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 C_1, 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 C_2F_5I.[4]

As illustrated in Figure l (left), following the adsorption of 0.6 L of C_2F_5I (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(^{63}-CuF) and 84(^{65}CuF) 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−C_2F_5 must be ruptured. The *315 K* state is primarily characterized by m/e 181($C_4F_7^+$), 131($C_3F_5^+$), 100($C_2F_4^+$), and 93($C_3F_3^+$). Their relative abundance agrees with the measured cracking pattern of CF_3-CF=$CFCF_3$(C_4F_8),[6] inferring single F abstraction at the α-carbon in perfluoroethyl,[7] Cu−$^α CF_2CF_3$ → Cu=$CFCF_3$ + 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($C_2F_4^+$) and 119($C_2F_5^+$) may arise from desorption of C_2F_5 radicals.[9] However, the lack of m/e 81($C_2F_3^+$) rules out a possible contribution from CF_2=CF_2(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 (>C_1) systems.[10] Second, a featureless trace of m/e 169($C_3F_7^+$) ensures the absence of perfluorobutane (C_4F_{10}), and the concurrence of m/e 93($C_3F_3^+$), 143($C_4F_5^+$), and 162($C_4F_6^+$) signals is attributable to unsaturated C_4F_6 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−C_2F_3 is invoked to account for the observed C_4F_6 recombinants at these temperatures; in other words, *two C−F bonds must be selectively activated* in the starting Cu−C_2F_5. The coverage-dependent study, shown in Figure l (right), manifests that at very low exposure the 425 K C_4F_6 is the sole fluorocarbon product. At high coverage, a crossover of
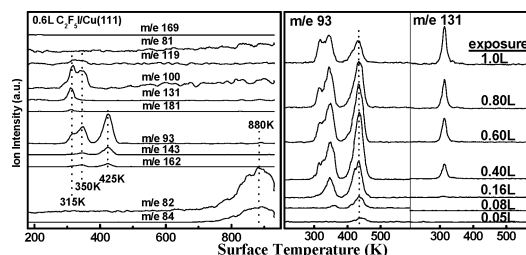

Figure 1. Left: Multiplex TPR/D spectra after the adsorption of 0.6 L of C_2F_5I on Cu(111) at 110 K. Right: The trend of m/e 93 and 131 signals shows change of C_4F_6 and C_4F_8 relative yields with increasing exposures.
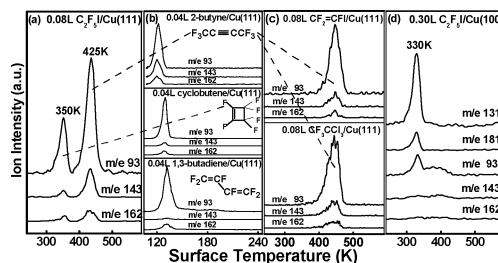

Figure 2. TPR/D traces of m/e 93, 143, and 162, representing C_4F_6 evolution from (a) C_2F_5I, (b) C_4F_6 isomers, (c, top) CF_2=CFI, and (c, bottom) CF_3CCl_3 adsorbed on Cu(111) at 110 K. The exposures are kept low enough to focus on the 425 K pathway. (d) TPR/D profiles after exposing C_2F_5I to Cu(100), indicating C_4F_6 is not formed on this surface.

yield from C_4F_6 to C_4F_8 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 C_2F_5I/Cu(111) are compared with those (Figure 2b) from the individually adsorbed hexafluoro-2-butyne, -cyclobutene, and -1,3-butadiene (C_4F_6 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 C_2F_3 intermediate, we used the readily available perfluoro*vinyl* iodide (CF_2=CFI, 97%, Lancaster) as a direct route to form Cu−C_2F_3. 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−$^α CF_2CF_3$ → Cu=$CF^β CF_3$ → Cu−CF=CF_2. But, the question remains: why is C_4-diene not observed, considering the fact that copper would promote coupling of Cu−CF=CF_2 (Ullman-type reaction)?[11] By losing two fluorine atoms from the α-carbon in Cu−CF_2CF_3, an alternative intermediate, *trifluoroethylidyne* (Cu≡C−CF_3) certainly deserves attention. Because d'Itri and co-workers reported identification of the surface

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$\equiv$C$-$CF$_3$ species formed upon adsorption and dechlorination of CCl$_3$CF$_3$ on a Pd/γ-Al$_2$O$_3$ catalyst,[7] TPR/D spectra were measured by exposing Cu(111) to CCl$_3$CF$_3$ (99%, Aldrich). The data shown in Figure 2c (bottom) also support the evolution of CF$_3$C$\equiv$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 C$_2$F$_5$I on 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 $\equiv$C$-$CF$_3$[12] or $-$CF$=$CF$_2$[13] moiety. In fact, the spectrum was identical with that produced by CF$_3$C$\equiv$CCF$_3$ adsorbed on 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 ν_s(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 C$\equiv$C group.[14] The strongly chemisorbed CF$_3$C$\equiv$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 C$_2$F$_5$I/Cu(111), it was not obvious whether the spectra represent 2-butyne (end product) or ethylidyne (intermediate).

It is generally accepted that ethylidyne is the favored intermediate against vinyl on close-packed fcc(111) surfaces where $\equiv$C$-$CH$_3$ prefers to sit at the *threefold hollow site* by forming three bonds with the metal surface.[16] If the generation of CF$_3$C$\equiv$CCF$_3$ and the intermediacy of Cu$\equiv$C$-$CF$_3$ on 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 Cu(100). In this vein, we measured the TPR/D spectra by dosing C$_2$F$_5$I on Cu(100). As illustrated in Figure 2d, only one desorption state arises at *330 K*, and CF$_3$C$\equiv$CCF$_3$ is indeed absent because of the lack of m/e 143 and 162 signals. Instead, CF$_3$CF$=$CFCF$_3$ accounts best for the relative peak intensities of m/e 181, 131, and 93.[6] This observed end product suggests that Cu$-$CF$_2$CF$_3$ is susceptible to the α-F elimination step only *once* on Cu(100), yielding surface $\equiv^\alpha$CF$-$CF$_3$ species[7] 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 C$_2$F$_5$/Cu-(111). While the fate of $\equiv$C$-$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 $\equiv$C$-$CF$_3$ on a metal surface. The electronegative CF$_3$ group weakens the orbital overlap between the metal and α-carbon in Cu$\equiv$CCF$_3$. Thus, on Cu(111) an unusual CC bond formation step becomes possible, 2Cu$\equiv$CCF$_3$ $\rightarrow$ Cu$\equiv$Cu + CF$_3$C$\equiv$CCF$_{3(ad)}$, reminiscent of a reverse metathesis-type reaction involving metal$-$metal multiple bonds to give alkylidyne complexes (Chauvin-like mechanism).[18] This coupling process can be relatively facile; therefore, as successive α,α-fluoride elimination of Cu$-$CF$_2$CF$_3$ takes place, the resulting Cu$\equiv$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 Cu$-$CF$=$CF$_2$ to CF$_3$C$\equiv$CCF$_3$ (Figure 2c, top) must be explained by the rapid isomerization from Cu$-$CF$=$CF$_2$ to Cu$\equiv$

CCF$_3$ on Cu(111). This type of vinyl-to-ethylidyne rearrangement was observed on a (111) surface of Pd.[19] Altogether, we propose the following mechanism:
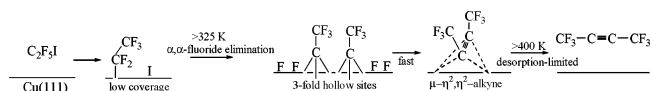
Ethyl ($-$CH$_2$CH$_3$) on transition-metal surfaces is dominated by the H-elimination from the β-position.[10] On the other hand, β-F elimination is favored by a semifluorinated ethyl ($-$CH$_2$CF$_3$) on Ag(111) to yield CH$_2=$CF$_2$.[20] Here we have established a different pathway available for the perfluorinated ethyl ($-$CF$_2$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$_2$R) bound to a metal center or surface (M), comprehensible by resonance such as M$-$CF$_2$R $\leftrightarrow$ M$^+=$CFR + F$^-$, or the back-donation of metal dπ electrons into the C$-$F antibonding orbital.[21] The removal of the second F atom from the β-carbon (M$=^\alpha$CF$-^\beta$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 Cu(111) the available threefold hollow sites are beneficial to the consecutive α-F abstraction to afford *trifluoroethylidyne*, 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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