

Dynamics of Complex-Forming Bimolecular Reactions

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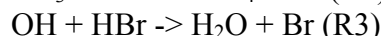
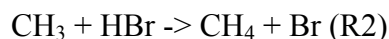
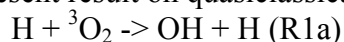
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Reactions in which two reactants form a strongly or weakly bound complex are ubiquitous in atmospheric and combustion chemistry. Theoretical description of such reactions is generally based on some version of statistical rate theories. However, dynamical methods are essential in finding out what actually happens in the reacting system and can help us establish the connection between the shape of the potential energy surface and the dynamics of the reaction.

We present result on quasiclassical trajectory calculations on reactions



In reactions R1a and R1b a strongly bound complex is formed. The trajectory calculations (1,2) showed numerous common dynamical features even though the topography of the potential surfaces is different except the presence of the deep potential well. This is found to occur partly because of the common features of the two potential surfaces, partly due to mechanical conservation rules, partly incomplete loss of memory in the complex. In reaction R1b a dominant fraction of trajectories tends to return to reactants after passing the barrier in the entrance channel and getting deeply immersed into the deep potential well of the HO₂ complex.

In reactions R2 and R3 weakly bound complexes are formed by the reactants and in both cases the barrier separating the potential well corresponding to the complex from the products is submerged below the bimolecular reactant level. Not all complexes form immediately products. There is a large fraction of collisions in which the partners linger around one another for a long time without entering the potential well which turns out to be prevented by the centrifugal barrier arising because of angular momentum conservation. excitation of reactant rotation and vibration reduces the rate. A significant fraction of trajectories return to reactants after passing the potential barrier and going halfway down on the slope of the potential surface on the product side of the potential surface. Reasons for these dynamical features will be discussed.

References

- (1) Szabó, P.; Lendvay, G. *J. Phys. Chem. A* **2015**, 119, 7180-7189.
- (2) Szabó, P.; Lendvay, G. *J. Phys. Chem. A* **2015**, 119, 12485–12497.