# Supplementary Information for: Influence of second-order saddles on reaction mechanisms

Komal Yadav, Renuka Pradhan, and Upakarasamy Lourderaj

School of Chemical Sciences, National Institute of Science Education and Research (NISER) Bhubaneswar, An OCC of Homi Bhabha National Institute, P.O. Jatni, Khurda, Odisha, India

Email: u.lourderaj@niser.ac.in

## Additional Computational Details

## 1. 1-pyrazoline

#### 1.1. Trajectories initiated from py region

For the trajectories initiated in the **py** region, the initial coordinates and momenta were chosen using the microcanonical normal mode sampling technique<sup>1</sup> for a given available energy. In the earlier report (Pradhan and Lourderaj, *Phys. Chem. Chem. Phys.*, 2019, **21**, 12837–12842), for the trajectories initiated from **py**,

$$E_{\text{avail}} = \Delta E_{\mathbf{TS4f}} + E_{\text{ZPE}} + E_{\text{vib}} + E_{\text{rot}} + RT$$

where,  $\Delta E_{\mathbf{TS4f}}$  is the energy of **TS4f** relative to **py**,  $E_{\text{ZPE}}$  is the zero-point energy of **TS4f**, and  $E_{\text{vib}}$ and  $E_{\text{rot}}$  are the average vibrational and rotational energies at the experimental temperature of 510.45 K for **TS4f**. *RT* is the energy along the coordinate for **TS4f**. **TS4f** corresponds to the highest-barrier transition state (found along the asynchronous path) for the denitrogenation of 1-pyrazoline.  $E_{\text{avail}}$  thus obtained was 119 kcal/mol. In the current work, to understand the dynamics of the system at higher energies, the trajectories were initiated in the **py** region for  $E_{\text{total}} = E_{\text{avail}} + E_{\text{excess}}$ , with  $E_{\text{excess}} =$ 11, 21, and 31 kcal/mol, corresponding to  $E_{\text{total}} = 130$ , 140, and 150 kcal/mol respectively. It should be noted that the *ab initio* classical trajectory simulations used in this study do not take care of the zero-point-energy of the system during the dynamics.

#### **1.2.** Trajectories initiated from sos region of 1-pyrazoline

To understand the post second-order saddle dynamics, a set of 40 trajectories were integrated from the **sos** of 1-pyrazoline with  $E_{\text{avail}} = 95.88$  kcal/mol. The trajectories were integrated by solving the classical equations of motion, and the forces were computed on-the-fly at CASSCF(4,4)/6-31+G\* level of theory.<sup>2,3</sup> The  $E_{\text{total}}$  available to the system was calculated as,

$$E_{\text{avail}} = 140.0 - \Delta E_{\text{sos}}$$

where  $\Delta E_{sos}$  is the energy difference between **py** and **sos** and is equal to 44.12 kcal/mol. These trajectories were then integrated in the forward and reverse directions for 600 fs each and stitched together to get a complete set. The initial coordinates for the forward and reverse directions are the same, and the directions are defined by the sign of momenta while choosing the initial conditions. If  $p_i^f$  is the sign of momenta chosen for the  $i^{\text{th}}$  component in the forward direction, then  $p_i^r = -p_i^f$  is the momenta chosen for the reverse direction for the  $i^{\text{th}}$  component. Out of the 40 trajectories initiated, 25 gave a complete set, i.e.,  $\mathbf{py/py'} \to \mathbf{sos} \to \mathbf{cyp/tmd/tmd'}$ . The trajectories accessing the  $\mathbf{tmd/tmd'}$  region are expected to undergo C-C bond formation and result in  $\mathbf{cyp}$ . The different pathways followed by these trajectories are given in Table S1.

### 2. 3,3,5,5-tetrachloro-1-pyrazoline

The potential energy profile for the system was mapped at CASSCF(4,4)/6-31+G<sup>\*</sup> level of theory.<sup>2,3</sup> The four orbitals in the active space include the two C-N  $\sigma$  and  $\sigma^*$  orbitals. The trajectories were integrated by solving the classical equations of motion, and the forces were computed on-the-fly at CASSCF(4,4)/6-31+G<sup>\*</sup> level of theory. The  $E_{\text{total}}$  available to the system was calculated at 510.45 K,

|    | Pathways  | No. of trajectories |
|----|---|---------------------|
| 1. | ${ m py} ightarrow{ m sos} ightarrow{ m tmd'}$                          | 6                   |
| 2. | $\mathbf{py}'  ightarrow \mathbf{sos}  ightarrow \mathbf{tmd}$          | 7                   |
| 3. | $\mathbf{p}\mathbf{y}'  ightarrow \mathbf{sos}  ightarrow \mathbf{cyp}$ | 3                   |
| 4. | $\mathbf{py}  ightarrow \mathbf{sos}  ightarrow \mathbf{cyp}$           | 7                   |
| 5. | ${ m py}  ightarrow { m ts0}  ightarrow { m sos}  ightarrow { m cyp}$   | 2                   |

Table S1: Pathways followed by various trajectories initiated from the **sos** region for  $E_{\text{total}} = 95.88$  kcal/mol

assuming a Boltzmann distribution of states at the  $Cl_{-sos}$ . The temperature of 510.45 K was chosen to compare the simulation results of 1-pyrazoline.<sup>4</sup> The total energy can be calculated as,

$$E_{\text{total}} = E_{\text{ZPE}} + E_{\text{vib}} + E_{\text{rot}} + 2RT$$

where,  $E_{\text{ZPE}}$ ,  $E_{\text{vib}}$ ,  $E_{\text{rot}}$  are the zero-point-energy, average vibrational energy, and average rotational energy at 510.45 K. RT is the energy along each of the orthogonal coordinate having negative curvature (Figure S7). The trajectories from the **Cl\_sos** were integrated in the forward and reverse direction using the same procedure described above for 1-pyrazoline.



Figure S1: The asynchronous denitrogenation pathways for 1-pyrazoline at  $CASSCF(4,4)/6-31+G^*$  level of theory via (a) planar like and (b) perpendicular like diazenyl diradicals. The **TS5** represents the transition state for a concerted denitrogenation pathway. This figure is taken from Pradhan and Lourderaj, *Phys. Chem. Chem. Phys.*, 2017, **19**, 27468-27477.



Figure S2: Potential energy profile for the synchronous denitrogenation of 3,3,5,5-tetrafluoro-1pyrazoline mapped at the CASSCF(4,4)/6-31+G\* level of theory. The four orbitals in the active space consists of the two C-N  $\sigma$  bonding and anti bonding orbitals. The relative energies are reported in kcal/mol.



Figure S3: Plot of  $\phi_s$  vs  $d_s$  projected on the 2D-potential energy surface for trajectories following the second order saddle pathway in the thermal denitrogenation of 1-pyrazoline for  $E_{\text{total}}$  of (a) 130, (b) 140, and (c) 150 kcal/mol.



Figure S4: Sample trajectories showing recrossing events from the **sos** for 1-pyrazoline with  $E_{\text{total}} = 150 \text{ kcal/mol}$ . The  $\phi_s$  vs  $d_s$  of the trajectories are projected on the 2D-potential energy surface of 1-pyrazoline. Recrossing events seen in (a) **sos** and **ts1** regions, (b) **sos** and **ts1'** regions, and (c) **ts1** and **sos** regions.



Figure S5: Trajectory lifetime distributions for the denitrogenation of 1-pyrazoline. The distributions are shown for (a) all the reactive trajectories, (b) trajectories following synchronous denitrogenation pathway, and (c) trajectories following asynchronous denitrogenation pathway, for the three total energies.



Figure S6: Distribution of average translational energy between the  $\mathbf{cyp}$  and  $N_2$  fragments of 1-pyrazoline for trajectories following synchronous, asynchronous, and SOS pathways for the three total energies.



Figure S7: Total energy available to the system (for 3,3,5,5-tetrachloro-1-pyrazoline) at a temperature of 510.45 K.

## References

- [1] W. L. Hase and D. G. Buckowski, Chem. Phys. Lett., 1980, 74, 284–287.
- [2] B. O. Roos, in Adv. Chem. Phys., John Wiley and Sons, Ltd, 1987, pp. 399–445.
- [3] T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, J. Comput. Chem., 1983, 4, 294–301.
- [4] R. Pradhan and U. Lourderaj, Phys. Chem. Chem. Phys., 2019, 21, 12837–12842.