Predicting the Mechanism and Products of CS_2 Capture by NH_3 - An Exemplar Benchmark Study

Shelbie A. Black[1], David A. Dixon[2] and Zachary R. Lee[1*]

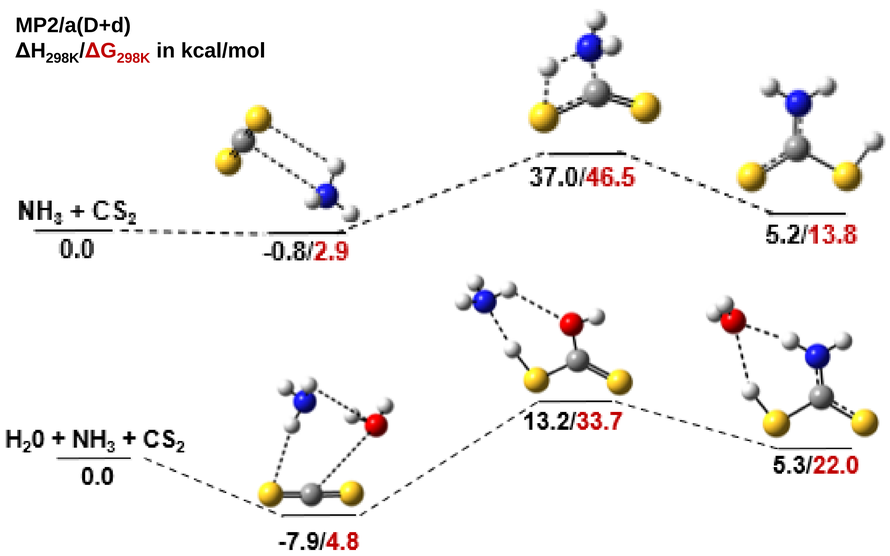
[1]*Department of Biology and Chemistry, Morehead State University*

[2]*Department of Chemistry and Biochemistry, The University of Alabama*

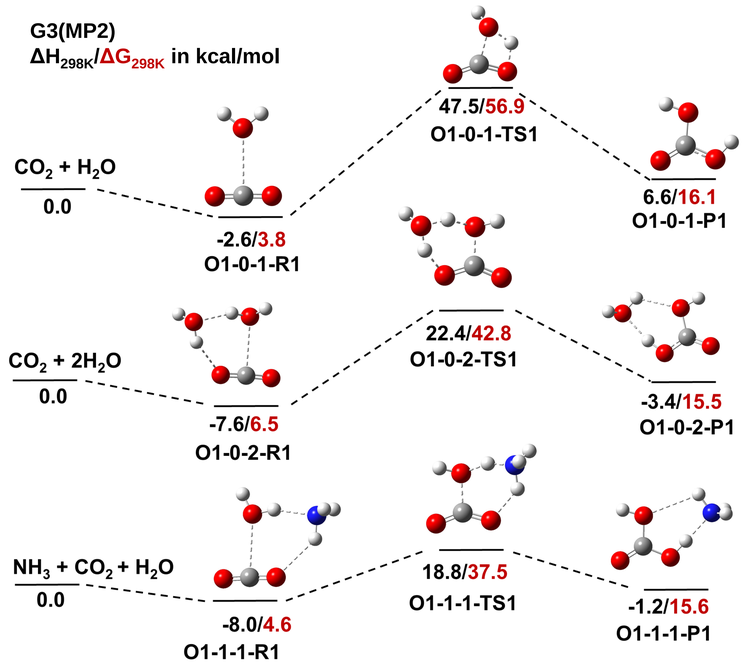
Overview

- Carbon disulfide is a toxic gas emitted from industrial plants and a common greenhouse gas. Acute poisonings from carbon disulfide are rare, but recurring exposure to low doses can have long term health effects (Kraackman, 2003).
- Currently, there are two approaches being considered for the removal of acid gas pollutants: (1) sequester these gases from the atmosphere or (2) remove these gases directly upon combustion (post-combustion).
- Potential energy surfaces (PES) for a series of CS_2 capture reactions by NH_3 in the presence H_2O were calculated at the MP2/a(D+d) evel in the gas phase.
- G3(MP2) and FPD calculations are in progress
- Extensive thermodynamic understanding of these mechanisms can help optimize conditions and amine substituents for practical CS_2 capture.
- Future research will examine the thermodynamics of CS_2 capture by multiple NH_3 and water molecules as well as with other amines in gas phase and aqueous solution.

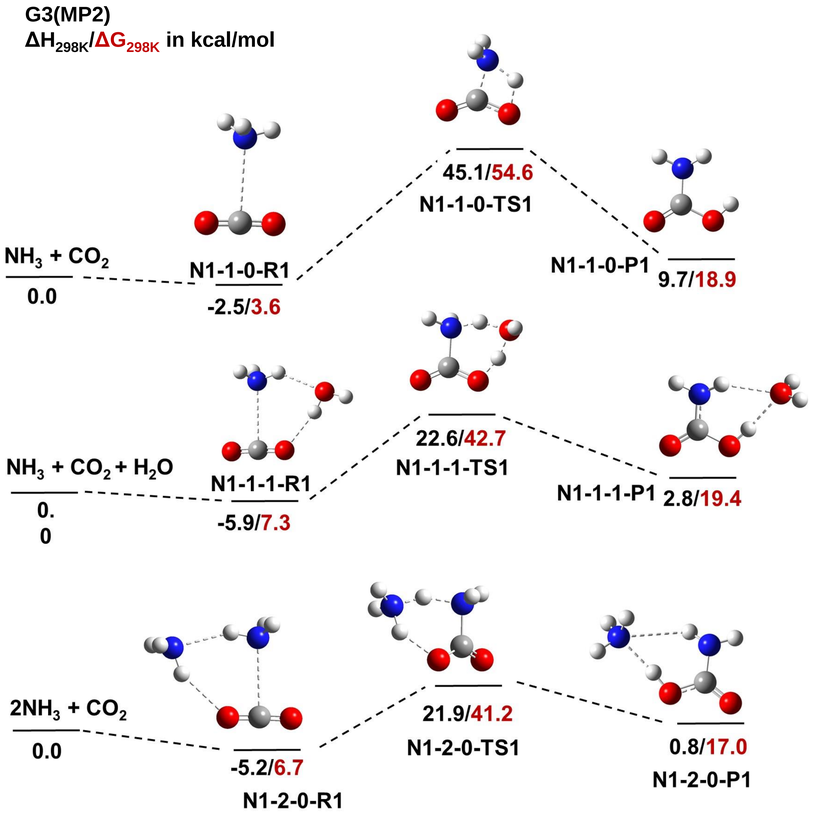
PES for H_2O-Catalyzed $H_2NC(=S)SH$ Formation



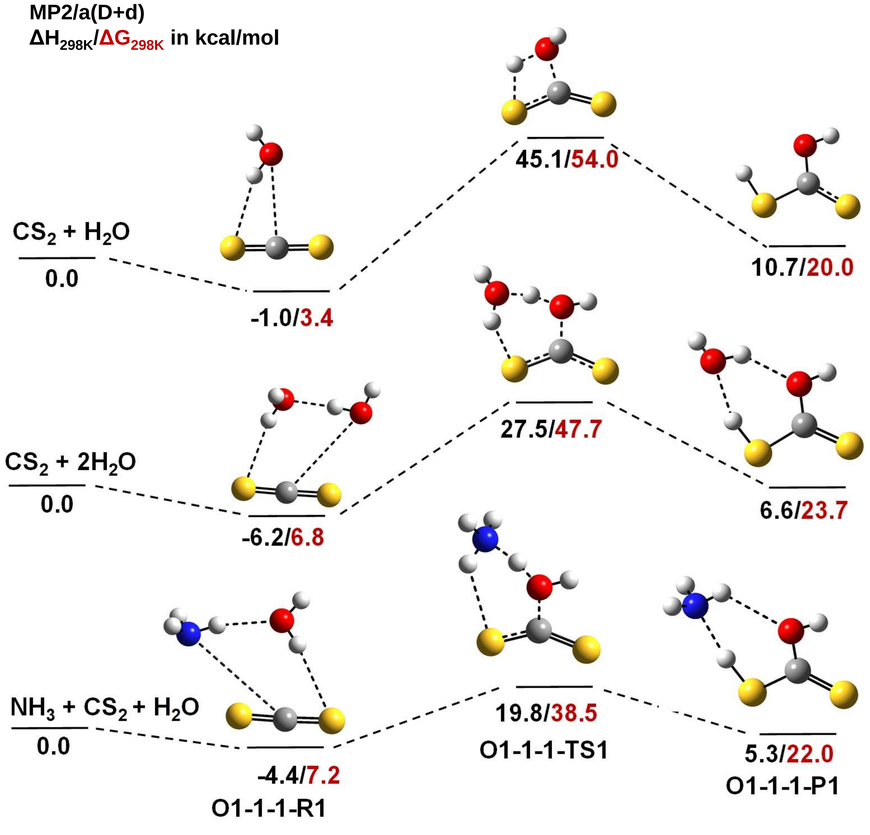
PES for NH_3-Catalyzed H_2CO_3 Formation



PES for NH_3Catalyzed H_2NCOOH Formation



PES for NH_3-Catalyzed $HOC(=S)SH$ Formation



Conclusions and Future Work

- Amine-catalyzed barriers are modest and significantly lower than H_2O-catalyzed.
- For both $H_2NC(=S)SH$ and $HOC(=S)SH$ formation, the higher proton affinity of NH_3 (204 kcal/mol) compared to H_2O (165 kcal/mol) correlates to an overall lower barrier for proton transfer than that of the H_2O-catalyzed processes.
- Consistent with previous work on CO_2 capture, our preliminary MP2 results suggest that NH_3 capture of CS_2 is more favorable than that of H_2O.
- G3(MP2), MP2/a(D+d)/COSMO, and $2NH_3/2H_2O$ Reaction Coordinate calculations are ongoing and currently in progress.

Acknowledgements

- This work was supported as part of UNCAGE-ME, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012577.

Works Cited

Kraakman, N. (2003). *Robustness of a Full-Scale Biological System Treating Industrial CS_2 Emissions*. Environmental Progress Volume 22.

Lee, Z. R., Quinn, L. J.; Jones, C. W.; Hayes, S. E.; Dixon, D. A. *Predicting the Mechanism and Products of CO_2 Capture by Amines in the Presence of H_2O* The Journal of Physical Chemistry A 2021 125 (45), 9802-9818