Abstract

The chemical evolution of interstellar clouds can be estimated over time using kinetic models. The Kinetic Database for Astrochemistry (KIDA) contains kinetic parameters for thousands of reactions for inclusion into gas phase and gas-grain models. Many of the reactions in this database have yet to be reviewed by experts for their accuracy, but are available to the public for general use. Investigation of some of the unsolved reactions revealed identical rate constants for a number of chemically distinct reactions as well as several values with suspicious rate constants for the temperature ranges listed. Rate constants for several unreviewed reactions from KIDA involving small organic molecules and compounds relevant to their formation were evaluated using the POLYRATE kinetics program in conjunction with the Gaussian 09 electronic structure modeling software. The results of these calculations were compared to the values reported in KIDA.

Reactions were selected from the KIDA database based on the following criteria: 1) the reaction had a recommendation of “Not rated value,” 2) the reaction was a bimolecular process exhibiting Arrhenius-type kinetics, 3) one or more of the species participating in the reaction contained organic components or fragments which would be relevant to the formation of other organic compounds, 4) the kinetic parameters were “surprising” — either the reaction had identical kinetic information to other reactions in the database (despite being chemically distinct processes), the reaction had sets of conflicting data, or the reference was not specific to the reaction.

Methods

Reactants, products, and transition states were optimized using the Gaussian 09 electronic structure modeling program at the MP2-2X6/31++G(d,p) level of theory. POLYRATE performed conventional and variational transition state theory calculations (canoncal and microcanonical) with zero, small, and large curvature tunneling corrections to estimate the rate constants, from the optimized structures via the Gassatte Gaussian/POLYRATE interface program.

Future Work

Several other reactions have been identified for further study. We have identified and optimized transition states for 11 additional reactions in the database with suspicious rates. We will determine rates for these reactions and then explore what effects the updated rate constants have on predicted abundances of a variety of components of interest.

References