Probing and Understanding Elementary Steps in Tribochemical Reactions

Alejandro Boscoboinik,¹⁾ Dustin Olson,¹⁾ Heather Adams,¹⁾ Nicholas Hopper¹⁾ and

Wilfred T. Tysoe ^{1)*}

¹⁾ Department of Chemistry and Biochemistry and laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

*Corresponding author: wtt@uwm.edu

The elementary steps in the surface tribochemistry of model lubricant additives is studied in ultrahigh vacuum (UHV) and the stress-dependent reactions rate is measured using a UHV atomic force microscope (AFM) and is accurately modeled using first-principles density functional theory (DFT) calculations.

Keywords: tribochemistry, quantum calculations, atomic force microscopy

1. Introduction

It is becoming increasing clear that tribochemical reactions of lubricant additives are mechanochemical processes induced at the sliding interface [1], yet the mechanism by which mechanochemical and tribochemical reactions occur are not well understood. The first theoretical analysis of the effect of stress on reaction rates was by Evans and Polanyi [2] who showed that the reaction rate increased exponentially with stress, which later became known to the chemistry community as the Bell model [3]. A knowledge of the elementary steps in the tribochemical reaction pathways is required to be able to test tribochemical model and develop theories to understand and predict mechanochemical reaction rates. This is accomplished in this work by investigating the mechanisms of a simple model tribochemical reaction consisting of dimethyl disulfide (DMDS) reacting with copper, and the decomposition of carboxylic acids with different functional groups on copper. The normal-stress dependent rate of decomposition of methyl thiolate on a Cu(100) simple crystal is measured using AFM, where it is confirmed that the reaction rate increases exponentially with applied stress as predicted by Evans and Polanyi. This system is sufficiently simple that it is amenable to analysis by DFT which enables the experimentally measured rates to be predicted quantitatively.

2. Methods

Experiments were carried out in UHV using a tungsten carbon ball sliding against a copper surface. The rate of reaction was measured using a UHV AFM by compressing an adsorbed overlayer with an AFM tip to mechanically induce decomposition. The results were analyzed using first-principles DFT calculations as implemented by the Vienna ab-initio simulation package (VASP).

3. Results

The surface reaction steps for DMDS decomposition are shown in Fig. 1. Reaction is initiated by S–S bond scission to form a stable adsorbed methyl thiolate species that decompose under shear [4]. The surface chemistry of adsorbed carboxylic acids is studied using similar strategies, where it is found that the chemistry is controlled by the reactivity of the carbonaceous group.



Figure 1: Reaction pathway for the mechanically induced decomposition of methyl thiolate species on copper.

4. Discussion

The rate of methyl thiolate decomposition (Fig. 1) under the influence of a normal stress is measured using an AFM and modeled by DFT (Fig. 2) where the calculations accurately predict the experimental reaction rate.



Figure 2: Illustration of the experimental and theoretical approach to modeling tribochemical reaction rates.

5. References

[1] N.N. Gosvami, J.A. Bares, F. Mangolini, A.R. Konicek, D.G. Yablon, R.W. Carpick, Mechanisms of antiwear tribofilm growth revealed in situ by single-asperity sliding contacts, Science, 348, 2015, 102-106.

[2] M.G. Evans, M. Polanyi, Some applications of the transition state method to the calculation of reaction velocities, especially in solution, Transactions of the Faraday Society, 31, 1935, 875-894.

[3] G. Bell, Models for the specific adhesion of cells to cells, Science, 200, 1978, 618-627.

[4] H. Adams, B.P. Miller, O.J. Furlong, M. Fantauzzi, G. Navarra, A. Rossi, Y. Xu, P.V. Kotvis, W.T. Tysoe, Modeling Mechanochemical Reaction Mechanisms, ACS Applied Materials & Interfaces, 9, 2017, 26531-26538.