

Theoretical studies on the dynamics of the $HO + HBr \rightarrow H_2O + Br$ reaction

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The reaction $HBr + OH \rightarrow H_2O + Br$ is an excellent model for complex-forming bimolecular reactions with a submerged barrier. Given its importance in the chemistry of atmosphere, many measurements have been conducted over the years. A highly accurate full dimensional ab initio potential energy surface has recently been published, so it is now possible to compare experiments with reaction dynamical calculations. Using this PES our goal is to account for the interesting classical dynamical and quantum mechanical effects shown by this reaction.

We have calculated the reaction rates over a wide range of temperature and found a strong non-Arrhenius behaviour: the activation energy is negative at low temperatures, zero at about 600 K, and positive at higher temperatures. We suggest that this is caused by the rotation of the reactants: rotational excitation of the HBr molecule rapidly decreases the reaction cross section at lower excitation levels ($J < 15$). The thermal rate coefficients were also calculated at several temperatures using the ring polymer molecular dynamics (RPMD) method, which is based on a semiclassical statistical rate theory and accounts for quantum mechanical effects.

The results of the two calculation methods agree well with each other and also with the experiments at the temperatures where experimental data are available. This tells us that the reaction rate is controlled by classical mechanical effects. The agreement between all of the points suggests that we can reliably calculate rate coefficients at high temperatures, too, complementing the experimental work in the literature to provide rate coefficients at flame temperatures.