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ORIGINAL PAPER

Influence of the Nature and Orientation of the Terminal Group on the Tribochemical Reaction Rates of Carboxylic Acid Monolayers on Copper

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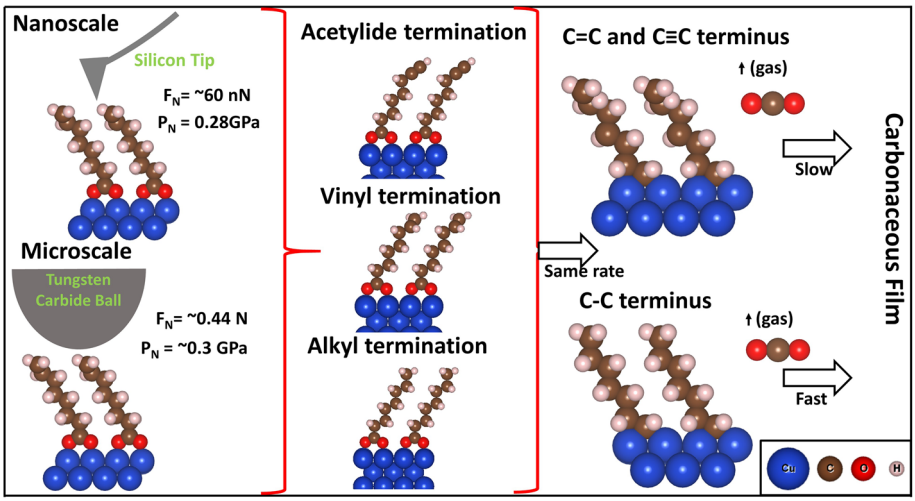
Abstract

The effect of changing the terminal functional group of C_7 and C_8 carboxylate species adsorbed on copper on the rate of tribochemical decomposition is investigated both in an ultrahigh vacuum tribometer and using an atomic force microscopy (AFM) tip, where the conditions are selected to provide similar normal stresses for both experiments. The carbon chains are terminated by alkyl, vinyl and acetylide groups, where the different chain lengths are selected to modify the orientation of the terminal π-orbitals. The pull-off forces measured by AFM are in accord with the calculated molecular structure but, despite this, the rates of tribochemical decomposition of all the adsorbed carboxylates are identical. However, the carbon is lost from the surface at different rates and this is ascribed to the different reactivities of the resulting carbonaceous species that are tribochemically produced at room temperature, but form thermally at ~ 650 K. This results in lower-energy barrier pathways, such as β-hydride elimination reactions, occurring preferentially compared to higher-activation-energy ones, such as coupling reactions. It is proposed that these rates are influenced by the ability of the terminal groups to access the copper surface and accounts for the relative reaction rates and the amount of carbon deposited onto the surface.

Graphical Abstract



Keywords Carboxylic acids · Copper · Tribochemistry · Auger spectroscopy · Atomic force microscopy

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1 Introduction

It is becoming increasingly clear that the chemistry of lubricant additives is dominated by mechanochemical processes [1–8] in which the potential energy surface is modified to change the rate of reaction [9–13]. This implies that the nature and stereochemistry of the chemical functionality at the sliding interface might be expected to influence the tribo/mechanochemical reaction rate. That is, the tribochemical reaction rates of films that bind to the substrate via an attachment point (AP), and to the moving counterface by a pulling point (PP), are likely to depend on the strengths of AP and PP binding relative to the activation energy of the tribochemical reaction [14]. For example, interactions with the counterface have recently been suggested to play a role in the mechanochemical etching of silicon [15] and molecular dynamics (MD) simulations, combined with first-principles density functional theory (DFT) calculations, have shown that carboxylic acids bind to tetrahedral amorphous carbon (ta-C) via a −COOH group AP, while the presence of a vinyl group PP in the carbonaceous chain can influence the tribochemical reactivity by binding to the moving counterface [16]. Furthermore, the rate was also influenced by the stereochemical ability of the vinyl group to access the counterface.

These effects are investigated in the following by systematically tuning the PP functionality while keeping the AP interaction constant by using carboxylic acids adsorbed on a copper substrate. Carboxylic acids deprotonate at room temperature when adsorbed on copper to bind strongly to the surface a bidentate η^2 configuration as a carboxylate [13, 17] (Fig. 1). Such fatty acids often act as friction modifiers by forming an adsorbed overlayer on the surface [16, 18–20], where the friction force is found to depend on the nature of the terminus of the hydrocarbon group and its surface orientation [21–23]. At higher stresses, tribochemical reactions of the adsorbed layer can form low-friction carbonaceous films [18, 19, 23–25] and thus, in this case, act as chemically reactive additives. Since many lubricant additives are functionalized by hydrocarbon groups to enable them to dissolve in the base oil, and since their removal has been implicated in their reaction to form tribofilms [26–29], studies of the tribochemistry of carboxylic acids on surfaces may be relevant to understanding how other additives operate.

The effect of the nature of the terminal group on the tribochemistry is investigated by adsorbing a series of C_7 and C_8 carboxylic acids with terminal alkyl, vinyl and acetylide groups onto copper, as illustrated in Fig. 1. The different hydrocarbon chain lengths influence the orientation of the terminal groups and consequently their steric ability to access the counterface and to provide a pulling

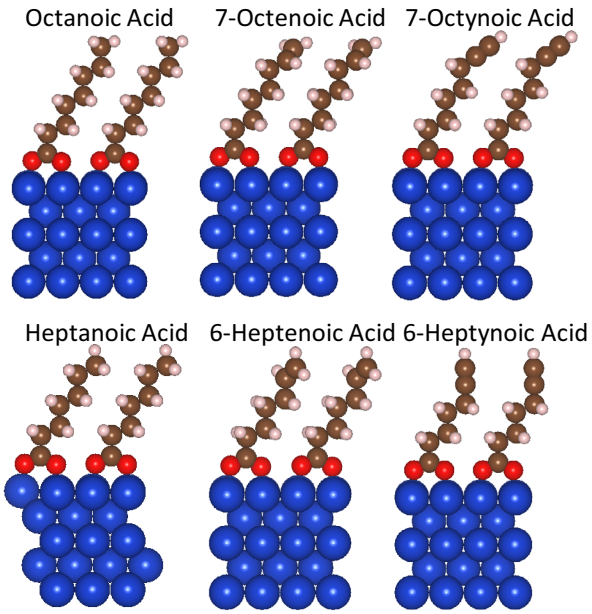

Fig. 1 Structures of various carboxylates adsorbed on a Cu(100) surface in a (2×2) units cell, assuming that the carboxylic acids adsorb on the surface via the carboxylate group as suggested by infrared spectroscopy [17]

point. For example, the terminal π-orbitals of 7-octenoic acid are more exposed, enabling them to bind more easily to a moving contact than those in 6-heptenoic acid. Similarly, the π-orbitals in 7-octynoic acid are likely to be more accessible than those in 6-hepytnoic acid, suggesting that their tribochemical reactivities may be different.

Experiments are carried out using an ultrahigh vacuum (UHV) tribometer [30] with a tungsten carbide ball that will not wear when rubbed against copper and tungsten carbide has been suggested to have catalytic properties akin to those found for noble metals (platinum and palladium) [31–33], and this concept has been borne out by UHV surface science studies [34, 35]. The tribochemical reaction rate is also measured by an atomic force microscope (AFM), which allows the interaction between the tip and the surface to be measured directly from the pull-off forces [36].

Carboxylic acids bind to copper via the formation of carboxylate species [17] and decompose via the evolution of carbon dioxide with the simultaneous formation of hydrocarbon fragments at temperature between 570 and 650 K in temperature-programmed desorption [37–42].

2 Experimental and Theoretical Methods

Experiments were carried out in two stainless-steel, ultrahigh vacuum (UHV) chambers operating at base pressures of ~ 2×10^{-10} Torr following bakeout, one for

AFM experiments [11] and the second for tribochemical measurements [43]. Briefly, the tribology chamber was equipped with a UHV-compatible tribometer, which simultaneously measures normal loads, lateral forces and the contact resistance between the pin and substrate. All tribological 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 [44]. The spherical tribopin (~ 1.27×10^{-2} m in diameter) was made from tungsten carbide containing some cobalt binder and could be cleaned by heating using electron bombardment in vacuo or by argon ion bombardment. The pin was attached to an arm that contained strain gauges to enable the normal and lateral forces to be measured. The arm was mounted to a rotatable $2\frac{3}{4}$" 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. Additional experiments were carried out by analyzing the tungsten carbide pin by X-ray photoelectron spectroscopy after argon ion bombardment using a spectrometer containing a hemispherical analyzer built by ThermoFisher (220i) with a focused monochromatic X-Ray source [12].

The copper samples (Alfa Aesar, 99.99% pure, 1 mm thick) were polished to a mirror finish using 1 μm diamond paste and then rinsed with deionized water and degreased ultrasonically in acetone before mounting in the UHV chamber. The copper foil and Cu(100) single crystal were cleaned using a standard procedure that consisted of argon ion bombardment (~ 1 kV, ~ 2 μA/cm^2) and annealing cycles, and the cleanliness of the samples was monitored using Auger spectroscopy.

The tribometer chamber contained a single-pass CMA for Auger analysis, and an argon ion bombardment source for sample cleaning and depth profiling. Auger spectra were either collected using the coaxial electron gun in the CMA with 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 high-resolution electron gun, which also enabled Auger elemental profiles to be obtained across the rubbed regions.

Experiments were performed by initially rubbing the tribopin against the clean copper sample (~ 1.7×1.7 cm^2 by ~ 1 mm thick) until a constant friction coefficient was obtained. This resulted in the formation of a wear track. The carboxylic acids were dosed through a Knudsen source connected to a dosing tube (with an internal diameter of 4×10^{-3} m) directed towards the sample so that the flux at the sample is enhanced. Experiments were carried out for saturated overlayers of the carboxylic acids on the copper surfaces, which were measured from the magnitude of the Auger signal versus dosing time.

The 7-octenoic acid (Sigma-Aldrich, ≥ 96.5% purity), octanoic acid (Sigma-Aldrich, ≥ 98.% purity), 6-heptenoic acid (Sigma Aldrich, ≥ 98.5% purity), heptanoic acid (Sigma Aldrich, ≥ 99.0% purity), 7-octynoic acid (Sigma Aldrich, 95.0% purity) and 6-heptynoic acid (Sigma Aldrich, 90.0% purity) were transferred to glass bottles and attached to the gas-handling system of the vacuum chamber, where they were subjected to several freeze–pump–thaw cycles.

Density functional theory (DFT) calculations were performed to predict the structures and conformations of the carboxylates (Fig. 1) with the projector augmented wave (PAW) method [45, 46] as implemented in the Vienna ab initio simulation package, VASP [47–49]. The exchange–correlation potential was described using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof [50]. A cutoff of 400 eV was used for the planewave basis set, and the wavefunctions and electron density were converged to within 1×10^{-5} eV. The first Brillouin zone was sampled with a $4 \times 4 \times 1$ Γ-centered k-point mesh. Geometric relaxations were considered to be converged when the force was less than 0.02 eV/Å on all unrestricted atoms.

3 Results

3.1 Tribochemical Reactions of Carboxylic Acids on Copper Measured in the UHV Tribometer

Tribochemical experiments were carried out by rubbing a carboxylate-covered surface with a cleaned tungsten carbide ball at a sliding speed of 4×10^{-3} m/s at a normal load of 0.44 N and by analyzing the rubbed region using Auger spectroscopy. Attempts were made to monitor the gas-phase products formed during sliding as done previously [4, 6, 7], but the residual background signal after sample dosing precluded such experiments from being carried out. Figure 2 shows the results of experiments for saturated overlayers of the series of carboxylic acids shown in Fig. 1 on copper. Here the surfaces were first rubbed to create a wear track and then saturated with the carboxylic acid, where the saturation dose was gauged by measuring the C KLL Auger spectral intensity as a function of exposure. The decrease in the amount of carbon on the surface as the surface is rubbed (■) for each carboxylic acid indicates that they undergo tribochemical reactions. In all cases, the signals decrease to a steady C/Cu Auger ratio after 50 passes and a fit to an exponential decay yields the number of passes to reduce the signal by 1/e, S_e scans, for each adsorbate. The results are summarized in Table 1. The exponential decay in carbon Auger signal suggests a first-order decomposition rate. The results indicate that the nature of terminal group

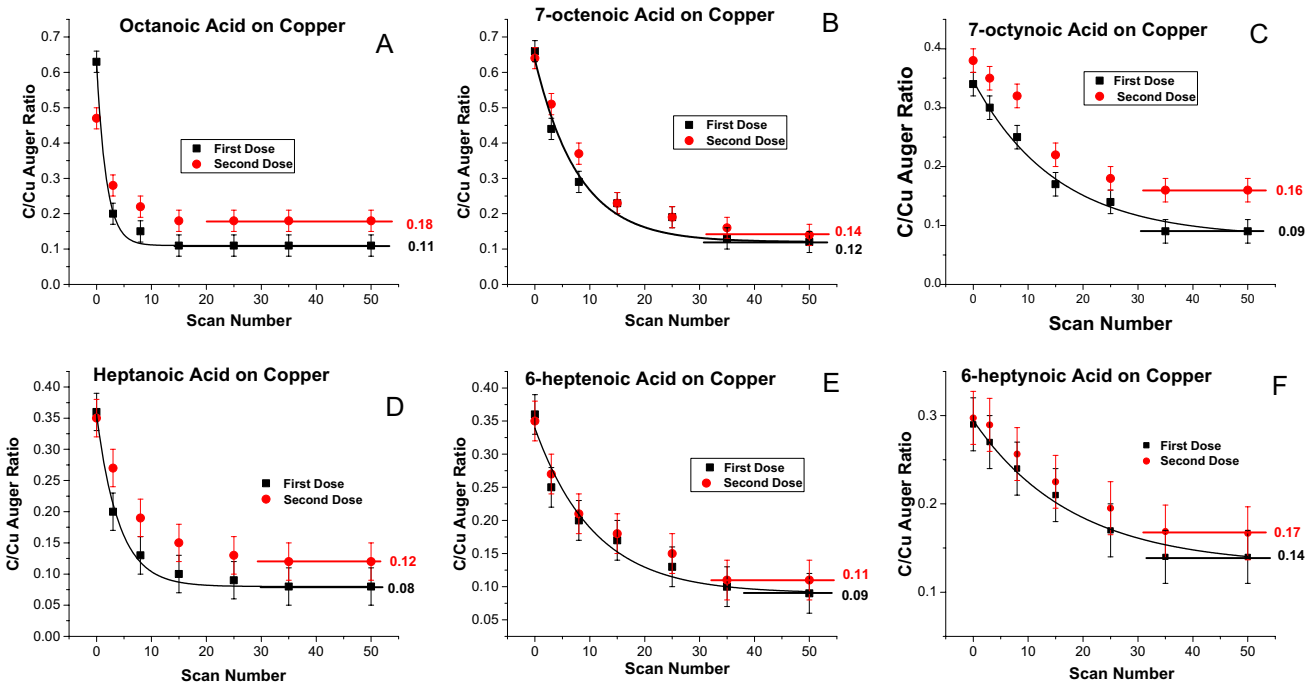

Fig. 2 Plot of the C/Cu Auger ratio in the wear tracks of saturated overlayers of carboxylic acids on a copper foil as a function of the number of passes at a normal load of 0.44 N and a sliding speed of 4×10^{-3} m/s, on a clean surface (■) and after a second dose of the carboxylic acid on the previously rubbed surface (●) for **A**; octanoate, **B**; 7-octenoate, **C**; 7-octynoate, **D**; heptanoate; **E**; 6-heptenoate and **F**; 6-heptynoate on copper (Color figure online)

Table 1 The number of scans at a load on 0.44 N at a sliding speed of 4×10^{-3} m/s to decrease the C KLL Auger intensity to 1/e of its original value for the adsorption of each of the carboxylic acids on copper, compared with the initial friction coefficient of the saturated overlayer of each compound

Compound	Carbon Removal Rate/Scan	Friction Coefficient
Octanoic Acid	1.8 ± 0.2	0.24 ± 0.06
7-Octenoic Acid	7.9 ± 1.1	0.32 ± 0.06
7-Octynoic Acid	15.2 ± 1.2	0.32 ± 0.06
Heptanoic Acid	4.1 ± 0.4	–
6-Heptenoic Acid	10.9 ± 1.7	–
6-Heptynoic Acid	18.1 ± 1.5	–

Table 2 The proportion of carbon on the surface after a tribological experiment and after temperature-programmed desorption

Compound	Carbon Ratio after Rubbing/%	Carbon Ratio after TPD/%
Octanoic Acid	11	36
7-Octenoic Acid	12	47
7-Octynoic Acid	9	84
Heptanoic Acid	8	46
6-Heptenoic Acid	9	49
6-Heptynoic Acid	14	82

has a significant influence on the tribochemical reaction rate with the trend for both series of carboxylic acids indicating that those with a saturated hydrocarbon terminus react most rapidly, those with a vinyl terminus react somewhat more slowly, while those with a terminal triple bond react the most slowly of all. However, this trend is exactly the reverse of the rates that would be expected by assuming that the molecules bridge between the substrate and the tip [16].

The experiments were repeated without cleaning the substrate or the pin (Fig. 2, ●) to assess how the presence of carbonaceous product influenced the reaction kinetics. These results are also plotted on the figure, where the signal decay rates are approximately identical to those of the first scan, but there is a slight increase in the amount of carbon on the surface. In all cases, as indicated in Table 2, the amount of carbon deposited on the surface by tribochemical reactions is much less than formed by the thermal deposition of the carboxylates, where the amount of thermally formed carbon is the least for alkyl functionalized carboxylic acids, somewhat larger for molecules with terminal carbon–carbon double bonds, and much larger both those with triple bonds.

The evolution in friction coefficient as a function of the number of passes for octanoic, 7-octenoic and 7-octynoic acid overlayers on clean copper is shown in Fig. 3. The initial friction coefficient of an octanoate overlayer on copper is 0.24 ± 0.06, remains constant for the first ~ 4 scans, and then increases with the number of passes to reach a constant value of ~ 0.5, corresponding to the friction coefficient of clean copper [4]. The presence of the 7-octenoate overlayer on the surface also reduces the initial friction coefficient to 0.32 ± 0.06 (Table 1), which remains constant for ~ 7 scans and then rises to a value of ~ 0.5 over the next ~ 50 scans. In the case of a 7-octynoate overlayer, the initial friction coefficient is 0.32 ± 0.06, and remains at this value for ~ 10 scans and then rises to a constant value of ~ 0.4. The duration of the initial, relatively low value of friction correlates well with the time required to reduce the amount of carbon on the surface to its asymptotic value (Table 1), suggesting the friction remains low while carbonaceous species are present on the surface, and then starts to increase, likely because the carbonaceous films formed on the surface by carboxylate decomposition are slowly restructuring. In addition, the presence of terminal unsaturation increases the friction in accord with the adsorbate structures (Fig. 1).

To provide further insights into the reactivity, the loss of oxygen from the surface as a function of the number of passes was also monitored and the results are displayed in Fig. 4. Note that the oxygen Auger signal is much smaller than the carbon signal because there is much more carbon than oxygen in the adsorbed layer, and the oxygen is buried at the surface, while the carbon is in the outermost layer. The amount of oxygen decreases at identical rates for all carboxylate overlayers with $S_e = 2.0 \pm 0.1$ scans, similar to the rate of carbon removal from octanoic acid (Table 1). All the oxygen is removed by ~ 8 scans indicating that the carboxylates reacts by evolving carbon dioxide from the surface [51]. This implies that there is little effect of varying the nature of the outermost functionality, and thus the nature of the pulling point, on the overall shear-induced rate of

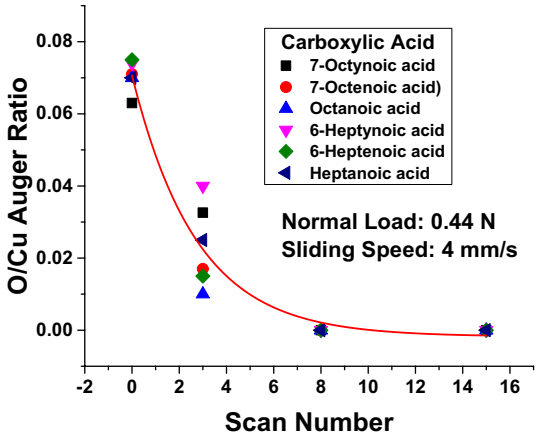

Fig. 4 Plot of the O/Cu Auger ratio in the wear track of a saturated overlayer of 7-octynoate (■), 7-octenoate (●), octanoate (▲), 6-heptynoate (▼), 6-heptenoate ♦) and heptanoate (◀) as a function of the number of passes at a normal load of 0.44 N and a sliding speed of 4×10^{-3} m/s (Color figure online)

decomposition of the carboxylic acids. This suggests that differences in the rates of carbon removal are caused by the rates at which the resulting hydrocarbon fragments react.

3.2 Tribochemical Reactions of Carboxylic Acids on Cu(100) Measured in UHV by Atomic Force Microscopy

To further test whether the nature of the terminal group influences the rate of tribochemical decomposition, this is measured by rubbing an AFM tip over the surface and by measuring the depth of the groove formed by rubbing using a silicon tip. The extent of interaction between the tip and the surface is measured using the pull-off forces.

The decomposition of the carboxylate films formed from the carboxylic acids shown in Fig. 1 on Cu(100) were studied by sliding an AFM tip at 120 nm/s on a saturated overlayer using an AFM tip with a nominal radius of ~ 8 nm at

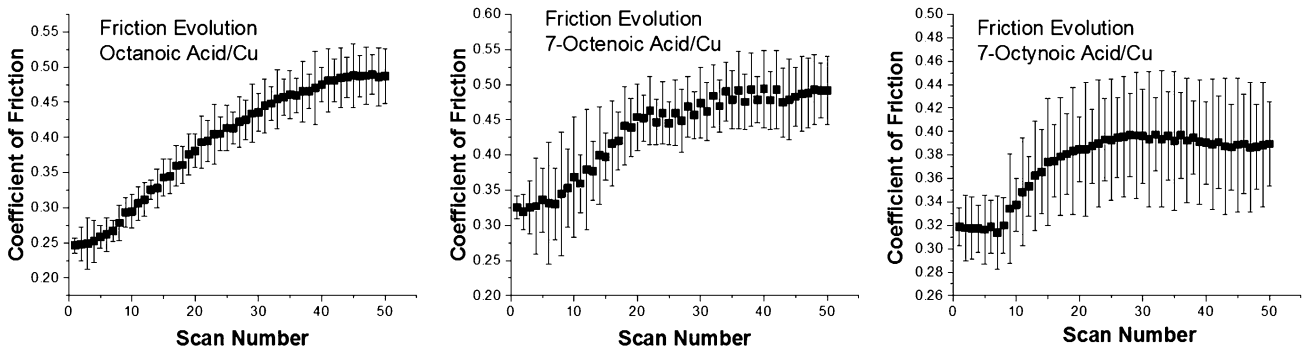

Fig. 3 Plot of the friction coefficient as function of the number of passes for a copper surface saturated with octanoic, 7-octenoic and 7-octynoic acids while rubbing at a normal load of 0.44 N at a sliding speed of 4×10^{-3} m/s

an applied normal load of 60 nN. Based on previous calibrations [11], this corresponds to a normal stress at the center of the contact of ~ 0.26 to 0.28 GPa. The reaction rate was obtained by periodically imaging the depth of the rubbed region using a non-perturbative load to measure the depth at the center of the track. The results are displayed in Fig. 5 for C_8 carboxylates and in Fig. 6 for C_7 carboxylates, which show that the groove increases in depth with the number of scans. The resulting traces can be fit to exponentials, suggesting first-order kinetics, agreeing with the tribometer results, and the characteristic number of scans for the exponential groove formation are identical for all carboxylic acids studied and is ~ 600 scans. These results are in accord with the data in Fig. 4 showing that the rates of oxygen removal, characteristic of the rate of carboxylate decomposition, are identical for all carboxylates, independent of the nature of the terminus.

The asymptotic depths at the center of the scan are ~ 200 to 250 pm for the C_7 carboxylic acids and from ~ 200 to ~ 350 pm for C_8 carboxylic acids. The DFT structures in Fig. 1 and of other carboxylic acids on copper [41, 42] suggests a molecular layer thickness of ~ 970 pm for C_8 chains and ~ 920 pm for the shorter carboxylates. The grooves are significantly shallower for carboxylic acids with unsaturated termini, and correlate with the amount of carbon remaining on the surface after the completion of the tribochemical reactions in Table 1. This suggest that at least part of the reason that the grooves are shallower than the length of the chain is that a significant amount of material is left on the surface after the tribochemical reaction is complete. It may also be that the compliant hydrocarbon film results in an underestimate of the film thickness.

To investigate whether the similarities in film removal rates are a result of the carboxylate films interacting similarly with the tip, the pull-off forces are compared in Fig. 7, plotted as a distribution of repeated measurements. They yield quite different values of the pull-off forces of 14 ± 4 nN for an octanoate overlayer compared with 31 ± 5 nN for the 7-octenoate film, consistent with the terminal C = C group in the 7-octenoate overlayer interacting more strongly than with the saturated alkyl terminus of the octanoate film.

The pull-off forces for heptanoic, 6-heptenoic and 6-heptynoic acids are all quite low and very similar to each other and are close to the values for heptanoic and octanoic acid. These results reflect the conformation of the termini of these carboxylate films in which the orientation of the terminal unsaturation does not allow it to interact with the tip (Fig. 1).

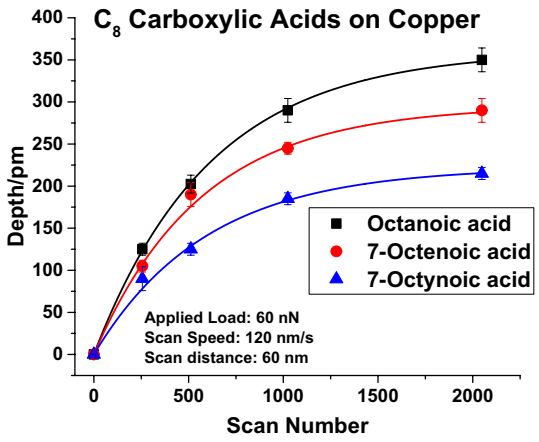

Fig. 5 Plot of the depth at the center of the wear track of saturated overlayers of octanoic acid (■), 7-octenoic acid (●) and 7-octynoic acid (▲) on Cu(100) measured using a silicon AFM tip as a function of the number of passes at an applied normal load of 60 nN, corresponding to a normal stress at the center of the contact, σ_0, of 0.28 GPa, and a scanning velocity of 120 nm/s (Color figure online)

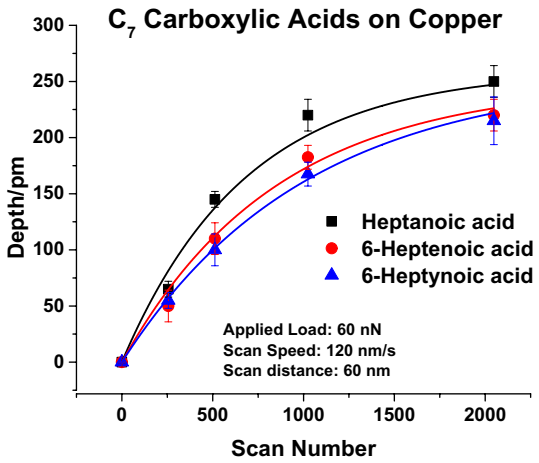

Fig. 6 Plot of the depth at the center of the wear track of saturated overlayers of heptanoic acid (■), 6-heptenoic acid (●) and 6-heptynoic acid (▲) on Cu(100) measured using a silicon AFM tip as a function of the number of passes at a normal load of 60 nN, corresponding to a normal stress at the center of the contact, σ_0, of 0.28 GPa, and a scanning velocity of 120 nm/s (Color figure online)

4 Discussion

These results indicate that intermediate length carboxylic acids adsorbed on copper to form carboxylates undergo tribochemical reactions to deposit carbonaceous species on the surface. In addition to carboxylic acids functioning as friction modifiers by forming protective adsorbed molecular overlayers [20], they can react at the interface to form lubricious carbonaceous films [18, 24, 25] and thus also function as friction-reducing additives. An important conclusion from this work is that this reaction is mechanochemically induced rather that the rate being accelerated by some other process such as interfacial heating since the temperature rise during sliding on copper under the conditions used here

is negligible. This is in accord with the predictions from simulations [16] and appears to be a common feature that the chemistry of lubricant additives is mechanochemically driven as, for example, for zinc dialkyl dithiophosphate (ZDDP) and phosphate esters [1, 2, 52, 53].

The complete removal of oxygen from the surface indicate that the tribochemical reaction is initiated by the cleavage of the bond between the carboxylate anchoring group and the hydrocarbon chain to form carbon dioxide that rapidly desorbs from the surface, along with the formation of a hydrocarbon radical, which then undergoes subsequent reactions on the surface [42, 54, 55]. It should be pointed out that an alternative reaction pathway has been identified for the decomposition of acetate species on copper in which forces exerted within the OCO plane mechanically induce the formation of an η^1-acetate species that reacts to evolve carbon monoxide and deposit oxygen on the surface [51]. However, the lack of oxygen deposition after tribochemical reaction of these longer-chain hydrocarbons suggest that this pathway is suppressed.

It has been postulated that an interaction between the terminus of the hydrocarbon chain (the pulling point) and the moving counterface (the ball or tip, to provide an attachment point) influences the tribochemical reaction rate [16], where the stronger binding of an unsaturated terminal group than a saturated alkyl groups to the tungsten carbide ball or AFM tip should result in higher forces being exerted, inducing higher reactivity.

The stereochemistry of this interaction was also investigated using carboxylates with C_7 and C_8 chains. While there was a dependence of the carbon removal rate on the nature of the hydrocarbon terminus (Fig. 2), none was found on the rate of oxygen removal, and therefore on the rate of tribochemical reaction and carbon dioxide evolution from the surface, while rubbing (Fig. 4). This result was confirmed by experiments using a silicon tip sliding on overlayers of various C_7 and C_8 carboxylates adsorbed on Cu(100) in UHV (Fig. 6), where the reaction rates, measured from the depths at the center of the grooves formed by sliding was essentially identical for all carboxylic acid overlayers, irrespective of the nature of the terminal group. However, the values of the pull-off forces (Fig. 7) for the C_7 and C_8 carboxylate overlayers are exactly what would be expected from their structures (Fig. 1), so that the identical reactivity, in particular, for the AFM experiments, cannot be ascribed to the forces being exerted on the overlayer being identical [19, 56]. Note that the AFM silicon tip exerting a normal load of ~ 60 nN produces a contact stress of ~ 0.26 GPa, which is in the same range as the contact pressures in the ball-on-flat geometry in the UHV tribometer, estimated to be between 0.1 and 0.4 GPa depending on the choice of contact model [57]. The two sets of experiments are performed under similar contact conditions.

The pull-off force for 7-octenoate (~ 31 nN) is larger than that for 6-heptenoate, which is the same as for the films formed from saturated fatty acids. This is due to steric effects in which the terminal π-orbital faces outwards in 7-octanoic acid, but is oriented parallel to the surface for 6-heptenoic acid, and is thus inaccessible to the counterface. Similarly, the π-orbitals of 7-octynoate can contact the tip to provide strong adhesion (with a pull-off force of ~ 37 nN), while the inaccessibility of the π-orbitals in 6-heptynoate means that it has a small pull-off force. The stereochemical trends were proposed from the simulations [16], but do not appear

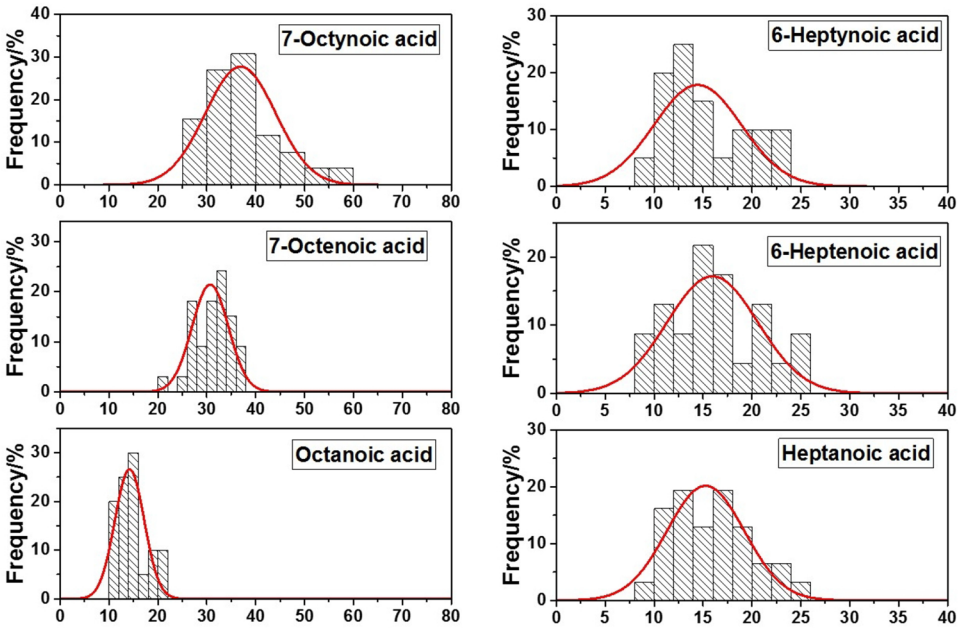

Fig. 7 Distributions of pull-off forces for saturated overlayers of carboxylic acids adsorbed on Cu(100) measured in ultrahigh vacuum using an atomic force microscope for 7-octynoic acid, 7-octenoic acid, octanoic acid, 6-heptynoic acid, 6-heptenoic acid and heptanoic acid

to lead to differences in the tribochemical reaction rates. It is possible that tip stresses on the adsorbed carboxylate overlayer could compress the films to cause distortions that change the orientation of the chain terminus. The film will be compressed at the tip approaches, but the normal stress decreases to zero at the tip detaches from the surface so that significant pressure-induced geometry changes are unlikely.

Nevertheless, the results in Fig. 2 do show different carbon removal rates that depend on the nature of the terminal group, but with a reverse order to that proposed by the MD simulations [16]. Since, based on the oxygen removal rate (Fig. 4), the tribochemical decomposition rates are identical for all carboxylic acids irrespective of the nature of the terminal group, these differences must be due to the different subsequent reactivities of the resulting hydrocarbon fragments. Alkyl species adsorbed on copper can either undergo a β-hydride elimination reaction to form an alkene, or hydrogenate to form alkanes, both of which occur below room temperature [58, 59], or undergo coupling reactions to form oligomeric species on the surface [55, 58–60]. However, the chain lengths of these hydrocarbons is sufficient for the terminus to be able to access the surface and modify their subsequent reactivity [41, 42]. Thus, alkyl terminal groups, with a CH_3 that does not interact strongly with the surface, will be able to undergo a facile and rapid β-hydride elimination reaction, with kinetics that are controlled by the rate that it is formed from the parent carboxylate (compare Figs. 2 A and 5 and 6) to deposit relatively little carbon on the surface (Table 2). In contrast, the presence of unsaturated terminal groups allows the hydrocarbon chain terminus to bind to the copper, thereby inhibiting the formation of the alkene products to facilitate further decomposition or coupling reactions to form carbonaceous species on the surface [54]. However, it is evident that, in general, the amount of surface carbon is less for the tribochemical decomposition of carboxylic acids on copper than for the thermal reactions [55] (Table 2). This is proposed to be due to the different temperatures at which the hydrocarbon fragments are formed, being thermally produced at ~ 650 K, but tribologically formed at room temperature [41, 42]. By definition, higher-activation-energy reactions will proceed relatively more quickly at higher temperatures than lower-barrier ones. Since the activation energies of coupling reactions, which deposit surface carbonaceous films, are greater than those for β-hydride elimination (which removes carbon from the surface), less carbon is formed tribochemically because the carbonaceous species are formed at lower temperatures.

Thus, there seem to be two major processes that influence tribochemical reaction selectivity. The major influence of an applied force is to accelerate the rate of the tribochemical reaction, but the effect depends on the direction of the applied force with respect to the potential energy surface. If the force is aligned with the lowest-energy reaction pathway, then it can be expected to result in an acceleration in the rate of the reaction. Carboxylic acids react thermally on copper to form η^2-acetate species that decompose at ~ 650 K to evolve gas-phase carbon dioxide by the plane of the carboxylate group tilting towards the surface to eventually weaken the C−C bond to eject a carbon dioxide molecule. Consequently, one mechanism by which the selectivity could be changed is if the direction of the force were orthogonal to this direction and aligned within the plane of the carboxylate group, which, as discussed above, induces a reaction to form carbon monoxide and adsorb oxygen on the surface [51].

The second origin of different tribochemical selectivities is due to the different temperatures at which reaction products are formed. The acceleration in the tribochemical reaction rate implies that products are formed at lower temperature compared to thermal reactions and thus increases the selectivity towards lower-activation-energy pathways.

Finally, the conclusion from this work, that carboxylic acid reaction rates do not depend on the strength of interaction of the molecular termini with the counterface, that is, is independent of the nature of the pulling-point interactions [16], seems counterintuitive. It would seem obvious that the stronger the interaction, the larger the shear forces that should be exerted, and thus the larger are the tribochemical reactions rates. Why this is not the case deserves some (perhaps speculative) discussion. One possibility is that the rate at which the shear force is applied during an experiment is very slow compared to the rate of molecular motion so that tribo- [11] and mechanochemical [61, 62] reaction rates can be calculated from quantum calculation under a static applied stress. This suggests that the shear motion of the counterface is effectively negligible compared to the molecular motion of the adsorbate. In the case of adsorbates on surfaces studied here, the reaction involves the adsorbate tilting towards the surface [57], which would be expected to depend on both normal and lateral forces. However, if the lateral motion is sufficiently slow it may be that the tilting motion, once initiated, is accelerated by the imposition of normal stress, similar to the normal-stress induced activation of methyl thiolate species on copper [11], resulting in rates that do not depend on the strength of the attractive interaction between the tip and the surface. Further work is required to test these ideas.

5 Conclusions

The effect of changing the nature and orientation of the terminal group on the tribochemical reaction rates of carboxylates adsorbed on copper are investigated for sliding of both a tungsten carbide ball and a silicon AFM tip using similar contact stresses. This represents a situation in which

the attachment point of the mechanically active species (the mechanophores) is kept constant while varying the nature of the pulling point. Values of the pull-off forces by AFM correlated with the presence and accessibility of π-orbitals in the terminal group, indicating that varying the nature of the pulling point does modulate the interaction with the counterface. Nevertheless, it is found that the rates of tribochemical reactions for the various carboxylate films, measured both in the UHV tribometer and by AFM, are identical. Yet, there are differences in the rates at which carbon is removed from the surface and in the amount of carbon deposited on the surface by the tribological reaction compared to the thermal one. This is ascribed to differences in the temperatures at which the thermal and tribochemical reactions occur, with the tribochemical reactions occurring at room temperatures and thermal reactions occurring at much higher ones. Such lower reaction temperatures will favor lower-activation-energy pathways and this constitutes an important mechanism by which selectivities in tribo- or mechanochemical reactions differ from thermal ones.

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Author Contributions All authors conceived of the study and analyzed the results. R.R. carried out UHV compatible tribometer and AFM experiments. R.B. performed TPD experiments. K.H. collected friction data by using a UHV compatible tribometer. Both R.B and N.H executed DFT calculations. W.T.T. wrote the manuscript and all the authors discussed and revised the manuscript.

Data Availability Data are available on request.

Ethical Approval All ethical responsibilities were respected by the authors.

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