

Surprising Energy Transfer Effects in Multi-Channel Complex Reactions in Multi-Component Baths

Michael P. Burke^{1,*}

¹ Department of Mechanical Engineering, Department of Chemical Engineering, and Data Sciences Institute, Columbia University, New York, NY, USA

* Corresponding author: mpburke@columbia.edu

Complex-forming reactions, which are ubiquitous in combustion and atmospheric chemistry, involve competition between reactive and energy transfer processes that depend on the surrounding gas mixture. Most mixtures of practical relevance are comprised of multiple components, introducing potential for both bimolecular reactions involving the rovibrationally excited intermediate and energy transfer effects from multiple mixture components. While bimolecular reactions of rovibrationally excited intermediates have been the subject of substantial recent attention in atmospheric (e.g. (1-4)) and combustion (e.g. (5)) environments, multi-component energy transfer may also have a substantial impact on kinetics in practical gas mixtures.

Multi-component energy transfer effects appear to be particularly important in combustion environments, where fuel, oxygen, intermediates, carbon dioxide, and water can all comprise significant fractions of the mixture. With the exception of oxygen, most of these other species are much stronger colliders than the main diluent (usually nitrogen). An extensive body of knowledge exists for multi-component effects on energy transfer in single-channel reactions (6,7), but multi-component effects in multi-channel reactions are significantly less understood.

As demonstrated here through master equation calculations using the PAPER code (8,9), these multi-channel reactions give rise to a number of unique manifestations of multi-component effects not captured by previous insights on single-channel reactions. In multi-channel reactions, not only are multi-component effects for some channels entirely opposite to effects for single-channel reactions, but also such effects can be substantially more pronounced. This talk will highlight some of the key results from studies on prototypical multi-channel reactions as well as explore the implications of the results for both interpreting fundamental experiments and modeling combustion kinetics.

References

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