Supplemental Information

Critical Stresses in Mechanochemical Reactions

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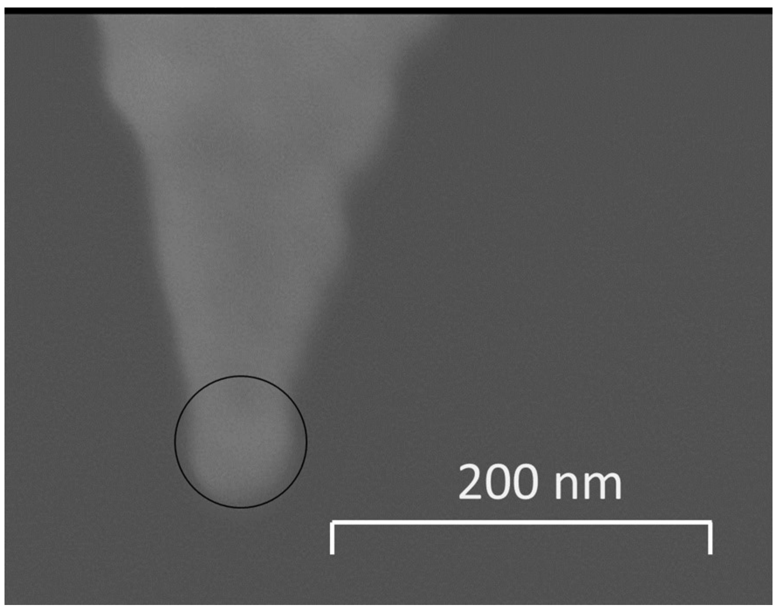

Figure S1: Electron microscope image of the AFM tip after wearing in and collecting data on the rate of stress-induced reactions in alkyl thiolates on Cu(100), which yields a tip radius $R =$ 35 ± 3 nm, which is larger than the nominal radius of ~8 nm, due to a running in of the tip during the mechanochemical reactions. Note, however, that the end of the tip maintains a spherical shape.

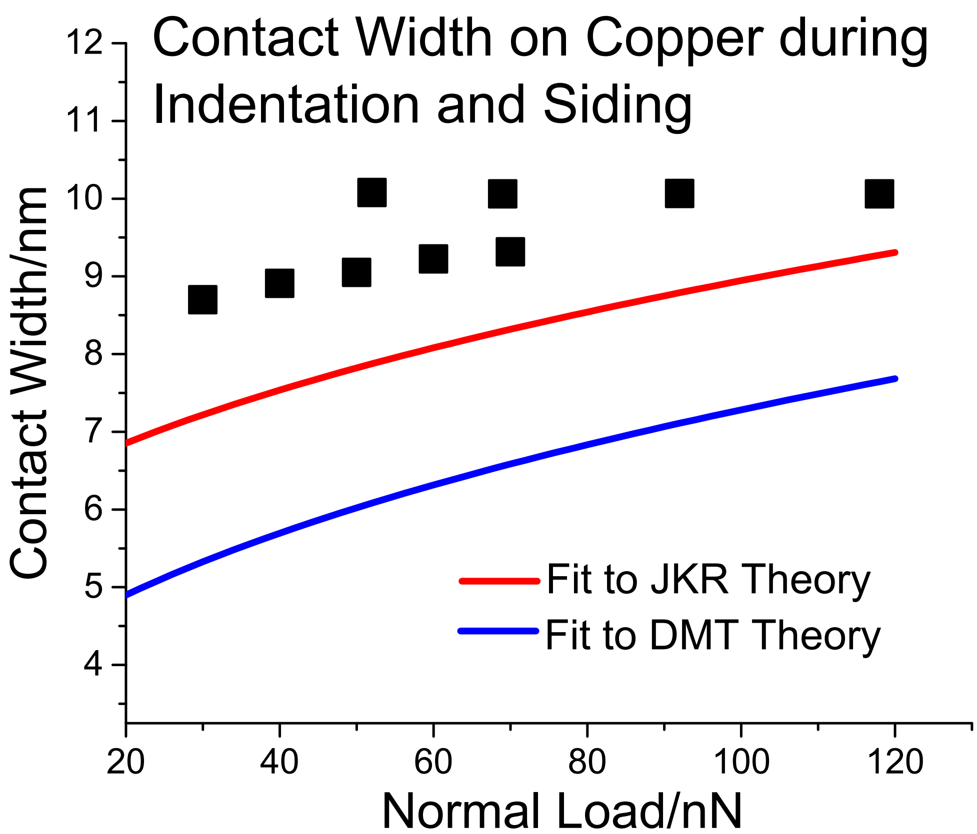

Figure S2: Plot of the contact widths measured either for indentation of the tip on the surface to make an indent [1] or from the width of the wear track during rubbing in the experiments performed here (■). It was shown previously that the shape of the indent was that expected for a Hertzian stress distribution where the depth of the indent was proportional to the stress-accelerated reaction rate as calculated using Bell theory.[2] The results were compared with the results predicted for a ball-on-flat geometry using a Young's modulus for copper of 100 GPa [3] with a Poisson ratio of 0.34, [4] and a Young's modulus of silicon of 125 GPa [5, 6] and a Poisson ratio of 0.265 to yield a value of $E^* = 70.2$ GPa. The contact area versus load was calculated using an average pull-off force of ~12 nN using JKR (——) and DMT (——) theory[7] and the results are shown plotted along with the experimental data. Corrections to take into account the presence of an alkyl thiolate overlayer had no significant effect on the results.

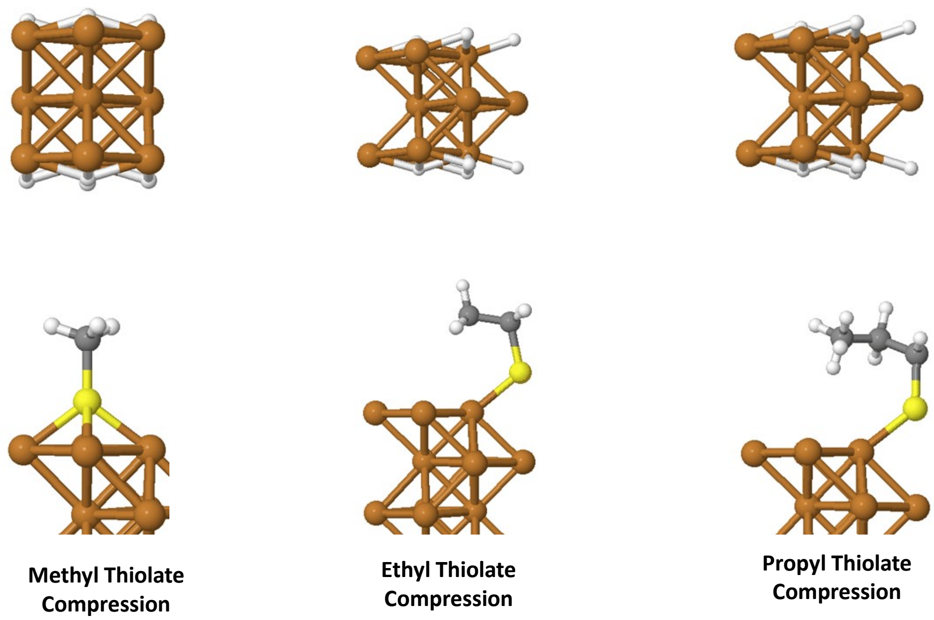

Figure S3: Movies of the evolution in the structures of methyl, ethyl and propyl thiolate compressed by Cu(100) slabs as the slabs are brought closer together.

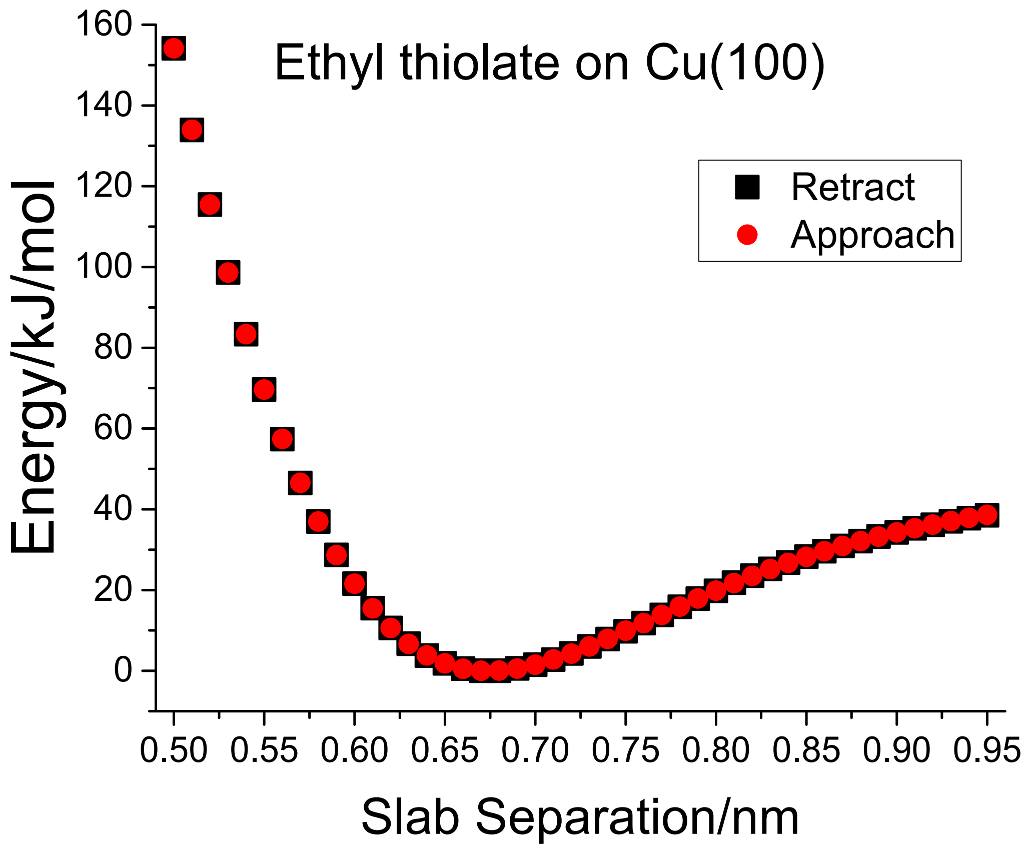

Figure S4: Plot of the energy versus slab separation for the compression of an ethyl thiolate species on Cu(100) as a function of the distance from a hydrogen-atom-covered Cu(100) surface for the approach (●) and retraction (■) of the two slabs. The lack of structural changes associated with the approach and retraction of the slabs is shown in Movie S3.

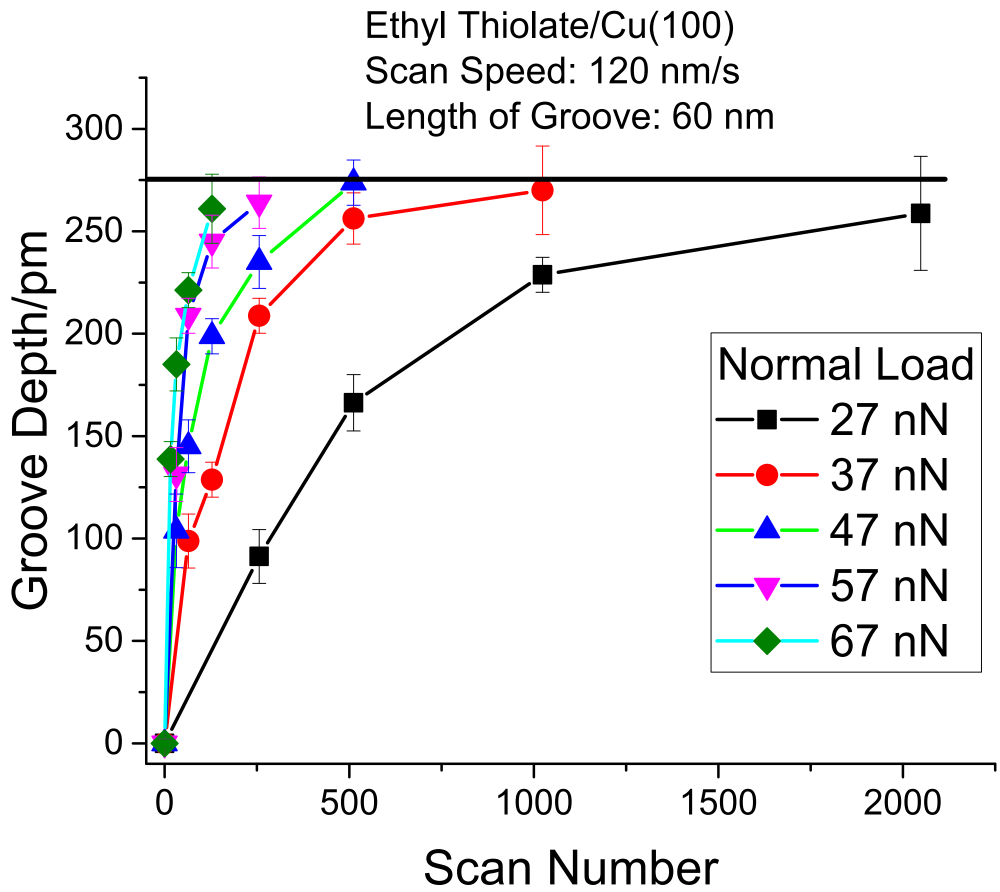

Figure S5: Plot of the depth of the wear track as a function of the number of passes over an ethyl thiolate saturated Cu(100) surface showing an exponential increase in the depth of the wear track, indicative of first-order reaction kinetics. The maximum depth for all mechanochemical reactions is ~275 pm, which agrees well with the calculated thickness of a methyl thiolate films.

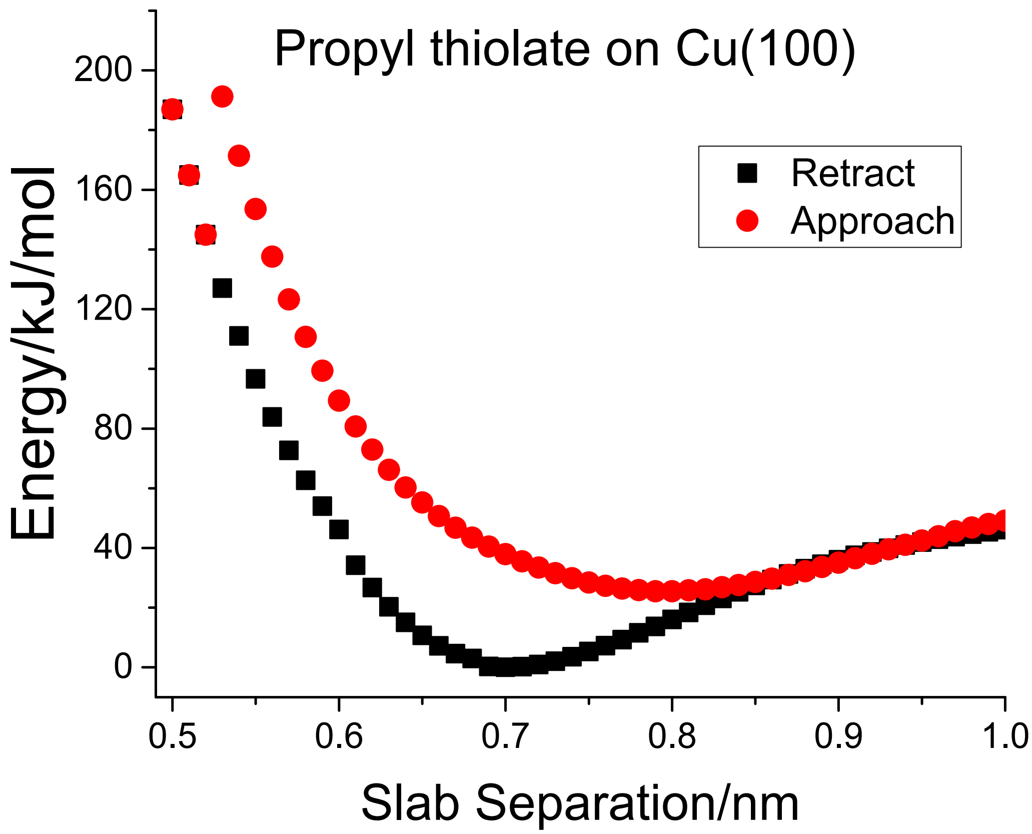

Figure S6: Plot of the energy versus slab separation for the compression of a propyl thiolate species on Cu(100) as a function of the distance from a hydrogen-atom-covered Cu(100) surface the approach (●) and retraction (■) of the two slabs. The structural changes associated with the approach and retraction of the slabs is shown in Movie S3.

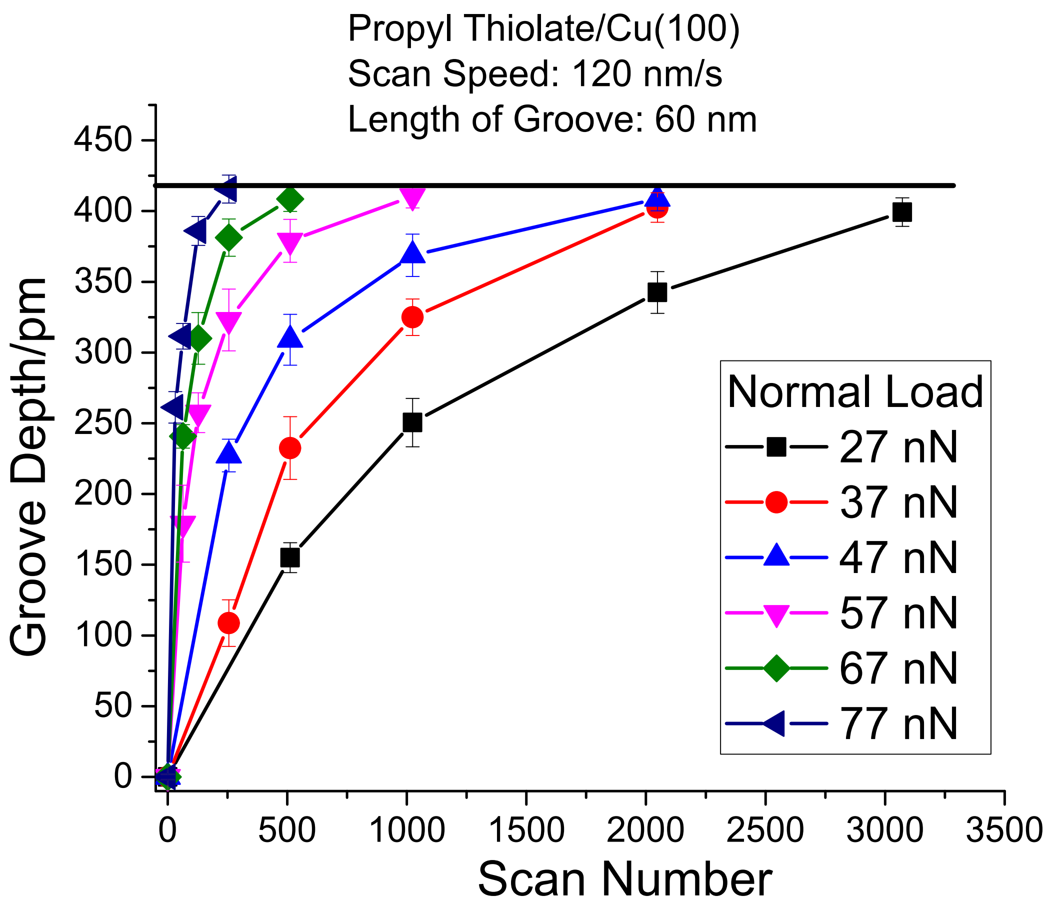

Figure S5: Plot of the depth of the wear track as a function of the number of passes over a propyl thiolate saturated Cu(100) surface showing an exponential increase in the depth of the wear track, indicative of first-order reaction kinetics. The maximum depth for all mechanochemical reactions is ~420 pm, which agrees well with the calculated thickness of a methyl thiolate films.

References

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