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ABORTIVE REACTION LEADS TO SELECTIVE ADSORBATE ROTATION

Yi-Fang Lai, Lydie Leung, Matthew J. Timm, Gilbert C. Walker and John C. Polanyi *

Abstract

Electron-induced dissociation of a fluorocarbon adsorbate CF$_3$ (ad) at 4.6 K is shown by Scanning Tunneling Microscopy (STM) to form directed energetic F-atom ‘projectiles’ on Cu(110). The outcome of collision between these directed projectiles and stationary co-adsorbed allyl ‘target’ molecules was found by STM to give rotational excitation of the target allyl, clockwise or anti-clockwise, depending on the chosen collision geometry. Molecular dynamics computation linked the collisional excitation of the allyl target to ‘abortive chemical reaction’, in which the approach of the F-projectile stretched an H-C bond lifting the allyl above the surface, facilitating isomerization from ‘Across’ to ‘Along’ a Cu-row.

Introduction

Bimolecular chemical reaction has been shown to occur if reagents collide with sufficient energy and a favorable orientation. Gas-phase studies of molecular collisions have provided insights in reaction dynamics, despite averaging over the reagent impact parameter (the miss-distance) and averaging over the angle of approach. Alignment of the reagents at a surface provides a means to restrict the impact parameter. Such surface-aligned reactions can occur between a recoiling reagent produced by photolysis or electron-induced dissociation, and a stationary adsorbed target molecule. Recent studies of this type employing Scanning Tunnelling Microscopy (STM) have shown that a molecular projectile, CF$_2$, can be aimed at a stationary target at different impact parameters. The ability to choose the impact parameter allows control over the collision outcome. At small impact parameter such collisions can result in a reactive outcome. In the case of an atomic projectile, an F-atom, the one-dimensional collision along its path with a CF$_3$ target resulted in a substitution reaction where the incoming atom ‘knocked-on’ an F-atom in the target. A directed to-and-fro knock-on reaction involving

* Corresponding author

Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, M5H 3H6, Canada. Email: john.polanyi@utoronto.ca

Department of Physical Chemistry, University of Graz, Heinrichstrasse 28, 8010 Graz, Austria
an F-atom projectile and a row of stationary targets has been shown to resemble the motion in a Newton’s cradle.\textsuperscript{19}

Here we report an STM study of collisions of an energetic F-atom projectile with a stationary allyl target on Cu(110), at impact parameters in the region of 1-2 Å. Almost half of these collisions led to rotation of the allyl from ‘Across’ to ‘Along’ a Cu-row. Molecular dynamics calculations gave evidence of abortive H-atom abstraction reaction as the cause of the observed efficient rotational isomerization of the allyl.

**Methods**

**Experimental**

All experiments were performed in a low-temperature UHV-STM (Omicron) with a base pressure of $< 3.0 \times 10^{-11}$ mbar. The Cu(110) sample was cleaned by repeated cycles of Argon sputtering (0.6 keV, 7 $\mu$A) and annealing at 800 K. The surface cleanliness, less than 1\% contaminants, was determined by STM. The constant-current mode was used to record the STM images at 4.6 K. The bias is given with respect to the sample. Both Iodotrifluoromethane (CF$_3$I; SynQuest, 99 \%) and allyl bromide (C$_3$H$_6$Br; Aldrich, 99 \%) were deposited via a capillary tube pointing to the Cu sample. Chemisorbed CF$_3$ were obtained from the thermal dissociation of CF$_3$I on Cu(110) at 79.5 K, as previously reported.\textsuperscript{17-19} The target molecule, allyl (C$_3$H$_5$), was then generated by dosing allyl bromide on the Cu sample, which dissociated upon adsorption at 11 K.

The F-atom projectile was produced from the electron-induced dissociation of CF$_3$. The STM tip was placed over the CF$_3$ radical with the feedback loop off. The current was recorded as a function of time at a constant bias of $+ 1.4$ V. A subsequent STM image showed the position of the products after the collision between the F-atom projectile and the allyl Across. The positions of the products following collision were obtained using the WSxM software.\textsuperscript{20}

**Theory**

Density Functional Theory (DFT) calculations, as implemented in the Vienna Ab initio Simulation Package (VASP),\textsuperscript{21,22} were performed on the SciNet supercomputer Niagara
The structure relaxations used the projected augmented method\textsuperscript{25,26} and the generalized-gradient approximation with the Perdew-Burke-Ernzerhof functional.\textsuperscript{27} A semi-empirical dispersion correction (DFT-D3) generated by Grimme was added to account for van der Waals interactions.\textsuperscript{28} The energy cutoff for the plane-wave basis was set to 400 eV. The Cu(110) surface was modelled by a (4 × 10) slab composed of 200 Cu-atoms in five layers, separated by a 17 Å vacuum layer. All atoms except for the bottom two layers were fully relaxed until the residual force on each atom was less than 0.01 eV/Å. The Tersoff-Hamann approximation\textsuperscript{29} was employed to produce the STM-image simulations, which were then visualized with the HIVE-STM program.\textsuperscript{30}

An Impulsive Two-State (I2S) model, described in detail elsewhere,\textsuperscript{12,13,31-33} was used to model the formation of the F-atom projectile. In the I2S model, the system is promoted from equilibrium on the ground state to a repulsive upper state by transferring an electron from the F-atom core to its valence shell, so as to reproduce the effect of added charge. Molecular dynamics (MD) were calculated for the excited system for a time, t*. Once the system was returned to the ground state, with the velocities and atomic positions obtained from the excited state, the dynamics were followed until a final state was reached. For the abortive reaction, the maximum allyl rotation was calculated with t* = 7.5 fs. For the abstraction reaction, the t* was set at 8.0 fs which was the minimum time needed to obtain the reaction products, HF and allyl radical. The MD calculations were performed using a time-step of 0.5 fs, under microcanonical conditions.

\textbf{Results and discussion}

On the Cu(110) surface the allyl was observed to have two adsorption geometries formed in equal numbers, with their long axes’ lying Across or Along the Cu rows. This observed ratio for the two geometries is consistent with that previously reported.\textsuperscript{34} The computed geometry for the allyl Across configuration places the curved-allyl over a four-fold hollow site, with the H-atoms of the terminal carbon-atoms of allyl adjacent to Cu-atoms. In the case of the allyl Along, the curved-allyl is centered over a Cu-atom along a Cu-row. Computational results gave an adsorption energy of 0.91 eV for the Across configuration, slightly lower than the 1.15 eV for the Along configuration, making the switch from Across to Along exoergic.
Figure 1: Experimental STM images (13.5 Å × 22.0 Å; 0.5 nA; −0.1 V) of (a) Initial and final state of allyl Across and co-adsorbed CF₃ on the Cu surface resulting in clockwise rotation of allyl Across to Along, and (b) Initial and final state of allyl Across and co-adsorbed CF₃ giving anti-clockwise rotation of allyl Across to Along. The white cross indicates the location of the electron pulse. The black balls indicate the calculated positions of the carbon atoms of the allyl Across and Along. Computed simulations and ball-and-stick models below each STM image show the calculated geometries of the reagents and products. The F-atom projectile is circled in red; its trajectory is indicated in the initial state by a red arrow. The resultant motion of the allyl from Across to Along is indicated in the final state by a curved arrow.

In Figure 1a, the initial state shows an STM image recorded at 4.6 K of CF₃ and allyl
Across, adsorbed as nearest neighbours. The allyl is located between Cu-rows 1 and 2, and the CF$_3$ is found adsorbed on Cu-row 2 (vertical dashed line). The CF$_3$ was found preferentially on the inside of the curved-allyl Across, as shown in the calculated geometry. The CF$_3$ is located on the right-hand of the allyl centre-of-mass, near the allyl C-atom denoted as 3. Localized ‘streaks’ observed between the curved side of the allyl and the CF$_3$ are indicative of long-range interactions between the F-atom and the neighbouring allyl. The final state shown in Figure 1a, was obtained by injecting 1.4 eV electrons from the STM tip into the CF$_3$ radical, at the location of the white cross. This led to electron-induced dissociation of a C-F bond, generating an F-atom projectile and a CF$_2$ at the surface as indicated in the figure.$^{15-19}$

The final state comprised an allyl Along and a CF$_2$ adsorbed on the same Cu-row 2, and an F-atom located on the adjacent Cu-row 1. The final position of the F-atom projectile indicated that the broken C-F bond was the one nearest to the allyl Across in the initial state, since the products of the electron-induced dissociation recoil along the bond direction.$^{35}$ The collision between the F-atom and the allyl Across occurred at negative impact parameter, with the recoiling F travelling towards C-atom 1 of allyl Across (to the left of the allyl centre-of-mass -- see calculated geometries in Fig. 1a). This collision resulted in a clockwise rotation of allyl from Across to Along. The calculated geometries in the simulations are in good agreement with observation, confirming the given assignment of the reagents and products.

The initial state in Figure 1b consists of an allyl Across located between Cu-rows 2 and 3, and a neighbouring CF$_3$ found on Cu-row 2 (vertical dashed line). In this case the collision between the F-atom and the allyl Across occurred at positive impact parameter, with the F-atom travelling towards C-atom 3 of allyl Across, resulting in an anti-clockwise rotation of the allyl. The final state STM image shows the allyl Along and the CF$_2$ radical adsorbed on the same Cu-row 2, and the F-atom on Cu-row 3 adjacent to the allyl. The initial and final states in Figure 1b are essentially mirror-images of those in Figure 1a.

In addition to rotation, translation of the allyl Along was observed by one or two unit-cells in the [110] direction, attributable in either case to attractive interactions between the allyl and the CF$_2$ radical. The allyl rotation was observed for ~ 41 % of collisions between the F-atom and the allyl. The balance of the cases gave no-rotation; $N_{\text{total}} = 114$ cases.
Molecular dynamics calculations were performed for the rotational energy-transfer between the F-atom projectile and the allyl Across (for which the initial state was shown in Fig. 1a). The impulsive two-state model employed to describe the electronic excitation of the CF$_3$ resulted in recoil of atomic F. The trajectories of the F-atom projectile and the terminal H-atom of allyl, are shown in Figure 2a, with visualizations of the initial, transition and final states. The F-atom recoiled from CF$_3$ with 0.82 eV, gained after the system had resided in the excited state for $t^* = 7.5$ fs, which is the maximum $t^*$ for abortive (failed) reaction.

On the neutral ground state, the F-atom projectile approached the allyl Across at an impact parameter of –1.3 Å and an angle of 65° from the [1 1 0] direction. As the F-atom travelled towards the allyl, at 81 fs the C-H bond extended by 0.26 Å (~ 23 %) due to the F-atom attracting the H-atom. Subsequently, the C-H bond returned to its original length, with energy released. The released energy was transferred to internal states of the allyl causing the H-atom to accelerate along the [1 1 0] direction. At 300 fs, the allyl target was computed to rotate 36.5°, about 1/3 of the experimentally observed rotation.

Figure 2b shows dynamical details of the 3D trajectory for the same H-atom of allyl Across shown in Figure 2a. The C-H bond-stretch induced by the F-atom projectile at 81 fs

**Dynamics of Abortive Reaction**

![Figure 2](image-url)

**Figure 2.** Dynamics of abortive reaction for the clockwise rotation of allyl. (A) Trajectories of the F-projectile (red) and the recoiling H-atom (black), with ball-and-stick models at 0, 81 and 300 fs. (B) 3-D trajectory of the recoiling H-atom during the rotation of allyl (in black), and ball-and-stick models at 0, 167 and 300 fs, showing concurrent 36.5° rotation of the allyl.
resulted in lifting of the allyl above the surface, freeing it to rotate and reach its maximum height at 167 fs. Simultaneously the allyl rotated in a clockwise direction, with the carbon atom furthest away from the collision acting as pivot. The allyl then travelled towards the Cu surface and bounced a second time at 211 fs.

Figure 3 shows the same dynamics as Figure 2, diagrammatically at successive times. Initially at $t = 0$ fs, the electron-induced dissociation of CF$_3$ was obtained by adding an electronic-charge to the F-atom of CF$_3$ adjacent to the allyl Across, as indicated by the ‘explosion’ in the C-F bond. At $t = 81$ fs, the I2S model shows the F-atom recoiling along the direction of the breaking C-F bond in CF$_3$. This F-atom projectile approached and interacted with the H, inside the curve of the allyl Across to form a transition state F--H--C. At 94 fs, the C-H was vibrationally excited, as evidenced by the C-H bond-stretch. Rotational momentum was gained as the allyl bounced from the surface; by 300 fs the allyl had rotated 36.5° clockwise.

The final state for anti-clockwise rotation observed in Fig. 1B was the result of a collision with the F-projectile at a positive impact parameter of + 1.3 Å. The molecular dynamics were a

**Dynamics of Abortive Reaction**: F-induced VIB and ROT in co-adsorbed allyl

<table>
<thead>
<tr>
<th>a) Initial State (IS)</th>
<th>b) Transition State (IS)</th>
<th>c) Allyl-H (VIB)</th>
<th>d) Allyl-H (VIB-ROT)</th>
</tr>
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<tbody>
<tr>
<td>$e^- + \text{CF}_3 \rightarrow \text{F} + \text{CF}_2$</td>
<td>F--H--C</td>
<td>94 fs</td>
<td>300 fs</td>
</tr>
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**Figure 3.** Computed molecular dynamics for clockwise rotation in the collision between an F-projectile and an allyl Across target, at a negative impact parameter $b = -1.3$ Å. The initial state ($t = 0$ fs) corresponds to that in Fig. 1A. The explosion marks the C-F bond excitation to anti-bond. The F-projectile is highlighted in red. The formation of the intermediate state is indicated by black dashed lines, linking F--H and H--allyl. The computed clockwise-rotated position of the allyl is shown at 300 fs.
mirror image of Figure 3, with the F-atom colliding at the right-end carbon of the allyl. This resulted in a maximum rotation of ~36.5° anti-clockwise.

The observed rotational excitation of the allyl is a consequence of the C-H bond-stretch. This C-H bond-stretch occurs en route to abstraction reaction in which the F-atom projectile would abstract the terminal H-atom of allyl. This abstraction reaction was not observed, since it is calculated to be endoergic by ~1 eV. Figure 4 shows the computed abstraction of the terminal H-atom of allyl for an F-atom projectile with an enhanced kinetic energy of 0.88 eV. The enhanced F-atom kinetic energy enabled abstraction of the H-atom to form HF. Abortive reaction (figs. 2 and 3) excited the C-H bond-stretch leading, in multiple encounters between the allyl and the surface, to rotation of the allyl from Across to Along.

Conclusions

We report an STM study of inelastic scattering in collisions F + allyl on Cu(110), at kinetic energies below and above the barrier to H-atom abstraction. Molecular dynamics showed
collision-induced rotation of the allyl target from Across the Cu-rows to Along, as observed. The
dynamics link this rotational isomerization to C-H bond extension in the allyl, along the path to
HF formation in a process we term ‘abortive’ reaction. Here, therefore, we show the importance
of the mixing of degrees of freedom in abortive reaction. The dynamics link the extension of the
C-H bond, which lifts the allyl product, with efficient ro-vibrational excitation. At translation
energies > 0.85 eV for the F-projectile, the potential-energy surface predicts abstraction reaction
to give HF.

Conflicts of interest
There are no conflicts of interest to declare.

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