MECHANISTIC MODEL OF OZONE FORMATION

A team of researchers is modeling ozone formation induced by volatile organic compounds.

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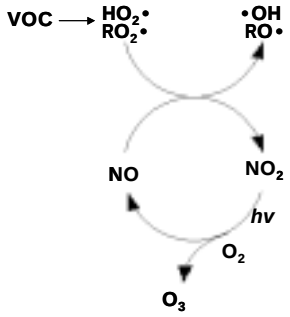
Objective: Emission of volatile organic compounds (VOC's) into the atmosphere leads to increases in the concentration of ambient ozone, a major component of photochemical smog. Therefore, the ability to determine the contribution of a selected VOC to ozone formation would be extremely valuable for both environmental and industrial reasons. To this end, a promising strategy is to create detailed mechanistic models based on kinetics and photochemistry, from which predictions of ozone production can be made.

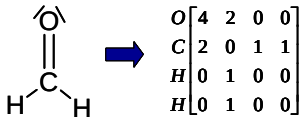
Approach: Large uncertainties in the reaction mechanism and the lack of quantitative rate constants for the majority of the elementary step reactions leading to the ozone formation prohibit their explicit description, while manual assembly of models of the implied complexity is extremely time-consuming. The Broadbelt group has overcome these difficulties by applying an automated approach, which involves transforming one set of data (reactants, reaction rules and a structure/property relationship) into another set of data (products and reactions) using graph theory representations of species and a computer. Based on this information, a mechanism with experimental and/or estimated rate constants is generated. Significantly, the ability to use this strategy is dependent on how well the chemistry of interest is known. The Broadbelt group addresses this issue by organizing the chemistry according to reaction families postulating that structurally related species undergo the same type of chemical transformations. As a result, a small set of reaction families can be used to summarize a complex multi-component reaction system.

Results: The Broadbelt group has incorporated sixteen reaction families inherent in atmospheric chemistry into the automated model. Data available in the literature are used to develop enthalpy-based linear free energy relationships for the reaction families with non-existing kinetic correlations. Semi-empirical and *ab initio* quantum calculations are performed to obtain thermodynamic data not available in the literature. Rate constants for a wide range of different reactions types are accurately estimated using linear free energy relationships along with properties obtained from quantum mechanical calculations. Four reaction families have been developed to account for photochemical reactions of peroxides, nitrates, aldehydes, and ketones. A group additivity approach similar to the one developed by Benson to estimate thermodynamic data is implemented to estimate absorption cross sections over the wavelength region of tropospheric interest and has proven to be in good agreement with the available experimental data for a range of molecules with different functional groups.

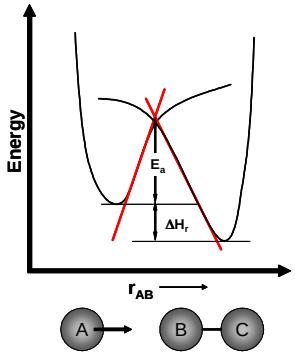
Selected Publications: Wong H-W, Li X, Swihart MT, Broadbelt, LJ, *J Chem Inf Comput Sci* **2002**, accepted; Broadbelt LJ, Stark SM, Klein MT, *Comput Chem Eng* **1996**, 20(2): 113; Broadbelt LJ, Stark SM, Klein MT, *Ind Eng Chem Res* **1995**, 34(8): 2566; Broadbelt LJ, Stark SM, Klein MT, *Ind Eng Chem Res* **1994**, 33(4): 790; Broadbelt LJ, Stark SM, Klein MT, *Chem Eng Sci* **1994**, 49(24B): 4991.



VOC's present in the atmosphere increase the NO to NO_2 conversion, which results in the formation of ozone.



A simple 4 x 4 matrix represents formaldehyde. The diagonal elements and off-diagonal elements represent non-bonding electrons and bond order between two atoms, respectively.



A reaction energy diagram of the reaction A + BC → AB + C illustrates how the Evans-Polanyi relationship relates the activation energy to the reaction enthalpy.