Theoretical Study on the Mechanism of the Reaction of Acetonitrile with its Radical Form

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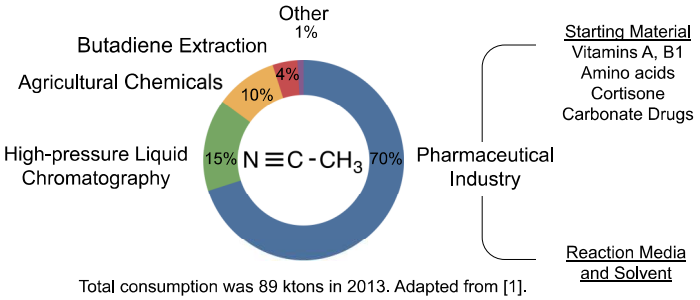
Motivation

Acetonitrile (CH_3CN) is a key intermediate used in the manufacturing of organic compounds. In the gas phase, organic synthesis could be mediated by radical species. Reactions of CH_3CN with halogens, hydroxyl group and hydrogen have been studied extensively. However, the effect of other nitrile species on the reaction mechanism remains elusive. Here, we investigate the reaction of CH_3CN with acetonitrile radical ($^{\bullet}CH_2CN$). We hypothesize that a dicarbonitrile could be formed in the presence of Chlorine radical ($^{\bullet}Cl$).

Applications of Acetonitrile



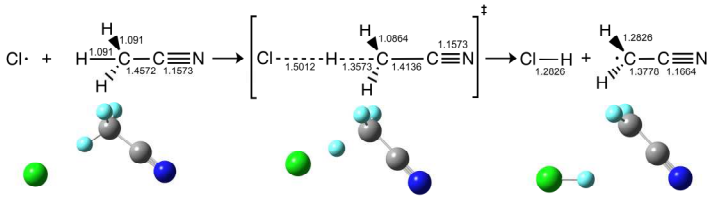
Total consumption was 89 ktons in 2013. Adapted from [1].

Method

- Density functional theory calculations using Gaussian 09 [2]:
  - Geometry optimization and frequency calculations at UB3LYP/6-311+G (2d,p) level
  - Transition state determination by finding single imaginary frequency
  - Minimum energy pathway construction by using stationary point energies

Results

Reaction of CH_3CN with $^{\bullet}Cl$



Energies in kJ/mol

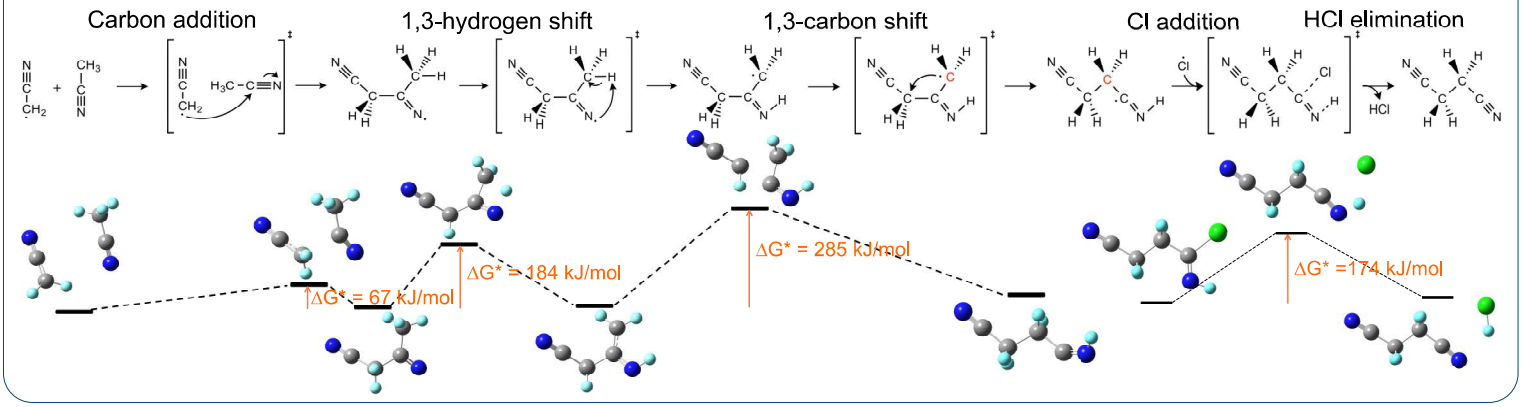
Method	$\Delta H°_{298K}$	ΔG^*
Calculated	-35.37	14.20
Theoretical [3]	-30.38	22.43
Experimental [4]	-34.77	17.74

UB3LYP/6-311++G (3df,2p) level at [3].

- Reaction enthalpy and potential energy barrier are in good agreement with the literature data.

Reaction of CH_3CN with $^{\bullet}CH_2CN$

- Isomerization via C1-C3 carbon shift has the highest energy barrier.
- This step is suggested as the slowest step of the reaction.



Conclusion

- Proposed mechanism reveals a possible route to synthesize succinonitrile.
- Molecular modeling approach provides a basis to elucidate a model for reaction kinetics.

References

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