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ORIGINAL PAPER

Inducing High-Energy-Barrier Tribochemical Reaction Pathways; Acetic Acid Decomposition on Copper

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Abstract

The surface tribological chemistry of acetic acid on copper is studied using an ultrahigh vacuum tribometer, supplemented by first-principles density functional theory calculations of the surface structure and reaction pathways. Acetic acid forms η^2-acetate species on bridge sites at room temperature as identified by reflection–absorption infrared spectroscopy. Rubbing the surface with a tungsten carbide ball reduces the amount of carbon and oxygen in the rubbed region at the same rates to leave some carbon and oxygen on the surface. This is different from the thermal decomposition pathway, where heating to ~ 580 K removes all oxygen, but leave a small amount of carbon on the surface. It is postulated that this arises because sliding along a direction aligned within the plane of the adsorbed acetate species can induce a high-energy-barrier pathway in which the η^2-acetate tilts to form an η^1-acetate that can react to form a bent $CO_2^{\delta-}$ species that decomposes to evolve carbon monoxide and deposit atomic oxygen on the surface. Repeated acetic acid dosing and rubbing reduces the total amount of acetic acid that can adsorb on the surface by ~ 50% after ~ 4 cycles, resulting is a stable, low-friction film. At this point, the adsorbed acetic acid is completely tribochemically removed. This suggests that adsorbed acetic acid can form a self-healing film in which any wear of the low-friction film will then allow it to be replenished by shear-induced decomposition of adsorbed acetate species.

Keywords Acetic acid · Cu(100) · Infrared spectroscopy · Density functional theory calculations · Mechanochemistry · Tribochemistry

1 Introduction

Long-chain carboxylic acids have been used as so-called boundary lubricants [1–5] in which a carboxylate self-assembled monolayer lowers friction by adsorbing strongly to the surface to prevent adhesion at the contacting interface [6]. The adsorbed carboxylic acids can also decompose under the influence of shear to form low-friction carbonaceous layers [7–10]. For example, low-friction films are formed from functionalized fatty acids such as elaidic and oleic acid [7–11] on tetrahedral amorphous carbon. Molecular dynamics (MD) simulations of short-chain (~ C_7) versions of these carboxylic acids reveal attachment of the carboxylic acid to one face of the contact via the −COOH functionality, with the simultaneous attachment of vinyl groups to the other face. The postulated formation of such molecular bridges results in large forces being exerted on the bridging carboxylic acid, which is proposed to facilitate its mechanochemical decomposition. Of particular interest is that the *cis* and *trans* conformations of these carboxylic acids show different tribochemical activities, likely because of steric constraints [12].

Being able to understand such tribochemical reaction mechanisms in the presence of fatty-acid containing lubricants requires an understanding of the surface chemical reactions being induced by interfacial shear. This is a particularly challenging problem because the commonly used surface analytical techniques cannot generally interrogate such buried solid–solid interfaces [13]. This issue is overcome in this work by following the evolution of surface composition using Auger spectroscopy as a function of the number of the times that the sample has been rubbed [14–16], or, in favorable cases, by monitoring

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the gas-phase products formed during sliding [14, 17] in ultrahigh vacuum. The variation in friction coefficient is also used as an in situ monitor of the rate of tribochemical reactions [18, 19]. This approach was used to follow the surface tribochemical pathways for the reaction of dimethyl disulfide with copper [20, 21]. In this case, the reaction is initiated by the formation of adsorbed methyl thiolates, which react both thermally and tribochemically to form small gas-phase hydrocarbon and adsorbed sulfur. Here, methyl thiolate decomposes on copper by the C−S bond tilting toward the surface to induce bond scission to deposit sulfur on the surface. This reaction pathway and the elementary-step kinetics have been used to model the overall rates of formation of a tribofilm during gas-phase lubrication [19, 20]. In this case, the rate of the thermal reaction is tribologically accelerated so that it occurs at room temperature much lower than the ~ 450 K at which it thermally decomposes. Similar strategies have been used to demonstrate that the tribochemistry of borate esters depends on its initial thermal surface reaction pathways [22, 23], and for identifying the tribochemical reactions of phosphite esters [24]. The thermal surface reaction pathways identified in the absence of sliding provided a basis for understanding the tribochemical reactions. A key aspect to being able to implement such a strategy is to be able to carry out the surface and tribochemical reactions under well-defined ultrahigh vacuum (UHV) conditions to ensure that the chemistry is not influenced by background gases.

As a precursor to studying the tribochemistry and the influence of chain functionalization of long-chain fatty acids, we first investigate the tribochemical reaction pathways of the simplest carboxylic acid, acetic acid, CH_3-COOH. Rather than studying the chemistry on tetrahedral amorphous carbon for which the mechanism was analyzed theoretically [12], the chemistry is studied instead on electrically and thermally conducting copper, where acetic acid has been shown previously to react to form carboxylate species [25], with the resulting carboxylate group being anchored strongly to the surface. This adsorption structure is analogous to the previously studied methyl thiolate species on copper that decomposes by tilting to induced C−S bond cleavage [18], where the reaction rate is accelerated by the imposition of normal and shear stresses [21]. However, there are some key differences. First, the acetate species decomposes on heating to ~ 580 K, with an activation energy of 180 kJ/mol with a pre-exponential factor of 2×10^{15} s^{-1} [26] and so is more stable on the surface that the methyl thiolate. This increased stability may render it tribochemically less reactive and this is investigated here. Second, the bidentate carboxylate species formed on copper [25] might be expected to react differently depending on the direction of the lateral force relative to the acetate molecular plane; sliding parallel to the plane may have a different influence than sliding perpendicular to it. This conjecture is investigated here by combining experiments with first-principles quantum calculation.

Some work has already been carried out on the surface chemistry of carboxylic acids adsorbed on copper. Near-edge X-ray adsorption spectroscopy (NEXAFS) has been used to investigate the adsorption of a range of carboxylic acids on Cu(111), where the structure was found to depend on the chain length [27, 28]. The deprotonation kinetics of carboxylic acids on copper have been investigated using fluorine-modified chains [29] and studies on the decomposition of isotopically labeled carboxylic acids on copper have shown that the reaction is initiated by the removal of carbon dioxide from the carboxylate group [30]. Acetic acid has been found to be relatively thermally stable on Cu(110) [26] and decomposes by simultaneously desorbing carbon dioxide, methane and ketene at 590 K in temperature-programmed desorption (TPD). Some hydrogen evolves at ~ 300 K from COOH group deprotonation and approximately 5% of the initial carbon remains on the surface after the completion of the reaction.

The following investigates the surface tribochemical reaction pathways of acetic acid on a copper foil rather than a single crystal because rubbing with the tungsten carbide ball damages the surface so that the use of single-crystal samples is prohibitively expensive. However, it has been shown that these cleaned and annealed copper foils exhibit sufficient order to display distinct (100) low-energy electron diffraction (LEED) patterns [31].

2 Experimental and Theoretical Methods

Experiments were carried out in ultrahigh vacuum (UHV) chambers operating at pressures of ~ 2.0×10^{-10} Torr after bakeout. Infrared spectra were collected using a Bruker Vertex 70 infrared spectrometer using a liquid-nitrogen-cooled, mercury cadmium telluride detector [32], which is relatively insensitive in the C−H stretching region of the spectrum. The complete light path was enclosed and purged with dry, CO_2-free air and spectra were collected for 1000 scans at 4 cm^{-1} resolution. The surface was exposed to acetic acid using a leak valve attached to the gas-handling line prior to collecting the infrared spectra and performing tribochemical measurements. The sample temperature was monitored by means of a chromel/alumel thermocouple spot-welded to the edge of copper foil, which enabled the temperature of the sample to be accurately measured.

Tribochemical experiments were also carried out in a UHV chamber operating at a base pressure of ~ 2×10^{-10} Torr following bakeout, which has been described in detail elsewhere [33]. Briefly, the chamber was equipped with a UHV-compatible tribometer, which simultaneously measures normal load, lateral force and the electrical contact resistance between the tip and substrate. All measurements were made using a sliding speed of ~ 4×10^{-3} m/s at a normal load of 0.44 N. Previous work has shown that the maximum interfacial temperature rise for a copper sample under these conditions is much less than 1 K [15] so that any changes found after rubbing the surface are tribochemically and not thermally induced. The spherical pin (~ 1.27×10^{-2} m diameter) was made from tungsten carbide containing some cobalt binder and could be heated by electron bombardment *in vacuo* or by argon ion bombardment in order to clean it and it was cleaned by heating for the experiments reported here. The pin was attached to an arm with attached strain gauges to enable the normal and lateral forces to be measured. The arm was mounted to a rotatable Conflat flange to allow the pin to be rotated to face a cylindrical-mirror analyzer (CMA) to enable Auger spectra of the pin surface to be obtained [34].

The copper foil was prepared by mechanical polishing using sandpapers of increasing grit size until no visible scratches were observed. This was followed by polishing using polycrystalline diamond paste until a visibly smooth surface was seen under a microscope. The samples were mounted in UHV to a precision x, y, z manipulator for measuring the elemental profiles across a rubbed region of the sample. Auger spectra were either collected using the coaxial electron gun in the CMA using an electron beam energy of 3 kV, or with a Staib model EK050M2 Microfocus electron gun. The chamber is also equipped with a channeltron secondary electron detector which allowed scanning electron microscopy (SEM) images of the wear scar to be collected using the microfocus electron gun. Auger elemental profiles were obtained across the rubbed regions to measure the loss of carbon or oxygen from the surface as a function of the number of times that the sample had been rubbed.

The copper foil sample was cleaned using a standard procedure consisting of Ar^+ bombardment with subsequent annealing to 850 K for 10 min. Ar^+ bombardment was performed at a background gas pressure of ~ 5.0×10^{-5} Torr at a 1 kV potential, while maintaining a ~ 2μA sample current. This process was repeated until the sample was determined to be sufficiently clean by AES where, in particular, no carbon or oxygen were detected on the surface. Acetic acid (Sigma-Aldrich, > 99.5% purity) was purified using several freeze–pump–thaw cycles and its cleanliness was judged by mass spectroscopy.

The adsorption geometry of acetic acid was calculated using periodic density functional theory (DFT) using the projector augmented wave (PAW) method as implemented in the Vienna ab-initio simulation package (VASP) code [35–37]. The exchange and correlation energies were calculated using the PBE3 (Perdew, Burke and Ernzerhof [38]) form of the generalized gradient approximation (GGA). The kinetic energy cutoff for all calculations was 400 eV. The wavefunctions and electron density were converged to within 1×10^{-5} eV, whereas geometric structures were optimized until the forces on the atoms were less than 0.01 eV/Å. Van der Waals interactions were implemented using the DFT-D3 method as described by Grimme et al. [39]. The reaction pathway and activation energy for acetate decomposition on copper were measured using the climbing nudged-elastic band (NEB) method [40, 41].

3 Results

To confirm that acetate species form on a copper foil when dosed at room temperature [42], infrared spectra were collected as a function of acetic acid exposure and the results are displayed in Fig. 1, where the background spectrum for the clean surface is also displayed. The spectra show an intense feature centered at 1437 cm^{-1} with a much less intense peak at 1028 cm^{-1}. These features have been identified previously for acetic acid adsorbed at room temperature on a Cu(100) surface [25] where the ν_S(COO) mode at 1437 cm^{-1} is associated with the formation of an acetate species and indicates that acetic acid has deprotonated on adsorption. The weak peak at 1028 cm^{-1} is due to a C−C stretching mode and, according to the surface selection rules [43, 44], its appearance suggests that the carbon–carbon bond is oriented with a component of the vibration being normal to the surface. Similarly, the asymmetric COO mode is completely absent indicating that the plane of the carboxylate group is oriented perpendicularly to the surface, in accord with the structure predicted by DFT (Figs. 6 and 7). This structure is analogous to that for methyl thiolate species on copper [31] suggesting that it should be susceptible to shear-induced decomposition.

To test this, a clean copper sample was rubbed ~ 50 times to create a wear track and to stabilize the friction coefficient before dosing with 2 L (1 L (Langmuir) = 1×10^{-6} Torr s) of acetic acid to saturate the surface with acetate species (Fig. 1). Note that neither carbon nor oxygen were found on the surface after this procedure. The surface was then rubbed with a tungsten carbide ball and the amount of carbon remaining within the rubbed region was measured using small-spot-size Auger spectroscopy as a function of the number of times that the sample had been rubbed. The results are shown in Fig. 2, which were collected after saturating an initially clean copper sample with acetic acid (■). The reduction in carbon Auger signal indicates that the adsorbed acetate is decomposing tribochemically. The exponential decay yields a value of the number of scans to reduce the amount of surface carbon to 1/e of its original amount of 6.6 ± 0.5 scans. However, this procedure does not completely remove all carbon from the surface and the final

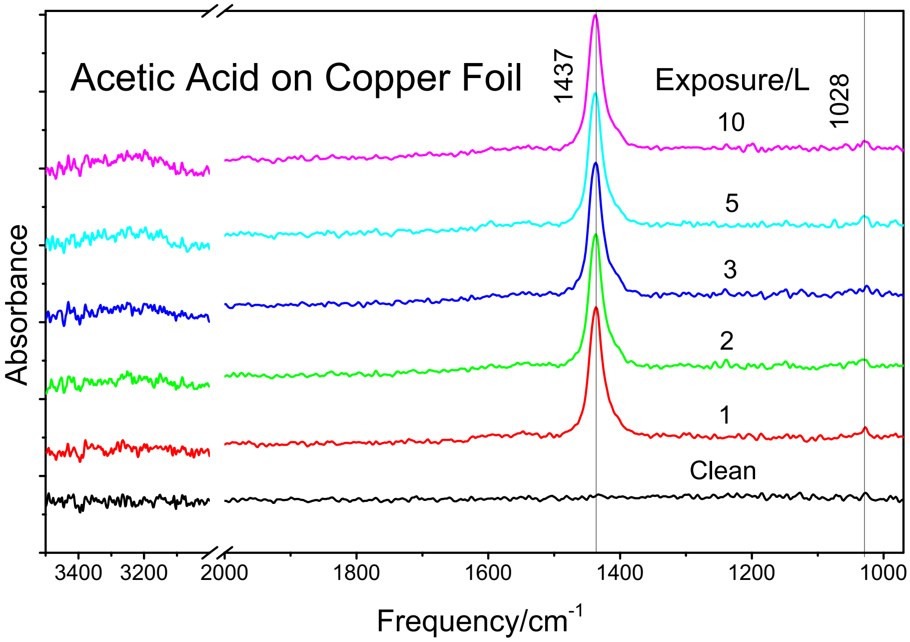

Fig. 1 Infrared spectra of a copper foil dosed at room temperature with acetic acid as a function of exposure in Langmuirs, where the exposures are displayed adjacent to the corresponding spectrum

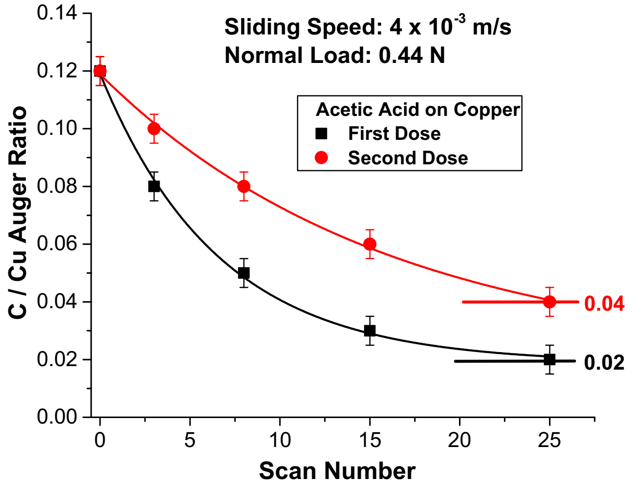

Fig. 2 Plot of the ratio of the C(KLL) peak-to-peak Auger signal measured in the center of a wear track on a copper foil surface to the Cu(LMM) peak-to-peak signal from the substrate after the surface was dosed with 2 L of acetic acid as a function of the number of times that the sample had been rubbed at a load of 0.44 N and a sliding speed of 4×10^{-3} m/s. The results are shown for adsorption on a clean surface (■), and after redosing without cleaning the surface (●)

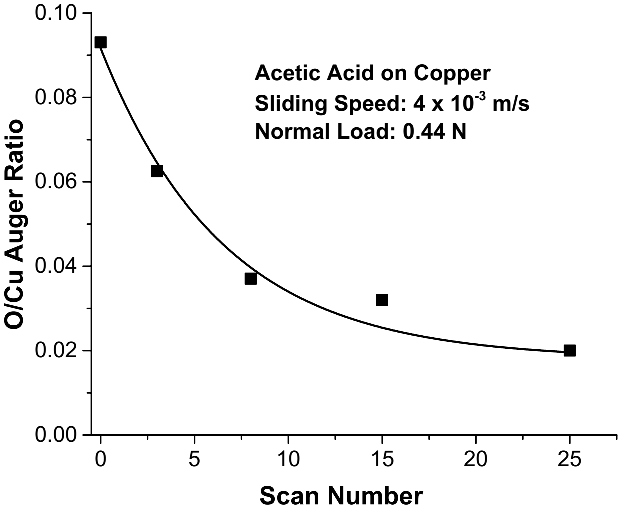

Fig. 3 Plot of the ratio of the O(KLL) peak-to-peak Auger signal measured in the center of a wear track on a copper foil surface to the Cu(LMM) peak-to-peak signal from the substrate after the surface was dosed with 2 L of acetic acid as a function of the number of times that the sample had been rubbed at a load of 0.44 N and a sliding speed of 4×10^{-3} m/s

C(KLL)/Cu(LMM) peak-to-peak Auger ratio after 25 scans is ~ 0.02 indicating that ~ 16% of the original carbon remains on the surface, significantly more than the ~ 5% remaining carbon after a TPD experiment after heating to ~ 650 K [26]. The relatively low intensity of the Cu Auger signal after the sample had been rubbed prohibited the lineshape from being used to identify the nature of the carbon on the surface.

Figure 3 shows that this is accompanied by the loss of oxygen from the surface where the number of passes to reduce the O(KLL)/Cu(LMM) ratio to 1/e of its original value is 6.6 ± 0.8 scans, identical to the rate of loss of carbon (Fig. 2), indicating that carbon and oxygen are removed simultaneously in the same tribologically induced reaction step. By measuring the relative carbon and oxygen Auger sensitivities of the Auger system used here by assuming a 1:1 C:O stoichiometry for the initially adsorbed acetate over layer indicates that the carbon:oxygen stoichiometry of the remaining film is 0.8 ± 0.1.

During a gas-phase lubrication, which consists of continually rubbing in the presence of the lubricant, the overall process depends on how the surface composition evolves as the tribochemical reaction proceeds. This is illustrated in Fig. 2, which shows the effect of redosing a sample that was previously rubbed 25 times with acetic acid without any intervening cleaning (●). Now the tribochemical reaction rate is slower (with a time to 1/e of ~ 16 passes) than on the clean surface, and the amount of carbon on the surface doubles. Note that attempts to measure the gas-phase products emitted into the chamber during rubbing were not successful in this case because of the small amount of residual acetic acid background in the chamber.

The effect of repeating this process is illustrated in Fig. 4, which plots the C/Cu Auger ratio after exposing the surface to 2L of acetic acid at room temperature (■) before rubbing the sample compared with the Auger signal after rubbing (●), as a function of the number of cycles. The data for the carbon coverage after rubbing represent the amount of strongly bound carbon remaining on the surface after the reactive species have been removed. However, the surface can still accommodate acetate species and the difference between the upper and lower curves represents the proportion of the copper surface that contains available adsorption sites. The first two points for dose 1 and 2 include the data shown in Fig. 2, and the amount of carbon remaining on the surface after rubbing increases approximately linearly up to ~ 4 doses, and then remains constant, while the amount of carbon that can adsorb on the surface increases slightly. At higher values of dose-and-rub cycle, the values remain constant and the surface can adsorb ~ 50% of the initial acetate coverage on the clean surface. This indicates that the tribochemical reaction selectivity increases as the surface becomes passivated so that acetate species initially adsorbed on clean copper decompose tribochemically to remove a portion of the surface species, but the reaction causes some carbon and oxygen to be deposited onto the surface. As the coverage of decomposition products increases, the saturation coverage of the adsorbed acetates is reduced by ~ 50% and no detectable carbon is added to the surface. This implies that all the acetate species are tribochemically removed from the surface and indicates that the film-formation rate of the simple model carboxylic acid gas-phase lubricant is self-limiting. Presumably if the oxygen- and carbon-containing film is worn away, this would allow more acetate species to adsorb and repair the film.

This surface chemistry has a profound influence on the frictional properties as shown in Fig. 5. The top curve displays the evolution in friction of an acetate overlayer on copper (■), which varies sigmoidally as a function of the number of times that the sample has been rubbed, from an initial value of ~ 0.5 for friction on an acetate-covered surface, increasing to a high value of ~ 1.5. Note that the curve cannot be fit to a kinetic model in which the acetate species decompose directly to the final film, but requires the inclusion of additional tribochemically induce reaction steps. The behavior of the film once it has reached steady state, after six dosing and rubbing cycles (●), shows a lower and approximately constant friction coefficient.

To obtain insights into the pathway for the reaction of acetate species on copper, DFT calculations of acetate decomposition were performed using the nudged-elastic

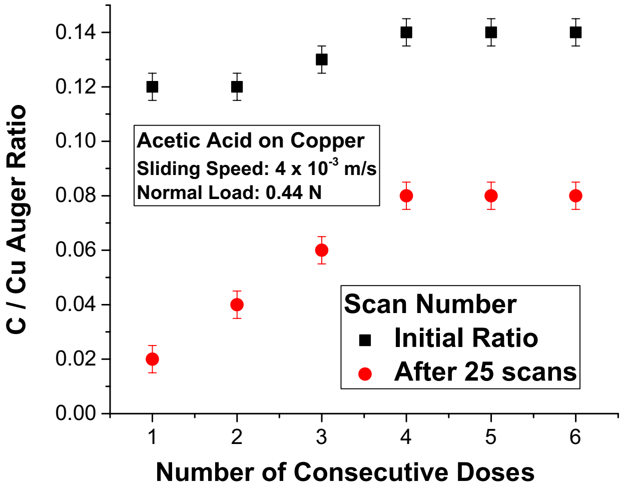

Fig. 4 Plot of the initial (■) and final (●) C(KLL)/Cu(LMM) Auger ratios after 25 rubbing cycles for repeated dosing of the surface without cleaning the sample between doses. Experiments were performed at a load of 0.44 N and a sliding speed of 4×10^{-3} m/s

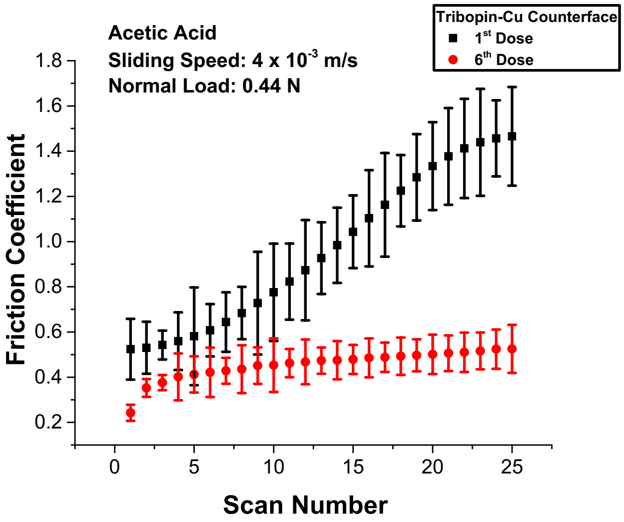

Fig. 5 Plot of the friction coefficient after the surface was dosed with 2 L of acetic acid as a function of the number of times that the sample had been rubbed at a load of 0.44 N and a sliding speed of 4×10^{-3} m/s. The results are shown for adsorption on a clean surface (■), and after redosing six times without cleaning the copper (●)

band method [40, 41]. The energy profile for the lowest-energy acetate decomposition pathway is displayed in Fig. 6. This reveals that the reaction occurs by the plane of the adsorbed acetate species tilting so that the methyl group approaches the surface until the CH_3—C bond is weakened, resulting in the deposition of a methyl group on the surface and the complete elimination of carbon dioxide into the gas-phase. This reaction pathway is analogous to the methyl thiolate decomposition reaction except that the weaker C—S bond causes the reaction to occur at much lower temperatures than the acetate decomposition and the weak binding of CO_2 compared to sulfur results in it desorbing from the surface as it is formed. This reaction sequence is shown as insets to Fig. 6. The calculated energy barrier is ~ 1.8 eV/molecule (173 kJ/mol), close to the value of 180 kJ/mol measured experimentally [26], suggesting that the NEB calculations correctly reproduce the reaction pathway.

However, the thermal reaction deposits carbon, but no oxygen, while the tribochemical reaction leaves a significant amount of oxygen on the surface (Fig. 3). To investigate the possibility that this is due to other shear-induced reactions, the reaction pathway and energy barrier were calculated for the acetate species tilting within the plane, perpendicular to the tilt direction for the lowest-energy pathway (Fig. 6). The results are shown in Fig. 7, which also displays the evolution in structure as the reaction proceeds. Now the energy barrier increases to 2.5 eV (240 kJ/mol), somewhat higher than the lowest-energy pathway, as expected. Here, shear causes one of the carboxylate oxygens to detach from the surface to initially form an η^1-acetate species that continues to tilt as the reaction proceeds. This induces the formation of a bent $CO_2^{\delta-}$ species that has been detected on copper at high CO_2 pressures [45, 46], which reacts to form CO and adsorbed oxygen.

4 Discussion

Acetic acid deprotonates to form an η^2-acetate species following adsorption on copper at room temperature, with the oxygen atoms of the acetate group bound to copper bridge site atoms as evidenced by infrared spectroscopy (Fig. 1) and DFT calculations (Figs. 6 and 7), in a behavior typical of the chemistry of carboxylic acids on transition-metal surfaces [42]. The most-stable structure involves bidentate binding to a surface bridge site with the C—C bond oriented perpendicular to the surface. The energy barrier calculated for acetic acid decomposition is ~ 173 kJ/mol (Fig. 6), consistent with the temperature at which carbon dioxide, methane and ketene evolve from the surface in TPD [26, 42]. This lowest-energy decomposition pathway involves the molecular plane tilting toward the surface (Fig. 6) to induce C—C bond scission to evolve carbon dioxide and form an adsorbed methyl group centered on a bridge site. Ketene also desorbs from the surface and is proposed to be due to the decomposition of surface species formed by acetate dimerization [26]. The trajectory of the decomposition pathway is coincident with the normal and shear forces exerted during sliding and is consistent with a tribochemical reaction pathway resulting in the simultaneous loss of carbon (Fig. 2) and oxygen (Fig. 3) with identical effective first-order rate constants of ~ 0.15/pass. This occurs by the stress reducing the energy barrier so that the reaction proceeds relatively rapidly at ~ 290 K [47].

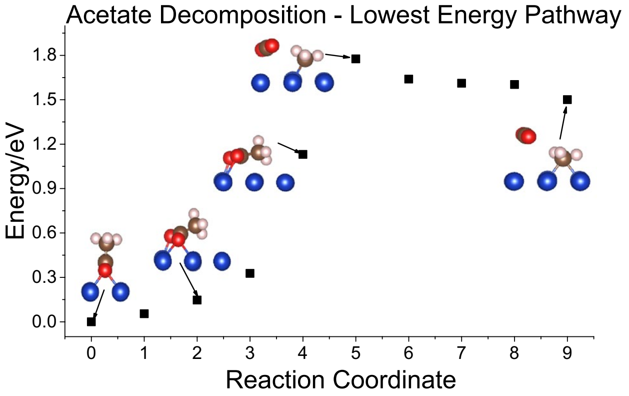

Fig. 6 Reaction energy profile that plots energy versus the reaction coordinate for the lowest-energy pathway for the decomposition of acetate species on a Cu(100) slab obtained using the nudged-elastic band method calculated using density functional theory. This pathway involves the vertical OCO–CH_3 plane of the adsorbed acetate species tilting toward the surface to evolve molecular carbon dioxide and deposit a methyl group on the surface. Shown on the figure are depictions of how the structure evolves as the acetate species decomposes

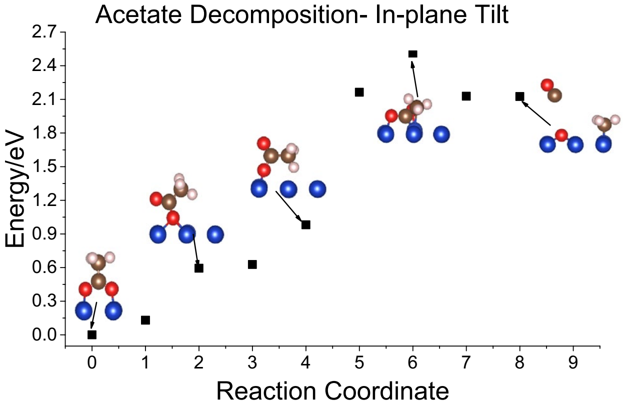

Fig. 7 Reaction energy profile that plots energy versus the reaction coordinate for a high-energy pathway for the decomposition of acetate species on a Cu(100) slab obtained using the nudged-elastic band method calculated using density functional theory. This reaction is initiated by a tilting within the vertical OCO–CH_3 plane of the adsorbed acetate species to evolve carbon monoxide and deposit atomic oxygen on the surface. Shown on the figure are depictions of how the structure evolves as the acetate species decomposes

This indicates that even quite stable anchored adsorbates are amenable to undergoing tribochemical reactions. However, the detection of residual oxygen on the surface after the completion of the reaction (Fig. 3) is not consistent with this model since the lowest-energy reaction should produce only carbon dioxide, which rapidly leaves the surface to remove all oxygen [26]. This suggests an alternative possibility that large stresses parallel to the plane of the adsorbed acetate induces the formation of monodentate acetate species, which then decomposes to form CO and adsorbed oxygen (Fig. 7) via a bent $CO_2^{\delta-}$ intermediate [45, 46].

The reaction also deposits methyl species onto the copper surface so that one of the main differences between the thermal and mechanochemical processes is the temperature at which the resulting methyl species are deposited on the surface, where they are formed thermally at ~ 590 K, but tribochemically at ~ 300 K. This will likely influence the subsequent reactions of the products.

Repeatedly adsorbing acetic acid on copper and rubbing results in the accumulation of carbon (Fig. 4) that produces a stable, low-friction film (Fig. 5). At this point, the surface can accommodate only ~ 50% of the acetate species found on clean copper. This indicates that the tribochemical reaction of acetic acid with copper forms a self-limiting, lubricious film that contains both carbon and oxygen. These results suggest that longer-chain hydrocarbons might undergo similar tribochemical reactions, and this is currently under investigation.

5 Conclusion

Acetic acid forms a bidentate acetate species when adsorbed on copper at room temperature. Rubbing in UHV causes the copper and oxygen Auger signals to decrease at the same rate to leave a surface film that contains carbon and oxygen, where the final carbon coverage is ~ 16% of that of the original acetate over layer with a stoichiometry of ~ $C_{0.8}O$. This indicates that acetate decomposition is tribologically induced, but that the reaction does not proceed exclusively by the thermal reaction pathway, which would leave no oxygen on the surface, and only ~ 5% of the original carbon, after thermally decomposing the acetate over layer. This effect is investigated using first-principles DFT calculations that show that the lowest-energy reaction proceeds by the plane of the adsorbed acetate tilting toward the surface to eliminate CO_2 and deposit methyl species on the surface with a calculated activation energy very close to that found experimentally. To test the possibility that a lateral force oriented along a direction within the plane of the adsorbed acetate molecule can lead to the deposition of oxygen on the surface, energy barrier calculations were carried out by constraining the acetate species to react by tilting within the plane. The calculated activation energy for this process is ~ 240 kJ/mol, only slightly higher than the lowest-energy reaction energy barrier, so that it is plausible that it is also tribochemically induced. This pathway involves the formation of an η^1-acetate species, which is the precursor for reaction to produce CO and atomic oxygen via a bent $CO_2^{\delta-}$ intermediate. This surface intermediate has been found previously following high-pressure adsorption on carbon dioxide on copper and found to decompose to evolve carbon monoxide and $O_{(ads)}$. Because the tribological experiments were carried out using polycrystalline copper, all acetate azimuthal orientations are likely to be present. This tribochemistry can be tested by rubbing an acetate-covered copper single crystal using an atomic force microscopy tip.

It is also found that the amount of acetic acid that can adsorb on the surface after rubbing decreases with an increasing number of dose-rub cycles, eventually reaching a steady-state coverage of ~ 50% of the initial acetate coverage after ~ 4 cycles. This implies that the surface is passivated such that the acetic acid adsorbs, but is completely removed from the surface when subsequently rubbed. The mechanism for this process is not known, but it must either be that the initial acetic acid is only weakly bound or that the methyl species formed by acetic acid decomposition reacts with high selectivity to remove all carbon. This final film has a relatively low and stable friction. Note that this observation suggests that such a film should be self-replenishing; removal of surface species will open up surface copper sites to form acetate species that once again deposits more carbon.

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