



Accurate FP-RF determination of OH reaction rate constants over atmospheric temperatures.

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One of the most important parameters in estimating the environmental impact of a trace gas emission is the residence time of the compound in the Earth's atmosphere, which (for many such compounds) is driven by their reaction with hydroxyl radicals (OH) in the troposphere. These atmospheric lifetimes are important for estimating ozone depletion potentials (ODPs) and global warming potentials (GWPs) of industrial compounds, which are key parameters utilized in regulatory considerations.

The critically evaluated photochemical databases for atmospheric modeling, the NASA/JPL (<http://jpldataeval.jpl.nasa.gov>) and the IUPAC (<http://www.iupac-kinetic.ch.cam.ac.uk>) generally cite recommend uncertainties in the 10%-60% range 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 are typically somewhat conservative because the evaluations are based on data from various laboratories obtained as far back as a few decades. Furthermore, the authors of the original experimental studies rarely provided estimates of the total combined uncertainties (statistical plus systematic) of the derived OH reaction rate constants. Thus, uncertainties in the laboratory derived photochemical properties of potential and current industrial trace gases still constitute major sources of uncertainty in estimating a compound's environmental impact.

The results of new accurate measurements of OH reaction rate constants over the temperature range of atmospheric interest will be presented and compared with the earlier data. A detailed inventory of the various sources of instrumental uncertainties related to our new flash-photolysis resonance fluorescence experiments will be presented and the statistical treatment of kinetic results will be discussed, thereby illustrating that total uncertainties in OH reaction rate constants can be as small as $\sim 2\%$.

The high precision of measurements conducted between 220 K and 370 K now allows us to clearly resolve real curvature in the Arrhenius plots for the OH rate constants of various hydrocarbons and halogenated hydrocarbons. This emphasizes the importance of direct reaction rate constant measurements at low atmospheric temperatures since extrapolations from higher temperature data can significantly underestimate the reactivity at the lower temperatures.