The chemistry of C₂ perfluoroalkyl iodide on the Cu(111) single crystal surface

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Abstract

The thermal chemistry of perfluoroethyl iodide (C₂F₅I) adsorbed on Cu(111) has been investigated by temperature-programmed reaction/desorption (TPR/D), reflection-absorption infrared spectroscopy (RAIRS), and X-ray photoelectron spectroscopy (XPS). I 4d and F 1s XPS spectra show that dissociative adsorption of C₂F₅I to form the surface-bound perfluoroethyl (Cu–C₂F₅) moieties occurs at very low temperature (T < 90 K), while the C–F bond cleavage in adsorbed perfluoroethyl (Cu–C₂F₅) begins at ca. 300 K. XPS and TPR/D studies further reveal that the reactions of CF₃(ad) on Cu(111) are strongly dependent on the surface coverage. At high coverages (P₀ ≥ 0.16 L exposure), the adsorbed perfluoroethyl (Cu–C₂F₅) evolves, via α-F elimination, into the surface-bound tetrafluoroethylidene moieties (Cu≡CF–CF₃) followed by a dimerization step to form octafluoro-2-butene (CF₃CF=CFCF₃) at 315 K as gas product. The surface-bound (Cu–C₂F₅) decomposes preferentially, at low coverages (P₀ ≤ 0.04 L), via consecutive α-F abstraction to afford intermediate trifluoroethylidyne (Cu≡CCF₃), resulting in the final coupling reaction to yield hexafluoro-2-butene (CF₃CF=CFCF₃) at 425 K. However, at middle coverages (ca. 0.08–0.16 L exposure), the adsorbed perfluoroethyl (Cu–C₂F₅) first experiences an α-F elimination and then prefers to loss the second F from β position to yield the intermediate of Cu–CF₂–CF=Cu (μ-η,η-perfluorovinyl), which may further evolve into hexafluorocyclobutene (CF₃CF=CFCF₃) at 350 K through cyclodimerization reaction. Our results have also shown that the surface reactions to yield the products, CF₃CF=CFCF₃ and CF₃C≡CCF₃, obey first-order kinetics, whereas the formation of CF₃CFCFCF₂ follows second-order kinetics.

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1. Introduction

In heterogeneous catalytic reactions the reaction products are strongly dependent on the surface intermediates adsorbed on the catalysts. The study of the adsorption phenomena on the catalyst surfaces is therefore of great importance to heterogeneous catalysis. In the past two decades the chemistry [1–5] and the reaction kinetics [6–8] of alkyl moieties below C₃ prepared by the dissociative adsorption of alkyl halides on transition-metal have been widely studied. These results show that the alkyl moieties of C₂ or C₃ decompose on transition-metal surface by β-hydrogen elimination to form olefins (ethylene or propylene) and no C–C coupling reactions have been observed [1–8]. Fluorine-substituted alkyl surface moieties have also drawn increasing attention because the replacement of hydrogen with fluorine can result in a marked change in the physical and chemical properties. Compared with hydrocarbon counterparts, for example, fluorocarbons are more resistant to chemical attack, exhibit higher thermal stability,
and are more reluctant to coordinate to metal centers [9]. It has been found that for the substitution of fluorine into the terminal methyl group of C₂ or C₃, the surface moieties adsorbed on the Cu(111) [10] or Ag(111) [11] surface also decompose via β-elimination mechanism, forming CF₂=CH₂ or CF₃CH₂=CH₂, and no carbon–carbon bond coupling reactions are observed. In a recent communication, however, we have found a novel mechanism, namely α-elimination, as well as coupling reaction, occurring in perfluoroalkyl moieties (CF₃–CF₂–Cu) adsorbed on Cu(111) [12].

In this article, we report our comprehensive results of the thermal chemistry of perfluoroethyl iodide (C₂F₅I) occurring on Cu(111) single crystal surface, including C–I bond dissociation, C–F bond dissociation and cleavage, and C–C bond formation. In particular, we will address the issues of surface intermediates, reaction pathways and products distribution of perfluoroethyl adsorbed on Cu(111).

2. Experimental section

TPR/D and RAIRS experiments were performed in a stainless steel ultrahigh-vacuum (UHV) chamber evacuated by a turbomolecular pump (Varian, 250 L/s), backed by combined oil-free molecular-drag and diaphragm pumps (Alcatel Drytel 31) to a base pressure of 1 × 10⁻¹⁰ Torr. The chamber was equipped with a sputter-cleaning ion source (Omicron ISE10) for crystal surface cleaning and a mass spectrometer (Hiden, 510amu) for residual gas analysis and detection of gas-phase products during temperature-programmed reaction/desorption (TPR/D) measurements. RAIRS was performed by taking the infrared beam from a Nicolet Magna 560FTIR spectrometer and focusing it at grazing incidence (85°) through a polarizer and a KBr window onto the Cu(111) in the UHV chamber. Gas dosing was accomplished through a 0.76-mm-i.d. stainless steel tube that was connected to a precision leak valve.

The disk-shaped Cu(111) crystal (10 mm in diameter, 2 mm thick, 5 N purity from Monocrystals) was first manually polished to a mirror finish by using alumina grits (in 1, 0.3, and 0.05 μm order) and then placed within the UHV system. The crystal was mounted on a molybdenum plate with four clips. Heating was achieved through radiation from a hot tungsten filament located at the back of the molybdenum plate. Active cooling was executed by feeding liquid nitrogen through a coil of stainless steel tubing into an OFHC copper block, to which the molybdenum plate is attached. With this mounting scheme, sample temperatures could be controlled from 100 to 1200 K and were measured by a chromel–alumel thermocouple (0.127 mm) whose junction was wedged into a hole on the edge of the crystal. To maintain a constant crystal temperature for a long period of time or to heat the crystal at a reproducible rate, a commercial temperature controller (Eurotherm 818P) consisting of a programmable proportional–integral–differential (PID) feedback circuit coupled to a DC power supply to regulate the heating of the tungsten filament was used.

After pump-down and bake-out of the chamber, the Cu(111) surface was cleaned by 3–4 cycles of Ar⁺ sputtering at room temperature for 30 min and at 900 K for 8 min, then annealed at 950 K for 3 min. The Ar⁺ beam voltage and current to the sample were typically 1 keV and 5–6 μA, respectively. Prior to each TPR/D experiment, the single crystal surface was exposed to gaseous reactants at 110 K by positioning the sample front approximately 3 cm from the doser. The pressure of the adsorbate in the chamber (measured by the ion gauge in this dosing geometry) multiplied by the dosing time constituted our measurement of the exposure, which was given in langmuirs (L) with 1 L = 1 × 10⁻⁶ Torr s. All mass scan and TPR/D spectra were taken with the mass spectrometer ionizer energy set at 70 eV.

The X-ray photoelectron spectroscopy (XPS) were recorded in an UHV chamber connected to a wide-range (10–1500 eV) spherical grating monochromator beamline at the Synchrotron Radiation Research Center in Hsin-Chu, Taiwan. The sample preparation and gas handling all followed standard procedures, and were described in detail above. Gas dosing was accomplished by background dosing, i.e. the leak value mouth is in back of the Cu(111) surface. The photomission counts and thermocouple readings were both interfaced to a personal computer for data acquisition and storage. The iodine 4d₃/₂, 4d⁵/₂, and fluorine 1s binding energies were calibrated against Cu 2p₃/₂ core levels, centered at 75 eV. For all XPS spectra, curve fitting is used to reveal the change in line shape. A mixed Gaussian (80%)/Lorentzian (20%) product function in conjunction with a linear background is found to reproduce observed spectra very well [13].

Perfluoroethyl iodide (C₂F₅I, 97%) and hexafluoro-1,3-butadiene (CF₃CF=CF₂, 99%) were obtained from Lancaster Synthesis. Hexafluoro-2-butyne (CF₂C=CCF₃, 98%) and hexafluoro-cyclobutene (CF₂CFCF₂CF₂, 98%) were purchased from SynQuest. All gaseous compounds above were used without additional purification. The purity of the closing gases was confirmed in situ by mass spectrometry.

3. Results and discussion

The thermal chemistry of C₂F₅I on Cu(111) was examined by performing TPR/D spectroscopy and X-ray photoelectron spectroscopy experiments. Thermal activation of adsorbed C₂F₅I on the copper surface gives mainly C–C coupling reaction productions, such as C₄F₈ and C₄F₆. Thermal desorption product CF₃=CF₂, resulting from β-F elimination was not detected, nor was any other stable C₁ or C₂ or C₃ molecules. Molecular desorption of C₂F₅I was only observed for the coverage approaching saturation, demonstrating the facile nature of the C–I bond-scission step.
3.1. C–I bond cleavage

I 4d XPS spectra from a Cu(111) surface obtained as a function of C\(_2\)F\(_5\)I coverage (by background dosing) at 90 K are shown in Fig. 1. Here, the dots represent the collected data after Shirley background subtraction, the solid lines are the curve fits to the data, and the various decomposed components are shown by the short dot lines. At low coverages (<4.0 L), as determined from the fitting process, the I 4d XPS spectrum can be decomposed into two components, centered at 49.29 and 51.07 eV, which correspond, respectively, to 4d\(_{5/2}\) and 4d\(_{3/2}\) binding energies of iodine bonded to Cu(111). When the coverage reaches 4.0 L (especially 5.0 L), however, clear features begin to develop at 50.80 and 52.62 eV, corresponding to the I 4d\(_{5/2}\) and I 4d\(_{3/2}\) core levels of C\(_2\)F\(_5\)I, respectively. These values are higher than those measured at low coverages, indicating that the C–I bond cleavage occurs and I–Cu bond forms on Cu(111) surface at low coverages. These results demonstrate that the temperature at which the C–I bond-scission step in C\(_2\)F\(_5\)I on Cu(111) surface takes place is less than 90 K, much lower than the value of 100–200 K observed in alkyl halides [1].

3.2. C–F bond activation and cleavage

As illustrated in Fig. 2, after adsorption of 0.25 L of C\(_2\)F\(_5\)I at 110 K the multiple-ion TPR/D spectroscopy gives two desorption states with peak maxima at 880 K. The states are featured by m/e 82 (\(^{63}\)CuF) and 84 (\(^{65}\)CuF), respectively, with a ratio of the peak heights matching the natural abundance of copper isotopes. The formation of volatile copper fluoride [14] implies that the substrate experiences an etching process. It also suggests that some of the C–F bonds (if not all) in Cu–C\(_2\)F\(_5\) must be ruptured. To determine the temperature at which C–F bound-scission step occurs, we have collected the F 1s XPS spectra after 1.5 L C\(_2\)F\(_5\)I (by background dosing) exposed to Cu(111) at 90 K and then annealed at indicated temperatures for about 10 s. The obtained temperature-dependent F 1s XPS spectra are presented in Fig. 3. At low temperatures (namely below 300 K), two peaks can be observed, indicating that two different types of fluorine atoms with significantly different chemical surrounding are present on the surface. Based on the F1s binding energy observed in fluoropolymers [15], the peak at 687.40 eV, with a larger fitted peak area (denoted as S\(_1\)), can reasonably be assigned to the terminal perfluoromethyl groups (namely α-F), while the peak centered at 685.84 eV, with a smaller fitted peak area (denoted as S\(_2\)), can be attributed to the fluorine bonded to alpha carbon (namely β-F). This peak assignment is also supported by the ratio of S\(_2\) to S\(_1\), a value of ~2/3 obtained. This value is exactly equal to the ratio of the number of α-F to that of β-F. These observations also indicate that no C–F bond cleavage occurs at temperatures less than 300 K. However, when the temperature reaches 300 K, a third peak centered at 683.08 eV with a fitted peak area being denoted as S\(_3\) clearly appears. This peak can be
assigned to F bonded to the Cu(111) surface, suggesting that the F–C bond-scission step begins at about 300 K. In addition, we found that the ratio of S2 to S1 at 300 K is reduced to \(\sim 0.52\), less than the value of 2/3, suggesting that the F–C bond-scission step begins at ca. 300 K.

indicate that the products are strongly dependent on the surface coverage.

To understand the coverage-dependent product distribution, we first analyze the TPR/D data of a 0.6 L coverage at which all the three desorption states (315 K, 350 K, and 425 K) are observed. As can be seen from Fig. 4(B), the 315 K state is mainly characterized by \(m/e\) 181 (\(C_4F_6^+\)), 131 (\(C_4F_4^+\)), 100 (\(C_4F_2^+\)), and 93 (\(C_2F_3^+\)). Their relative intensity is consistent with the cracking pattern of \(CF_3CF=CFCF_3\) (\(C_4F_8\)) detected by backfilling the chamber with pure \(CF_3CF=CFCF_3\) gas. This suggests that the 315 K product is \(CF_3CF=CFCF_3\). The 350 K desorption state is featured by \(m/e\) 119 (\(C_2F_3^+\)), 100 (\(C_2F_2^+\)), 162 (\(C_4F_4^+\)), 143 (\(C_4F_3^+\)) and 93 (\(C_2F_3^+\)). From the reports of fragmentation patterns in National Institute of Standards and Technology (NIST) Chemistry WebBook, we find that the intensity ratios among the fragments 162 (\(C_4F_6^+\)), 143 (\(C_4F_4^+\)) and 93 (\(C_2F_3^+\)) observed in our TPR/D experiments agree well with those resulting from the unsaturated \(C_4F_6\). Therefore, we believe that the concurrence of \(m/e\) 93 (\(C_3F_7^+\)), 143 (\(C_4F_5^+\)), and 162 (\(C_4F_4^+\)) signals originates from the unsaturated \(C_4F_6\) compounds, which is indeed confirmed by our TPR/D experiments with \(CF_3CFCF_3\), \(CF_2CFCFCF_2\), and \(CF_2=CF=CF=CF_2\) being individually adsorbed on Cu(111) [see Fig. 4(C)].

The other fragments of the 350 K desorption state, \(m/e\) 119 (\(C_2F_3^+\)) and 100 (\(C_2F_2^+\)), may come from: (i) the compounds (possible products) such as \(C_2F_4\), \(C_3F_6\), \(C_4F_8\), \(C_6F_{16}\) isomers (\(CF_3C=CFCF_3\), \(CF_2CFCFCF_2\), \(CF_2=CF=CF=CF_2\)), \(C_3F_6\) isomers [\(CF_3CF=CFCF_3\), \(CF_2=CF=CF=CF_2\), \(CF_2CF2CF2CF2\) (octafluorocyclobutane)] and \(C_4F_{10}\), and (ii) the desorption of radicals (\(C_2F_3\)). The absence of \(m/e\) 81 (\(C_2F_3^+\)) [see Fig. 4(B)], a characteristic fragment ion of \(C_2F_4\), indicates that there is no such a product \(C_2F_4\), which can be in principle formed via F-elimination from \(\beta\) position of \(^{12}C_4F_6^{18}C_4F_6^{18}\) on Cu(111), as the hydrocarbon alkyl group does [1–3,16,17]. The lack of \(m/e\) 131 (\(C_3F_7^+\)) fragment peak at 350 K [see Fig. 4(B)], a characteristic fragment peak of \(C_2F_6\), \(C_2F_8\) isomers, or \(C_3F_{10}\) excludes the possibility of the fragments 119 (\(C_2F_3^+\)) and 100 (\(C_2F_2^+\)) from \(C_4F_6\), \(C_3F_8\) isomers and \(C_3F_{10}\). Our results have also shown that the fragments 119 (\(C_2F_3^+\)) and 100 (\(C_2F_2^+\)) are not from \(C_3F_8\) because of the absence of \(m/e\) 169 (\(C_3F_6^+\)), a characteristic fragment ion of \(C_3F_8\), in the TPR/D spectra [see Fig. 4(B)]. Moreover, as shown in Fig. 4(C), the peaks of \(m/e\) 119 (\(C_2F_3^+\)) and 100 (\(C_2F_2^+\)) are not included in the cracking patterns of \(C_4F_6\) isomers (\(CF_3C=CFCF_3\), \(CF_2CFCFCF_2\), \(CF_2=CF=CF=CF_2\)), indicating that the fragments of \(m/e\) 119 (\(C_2F_3^+\)) and 100 (\(C_2F_2^+\)) do not originate from \(C_4F_6\) isomers. Thus, the possibility of the fragments 119 (\(C_2F_3^+\)) and 100 (\(C_2F_2^+\)) stemming from the desorption of radicals (\(C_2F_3\)) should be taken into account. An previous study on the thermal chemistry of \(C_2F_4\) on Ni(100) at 340 K indicates that above 75% saturation of the first layer, the availability of surface sites for decomposition decreases to a level where some adsorbed \(C_2F_4\) remains intact and
desorbs as such [18]. Considering higher coverage (0.6 L) in our experiments (see Fig. 7 where the saturation-exposure of \( \text{C}_2\text{F}_5\text{I} \) on the Cu(111) surface is about 1.0 L), therefore, we speculate that the fragments [119 \((\text{C}_2\text{F}_5^+)^+\), 100 \((\text{C}_2\text{F}_4^+)^+\)] probably stem from the desorptions of radicals \((\text{C}_2\text{F}_5^+)\), where the fragment \(m/e\) 100 \((\text{C}_2\text{F}_4^+)^+\) of fluorocarbon radicals may originates from the loss of one fluorine atom during electron-impact ionization [18].

For the 425 K desorption state, we can also find a same fragment set containing \(m/e\) 93 \((\text{C}_3\text{F}_3^+)^+\), 143 \((\text{C}_4\text{F}_5^+)^+\), and 162 \((\text{C}_4\text{F}_6^+)^+\) as the 350 K desorption state has. However, the difference in relative fragment abundance between two desorption states suggests that the desorption states observed at 350 and 425 K are not corresponding to the same product. In order to determine the structures of unsaturated \(\text{C}_4\text{F}_6\) products observed at 350 and 425 K, we have made a comparison between the TPR/D profiles of \(m/e\) 93, 143, and 162 from \(\text{C}_2\text{F}_5\text{I}/\text{Cu}(111)\) (see Fig. 4(B)) and those from individually absorbed \(\text{C}_4\text{F}_6\) isomers, namely, hexafluoro-2-butyne \((\text{CF}_3\text{C}==\text{CCF}_3)\).
hexafluoro-cyclobutene (CF₂CFCF₂), and hexafluoro-1,3-butadiene (CF₂=CF–CF=CF₂) (see Fig. 4(C)). Based on the peak intensity ratios of the fragments of the products and C₃F₆ isomers determined by our mass spectrometer, we can assign the 425 K major product to hexafluoro-2-butene and 350 K species to hexafluoro-cyclobutene.

The above analyses reveal that the coverage-dependent products observed at 315, 350, and 425 K, are, respectively, CF₃CF=CFCF₂, CF₂CFCFCF₂ (hexafluoro-cyclobutene), and CF₂C≡CCFCF₃. A detailed product distribution as a function of the coverage can be found in Fig. 5 (A) and (B). From these figures we can find that at very low coverages, e.g. ≤0.04 L, the 425 K CF₂C≡CCFCF₃ is the sole fluorocarbon product. At high coverages, however, a crossover of yield from C₄F₆(CF₃CF–CF₂) (see Fig. 4 (C)) can be observed on perfluoroethyl iodide (C₂F₅I) (315 K), CF₂CFCF₂ (350 K), and CF₃CF₂ (315 K), CF₃CF₂, and CF₄ (major fragment C₃F₅) from C₄F₈(CF₃CF–CF₂) to C₄F₆(CF₃CF=CCFCF₃) can be observed.

3.3.2. Surface intermediates and reaction pathways

Our TPR/D results have shown that depending on the coverage, three main products, namely, CF₂CF=CCFCF₃ (315 K), CF₂CFCFCF₂ (350 K), and CF₂C≡CCFCF₃ (425 K) can be observed on perfluoroethyl iodide (C₂F₅I) adsorbed on Cu(111). According to the XPS and TPR/D results that the first C–F bond cleavage might occur at a carbon and no m/e 81 (C₃F₅) fragment (a fragment from CF₂=C≡F species that can be produced by β-F elimination) was detected, we believe that the product of CF₂CF=CCFCF₃ is formed by the following pathways. First, the C₂F₅(ad) on Cu(111) loses one F at each step, e.g. 0.04 L, the 425 K CF₂C≡CCFCF₃ is limited by the rate of C–F bond dissociation. The preference to α-F elimination, rather than β-F elimination, in perfluoroethyl (–CF₂CF₃) is rarely observed in hydrocarbon (–CH₂CH₃) or semifluorinated ethyl (–CH₂CF₃) where the β-F elimination dominates to yield CH₃=CH₂ or CH₂=CF₂ [11,21,22]. Fluorocarbons are more stable than their hydrocarbon counterparts, but the reactivity of fluoroalkyl groups is dramatically changed by coordination to a transition metal. Upon coordination to a transition metal, the α-CF bonds are significantly weakened [23]. Hence, we believe this difference between fluoroalkyl groups and their hydrocarbon counterparts is initiated by the exceptionally labile α-CF bonds in the fluorocarbon group (CF₂R) bound to a metal center or surface (M), comprehensible by resonance, stemming from the ability of the fluorne atom to function as both a σ-acceptor and a π-donor [24], such as M–CF₂R⇔M⁺ = CFR + F⁻, or the back-donation of metal dπ electrons into the C–F antibonding orbital.

For the product of CF₂CFCFCF₂ (350 K), the recombination of the intermediate species (C₃F₃(ad)) is logically invoked for its formation. The most possible structures of C₃F₃(ad) for CF₂CFCFCF₂ formation are CF₃C≡Cu (trifluoroethylidyne), CF₃=CF–Cu (perfluorovinyl), and Cu–CF₂–CF=Cu (μ-η,η-perfluorovinyl). It is generally accepted that CF₃C≡Cu has a propensity to sit at the threefold hollow site by forming three bonds with the metal surface, as the hydrocarbon counterpart does. The clean Cu surface is very reactive toward C–F bond cleavage, and at low CF₀C₀ exposure rapid elimination of two α-F atoms results in the stabilization of CF₃C≡Cu species on threefold site. But, similar to CH₂C≡Cu which is stable to above 400 K on Pt(1 1 1) [1], these species may not react further in vacuum in the absence of a high surface coverage of hydrogen [1,25] because of their orientation with respect to the surface (C–F bonds are located far from the surface) and high bonding energy to the surface. As far as the molecular structure is concerned, it is more reasonable to postulate perfluorovinyl than trifluoroethylidyne as the intermediate species for the formation of CF₂CFCFCF₂. To identify the possible surface intermediate, perfluorovinyl, we have used perfluorovinyl iodide (CF₂=CFI, 97%, Lancaster) as a direct route to form CF₂CFCFCF₂. As displayed in Fig. 4(A) (bottom), the traces of m/e 93, 143, and
162 are indeed observed in the TPR/D spectra of CF$_2$=CFI/Cu(1 1 1). However, one set of the peaks appears at 375 K, not 350 K as observed in the TPR/D results of C$_2$F$_3$I/Cu(1 1 1) [see Fig. 4(A) (middle)]. Moreover, the peak intensity ratios of these traces (m/e 93, 143, and 162) at 375 K differ from those at 350 K [the fragmentation ratios at 350 K are consistent with those in the TPR/D results of hexafluorocyclobutene/Cu(1 1 1) shown in Fig. 4(C) (middle)]. Further examination also reveals that the peak height ratio between 375 K and 425 K peaks of m/e 93 fragment [see Fig. 4(A) (bottom)] is much larger than that between 350 K and 425 K peaks [see Fig. 4(A) (middle)]. These observations clearly show that CF$_2$=CF=Cu is not the possible intermediate species for CF$_2$CFCFCF$_2$ formation. Thus, last intermediate, Cu–CF$_2$–CF=Cu (μ-η,η-perfluoro vinyl), certainly deserves attention. Due to the destabilizing repulsive interactions of the fluorine lone pairs with filled π orbitals on adjacent carbon atoms, fluorine has a propensity to reside on sp$^3$ rather than sp$^2$ carbon centers [23]. As such, the intermediate, Cu$^+$=CFCF$_3$, may prefer to form Cu–CF$_2$–CF=Cu (μ-η,η-perfluorovinyl) rather than to yield perfluorovinyl (Cu–CF–CF$_3$) via β-F elimination. At middle coverages (ca. 0.08–0.16 L exposure) the formed Cu–CF$_2$–CF=Cu (μ-η,η-perfluorovinyl) can evolve into hexafluorocyclobutene through a cyclodimerization reaction. However, at both low and high coverages the intermediate Cu–CF$_2$–CF=Cu (μ-η,η-perfluorovinyl) does not result in the formation of hexafluorocyclobutene. The reason for this is that at low coverages the surface has a lot of sites to adopt F and Cu–CF$_2$–CF=Cu (μ-η,η-perfluorovinyl) species may decompose completely to C and F atoms, while at high coverages there are not enough sites on the surface so that the reaction is limited by dissociation of only one α-F bond that results in the perfluoro-2-butene formation.

Last product, CF$_3$C=CCF$_3$, is possessed of the highest desorption temperature (425 K). The absence of the 1065–1077 cm$^{-1}$ (ν(C–F)) peak [19], as shown in Fig. 6(A) and (B), indicates that at 400 K there is no tetrafluoroethylidene (Cu=CCF$_3$) on the Cu(1 1 1) surface. In other words, the 1210 cm$^{-1}$ (ν$_l$(CF$_3$)) [see Fig. 6(A) and (B)] peak should be designed to trifluoroethylidyne (Cu=CCF$_3$) [19], which is formed by consecutive α-F elimination from the adsorbed perfluoroethyl (Cu–C$_2$F$_3$). In our previous work [12], we thought that the dimerization reaction of Cu=CCF$_3$ for the formation of CF$_3$C=CCF$_3$ takes place on the Cu(1 1 1) surface. However, the results shown in Fig. 4C indicate that there is no molecularly adsorbed CF$_3$C=CCF$_3$ on the surface above 150 K. Moreover, by analogy with C=CH$_3$ which is stable to above 400 K on Pt(1 1 1) [1], the surface intermediate ethyldiene (Cu=CCF$_3$) formed at low CF$_3$CFI exposures should not couple until above 400 K on the Cu(1 1 1) surface because of low mobility and high stability (namely lock of vacant adjacent threefold sites and high bonding energy to the surface). Therefore, it is more reasonable to propose that the formation of CF$_3$C=CCF$_3$ should occur in the gas phase by the dimerization of the CF$_3$C= radicals which desorb at the temperatures above 400 K. The absence of CF$_3$ traces in mass-spectra may be because of a low CF$_3$C= ionization probability.

As shown in Fig. 5(A) and (B), similar to the product of CF$_3$CF=CCF$_3$, the peak temperature for CF$_3$C=CCF$_3$ (425 K) does not change with increasing the exposure, showing the characteristic of first-order kinetics. This indicates that the reaction for the generation of CF$_3$C=CCF$_3$ in the gas phase by the coupling process of the radicals (≡C–CF$_3$) is fast and the desorption of the radicals from the Cu(1 1 1) surface is the rate-determining step for the CF$_3$C=CCF$_3$ formation. However, the peak temperature of hexafluorocyclobutene (CF$_3$CFCFCF$_3$) decreases as the surface coverage increases, shifting from 350 to 338 K. This typical feature of second-order kinetics [26] suggests that the desorption of CF$_3$CFCFCF$_2$ is fast with the surface reaction process invoking two intermediates [Cu–CF$_2$–CF=Cu (μ-η,η-perfluorovinyl)] being the rate-determining step.

To further gain insight into the thermally activated mechanism for CF$_3$F$_4$ conversion on Cu(1 1 1), the peak heights of desorption products at various coverage in TPR/D profiles shown in Fig. 5(A) and (B) were quantified. Provided in Fig. 7 are plots for 315 K octafluoro-2-butene (represented by $m/e$ 131 (C$_4$F$_7$)) and hexafluorocyclobutene (represented by $m/e$ 93 C$_3$F$_7$) desorption peak heights as a function of Cu(1 1 1) exposure to perfluoroethyl iodide. The peak height of CF$_3$C=CCF$_3$ desorption (425 K) rises with increasing the coverage up
to 0.4 L, and then goes down at 0.6 L and levels off to a constant value about 450 counts/s from 1.0 L to 1.5 L. The peak height of CF₂CFCFCF₂ desorption (350 K) displays a similar behavior to that of 425 K desorption up to 0.8 L, and then suddenly goes down to a constant value ca. 530 counts/s at higher exposures. Two reasons are believed to be responsible for the reduction in the peak heights of desorption products F₃CC≡CCF₃ and CF₂CFCFCF₂. First, the intermediates Cu≡C–CF₃ and Cu–CF₂=CF≡Cu (μ-η,η-perfluorovinyl) needed for the formation of the products CF₃C≡CCF₃ and CF₂CFCFCF₂ requires more empty surface sites for their formation. The decrease in empty surface site at high coverages can lead to a decay in peak height of the product desorption. Second, after the first α-elimination and the formation of Cu≡CF–CF₃, the competition may occur between the Cu≡CF–CF₃ coupling reaction to form octafluoro-2-butene CF₃CF=CCFCF₃ and the second α-F or β-F elimination to form Cu≡C=CF₃ or Cu–CF₂=CF≡Cu (μ-η,η-perfluorovinyl). As illustrated in Figs. 5 and 7, it is clear that high coverage is favorable for the Cu≡CF–CF₃ coupling reaction. The result is obviously related to the fact that the number of neighboring Cu≡CF–CF₃ intermediates increases with increasing the coverage and thus coupling reactions have a higher chance to occur at higher coverages. In addition, the observed phenomenon that at high coverages (≥1.0 L) the peak height of CF₃CF=CCFCF₃ almost keeps unchanged with increasing the coverage may be attributed to the saturated adsorption of perfluoroethyl iodide (C₂F₅I) on the Cu(111) surface.

Based on the above investigations, we propose the following mechanism for the chemistry of perfluoroethyl iodide on Cu(111) (see Scheme 1). Perfluoroethyl iodide first undergoes a C–I bond dissociation step to yield perfluoroethyl moieties directly bonded to Cu(111). This step is completed below 90 K. When the temperature reached ca. 300 K, perfluoroethyl (–CF₂–CF₃) adsorbed on Cu(111) begin to lose a fluorine by α-F elimination. After forming the intermediate of perfluoroethylidene (Cu≡CF–CF₃) by α-F elimination, the competition may take place between the coupling reaction to form octafluoro-2-butene (CF₃CF=CCFCF₃) and α-F or β-F elimination to yield trifluoroethylidyne intermediate for the formation of CF₃C≡CCF₃ (425 K) or Cu–CF₂=CF≡Cu (μ-η,η-perfluorovinyl) for the generation of CF₂CFCFCF₂ (350 K). Our TPR/D data show that high coverage is beneficial to the perfluoroethylidene coupling reaction and low coverage is favorable for the second α-F elimination. The middle coverage (ca. 0.08–0.16 L exposure), however, is good for β-F elimination. Therefore, at low coverages (<0.04 L exposure) hexafluoro-2-butyne is the sole product, at

Scheme 1. The mechanism proposed for the chemistry of perfluoroethyl iodide on Cu(111).
middle coverages (ca. 0.08–0.16 L exposure) the desorption products, hexafluoro-cyclobutene (CF₂CFCF₂F) at 350 K and hexafluoro-2-butyne (CF₃C≡CCF₃) at 425 K, are observed; and at higher coverage (≥0.16 L exposure), besides the products of CF₃C≡CCF₃ and CF₂CFCF₂F, CF₃CF₃CFCF₃ is also detected.

4. Conclusion

We have investigated the surface reaction of perfluoro-ethyl iodide adsorbed on Cu(111). It has been found that the dissociative adsorption of C₂F₅I to form the Cu–C₂F₅ moieties occurs at very low temperature (T < 90 K), while the C–F bond cleavage in adsorbed perfluoroethyl (Cu–C₂F₅) begins at ca. 300 K. Our results have also revealed that the first C–F bond cleavage to yield the surface-bound tetrafluoroethylidene moieties (Cu≡CF–CF₃) takes place at the α-C position, rather than β-C position, and depending on the surface coverage the formed Cu≡CF–CF₃ species can produce different products. At high coverages the formation of CF₃CF≡CFCF₃ by the coupling reaction of Cu≡CF–CF₃ is predominant. At middle coverages (ca. 0.08–0.16 L exposure) the cyclodimerization reaction of the formed intermediate, Cu–CF₂–CF≡Cu (μ-η,η-per-fluorovinyl), by the loss of F from Cu≡CF–CF₃ via β-elimination yields CF₂CFCF₂F, while at low coverages the intermediate of Cu≡C–CF₃ formed by further eliminating F from α-C position in Cu≡CF–CF₃ can evolve into CF₃C≡CCF₃ through the gas phase coupling reaction of the intermediate ≡CCF₃. The surface reactions of forming the products CF₃CF≡CFCF₃ and CF₂CFCF₂F are found to obey first-order and second-order kinetics, respectively. It is also shown that the surface reaction process from the intermediate Cu≡CCF₃ to gas product CF₃C≡CCF₃ follows first-order kinetics with the intermediate ≡CCF₃ desorption being the rate-limiting step.

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