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Mechanism of β-Hydride Elimination in Adsorbed Alkoxides

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Abstract: The fluorinated ethanols $F_nCH_{3-n}CH_2OH$ (n = 0–3) form fluorinated ethoxides when adsorbed on oxidized Cu(111), Cu(110), Cu(100), and Ag(110) surfaces. The fluorinated ethoxides decompose at elevated temperatures by β-hydride elimination to yield fluorinated acetaldehydes. Inclusion of fluorine in the methyl group systematically lowers the rates of β-hydride elimination, increasing decomposition temperatures by as much as 150 K. Measurements of the equilibrium constants between adsorbed ethoxides and of their decomposition kinetics on the Cu(111) surface serve to quantify the effects of fluorine on both the heats of dissociative adsorption of the ethanols and the activation barrier for β-hydride elimination. Fluorination has little effect (~2 kcal/mol) on the heat of formation of the ethoxides but has a much larger (~15 kcal/mol) destabilizing effect on the transition state for β-hydride elimination. This results from an electronic effect in which the trifluoromethyl group in the ethoxide destabilizes a transition state of the form $C^{\delta+}\cdots H^{\delta-}$ having net positive charge on the β-carbon atom.

1. Introduction

The β-hydride elimination reaction plays an important role in numerous reaction mechanisms in both surface chemistry and organometallic chemistry. In this work we have been able to use a set of fluorinated ethoxides to examine the nature of the transition state for the β-hydride elimination process. Previous investigations have demonstrated that alkoxide decomposition on Ag and Cu surfaces proceeds via β-hydride elimination, yielding aldehydes as products.[1-3] We will demonstrate that fluorination of the methyl group influences the kinetics of β-hydride elimination by destabilizing the transition state, increasing the reaction barrier, and thus lowering the rate of β-hydride elimination. The key to this work lies in the fact that we have chosen a system and a set of measurements which allow us to determine both the influence of fluorine on the heat of formation of the ethoxides and its influence on the kinetics of β-hydride elimination. This is fundamentally possible only because we have been able to find a system in which the initial-state ethoxide is stable over a very wide temperature range (200–360 K) and in which fluorine has an extremely large influence on the reaction barrier (~13 kcal/mol).[4]

Our results indicate that the transition state for the β-hydride elimination reaction involves charge separation in the direction $C^{\delta+}\cdots H^{\delta-}$ and have broad ranging implications. This reaction is important in numerous catalytic dehydrogenation processes involving both alkoxides and alkyl groups.[5,6] Its reverse is the first step in olefin hydrogenation reactions under both heterogeneous and homogeneous conditions.[7,8] Besides the fundamental interest in understanding the nature of the transition state for a reaction of this importance, understanding the nature of charge separation in the transition state allows us to predict the effects of numerous substituents on the kinetics of this reaction in a variety of molecules. Furthermore, the influence of fluorination on surface reaction kinetics is of current interest due to the importance of fluorocarbons for high-temperature tribological applications.[9] Fluorocarbon amphiphiles such as the alcohols and the acids are candidates for use as boundary layer additives in the perfluoropolyalkyl ether (PFAE) fluids used as high-temperature lubricants. The work presented here both demonstrates and explains in fundamental terms the increased thermal stability imparted by fluorine to surface alkoxides.

Study of the chemistry of methanol on the clean and oxidized Ag and Cu surfaces was originally motivated by the importance of these metals in partial oxidation catalysis.[1,5] The original studies showed that methanol adsorbs reversibly on the clean Ag(110) and Cu(111) surfaces. Methanol also adsorbs molecularly on the Cu(100) and Cu(110) surface but behaves slightly differently in that during heating ~5% of the monolayer decomposes to form methoxide rather than desorbing. The surface chemistry of ethanol and the longer chain alcohols is quite similar, although it has not been studied in the same detail.[2,10]

On the preoxidized Ag and Cu surfaces, methanol is deprotonated to form methoxide.[1,3] This process has been discussed in terms of "dual site mechanism" in which the active site consists of a Lewis acid–Lewis base pair. The metal ion serves as the adsorption site for the alkoxide, while the oxygen serves as the adsorption site for the hydroxyl proton. Methanol and adsorbed oxygen react to form water, which desorbs during heating. The methoxide then decomposes during heating by cleavage of a C–H bond to generate formaldehyde. The hydrogen produced during decomposition can either recombine and desorb as H_2 or hydrogenate methoxide to form methanol, which also desorbs rapidly. Little is known about the details of the methoxide decomposition step other than the fact that it is, indeed, rate limited by the C–H bond-breaking step. This has been determined on the Cu(111) surface using scanning kinetic spectroscopy to measure the decomposition kinetics of both CH_3O–Cu and CD_3O–Cu.[3] The observation of an isotope effect reducing the rate of formaldehyde desorption indicates that C–H (or C–D) bond breaking is the rate-limiting step in these reactions and that the desorption process is rapid by comparison.

The chemistry of ethanol on the oxidized Ag and Cu surfaces is similar in that it is deprotonated to form the ethoxide.[2] This then decomposes by breaking of a β-C–H bond to generate acetaldehyde. Acetaldehyde desorption is rapid and serves as a direct measure of the β-hydride elimination kinetics. It should be noted

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(1) (a) Wachs, I. E.; Madix, R. J. *Surf. Sci.* **1978**, *76*, 531. (b) Sexton, B. A.; Hughes, A. E.; Avery, N. R. *Surf. Sci.* **1985**, *155*, 366. (c) Bowker, M.; Madix, R. J. *Surf. Sci.* **1980**, *95*, 190. (d) Madix, R. J. *Adv. Catal.* **1980**, *29*, 1.

(2) (a) Wachs, I. E.; Madix, R. J. *Appl. Surf. Sci.* **1978**, *1*, 303. (b) Bowker, M.; Madix, R. J. *Surf. Sci.* **1982**, *116*, 549. (c) Sexton, B. A. *Surf. Sci.* **1979**, *88*, 299.

(3) Russel, J. N., Jr.; Gates, S. M.; Yates, J. T., Jr. *Surf. Sci.* **1985**, *163*, 516.

(4) Parker, B.; Zhang, R.; Dai, Q.; Gellman, A. J. In Applications of Surface Science and Advances in Tribology; Chung, Y., Homola, A. M., Street, G. B., Eds.; ACS Symposium Series 485; American Chemical Society: Washington, DC, Chapter 11.

(5) Forzatti, P.; Tronconi, E.; Pasquon, I. *Catal. Rev. Sci. Eng.* **1991**, *33* (2), 109.

(6) Garibyan, T. A.; Margoli, L. Y. *Catal. Rev. Sci. Eng.* **1989**, *31* (4), 355.

(7) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134 and references therein.

(8) Tanaka, K. *Adv. Catal.* **1985**, *33*, 99.

(9) (a) Jones, W. R.; Biershenk, T. R.; Juhlke, H. K.; Lagow, R. J. *Ind. Eng. Chem. Res.* **1988**, *27*, 1497. (b) Snyder, C. E.; Gschwender, L. J.; Tamborski, C. *Lubr. Eng.* **1981**, *37* (6), 344. (c) Snyder, C. E.; Gschwender, L. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22* (3), 383.

(10) (a) Dai, Q.; Gellman, A. J. *Surf. Sci.* **1991**, *257*, 103. (b) Zhang, R.; Gellman, A. J. *J. Phys. Chem.* **1991**, *95*, 7433.

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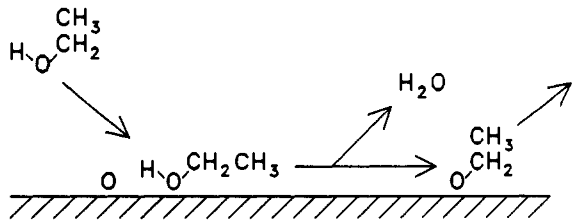

that by β-hydride elimination we refer to breaking of a C–H bond adjacent to the oxygen atom in the ethoxide. The approach that we have taken in this work is to use substituent effects as a probe of the transition state for this reaction. The basic nature of the problem imposes two requirements on the system used for study. First, it must be possible to determine the effects of the substituent on the activation barrier by measuring the temperature dependence of the reaction rate. Second, it must be possible to determine the influence of the substituent on the energetics of the reactant in order to separate the contributions of initial-state effects and transition-state effects. The fluorinated ethanols serve as good candidates for the study of the ethoxide decomposition process because fluorination of the methyl group increases its electronegativity and hence stabilizes negative charge or destabilizes positive charge on the β-carbon atom during C–H bond breaking. As a result, fluorination of the methyl group will have a strong influence on the reaction kinetics if there is charge on the β-carbon in the transition state.

An important aspect of our choice of ethanols for this study is that we are able to determine the influence of fluorination on the heat of formation of the initial-state alkoxide from gas-phase ethanol. In a series of experiments using a variety of acids on both Ag and Cu surfaces, Madix et al. have shown that the rates of displacement of weak acids by strong acids on these surfaces is quite rapid.[11] Displacement is sufficiently rapid that it is possible, for example, to completely displace methoxide with formate under ultra-high-vacuum (UHV) conditions. These high displacement rates have allowed us to measure equilibrium constants for the displacement of ethoxide by trifluoroethoxide at various temperatures and thus to determine the influence of fluorination on the heat of dissociative adsorption of ethanol and fluorinated ethanols. We will demonstrate that fluorine has little influence (~2 kcal/mol) on the heat of dissociative adsorption while it has a much greater influence on the activation barrier for β-hydride elimination (13 kcal/mol). The increase in the barrier to β-hydride elimination arises from electronic destabilization of the transition state, which involves charge separation in the direction $C^{\delta+}\cdots H^{\delta-}$. Increasing the electronegativity of the methyl group by adding fluorine increases the energy of the cationic β-carbon atom.

2. Experimental Section

All experiments were performed in two ultra-high-vacuum chambers equipped with optics for low electron energy diffraction (LEED) and Auger electron spectroscopy (AES) and quadrupole mass spectrometers for making desorption measurements. In addition, the chambers contained Ar^+ ion guns for sample sputtering and several leak valves fitted with capillary array dosers for introduction of gases into the chamber. One chamber contained the high-resolution electron energy loss (HREEL) spectrometer for vibrational spectroscopy of the adsorbed ethoxides.

The alcohols used in this work were CH_3CH_2OH (Mallinckrodt), FCH_2CH_2OH (Lancaster Synthesis), F_2CHCH_2OH (PCR Inc.), and F_3CCH_2OH (Lancaster Synthesis). These were purified by cycles of freezing, pumping, and thawing to remove high vapor pressure contaminants.

The quadrupole mass spectrometer used for desorption measurements was housed in a shield with a $^3/_8$-in. tube as an aperture to the ionizer. Desorption measurements were made by positioning the sample 2–3 mm from the front of the aperture and then heating the sample while monitoring several ion fragments with the mass spectrometer. Heating was controlled by computer, using a proportional/differential feedback routine to maintain a constant heating rate.

The HREEL spectra were taken with the sample at 100 K. To obtain vibrational spectra of the alkoxides, the crystals were heated to 250 K following alcohol adsorption on the preoxidized surface. This procedure desorbs water and unreacted alcohols, leaving only the alkoxide on the surface. The beam energy was always 5.5 eV, and the elastic peak intensities varied from 10^4 to 10^5 cps. The data collection time was 1 s/channel, which required a total scan time of 20 min.

All crystals used here were oriented on both faces, cut, and polished using standard techniques. These samples were spot welded between two Ta or Pt wires on a small sample holder which was then mounted on the end of a manipulator. The manipulator allows cooling of the sample to 100 K and resistive heating to >1000 K, with the sample temperature being measured using a chromel–alumel thermocouple spot welded to the side of the crystal. The crystal surfaces were cleaned by Ar^+ ion sputtering at 1000 eV and annealing in oxygen to remove carbon. Surface cleanliness was checked by Auger spectroscopy, and surface order was checked using LEED. In the case of the Ag(110) surface, cleanliness was also checked by adsorption of O_2 followed by heating in front of the mass spectrometer. The surface was deemed to be clean when there was no CO_2 desorption and oxygen desorption at 575 K was observed. Preoxidizing the surfaces was done under various conditions. The Ag(110) and Cu(110) surfaces were held at 300 K, the Cu(100) surface at 470 K, and the Cu(111) surface at 600 K during exposure to oxygen. The oxygen exposures were controlled to optimize the yield of acetaldehyde from the surface following exposure to ethanol.

The Cu(111) surface was used for most of the measurements in this work. After each reaction the surface was prepared by annealing at 1000 K for 20 s followed by exposure to 0.5 L of oxygen at 600 K in front of a stainless steel tube doser. Ethoxides were then produced by exposure of the surface at 200 K to ethanol or fluorinated ethanols using a capillary array doser. The ethanols are deprotonated by surface oxygen to form adsorbed ethoxide and water. At 200 K the water desorbs into vacuum. The temperature of the crystal was controlled by computer, allowing the annealing and dosing temperatures to be reproduced to within 2 K and held constant within this tolerance. The β-hydride elimination kinetics were then measured using a quadrupole mass spectrometer to monitor desorption of acetaldehyde and fluorinated acetaldehydes from the surface during heating. Heating rates were also controlled by computer and ranged from 0.5 to 20 K/s. In all cases a number of fragments including the parent ion were used to identify the desorbing product as the aldehyde.

In addition to exposing the surface to pure ethanol or fluorinated ethanols, a number of experiments were performed in which the preoxidized Cu(111) surface was exposed to mixtures of ethanols. The exposures were performed with the crystal held at temperatures in the range of 200–300 K to establish equilibria between the alkoxides formed on the surface. As an example, high exposure (>20 L) of the surface to a mixture of ethanol and trifluoroethanol results in the formation of an overlayer of ethoxide and trifluoroethoxide in equilibrium with the gas phase. The relative concentrations of the two ethoxides can be determined by measurement of the relative amounts of acetaldehyde and trifluoroacetaldehyde desorbing from the surface in a desorption experiment. In reality we measure the ratio of two integrated desorption peaks (for example, $I_{H3}:I_{F3}$), which is proportional to the ratio of the ethoxide coverages ($\theta_{H3}:\theta_{F3}$). Here θ_{H3} denotes the coverage of ethoxide and θ_{F3} denotes the coverage of trifluoroethoxide. The success of these equilibrium experiments rested on several factors. The first was the efficiency of the dosers used to expose the Cu(111) surface to the alcohols. These were capillary arrays ($l/d = 200$) mounted on the ends of tubes leading to leak valves. Comparison of the amount of ethanol adsorbed from a 0.1-L background exposure and exposure with the crystal ~5 mm from the doser (normal operating position) indicates that the enhancement factor is ×300. This means that the 0.1-L exposure used to achieve equilibrium between ethoxide and trifluoroethoxide corresponds to a true exposure of ~30 L. Another important factor was the 4000 L/s pumping speed of the cryopump used on the chamber in which these experiments were performed. This maintained the base pressure of the chamber at 2×10^{-10} Torr during these experiments. Most of the equilibrium exposures were performed with a background pressure of 1.0×10^{-9} Torr. During an exposure, the crystal was positioned immediately in front of the doser and held at a temperature between 200 and 300 K. Once the exposure had been completed, the crystal was immediately moved away from the doser and positioned in front of the mass spectrometer while being held at the exposure temperature. By stopping the exposure to the gas-phase ethanol mixture, the crystal is left covered with a mixture of ethoxides, the relative coverages of which can be measured by desorption. Provided that there is no change in the surface composition in the time between exposure and the desorption measurement, the yield of acetaldehyde and fluorinated acetaldehydes from the surface will

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(11) (a) Barteau, M.; Madix, R. J. *Surf. Sci.* **1982**, *120*, 262. (b) Jorgenson, S. W.; Madix, R. J. *Surf. Sci.* **1983**, *130*, L291.

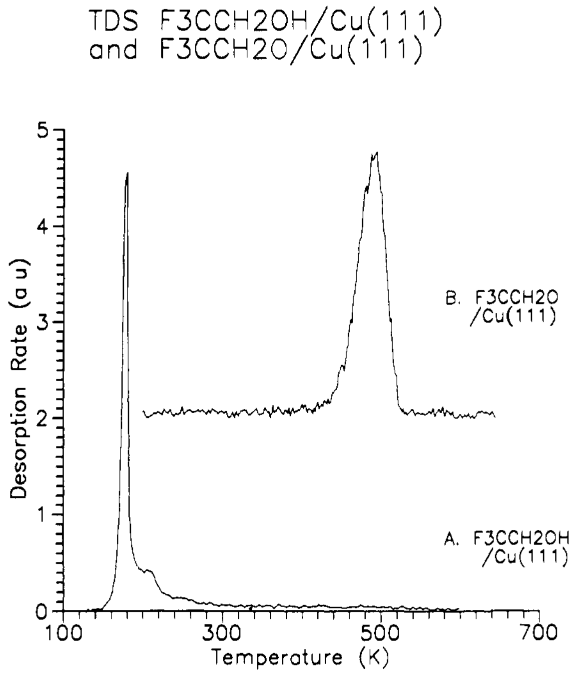

Figure 1. (A) Thermal desorption of F_3CCH_2OH on Cu(111) surface. $m/q = 31$ amu, $\beta = 5$ K/s. (B) Thermal desorption of F_3CCH_2OH on preoxidized Cu(111). Desorbing species is F_3CCHO from $F_3CCH_2O_{(ad)}$ decomposition. $m/q = 98$ amu, $\beta = 5$ K/s.

be representative of the ethoxide coverages on the surface during exposure to the mixture of gas-phase ethanols. At temperatures between 200 and 300 K, the ethoxide decomposition rate is extremely slow, so none of the surface ethoxide is lost to decomposition in the time between exposure and the desorption measurement. The entire exposure to ethanols in the background in the time between equilibrium exposure and thermal desorption was <0.1 L. Since the approach to equilibrium is quite slow, this background exposure is well below that needed to effect the equilibrium ethoxide concentrations on the surface. In some instances, equilibria were established by starting with a surface covered with a one-component overlayer of an ethoxide. These were produced by exposure of the surface to 30 L of the precursor ethanol at 200 K using a second capillary array doser in the chamber. With the surface thus saturated with one of the ethoxides, the crystal was then exposed to the mixture in the first doser.

3. Results

3.1. Trifluoroethanol on the Cu(111) Surface. Studies of the straight-chain hydrocarbon alcohols $CH_3(CH_2)_nCH_2OH$ and the fluorocarbon alcohols $CF_3(CF_2)_nCH_2OH$ on the Cu(111) surface have shown that the important aspects of their surface chemistries are identical.[13] On the clean surfaces these species adsorb reversibly and desorb intact during heating. Figure 1a shows the desorption of trifluoroethanol from the Cu(111) surface during heating. Desorption of the monolayer occurs at 180 K, which is slightly lower than the desorption temperature of ethanol (190 K). This behavior is also observed on the clean Ag(110) surface. On the Cu(100) and Cu(110) surfaces, a small fraction of the trifluoroethanol forms trifluoroethoxide, which decomposes during heating (495 K) to form trifluoroacetaldehyde. This difference between the Cu(111) surface and the Cu(100) and Cu(110) surfaces has also been observed with the hydrocarbon alcohols.[1]

On the oxidized Cu(111) surface, trifluoroethanol adsorbs irreversibly by deprotonating to form trifluoroethoxide and water. During heating, the water desorbs at ~200 K, leaving the trifluoroethoxide monolayer on the surface. This decomposes at high temperatures (495 K) by β-hydride elimination. Figure 1b shows the desorption of trifluoroacetaldehyde following the decomposition of trifluoroethoxide on the Cu(111) surface. Acetaldehyde and the fluorinated acetaldehydes have all been identified by monitoring desorption of both the parent ion in the mass spectrometer and the $m/q = 29$ amu signal resulting from the HCO^+ fragment.

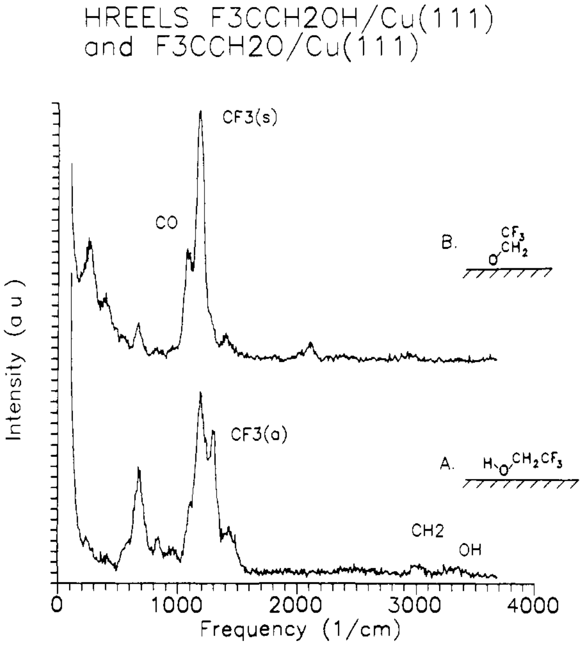

Figure 2. (A) HREELS of F_3CCH_2OH on Cu(111) ($I_{el} = 0.7 \times 10^5$ cps, FWHM = 75 cm^{-1}). (B) HREELS of F_3CCH_2O on Cu(111) ($I_{el} = 1.1 \times 10^5$ cps, FWHM = 70 cm^{-1}). $E_i = 5.5$ eV.

The vibrational spectra of both trifluoroethanol and trifluoroethoxide on the Cu(111) surface are shown in Figure 2. The spectrum of trifluoroethoxide was obtained after first exposing the preoxidized surface to trifluoroethanol at 100 K and then heating to 250 K to desorb water and unreacted alcohol. The sample was then cooled to 100 K before collecting the HREEL spectrum. Heating the sample to higher temperatures before taking the HREEL spectrum does not have any effect until one reaches the decomposition/desorption temperature range (495 K). The vibrational spectrum of trifluoroethanol adsorbed on the clean surface (Figure 2a) is only slightly perturbed from that of the liquid-phase species.[12] The dominant modes in the spectrum are the O–H stretch (3300 cm^{-1}), C–H stretch (3000 cm^{-1}), CH_2 deformation (1430 cm^{-1}), CF_3 stretches (1290 (asym) and 1185 cm^{-1} (sym)), C–O stretch (1090 cm^{-1}), CH_2 rock (950 cm^{-1}), C–C stretch (830 cm^{-1}), O–H bend (680 cm^{-1}), and CF_3 deformation (~600 cm^{-1}). The assignment is based on comparison with IR and Raman spectra of the liquid.[12] The formation of trifluoroethoxide on the preoxidized Cu(111) surface is indicated by the loss of the O–H stretch mode at 3300 cm^{-1}. The appearance of the mode at 260 cm^{-1} is indicative of the formation of the Cu–O bond. Although the C–H stretch at 3000 cm^{-1} is extremely weak, the presence of the CH_2 group is indicated by the deformation mode at 1400 cm^{-1}. The important features of these spectra have also been observed in the HREEL spectra of trifluoroethanol and trifluoroethoxide on both the Ag(110) and Cu(100) surfaces.[13] The other obvious feature of the trifluoroethoxide spectrum is the absence of the asymmetric CF_3 stretch mode (1290 cm^{-1}) and the dominance of the CF_3 symmetric stretch at 1185 cm^{-1}. These modes have been shown to be dipole active scatterers, and the absence of the asymmetric stretch is attributed to reorientation of the molecule such that the C–C bond is aligned along the surface normal, resulting in screening of the asymmetric mode of the CF_3 group.[13,14] The two geometries are depicted in Figure 2. The reorientation of the C–C bond on going from trifluoroethanol to trifluoroethoxide is also observed on the Ag(110) and Cu(100) surfaces.[13]

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(12) Travert, J.; Lavalley, J. C. *Spectrochim. Acta* **1976**, *32A*, 637.

(13) (a) Dai, Q.; Gellman, A. J. *J. Phys. Chem.* **1991**, *95*, 9443. (b) Dai, Q.; Gellman, A. J., to be published.

(14) (a) Harris, D. C.; Bertolucci, M. D. An Introduction to Vibrational and Electronic Spectroscopy; Oxford Univ. Press: New York, 1978. (b) Ibach, H.; Mills, D. L. Electron Energy Loss Spectroscopy and Surface Vibrations; Academic Press: New York, 1982.

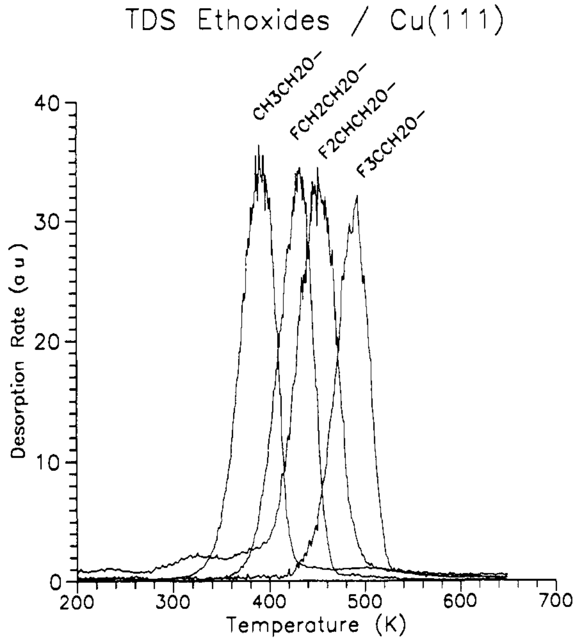

Figure 3. Thermal desorption of CH_3CHO, FCH_2CHO, F_2CHCHO, and F_3CCHO during decomposition of ethoxides on Cu(111). Masses monitored were m/q = 43, 62, 80, and 98 amu, β = 5 K/s.

Table I. Kinetic Parameters for β-Hydride Elimination in Alkoxides on the Cu(111) Surface

alkoxide	T_p of desorption peak max (β = 5 K/s)	E_a (kcal/mol)	log ν_{10} (s^{-1})	ϵ
CH_3O	428 K	(32.4 ± 1.2)^a	(16.2)^a	
CH_3CH_2O	390 K	29^b (27.0 ± 1.0)	15.2^b (14.7)	0.045^b
FCH_2CH_2O	432 K	33 (32.4 ± 1.0)	16.0 (16)	0.048
F_2CHCH_2O	452 K	35 (34.0 ± 1.3)	16.2 (16)	0.045
F_3CCH_2O	495 K	42 (41.0 ± 1.4)	17.9 (17.8)	0.032

[a] Parameters from fitting of data to $k = \nu \exp(-E_a/RT)$ in Figure 4. [b] Parameters from fitting to spectra simulated using $k = \nu \exp[-E_a(1 - \epsilon\theta)]$.

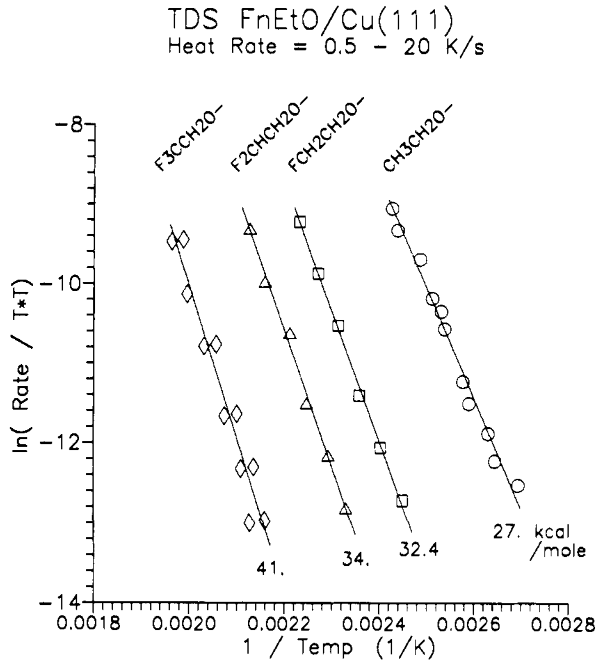

Figure 4. ln (β/T_p^2) vs $1/T_p$ for desorption of acetaldehyde and fluorinated acetaldehydes during decomposition of ethoxide and fluorinated ethoxides on Cu(111) heated at rates from 0.5 to 20 K/s.

The vibrational spectra of ethanol on the Cu(111) surface indicate that its surface chemistry is similar to that of trifluoroethanol in the sense that one observes the disappearance of the features due to the OH modes once ethoxide has been formed. The important difference, of course, is that whereas ethoxide decomposes at 390 K, trifluoroethoxide decomposes at 495 K. Fluorination of the methyl group results in a pronounced increase in thermal stability. The primary differences between the Ag and the Cu surfaces is that the ethoxide decomposition reactions all occur at temperatures ~100 K lower on the Ag(110) surface than they do on the Cu surfaces. The increase in thermal stability of fluorocarbon versus hydrocarbon alkoxides is also observed for the longer-chain species.[13]

3.2. Ethoxide Decomposition Kinetics. The decomposition rates of ethoxides adsorbed on the Cu(111) surface are systematically lowered as fluorine is substituted into the methyl group. Figure 3 shows the desorption of acetaldehydes following the decomposition of ethoxide and monofluoro-, difluoro-, and trifluoroethoxide on the Cu(111) surface. The decomposition reactions during heating at 5 K/s gives rise to peak desorption temperatures which increase by >100 K on going from ethoxide to trifluoroethoxide. The peak temperatures are listed in Table I.

In order to distinguish between the influence of fluorination on the preexponent of the rate constant for β-hydride elimination and its effect on the activation barrier, we have measured the ethoxide decomposition kinetics using heating rates between 0.5 and 20 K/s. Figure 4 plots $\ln(\beta/T_p^2)$ against $1/T_p$ (β = heating rate, T_p = peak desorption temperature) which yields a line of slope $-E_a/R$ for a first-order process. The preexponent can then be evaluated separately.[15] Both E_a and ν are listed in parentheses in Table I for each of the ethoxides. Also listed are the kinetic parameters measured for the decomposition of methoxide to formaldehyde on the Cu(111) surface.

In addition to using the simple first-order model to find the kinetic parameters for decomposition, we have simulated the desorption process and fit the calculated spectra to the real data. The desorption spectra for all heating rates have been fit to a single first-order desorption rate law with a rate constant of the form

$$k = \nu \exp[-E_a(1 - \epsilon\theta)/RT]$$

where θ is the ethoxide coverage, ν is the preexponent, and $E_a(1 - \epsilon\theta)$ is the reaction barrier. The term $(1 - \epsilon\theta)$ includes the coverage dependence of the desorption/decomposition energy to account for interactions between adsorbates. The results of this fitting procedure are listed in Table I and agree very closely with those obtained from the simple first-order analysis. The values of ϵ are all ~0.04, indicating a slight dependence (repulsive) of the activation energy on coverage. The repulsive interaction causes the activation energies found from the simple first-order coverage-independent analysis to be slightly lower than those found by fitting the data with a coverage-dependent activation energy. Although fluorination of the methyl group in ethoxide increases the preexponent from 10^{15} to 10^{18} s^{-1}, it is quite apparent that the dominant effect on the β-hydride elimination kinetics comes about from its influence on the reaction barrier, which is increased from 29 to 42 kcal/mol.

The increase in the activation barrier for ethoxide decomposition has also been observed on the Cu(100), Cu(110), and Ag(110) surfaces. Figure 5 illustrates the desorption of acetaldehydes from the Ag(110) surface resulting from decomposition of ethoxides. As in the case of the Cu(111) surface, there is an increase in the desorption temperature as the methyl group is fluorinated. The effect is even more pronounced on the Ag(110) surface in the sense that T_p increases by ~150 K on going from ethoxide to trifluoroethoxide. A second difference is that in all cases the rates of β-hydride elimination are greater on the Ag(110) surface than on the Cu surfaces.

3.3. Ethanol–Ethoxide Equilibrium. To understand the role that fluorine plays in decreasing the rates of β-hydride elimination in the ethoxides, it is necessary to determine whether its influence

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

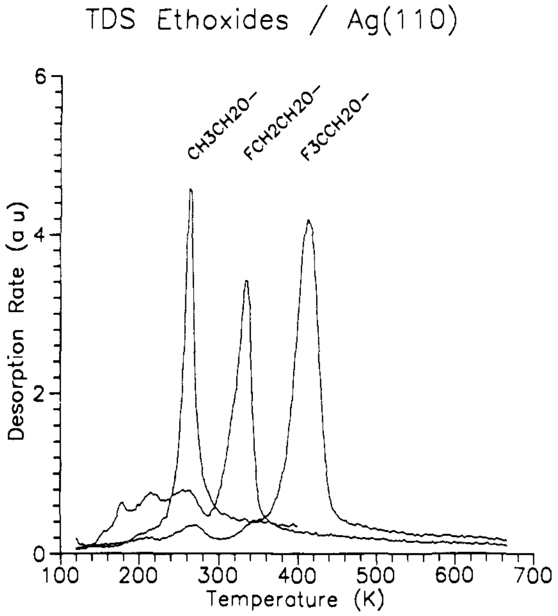

Figure 5. Thermal desorption of CH_3CHO, FCH_2CHO, and F_3CCHO during decomposition of ethoxides on Ag(110). Masses monitored were $m/q = 29$ amu, $\beta = 5$ K/s.

is on the energetics of the initial state or the transition state. The importance of the system that we have chosen to study is that we are able to observe both the displacement of ethoxide by trifluoroethanol and the displacement of trifluoroethoxide by ethanol on the Cu(111) surface under UHV conditions. This allows us to reach equilibrium in reaction 1 quite rapidly. The heat of

$$CH_3CH_2OH_{(g)} + F_3CCH_2O_{(ad)} \rightleftharpoons CH_3CH_2O_{(ad)} + F_3CCH_2OH_{(g)} \quad (1)$$

reaction gives the difference between the heats of dissociative adsorption of the ethanols.

$$CH_3CH_2OH_{(g)} \rightarrow CH_3CH_2O_{(ad)} + H \qquad \Delta H_{H3}$$

$$H + F_3CCH_2O_{(ad)} \rightarrow F_3CCH_2OH_{(g)} \qquad -\Delta H_{F3}$$

The experiments performed to find the heat of reaction 1 have consisted of exposing the preoxidized Cu(111) surface to a gas-phase mixture of ethanol and trifluoroethanol with the crystal held at temperatures between 200 and 300 K. The equilibrium constant for the reaction is given by

$$K = P_{F3}\theta_{H3}/P_{H3}\theta_{F3}$$

$$= (P_{F3}/P_{H3}) \times (\theta_{H3}/\theta_{F3})$$

(P_{F3} = F_3CCH_2OH pressure, P_{H3} = CH_3CH_2OH pressure, θ_{F3} = $F_3CCH_2O_{(ad)}$ coverage, θ_{H3} = $CH_3CH_2O_{(ad)}$ coverage.) Using a solution with a fixed ratio of ethanol and trifluoroethanol, the ratio of the gas-phase pressures P_{F3}/P_{H3} will be constant and independent of crystal temperature. The equilibrium constant can be measured at different temperatures by determining the ratio of the ethoxide coverages θ_{H3}/θ_{F3} at equilibrium. This is done by desorbing the mixture of ethoxides into the mass spectrometer. Since ethoxide and trifluoroethoxide decompose at much different temperatures and also yield different fragments in the ionizer of the mass spectrometer, it is quite simple to separate the relative contributions of each in the desorption spectrum.

In practice, it is very difficult to obtain a measure of the true equilibrium constant (K) for reaction 1. On the one hand, it would be necessary to know the true ratio of the pressures of the ethanols (P_{F3}:P_{H3}) in the gas phase over the surface. This is complicated by the need to know the pressures over the liquid mixture, the rates of effusion through the doser, and finally the pumping speed for each ethanol in the mixture. Furthermore, it is quite possible that the effective pressures in the chamber vary with respect to position in front of the capillary array doser, and some variation in equilibrium ethoxide coverages was observed if the crystal position was varied. A second complication arises from the need to obtain measurements of the ratio of the coverages of the ethoxides (θ_{H3}:θ_{F3}) from the aldehyde desorption spectra obtained during their decomposition. This would require calibration of the mass spectrometer signal and knowledge of the relative pumping speeds of the aldehydes. The task of measuring K in absolute terms is almost impossible.

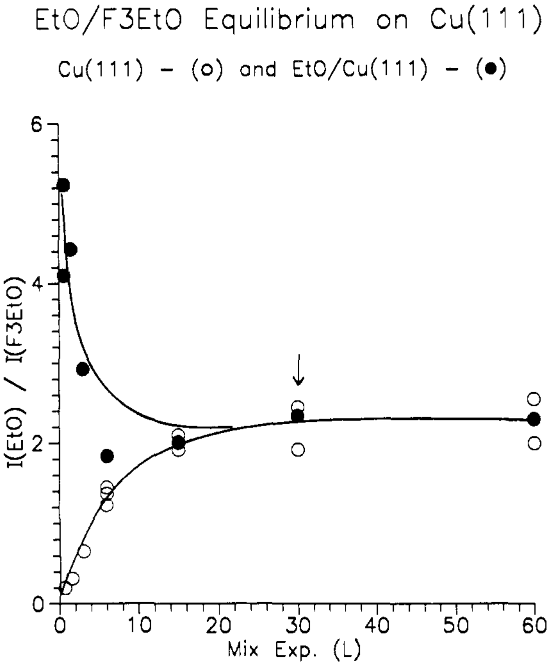

Figure 6. Ratio of ethoxide to trifluoroethoxide desorption signals on the Cu(111) surface following increasing exposure to vapor from a 1:6 solution of ethanol and trifluoroethanol. The open circles (○) are the signal ratios obtained starting with a clean, preoxidized Cu(111) surface. The solid circles (●) are obtained starting with a surface saturated with ethoxide before exposure to the mixture. The ethoxide-to-trifluoroethoxide signal ratio approaches the same equilibrium value starting with both surfaces. Exposures were made at 200 K.

However, provided that the ratio of the gas-phase ethanol pressures is kept as a constant by using the same mixture and the same crystal position during exposure, it is not necessary to know any other parameters to obtain the heat of equilibrium for reaction 1. Since we ultimately determine the equilibrium heat of reaction from d ln $(K)/d(1/T)$, it is only necessary to measure quantities which are proportional to the true coverages. If the signals for ethoxide and trifluoroethoxide desorption yields are I_{H3} and I_{F3}, respectively, then we can define a pseudoequilibrium constant

$$K' = I_{H3}/I_{F3} \propto \theta_{H3}/\theta_{F3} \propto (P_{F3}/P_{H3})(\theta_{H3}/\theta_{F3}) = K$$

which we measure directly. This is proportional to the true equilibrium constant, and d ln $(K')/d(1/T)$ will yield the heat of reaction.

A key issue to which we have devoted our attention is demonstrating that one can reach true equilibrium with the types of exposures that are feasible under ultra-high-vacuum conditions. Figure 6 shows the ratio I_{H3}:I_{F3} obtained following various exposures of a Cu(111) surface at 200 K to a gas-phase mixture of vapor obtained from a solution containing a 1:6 ratio of ethanol to trifluoroethanol. The circles give the I_{H3}:I_{F3} ratios obtained starting with an initially clean, preoxidized surface and have been determined by integrating the signal from the $m/q = 29$ amu fragment during decomposition of both ethoxide and trifluoroethoxide. In order to obtain relatively low exposures (<10 L) with some control and reproducibility, this set of exposures was made with the sample positioned ~25–30 mm from the capillary array doser, thereby reducing its enhancement of the gas-phase pressure.

At low exposures the surface is covered predominantly by trifluoroethoxide. It is important to note that the surface is saturated with the ethoxides at exposures of <2 L and that the

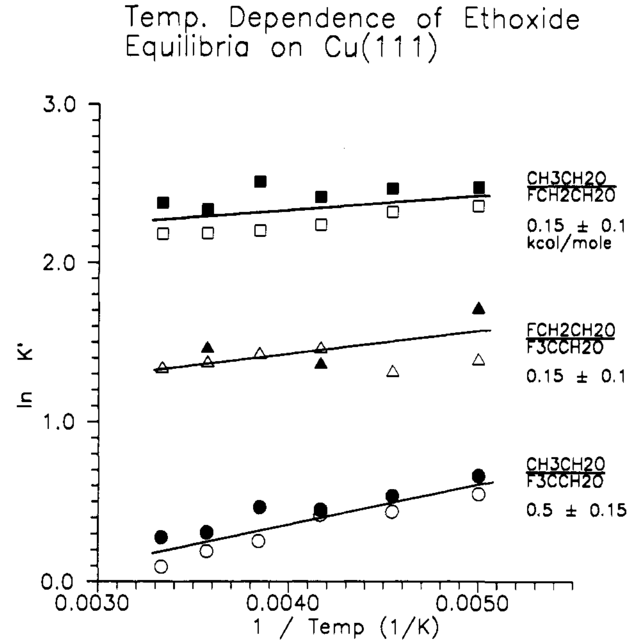

Figure 7. ln (K') vs $1/T$ for mixtures of ethanol, monofluoroethanol, and trifluoroethanol on the Cu(111) surface. K' is the ratio of desorption signals of the two ethoxides on the surface and is proportional to the equilibrium constant K for reaction between gas-phase ethanols and surface ethoxides. The slopes in kcal/mol are given on the figure. Exposure was 30 L.

subsequent increase in the I_{H3}:I_{F3} ratio is a direct observation of the displacement of trifluoroethoxide by gas-phase ethanol. As the exposure is increased, trifluoroethoxide is replaced by ethoxide until equilibrium is approached and I_{H3}:I_{F3} ceases to change. The exposures have been continued to 150 L without observing any further change in the I_{H3}:I_{F3} ratio.

In order to demonstrate that we have reached true equilibrium, we have also started with a surface saturated with ethoxide. The filled circles in Figure 6 show the I_{H3}:I_{F3} ratio following exposure of an ethoxide saturated Cu(111) surface to the ethanol/trifluoroethanol mixture. Initially the surface is covered with ethoxide, but as the exposure is increased ethoxide is replaced with trifluoroethoxide until the ratio I_{H3}:I_{F3} reaches the same equilibrium value as is found on the surface initially saturated with trifluoroethoxide. In this fashion, we have been able to approach equilibrium from both sides. The exposure used for subsequent measurements of the equilibrium constant is 30 L (marked with an arrow in Figure 6) and is clearly sufficient to reach equilibrium. The measurements in Figure 6 were made with the crystal at 200 K, which is the low end of the temperature range over which we have made equilibrium measurements. We expect equilibrium to be reached more rapidly at the higher temperatures, although in practice we observed no significant difference in the exposures needed to reach equilibrium.

3.4. Relative Heats of Ethoxide Formation. The differences in the heats of ethoxide formation from gas-phase ethanol can be determined from the temperature dependence of the equilibrium constant for reaction 1. We have made measurements of the pseudoequilibrium constants (K') using all three possible mixtures of ethanol, monofluoroethanol, and trifluoroethanol over a temperature range of 200–300 K. Figure 7 plots ln(K') against $1/T$ for each of the three mixtures. Since K' is proportional to K, the slopes of these lines give the equilibrium heat of reaction, however, the absolute magnitudes of K' are of no significance since they were obtained by monitoring different ion fragments for each decomposition reaction.

The ethanol/trifluoroethanol solution had a concentration ratio of 1:6. The open-circle points were obtained starting with a preoxidized Cu(111) surface. In this instance the surface is initially covered with trifluoroethoxide early in the exposure and then approaches equilibrium as the exposure is continued and the trifluoroethoxide is displaced by ethoxide. The solid-circle points were obtained on surfaces that were first saturated with ethoxide before exposure to the mixture. In this fashion, the data plotted in Figure 7 provide both upper and lower bounds on the equilibrium constant at each of the temperatures used.

Table II. Gas-Phase Heat Capacities (cal/mol/K)

compd	exptl[19]	MOPAC VI
CH_3CH_3	12.6	12.0
CH_3CF_3	18.7	18.3
CH_3CH_2OH	15.6	15.3
FCH_2CH_2OH		16.8
F_3CCH_2OH		21.5

The slope of the plot is $\delta_{H3/F3} = 0.5 \pm 0.15$ kcal/mol, favoring formation of ethoxide over trifluoroethoxide. The data for the other two mixtures are plotted in the same fashion. It is important to note that the slopes for the three mixtures are self consistent in that the heats of reaction for the ethanol/monofluoroethanol ($\delta_{H3/FH2} = 0.15 \pm 0.1$ kcal/mol) and the monofluoroethanol/trifluoroethanol ($\delta_{FH2/F3} = 0.15 \pm 0.1$ kcal/mol) mixtures add up to the heat of reaction for the ethanol/trifluoroethanol mixture ($\delta_{H3/F3} = 0.5 \pm 0.15$ kcal/mol).

Obtaining the heats of reaction actually requires a small correction, since in our experiment the gas phase is at 300 K while the surface temperature is being varied. The equilibrium constant that we have measured is

$$K = \left[\frac{P_{F3}{}^{300}}{P_{H3}{}^{300}}\right]\left[\frac{\theta_{H3}{}^{T}}{\theta_{F3}{}^{T}}\right]$$

where we have used superscripts to denote the temperature of the gas and the surface. The true equilibrium constant from which we wish to obtain the heat of reaction 1 is

$$K_{eq} = \left[\frac{P_{F3}{}^{T}}{P_{H3}{}^{T}}\right]\left[\frac{\theta_{H3}{}^{T}}{\theta_{F3}{}^{T}}\right]$$

$$= \left[\frac{P_{F3}{}^{T}}{P_{H3}{}^{T}}\right]\left[\frac{P_{H3}{}^{300}}{P_{F3}{}^{300}}\right]\left[\frac{P_{F3}{}^{300}}{P_{H3}{}^{300}}\right]\left[\frac{\theta_{H3}{}^{T}}{\theta_{F3}{}^{T}}\right]$$

$$= K_g \cdot K$$

where K is the constant that we have measured. K_g is the constant for the reaction

$$CH_3CH_2OH_{(g)}{}^{T} + F_3CCH_2OH_{(g)}{}^{300} \rightleftharpoons CH_3CH_2OH_{(g)}{}^{300} + F_3CCH_2OH_{(g)}{}^{T}$$

the heat of which is given by

$$\Delta H_g = (C_{F3} - C_{H3})(T - 300)$$

C_{F3} and C_{H3} are the heat capacities of trifluoroethanol and ethanol, respectively. The heat capacity of trifluoroethanol should be higher than that of ethanol. We have not found an experimental value for C_{F3} and so have resorted to the use of a molecular mechanics package (MOPAC VI) to obtain an estimate. Table II lists experimental values of the heat capacities and the molecular mechanics predictions for several hydrocarbons and fluorocarbons. The predictions appear to be fairly accurate, and the difference in the heat capacities of trifluoroethanol and ethanol is ~6 cal/mol/K. The true equilibrium heat of reaction is finally given by

$$\Delta H_{eq} = -\frac{d\ln(K_{eq})}{d(1/T)}$$

$$= -\left(\frac{d\ln(K_g)}{d(1/T)}\right) - \left(\frac{d\ln(K)}{d(1/T)}\right)$$

$$= -(C_{F3} - C_{H3}) \times 300 - \delta$$

$$= -2.3 \text{ kcal/mol}$$

This is actually an over estimate since the heat capacities decrease

Table III. Gas-Phase Heats of Acidity for Fluorinated Alcohols and Acids:[16] $AH_{(g)} \rightarrow A^-_{(g)} + H^+_{(g)}$

R	ΔH (kcal/mol)	
	RCH_2OH	RCO_2H
H	379.2	345.2
CH_3	376.1	348.5
FCH_2	371.0	337.6
F_2CH	367.0	330.0
F_3C	364.4	322.7

with temperature and we have assumed a constant value between T and 300 K. The corrected heat of equilibrium for the reaction involving ethanol and monofluoroethanol is −0.6 kcal/mol.

The corrections due to the heat capacities still leave equilibrium favoring the formation of ethoxide over the fluorinated ethoxides. The important point, having the greatest implication for our understanding of the β-hydride elimination reaction, is that the equilibrium heats of reaction 1 are much smaller than the influence of fluorine on the kinetics for the β-hydride elimination reaction.

4. Discussion

4.1. Energetics of β-Hydride Elimination. The primary goal of this work has been to understand the influence of fluorine on the energetics of β-hydride elimination in adsorbed ethoxides and from that to understand the nature of the transition state for this reaction. It is quite clear from the kinetic measurements of ethoxide decomposition to acetaldehyde that fluorination of the methyl group has an enormous influence on the reaction kinetics, raising the decomposition barrier from 29 kcal/mol in ethoxide to 42 kcal/mol in trifluoroethoxide. The increase in the activation barrier for this process can be the result of a lowering of the initial-state energy, an increase in the transition-state energy or some combination of both effects. The influence of fluorine on the energetics of the initial-state ethoxide and the transition state will depend on the nature of charge distribution in the two. In simple terms, fluorination of the methyl group increases its electronegativity, thereby energetically destabilizing positive charge in the molecule and stabilizing negative charge.

The extent to which fluorination of ethanol can, in principle, stabilize the initial-state ethoxide can be estimated from the gas-phase heats of acidity of the ethanols. These are known for

$$F_nCH_{3-n}CH_2OH_{(g)} \rightleftharpoons F_nCH_{3-n}CH_2O^-_{(g)} + H^+_{(g)}$$

all four ethanols and are listed in Table III.[16] As can be seen, fluorination stabilizes the ethoxide anion by 12 kcal/mol. Measurements of the displacement of one acid by another on the Cu and Ag surfaces have shown that the relative ordering of acid strengths is the same as that observed in the gas phase.[11] In the extreme case in which ethoxide adsorbed on the Cu(111) surface is considered to be purely anionic and there are no screening effects due to the metal, the influence of fluorination on the initial state could account almost entirely for the increase in the barrier to β-hydride elimination. If the influence of fluorine on the activation barrier arises purely from its influence on an ionic initial state, then the energies of the transition states would not differ. In this case the equilibrium constant for reaction 1 would vary from 10^{-13} to 10^{-9} in the temperature range from 200 to 300 K, favoring trifluoroethoxide over ethoxide on the surface.

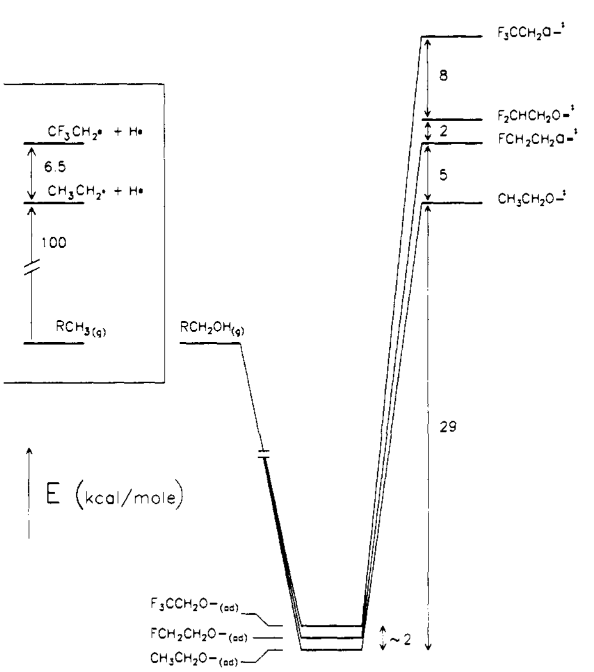

Figure 8. Relative heats of formation of fluorinated ethoxides from gas-phase ethanols and activation energies for β-hydride elimination in fluorinated ethoxides on the Cu(111) surface. The influence of fluorine on the transition-state barrier is much greater than on the heat of formation of the ethoxides. The inset at the upper left illustrates the influence of CF_3 groups on the strengths of adjacent C–H bonds. The homolytic C–H bond strength in CF_3CH_3 is 6.5 kcal/mol greater than that in CH_3CH_3.

Although we have already noted that measurement of the true equilibrium constant (K) is extremely difficult, it is worth making an order-of-magnitude estimate of its value from the data in Figure 6. The room temperature vapor pressures of trifluoroethanol and ethanol are 75 and 60 Torr, respectively, or roughly equal.[19] The mixture contained a 6:1 ratio of trifluoroethanol to ethanol in the liquid. Assuming that the solution behaves ideally, the ratio of the vapor pressure over the liquid would be 7.5:1. Further assuming that the rates of effusion through the doser and the pumping speed are identical, the ratio of the ethanol and trifluoroethanol pressures over the sample is $P_{F3}/P_{H3} \approx 10$. This is consistent with the ratio of the desorption signals of ethoxide and trifluoroethoxide from the surface following low exposures to the mixture ($I_{H3}/I_{F3} = 0.15$). Finally, if we assume that the cross sections for formation of the $m/q = 29$ amu fragment ion (HCO^+) from both acetaldehyde and trifluoroacetaldehyde are equal, then the desorption signals obtained by monitoring the $m/q = 29$ amu fragment yield the ratio of the coverages of ethoxide and trifluoroethoxide on the surface (θ_{H3}/θ_{F3}). At equilibrium the ratio of the signals obtained from ethoxide and trifluoroethoxide is $I_{H3}/I_{F3} = 2$. The final rough estimate of the magnitude of the equilibrium constant at 200 K yields

$$K \approx 20$$

Besides being far off the estimate based on the 12 kcal/mol difference in the gas-phase heats of acidity of the ethanols, our estimate favors ethoxide formation over trifluoroethoxide formation. Furthermore, we find that rather than varying by 4 orders of magnitude over the temperature range of 200–300 K, the equilibrium constant varies by only a factor of 2.

In the work performed here we have been able to make direct measurements of the relative heats of dissociative adsorption of the ethanols. This has been due, in part, to the rapid displacement kinetics which allow equilibrium between the gas-phase alcohols and ethoxides to be established with feasible exposures to the surface. The other important factor is that the relative coverages of the ethoxides at equilibrium can be determined quite easily since the decomposition products desorb at much different temperatures and are identified quite easily using mass spectrometry. The results show quite clearly that fluorination of the methyl group has little influence on the heat of dissociative adsorption of ethanol to form ethoxide. Figure 8 illustrates the energetics of the ethoxide formation and β-hydride elimination processes. The heat of formation of ethoxide from ethanol is actually slightly greater than the heat of formation of trifluoroethoxide from trifluoroethanol.

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(16) Bartmess, J. E.; McIver, R. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2., Chapter 11.

(17) (a) Zhdanov, V. P.; Pavlicek, J.; Knor, Z. *Catal. Rev. Sci. Eng.* **1988**, *30* (4), 501. (b) Baetzold, R. C.; Somorjai, G. A. *J. Catal.* **1976**, *45*, 94.

(18) Forbes, J. G.; Gellman, A. J., to be published.

(19) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K.; Nutell, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11* (2), 2–95.

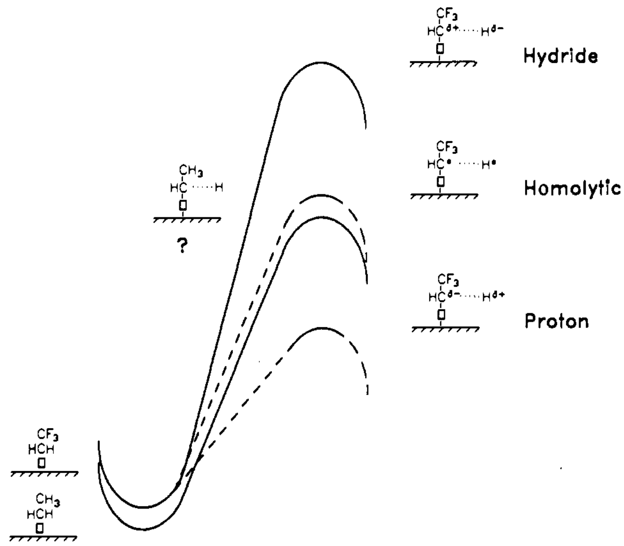

Figure 9. Illustration of possible transition states for decomposition of ethoxide to acetaldehyde and the influence of fluorine on the transition-state energetics. The destabilization of the homolytic transition state is expected to be <6.5 kcal/mol. The 13 kcal/mol increase in the activation barrier resulting from fluorination of the methyl group indicates that charge separation in the transition state leaves the β-carbon with net positive charge and the hydrogen atom with net negative charge.

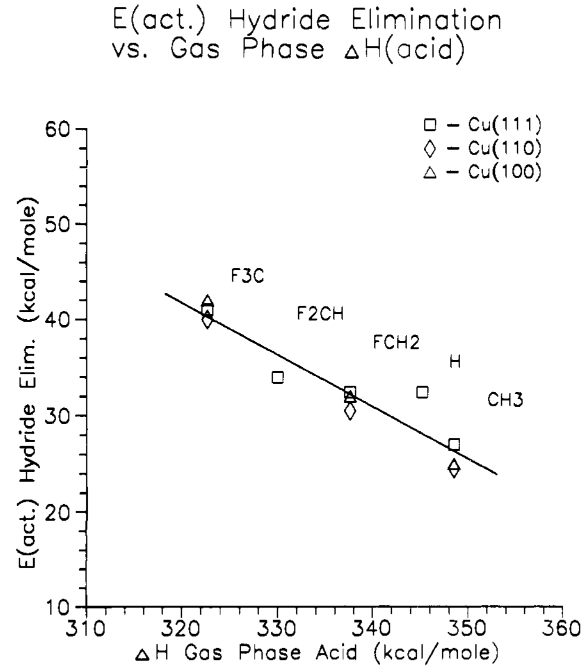

Figure 10. Free energy relationship between the gas-phase heats of formation of carboxylate anions with H, CH_3, FCH_2, F_2CH, and F_3C substituents and the activation energy for β-hydride elimination in alkoxides on Cu(111), Cu(100), and Cu(110) surfaces. The relationship gives $\rho = -0.5$, indicating a substituent influence on hydride elimination that is opposite the stabilization of the carboxylates and weaker in magnitude.

The influence of fluorine on the β-hydride elimination kinetics clearly arises from its influence on the energetics of the transition state, which is destabilized by ~15 kcal/mol in trifluoroethoxide.

In order to appreciate the significance of the energy difference in the transition state, it is necessary to know the influence of the trifluoromethyl group on the homolytic C–H bond strength at an adjacent carbon atom. This number is unknown in the case of the ethanols, however, it is known for CH_3CH_3 and CF_3CH_3 in the gas phase. The inset in the upper left-hand corner of Figure 8 illustrates the fact that the fluorine increases the homolytic C–H bond strength in ethane by 6.5 kcal/mol.[20] In other words, the trifluoromethyl group destabilizes the transition state for β-hydride elimination in ethoxide by a significantly greater amount than it destabilizes the ethyl radical generated by dissociation of a C–H bond in ethane.

4.2. Transition State for β-Hydride Elimination. The increased electronegativity of the trifluoromethyl group in trifluoroethoxide serves to destabilize an anionic transition state. Figure 9 illustrates the types of charge separation that one can envision in the transition states for deprotonation, homolytic dissociation, and hydride elimination and the influence that one might expect fluorine to have on the energetics of these states. If the process were a deprotonation reaction, then the trifluoromethyl group would stabilize the transition state and increase the rate of ethoxide decomposition. The trifluoromethyl group is expected to destabilize the transition state for a homolytic bond-breaking process; however, the upper limit on this destabilization should be 6.5 kcal/mol. This is our estimate of the difference in the homolytic C–H bond strengths at the β-carbon based on the difference in the gas-phase C–H bond strengths of CH_3CH_3 and CF_3CH_3.[20] Since the barriers for decomposition are only ~30% of the C–H bond strength, the influence of fluorine on the energy of a homolytic transition state should be less than 6.5 kcal/mol and certainly much less than the 15 kcal/mol destabilization that we have observed. The results of our work on ethoxide decomposition indicate that the process is best described as a hydride elimination with a transition state of the form $C^{\delta+}\cdots H^{\delta-}$. The magnitude of the charge separation is, of course, not known. As an extreme case for calibration, however, one can examine the influence of fluorination on the gas-phase heats of acidity of the acetic acids (Table III). In this case, the purely anionic carboxylate group is stabilized by 26 kcal/mol by fluorination of the methyl group.

A second interesting result of the kinetic measurements of this work is the demonstration that the preexponential factor for the β-hydride elimination reaction increases by 3 orders of magnitude (Table I) as a result of fluorination of the methyl group. There are a number of possible explanations for preexponential factors that deviate significantly from 10^{13} s^{-1}. The usual transition-state argument for this implies that the transition state is more loosely bound for the fluorinated ethoxides than for ethoxide. As a result the transition-state partition function is greater for the fluorinated ethoxides.[17] This phenomenon appears to be a general property of fluorination of surface species. We have found that in the β-hydride elimination reaction of propyl on the Cu(111) surface, fluorination of the methyl group also increases the reaction rate preexponent by 3 orders of magnitude. Fluorination of the methyl group in adsorbed propyl also increases the β-hydride elimination barrier by 8.5 kcal/mol.[18]

The primary conclusion of this work has been that the transition state for β-hydride elimination in adsorbed ethoxide has a positive charge on the β-carbon atom. The effect of fluorine on the methyl group is to energetically destabilize this transition state. This can be quantified to some extent by establishing a linear free energy relationship between this effect and the degree to which methyl and fluorinated methyl groups stabilize carboxylic acids. Table III contains the gas-phase heats of acidity of formic, acetic, and monofluoro-, difluoro-, and trifluoroacetic acids.[16] In the gas phase, fluorination of the methyl group serves to stabilize the acetate anion by 26 kcal/mol. The degree of stabilization with respect to acetate yields a parameter analogous to the σ parameter of the Hammett equation used to quantify the influence of substituents on benzoic acids in aqueous solution. Figure 10 plots the β-hydride elimination barriers for methoxide and ethoxides on the Cu surfaces against the gas-phase heats of acidity of the corresponding carboxylic acids. The two quantities are roughly correlated ($r^2 = 0.9$) with a slope of $\rho = -0.5$. The significance of the sign of ρ is simply to quantify the fact that fluorination of the methyl group in the ethoxides has an effect on the kinetics of β-hydride elimination which is opposite to its effect on the stability of the acetate anions. In other words, the charge buildup at the β-carbon in the transition state for β-hydride elimination

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(20) Lide, D. Handbook of Chemistry and Physics; CRC Press: Boca Raton, FL, 1992; Chapter 9.

is positive. Secondly, the magnitude of ρ (<1) indicates that the charge buildup is lower than that found in the gas-phase carboxylate anion. The demonstrated relationship between the gas-phase heats of acidity of the acetic acids and the activation barriers for β-hydride elimination in adsorbed ethoxides allows prediction of the rates of decomposition in other alkoxides.

The implications of this work extend beyond β-hydride elimination in ethoxides on the Cu(111) surface. Similar influences of fluorination have been observed in the ethoxides on the Cu(110), Cu(100), and Ag(110) surfaces. They have also been observed in the longer chain hydrocarbon and fluorocarbon alkoxides on the Ag(110) and Cu(100) surfaces.[10,13] We have also been able to study the influence of fluorination on β-hydride elimination in alkyl groups adsorbed on the Cu(111) surface. The activation barrier for β-hydride elimination of 3,3,3-trifluoropropyl to 3,3,3-trifluoropropylene is 8.5 kcal/mol higher than for the reaction of propyl to propylene.[18]

Studies using much different approaches also suggest that the transition state is really described as hydride elimination. Theoretical studies of β-hydride elimination in alkyl groups on Al surfaces suggest a four-center transition state in which the hydrogen carries net negative charge.[21] Finally, results similar to ours have been found in a study of the insertion of olefins into Nb–H and Ta–H bonds in a homogeneous phase.[7] This reaction is the microscopic reverse of β-hydride elimination, and the effects of substituents have also lead to the conclusion that the transition state for the reaction involves charge separation of the form $C^{\delta+}\cdots H^{\delta-}$.

5. Conclusions

We have demonstrated that fluorination of the methyl group in ethanol exerts an influence on both the heat of dissociative adsorption to form ethoxides on the Cu(111) surface and on the kinetics of β-hydride elimination in these species. The influence of fluorine on the heat of reaction forming ethoxides from gas-phase ethanols is quite small (~2 kcal/mol). By comparison, the influence on the kinetics of β-hydride elimination is relatively large, increasing the barrier from 29 kcal/mol in ethoxide to 42 kcal/mol in trifluoroethoxide. This indicates that the influence of fluorine is on the transition-state energetics. The description of the transition state is one in which positive charge builds up on the β-carbon atom ($C^{\delta+}\cdots H^{\delta-}$) and is destabilized by fluorination of the methyl group. The magnitude of the ρ parameter in the free energy relationship between the reaction barrier for β-hydride elimination and the stabilization of gas-phase acetate by fluorination indicates that the charge buildup in the transition state is much lower than is observed in the gas-phase acetate anion.

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(21) (a) Higishi, G. S.; Raghavachari, K.; Steigerwald, M. *J. Vac. Sci. Technol.* **1990**, *B8*, 103. (b) Chan, A. W. E.; Hoffmann, R. *J. Vac. Sci. Technol.* **1991**, *A9* (3), 1569.

Surface Organometallic Chemistry of Tin: Reactivity of Tetraalkyltin Complexes and Tributyltin Hydride toward Silica

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Abstract: Tetraalkyltin complexes, SnR_4 (R = Me, Et, *i*-Pr, Bu), and tributylhydridotin were reacted with the surface of partially dehydroxylated silica. Interaction between the complexes and the silica surface was followed by IR and ^{13}C and ^{119}Sn MAS NMR spectroscopies and analysis of the evolved gases. At room temperature, all the studied complexes are physisorbed: a hydrogen-type bonding between the terminal methyl group of the alkyl ligands and/or the hydride ligand and the surface silanol groups is evidenced. Above 100 °C, with silica dehydroxylated at 500 °C ($SiO_2(500)$), a reaction occurs, leading to the formation at 200 °C of essentially one surface complex, $\gg SiO–SnR_3$ (**1**) with evolution of 1 mol of alkane per mol of surface tin. **1** is already formed at room temperature by reaction of silica with Bu_3SnH; the reaction is slow and liberates 1 mol of H_2/mol of surface Sn. At low surface coverage, and for R $\neq$ Me, the alkyl ligands of **1** are folded toward the surface, interacting with it via hydrogen-type bonding. The same interaction and reaction are observed when the surface of silica is less dehydroxylated, $SiO_2(200)$: nevertheless **1** is less stable, probably due to the availability of surface silanol groups in the neighborhood of **1**.

Introduction

Tin inorganic and organometallic complexes are widely used in the field of catalysis (transesterification and polyurethane foam and silicone elastomers production)[1] and as efficient modifiers of supported metal particles.[2] The bimetallic solids obtained in the latter case present new properties, high conversions, and high selectivities for a number of reactions, particularly in the field of synthesis of fine chemicals.[3] Yet, the reactions occurring during the synthesis of such catalysts are not well understood, due to the high complexity of such multicomponent systems. In particular,

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[‡] Institut Francais du Pêtrole.

(1) See for example: (a) *Organotin Chemistry*, I. Omae: *Journal of Organometallic Chemistry Library*, Elsevier, Amsterdam, 1989; vol. 21, pp 321. (b) Evans, C. J. In *Chemistry of Tin*; Harrison, P. G., Ed.; Blackie: Glasgow, Scotland, 1989; pp 421.

(2) (a) Weisang, J. E.; Engelhard, P. Fr. Pat. 2031984, 1968. (b) Jacobsen, R. L. US Pat. 3577474, 1977. (c) Coq, B.; Figueras, F. *J. Catal.* **1984**, *85*, 197. (d) Sarkani, A.; Guczi, L.; Weiss, A. H. *Appl. Catal.* **1984**, *10*, 369. (e) Bursian, N. R.; Zharker, B. B.; Kagan, I. B.; Lastoukin, G. A.; Potkletnova, M. M. Proceedings of the 8th International Congress on Catalysis, Berlin; Verlag Chemie: Weinheim, Germany, 1984; Vol. 2, pp 481.

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