

Tracing the Minimum Free Energy Path

Sheng-Yong Yang, Paul Fleurat, Jordan Hristov and Tom Ziegler*

Department of Chemistry, University of Calgary, University Drive 2500, Calgary,
Alberta, Canada T2N 1N4

Abstract

Recent studies have shown that a chemical reaction pathway at finite temperature can deviate significantly from the Intrinsic Reaction Coordinate (IRC) at 0K [For example, see *Science* 2003, 299, 1555-1557]. This would imply that in order to understand a real chemical reaction, exploring the minimum free energy path on the free energy surface (FES) is necessary and important. A scheme tracing the IRC on the FES based on the *ab initio* molecular dynamic (AIMD) simulations is presented in this contribution. Two S_N2 reactions, ie. (1) $\text{NH}_3 + \text{BH}_3 \cdot \text{NH}_3 \rightarrow \text{NH}_3 \cdot \text{BH}_3 + \text{NH}_3$, (2) $\text{HO}^- + \text{CH}_3\text{F} \rightarrow \text{CH}_3\text{OH} + \text{F}^-$, are exemplified to trace the IRC paths on their FESs. The results show that the IRCs of the two reactions at 300K differ from the ones at 0K. The reaction 1, which is a S_N2 reaction at 0K, will shift to S_N1 at higher temperatures. For reaction 2, the potential energy surface exhibits a deep minimum in the product exit channel arising from the $\text{CH}_3\text{OH} \cdots \text{F}^-$ hydrogen-bonded complex. However at finite temperatures this minimum disappears on the free energy surface, and the system can dissociate directly. The finding of this study shows that a new reaction mechanism might result when temperature effect is considered.