Multi-Channel Chemically Activated Reactions: Comparison of Troe's Weak Collision Model and Exact Solution of Collisional Energy Transfer by Monte Carlo Method

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Knowledge of the collisional energy transfer for a large number of multi-channel unimolecular and chemically activated reactions is often required to successfully model chemically reacting systems. Much progress has been made in our understanding of the collisional energy transfer process[1-5]. Early studies have questioned the "strong collision" hypothesis, which allowed for large energy transfer during collisions. It is known that inefficient collision energy transfer causes the population distribution of molecules above the threshold energy to deviate from the Boltzmann distribution. This results in a pressure fall-off of the thermal rate constant that is different from that predicted using the strong collision approach. For this reason, the strong collision model has in general been abandoned and collisions are effectively treated as "weak collisions".

Kineticists have employed Troe's modified strong collision model[6] to account for weak collisions. In this treatment, a collision efficiency factor β_c is introduced. This factor relates the weak collision rate constant with the strong collision rate constant through $k^{wc} = \beta_c\, k^{sc}$. Although Troe's treatment was intended for use only with single-channel unimolecular reaction, it has been nevertheless used for multi-channel reactions. In recent years, it was recognized that while Troe's collision efficiency factor is simple to calculate, for multi-channel unimolecular reactions the treatment represents a gross simplification of the collision process and the accuracies of the resulting thermal rate constants are highly questionable. Direct solution of master equation[7,8] of collisional energy transfer is a logical approach for multi-channel unimolecular and chemically activated reactions. Nevertheless it is far from trivial to analyze a reaction network of arbitrary complexity and to solve the collision energy transfer coupled with the isomerization of vibrationally excited adducts for such a reaction network.

Here, we approach the solution of master equation of collisional energy transfer and the estimation of thermal rate constants using a Monte Carlo method[9] based on Gillespie's exact stochastic method[10-12]. Our computational capability resolves reaction networks of arbitrary complexity. In this work, we compare the rates computed using the Monte Carlo approach and Troe's modified strong collision method. Rates have been computed for the chemically activated reaction of OH + CO $\rightarrow$ products[13], C_2H_2 + CH_3 $\rightarrow$ products[14] and C_6H_6 + O $\rightarrow$ products. Results show that the rate constants are systematically overpredicted for the stabilization channels by Troe's weak collision model, and as expected, the extent to which the rates are overpredicted increases as the stabilization rates deviate further from their high-pressure limits. On the other hand, the modified strong collision model is sufficiently accurate for rate estimation under many practical conditions.

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