

Molecular structure and environment dependence of shear-driven chemical reactions: Tribopolymerization of methylcyclopentane, cyclohexane and cyclohexene on stainless steel

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Abstract

Tribochemistry, which is another name of mechanochemistry driven by shear, deals with complex and dynamic interfacial processes that can lead to facilitation of surface wear or formation of beneficial tribofilms. For better mechanistic understanding, we investigated the reactivity of tribopolymerization of organic molecules with different internal ring strain energy (methylcyclopentane, cyclohexane, and cyclohexene) on a stainless steel (SS) surface in inert (N₂), oxidizing (O₂), and reducing (H₂) environments. On the clean SS surface, precursor molecules were found to physisorb with a broad range of molecular orientations. In inert and reducing environments, the strain-free cyclohexane showed the lowest tribochemical activity among the three tested. Compared to the N₂ environment, the tribochemical activity in H₂ was suppressed. In the O₂ environment, only cyclohexene produced tribofilms and methylcyclopentane and cyclohexane did not. When tribofilms were analyzed with Raman spectroscopy, the spectral

1 features of diamond-like carbon (DLC) or amorphous carbon (a-C) were observed due to
2 photochemical degradation of triboproducts. Based on infrared spectroscopy, tribofilms were
3 found to be organic polymers containing oxygenated groups. Whenever polymeric tribofilms were
4 produced, wear volume was suppressed by orders of magnitudes but not completely to zero. These
5 results supported the previously suggested mechanisms which involved surface oxygens as a
6 reactant species of the tribopolymerization process.

8 **Introduction**

9 Tribochemistry is the study of chemical reactions that are facilitated by friction at a sliding
10 interface. Tribochemical reactions could result from frictional heat or the exposure of highly
11 reactive sites and dangling bonds [1-5]. When frictional heating and surface wear are negligible,
12 tribochemical reactions occur via direct mechanical activation of interfacial molecules or atomic
13 sites in the sliding interface [6-8]. It has been shown that tribofilms formed from tribochemical
14 reactions of lubricant additives prevent the direct contact of asperities on the mating surfaces,
15 hence minimizing friction and wear [9-12]. The prototypical film forming material is zinc
16 dithiophosphate (ZDDP), a widely-used anti-wear additive that decomposes upon frictional shear
17 to form a tribofilm that can protect surfaces and reduce wear [13-15]. However, thermal
18 decomposition products of ZDDP in internal combustion engines of automobile can deteriorate the
19 performance of the catalytic converter in the exhaust line [10, 16]. Thus, developing alternative
20 anti-wear additives is imperative, but this requires better understanding of tribochemical reaction
21 pathways and the mechanisms that lead to the formation of functional tribofilms.

22 Shear-induced tribofilm formation can vary depending on applied stress, molecular structure of
23 reactants, environmental gas, and surface chemistry of materials involved [13, 17-21]. Numerous
24 tribochemistry investigations have demonstrated an exponential relationship between applied

1 stress or mechanical force and reaction rate or yield [13, 22-26]. For example, the growth of
2 tribopolymer from α -pinene on dehydroxylated silica in N_2 was found to have an exponential
3 relationship with applied stress [23]. In a study of wear reduction by cyclopropylcarboxylic acid
4 (CPCa), which has a highly strained three-membered ring, the zero-stress activation energy was
5 found to be comparable to the C-C bond dissociation energy within cyclopropane, indicating that
6 opening of the 3-membered ring was involved in tribochemical activation [27, 28]. In the
7 tribochemical polymerization study of α -pinene, pinane, and n-decane, the tribochemical activity
8 was found to be the highest for α -pinene which has the highest ring strain due to the presence of
9 the 4-membered ring and a double bond in the 6-membered ring [11]. Reactive molecular dynamics
10 (MD) simulations showed that the double bond in the ring can provide a reaction path that is not
11 accessible in thermal reaction conditions [29]. This computational study also suggested that the
12 structural deformation of reacting species by shear may contribute to the mechanical activation of
13 tribochemical reactions [29].

14 In addition to quantifying the tribochemical reactivity of organic molecules, it is also important
15 to chemically characterize the produced tribofilms. In the literature, Raman spectroscopy has been
16 extensively employed to analyze tribofilms formed from organic precursors [14, 28, 30-36].
17 Vibrational spectral features reported for such tribofilms often showed two broad bands at ~ 1370
18 cm^{-1} and $\sim 1580 cm^{-1}$, which are very similar to characteristic bands of amorphous carbon (a-C) or
19 diamond-like-carbon (DLC) materials [14, 28, 30-36]. Since these carbon materials are well
20 known to reduce friction and wear, their formation could explain the good lubrication efficiency
21 with substantial wear reduction in tribochemistry studies of organic precursors [30, 36, 37].
22 However, it should be noted that a-C and DLC are usually produced by high-energy physical or
23 chemical vapor deposition processes or pyrolysis at extremely high temperatures [38, 39]. Thus,
24 their formation must be tested and confirmed (or disputed) via independent analysis [40]. For a

1 better understanding of tribochemical mechanism, having knowledge of the chemical nature of
2 tribofilms is critical.

3 In this work, we studied the molecular structure dependence of tribopolymerization reactions of
4 adsorbed organic precursors and demonstrated several methods for characterizing the tribofilm
5 products. Vapor phase lubrication (VPL) has been demonstrated to effectively minimize friction
6 and wear of various inorganic surfaces [16, 37, 41-47]. In VPL, lubricating molecules are delivered
7 to the sliding interface via adsorption from the gas phase. Since there is no liquid solvent,
8 tribochemical reaction products with vapor pressure lower than the delivered precursor molecule
9 will remain on the surface, which allows further characterization of triboproducts [2, 4, 22, 48-50].
10 Here, methylcyclopentane ($\text{CH}_3\text{-c-C}_5\text{H}_9$), cyclohexane ($\text{c-C}_6\text{H}_{12}$), and cyclohexene ($\text{c-C}_6\text{H}_{10}$) were
11 chosen to evaluate the reactivities of cyclic compounds with a 5-membered ring versus a 6-
12 membered ring, as well as the impact of C=C double bond in the 6-membered ring. The ring strain
13 is smaller in the cyclohexane than the cyclopentane [51]. In addition to precursor molecular
14 structures, the effect of surrounding gas – inert (dry N_2), reducing (10% H_2 in N_2), and oxidizing
15 (O_2) environment – was also evaluated. To investigate the interaction between organic vapors and
16 the surface, polarization-modulation reflection absorption infrared spectroscopy (PM-RAIRS) and
17 MD simulations were used to measure the adsorption isotherms and geometry, respectively, of
18 cyclic hydrocarbons on stainless steel surfaces at ambient temperature. The produced tribofilms
19 were analyzed with energy-dispersive X-ray (EDX) mapping for elemental composition, as well
20 as Raman and infrared spectroscopy for chemical structures.

22 **Methods**

23 **Experimental Methods**

24 A bidirectional ball-on-flat tribometer was used to study tribochemical reactions of

1 methylcyclopentane (97%; Sigma-Aldrich), cyclohexane ($\geq 99\%$; Sigma-Aldrich) and
2 cyclohexene (99%; Thermo Scientific) in dry N₂ (moisture volume concentration ~ 18 ppm), dry
3 O₂ (purity 99.994%) and dry H₂ (10% in N₂) gas environments. A schematic of the setup designed
4 to conduct tribotests is shown in Figure S1. The bearing-grade ball (diameter = 3mm) and substrate
5 were AISI 440C stainless steel (SS; McMaster-Carr). The substrate was polished to RMS
6 roughness of roughly 20 nm using various grits of sandpaper and a 0.03 μm alumina colloidal
7 solution. The RMS roughness of the ball was ~ 6 nm [52]. The substrate and ball were both rinsed
8 with ethanol followed by water and UV/Ozone for 30 minutes prior to tribo-testing [47]. The
9 applied normal load was kept at 0.5 N. At this load the maximum Hertzian contact pressure was
10 calculated to be ~ 0.45 GPa. The sliding speed was kept at 3 mm/s, so the average increase of flash
11 temperature was less than 5 °C [11, 17]. The length of the sliding track was 2.3 mm. The saturated
12 vapor stream of each precursor was produced by flowing dry N₂, dry O₂ or dry H₂ (10% in N₂)
13 into a flask containing the corresponding liquid, and a target partial pressure relative to its
14 saturation (P/P_{sat}) was obtained by mixing the vapor-free gas stream with the saturated vapor
15 stream at the corresponding ratio [25, 52]. The adsorption isotherms of organic vapor on polished
16 stainless steel (SS) surface were studied with PM-RAIRS. For PM-RAIRS experiment, a
17 ThermoNicolet Nexus 670 spectrometer equipped with an MCT detector and a Hinds Instrument
18 photoelastic modulator was used. The modulator generated the P- and S-polarizations, alternating
19 at 50 kHz of the incident IR beam. The P-polarization has the electric field parallel to the incidence
20 beam plane, while the S-polarization has the field perpendicular to the plane [53, 54]. The P+S
21 sum signal gives the vibrational spectrum of mostly gaseous species, while the (P-S)/(P+S) signal,
22 difference normalized with total signal, solely provides the vibrational spectrum of the adsorbed
23 species [53, 55]. The spectral resolution was set at 4 cm^{-1} for the SS experiment. For comparison,
24 another PM-RAIRS measurement was done for a gold (Au) surface with a 1 cm^{-1} resolution. All

spectra shown in this study were normalized with the spectrum collected with a clean surface in dry N₂ or O₂ spectrum as the background.

Tribofilms accumulated on the sliding track were imaged with atomic force microscopy (AFM; Digital instrument, Multimode). The imaging was done in tapping-mode with Bruker TESPA-V2 probes. Tribopolymerization yield was then estimated by calculated the volume above the reference plane, which was the pristine SS substrate surface outside the sliding track [11]. 3D optical profilometry (Zygo NewView 7300) was used to image the topography of the sliding track to estimate the wear volume after solvent-rinsing of triofilms produced and accumulated from 600 reciprocating cycles of sliding.

A Bruker Hyperion 3000 IR Microscope coupled to an IFS 66/s spectrometer was used for IR analysis. A reflective objective lens 15× (NA=0.4) was used to analyze an area of 50×50 μm². The IR spectra were collected with 4 cm⁻¹ resolution and averaged over 400 scans. For Raman analysis, a Horiba LabRam HR Evolution Vis-NIR system with an objective lens 100× (NA=0.9) was used. In Raman data collection, the acquisition time was 1s and the data were accumulated 10 times. Elemental analysis of the tribofilm via energy-dispersive x-ray (EDX) mapping was carried out using an Apreo S system (Thermo Fisher Scientific) with an electron accelerating voltage of 15kV.

Computational Methods

Molecular dynamics (MD) simulation was used to study the adsorption of cyclohexane, cyclohexene, and methylcyclopentane on amorphous Fe₂O₃ and Fe₃O₄ surfaces. The surface of a stainless-steel sample is known to be covered with a thin oxide layer that contains both chromium oxides and iron oxides. Analysis of such oxide layer on stainless-steel using SEM/EDX and XPS in previous literature has shown the iron content to be at least three times higher than chromium content after the mechanical polishing [56, 57]. Also, ex-situ XPS and TEM analysis of wear tracks formed on bearing steel revealed the presence of FeO, Fe₂O₃, Fe₃O₄ at the surface [58, 59].

Therefore, given the limitations of reactive MD simulations (size scale and availability of potentials), the surface of steel is usually approximated as iron oxide (Fe_2O_3 and Fe_3O_4) [58, 60-62]. Two model systems were designed using QuantumATK [63], one for monolayer coverage and the other for sub-monolayer coverage on the iron oxide. The model for monolayer coverage contained 100 molecules of one of the three precursors, while the system for sub-monolayer coverage contained 30 molecules.

The amorphous iron oxide slabs were created using a heat and quench method that involved heating a crystalline Fe_2O_3 or Fe_3O_4 slab to 4000 K and then cooling it back to room temperature. Next, a vacuum region was inserted on top of the slabs to create surfaces. The amorphous surfaces were then passivated through reactions with water molecules until the number of reactions between the water and the surface reached steady state. The final dimensions of the amorphous slabs were $5 \text{ nm} \times 5 \text{ nm} \times 1.3 \text{ nm}$ (length $\times$ width $\times$ thickness). The positions of atoms at the bottommost 0.4 nm of each slab were fixed. The organic molecules were placed randomly about 1 nm above the surface.

The simulation process started with energy minimization, followed by dynamic simulations of thermal equilibration at 300 K. Then the system temperature was increased to 450 K at 0.1 K/ps heating rate. This heating rate has been used previously to capture the adsorption process of tricresyl phosphate [64]. A repulsive wall was placed at the top of the simulation box to prevent atoms from leaving the simulation box. The canonical ensemble (NVT) was applied to all unconstrained atoms and charge equilibration was performed throughout the simulation. The initial simulation box dimensions were $5 \times 5 \times 6 \text{ nm}^3$ with periodic boundary conditions along the surface and fixed boundaries in the surface-normal direction.

The interactions between atoms were modeled using the ReaxFF force field [65, 66] with a set of parameters previously developed for Fe/P/O/C/H [67]. This force field has previously been used

to simulate phosphorus-containing organic molecules on Fe, Fe₂O₃, and Fe₃O₄, where the adsorption and dissociation energies were reproduced accurately [62, 64, 67]. The time step for dynamics was 0.25 fs. All simulations were performed using the Large Atomic/Molecular Massively Parallel Simulation (LAMMPS) software [68]. Postprocessing was carried out using in-house python scripts and OVITO software [69].

Results and Discussion

Adsorption of precursors on SS surface in VPL condition

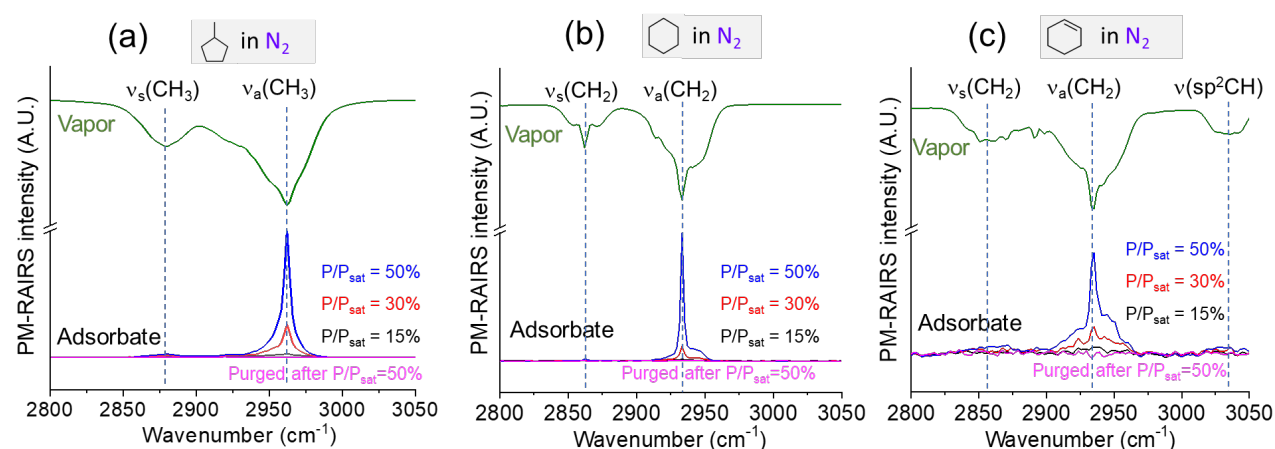


Fig. 1 PM-RAIRS spectra of (a) methylcyclopentane, (b) cyclohexane, and (c) cyclohexene adsorbed on the stainless-steel surface at $P/P_{\text{sat}}=15\%$ (black), 30% (red), 50% (blue) and then after purging out organic vapor with N₂ (magenta). For comparison, the vapor phase spectrum of each precursor (green) is also shown. Above 50% P/P_{sat} , the vapor phase signal was saturated in our in-situ cell, so PM-RAIRS measurement could not be done. The PM-RAIRS spectra of the same precursors measured in O₂ as well as the PM-RAIRS spectra measured with a gold substrate are shown in Figure S2. (Color figure online)

First, it is important to know how precursor molecules supplied through the vapor phase are adsorbed on the substrate surface. For that purpose, PM-RAIRS analysis was performed since this technique could selectively detect the vibrational spectrum of molecular species adsorbed on metal surfaces that are in equilibrium with the same molecules in the gas phase [54]. Figure 1 shows the

PM-RAIRS spectra of methylcyclopentane, cyclohexane, and cyclohexene adsorbed on the SS surface. For comparison, the vapor phase spectra of the precursors are also plotted in Figure 1.

In Figure 1a, the gas phase spectrum of methylcyclopentane shows both symmetric and antisymmetric stretch modes of the CH₃ group at 2878 cm⁻¹ and 2962 cm⁻¹, respectively, along with broad side bands or shoulders due to rovibrational excitations [70]. In contrast, the PM-RAIRS spectra of the methylcyclopentane adsorbed on the SS surface show only one sharp peak at 2962 cm⁻¹, which is the asymmetric stretch (ν_a) mode of CH₃, and the symmetric stretch (ν_s) peak of CH₃ is negligible at 2878 cm⁻¹. The same trend was observed in the higher-resolution PM-RAIRS spectra of methylcyclopentane adsorbed on the Au surface (Figure S2). On metallic surfaces with free electrons in the conduction band, only the surface-normal component can be detected in PM-RAIRS and the vibrational mode parallel to the surface is not detected due to the screening by the image charge in the substrate [71]. Thus, the absence of the CH₃ symmetric stretch peak means that the CH₃ side group of methylcyclopentane is parallel to the surface. In the PM-RAIRS spectra of the methylcyclopentane adsorbed on SS, side band tails with small intensities due to rovibrational broadening are still noticeable around the CH₃ asymmetric stretch peak. The CH₂ asymmetric vibration peak is not observed at ~2935 cm⁻¹, because its IR absorption cross-section is small (so its intensity is much smaller than the CH₃ asymmetric peak in the vapor phase spectrum).

In the PM-RAIRS spectra of cyclohexane adsorbed on the SS surface shown in Figure 1b (and on Au in Figure S2 as well), the CH₂ asymmetric peak (ν_a) is very strong at 2935 cm⁻¹. The CH₂ symmetric peak (ν_s) of the adsorbate spectrum is negligible at 2860 cm⁻¹, while it is quite strong in the gas phase spectrum (again with the broad rovibrational bands in both side of the peak). In the case of cyclohexene (Figure 1c), the stretch mode of the sp² C-H group can be seen at ~3040 cm⁻¹ in the vapor phase spectrum, but this peak is very weak in the PM-RAIRS adsorbate spectrum.

1 This means that the C=C double-bond of cyclohexene is preferentially parallel to the surface.
 2 Similar to the methylcyclopentane case, the weak rovibrational side bands are evident around the
 3 CH₂ asymmetric stretch peak in the PM-RAIRS of cyclohexane and cyclohexene adsorbed on the
 4 SS surface.

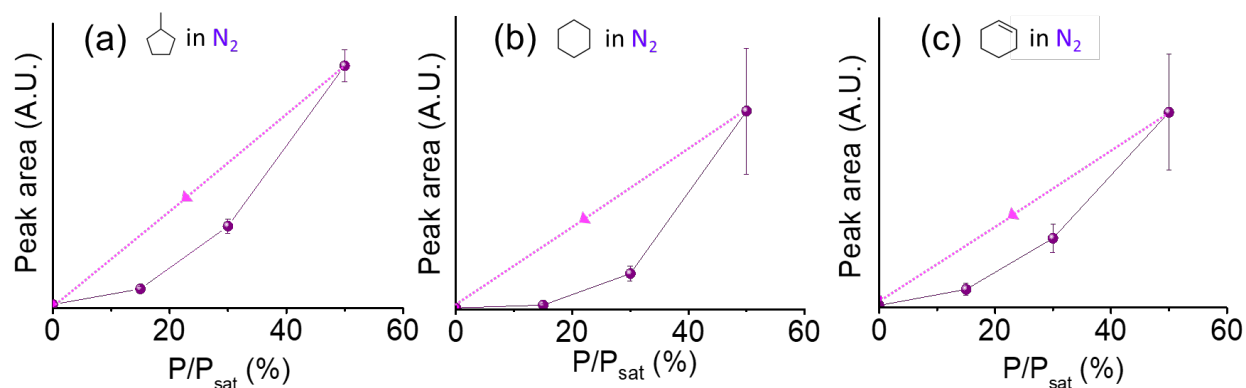


Fig. 2 Peak areas of the C-H stretch modes of the adsorbate spectra of (a) methylcyclopentane, (b) cyclohexane, and (c) cyclohexene as a function of relative partial pressure (P/P_{sat}). The arrow (Magenta) indicates the data measured upon purging of the vapor after $P/P_{\text{sat}}=50\%$ measurement. Error bars are the standard deviation from three different measurements.

In Figure 2, the peak areas of the PM-RAIRS spectra are plotted as a function of relative partial pressure (P/P_{sat}) of each precursor molecule in the gas phase. The PM-RAIRS peak area is proportional to the surface coverage; thus, this plot is effectively equivalent to the adsorption isotherm [72]. The maximum P/P_{sat} employed in this study was 50%; beyond this, the vapor phase signal of the PM-RAIRS measurement was saturated. In this P/P_{sat} range, the adsorbate signal intensity (peak area) increases nonlinearly with a concave curvature [73-75]. This is characteristic of a type-III adsorption isotherm, which is observed when the adsorbate-substrate interaction is weaker than the adsorbate-adsorbate interaction [73, 76]. When the precursor vapor was purged out, the PM-RAIRS signal decreased to the initial baseline, indicating that there was no residue or chemisorbed species on the SS substrate surface. In other words, the SS surface was inert, i.e., did

not react with the precursor molecules studied here at room temperature. All molecules were physisorbed in the absence of associated shear force, suggesting that the interaction between cyclic hydrocarbon and SS is primarily governed by Van der Waals force; thus, any species remaining on the surface after frictional shear must be formed via tribochemical reactions.

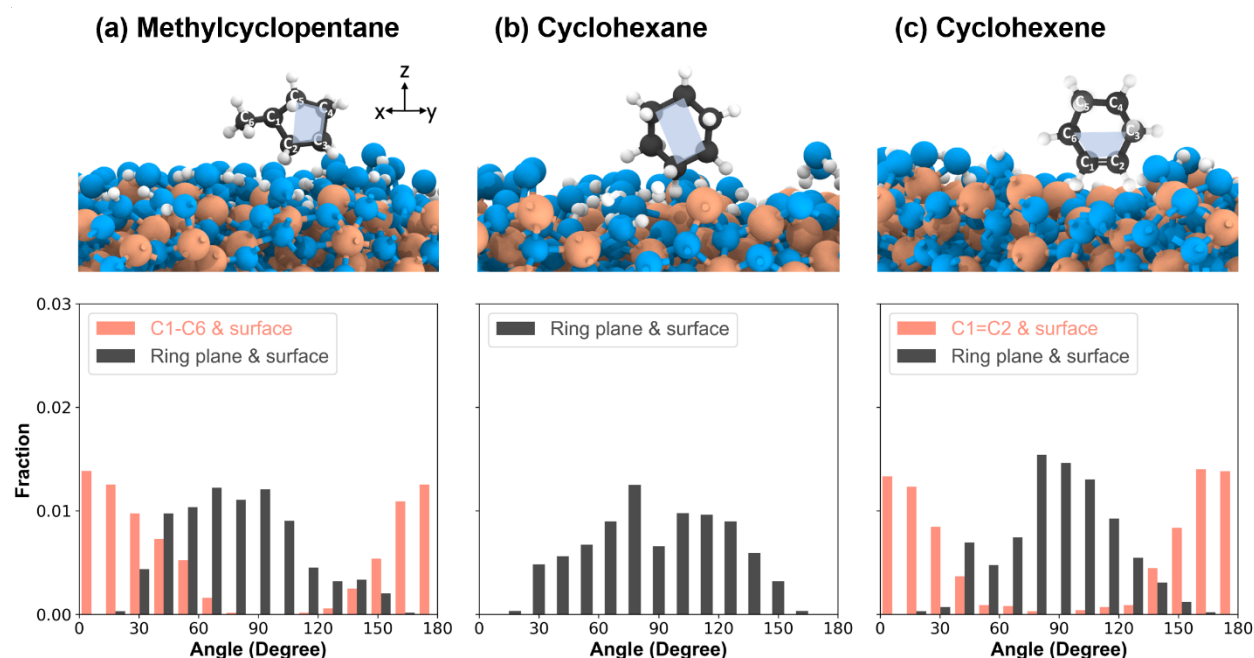


Fig. 3 MD simulation results of (a) methylcyclopentane, (b) cyclohexane, and (c) cyclohexene on an amorphous Fe_2O_3 surface and sub-monolayer coverage. The upper row of the figure shows simulation snapshots of representative adsorbed molecules. The white, black, blue, and brown spheres represent H, C, O, and Fe atoms, respectively. The C atoms in methylcyclopentane and cyclohexene are numbered from 1 through 6 according to IUPAC convention. The blue trapezoid inside a molecule shows the four atoms used to define the plane of the ring. The black bars in the bottom row represent the distributions of the ring plane tilt angle, i.e., angle between the surface (XY plane) and the ring plane, while the orange bars represent the distributions of the angle between the surface and the C1-C6 methyl group side chain in (a), or C1=C2 double bond in (c).

To better understand the molecular adsorption geometry, reactive MD simulations were carried out simulating the adsorption process of the three precursor molecules on iron oxide surfaces. No chemisorption of the molecules was observed on stoichiometric hematite (Fe_2O_3) and magnetite

(Fe₃O₄) surfaces in the reactive simulations; only molecular physisorption occurred. The orientation of the physisorbed molecules were investigated by analyzing the ring plane tilt angle of those molecules with respect to the surface. Further, the positions of the C1-C6 side chain of methylcyclopentane and C1=C2 double bond of cyclohexene were characterized by analyzing the angle they made with the substrate surface. The trends observed in the results for monolayer coverage on Fe₂O₃ and Fe₃O₄, shown in Figure S3, were similar to the trends observed in the results for simulations with Fe₂O₃ surface in sub-monolayer coverage, which is shown in Figure 3.

In all simulations, the orientation angle distributions of the C1-C6 side group of methylcyclopentane and the C1=C2 double bond of cyclohexene (Figure 3, Figure S3, orange bars) are centered around 0° and 180°, which is consistent with the experimental finding from the PM-RAIRS analysis (Figure 1). A very weak band in the C=C double bond region in the PM-RAIRS spectrum of the 50% P/P_{sat} case was observed (Figure 1c). This observation was supported by the MD simulation results that some C=C bonds were tilted away from 0 and 180°. Although quantitative correlations between the PM-RAIRS signal intensity and the tilt angle distribution from MD cannot be made, the C=C peak intensity relative to the CH₂ asymmetric mode was quite small in the PM-RAIRS spectra of adsorbates compared to the gas phase spectrum (Figure 1c), suggesting that most of the C=C double bonds were laying parallel to the surface. The distributions for the ring plane tilt angles with respect to the surface in Figure 3 and Figure S3 (black bars) averaged around 90°, suggesting that the precursor molecules adsorbed on oxide surfaces were tilted. This is somewhat different from the cryogenic temperature condition in which cyclic organic molecules typically adsorb with their molecular planes parallel to the surface [77]. All distributions reported in Figure 3 and Figure S3 have standard deviations of at least 25°. Such broad distributions are probably consequences of dynamic interactions among adsorbates which are in

equilibrium with the gas phase molecules at 300 K. This is because the interactions between adsorbates are stronger than interactions with the substrate, which is the characteristic of type-III adsorption isotherm.[73, 76] The dynamic equilibrium with the gas phase molecules may explain the presence of weak rovibrational features in the PM-RAIRS spectra of adsorbate species (Figure 1) which are absent in the spectra of adsorbates on metal surfaces at cryogenic temperatures [78-80].

VPL efficiency and tribopolymerization yield

When the molecule of interest shows the type-II adsorption isotherm, the VPL study is typically carried out in the P/P_{sat} condition at which the formation of monolayer coverage is assured [72, 81]. However, due to the type-III adsorption isotherm (Figure 2), it could not be determined the P/P_{sat} forming the monolayer coverage of precursors on the clean SS surface [72]. Therefore, we conducted VPL experiments of cyclohexene in N_2 at 15%, 30% and 60% P/P_{sat} , and the results are shown in Figure 4. The friction coefficient at 15% P/P_{sat} was 0.35, which was higher than at 30% and 60% P/P_{sat} (around 0.23), but still lower than in the precursor-free environment. Although the wear volume per length was similar at 15%, 30%, and 60% P/P_{sat} , the sliding track at 15% P/P_{sat} ($S_q = 0.18 \mu\text{m}$) was rougher than that at higher P/P_{sat} ($S_q = 0.04 \mu\text{m}$), implying that the precursor partial pressure (or adsorbate surface coverage) was not high enough to readily form tribopolymers which protected the surface from mechanical wear. When P/P_{sat} was increased from 30% to 60%, the reaction yields increased because there were more reactant molecules adsorbed on the surface (Figure S4). Furthermore, it was empirically found that when P/P_{sat} was 30% or above, all three precursors provided sufficient lubrication, as determined by the ability to suppress wear of the substrate in dry N_2 environment [72]. Since the focus of this study was to test the dependence of precursor molecular structure on tribochemistry, we performed all tribochemical measurements at

$P/P_{\text{sat}} = 30\%$. Since the adsorbate-adsorbate interaction is favored (as implied from the type-III adsorption isotherm in Figure 2), it was expected that once tribopolymerization was initiated, leaving a small amount of polymer in the sliding track, the precursor vapor would readily absorb into the polymer, facilitating further reactions in subsequent sliding cycles [11]. Also, it is commonly known that organic vapors with molecular structures similar to a polymer can readily dissolve (or absorb) into the polymer and act as a plasticizer [82]. This effect has been confirmed in our previous study of tribopolymerization of α -pinene of the tribopolymer [11].

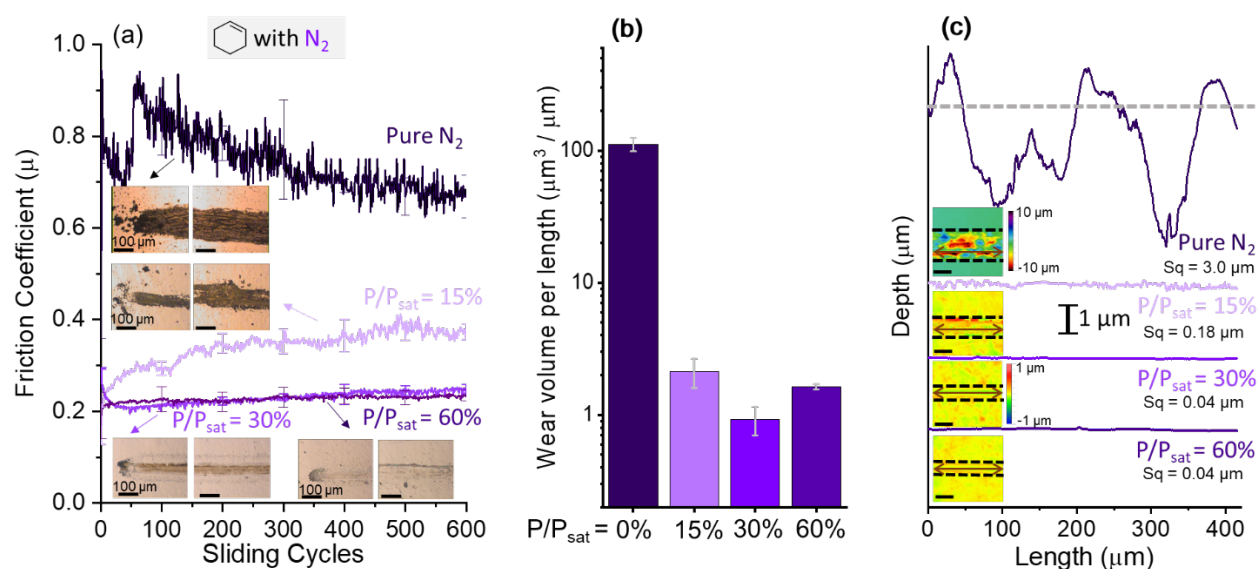


Fig. 4 (a) Friction coefficient measured on SS in dry N₂ without and with 15%, 30%, and 60% P/P_{sat} of cyclohexene. Optical microscope images of the sliding tracks formed in each vapor environment are also shown. (b) Wear volume per length of the sliding track measured with images taken by 3D profilometry after removing the tribopolymers with acetone. (c) Depth profiles along the sliding tracks formed in different vapor environments. The root mean square roughness (S_q) of each slide track is also reported.

Figure 5a compares the coefficient of steady-state friction of the self-mated 440C SS surface in different vapor conditions. Figure 5b depicts the wear volume per reciprocating sliding cycle (i.e.,

1 wear rate) calculated after 600 bidirectional sliding at the applied contact stress of ~ 450 MPa. In
2 the absence of precursor vapor, the coefficient of friction was around 0.7, and the surface exhibited
3 severe wear [53, 72]. When significant wear occurred, the sliding track appeared dark in the optical
4 image due to light scattering from the rough surface, and particulate debris were accumulated
5 around the sliding track (Figure S5). In N_2 and H_2 environments, the presence of all three
6 precursors tested at $P/P_{\text{sat}} = 30\%$ reduced the friction coefficient to approximately 0.23, which was
7 close to a typical value reported for VPL of organic molecules [29, 81]. The friction coefficient
8 gradually reached to a steady-state value within 50 cycles and stayed constant until stopping the
9 measurement at 600 cycles (Figure S6). The wear volume per length also decreased by about three
10 orders of magnitude compared to the precursor-free environment (Figure 5b; details about the wear
11 calculation in Figure S7). In addition, triboproducts with iridescent color could be seen in optical
12 microscopy images, which is typical of polymeric tribofilms with varying thickness [11]. When
13 O_2 was used as the carrier gas, methylcyclopentane and cyclohexane did not show any significant
14 change in friction as compared to the precursor-free environments (Figure 5a) and wear volumes
15 were about two orders of magnitude higher than in N_2 and H_2 environments (Figure 5b). Only
16 cyclohexene could provide sufficient VPL along with formation of lubricious tribofilms that could
17 be seen with optical microscopy.

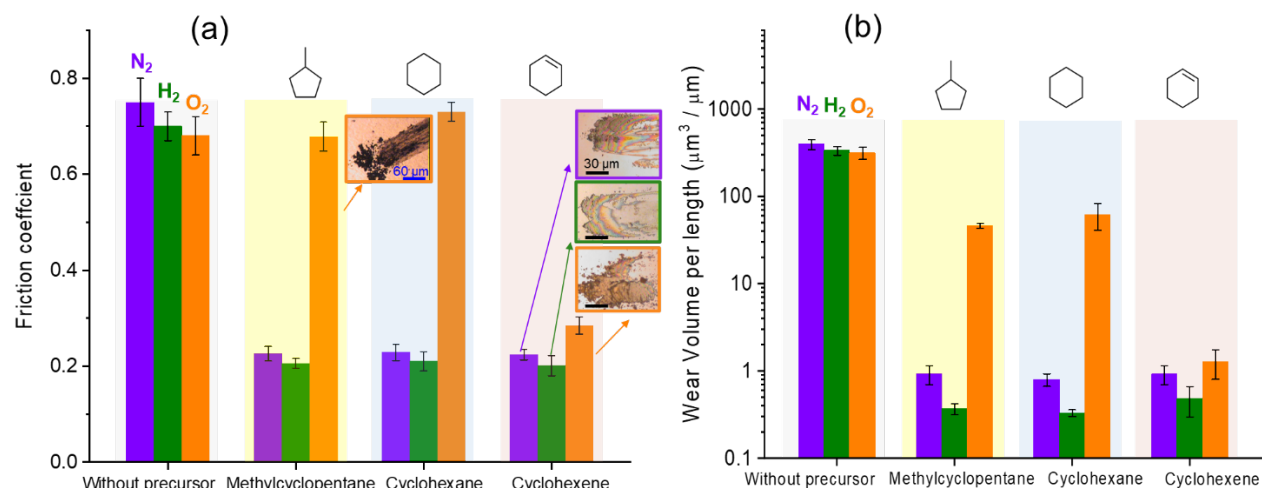


Fig. 5 (a) Friction coefficient measured on SS in dry N_2 , O_2 , and H_2 without and with 30% P/P_{sat} of methylcyclopentane, cyclohexane, and cyclohexene. The error bars are standard deviations from more than five independent measurements. The optical microscope images show wear tracks formed in cyclohexane test in O_2 , and tribopproducts produced from cyclohexene and piled up at one end of the sliding track; images of other precursors are not shown. (b) Wear volume on the slide track measured with optical profilometry after 600 reciprocating cycles and removing tribopproducts with acetone.

Since the pristine SS surface was chemically inert in the absence of any frictional shear in the vapor environments tested (Figures 1 and 2), the tribofilms can be attributed to the product of tribopolymerization of physisorbed molecules taking place upon frictional shear by the counter-surface. The tribopolymerization yield was determined by estimating the volume of the tribofilm above the reference plane using tapping-mode AFM (details about the yield calculation in Figure S7). Figure 6a shows AFM images of the endpoints and middle of sliding tracks after tribopolymerization reactions of cyclohexene in N_2 , O_2 , and H_2 environments. The AFM images of tribofilms produced from the methylcyclopentane and cyclohexane precursors in N_2 and H_2 environments are shown in Figure S8.

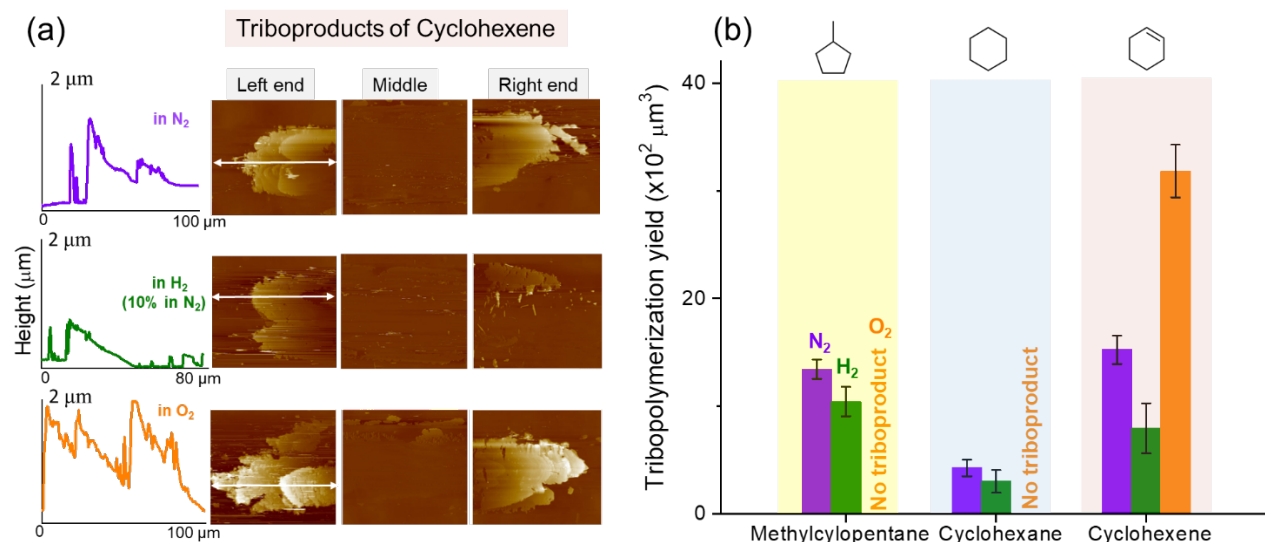


Fig. 6 (a) AFM images ($100\ \mu\text{m} \times 100\ \mu\text{m}$ in N₂ and O₂ or $80\ \mu\text{m} \times 80\ \mu\text{m}$ in H₂) of the left end, middle, and right end of the slide track after 600 reciprocating cycles of interfacial sliding in 30% P/P_{sat} cyclohexene in N₂, H₂, and O₂ environments. The height profiles of the products at the left ends are also shown. (b) Total amount of triboprecipitates was calculated by integrating the volume above the substrate surface plane. The error bars are standard deviations from three independent measurements.

Figure 6b compares the tribopolymerization yields at the same applied load, sliding speed, and sliding distance for different precursor molecules in inert (N₂), reducing (10% H₂ in N₂), and O₂ gas environments. The amount of tribopolymer material adhered to SS ball was negligible compared to that on the substrate, so only the volume of tribopolymers on the substrate were calculated (Figure S9). In N₂, cyclohexane showed the lowest yield among the three precursors tested. In H₂, the overall yields decreased by ~50% as compared to the inert gas environment, but the relativity trend among three precursor molecules was the same as the N₂ case. In O₂, methylcyclopentane and cyclohexane did not produce any measurable amount of tribopolymer, and only cyclohexene produced the tribopolymer. The tribopolymerization yield of cyclohexene in the O₂ environment was about ~50% higher than that in the N₂ environment.

Chemical analysis of tribopolymerization products

The ends of the sliding tracks, where tribopolymerization products were accumulated, were analyzed with EDX mapping. Figure 7 compares the elemental compositions determined from EDX mapping of the track ends after VPL testing of the three precursors for 600 reciprocating cycles in inert (N_2), reducing (10% H_2 in N_2), and oxidizing (O_2) environments. As a reference, the chemical composition of the 440C SS measured outside the sliding track is also shown [83]. In the absence of precursor vapors, EDX analysis revealed the uptake of a large amount of oxygen without an increase in carbon. This must be due to oxidation of wear debris formed during shearing [17, 50]. It is possible that the wear debris was oxidized by a trace amount of oxygen in the test environment during the tribotesting or by air during the sample transfer for ex-situ analysis.

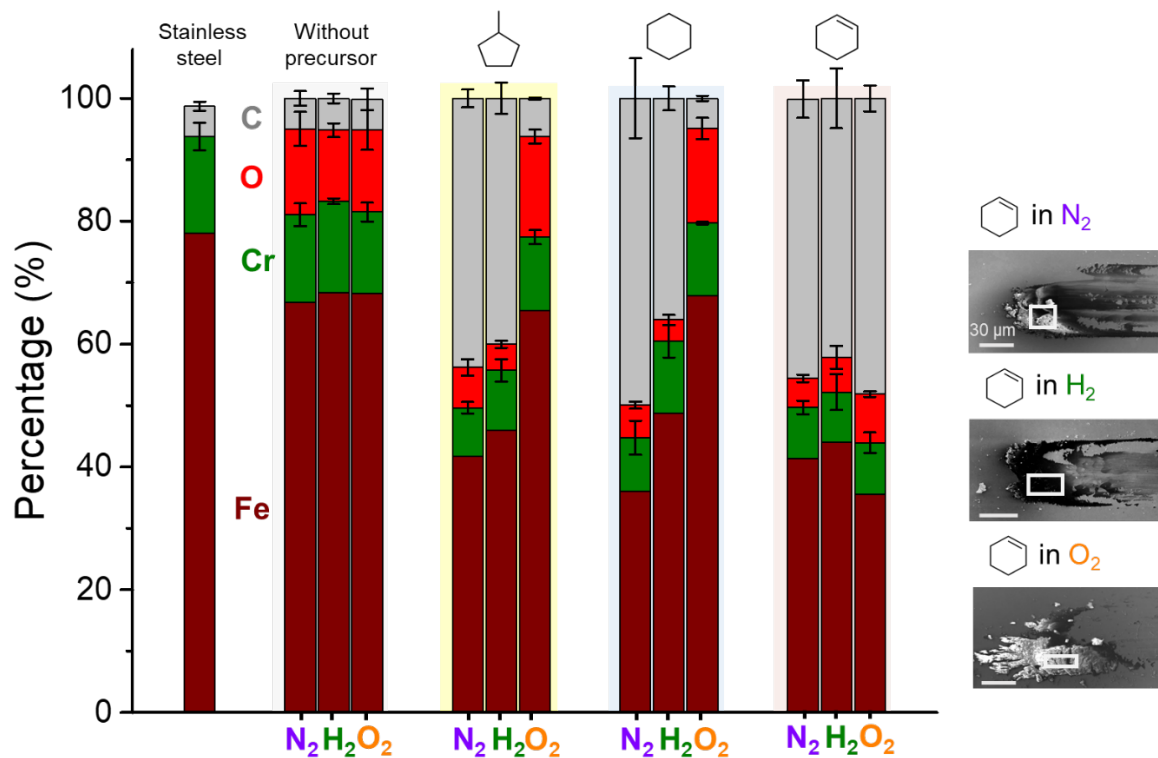


Fig. 7 Elemental composition calculated from EDX mapping of the tribofilm region at the end of the sliding track formed after 600 reciprocating cycles in 30% P/P_{sat} of precursor vapors in inert

(dry N₂), reducing (10% H₂ in N₂), and oxidizing (dry O₂) gas environments. The error bars are standard deviations from three different sliding tracks. Examples of analyzed areas are identified by white boxes in the SEM images shown in the right. More examples of EDX mapping at various locations for one sliding track are shown in Figure S10.

In the cases of methylcyclopentane and cyclohexane in O₂, the chemical compositions detected with EDX are similar to the severe wear cases observed in the friction test without precursors. This is consistent with the inefficiency of VPL by these precursors in O₂, as shown in Figure 5. In the cases where tribofilms were formed (Figure 6) and friction and wear were greatly reduced (Figure 5), EDX indicated the accumulation of carbon-containing species at the ends of sliding tracks. The iron and chromium signals in these regions are primarily from the substrate beneath the tribofilms, as the probe depth of EDX is larger than the tribofilm thickness (less than 2 μm; Figure 6) [84, 85]. EDX also found the presence of oxygen in tribofilms formed by oxygen-free precursors in N₂ and H₂ environments. Tribochemical reaction pathways studied by ReaxFF-MD suggested that methylcyclopentane, cyclohexane and cyclohexene react with surface oxygen to form the final triboproducts [86]. Determining whether these oxygen species are due to wear debris or incorporated into the tribopolymers required molecular spectroscopy.

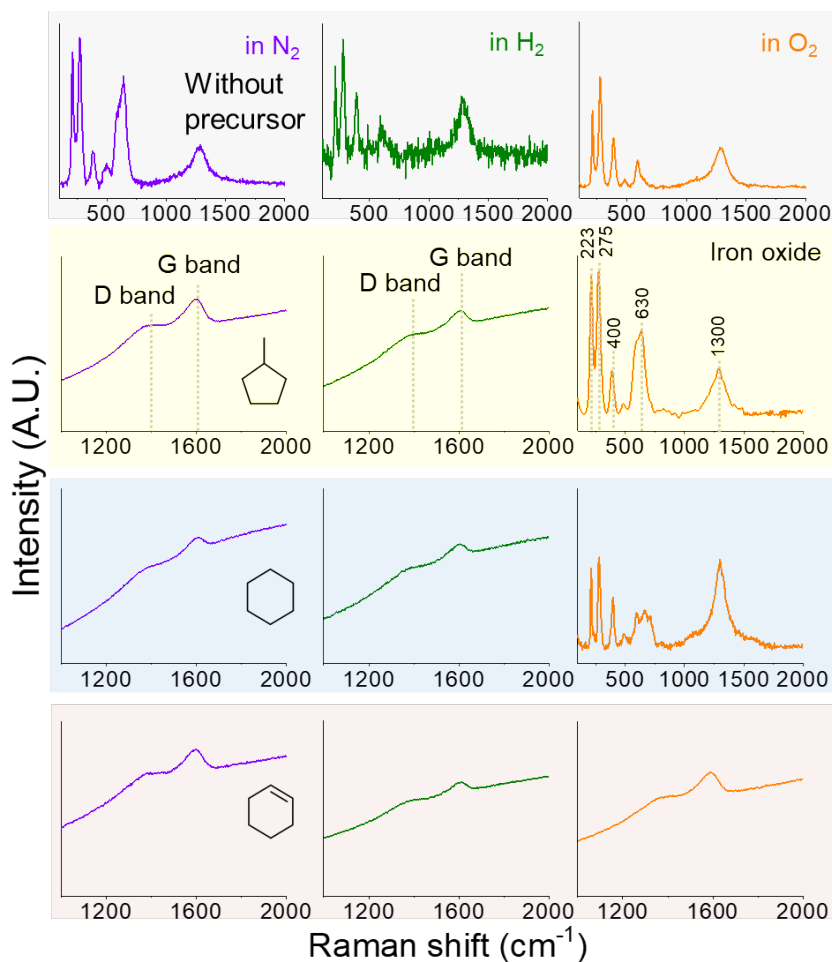


Fig. 8 Raman spectra collected at the end of the sliding tracks where tribofilms or wear debris were piled up after 600 reciprocating cycles in 30% P/P_{sat} of precursor vapors in inert (dry N₂), reducing (10% H₂ in N₂), and oxidizing (dry O₂) gas environments. Excitation wavelength = 532 nm; laser power = 2.05 mW; objective lens = 100x (NA = 0.9). The reference spectra of hematite (Fe₂O₃) and magnetite (Fe₃O₄) are shown in Figure S11.

In the tribochemistry literature, Raman analysis has been frequently employed for vibrational spectroscopic analysis of tribofilms formed from organic precursors [9, 27, 30-32, 34-36, 87-90]. Many previous studies reported the formation of a-C or hydrogenated DLC due to frictional activation of organic precursors and hypothesized that these carbon films formed *in situ* are responsible for lubrication and wear prevention [9, 27, 34-36, 88, 90]. To compare with such previous reports, we performed micro-Raman analysis of the tribofilms (Figure 8).

1 In the wear tracks formed in the absence of precursor molecules in the gas phase, the spectral
2 features characteristic of hematite (Fe_2O_3) and magnetite (Fe_3O_4) were observed (Figure S11) [91,
3 92]. After VPL testing for methylcyclopentane and cyclohexane in O_2 , the slide track also showed
4 the same oxide bands, although the relative intensities of the peaks at 630 cm^{-1} and 1300 cm^{-1} were
5 slightly different. These results confirmed that methylcyclopentane and cyclohexane could neither
6 prevent the wear of SS surface (Figure 5) nor produce tribopolymers (Figure 6) in the O_2
7 environment.

8 As can be seen in Figure 8, all tribofilms identified in with AFM (Figure 6) exhibited Raman
9 spectra with broad D-band and G-band characteristic of a-C or H-DLC. Although this might be
10 viewed as ‘consistent with previous literature’, we concluded that the vibrational spectral features
11 of a-C or H-DLC were due to photochemical degradation of tribopolymerization products based
12 on the following control experiments. Details of the control experiments conducted to dispute the
13 hypothesis of tribochemical synthesis of a-C or H-DLC are given elsewhere [40].

14

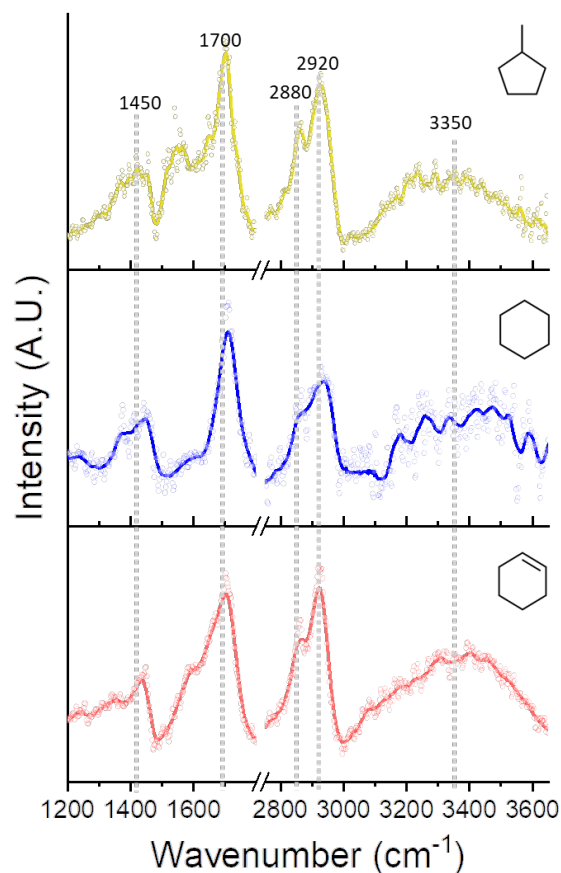


Fig. 9 FTIR spectra of tribopproducts produced after tribotesting in VPL of methylcyclopentane, cyclohexane and cyclohexene in N₂. Micro-IR objective lens = 15x; analyzed area = 2500 μm². (Color figure online)

To obtain molecular spectral features without the photochemical artifact, tribopolymers produced from methylcyclopentane, cyclohexane, and cyclohexene in the N₂ environment were analyzed with IR spectroscopy coupled with microscopy. As shown in Figure 9, all tribopolymers formed from these three precursors exhibited similar vibrational spectral features: broad bands at ~1450 cm⁻¹ which can be attributed to CH₂ bending modes and two bands at 2880 cm⁻¹ and 2920 cm⁻¹ that could be ascribed to symmetric and asymmetric stretches of alkyl groups, respectively. There was no discernable peak at ~3030 cm⁻¹ in the IR spectrum of the tribopolymers formed from cyclohexene, indicating that the C=C double-bonds are all converted to single bonds or dissociated

1 during the tribopolymerization process [29, 86]. All tribopolymers showed a strong peak at ~ 1700
2 cm^{-1} and a broad band spanning from 3100 cm^{-1} up to 3700 cm^{-1} , indicating that they have carbonyl
3 ($\text{C}=\text{O}$) and hydroxyl ($\text{O}-\text{H}$) groups. The precursor molecules do not have any oxygenated
4 functional groups. Thus, they must come from the substrate. In fact, previous tribochemistry
5 studies of α -pinene and pinane have also reported that the tribopolymers contained oxygenated
6 functional groups [11, 20, 29, 93, 94], and those groups must originate from the involvement of
7 surface oxygen atoms in tribochemical reactions [22, 23, 29].

9 *Molecular structure dependence and environmental effect of tribopolymerization*

10 In inert gas environment (N_2), the tribopolymerization yield was lower for cyclohexane as
11 compared to methylcyclopentane and cyclohexene (Figure 6). It is known that, among
12 cycloalkanes, cyclohexane with the 6-membered ring has the lowest ring strain [95]. Thus, our
13 result is consistent with the hypothesis that the ring strain of a precursor plays a role in
14 tribochemical activation [51]. Reactive MD simulations have shown that, prior to tribochemical
15 reaction, reactants undergo some physical deformation deviating from their equilibrium
16 conformation [22, 29]. ~~It is conceivable that the molecules with higher internal strain energy would~~
17 ~~be more susceptible to such deformation.~~ Therefore, the molecules with higher internal strain
18 energy have higher reactivity, which may be related to their susceptibility to physical deformation.

19 In the reducing environment (H_2), the relative effect of molecular structure of precursors was
20 similar to the trend found in the N_2 environment, but the overall yield was lower than the N_2 case
21 (Figure 6). Reactive MD simulations suggested that the initial tribochemical activation step of
22 cycloalkane involves dehydrogenation reaction by the surface oxygen [86]. In the presence of H_2
23 in the surrounding gas, it is likely that such dehydrogenation reactions may be suppressed because,
24 even if surface oxygens are activated by frictional shear, they could react with H_2 impinging from

the gas phase, forming stable hydroxyl groups. Our previous study showed that fully hydroxylated silica surface is not highly reactive, as compared to dehydroxylated surface, toward tribochemical reaction of another organic precursor (α -pinene) [23].

In the oxidative environment (O_2), all three molecules physisorb as readily as in N_2 (Figure S2), but only the tribochemical reactions of cyclohexene can be activated effectively. In the case of cyclohexene, the oxidative chemisorption can occur at shear-activated surface sites through the C=C double bond [29, 86]. Once the precursor molecule is chemisorbed, it can be associated with other molecules during sliding [24, 28, 72, 81, 86]. The fact that tribochemical reactions of cycloalkane are negligible in O_2 indicates that dehydrogenative chemisorption is suppressed or passivated if the reactive surface sites are reacted with O_2 impinging from the gas phase. The competition of reaction sites between cycloalkane and O_2 is supported by the results shown in Figure S12. When the partial pressure of cyclohexane was increased from 30% to 45% or 80% in the O_2 environment, the friction coefficient, wear volume, and Sq of sliding track decreased, which was accompanied by formation of tribopolymers. But the tribopolymerization yield was still quite low, compared to the N_2 environment. Even if iron atoms are momentarily exposed at the worn surface, they are likely to be oxidized by O_2 impinging from the gas phase. Overall, the oxygen competed with cycloalkane for reaction sites on SS and, thus, tribochemical reactions of cycloalkane may not occur readily [33, 50, 96-98].

Conclusion

The effects of molecular structure (methylcyclopentane, cyclohexane, and cyclohexene) and ambient gas (N_2 , O_2 , and H_2) on tribochemical reactivity on stainless steel were investigated. Under the experimental conditions in this study, it was found that the more strained molecules (methylcyclopentane and cyclohexene) exhibited higher reaction yield than the nearly-strain-free

molecule (cyclohexane) in all environmental conditions. This supports the hypothesis that the internal ring strain of a molecule can impact tribochemical reactivity. ~~since reacting species with higher internal strain are more susceptible to shear-induced structural deformation deviating from thermodynamic equilibrium conformation.~~

Moreover, tribochemical reactivities in reducing (H_2) and oxidizing (O_2) environments were different to that in an inert (N_2) environment. Hydrogen could impede dehydrogenative reactions of the cyclic hydrocarbons by surface O atoms, and thus the reactivities were suppressed in H_2 as compared to N_2 . In an oxidizing environment, dehydrogenative chemisorption of methylcyclohexane and cyclohexane were impeded, thus preventing the formation of tribopolymers, and resulting in severe wear. In contrast, tribopolymerization of cyclohexene, which could be activated by the oxidative chemisorption of $\text{C}=\text{C}$, was facilitated in O_2 . Vibrational spectroscopic analysis of tribofilms showed that they are polymeric species containing $\text{C}=\text{O}$ and OH groups. The presence of oxygenated groups in the formed tribopolymers supported the previously suggested mechanisms which involved the surface oxygen in the intermediate step.

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