

Reply to "Comment on 'Anisotropy of Shear-Induced Mechanochemical Reaction Rates of Surface Adsorbates; Implications for Theoretical Models'"

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INTRODUCTION

Quapp and Bofill voiced several issues with our paper published in *The Journal of Physical Chemistry*¹ in which we postulated that the use of the force-displaced stationary points (FDSPs) to describe the reaction pathway under the influence of an external force can be approximated by the steepest-descent pathway (SDP) from the transition state to the initial (reactant) state,² an approximation that would significantly facilitate the analyses of mechanochemical reaction rates. The paper illustrates the postulate using a 4-fold analytical function of a model potential energy surface (PES)³ to show that the solution of the FDSP (also called a Newton trajectory by Quapp and Bofill) is similar to that derived from a SDP. It should be emphasized that the model potential is not intended to reproduce the PES for the experimental methyl thiolate decomposition reaction but is intended as an illustration of the validity of the postulate. The results from the postulate are particularly valid at low loads that are most relevant to those encountered in stress-induced reactions where the energy barrier decreases from that of the stress-free state and where the reaction over the reduced barrier is thermally driven. This differs from the assertion by Quapp and Bofill that the goal of mechanochemical theories is to calculate a bond-breaking point that occurs at the critical stress at a bifurcation point when the activation energy decreases to zero and the reaction thus occurs spontaneously at zero Kelvin. Such a critical force is used in the Prandtl–Tomlinson theory of friction.^{4–7} While reducing the energy barrier to zero may be the goal of single-molecule pulling experiments, most bulk mechanical reactions occur by lowering the barrier so that the reaction can proceed at a reasonable rate at a modest temperature, unusually room temperature, hence the use of the Bell model in mechanochemistry.^{8–10}

A straightforward consequence of the above postulate is that the reduction in activation barrier should depend on the component of the force vector along the SDP. This is tested experimentally using a simple mechanochemical reaction consisting of the decomposition of methyl thiolate species adsorbed on a Cu(100) single crystal surface. It decomposes by C–S bond scission to form small gas-phase hydrocarbons

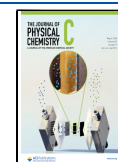
and deposit sulfur on the surface.^{11–14} This is followed by a step in which the sulfur is transported into the subsurface region^{15,16} to regenerate a clean Cu(100) surface that enables the mechanochemical reaction cycle to continue. This simple system enables the mechanochemical reaction rate to be measured as a function of the azimuthal direction on a well-ordered single crystal substrate using an atomic force microscope (AFM) tip sliding over the surface at room temperature to accelerate the rate of the mechanochemical reaction. The measured azimuthal dependence of the mechanochemical reaction rate agrees well with the postulated use of the SDP to analyze mechanochemical kinetics, thus suggesting that the postulate is correct, at least in this simple case. We note this is not claimed to be true in all cases and concede that there may well be complex Born–Oppenheimer potential energy topologies that do not obey this postulate. However, we do agree with Quapp and Bofill that there is a lack of mechanochemical rate measurements on well-characterized reaction systems that will allow theories to be developed and tested. Making such measurements and developing theories that describe the results is a central goal of our research.

In our view, there are two main objections raised by Quapp and Bofill. The first is that they contend that the SDP and the FDSP (their Newton trajectories) are different in all “thinkable” cases. This may formally be true, but the agreement between the predictions from our postulate and our experimental results implies that it may at least be true for simple, practically occurring reactions. Second, they argue that the angle at which the rate is a maximum does not lie along the lowest-energy pathway of the model potential energy surface. They conclude, therefore, that we are not measuring the mechanochemical decomposition of methyl thiolates species

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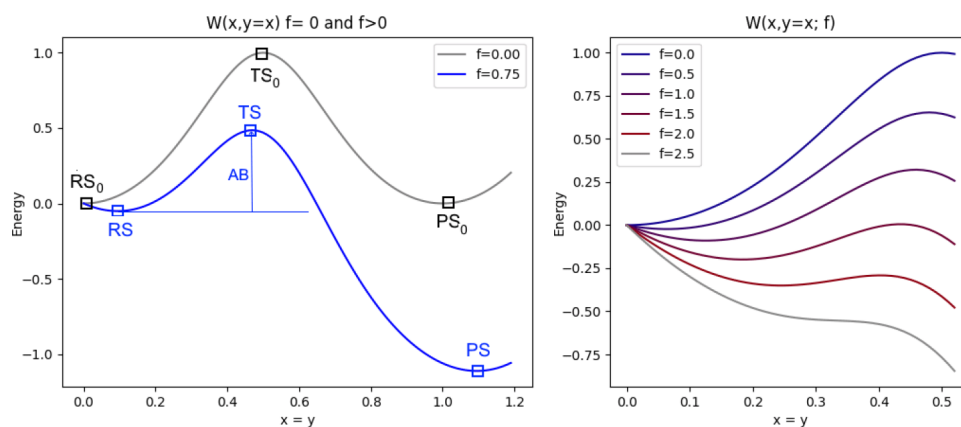


Figure 1. Evolution of the energy profile along the SDP ($x = y$) as a function of x for different values of the radial force f .

but rather some other reaction such as the sliding of the methyl thiolates over the surface. We appreciate the comments because they allow us to clarify the situation and to present a more detailed analysis of the model PES to compare the results of the variation in activation barrier using the FSDPs and the steepest-descent pathway in more detail than in the original paper. We also explain more clearly the evidence for the reaction occurring by shear-facilitated C–S bond scission rather than by any other reaction, including the reactant being pushed across the surface by the AFM tip.

RESULTS AND DISCUSSION

Analysis of the Effect of an Applied Force on a Model Remoisenet–Peyrard Potential Energy Surface. Quapp and Bofill express doubts about our use of the Remoisenet–Peyrard (RP) model potential.³ We emphasize again that this was used as an illustration of the postulate applied to a model PES, and is not expected to exactly reproduce the experimental potential. However, we are grateful for the opportunity to describe the analysis and its conclusions in greater detail. The original RP potential (that is, without an applied external force) is symmetric with respect to the $x = y$ axis, which also represents the SDP from RS_0 ($x = y = 0$) to TS_0 ($x = y = 0.5$) joined by a sinusoidal energy profile. When an external force f is applied along this (radial) direction, the symmetry remains the same, but the reaction and transition states move to the right and left, respectively. This is represented in Figure 1 for $r = 0.5$, where r is the parameter that controls the shape of the RP potential.

The corresponding evolution of the locations of the reaction- and transition-states (x_{RS} and x_{TS}) as well as the corresponding energies, w_{RS} and w_{TS} , are represented graphically in Figure 1, finally allowing the evaluation of the f dependence of the energy barrier as a function of the radial force f , which is in fact the final goal of this analysis.

When the applied force is not radial but inclined at some angle θ with respect to the diagonal $x = y$, the mirror symmetry is, of course, broken so that the FDSP (or Newton trajectory) no longer coincides with the diagonal SDP. This is shown in Figure 2 for $\theta = 30^\circ$. Here, the FDSPs (or Newton trajectories) are plotted as a function of the applied force f , where they approach each other to coalesce at some critical force, f_C at which the activation barrier tends asymptotically to zero when the reaction would occur spontaneously at 0 K. To more clearly illustrate the pathways for different force angles,

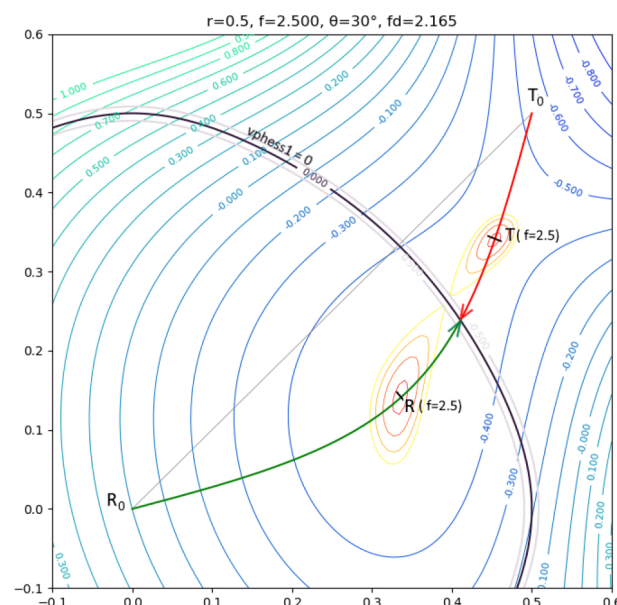


Figure 2. Contour plot of the RP potential for a force $f = 2.5$ aligned at $\theta = 30^\circ$ to the SDP ($f = 2.5$, $f \cos \theta = 2.165$) with the corresponding modified reaction and transition states. Contour plots of $|\nabla W|$ around these two local extrema are shown in orange. On this diagram are also represented the evolution of the reaction state (green) and the transition state (red) when the applied force increases from 0 to its limiting value of 3.05 where reaction and transition states merge and disappear while the energy barrier decreases to zero and the reaction occurs spontaneously at 0 K. This critical point is also located on the black curve corresponding to a vanishing eigenvalue of the Hessian.

of the force-dependent pathways such as those displayed in Figure 2 are shown in the Supporting Information section.

Measuring this critical force for the cleavage of chemical bonds is the goal of many single-molecular pulling experiments. As Quapp and Bofill suggest, this illustrates that the FDSP is indeed quite different from the SDP. Yet projecting all the energy profiles on the diagonal SDP provides a good approximation as shown in Figure 3, which shows that the force dependence of the energy barrier may be accurately obtained from the radial case at $\theta = 0^\circ$. Note that the agreement between the curves is excellent for decreases in energy barriers up to $\sim 50\%$ of the value of the initial energy barrier. However, there are significant variations in the values of the critical forces as the directions of the forces change, in

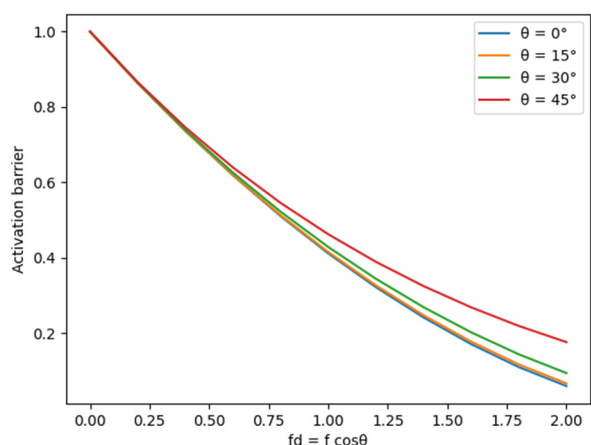


Figure 3. Evolution of the activation barrier as a function of $fd = f \cos \theta$ (the radial component of the applied force) for different values of the orientation θ of the applied force. This shows that even if the actual FDSP may differ significantly from the SDP, using the latter pathway (i.e., using the blue curve, $\theta = 0^\circ$) will provide a good approximation to that obtained from the FDSP.

particular as the angle approaches 45° . While these differences may be important for the large forces exerted by an atomic force microscope tip on a single molecule that may be capable of spontaneously cleaving bonds in the molecule, macroscale mechanochemical reactions are more likely to occur with smaller forces exerted on individual molecules. In this regime, the lines collapse onto a single curve.

More generally, the initial reaction state RS_0 and transition state TS_0 are local extrema of the initial potential energy function $W_0(x)$, and comprise a minimum for the reactant and a saddle point for the transition states. When an external force f is applied, as noted by Quapp and Bofill, this potential becomes $W_f(x) = W(x) - f \cdot x$, which obviously changes the positions of the reaction and transition states. Neglecting these

changes in position, the new energy barrier is simply obtained from

$$\Delta W = W_f(TS_0) - W_f(RS_0) = W(x_{TS_0}) - f \cdot x_{TS_0} - (W(x_{RS_0}) - f \cdot x_{RS_0}) = \Delta W_0 - f(x_{TS_0} - x_{RS_0})$$

and is essentially the Bell approximation⁸ in which the energy barrier decreases in proportion with the applied force, and is in accord with the initial linear decrease in energy with applied force shown in Figure 3. The utility of this approach is that the SDP and the associated reactant- and transition-state structures are relatively easy to obtain using standard quantum software packages,^{14,17–19} while developing a full Born–Oppenheimer PES for even simple reactions to be able to directly compute FDSPs or Newton trajectories is much more computationally expensive. While such more precise computations may be required for establishing the critical behavior, most practical mechanochemical reactions, including those carried out in the work that is the subject of Quapp and Bofill's comment,¹ are thermally driven over a mechanically reduced activation barrier for which the postulate that we make and test in that manuscript is a much more practical and easier to apply than the Newton trajectories proposed by Quapp and Bofill.

This approach can also be extended to take into account the evolution of the positions of the reaction and transition states but requires a knowledge of the initial potential energy profile $W(x)$. However, for small values of the force f , the evolution of TS and RS can be obtained by simple a Taylor series expansion of W around TS_0 and RS_0 , and this only requires an evaluation of the Hessians of W at TS_0 and RS_0 . This extended-Bell approximation⁹ is exemplified in Figure 4. We believe that it is an appropriate approach to solving practical mechanochemical problems in which the applied force induces only modest decreases in the activation barrier from that found at zero force.

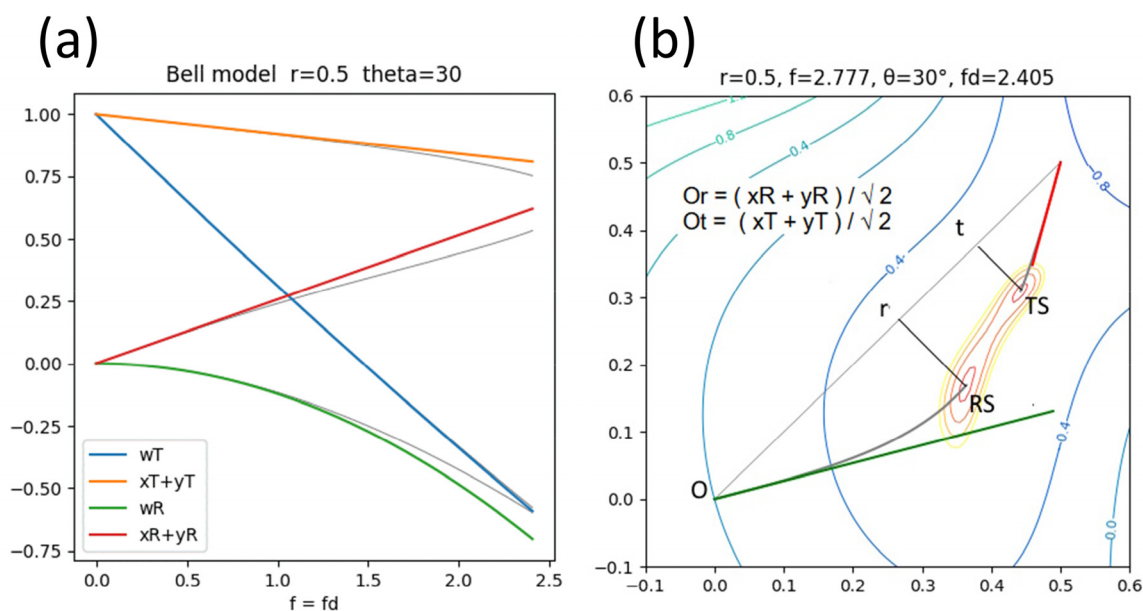


Figure 4. Illustration of the Bell approximation. Figure 4a shows the evolution of the energies, $W(T)$ (blue) and $W(R)$ (green) according to the Bell approximation as compared to the one obtained using the FDSP in gray (gray). In red and orange are shown the corresponding evolutions of $x(T) + y(T)$ and $x(R) + y(R)$, the radial projections of RS and TS . Figure 4b shows the Bell approximation of the FDSP for $fd = 2.405$.

Evidence for the Mechanochemical Reaction Pathway on Cu(100) Substrates. The elementary reaction steps for the shear-induced mechanochemical decomposition of methyl thiolates adsorbed on copper were first established by rubbing a tungsten carbide ball under ultrahigh vacuum (UHV) conditions. Traditional surface science experiments were first used to establish the thermal reaction pathways of alkyl thiolates on copper using a combination of temperature-programmed desorption (TPD), and infrared and X-ray photoelectron spectroscopies.²⁰ The thiolate was found to bind with the C–S bond perpendicular to the surface and decompose at ~ 450 K to desorb small hydrocarbons and to leave no carbon, but a monolayer of sulfur on the surface²¹ after the reaction was complete. Density functional theory (DFT) calculations, using the nudged-elastic band method^{17,19} showed that the reaction occurred by the C–S bond tilting with respect to the surface, causing it to weaken and eventually cleave.²² The calculated activation barrier was ~ 100 kJ/mol, in good agreement with the results from TPD measurements and the molecular terminus moves along the $[110]$ direction on the Cu(100) substrate.

The mechanochemical reaction mechanism was measured in several ways. The gas-phase products formed by rubbing were monitored using a quadrupole mass spectrometer placed inside the UHV chamber and close to the sample¹¹ and were identical to those found for the thermal reaction, indicating that they react in the same way, but at room temperature rather than 450 K. The composition of the rubbed region was also measured as a function of the number of passes over the surface using Auger spectroscopy, and it was found that the sulfur was completely removed, in contrast to the thermal behavior. This was shown to be due to the surface sulfur being transported into the subsurface region²³ and the mechanism by which this process occurred was investigated.¹⁶ The rates of the elementary mechanochemical reaction steps were measured in greater detail^{13,22} and used to model the sulfide film-formation kinetics.¹⁴ Further evidence that this was a mechanically induced reaction comes from the fact that carboxylate species adsorbed on copper, where the decomposition activation energy is ~ 160 kJ/mol,²⁴ requires more rubbing cycles than methyl thiolates under the same conditions to remove the overlayer.^{25–27}

The reaction rate has also been measured using an AFM tip under compressive stresses.²⁸ Such stresses can only accelerate the rate of the mechanochemical reaction, but cannot induce lateral sliding. Quapp and Bofill question whether this decomposition reaction also occurs under shear with the AFM. We expected this to be the case because the loads on the AFM tip were selected to be in the same range as in the UHV apparatus.^{22,28} They suggest that other degrees of freedom might contribute based on our molecular dynamics simulations,²⁹ but these simulations were carried out at much higher temperatures than in the experiments to accelerate the reaction rates to enable rare events such as chemical reactions to be captured.

Despite this, we were also concerned that another reaction might have been occurring. Consequently, several pieces of corroborative evidence were collected to confirm that methyl thiolate reacts on copper in the same way as in the UHV apparatus, and not by diffusing across the surface or by some other route. First, in the images of the troughs produced by rubbing (Figure S3 in the Supporting Information of reference¹), there is no evidence of the accumulation of

additional material at the ends of the stroke as would be expected if adsorbates were pushed to the end of the trough. Second, about 300 scans were required to remove the methyl thiolate overlayer (Figure 1, ref. 1), while ~ 2000 scans were needed to remove a carboxylate overlayer^{26,27} in accord with their relative reaction activation barriers. Third, the final depths of the grooves corresponded to those expected for the removal of a methyl group from an adsorbed methyl thiolate species on copper. Fourth, the results in Figure S1 of the Supporting Information section of reference 1 are specifically designed to address this issue. This shows the results of measurements of the friction force using the AFM tip at low loads after a patch of the overlayer had been rubbed at higher loads to induce mechanochemical reactions. This shows the clear formation of a sulfur overlayer, where its characteristic friction force was measured by thermally decomposing a methyl thiolate overlayer (as shown in Figure S2 of ref. 1). The correspondence between the UHV AFM data and that for UHV ball-on-flat sliding is confirmed by the friction force increasing further due to the formation of bare copper as the sulfur is transported into the subsurface region of the sample. We feel that these results collectively provide very strong evidence that we are following a reaction in which the adsorbed methyl thiolate reacts under shear to form a sulfur overlayer.

Quapp and Bofill further question the fact that the maximum rate in Figure 4 of ref. 1 does not align with the direction of the steepest-descent pathway. Confusion may have occurred because the directions were mislabeled during a revision of the inset, and that figure is now presented correctly here as Figure 5.

They concede that we have correctly calibrated the sliding directions of the AFM tip on the Cu(100) surface. In fact, this was independently tested by two students by defining surface lattice directions using low-energy electron diffraction

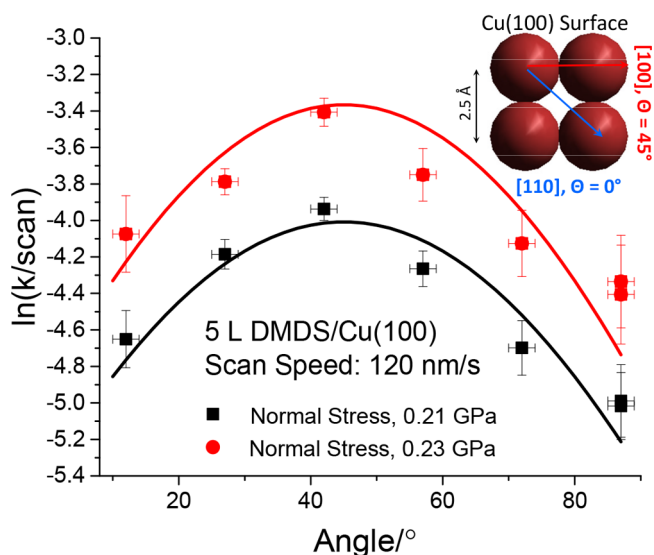


Figure 5. Plot of $\ln\left(\frac{k}{\text{scan}}\right)$ where k is the rate constant for the shear-induced decomposition of methyl thiolate species on Cu(100) as a function of scanning angle relative to the $[110]$ directions, illustrated as an inset to the figure. Experiments were carried out at normal stresses of 0.21 GPa (black) and 0.23 GPa (red). The solid lines plotted with the data are fits assuming that $\ln(k_0) \approx -8.7$.

(LEED), and the results were independently verified by an expert in LEED.³⁰

The observation that the mechanochemical reaction rate is a maximum at an scanning angle of 45° relative to the [110] directions is addressed on Page 11590 of ref. 1 It is due to the fact that the surface has 4-fold symmetry so that there are degenerate orthogonal reaction pathways that can be simultaneously activated to give the maximum rate at 45° to the SDP.

CONCLUSIONS

We address the issues raised by Quapp and Bofill in their Comment on our paper. We have emphasized the care that we have taken in establishing the mechanochemical reaction pathway for the decomposition of methyl thiolate species adsorbed on a Cu(100) substrate and reiterated the evidence for the reaction pathway both from previous experiments carried out in UHV, and from additional work carried out in ref. 1. Quapp and Bofill's concerns with our analysis of the RP potential has allowed us to illustrate the analysis in greater detail to show that using the postulate that the initial and transition state structures connected by a SDP can be used to calculate the variation in activation barrier with applied stress at low stresses is correct. The analysis is relevant to those stresses that result in a reduction in activation barrier up to ~50% of its original value but is indeed less accurate in predicting the forces at which the barrier decreases to zero. However, while such high-stress regimes may be useful for single-molecule pulling experiments, our the lower-force results are more relevant to the forces that can be attained both in the AFM compression experiments shown in ref. 1 and for practical mechanochemical synthesis for which the Bell⁸ and extended-Bell⁹ models apply.^{28,31–33} The approach that we suggest will enable the rates of mechanochemical reactions to be calculated more easily.

As indicated by Karl Popper, the scientific method requires a hypothesis that is both testable and falsifiable,³⁴ and that is exactly what we have done by providing experimental results that are in agreement with the predictions from our postulate. In this spirit, we suggest that a more valid scientific approach than criticizing our work through their Comment would have been to have calculated the Newton trajectories for a computed Born–Oppenheimer PES for the relatively simple decomposition reaction of methyl thiolate on Cu(100) and have used those results to reproduce the experimental angular dependence and illustrate how it differed from our approach.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.3c00756>.

Description of movie contents (PDF)

Illustrations of the FDSPs at various angles (ZIP)

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Notes

The authors declare no competing financial interest.

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