10^4$ Hz, fwhm = 75 cm⁻¹). (B) HREEL spectrum of propyl on the Cu(111) surface formed by adsorption of propyl iodide at 120 K followed by heating to 180 K ($I_{el} = 1 \times 10^5$ Hz, fwhm = 60 cm⁻¹).

Table I. Comparison of the Vibrational Frequencies for Liquid Propyl Iodide (IR) and Propyl Iodide Adsorbed on the Cu(111) Surface (HREELS)

mode[a]	$CH_3CH_2CH_2I$ liquid[b]	multilayer $CH_3CH_2CH_2I$/Cu(111)	monolayer $CH_3CH_2CH_2$/Cu(111)
CI stretch (G)	503 cm⁻¹	510	
CI stretch (T)	592	590	
CH_2 rock (G)	764	770	
	816	850	
CC stretch	1020	1030	1010
CH_2 wag (T)	1185	1195	1150
CH_2 wag (G)	1195		
CH_3 sym def	1380		1360
CH_2 scissor (T)	1428		
CH_2 scissor (G)	1435		
CH_3 asym def	1456	1450	1445
CH_2 scissor	1460		
$C_\alpha H_2$ stretch (soft)			2730
CH_2, CH_3 stretch		2950	2935

[a] G and T refer to gauch and trans conformations. [b] Reference 14.

Heating to 180 K results in desorption of the multilayer leaving propyl groups and iodine on the surface. The vibrational spectrum of propyl on the surface is shown in Figure 1B. It is not possible to resolve the ν_{Cu-I} or ν_{Cu-C} modes in the low-frequency range of the spectrum; however, the dissociation of the C–I bond and formation of the propyl group can be inferred from the observation of the softened ν_{CH_2} mode at 2730 cm⁻¹. This mode has been observed in alkyl groups on several surfaces and arises from the α-CH_2 bonds.[11] The features at 1360 and 1445 cm⁻¹ arise from the $\nu_{CH_3}{}^{s}$ and $\nu_{CH_3}{}^{as}$ modes, respectively. The peak at 1445 cm⁻¹ may also have some contribution from the CH_2 scissor modes.

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Table II. Comparison of the Vibrational Frequencies for Liquid Trifluoropropyl Iodide (IR) and Trifluoropropyl Iodide Adsorbed on the Cu(111) Surface (HREELS)

mode[a]	CF_3CH_2-CH_2I liquid[b]	multilayer $CF_3CH_2CH_2I$/Cu(111)	monolayer $CF_3CH_2CH_2$/Cu(111)
CF_3 rock		375 cm^{-1}	
CF_3 asym def	576	575	560
CF_3 sym def	680		660
CH_2 rock (G)	738	725	
CC stretch sym (G, T)	837	835	825
CH_2 rock (G)	927	925	
CC stretch asym (G)	1073[c]	1075	
CF_3 stretch sym	1153	1160	1170
CF_3 stretch asym	1265	1265	1265
CH_2 scissor (T)	1365	1365	1350
CH_2 scissor (G)	1425	1425	
CH_2 stretch	2957	3000	2985

[a] G and T refer to the gauche and trans conformations. [b] Vibrational frequencies obtained from liquid phase IR of $CF_3CH_2CH_2I$ and assigned by comparison with the spectrum of $CF_3CH_2CH_2I$.[15] [c] In 1,1,1-trifluoro-3-chloropropane the CC asymmetric stretch of the trans conformation is ~10 cm^{-1} lower than that of the gauche conformation, but it is weak.

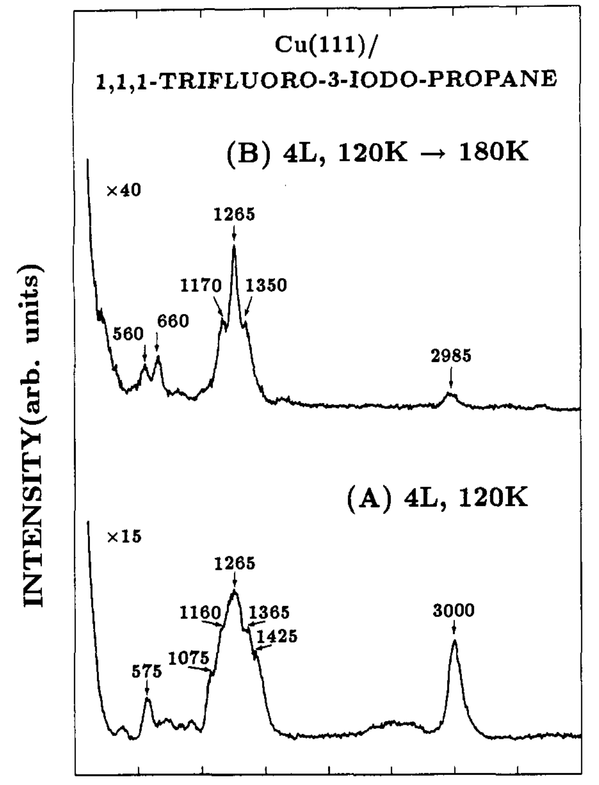

Figure 2. (A) HREEL spectrum for multilayer trifluoropropyl iodide adsorbed on the Cu(111) surface at 120 K (I_{el} = 9.2 × 10^3 Hz, fwhm = 70 cm^{-1}). (B) HREEL spectrum of trifluoropropyl on the Cu(111) surface formed by adsorption of trifluoropropyl iodide at 120 K followed by heating to 180 K (I_{el} = 2.3 × 10^4 Hz, fwhm = 60 cm^{-1}).

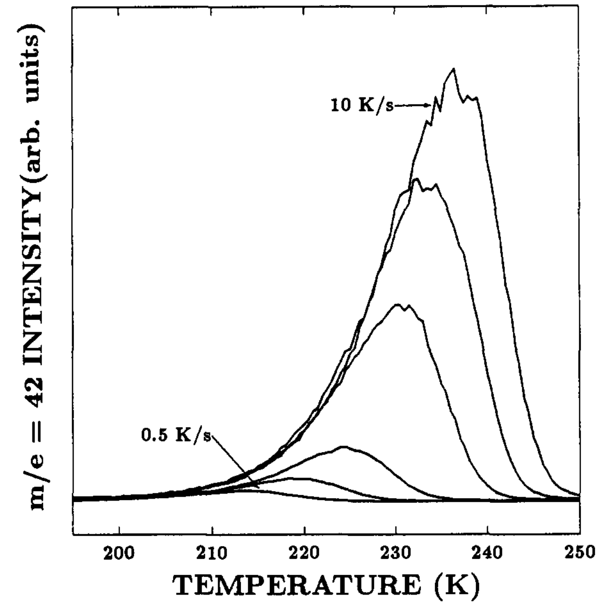

Figure 3. TPR spectra of propylene from the Cu(111) surface following adsorption of propyl iodide at 120 K with an exposure of 0.1 L. The heating rates vary from 0.5 to 10 K/s. m/q = 42 amu (parent ion).

The origin of the feature at 1600 cm^{-1} is unknown. In previous work in which propyl groups were generated from propyl bromide (1-bromopropane, $CH_3CH_2CH_2Br$) and propyl iodide the $\nu_{CH_3}{}^{as}$ mode was almost completely absent indicating that the C–C bond was aligned along the surface normal.[10,11] In our spectrum we are able to resolve a feature at 1445 cm^{-1} although it is lower in intensity than the $\nu_{CH_3}{}^{s}$ mode at 1360 cm^{-1}. This indicates either that the terminal C–C bond in the propyl group is tilted away from the surface normal or that the feature at 1445 cm^{-1} arises from the CH_2 scissors mode. In instances in which the terminal C–C bond is thought to lie parallel to the surface, the $\nu_{CH_3}{}^{as}$ mode dominates this region of the spectrum.[11] It is possible that orientation is sensitive to coverage and that small differences in coverage (orientation) are responsible for the differences between the spectrum in Figure 1B and that in ref 11.

The HREEL spectrum of the trifluoropropyl iodide multilayer on the Cu(111) surface at 120 K is shown in Figure 2A. The spectrum contains many of the modes expected on the basis of comparison with the liquid-phase IR spectrum of trifluoropropyl chloride (1-chloro-3,3,3-trifluoropropane, $CF_3CH_2CH_2Cl$).[19] The observation of the CH_2 scissors modes at 1365 and 1425 cm^{-1} indicates the presence of both *gauche* and *trans* conformers in the multilayer. The spectrum of the species which we believe to be adsorbed trifluoropropyl is shown in Figure 2B and is quite simple. The intensity of the ν_{CH} modes is very low and in some spectra they could not be observed at all. The dominant features are the $\nu_{CF_3}{}^{s}$ and $\nu_{CF_3}{}^{as}$ modes at 1170 and 1265 cm^{-1}, respectively. These are in the same positions as those observed for trifluoroethanol and trifluoroethoxide on the Cu(111) surface.[13,20] Angle resolved measurements in the ethoxides have shown that the ν_{CF_3} modes are dipole active. The fact that both are observed in the trifluoropropyl group indicates that the C–C bond in the trifluoropropyl group is tilted away from the surface normal as in the case of the propyl groups. The mode at 1350 cm^{-1} must arise from the CH_2 groups in the alkyl chain and is consistent with the position expected for the CH_2 scissors mode in the *trans* form of the alkyl chain.

The HREELS spectra shown in Figures 1 and 2 were taken at high propyl coverage. Unfortunately, it was not possible to obtain good spectra of the low coverage species which were used for the desorption measurements. The spectra that we have obtained do indicate the formation of propyl and trifluoropropyl groups on the surface, and these propyl groups at high coverage do decompose by β-hydride elimination to yield propylene and trifluoropropylene.

2. β-Hydride Elimination of Propyl to Propylene. Figure 3 shows the desorption of propylene produced by β-hydride elimination in propyl groups on the Cu(111) surface. The propyl

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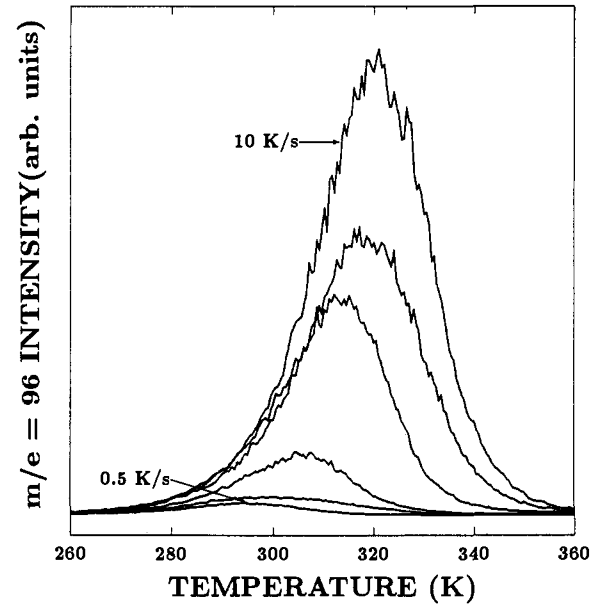

Figure 4. TPR spectra of trifluoropropylene from the Cu(111) surface following adsorption of trifluoropropyl iodide at 120 K with an exposure of 0.1 L. The heating rates vary from 0.5 to 10 K/s. $m/q = 96$ amu (parent ion).

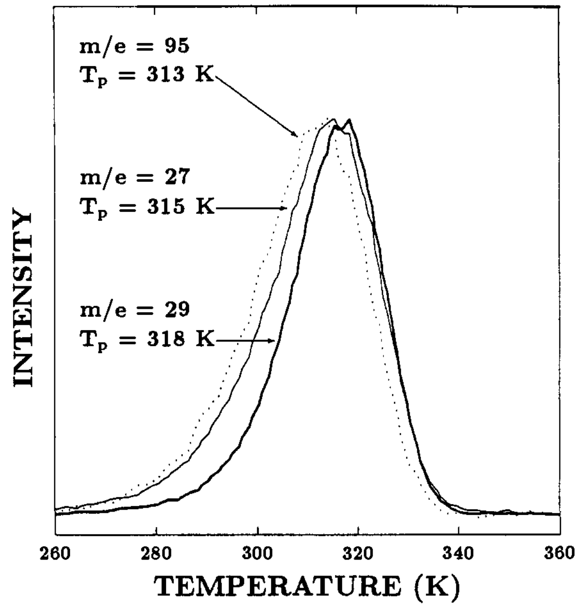

Figure 5. TPR spectra of trifluoropropylene ($m/q = 95$ and 27 amu) and trifluoropropane ($m/q = 27$ and 29 amu) from the Cu(111) surface following adsorption of propyl iodide at 120 K with an exposure of 0.05 L. The heating rate is 1 K/s. The spectra have been scaled to have the same amplitude.

groups have been generated by exposure to 0.1 L of propyl iodide with the surface at 120 K. Temperature programmed reaction (TPR) spectra of propylene production have been obtained by monitoring the signal at $m/q = 42$ amu during heating at rates from 0.2 to 20 K/s. The $m/q = 42$ amu fragment shown in Figure 3 belongs to the parent ion of propylene. The decomposition of propyl groups on Cu(110) and Cu(111) surfaces has been studied in some depth by others and propylene has also been identified as the reaction product in these studies on the basis of it fragmentation pattern in the mass spectrometer.[8,9] The β-hydride decomposition mechanism has been determined on the basis of deuterium labeling studies. For exposures to ≤ 0.1 L of propyl iodide the production of propylene displays first-order kinetics in that the desorption peak temperature is independent of exposure (coverage). Complications arise at higher exposures (coverages) as the peak shifts to higher temperatures and the decomposition rate at low temperatures (220–230 K) actually decreases. This effect has been observed in the case of butyl decomposition to butylene on the Cu(111) surface and propyl decomposition to propylene on the Cu(110) surface and has been ascribed to site blocking.[9,12] At high coverages alkyl groups block the hydrogen adsorption sites needed for β-hydride elimination resulting in a decrease in decomposition rate and an increase in the peak temperature for alkene desorption. We have been careful to make our measurements of β-hydride elimination kinetics using low exposures of propyl iodide (0.1 L) to avoid the complications arising at high propyl coverages.

Figure 4 shows the TPR spectra obtained during decomposition of trifluoropropyl groups on the Cu(111) surface. The trifluoropropyl groups were generated by exposure to 0.1 L of trifluoropropyl iodide at 120 K. The spectra were obtained by monitoring the $m/q = 96$ amu signal during heating at rates varying from 0.2 to 10 K/s. Identification of the reaction product is complicated by the fact that there appear to be two reaction products as shown by comparison of the $m/q = 27$, 29, and 95 amu signals in Figure 5. These appear to be trifluoropropylene and trifluoropropane both of which have a number of common ion fragments. Identification of one of the reaction products as trifluoropropylene has been made by observation of the product fragmentation pattern which includes the parent ion at $m/q = 96$ amu, $CF_3C_2H_2^+$ at 95 amu, CF_3^+ at 69 amu, and $CH_2{=}CH^+$ at 27 amu as major fragments. In addition to trifluoropropylene we observe the formation of trifluoropropane ($CF_3CH_2CH_3$) arising from the hydrogenation of the trifluoropropyl groups by hydrogen released onto the surface by β-hydride elimination. This can be identified on the basis of the observation of its parent ion and of the $CH_3CH_2^+$ fragment at $m/q = 29$ amu. Trifluoropropane evolution is observed at slightly higher temperatures than trifluoropropylene production. The TPR spectra obtained by monitoring the signals at $m/q = 95$ and 27 amu (trifluoropropylene) and $m/q = 29$ and 27 amu (trifluoro-propane) fragments are shown in Figure 5. In the case of propyl decomposition at low coverages ($T \approx 225$ K) there is no simultaneous hydrogenation of propyl to give propane. It is only at high coverages when the decomposition reaction is shifted to higher temperatures by site blocking ($T \approx 250$ K) that propane formation is observed.

The formation of gas-phase propylene and trifluoropropylene from propyl and trifluoropropyl groups is rate limited by β-hydride elimination kinetics. Adsorption of propylene and trifluoropropylene followed by heating results in desorption at temperatures below 200 K. The kinetics of propylene and trifluoropropylene desorption during propyl and trifluoropropyl decomposition can, as a result, be used as measures of the kinetics of β-hydride elimination.

Comparing Figures 3 and 4 it is immediately apparent that the rate of β-hydride elimination in trifluoropropyl is much lower than that in propyl. Although the product desorption profiles from the two reactions are slightly different and may be influenced by some coverage dependence of the reaction rate constant, this effect is minor compared to the absolute difference in the rate constants for β-hydride elimination in propyl and trifluoropropyl. At any given heating rate the peak temperature for trifluoropropylene production is ~80 K higher than that for propylene production. The kinetic parameters for the β-hydride elimination reactions have been determined by a first-order analysis by plotting $\ln(T_p^2/\beta)$ versus $1/T_p$ in Figure 6. "T_p" is the temperature of the peak desorption rate and "β" is the heating rate used to obtain the TPR spectrum. The barrier to β-hydride elimination increases from 12.6 ± 0.4 kcal/mol in adsorbed propyl to 21.0 ± 0.7 kcal/mol in trifluoropropyl. The increase in the decomposition barrier is compensated by an increase in the reaction pre-exponent from $10^{11.8\pm0.4}$ to $10^{14.3\pm0.6}$ s^{-1}. These effects of fluorination are similar

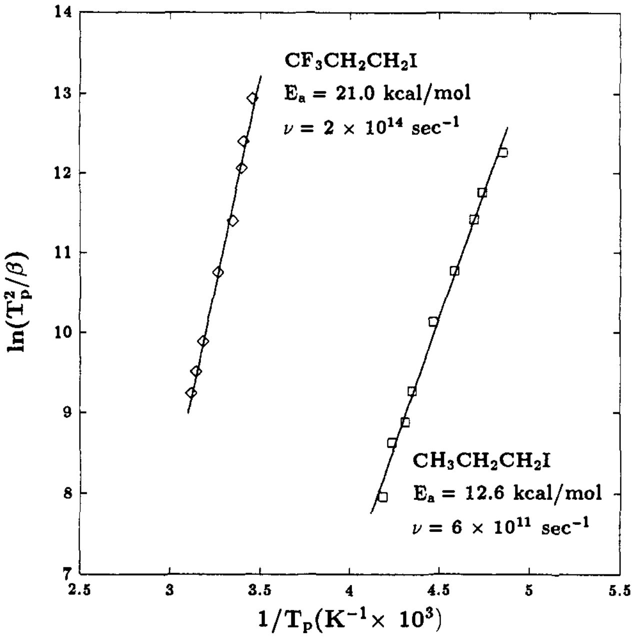

Figure 6. Plot of $\ln(T_p^2/\beta)$ vs $1/T_p$ for propylene and trifluoropropylene during decomposition of propyl and trifluoropropyl groups on the Cu(111) surface. The heating rate (β) was varied from 0.2 to 20 K/s for propyl decomposition and 0.2 to 10 K/s for trifluoropropyl decomposition. The slope of each line gives the activation barrier (E_a/R) for the β-hydride elimination reaction.

to those observed in the ethoxide decomposition reaction on the Cu(111) surface. Fluorination of the methyl group in ethoxide results in an increase in the β-hydride elimination barrier from 27 to 41 kcal/mol. As in the propyl decomposition reaction the pre-exponent for β-hydride elimination in ethoxides also increases by three orders of magnitude when the terminal methyl group is fluorinated.[13]

4. Discussion

1. Energetics of β-Hydride Elimination. The kinetics of β-hydride elimination in adsorbed propyl groups are dramatically influenced by fluorination of the terminal methyl group (γ-carbon) adjacent to the dissociating β-CH bond. The reaction barrier in trifluoropropyl is 8.4 kcal/mol greater than that in propyl. The issue that we wish to address first is whether or not this increase is due to the influence of fluorination on the transition state energetics or on the heat of formation of the propyl groups from the gas-phase propyl iodides. To show that it is in fact an influence on the transition state we must argue that the influence of the terminal trifluoromethyl group on the heat of dissociative adsorption of propyl iodide is significantly less than the 8.4-kcal/mol influence on the β-hydride elimination barrier.

The extreme electronegativity of fluorine causes it to stabilize anionic species and to destabilize cations. In earlier work we have studied the energetics of the formation of fluorinated ethoxides from fluorinated ethanols. The ethoxides are analogous to the propyl groups but form more polar adsorbate–metal bonds. If the adsorbate is ionic then the trifluoromethyl group will have a large influence on the heat of formation from a neutral gas-phase species. As an extreme case consider the influence of fluorination on the energetics of formation of gas-phase ethoxide anions by deprotonation of ethanols.

$$CH_3CH_2OH(g) \rightarrow CH_3CH_2O^-(g) + H^+(g)$$

The gas-phase heat of acidity for ethanol is 376.1 kcal/mol while that for trifluoroethanol is 364.4 kcal/mol.[21] Fluorination of the methyl group stabilizes the gas-phase ethoxide anion by ~12 kcal/mol. In the extreme case that the adsorbed ethoxide is considered purely anionic one might expect the same degree of stabilization of CF_3CH_2O–(ad) over CH_3CH_2O–(ad). This issue has been addressed by measuring the temperature dependence of the equilibrium constant for the reaction

$$CF_3CH_2OH(g) + CH_3CH_2O\text{–}(ad) \rightleftharpoons CF_3CH_2O\text{–}(ad) + CH_3CH_2OH(g)$$

on the Cu(111) surface. The heat of equilibrium is the difference in the heats of dissociative adsorption of the ethanols to form ethoxides. We have shown that there is very little difference (~2 kcal/mol) in the heats of dissociative adsorption of ethanol and trifluoroethanol.[13] In other words, fluorination of the methyl group in the ethoxides has little influence on the Cu–O bond strength. The Cu–C bond formed via dissociative adsorption of propyl iodide is expected to be less ionic than the Cu–O bond in the ethoxides and, as a result, fluorination of the methyl group should have little influence on the heat of formation of propyl and trifluoropropyl groups from the propyl iodides.

The interactions of the alkyl chains of these adsorbates with the surface are quite weak. Furthermore, the influence of fluorination on the interaction of the alkyl chain with the surface has been found to be quite small and certainly cannot account for an 8.4-kcal/mol difference in the heat of dissociative adsorption. Measurements of the reversible heats of adsorption of the straight chain alcohols on clean Ag(110) and Cu(100) surfaces have shown that the heat of interaction of the alkyl chains with the surface is ~1.2 ± 0.1 kcal/mol per CH_2.[22,23] The same number has also been obtained from reversible adsorption of the alkyl chlorides on the Cu(111) surface.[10] Similar measurements with the fluorinated alcohols on the Ag(110) and Cu(100) surfaces have shown that the heat of interaction of the fluorinated alkyl chains with these surfaces is 0.8 ± 0.1 kcal/mol per CF_2.[20,23] The minor influence of fluorination on the reversible heats of adsorption of ethanol and trifluoroethanol indicates that the contributions due to the dipole moment of the CF_3 group are quite small. Either its attractive interaction with its image in the metal surface is very weak or it is roughly canceled by dipole–dipole repulsions within the overlayer. The net influence of fluorination is to weaken the interaction of alkyl chains with the surface, and it cannot account for the differences in the barriers to β-hydride elimination in propyl and trifluoropropyl groups.

A final number of interest is the influence of an adjacent CF_3 group on the strength of a C–H bond. The C–H bond strength in gas-phase CF_3CH_3 is 106.7 kcal/mol which is 6.5 ± 1.5 kcal/mol greater than in CH_3CH_3 (100.3 kcal/mol).[24] The influence of a CF_3 group on the strength of a covalent Cu–C bond which is removed by two C–C bonds is expected to be significantly smaller.

Our discussion of the energetics of the β-hydride elimination process in adsorbed propyl is summarized in Figure 7. As in the case of the ethoxides on the Cu(111) surface we believe that the influence of the trifluoromethyl groups on the heat of dissociative adsorption of propyl iodide is quite small (~1 kcal/mol). By comparison the 8.4 kcal/mol barrier difference in the β-hydride elimination reaction is much larger and arises predominantly from transition state effects. The transition state is energetically destabilized by the substitution of fluorine into the adjacent methyl group. This is the same conclusion reached in our study of the β-hydride elimination reaction in adsorbed ethoxides on the Cu(111) surface.[13]

2. The Transition State for β-Hydride Elimination. The destabilization of the transition state for β-hydride elimination by fluorination of the adjacent methyl group has important implications on the nature of the transition state. Clearly the

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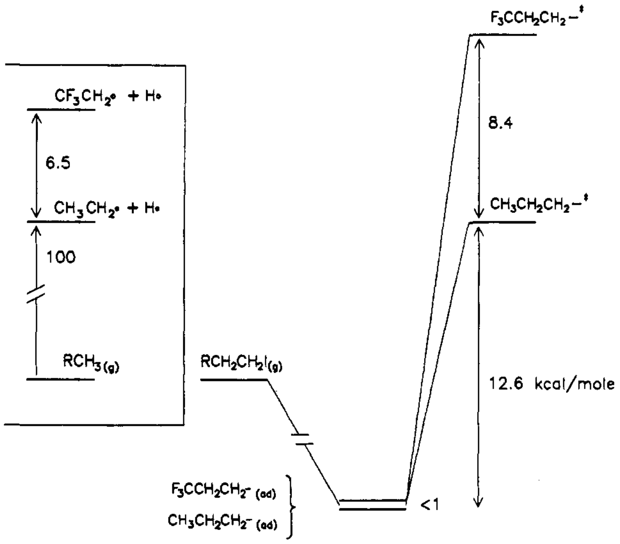


Figure 7. Illustration of the energetics of propyl and trifluoropropyl formation and decomposition on the Cu(111) surface. The influence of fluorine on the heat of formation of the propyl groups from the gas-phase iodide is taken to be quite small. The influence of fluorine in the reaction barrier is the result of its influence on the energetics of the transition state. The insert to the left shows the influence of fluorination on the C–H bond strength in ethane.

reaction cannot be thought of as deprotonation since one would expect fluorination to lower the reaction barrier by stabilizing the anionic C_β atom that would be generated in the process. As an example take the case of acetic acid in which fluorination of the methyl group lowers the gas phase heat of acidity by 26 kcal/mol by stabilizing the carboxylate anion.[21] In fact, the effect of fluorination on deprotonation kinetics has been observed on the Ag(110) surface.[14,15] In this instance fluorination of the methyl group stabilizes the anionic transition state ($CF_3CO_2^{\delta-}\cdots H^{\delta+}$) so that the barrier to deprotonation is lower in trifluoroacetic acid than in acetic acid.

The homolytic C–H bond strength in CF_3CH_3 is 6.5 kcal/mol greater than the strength of the C–H bond in CH_3CH_3.[24] This sets an extreme upper limit on the influence that fluorine might be expected to have on the barrier to a homolytic bond breaking reaction on the Cu(111) surface. Since the barrier to β-hydride elimination in adsorbed propyl is only ~15% of the C–H bond strength the influence of the trifluoromethyl group on the barrier to homolytic bond breaking should be a small fraction of its influence on the homolytic bond strength. In the simplest approximation the influence of the trifluoromethyl group on a homolytic transition state would be 15% of its influence on the homolytic bond strength or ~1 kcal/mol. In any case the influence of the trifluoromethyl group on the barrier to homolytic breaking of the β-CH bond should be substantially less than 6.5 kcal/mol and certainly less than the 8.4 kcal/mol destabilization that we observe.

The conclusion of this discussion is that the transition state for propyl decomposition should truly be thought of as a hydride elimination process in which the β-carbon atom is partially cationic. Figure 8 illustrates the reaction barrier and transition state for breaking the C_β–H bond in adsorbed propyl. Also shown are the expected influences of fluorination on transition states involving deprotonation, homolytic dissociation, and a transition state which would be truly described as hydride elimination. The data presented in this paper are clearly consistent with the picture of hydride elimination having a transition state with charge separation of the form $C_\beta^{\delta+}\cdots H^{\delta-}$. The electronegativity of the trifluoromethyl group in trifluoropropyl serves to destabilize this transition state with respect to the same transition state in adsorbed propyl.

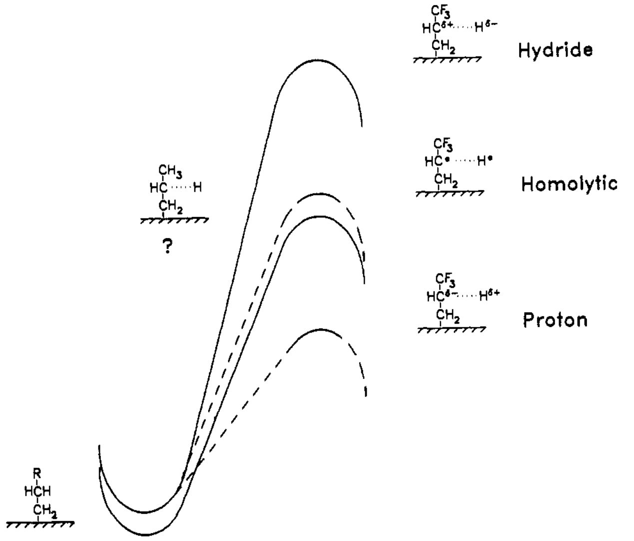
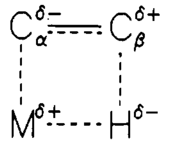


Figure 8. Illustration of the possible transition states for β-hydride elimination in propyl groups on the Cu(111) surface. In the case of deprotonation the reaction barrier is expected to drop. Fluorination should result in a small increase in the energy of the transition state for homolytic dissociation. The transition state consistent with our observations is one of hydride elimination which is energetically destabilized by fluorination of the methyl group.

A final issue that can be addressed is the rationale for the nature of the transition state. Measurements of both the forward and the reverse rates of propyl decomposition to propylene lead to an estimate of the heat of reaction at ΔH = 7 ± 4 kcal/mol.[25] The forward reaction, β-hydride elimination, is endothermic. This then suggests that the transition state for the reaction is "late" and resembles the Cu–H product which one can formally think of as a metal–hydride.

This type of transition state is consistent with the results of our work on the β-hydride elimination reaction in adsorbed ethoxides on the Cu(111) surface.[13] There the influence of fluorination was to increase the transition state energy by ~15 kcal/mol which is substantially higher than the influence of fluorine on the homolytic C–H bond strength. The same conclusions regarding the nature of the transition state have been reached on the basis of theoretical studies and experimental studies on surfaces and in organometallic complexes. Studies on the Al(100) surface show that in alkyls with primary, secondary, and tertiary β-carbon atoms the barrier to β-hydride elimination decreases with increasing methyl substitution.[26] Methyl groups adjacent to the C_β–H bond serve to stabilize the cationic transition state, lowering the reaction barrier. The effect is not nearly as marked as the effect of fluorination which we have observed and may be complicated by the steric effects associated with the use of the bulkier methyl substituents. The results on the Al surfaces combined with molecular orbital calculations[27,28] also suggest a reaction involving hydride elimination which has been described in terms of a four-center transition state with a cationic β-carbon atom.



Finally, the insertion of olefins into metal–H bonds has been studied in a set of Nb–H and Ta–H complexes. This reaction is the microscopic reverse of the β-hydride elimination reaction described here. On the basis of measurements of both equilibrium heats of reaction and reaction kinetics a transition state has been described which is identical with that shown above.[29]

5. Conclusions

On the Cu(111) surface propyl and trifluoropropyl groups decompose by β-hydride elimination to produce propylene and trifluoropropylene, respectively. The influence of fluorine is to increase the reaction barrier by destabilizing the transition state. This destabilization is expected in a transition state which would be truly described as a β-hydride elimination with charge separation of the form $C_\beta^{\delta+}\cdots H^{\delta-}$. The electronegativity of the trifluoromethyl group energetically destabilizes the cationic β-carbon.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research under Grant No. AFOSR 89-0278. A.J.G. holds a Fellowship in Science and Engineering from the David and Lucile Packard Foundation and is an A.P. Sloan Foundation research fellow.

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