

## Selective and Facile C–F Bond Activation of Trifluoromethyl Groups on Cu(111)

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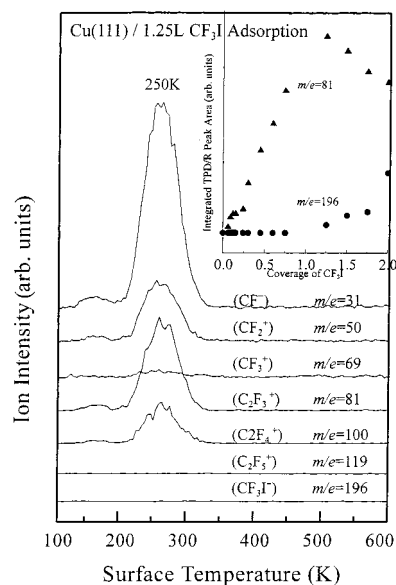
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Received May 13, 1999

Activation of the strongest bond that carbon can form, the C–F bond, remains a topic of recent interest.<sup>1</sup> It has long been known that interaction of fluorocarbons with a metal center may ultimately lead to the cleavage of such robust bonds. Catalytic activation of C–F bonds by metal complexes in solution is the subject of several reviews.<sup>2,3</sup> Trifluoromethyl transition-metal complexes draw our particular attention because M–CF<sub>3</sub> species have been recognized as precursors to M=CF<sub>2</sub> (difluorocarbene) complexes.<sup>4</sup> We are interested in such problems regarding controlled C–F activation of small fluorocarbons bound to metal surfaces. The chemistry of trifluoromethyl groups adsorbed on metal single-crystal surfaces was explored by the reactions of trifluoromethyl iodide (CF<sub>3</sub>I) with Ni,<sup>5–7</sup> Ru,<sup>8,9</sup> Pt<sup>10,11</sup>, and Ag.<sup>12</sup> Except for silver (CF<sub>3</sub> desorbs as a radical), experimental results revealed that the C–F bonds could be ruptured, however, in either uncontrolled fashion or at high temperatures. Removal of a single fluorine atom from the CF<sub>3</sub> fragment could not be achieved with high selectivity, as displayed for metal complexes.

We speculate that the choice of metal surfaces might be pivotal. Here we report a novel C–F activation in chemisorbed CF<sub>3</sub> moieties using a Cu(111) surface. The key findings of this work are 2-fold: First, only one C–F bond in the trifluoromethyl is broken, suggesting *selective activation* of carbon–fluorine bonds rather than complete defluorination, and the formation of a *difluorocarbene intermediate* on the surface. Without other competing reaction channels, all the CF<sub>3</sub> groups undergo this mild C–F decomposition pathway at and below the monolayer coverage. Second, C–F bonds are cleaved by the copper surface *below 160 K*. This low reaction temperature can be translated, in kinetics terms, into small activation energy; therefore, remarkably *facile* bond activation is implied.

The experiments were performed in an ultrahigh vacuum chamber described in detail elsewhere.<sup>13</sup> In brief, the system is equipped with an ion sputtering gun and a retarding-field analyzer for both Auger electron spectroscopy and low-energy electron diffraction. A quadrupole mass spectrometer is shielded in a differentially pumped cylindrical cage assembly with an aperture



**Figure 1.** Multiple-ion TPR/D spectra of  $m/e$  31 ( $\text{CF}^+$ ), 50 ( $\text{CF}_2^+$ ), 69 ( $\text{CF}_3^+$ ), 81 ( $\text{C}_2\text{F}_3^+$ ), 100 ( $\text{C}_2\text{F}_4^+$ ), 119 ( $\text{C}_2\text{F}_5^+$ ), and 196 ( $\text{CF}_3\text{I}^+$ ) after the adsorption of 1.25 L of  $\text{CF}_3\text{I}$  on Cu(111) at 110 K. Ions were monitored with the mass spectrometer ionizer energy set at 70 eV. The heating rate was 2 deg K/s. It should be noted that the current levels on the Cu(111) were less than 1 nA with our experimental configurations; therefore, the desorption features were surely not stimulated by electrons emitted from the ion source of the mass spectrometer. The inset shows the integrated peak areas, calculated from  $m/e$  81 (tetrafluoroethylene formation) and 196 (molecular desorption) TPR/D features, as a function of  $\text{CF}_3\text{I}$  exposure.

of 2 mm diameter to conduct temperature-programmed reaction/desorption (TPR/D) studies.  $\text{CF}_3\text{I}$  has been widely used as a source of adsorbed  $\text{CF}_3$  moieties on a variety of metal surfaces<sup>5–12</sup> because the C–I bond is weak, and is known to break readily upon adsorption, yielding the desired  $\text{CF}_3$  species. As illustrated in Figure 1, multiple-ion TPR/D survey shows a featureless trace of  $m/e$  196 following the adsorption of 1.25 L (1 L =  $10^{-6}$  Torr s) of  $\text{CF}_3\text{I}$  at 110 K. This observation indicates no molecular desorption occurs from the surface at this exposure, suggesting that all the adsorbed  $\text{CF}_3\text{I}$  undergo C–I bond scission. Because the ion signals of  $\text{CF}_3^+$  ( $m/e$  69) and  $\text{C}_2\text{F}_5^+$  ( $m/e$  119) are also absent, the possibility of forming the  $\text{CF}_3$  free radical, perfluoromethane, and perfluoroethane can be ruled out. The only desorption state is featured by  $m/e$  31 ( $\text{CF}^+$ ), 50 ( $\text{CF}_2^+$ ), 81 ( $\text{C}_2\text{F}_3^+$ ), and 100 ( $\text{C}_2\text{F}_4^+$ ) with peak maxima at 250 K. The relative ion abundance of these desorption profiles nearly duplicates the fragmentation pattern of tetrafluoroethylene ( $\text{CF}_2=\text{CF}_2$ ).<sup>14</sup> Intuitively, coupling of two difluorocarbene ( $\text{CF}_2$ ) units would afford tetrafluoroethylene. The intermediacy of a *surface-bound difluorocarbene*,  $\text{CF}_2(\text{ad})$ , can be invoked to account for the observed product. The lack of  $\text{CF}_3$ ,  $\text{CF}_4$ , and  $\text{C}_2\text{F}_6$  suggests complete conversion from  $\text{CF}_3(\text{ad})$  to  $\text{CF}_2(\text{ad})$ .  $\text{CF}_2(\text{ad})$  restricts itself from being further decomposed into  $\text{CF}(\text{ad})$  and carbidic carbon because the Auger data reveal the disappearance of carbon signal above 250 K, which coincides with the desorption of  $\text{CF}_2=\text{CF}_2$ . The fate of fluorine atoms on the surface, resulting from the selective C–F bond activation  $\text{CF}_3(\text{ad}) \rightarrow \text{CF}_2(\text{ad}) + \text{F}(\text{ad})$ , eventually leads to etching of the substrate by evolving  $\text{CuF}$  in the gas phase above 700 K (TPR/D data are not shown here). Surface-bound iodine due to the initial C–I bond dissociation ultimately desorbs as iodine atoms in a broad temperature range from 600 to 900 K.

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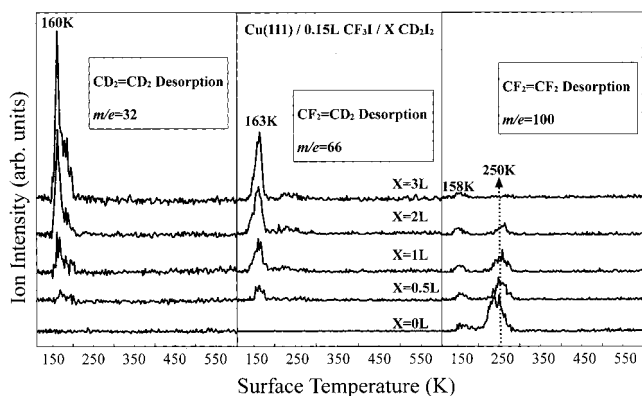
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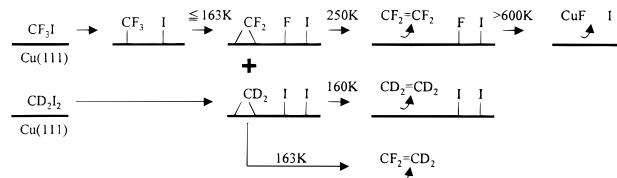
**Figure 2.** TPR/D spectra of three different types of ethylene due to competing carbene coupling reactions after exposing the Cu(111) surface, which was preadsorbed with 0.15 L of  $\text{CF}_3\text{I}$ , to an  $X$  amount of  $\text{CD}_2\text{I}_2$  ( $X = 0, 0.5, 1, 2, 3$  L exposures). The representative ions are  $m/e$  32 ( $\text{CD}_2=\text{CD}_2^+$ , left), 66 ( $\text{CF}_2=\text{CD}_2^+$ , middle), and 100 ( $\text{CF}_2=\text{CF}_2^+$ , right), respectively. It should be noted that the tiny feature at 158 K in all the  $\text{CF}_2=\text{CF}_2$  ( $m/e$  100) spectra resulted from traces of tetrafluoroethylene impurity in the  $\text{CF}_3\text{I}$  gas manifold.

The reaction scheme described above holds for all the  $\text{CF}_3\text{I}$  exposures below 1.25 L. Due to active-site availability, intact molecular desorption starts to compete with tetrafluoroethylene formation in the TPR/D spectra at higher doses. As shown in the inset of Figure 1, according to the uptake curves of  $\text{C}_2\text{F}_3^+$  ( $m/e$  81) and  $\text{CF}_3\text{I}^+$  ( $m/e$  196), it is reasonable to assign 1.25 L to the saturation coverage of one monolayer (ML) of  $\text{CF}_3\text{I}$ .

The intermediacy of  $\text{CF}_{2(\text{ad})}$  deserves further scrutiny. We can verify this intermediate state based upon purely chemical evidence. Our approach, borrowed from the concept of “carbene scavengers”, utilizes a labeled substance that is added to the surface to counteract the self-coupling of  $\text{CF}_{2(\text{ad})}$  (if any) and meanwhile to remove difluorocarbene as an easily identifiable species. Here this substance is chosen to be deuterium-labeled diiodomethane ( $\text{CD}_2\text{I}_2$ ), a well-known precursor for generating surface methylene. The chemistry of  $\text{CD}_2\text{I}_2$  on Cu surfaces studied by Chiang et al.<sup>15</sup> reveals facile dissociation of C–I bonds to form  $\text{CD}_{2(\text{ad})}$  followed by methylene recombination, yielding  $\text{CD}_2=\text{CD}_2$  as the sole gas-phase product. Figure 2 juxtaposes the TPR/D spectra of three different types of ethylene,  $\text{CF}_2=\text{CF}_2$  ( $m/e$  100, right panel),  $\text{CF}_2=\text{CD}_2$  ( $m/e$  66, middle panel), and  $\text{CD}_2=\text{CD}_2$  ( $m/e$  32, left panel), in a series of experiments by adding various amounts of  $\text{CD}_2\text{I}_2$  (scavengers) on Cu(111) which was preadsorbed by 0.15 L of  $\text{CF}_3\text{I}$  ( $\sim 1/10$  ML). These data demonstrate that the formation of  $\text{CF}_2=\text{CF}_2$  (250 K), originating from  $\text{CF}_{3(\text{ad})}$ , is being suppressed and finally blocked entirely as a function of increasing  $\text{CD}_{2(\text{ad})}$ . Concomitantly, yields of  $\text{CD}_2=\text{CD}_2$  from recombination of  $\text{CD}_{2(\text{ad})}$  at 160 K are found to increase. The most informative results consist of the emerging  $\text{CF}_2=\text{CD}_2$ , which is responsible for the descending yields of  $\text{CF}_2=\text{CF}_2$ . This cross-coupling product

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ensures the presence of surface difluorocarbene, which imperatively demands that C–F bond cleavage proceed in a selective fashion. Furthermore, the 163 K liberation of  $\text{CF}_2=\text{CD}_2$  reflects that the C–F bond in  $\text{CF}_3$  has already been activated *prior to* or *at* this temperature. That  $\text{CF}_2=\text{CF}_2$  formed at 250 K is thus rate limited by the  $\text{CF}_2$  coupling step instead of C–F activation. It is apparent that the addition of scavengers helps to place the kinetic upper limit for the C–F activation more accurately by 90 K (163 vs 250 K). In summary, we propose the following mechanism to delineate the aforementioned events and relevant kinetic information:



The role of Cu(111), the substrate used in this study, merits comment. The catalytic activity of atomically clean copper surfaces under ultrahigh vacuum (UHV) conditions can be classified into two categories. The first encompasses dehydrogenation reactions, such as  $\alpha$ - and  $\beta$ -elimination in alkyl groups.<sup>16</sup> Methyl ( $\text{CH}_3$ ) is stable on the copper surface until approximately 450 K, where a number of competing reactions occur, including  $\alpha$ -hydrogen elimination to yield a methylene ( $\text{CH}_2$ ) intermediate. Therefore, a similar reactivity toward  $\text{CF}_3$  is somewhat expected; however, the extremely low temperature for the C–F activation and the total domination of this reaction route are unusual. The second category is associated with the facile C–C coupling reactions to evolve alkanes<sup>17,18</sup> and alkenes.<sup>17,19</sup> This reactivity becomes a mechanistic probe that allows us to approach the kinetic limit for the C–F bond activation as exact as possible.

Activation of saturated C–F bonds has been investigated by trifluoromethyl groups chemisorbed on Cu(111). To our knowledge, this is the first example capable of readily and selectively cleaving a single C–F bond to transform  $\text{CF}_3$  into  $\text{CF}_2$  moieties on a well-defined metallic surface under UHV ambiances. In perspective, this discovery provides a convenient method for generating difluorocarbene intermediates. A variety of surface reactions involving carbenes, such as abstraction, addition, and insertion, can be studied and compared with its hydrocarbon counterpart, methylene, to give insight into the effects of fluorination on reactivity.

**Acknowledgment.** This research was supported by the National Science Council of the Republic of China under Contract No. 88-2113-M-110-013.

#### JA991596X

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