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A Unique Reaction Pathway of Fluorine-Substituted Ethyl Groups on Cu(111): Successive α,α -Fluoride Elimination

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Replacement of hydrogen with fluorine usually results in a marked change in the physical and chemical properties of fluorocarbons. Numerous studies have shown that fluorinated radicals and their metal complexes have structures and reactivities deviating from their hydrocarbon counterparts.^{1–3} Surface studies of adsorbed perfluoroalkyl moieties beyond C₁, in comparison, remain largely unexplored. Here we report a surface reaction study of the fluorine-substituted ethyl groups on Cu(111) that displays novel reaction pathways driven by α -elimination, instead of β -elimination found commonly in hydrocarbons.

Temperature-programmed reaction/desorption (TPR/D) and reflection absorption infrared spectroscopy (RAIRS) were conducted in an in-house ultrahigh vacuum chamber. X-ray photoemission spectra (XPS) were acquired in the wide-range spherical grating monochromator beamline at NSRRC. The surface-bound perfluoroethyl moieties were prepared by the dissociative adsorption of C₂F₅I.⁴

As illustrated in Figure 1 (left), following the adsorption of 0.6 L of C₂F₅I (98%, SynQuest) at 110 K, multiple-ion TPR/D survey shows *four* desorption states with peak maxima at 315, 350, 425, and 880 K, respectively. The 880 K state is featured by *m/e* 82(⁶³CuF) and 84(⁶⁵CuF) with a peak height ratio matching the natural abundance of copper isotopes; hence, the substrate is etched through forming volatile copper fluoride.⁵ Here the origin of the fluorine atoms hints that some, if not all, of the C–F bonds in Cu–C₂F₅ must be ruptured. The 315 K state is primarily characterized by *m/e* 181(C₄F₇⁺), 131(C₃F₅⁺), 100(C₂F₄⁺), and 93(C₃F₃⁺). Their relative abundance agrees with the measured cracking pattern of CF₃–CF=CFCF₃(C₄F₈),⁶ inferring single F abstraction at the α -carbon in perfluoroethyl.⁷ Cu– α CF₂CF₃ → Cu=CFCF₃ + Cu–F, followed by a dimerization step.⁸ The 350 K desorption state can be understood in terms of product mixtures. First, the observation of *m/e* 100(C₂F₄⁺) and 119(C₂F₅⁺) may arise from desorption of C₂F₅ radicals.⁹ However, the lack of *m/e* 81(C₂F₃⁺) rules out a possible contribution from CF₂=CF₂(*m/e* 100), a direct result from β -F elimination. This clear preference to α -elimination, rather than β -elimination, is rarely observable in hydrocarbon (>C₁) systems.¹⁰ Second, a featureless trace of *m/e* 169(C₃F₇⁺) ensures the absence of perfluorobutane (C₄F₁₀), and the concurrence of *m/e* 93(C₃F₃⁺), 143(C₄F₅⁺), and 162(C₄F₆⁺) signals is attributable to unsaturated C₄F₆ compounds. The above three fragments are also found in the pronounced 425 K desorption state, however, with different relative intensities. Logically, the intermediacy of Cu–C₂F₃ is invoked to account for the observed C₄F₆ recombinants at these temperatures; in other words, *two C–F bonds must be selectively activated in the starting Cu–C₂F₅*. The coverage-dependent study, shown in Figure 1 (right), manifests that at very low exposure the 425 K C₄F₆ is the sole fluorocarbon product. At high coverage, a crossover of

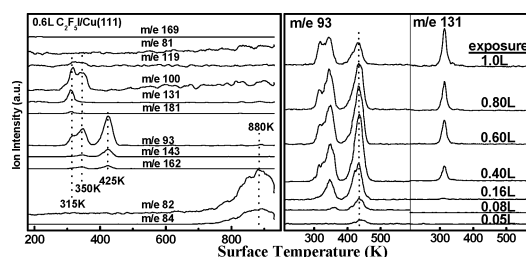


Figure 1. Left: Multiplex TPR/D spectra after the adsorption of 0.6 L of C₂F₅I on Cu(111) at 110 K. Right: The trend of *m/e* 93 and 131 signals shows change of C₄F₆ and C₄F₈ relative yields with increasing exposures.

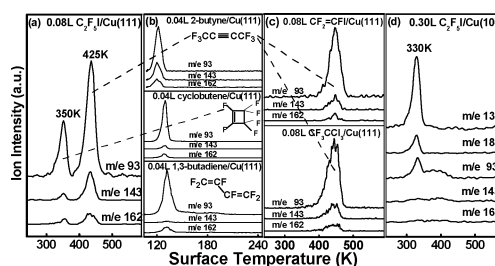


Figure 2. TPR/D traces of *m/e* 93, 143, and 162, representing C₄F₆ evolution from (a) C₂F₅I, (b) C₄F₆ isomers, (c, top) CF₂=CFI, and (c, bottom) CF₃CCl₃ adsorbed on Cu(111) at 110 K. The exposures are kept low enough to focus on the 425 K pathway. (d) TPR/D profiles after exposing C₂F₅I to Cu(100), indicating C₄F₆ is not formed on this surface.

yield from C₄F₆ to C₄F₈ is noted, consistent with the requirement for more empty surface sites in the process of making the former species.

In Figure 2a, the TPR/D profiles of *m/e* 93, 143, and 162 resulting from C₂F₅I/Cu(111) are compared with those (Figure 2b) from the individually adsorbed hexafluoro-2-butyne, -cyclobutene, and -1,3-butadiene (C₄F₆ isomers, 98%, SynQuest). On the basis of the fragmentation ratios determined by our mass spectrometer, it is safe to assign the 425 K major product to 2-butyne and the 350 K species to cyclobutene. To further identify the postulated surface C₂F₃ intermediate, we used the readily available perfluorovinyl iodide (CF₂=CFI, 97%, Lancaster) as a direct route to form Cu–C₂F₃. As displayed in Figure 2c (top), traces of *m/e* 93, 143, and 162, characteristic of hexafluoro-2-butyne, are indeed observed, yet appear *only* at 425 K. Despite the essential difference between perfluoroethyl and perfluorovinyl, the outcome of the same end product at 425 K seems to suggest that perfluoroethyl undergoes sequential fluoride elimination from the α - and β -carbons to render perfluorovinyl, namely, Cu– α CF₂CF₃ → Cu=CF ^{β} CF₃ → Cu–CF=CF₂. But, the question remains: why is C₄-diene not observed, considering the fact that copper would promote coupling of Cu–CF=CF₂ (Ullman-type reaction)?¹¹ By losing two fluorine atoms from the α -carbon in Cu–CF₂CF₃, an alternative intermediate, *trifluoroethylidyne* (Cu=C–CF₃) certainly deserves attention. Because d'Itri and co-workers reported identification of the surface

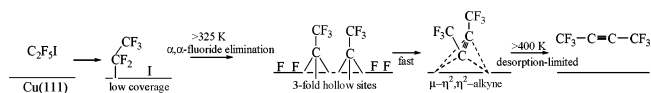
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$\equiv\text{C}-\text{CF}_3$ species formed upon adsorption and dechlorination of CCl_3CF_3 on a $\text{Pd}/\gamma\text{-Al}_2\text{O}_3$ catalyst,⁷ TPR/D spectra were measured by exposing $\text{Cu}(111)$ to CCl_3CF_3 (99%, Aldrich). The data shown in Figure 2c (bottom) also support the evolution of $\text{CF}_3\text{C}\equiv\text{CCF}_3$ at 425 K. In principle, the controversy about the reaction intermediacy can be resolved by direct surface spectroscopic methods. RAIR spectra taken after annealing $\text{C}_2\text{F}_5\text{I}$ on $\text{Cu}(111)$ showed dramatic changes at 400 K (near the onset of 2-butyne desorption), where only two absorption bands were present: 1410 and 1210 cm^{-1} , but they did not match the signature vibrations of either a surface $\equiv\text{C}-\text{CF}_3$ ¹² or $-\text{CF}=\text{CF}_2$ ¹³ moiety. In fact, the spectrum was identical with that produced by $\text{CF}_3\text{C}\equiv\text{CCF}_3$ adsorbed on $\text{Cu}(111)$ and annealed to 400 K, where the 1410 cm^{-1} band is, rather, attributed to the ν_{CC} and the 1210 cm^{-1} band is ascribed to the $\nu_s(\text{CF}_3)$ mode. The large red-shift of the CC stretching mode indicates that the symmetric alkyne is strongly perturbed upon adsorption, leading to a reduced bond order of its $\text{C}\equiv\text{C}$ group.¹⁴ The strongly chemisorbed $\text{CF}_3\text{C}\equiv\text{CCF}_3$ may adopt a $\mu-\eta^2, \eta^2$ binding geometry discovered in metal-alkyne complexes, in which the ligand is bonded to two metal centers, with the C-C axis perpendicular to the metal-metal axis as a tetrahedral form.¹⁵ In C1s XPS, we expected that the exact number of F atoms bonded to C atom for the surface-bound fluorocarbon species can be discerned because of a significant core-level shift exerted by the highly electronegative fluorine. Although only one type of C-F bonding environment, CF_3 (C1s binding energy at 291.3 eV), was observed between 350 and 400 K for $\text{C}_2\text{F}_5\text{I}/\text{Cu}(111)$, it was not obvious whether the spectra represent 2-butyne (end product) or ethynylidyne (intermediate).

It is generally accepted that ethynylidyne is the favored intermediate against vinyl on close-packed fcc(111) surfaces where $\equiv\text{C}-\text{CH}_3$ prefers to sit at the *threefold hollow site* by forming three bonds with the metal surface.¹⁶ If the generation of $\text{CF}_3\text{C}\equiv\text{CCF}_3$ and the intermediacy of $\text{Cu}\equiv\text{C}-\text{CF}_3$ on $\text{Cu}(111)$ do correlate, we anticipate that the 425 K pathway will not occur on a more open surface devoid of threefold hollow sites, such as $\text{Cu}(100)$. In this vein, we measured the TPR/D spectra by dosing $\text{C}_2\text{F}_5\text{I}$ on $\text{Cu}(100)$. As illustrated in Figure 2d, only one desorption state arises at 330 K, and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ is indeed absent because of the lack of m/e 143 and 162 signals. Instead, $\text{CF}_3\text{CF}=\text{CFCF}_3$ accounts best for the relative peak intensities of m/e 181, 131, and 93.⁶ This observed end product suggests that $\text{Cu}-\text{CF}_2\text{CF}_3$ is susceptible to the α -F elimination step only *once* on $\text{Cu}(100)$, yielding surface $=\text{CF}-\text{CF}_3$ species⁷ that couple to form a perfluoroalkene at lower temperatures.¹⁷ The surface-specific result should lend strong support to the α, α -fluoride elimination imperative for $\text{C}_2\text{F}_5/\text{Cu}(111)$. While the fate of $\equiv\text{C}-\text{CH}_3$ intermediate is high-temperature decomposition in conjunction with a surface carbon buildup, it might be hard to maintain the metal-carbon bond integrity for $\equiv\text{C}-\text{CF}_3$ on a metal surface. The electronegative CF_3 group weakens the orbital overlap between the metal and α -carbon in $\text{Cu}\equiv\text{CCF}_3$. Thus, on $\text{Cu}(111)$ an unusual CC bond formation step becomes possible, $2\text{Cu}\equiv\text{CCF}_3 \rightarrow \text{Cu}\equiv\text{Cu} + \text{CF}_3\text{C}\equiv\text{CCF}_3(\text{ad})$, reminiscent of a reverse metathesis-type reaction involving metal-metal multiple bonds to give alkynylidyne complexes (Chauvin-like mechanism).¹⁸ This coupling process can be relatively facile; therefore, as successive α, α -fluoride elimination of $\text{Cu}-\text{CF}_2\text{CF}_3$ takes place, the resulting $\text{Cu}\equiv\text{CCF}_3$ readily converts to a tightly surface-bound ($\mu-\eta^2, \eta^2$)- C_4 -alkyne (the only IR recognizable species). The overall reaction path is rate-limited by the product desorption step, following first-order kinetics (see the unchanged peak temperature with increasing exposure in Figure 1). The last puzzle about the pathway from $\text{Cu}-\text{CF}=\text{CF}_2$ to $\text{CF}_3\text{C}\equiv\text{CCF}_3$ (Figure 2c, top) must be explained by the rapid isomerization from $\text{Cu}-\text{CF}=\text{CF}_2$ to $\text{Cu}\equiv$

CCF_3 on $\text{Cu}(111)$. This type of vinyl-to-ethynylidyne rearrangement was observed on a (111) surface of Pd.¹⁹ Altogether, we propose the following mechanism:



Ethyl ($-\text{CH}_2\text{CH}_3$) on transition-metal surfaces is dominated by the H-elimination from the β -position.¹⁰ On the other hand, β -F elimination is favored by a semifluorinated ethyl ($-\text{CH}_2\text{CF}_3$) on $\text{Ag}(111)$ to yield $\text{CH}_2=\text{CF}_2$.²⁰ Here we have established a different pathway available for the perfluorinated ethyl ($-\text{CF}_2\text{CF}_3$) where α -elimination prevails, and thus two C-F bonds adjacent to the surface are selectively activated. We believe this difference is initiated by the exceptionally labile α -CF bonds in the fluorocarbon group (CF_2R) bound to a metal center or surface (M), comprehensible by resonance such as $\text{M}-\text{CF}_2\text{R} \leftrightarrow \text{M}^+=\text{CFR} + \text{F}^-$, or the back-donation of metal $d\pi$ electrons into the C-F antibonding orbital.²¹ The removal of the second F atom from the β -carbon ($\text{M}=\alpha\text{CF}-\beta\text{CF}_3$) is usually hindered by the relative difficulty in breaking a C-F bond for compounds with two or more F atoms attached to the same carbon.²² Further, on $\text{Cu}(111)$ the available threefold hollow sites are beneficial to the consecutive α -F abstraction to afford *trifluoroethynylidyne*, resulting in the final coupling product. We foresee that pathways involving α -elimination steps may prove to be quite general for fluorine-substituted alkyl groups bound to metal surfaces.

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