# Probing the Internal Competition between α- and β-Elimination by Fluorine Substitution in Adsorbed Ethyl Groups on Cu(100)

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*Received: September 21, 2005*

Key factors affecting the competition between α- and β-elimination channels for adsorbed ethyl groups on a metal surface were probed by fluorine substitution. The thermal desorption products and temperatures resulting from ethyl, 2,2,2-trifluoroethyl, 1,2,2,2-tetrafluoroethyl, 1,1,2,2-tetrafluoroethyl, and pentafluoroethyl moieties adsorbed on Cu(100) provided the information about the dominant reactions and a measure of the relative rates. The alterations of number and positions of the fluorine substituents revealed that the eclipsed interactions and hyperconjugation in the transition states can determine the kinetic barriers and allowed access to the separate pathways.

Thermally induced β-H elimination may be the most predominant reaction pathway for alkyl groups bound to metal centers in organometallic compounds[1] and on surfaces.[2] Hydrogen elimination from the α-carbon is generally much less favorable. Their kinetic difference can be probed by using surface-bound methyl (with no β-hydrogen) and ethyl moieties. A large variation in the peak maxima in temperature-programmed desorption (TPD) for β- (250 K) against α-elimination (470 K) was obtained on Cu(100).[3] Converting a C−H bond to a C−F bond in a molecule is, from the viewpoint of altering molecular shape and size, the minimum possible change. However, fluorine-substituted compounds often do not mimic their unsubstituted versions in a wide range of chemical processes. For example, α-F elimination prevails over β-elimination in the decomposition of perfluoroalkyl complexes[4] and surface species.[5,6] It has been shown that the $C_\alpha$−F bond adjacent to the metal in copper surface-bound perfluorinated methyl[5] and ethyl[6] is susceptible to chemical activation, in which $CF_3CF_2$−Cu (315 K) occurs at a much slower rate than $CF_3$−Cu (160 K). Thus, it is very intriguing why $CF_3CF_2$−Cu (β-fluorine available) eschews β-elimination in favor of α-elimination. To systematically understand the rate-limiting factors that hinder the β-elimination processes for the chemisorbed fluorine-substituted ethyl groups, a set of five alkyl and fluoroalkyl iodides, including $CH_3CH_2I$, $CF_3CF_2I$, $CF_3CH_2I$, $CHF_2CF_2I$, and $CF_3CHFI$, were utilized to produce a variety of ethyl fragments on Cu(100) via dissociative adsorption.[7,8] TPD experiments were performed in an ultrahigh vacuum chamber to identify the two competing α- and β-elimination pathways and to extract their kinetic data.

First, $C_2H_5I$ and $C_2F_5I$, elected as the benchmark compounds for the relative rates of the β-elimination, were analyzed. In Figure 1B the TPD data after exposing the clean Cu(100) to 0.01 L $CH_3CH_2I$ (99%, Aldrich) indicate the expected $CH_2=$

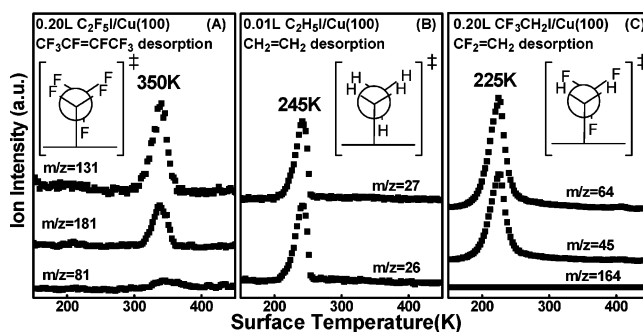* E-mail: cmc@mail.nsysu.edu.tw. Phone: 886-7-5253939, Fax: 886-7-5253908.

**Figure 1.** TPD spectra for submonolayer coverages of pentafluoroethyl iodide, ethyl iodide, and 2,2,2-trifluoroethyl iodide on Cu(100). Shown in (A) are traces for the end-product of α-fluoride elimination pathway ($C_4$-alkene). Shown in (B) and (C) are features for the formation of $C_2$-alkene via β-elimination channel. The heating rate is 2 K/s. The schematic diagrams are Newman projections of the planar eclipsed transition states for β-elimination on a surface.

$CH_2$ evolution resulting from C−I bond scission and β-H elimination. Ethylene is evidenced by $m/z$ 26 ($C_2H_2^+$) and 27 ($C_2H_3^+$) signals, with a peak temperature at 245 K. In Figure 1A, following the adsorption of 0.2 L $CF_3CF_2I$ (98%, SynQuest), one desorption state arises at 350 K. The formation of $CF_3$-$CF=CFCF_3$ ($C_4F_8$) accounts best for the observed relative abundances of $m/z$ 181 ($C_4F_7^+$) and 131 ($C_3F_5^+$).[9] Together with the trace of insignificant contribution from $m/z$ 81 ($C_2F_3^+$, major fragment of $CF_2=CF_2$), this end $C_4$-coupling product suggests that $CF_3CF_2$−Cu prefers to have its fluorine removed from the α-carbon rather than the β-position, then a dimerization step follows.[10] Nevertheless, this desorption maximum temperature 350 K should place a kinetic lower limit for the alternate β-elimination route, despite the fact that the reaction is actually superseded by α-elimination. This subtle switch in mechanism must be rationalized by the influence of fluorine on the reaction barriers. Elegant studies by Gellman[11] have demonstrated that the transition state (TS) for β-H elimination is hydride-like with

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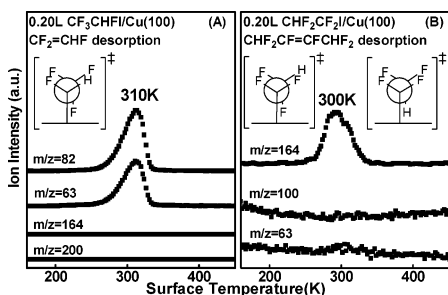*J. Phys. Chem. B, Vol. 109, No. 46, 2005* **21487**



**Figure 2.** TPD spectra for 1,2,2,2-tetrafluoroethyl iodide (A) and 1,1,2,2-tetrafluoroethyl iodide (B) on Cu(100). Both compounds gave chemisorbed ethyl groups with four fluorine substituents, which, however, are distributed differently between the $\alpha$- and $\beta$-carbons.

charge separation in the form of $C_\beta{}^{\delta+}\cdots H^{\delta-}\cdots M^{\delta+}$. It is quite plausible that $\beta$-fluoride elimination in $CF_3CF_2$−Cu would also adopt the $C_\beta{}^{\delta+}\cdots F^{\delta-}\cdots Cu^{\delta+}$-type TS, where the two remaining electron-withdrawing fluorine atoms bound to the cationic $\beta$-carbon can energetically destabilize the TS, rendering a barrier so high that the $\alpha$-elimination takes over. In this vein, we expect that neither would $CF_3CH_2$−Cu, with three F atoms attached to the $\beta$-carbon, undergo $\beta$-fluoride elimination because its electron-deficient TS is subject to the same amount of inductive effect. Figure 1C illustrates the TPD results obtained from adsorbing 0.2 L $CF_3CH_2I$ (99%, Aldrich) on Cu(100). To our surprise, the spectra show the $\beta$-fluoride elimination product $CF_2$=$CH_2$, characterized by the desorption features of $m/z$ 64 ($C_2H_2F_2{}^+$) and 45 ($C_2H_2F^+$). The anticipated $\alpha$-elimination, along with a subsequent coupling reaction to yield $CF_3CH$=$CHCF_3$, can be ruled out by the lack of $m/z$ 164 ($C_4H_2F_6{}^+$) ion signals. Further, the TPD maximum temperature is 225 K, lower than that in Figure 1B, representing that $\beta$-elimination from $CF_3CH_2$−Cu is even more facile than from $CH_3CH_2$−Cu. Explanation for these apparent dichotomies requires us to assess other factors in the reaction energetics.

It is also known that $\beta$-elimination proceeds via a cyclic TS,[12] where the two carbon atoms ($C_\alpha$ and $C_\beta$), the $\beta$-atom (H or F), and the surface metal atom(s) are coplanar. When such a geometric constraint is imposed on the transition states of the above three surface ethyl moieties (see the Newman projections in Figure 1), the eclipsed structures reveal that on adjacent carbons there are (1) two pairs of CF/CF interaction in $CF_3$-$CF_2$−Cu, (2) two pairs of CH/CH interaction in $CH_3CH_2$−Cu, and (3) two pairs of CH/CF interaction in $CF_3CH_2$−Cu. We speculate that these different interactions play a major role in determining the TS energies because the destabilization due to repulsions would appear much more severe as the distance between $C_\alpha$ and $C_\beta$ becomes shorter in the TS (forming a CC double bond eventually). Although it is debatable whether the nature of the instability of an eclipsed conformer, as opposed to the staggered, is attributed to conventional steric hindrance or vicinal hyperconjugation,[13] the CF/CF eclipsed interaction might be a less favorable interaction with respect to CH/CH, leading to a higher-energy TS, whereas the CH/CF is somewhat more favorable. By recognizing this trend of interaction (CF/CF > CH/CH > CF/CH)[14] and assuming similar initial states, the relative barrier heights are thus $CF_3CF_2$−Cu > $CH_3$-$CH_2$−Cu > $CF_3CH_2$−Cu, which coincide well with the relative rates for $\beta$-elimination gleaned from the TPD data (350 K > 245 K > 225 K). To further test if $\beta$-elimination can be accessible by fine-tuning the barrier height, $CF_3CHF$−Cu is chosen as an indicator because its eclipsed TS (see the schematic in Figure 2A) bears only one pair of adverse CF/CF interaction. Figure 2A displays that only the product of $\beta$-elimination is
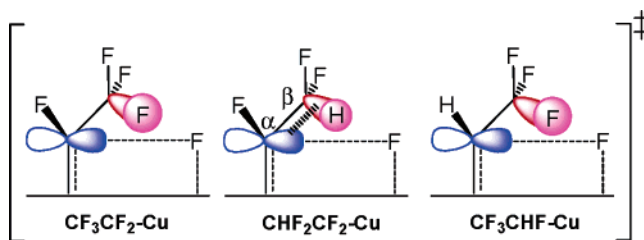
detected in TPD after dosing 0.2 L $CF_3CHFI$ (98%, Fluorochem) on Cu(100). The $C_2$-alkene, $CF_2$=$CHF$, is clearly observable by the $m/z$ 82 ($C_2HF_3{}^+$) and 63 ($C_2HF_2{}^+$) desorption peaks at 310 K. The TPD traces devoid of $m/z$ 164 ($C_4H_2F_6{}^+$) and 200 ($C_4F_8{}^+$), indicating the absence of $CF_3CH$=$CHCF_3$ and $CF_3$-$CF$=$CFCF_3$, exclude both $\alpha$-fluoride and $\alpha$-hydride eliminations from $CF_3CHF$−Cu. Here the revival of $\beta$-elimination and the lower reaction temperature (310 K vs 350 K) in contrast with $CF_3CF_2$−Cu made a strong argument about the correlation between the number of destabilizing CF/CF pair interactions in the TS and the $\beta$-elimination barrier heights.

$CHF_2CF_2$−Cu bears a strong resemblance to $CF_3CHF$−Cu except for the hydrogen changing position from the $\alpha$- to the $\beta$-carbon; therefore, two possible scenarios in the TS of $\beta$-elimination deserve scrutiny: (1) two pairs of CF/CF eclipsed interaction exist for $\beta$-H elimination, and (2) one pair of CF/CF repulsion is present for $\beta$-F elimination (see Newman projections in Figure 2B). Concerning case (1), the TPD data following 0.2 L $CHF_2CF_2I$ (98%, Fluorochem) adsorption on Cu(100) yield no trace of $CF_2$=$CF_2$ ($m/z$ 100) in Figure 2B is not unexpected because the barrier height should be large. Curiously, TPD signals from the $\beta$-F elimination product, $CHF$=$CF_2$ ($m/z$ 63), are also missing! Instead, the appearance of $m/z$ 164 ($C_4H_2F_6{}^+$), indicative of a recombinant $CHF_2CF$=$CFCHF_2$ product, implicates the opening up of the $\alpha$-F elimination pathway. It is noteworthy that this $\alpha$-elimination end-product shows a peak at 300 K, which is 10 K lower than the $\beta$-elimination temperature resulting from its nearly identical counterpart (Figure 2A), and 40 K lower in terms of $\alpha$-elimination originated from $CF_3CF_2$−Cu (Figure 1A). The rationale is that relative to $CF_3CF_2$−Cu (350 K) the activation energy of $CHF_2CF_2$−Cu for $\alpha$-elimination (300 K) must be reduced so much that even the $\beta$-elimination channel (310 K) cannot emulate. Here we propose a hypothetical transition state for $\alpha$-elimination (see Scheme 1), where the $\alpha$-carbon almost becomes $sp^2$-hybridized to facilitate the formation of a double bond with the surface copper atom, and one of the $C_\alpha$−F bonds, meanwhile, is on the verge of breaking down (a metal-ethylidene like species). In this type of TS for $CHF_2CF_2$−Cu, the electron density in the $C_\beta$−H sigma bond can spread out into the empty p orbital of the $\alpha$-carbon (hyperconjugation). In addition, this delocalization of the $\sigma$-bond electrons requires the C−H bond to align properly, leading the remaining two fluorine atoms on the $\beta$-carbon into positions adverse to $\beta$-elimination. In contrast, both $CF_3CF_2$−Cu and $CF_3CHF$−Cu have only $C_\beta$−F sigma bonds. Fluorine atoms hold onto the electron clouds more tightly, so it is most unlikely that the vicinal hyperconjugation will occur in their $\alpha$-elimination TS, resulting in higher kinetic barriers relative to $CHF_2CF_2$−Cu.

Fluorine substitution effects have been used successfully to probe the nature of transition states in many elementary reactions on single-crystal surfaces.[15] Here by judiciously altering the number and position of the fluorine substituents in the ethyl groups bound to Cu(100), we demonstrate that the destabilizing

**SCHEME 1**

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eclipsed interactions and the stabilizing vicinal hyperconjugation contribute significantly to the transition state energetics in the $\beta$-elimination and $\alpha$-elimination, respectively. Our results also strengthen the concept that the small difference in height between barriers leading to separate reaction pathways is influential to the selectivity.[16,17]

## References and Notes

(1) Davidson, P. J.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976**, *76*, 219.

(2) For a superb review, see: Zaera, F. *Prog. Surf. Sci.* **2001**, *69*, 1.

(3) Jenks, C. J.; Bent, B. E.; Zaera, F. *J. Phys. Chem. B* **2000**, *104*, 3017.

(4) Kiplinger, J. L.; Richmond, T. G.; Osterberg, C. *Chem. Rev.* **1994**, *94*, 373.

(5) Hou, Y.-C.; Chiang, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 8116.

(6) Chiang, C.-M.; Lu, D.; Huang, J.-T.; Hwang, C.-C.; Cho, C.-C.; Fan, L.-J.; Yang, Y.-W. *J. Am. Chem. Soc.* **2004**, *126*, 12242.

(7) Buelow, M. T.; Gellman, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 1440.

(8) Zaera, F. *Acc. Chem. Res.* **1992**, *25*, 260.

(9) The fragmentation ratios were determined by our mass spectrometer while backfilling the chamber with pure $C_4F_8$ gas.

(10) Wu, G.; Stacchiola, D.; Kaltchev, M.; Tysoe, W. T. *J. Am. Chem. Soc.* **2000**, *122*, 8232.

(11) Forbes, J. G.; Gellman, A. J. *J. Am. Chem. Soc.* **1993**, *115*, 6277.

(12) Teplyakov, A. V.; Bent, B. E. *J. Am. Chem. Soc.* **1995**, *117*, 10076.

(13) Pophristic, V.; Goodman, L. *Nature* **2001**, *411*, 565.

(14) There is an at least 6.6 kcal/mol difference in the activation energy between $CF_3CF_2-Cu$ and $CH_3CH_2-Cu$ for $\beta$-elimination processes (first-order kinetics and $10^{13}$ s$^{-1}$ prefactor at 300 K), implicating that one pair of CF/CF eclipsed interaction is 3.3 kcal/mol larger than CH/CH. Similarly, CH/CF interaction would be 0.6 kcal/mol less than CH/CH based on the TPD data from $CF_3CH_2-Cu$. Calculations for barriers of internal rotations about the C−C axis in fluorinated propanes showed the same qualitative trend of interactions in the eclipsed conformations, but underestimated their quantitative differences. For details, see: Yamada, T.; Bozzelli, J. W.; Berry, R. J. *J. Phys. Chem. A* **1999**, *103*, 5602.

(15) Gellman, A. J. *Acc. Chem. Res.* **2000**, *33*, 19.

(16) Zhao, Q.; Zaera, F. *J. Am. Chem. Soc.* **2003**, *125*, 10776.

(17) Zaera, F. *Appl. Catal. A* **2002**, *229*, 75.