

# Theoretical studies of the dynamics of complex-forming bimolecular reactions

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In the  $\text{H} + \text{O}_2$  reaction a complex,  $\text{HO}_2$  is formed. On the potential surface of the first excited electronic state the reactants need to surpass a barrier before getting into the potential well. Detailed dynamics calculations show that for this reaction, the conditions of applicability of transition state theory are not met. On one hand, the entrance barrier is crossed twice by 80% of trajectories; on the other, the electronically excited  $\text{HO}_2$  does not behave statistically.

The  $\text{CH}_3 + \text{HBr} \rightarrow \text{CH}_4 + \text{Br}$  and reverse reaction, in addition to being a prototype complex-forming bimolecular reaction, play crucial role in the determination of heats of formation of free radicals. The activation energy of the forward reaction is negative. The potential energy surface of the reaction is characterized by a van der Waals complex, separated from the products by a submerged barrier. Statistical rate theories with proper parameter setting do reproduce the negative activation energy, however, the applicability of such theories has not been justified. Extending the potential surface of Czakó, we performed full-dimensional quasiclassical trajectory calculations on the reaction. The results show that the low-temperature negative activation energy turns into positive slightly above room temperature. The van der Waals complex is found not to behave statistically.