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Heat, Load and Shear Driven Reactions of Di-*tert*-butyl Disulfide on Fe(100)

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Keywords: Mechanochemistry, Shear-Driven Reactions, Film Formation

Abstract

The surfaces of lubricated mechanical components operating under extreme conditions are protected by films that form in the presence of additives in lubricant formulations. Film formation is believed to be accelerated by heat, load, and shear force in the sliding interface, but the individual contributions of these factors are poorly understood. In this study, we use reactive molecular dynamics simulations to deconvolute the effects of heat, load, and shear force on chemical reactions between di-*tert*-butyl disulfide, an extreme-pressure additive in lubricants, and Fe(100), a model approximation of the ferrous surfaces of mechanical components. The reaction pathway is characterized in terms of the number of chemisorbed sulfur atoms and the number of released *tert*-butyl radicals during heat, load and shear stages of the simulation. Chemisorption is limited by accessibility of reaction sites, so shear accelerates the reaction by facilitating movement of radicals to available sites. Analysis of *tert*-butyl radical release in the context of an Arrhenius-based model for mechanochemical reactions shows that shear lowers the energy barrier for reactions, implying that, in lubricated contacts, the effect of shear will be significant at lower temperatures, which are expected to arise under moderate sliding conditions.

Introduction

The surfaces of moving mechanical components are protected from damage during operation by films that form when lubricant additives are present between the sliding surfaces. Analysis of these protective films has shown that they are composed of elements from both the lubricant additives and the surface material [24, 30, 32, 27, 29]. The implication is that the films are formed through chemical reactions between the additives and surfaces. Some of these films do not form or only form very slowly if the surface is simply immersed in a lubricant with additives under ambient to moderate conditions [5, 19, 15]. Accordingly, the common understanding is that these reactions are driven by factors that arise in the sliding contact. Physical factors in sliding contacts include temperature, load and shear force [10, 9, 36, 6]. First, frictional sliding results in heat generation, which can drive film-forming chemical reactions thermally. Second, normal loads on relatively small contact patches can result in high pressures, which place reactants in closer proximity, thereby facilitating chemical reactions. Lastly, shear forces are always present in sliding interfaces and are believed to contribute to film growth through mechanochemical reactions.

Numerous studies have now shown that shear force can drive chemical reactions on surfaces; for example, film growth from reactions between zinc dithiophosphate and steel, [8, 7, 36, 18] cleavage of oxygen and fluorine from graphene, [4] or dissociation of methyl thiolate from a copper surface [1]. These observations are consistent with a modification of the Arrhenius model in which a force applied along the reaction coordinate lowers the energy barrier for a reaction, thus accelerating chemical reactions. Although this model is typically used to describe the effect of normal force, it has been applied to capture shear-driven reactions [33]. However, the mechanism by which shear accelerates reactions is still a subject of active research. For example, it is not known whether shear simply drives reactions to occur faster through the same pathway as observed thermally, or if shear enables reaction pathways that are not available thermally. There is some evidence of the latter from vapor phase lubrication experiments complemented by reactive molecular dynamics simulations [35, 13], but not specifically related to reactions between lubricant additives and surfaces. Studies of additive-surface interactions have suggested that the first step of film formation is additive decomposition, which leads to generation of radicals that interact and react with the surface [5, 15]. Decomposition is believed to be the first reaction step for thermal- and shear-induced films, which is supported by the observation that both films have similar compositions [30, 15, 29]. Therefore, it is difficult to differentiate or isolate the effects of heat and shear on film formation. Further, it is likely that the relative contribution of these two effects depends on interface conditions, and it has been proposed that film formation is thermally driven under extreme pressure conditions and driven by shear under moderate conditions [6].

Protective films frequently contain sulfur, and this element is incorporated in many surface-active additives that are critical components of common lubricant formulations. The sulfur reacts with the surfaces, typically steel, during

operation to form iron-sulfide-based films [28, 22]. However, the mechanisms through which these films form are still poorly understood, due in part to challenges with experimental investigation of additive-surface interactions. This limitation suggests the use of simulations that can capture reaction pathways at the atomic scale. In a previous study, we used reactive molecular dynamics (MD) simulations to study the thermal contribution to film formation for di-*tert*-butyl disulfide on an Fe(100) surface [23]. The simulations were used to identify the thermally driven reaction pathway as follows: S–S bonds in the di-*tert*-butyl disulfide break, S atoms in *tert*-butyl sulfide bind to the Fe(100) surface, and then S–C bonds break enabling the release of *tert*-butyl groups. These steps are consistent with the reaction pathway previously proposed for sulfur-containing molecules and iron, based on previous experimental measurements [11]. Simulations at various temperatures showed that the rate limiting step was the S–C bond scission and that significant detachment of *tert*-butyl radicals did not occur until the temperature was increased to 700 K or higher. However, film formation from organic disulfides has been observed in sliding contacts at significantly lower system temperatures [21, 17, 2], suggesting that other factors in addition to heat contribute to films observed at sliding contacts.

In practice, film formation from di-*tert*-butyl disulfide on ferrous surfaces is likely driven by a combination of heat, load and shear. However, these effects cannot be isolated experimentally since all of them are occurring simultaneously, hidden from view in a sliding interface. The inability to differentiate the roles of individual contributions to film formation limits efforts to develop optimized lubricant additives or additives with application-specific film formation properties. To address this, here we use simulations to deconvolute the effects of heat, load and shear on chemical reactions between di-*tert*-butyl disulfide and Fe(100). Specifically, reactive MD simulations that capture the formation and breaking of covalent bonds are used to characterize the key steps along the reaction pathway leading to film formation.

Method

The initial atomic configurations of di-*tert*-butyl disulfide molecules (Fig. 1a) were obtained from PubChem [16]. These molecules were confined between two bcc Fe(100) slabs were created using Virtual NanoLab [26] and Packmol [20]. Energy minimization and molecular dynamics were performed using the open-source MD code LAMMPS [25]. All visualizations were done using OVITO [34]. Post processing and data analysis were performed using scripts written in Python.

Two bcc Fe(100) slabs with dimensions of $3.4 \times 3.4 \times 1$ nm were created and positioned in the model with a 2 nm gap between them in the z -direction. The Fe(100) surfaces were model approximations of steel on which the iron oxide layer is worn off during sliding. This simplification also facilitated analysis of reaction pathways, which were same everywhere on the surfaces, in contrast to reactions that occur on irregular surfaces such as amorphous iron oxide where

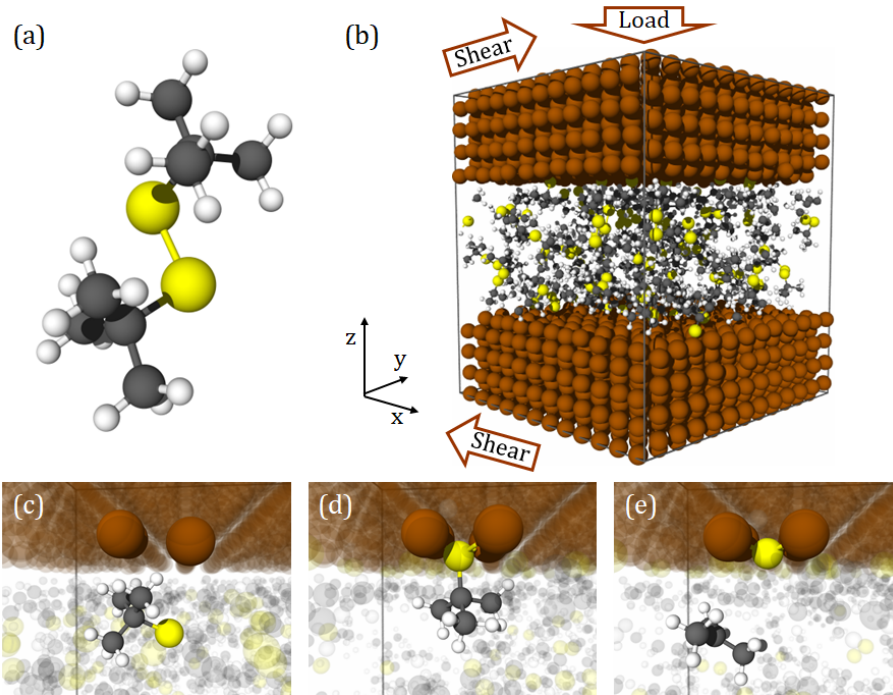


Figure 1: Snapshots of (a) the di-*tert*-butyl disulfide molecule and (b) the simulation domain shortly after the initial equilibration. Close-up views of specific steps in the pathway leading to the formation of iron sulfide are shown in (c) to (e), where all atoms except those involved in the reaction are faded out: (c) di-*tert*-butyl disulfide approaches the iron surface; (d) formation of Fe-S bonds by chemisorption of the *tert*-butyl sulfide radical on the iron surface; and (e) breaking of the S-C bond, leading to detachment of a *tert*-butyl radical. Sphere colors represent yellow – S, gray – C, white – H and brown – Fe.

many different pathways can be observed [14, 12]. Then, 54 di-*tert*-butyl disulfide molecules were randomly distributed in the gap. The model fluid consisted only of additive molecules, i.e., no base oil, to limit the size of the simulation and increase the number of additive-surface interactions. A snapshot of the simulation after the initial equilibration is shown in Fig. 1b. The boundary conditions were periodic in the directions in the plane of the iron surfaces (x and y) and fixed in the surface-normal direction (z). The atoms in the bottom atomic layer of the lower slab and the top atomic layer of the upper slab were treated as rigid bodies to facilitate imposing the desired kinematics to the system.

Atomic interactions were modeled using the ReaxFF force field [3] with a previously developed parameter set for Fe/S/C/H/O [31]. This parameter set was shown to accurately reproduce adsorption energies calculated using density functional theory (DFT) for di-*tert*-butyl disulfide and its radicals on Fe(100) [23].

The temperature was controlled using a Langevin thermostat with a damping parameter of 25 fs, acting only on the two layers of Fe atoms adjacent to the fixed atoms in both slabs. The di-*tert*-butyl disulfide molecules and the three layers of Fe atoms adjacent to these molecules were integrated in the microcanonical ensemble with a time step of 0.25 fs, and their temperature was controlled indirectly via the thermostat applied to the adjacent atoms.

To isolate the effects of heat, pressure, and shear on reactions between the di-*tert*-butyl disulfide and the iron surfaces, simulations were run in three stages. Following energy minimization, simulations without normal load or shear were run for 2 ns each at constant temperatures of 300, 400, 500, 600, and 700 K. After completion of the first stage, a normal load was applied to the atoms in the rigid body of the top wall. The top wall moved in $-z$ -direction in response to this load, reaching a final constant pressure of 1 GPa. All five temperature cases were subject to this pressure for another 2 ns. Keeping the pressure at 1 GPa, the top and bottom iron slabs were then moved laterally in opposite directions at speeds of $v_x = \pm 5$ m/s. The component of the kinetic energy in the z -direction was excluded from the temperature calculation during the load stage and the x -direction component was excluded in the load and shear stages. Shear simulations were run at all five temperatures for 2 ns. During all simulations, the positions and bond orders of the atoms were recorded every 1.25 ps. A covalent bond was identified as a bond order of at least 0.3. The three previously identified key steps in the reaction pathway [23] are illustrated in Fig. 1c–e. The first step, dissociation of the S-S bond, occurs rapidly at all temperatures as soon as the molecules approach one of the surfaces, and chemisorption occurs immediately after, typically within 1–2 ps. Therefore, we tracked the reaction in terms of the latter two steps: chemisorption of *tert*-butyl sulfide and *tert*-butyl radical release. Chemisorption was calculated as the number of S atoms having at least one S-Fe bond. Radical release was calculated from the difference between the number of S-C bonds at the start of the simulation and that number at each time step as the simulation ran.

Results and discussion

Figure 2 shows the number of chemisorbed S atoms and the number of *tert*-butyl radicals released from the surface during the three stages of the simulation at temperatures between 300 and 700 K. Generally, these results show that both chemisorption (Fe-S bond formation) and *tert*-butyl release (S-C bond breaking) were accelerated by temperature, load, and shear. Note that the maximum possible number of chemisorbed S atoms and released *tert*-butyl groups was 108, limited by the number of di-*tert*-butyl disulfide molecules in the system. The trends observed during each stage of the simulation are analyzed in more detail below.

The system was initially subject to heat without load or shear for 2 ns. As shown in Fig. 2a, chemisorption occurred rapidly at the onset of the simulation at any temperature due to the availability of reaction sites on the iron surface.

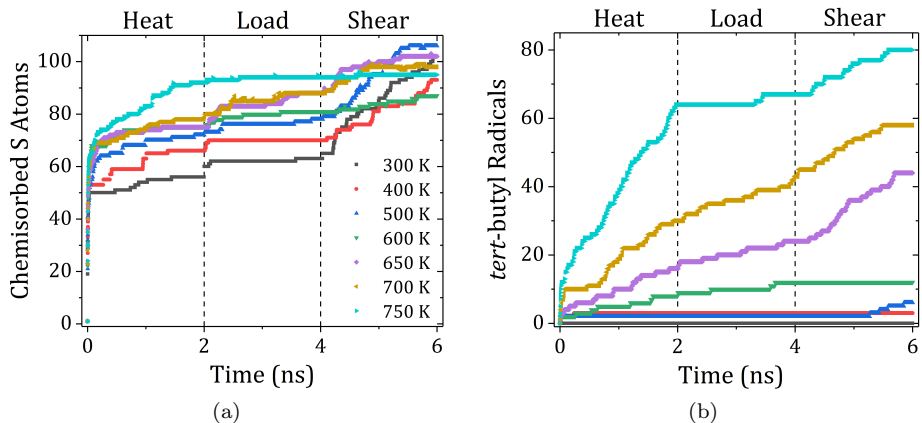


Figure 2: Number of (a) chemisorbed sulfur atoms and (b) *tert*-butyl radicals as functions of time during the heat, load, and shear stages of the simulation at temperatures between 300 and 750 K.

During the heat stage, the number of released *tert*-butyl radicals, shown in Fig. 2b, was relatively small (<3), except at the higher temperatures (≥ 600 K), consistent with our previous study of thermal film growth [23]. At the end of the heat stage, both the number of chemisorbed S atoms and released *tert*-butyl radicals increased monotonically with temperature.

Applying a normal load caused a small, sharp increase in chemisorption, as the *tert*-butyl sulfide groups were forced into nearby available reaction sites. However, the change in number of chemisorbed S atoms during the load stage was relatively small, with an increase of between 4 and 10 atoms relative to the end of the heat stage. Also, the number of chemisorbed S atoms was a monotonic function of temperature at the end of the load stage. The number of *tert*-butyl radicals slightly increased during the load stage, indicating that load does not significantly accelerate this reaction step. At the end of the load stage, additional release of *tert*-butyl radicals were only observed at 600 K and higher.

Finally, when shear was applied, the number of chemisorbed S atoms again increased rapidly, as *tert*-butyl sulfide groups were translated along the surface until they reached available reaction sites. The effect of shear was more significant than that of load, with an increase in chemisorption of between 6 and 39 atoms relative to the end of the load stage. This trend was also evident at some temperatures for the detached *tert*-butyl groups, which exhibited a sharp increase at 700 K at the onset of shear, and at 500 K approximately half-way through the shear stage. Therefore, at the end of the shear stage, detachment of *tert*-butyl radicals was observed at temperatures of 500 K and higher. However, the number of chemisorbed S atoms at the end of the shear stage was no longer monotonic with temperature. This is attributed to the presence of *tert*-butyl

radicals at higher temperatures, which, in some cases, impeded the motion of *tert*-butyl sulfide groups, hindering their ability to reach available reaction sites on the surface.

Considering chemisorption, the results above show that this reaction is accelerated by heat, load, and shear. We observed that all S atoms chemisorbed at the hollow sites on the Fe(100) surfaces. The binding energy for this process has been reported to be -74.1 kcal/mol from DFT calculations and -87.6 kcal/mol from ReaxFF calculations [31]. This is consistent with the rapid chemisorption observed at the start of simulations at any temperature. Therefore, the limiting factor for chemisorption is the ease with which *tert*-butyl sulfide groups can reach reaction sites on the surface. Heat provides more thermal energy that enables molecules to move to available reaction sites, load drives molecules downward toward nearby reaction sites, and shear moves molecules laterally on the surface toward sites further from their original position. Lateral movement was quantified in the simulations as the maximum mass diffusivity of the S atoms in the *tert*-butyl sulfide groups. During the heat stage, the maximum diffusivity was calculated to be 1.2 nm²/ns at 300 K and 26 nm²/ns at 700 K, so thermal motion enabled translation of the radicals. Load did not affect diffusivity at any temperature. Shear, however, significantly increased molecular movement; for example, at 300 K, the diffusivity increased from 1.2 nm²/ns during the heat stage to 160 nm²/ns during the shear stage of the simulation. This is significantly higher than in either of the other two stages, supporting the hypothesis that shear accelerates chemisorption by facilitating movement of molecules to available reaction sites on the surface.

Increasing sulfur coverage on the surface is expected to correspond to lower friction, so the effect of shear to increase chemisorption in our simulations should also correspond to a decrease in friction. To confirm this, the coefficient of friction (CoF) was calculated as the force in the *x*-direction on the fixed atoms of the upper slab divided by the normal load. The CoF was averaged over the first and last 0.5 ns of the shear stage at 300 K. The CoF decreased from 0.25 to 0.11, confirming the beneficial effect of sulfur coverage and the role of shear to cause an increase in that coverage.

The release of *tert*-butyl radicals through breaking of C–S bonds is accelerated by heat and shear, but via a different mechanism than the chemisorption. A previous study of the decomposition of methyl thiolate species on Cu(100) showed that the energy barrier for reaction was lowered by 40% due to shear [1]. Further, complementary DFT calculations of the decomposition process revealed that the methyl group moved laterally relative to the Cu(100) surface during the reaction; since shear force is in this same direction, the reaction can be accelerated by the mechanical force [1]. The results we observed for di-*tert*-butyl disulfide on Fe(100) may be explained by the same phenomena, where a mechanical force acting along the reaction coordinate lowers energy barriers to accelerate reactions.

The model for mechanochemical processes is written as follows [33]:

$$r_y = A \exp\left(-\frac{\Delta E - \Delta E^*}{k_B T}\right), \quad (1)$$

where r_y is the reaction yield, A is a coefficient, ΔE is the activation energy, ΔE^* is the amount by which the energy barrier is reduced by the mechanical force, k_B is the Boltzmann constant, and T is temperature. Taking the natural logarithm, this can be re-written as [35, 13]:

$$\ln(r_y) = \ln(A) - \left(\frac{\Delta E - \Delta E^*}{k_B T}\right) \quad (2)$$

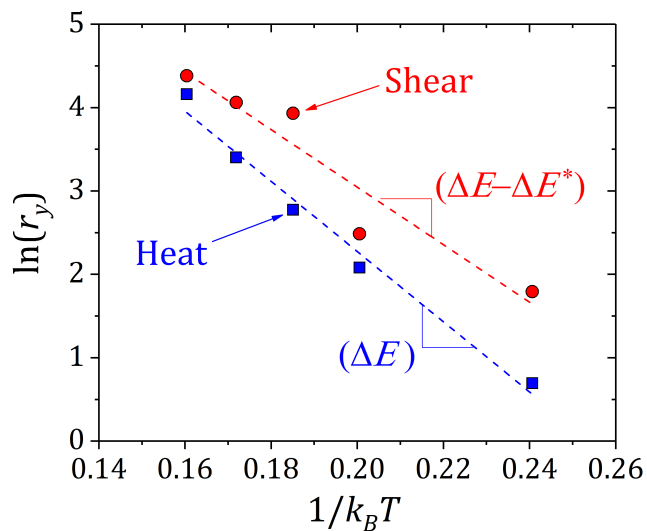
The reaction yield was approximated from our results (Fig. 2b) as the number of *tert*-butyl radicals at the end of each stage of the simulation. Then, the energy barrier ($\Delta E - \Delta E^*$) can be estimated as the slope of a linear fit of $\ln(r_y)$ vs. $1/(k_B T)$, as shown in Fig. 3a.

In the heat stage, there is no mechanical contribution, so $\Delta E^* = 0$. During this stage of the simulations, reactions were observed at 600 K and above. Fitting the data at these temperatures led to a calculated ΔE of 10.1 kcal/mole. In the shear stage, reactions were observed at 500 K and above. These data points were fit to Eq. (2) to give a slope of 8.2 kcal/mole, indicating that $\Delta E^* = 1.9$ kcal/mole. These results show that shear can lower the energy barrier for this reaction. As described previously [1], this is possible because the reaction occurs through lateral movement of the C atom relative to the surface, as shown in Fig. 3b. Shear force acts on the *tert*-butyl sulfide radical in the same direction and so can accelerate the reaction. Since the radical has no preferred orientation in the xy -plane when bonded to the iron surface, shear in any direction will have the same effect.

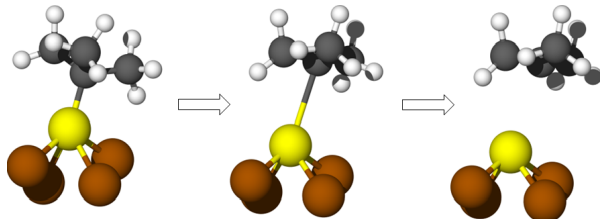
Finally, the results show that the relative contributions of heat and shear depend on temperature. Specifically, as shown in Fig. 3a, at lower temperatures the reaction yield is much higher with shear than without, but this difference is not observed at higher temperatures. This observation is consistent with the suggestion from previous experimental work that protective film formation is thermally driven under extreme pressure conditions (where friction heating is likely to be significant) and driven by shear under moderate conditions (lower frictional heating) [6].

Conclusions

In summary, reactive MD simulations of di-*tert*-butyl disulfide confined between Fe(100) surfaces was used to explore the effects of heat, load, and shear on chemical reactions that are the precursors to film formation. Results showed that all three factors accelerated the key steps in the reaction pathway, S chemisorption and *tert*-butyl radical release. Chemisorption was limited only by the ability of *tert*-butyl sulfide radicals to reach available reaction sites on the Fe(100) surface,



(a)



(b)

Figure 3: (a) Natural log of the reaction yield as a function of inverse temperature for the heat and shear stages of the simulation. The data is fit to Eq. (2) such that the fit slope is the reaction energy barrier. When only heat is available to drive the reaction, the energy barrier is ΔE ; adding shear decreases that barrier by ΔE^* . (b) Representative snapshots from the simulation showing that S-C dissociation occurs through lateral movement of the C atom relative to the surface, enabling shear to accelerate the reaction.

which was facilitated by thermal energy (heat), downward motion toward near sites (load) and lateral motion to further reaction sites (shear). The *tert*-butyl release step was driven by heat and shear, where shear lowered the energy barrier for reaction mechanically. Results confirmed previous suggestions that film formation reactions may be driven thermally and mechanically, where the role of the mechanical force is significant under moderate conditions where frictional heating will be relatively small.

acknowledgement

This work was supported by the Austrian COMET-Program (Project K2, XTri-bology, no. 849109) and carried out at the “Excellence Centre of Tribology” (AC2T research GmbH). The government of Lower Austria supported the endowed professorship tribology at the TU Vienna (Grant no. WST3-F-5031370/001-2017).

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