

Single water molecule catalysis of hydrogen abstraction reactions

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Atmospheric reactions have traditionally been divided into gas-phase and condensed-phase reactions. Elementary gas-phase reactions are typically assumed to involve at most two reactant molecules, with possible third bodies only playing the role of inert collision partners. Recent computational and experimental evidence has begun to modify this picture, as clustering (complexation) of reactants with molecules such as water has been shown to have a significant catalytic effect on some reaction rates (1,2).

In this work we present a computational study of the effect of a single water molecule on hydrogen abstraction by OH from small, saturated organic compounds. The hydrogen donors include amines, alcohols and fluorinated species. For molecules containing polar functional groups the transition state typically has a structure as shown on the left-hand side of Figure 1. Water molecules may stabilize the transition state by forming a ring structure as shown on the right-hand side of Figure 1. Our calculations indicate that the stabilization on the transition state electronic energy is at most a few kcal/mol. This stabilizing effect is diminished when zero point vibrational energy and entropy is included, and we predict that almost no catalytic effect should be observable at room temperature for any of the systems studied. Decreasing the temperature attenuates the entropic cost to be overcome for all compounds, and a catalytic effect might become evident below 100 K.

Since simultaneous three-body collisions in the atmosphere are extremely improbable, a necessary precondition for water catalysis is that water is already complexed with either the molecule being oxidized or with OH. Our results suggest that neither OH nor any of the studied compounds form a sufficiently strong complex with water to be significantly hydrated at temperatures and humidities encountered in the troposphere. Even though the intrinsic water catalysis for some of these reactions may be significant at lower temperatures, the net water catalysis in the atmosphere will still be minor, because the absolute water concentration and in turn the abundance of the hydrated complex decreases rapidly with decreasing temperature. In laboratory experiments, where the hydrated complexes can be generated in a jet prior to reaction, it might be possible to observe these intrinsic catalytic effects of water.

References

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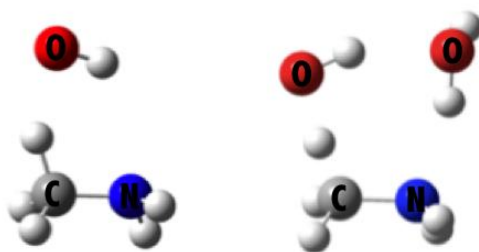


Figure 1. Transition states for the oxidation of methylamine by OH in the absence (left) and presence (right) of a water molecule.