Accuracy of OH Reaction Rate Constants Determination over Atmospheric Temperatures.

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One of the most important parameters in estimating the environmental impact due to emission of a compound is its residence time in the atmosphere, which is driven by the reaction of a compound with hydroxyl radicals (OH) for many atmospheric trace gases. The atmospheric lifetime is important for estimating ozone depletion potential (ODP) and global warming potential (GWP) of industrial compounds which are needed for evaluation of their environmental impact and regulatory purposes.

The sources of critically evaluated photochemical data for atmospheric modeling, NASA/JPL Publications and IUPAC Publications, recommend uncertainties within 10%-60% for the majority of OH reaction rate constants with only a few cases where uncertainties lie at the low end of this range. These uncertainties can be somewhat conservative because evaluations are based on the data from various laboratories obtained during the last few decades. Nevertheless, even the authors of the original experimental works rarely estimate the total combined uncertainties of the published OH reaction rate constants to be less than ca. 10%. Thus, uncertainties in the photochemical properties of potential and current atmospheric trace gases obtained under controlled laboratory conditions still may constitute a major source of uncertainty in estimating the compound's environmental impact.

The purpose of the presentation is to illustrate the potential for obtaining more accurate laboratory OH reaction rate constant data over the temperature range of atmospheric interest. Both data scattering and systematic uncertainty associated with instrumental measurements contribute to the total uncertainty of the rate constant. Although data scattering does not obviously obey the normal distribution, the statistical uncertainty is usually calculated to present the results of kinetic measurements. The scattering of measured rate constants in the Arrhenius plot should be consistent with their individual uncertainties and can serve as complementary evidence of the measurement precision. Then, the statistical tests can be applied to proof the temperature dependence derived from the fit to the experimentally obtained data. The detailed inventory of various sources of instrumental uncertainty yields the total uncertainty of the OH reaction rate constant, which can be as small as ~2% in our flash photolysis – resonance fluorescence experiments.

The high precision of kinetic measurements allows reliable determination of weak temperature dependences of the rate constants and clear resolution of the curvature of the Arrhenius plots for the OH reaction rate constants of various compounds. The results of OH reaction rate constant determinations between 220 K and 370 K will be presented.

References

(1) Orkin, V.L.; Martynova, L.E.; Ilichev, A.N. *J. Phys. Chem. A* **2010**, 114, 5967-5979.
(2) Orkin, V.L.; Khamaganov, V.G.; Martynova, L.E.; Kurylo, M.J. *J. Phys. Chem. A* **2011**, 115, 8656-8668.