Bond selectivity in electron-induced reaction due to directed recoil on an anisotropic substrate

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Bond-selective reaction is central to heterogeneous catalysis. In heterogeneous catalysis, selectivity is found to depend on the chemical nature and morphology of the substrate. Here, however, we show a high degree of bond selectivity dependent only on adsorbate bond alignment. The system studied is the electron-induced reaction of meta-diiodobenzene physisorbed on Cu(110). Of the adsorbate’s C-I bonds, C-I aligned ‘Along’ the copper row dissociates in 99.3% of the cases giving surface reaction, whereas C-I bond aligned ‘Across’ the rows dissociates in only 0.7% of the cases. A two-electronic-state molecular dynamics model attributes reaction to an initial transition to a repulsive state of an Along C-I, followed by directed recoil of C towards a Cu atom of the same row, forming C-Cu. A similar impulse on an Across C-I gives directed C that, moving across rows, does not encounter a Cu atom and hence exhibits markedly less reaction.
ond-selective chemistry due to differences in energy barriers continues to play a major part in the understanding of thermal heterogeneous catalysis. A notable advance in recent years has been the employment of selective excitation of a molecule incident on or present on a surface as a means to influence the reaction probability. For vibrationally and translationally excited gaseous beams incident on metal surfaces, reactions have been reported to be mode-specific, bond-selective, and gas-phase alignment-dependent. In the case of molecules adsorbed at surfaces, electrons from scanning tunnelling microscopy (STM) have been employed to excite vibrationally or electronically the adsorbate, resulting in molecular translation, rotation, and desorption. The breaking of a selected chemical bond in the adsorbate has also been achieved by varying the electron energy or, for extended adsorbates, the excitation location.

Here, we show a high degree of bond selectivity due to a cause, to our knowledge, that has not previously been noted, namely the directed recoil of products formed as a result of electron-induced surface reaction. The approach is quite general since directed recoil of products along what was the prior bond direction has been widely reported. When the directed recoil occurs at an anisotropic surface, we find bond-selective surface reaction occurs. We show that different alignments, even of a chemically identical bond, can result in a hundred-fold alteration in reaction probability, with corresponding bond selectivity. The example given is that of an electron from an STM tip impinging on a single meta-diodobenzene (mDIB) molecule on Cu(110) giving two orders of magnitude greater probability of breaking a carbon-iodine (C-I) bond lying ‘Along’ (AL) a Cu row than the C-I that lies ‘Across’ (AC) the rows. Molecular dynamics (MD) calculations employing an approximate anionic potential, followed by impulsive recoil across a ground potential computed by density functional theory (DFT) reproduce the observed bond selectivity, explaining it as due to directed recoil across the anisotropic surface of the Cu.

Results

Experiment. Experiments were performed on a Cu surface held at 4.6 K. Two physisorbed states of mDIB were observed: one termed ‘Row’ and the other ‘Diagonal’, the latter being the principal subject of the present report. An STM image of the Diagonal adsorption state on Cu(110) is shown in Fig. 1a, with a theoretical simulation directly below.

From the simulation, the benzene ring is located at a short-bridge site with one C-I directed along the Cu row and the other at 126° from the Cu row (measured clockwise from [110]), leading to the two lobes that were observed, corresponding to the two C-I bonds with I atoms located atop Cu atoms, as evident in the simulated STM image. The bond lengths of both C-I bonds in the physisorbed state were computed as ~2.1 Å, and the heat of adsorption as 1.0 eV. This Diagonal adsorption state was also predicted by a computational study performed by Panosetti and Hofer. The midpoint between the two lobes in Fig. 1a, EXPT, is indicated by a white cross used as the origin of the spatial distribution of the products following electron-induced reaction; see Fig. 1a-c.

Electron-induced reaction of physisorbed mDIB was initiated by tunnelling electrons from the STM tip placed over the centre of the intact physisorbed reagent at a sample bias of 1.0 V. The experimental findings are illustrated in Fig. 1, with, at left, sample STM images for the initial and final states of the major reaction path breaking the C-I bond AL the Cu rows, and, at the right, the minor path breaking the C-I bond directed AC the Cu rows. For 139 reactive cases, the breaking of only one of the two C-I bonds was observed, namely, the AL bond of the physisorbed mDIB, in preference to the AC bond. The bond selectivity amounted to a 99.3% probability for C-I(AL), as against 0.7% for the alternate C-I(AC).

A representative case of C-I(AL) bond breaking is shown in Fig. 1b. The reaction products are a chemisorbed I atom and a chemisorbed iodophenyl (IPh). A comparison between experiment (Fig. 1b, EXPT) and theory (Fig. 1b, TH and PIC) allowed us to identify the binding sites of both products with respect to the prior mDIB. The I atom was found at the closest four-fold hollow site adjacent to the initial I atom position in the reagent. The IPh product was bound to the atop Cu atom underneath the
reagent mDIB (green dashed circle, Fig. 1b, PIC). The I atom and IPh were found to recoil in opposite directions AL the Cu row (Supplementary Fig. 1a and Supplementary Note 1), as expected for the dissociation of C-I(Al) aligned along the row. The most probable recoil distance of the I atom measured from the white cross of Fig. 1 was 4.7 Å. Figure 1c and Supplementary Fig. 1b show the minor path consisting of 1 out of 139 cases. In this case, the products were found to recoil in the opposite direction AC the rows (Supplementary Note 1), from which we conclude that the bond dissociated was C-I(AC).

The observed strong preference for the breaking of C-I(Al) rather than C-I(AC) shows that the electron-induced reaction of the Diagonal physisorbed mDIB is markedly bond-selective. As the reaction of Row physisorbed mDIB did not exhibit any detectable bond selectivity between its symmetrical C-I bonds, the bond-selective reaction of Diagonal is attributed to its asymmetric adsorption geometry. This reactive bond selectivity will be examined below by the MD theory.

The number of electrons involved in triggering a reactive event was determined experimentally for the major path by measuring the average reaction rate as a function of the tunnelling current in the range of 0.6–18 nA, at a constant sample bias of +1.3 V. As shown in Fig. 2a, the reaction rate scaled linearly with the tunnelling current, evidencing a one-electron process. This linear relationship also excludes an electric field effect as a major cause of reaction.

As in previous studies of the electron-induced reaction of aryl iodides by ~1 eV electrons on Cu(110), we ascribe the reaction to adsorbate electronic excitation. The computed projected density of states is shown in Fig. 2b. It exhibits a nodal plane between carbon and iodine atoms for the lowest unoccupied molecular orbital (LUMO), indicative of a σ* antibonding character with respect to the C-I bond. This C-I antibonding orbital was computed to be 0.8 eV above the Fermi level. The yield for electrons of ~1.3 eV was measured as ~10⁻⁹ reactive events per electron for the major path. The high single-electron energy of at least 1.0 eV required to give reaction argues against vibrational excitation as the source of induced reaction.

Theory. The observed bond selectivity can be understood in terms of the different recoil directions of the AL and AC fragments following an electron-induced repulsive impulse in the LUMO of one or the other C-I bond, leading to different reaction paths across the anisotropic Cu(110) surface. As in previous work we used the ‘Impulsive Two-State’ (I2S) model to simulate the MD of the electron-induced reaction. In this two-electronic state model, the MD was first followed for the 192-atom system on an approximate anionic repulsive potential-energy surface (PES) obtained by the transfer of an electron to the valence shell of a halogen atom for a period of femtoseconds (a time t*). Thereafter, the atoms were returned with their accumulated momenta to the ab initio DFT ground PES for MD over a period of picoseconds needed to reach the reacted final states. In the present case, the added charge comprises one electron at the I atom of C-I(Al) to favour breaking of that bond, or alternatively one electron at the I atom of C-I(AC) to favour the alternate bond breaking.

Figure 3a shows the dynamics for an electron added at C-I(Al), using the minimum t* of 20 fs required for reaction. Figure 3a shows that the impulse, with momenta carried over to the ground PES, stretched C-I(Al) causing it to break at ~150 fs concurrently with the formation of the C-Cu (i.e., IPh-Cu) and I-Cu bonds. The distance versus time plot of Fig. 3a in the panel below shows bond extension of C-I(Al) from its initial separation of 2.1 Å to a 3.0 Å, accompanied by the formation of C-Cu and I-Cu bonds at their equilibrium separations (all equilibrium separations being indicated by horizontal dotted lines). Figure 3b shows that for the same t* the placing of one electron in the I atom of the alternate C-I(AC) bond did not break that C-I bond. This failure to break C-I(AC), as evident from the distance versus time plot of Fig. 3b, is connected with the larger separation between the C atom of C-I(AC) from its nearest Cu atom neighbour (C-Cu is 2.3 Å in the AL case, 3.0 Å for AC). We show below that this difference in C-Cu separation is significant for the extent of C-Cu binding energy.

In Fig. 4, we superimpose the MD taken from a full calculation of the motion of the 192 atoms onto a two-dimensional cut through the potential-energy hypersurface that gives the dependence of the potential energy on the two C-I separations. In drawing this PES we have kept the angle between the two C-I
carbon of the C-I bond: C-I(AL) in (a). The C-Cu bond separation is measured from the Cu atom nearest to the C atom of C-I(AL). The yellow arrow in the trajectories encompass the 20 fs duration of the repulsion on the anionic PES; the red line indicates the subsequent ∼3 ps motion on the ground PES. I2S, Impulsive Two-State.

We attribute the lower barrier along C-I(AL) to the greater C-Cu binding, and hence greater stabilization along this coordinate than along C-I(AC) (see Fig. 3a, b which show the bond-length versus bond-order (n) relationship for atomic pairs33, which gives n = 0.5 for C-Cu at the transition state (C-I(AL) = 3.0 Å) in Fig. 4a as compared with n = 0.3 for C-Cu at the transition state (C-I(AC) = 3.0 Å). For a computed ∼3.0 eV bond energy of C-Cu, this leads to ∼0.6 eV greater stabilization due to C-Cu binding in the AL coordinate than the AC coordinate. Accordingly, the lower barrier for the C-I(AL) (0.7 eV) than C-I(AC) (>1.2 eV) in Fig. 4 can be ascribed to stronger C-Cu binding and hence greater stabilization AL rather than AC. This finding shows that the binding of the products to the surface, late in the course of reaction, can influence reaction barriers with resultant bond selectivity.
The trajectories shown in Fig. 4 are taken from the motion on the full potential, with the two C-I bond separations plotted here on the ‘fixed bond-angle’ PES whose energy contours are shown. Bond selectivity is caused by the impulsive motion on the anionic PES, which impedes the system on the ground PES to stretch C-I(AL) giving surface reaction over a 0.7 eV barrier along \( r_1 \), but does not stretch C-I(AC) sufficiently to surmount the higher barrier along \( r_2 \). The low barrier for C-I(AL), as indicated above, is due to the proximity of an underlying Cu atom along the row direction, stabilizing the system through C-Cu bond formation.

It should be noted that the bond selectivity being reported is specific to the impulsive dynamics (see Fig. 4) being a consequence of the directed recoil of the atoms liberated in electron-induced reaction. The C-I bond breaking could also in principle be obtained thermally, although this was not studied here. We have, however, calculated, \( ab \ initio \), the different energy barriers to reaction for the individual breaking of the two C-I bonds by C-I extension along the alternative minimum-energy paths of the ground PES. The computed barrier heights relevant to thermal reaction were found to be 0.3 eV for the previously favoured AL C-I and 0.2 eV for the previously disfavoured AC C-I. Thermal reaction is therefore predicted to exhibit a modest bond selectivity but in the opposite sense to that observed and modelled here for electron-induced reaction.

Discussion

The high degree of bond selectivity in electron-induced surface reaction reported here is linked to directed recoil in relation to the anisotropy of the substrate, resulting in stronger bonding to the substrate when one bond is broken than the other. We anticipate similar bond-selective reaction for electron-induced processes on other anisotropic surfaces, the cause being the greater proximity of a substrate atom to one bond in an adsorbate than to another. This proximity leads in the present instance to 100 × greater reactivity for the adsorbate bond more closely adjacent to a substrate atom, despite the fact that the bonds being broken in the reaction are chemically identical. The proximity, in turn, is determined by the geometry of the physisorbed adsorbate relative to the substrate atoms. Directed recoil together with substrate anisotropy can therefore be expected to lead to bond selectivity in other electron-induced surface reactions, for example, in chemical reactions at surfaces being subjected to generalized electron radiation, in an extension of conventional heterogeneous catalysis.

Method

Experiment. The experiments were conducted at 4.6 K, using an ultrahigh vacuum Omicron low-temperature STM with a base pressure of \( < 3 \times 10^{-11} \) mbar. The Cu(110) surface was prepared by cycles of Ar\(^+\) sputtering (0.6 keV) and annealing (800 K). mDIB (98%; Sigma-Aldrich) was outgassed by 3–4 cycles of freeze pump. Deposition was at 800 K. mDIB (98%; Sigma-Aldrich) was outgassed by 3–4 cycles of freeze pump. Deposition was at 800 K. mDIB (98%; Sigma-Aldrich) was outgassed by 3–4 cycles of freeze pump. Deposition was at 800 K. mDIB (98%; Sigma-Aldrich) was outgassed by 3–4 cycles of freeze pump. Deposition was at 800 K. mDIB (98%; Sigma-Aldrich) was outgassed by 3–4 cycles of freeze pump. Deposition was at 800 K. mDIB (98%; Sigma-Aldrich) was outgassed by 3–4 cycles of freeze pump. Deposition was at 800 K. mDIB (98%; Sigma-Aldrich) was outgassed by 3–4 cycles of freeze pump. Deposition was at 800 K. mDIB (98%; Sigma-Aldrich) was outgassed by 3–4 cycles of freeze pump. Deposition was at 800 K.
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Author contributions
K.A., K.H. and L.L. contributed equally to this work. J.C.P. designed and supervised the project. K.A., K.H., L.L., A.C. and F.C. collected the STM data. K.A., K.H., L.L. and A.C. analysed the STM data. K.A. conducted the ab initio calculations. All the authors contributed to the manuscript.

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