

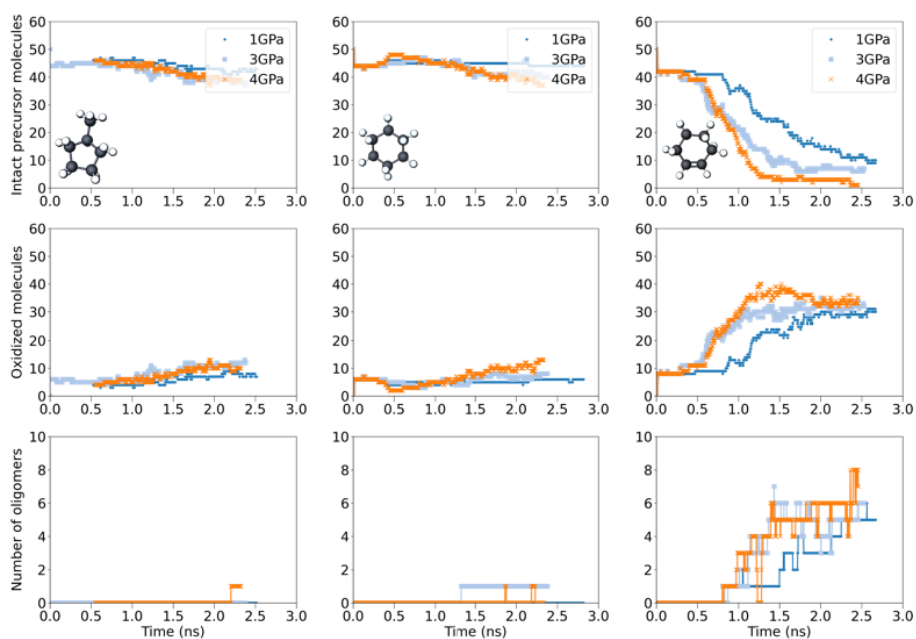
## Supplementary Information

### Shear-Activated Chemisorption and Association of Cyclic Organic Molecules

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**Figure S1:** Evolution of the number of intact precursor molecules (top row), corresponding change in the number of oxidized species (middle row), and formation of oligomers (bottom row) in simulations at 1, 3, and 4 GPa and 300 K. Methylcyclopentane (left column) and cyclohexane (middle column) molecules were mostly unreactive while cyclohexene (right column) molecules participated in many shear-driven reactions at any pressure. Sliding started from approximately 0.75 ns, after the system was equilibrated and compressed to the target pressure.

#### Activation volume

The rate of mechanochemical reaction can be expressed as an Arrhenius-type function, commonly known as the Bell model<sup>1</sup>:

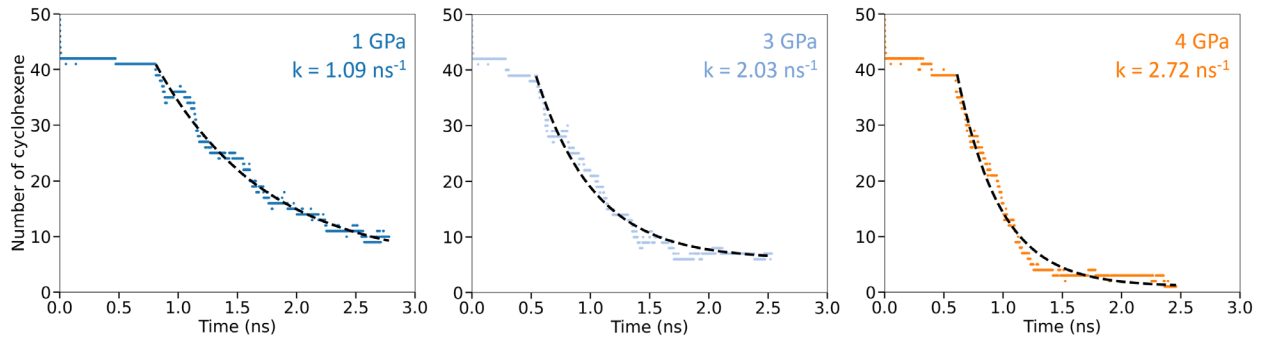
$$k = A \exp\left(-\frac{E_a - \tau\Delta V^*}{K_B T}\right) \quad (\text{S1})$$

where,  $k$  is reaction rate constant,  $\tau$  is shear stress,  $\Delta V^*$  is activation volume,  $A$  is the pre-exponential factor,  $E_a$  is activation energy,  $T$  is temperature, and  $K_B$  is the Boltzmann's constant.

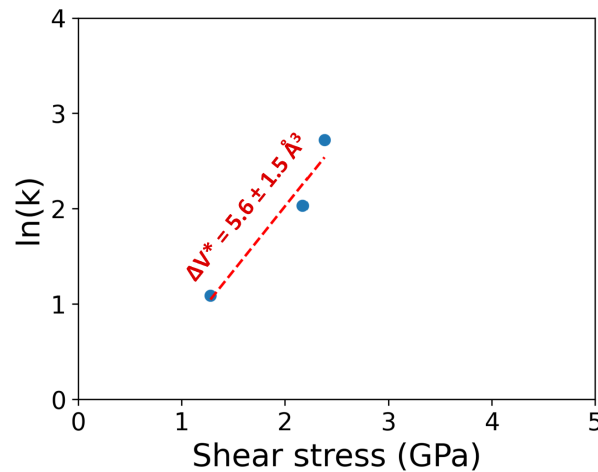
Taking natural log on both sides of Eq. S1 gives:

$$\ln(k) = \tau \frac{\Delta V^*}{K_B T} + \left( \ln(A) - \frac{E_a}{K_B T} \right) \quad (S2)$$

Therefore, on a semi-log plot of the reaction rate constant against the shear stress, the slope can be used to estimate  $\Delta V^*$ . The reaction rate constant,  $k$ , can be calculated by fitting the number of unreacted precursor molecules in the simulation to the first order kinetics equation. Shear stress,  $\tau$ , in the simulation can be calculated from the friction force on the upper slab and the contact area.



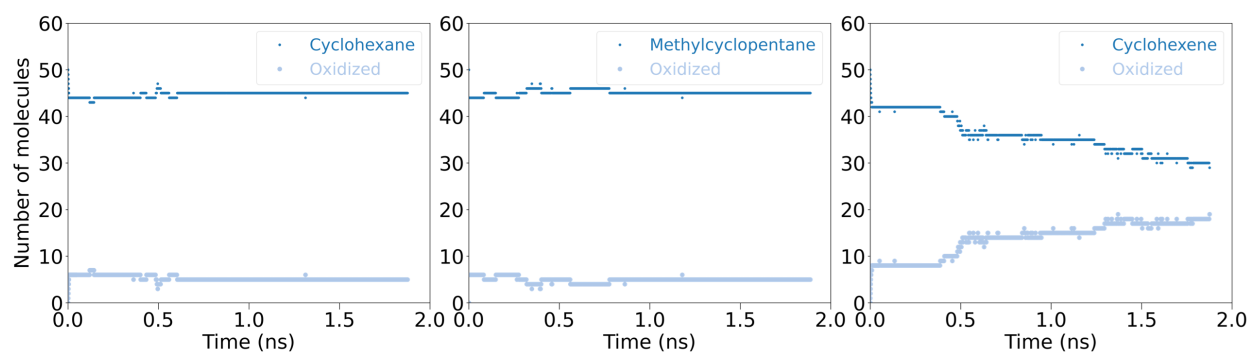
**Figure S2.** Reaction rate constant ( $k$ ) for oxidative chemisorption of cyclohexene calculated from the first order kinetics in sliding simulations at 1, 3, and 4 GPa and 300 K. The colored lines show the number of intact cyclohexene molecules in the sliding simulations and the black lines are fits of the data to the first order kinetics equation. As reactions were driven mainly by shear stress, only the data from the 2 ns of sliding were used for fitting.



**Figure S3:** Calculation of the activation volume of cyclohexene from the slope of a semi-log plot of the reaction rate constant vs. the shear stress, per Eq. S2. Shear stresses in the simulations were calculated from the friction force on the upper slab and the contact area.

## Heating simulations

To compare the shear-driven reactions with thermal reactions, heating simulations were performed for all three precursors. The model systems for the heating simulations were the same as those used in the sliding simulations, described in the methods section of the paper. The simulation protocol for the heating simulations was as follows: energy minimization and system equilibration at 300 K, moving the upper slab towards the bottom slab until the pressure at the interface reached  $\sim 0.5$  GPa (tensile), fixing the positions of the slabs, ramping up the temperature to 900 K at 1 K/ps heating rate, and finally, production simulation at 900 K without applying any additional normal pressure or sliding motion.



**Figure S4:** Evolution of the number of intact methylcyclopentane, cyclohexane, and cyclohexene molecules and corresponding change in the number of oxidized species in the heating simulations. The systems were heated from 300 K to 900 K at 1 K/ps heating rate starting from 0.28 ns. The constant temperature simulations at 900 K were run from 0.88 ns.

## References

- 1 G. I. Bell, *Science*, 1978, **200**, 618–627.