Atomic Tunneling in the *Chugeav Elimination* Reaction

Victor Siev and Dr. Edyta Greer

Introduction

It is widely accepted by experimentalists and theoreticians that H-atom tunneling contributes to increasing the rates of many types of chemical reactions. However, heavy-atom tunneling is often assumed/deemed to be miniscule except in reactions at cryogenic temperatures, where “narrower” reaction barriers allow tunneling to compete. Thus, we propose that thermally-activated heavy-atom tunneling is largely neglected or at least underreported in the organic chemistry literature. We think that TAHAT can potentially take place at room temperatures or slightly above, through the narrow part of the barrier near the saddle point, not at the restrictive “thick” base of the barrier. Consequently, there is a critical need for the determination of the extent of this effect within many types of reactions, such as in carbon–carbon bond forming processes.

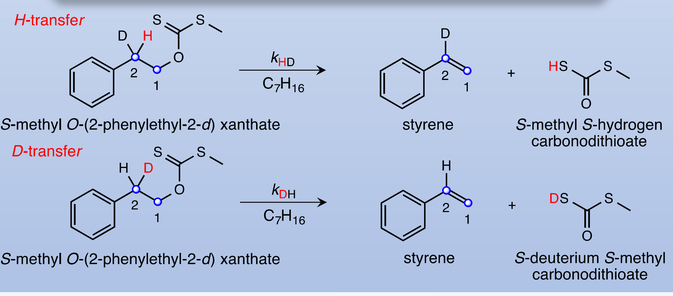
Hypothesis

Our working hypothesis is that TAHAT increases the rate of the intramolecular E2 elimination reactions in the Chugaev Elimination Reaction. The width of the barrier near the transition state (TS) is proposed to be narrow and thus allow for tunneling to contribute to the rate near the crest.

Methods and Materials

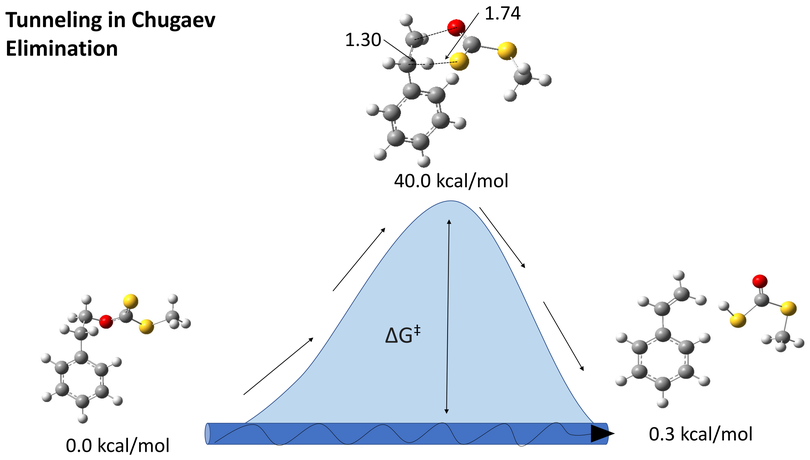
- The reactants and products were generated and visualized using Gaussian program package 5.0.9, and optimized with Gaussian 16 using B3LYP functional and the 6-31g(d,p) basis set to reproduce geometrics and energetics of structures.
- Transition states were found via local minima calculations in Gauss 16.
- Results were verified using vibrational frequency calculations and reactions mapped using intrinsic reaction coordinate calculations, which confirm the correct relative minima for each reaction.
- All further data was obtained using POLYRATE calculations. Results and graphs were made using excel.

Figures and Results



- The Chugaev elimination reaction begins with a xanthate. This structure is an intermediate that rearranges into an alkene and methanothiol.

Tunneling in Chugaev Elimination



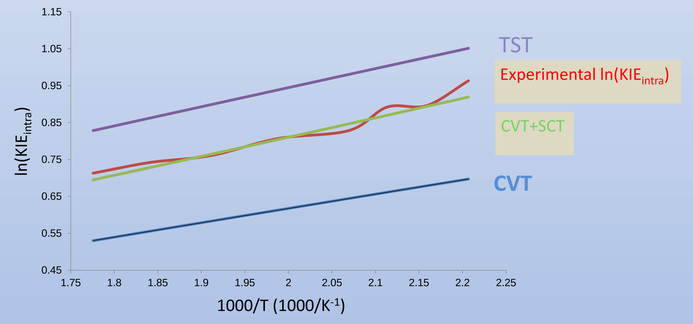
- This phenomenon is known as tunneling (above). Tunneling is possible by the wave/particle duality of objects. The less massive the object is, the higher it’s vibrational frequency and the more prevalent the wave character[5]. Waves can pass through barriers at much lower energies than particles[4]. Therefore, the lighter the atom, the more tunneling contributes to the reaction rate.

Experimental vs Computed KIE_{intra}

M06-2X/6-31+G**

			$KIE_{intra} = k_{HD}/k_{DH}$		$KIE_{inter} = 2k_{HH}/(k_{HD} + k_{DH})$	
T (°C)	T (K)	1000/T (K^{-1})	Experiment[a]	CVT+SCT	Experiment[a]	CVT+SCT
180	453.15	2.21	2.62±0.05	2.51	2.49±0.08	1.60
190	463.15	2.16	2.45±0.04	2.44	2.13±0.15	1.58
200	473.15	2.11	2.44±0.02	2.39	1.96±0.19	1.57
210	483.15	2.07	2.29±0.04	2.33	1.86±0.09	1.55
230	503.15	1.99	2.24±0.01	2.23	1.73±0.06	1.52
250	523.15	1.91	2.14±0.02	2.15	1.56±0.07	1.50
270	543.15	1.84	2.10±0.01	2.07	1.56±0.07	1.48
290	563.15	1.78	2.04±0.01	2.00	–	1.46

Arrhenius plot of $\ln(KIE_{intra})$ vs 1000/T

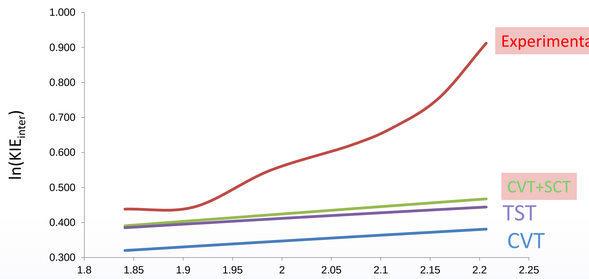


***Notice*:** excellent agreement between Experimental and CVT + SCT values of $\ln(KIE_{intra})$

Experimental vs Computed KIE_{inter}

			$KIE_{inter} = 2k_{HH}/(k_{HD} + k_{DH})$		
T (°C)	T (K)	1000/T (K^{-1})	Experiment[a]	TST	CVT	CVT+SCT
180	453.15	2.21	2.49±0.08	1.56	1.46	1.60
190	463.15	2.16	2.13±0.15	1.55	1.45	1.58
200	473.15	2.11	1.96±0.19	1.54	1.44	1.57
210	483.15	2.07	1.86±0.09	1.53	1.43	1.55
230	503.15	1.99	1.73±0.06	1.51	1.41	1.52
250	523.15	1.91	1.56±0.07	1.49	1.39	1.50
270	543.15	1.84	1.56±0.07	1.47	1.38	1.48
290	563.15	1.78	–	1.45	1.36	1.46

Arrhenius plot of $\ln(KIE_{inter})$ vs 1000/T



***Notice*:** disagreement between Experimental and CVT + SCT values of KIE_{inter}

Discussion

- There is significant agreement between experimental and computational intramolecular kinetic isotope effects. These kinetic isotope effects prove that tunneling plays and active role in the rate of the Chugaev reaction.
- Further research is underway to rectify disagreements shown in intermolecular KIE’s and tunneling in heavy atoms; Carbon, Oxygen and Sulfur

Conclusion

The results show that H/D tunneling plays a large role in the rate of Chugaev elimination reactions. By becoming more familiar with tunneling in elimination reactions, we will be able to improve the synthetization of small molecule medicines. Currently, the role of tunneling in many different reactions remains unknown. However, these findings suggest that atomic tunneling may play a large role in the reaction rate of many organic reactions. Further research is required to show the effects of heavy atom tunneling such as Carbon, Oxygen, and Sulfur.

Works Cited

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[a] experimental KIE_{intra} reported by Li, X.; York, D. M.; Meyer, M. P. Quantum Suppression of Intramolecular Deuterium Kinetic Isotope Effects in a Pericyclic Hydrogen Transfer Reaction. *J. Phys. Chem. A* **2019**, *123*, 3647-3654, Table S3, SI.

Acknowledgements

We acknowledge support from the NSF (CHE-1956098) and PSC CUNY (63367-00 51