

Some results of higher accuracy measurements of OH reaction rate constants.

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Rate constants of OH reactions with hydrocarbons and halogenated hydrocarbons can be determined with an accuracy of 2-3% over the temperature range between 220 K to 370 K. This was demonstrated in studies of OH reactions with various both halogenated and non-substituted organics including alkanes, alkenes, alcohols, and ethers. Lower data scattering allows rigorous statistical analysis of the results and reveals often missing details of the reactivity such as the dependence of the rate constant on the temperature, pressure, and the reactant molecular structure.

(i) The temperature dependence of both H-abstraction and OH-addition reactions exhibits a noticeable curvature in the Arrhenius plot. (ii) The reactivity of stereo-isomers of unsaturated compounds can be substantially different and exhibit very different temperature dependences. (iii) The temperature dependence of the OH-addition rate constants, which are approaching the collision factor has been studied. (iv) Unexpected pressure dependence of OH-addition reaction rate constants was found in case of C4 alkenes.

The accuracy of OH kinetic data is of primary importance for the purpose of comprehensive atmospheric modeling of compound's fate and its impact on the atmosphere, such as residence time in the atmosphere, stratospheric ozone depletion, global warming, and local pollution.