2.126 Linking theoretical kinetic studies with laboratory and chamber experiments.

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Abstract:

Though much of our understanding of the chemistry of the atmosphere is derived from experimental studies, the elementary reactions that govern atmospheric chemistry are not always readily studied by experimental methodologies. Theoretical studies, combining quantum chemical characterization of the reaction properties with theoretical kinetic prediction of temperature- and pressure-dependent rate coefficients and product distributions, offer a highly complementary approach to experimental studies, able to investigate some intermediates and reaction conditions that are hard to access practically. A number of theoretical kinetic studies are presented where theoretical predictions contributed to the interpretation of experimental observations and/or the development of the kinetic model. The reaction systems touched upon includes H-migration in alkyl peroxy radicals, the catalytic conversion of fluoridated products, and the reactions of Criegee intermediates.
The reactivity trends discovered for a given reaction class from theoretical calculations, laboratory studies, environmental chamber studies, field data, and modeling, should ultimately be combined and summarized in Structure-Activity relationships (SARs). These allow kinetic model development for novel, complexly substituted compounds and intermediates without the need for direct studies of each reaction step. While SARs are available for many reaction classes, their field of applicability and their reliability is often not fully understood; e.g. existing SARs often struggle with multi-functionalized compounds. A brief overview of current SAR development, and the role of theoretical calculations therein, will be presented.