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Determination of temperature dependent rate coefficients of the reaction of hydroxyl radicals with volatile organic compounds using a new OH reactivity instrument

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Accurate knowledge of the rate coefficient of the reaction of volatile organic compounds (VOCs) with the hydroxyl radical (OH) is fundamental for understanding atmospheric chemical processes and for predictions of air quality forecasting models. Nevertheless, the temperature dependence of reaction rates of many organic compounds is not well investigated as measurements are challenging.

In this work, we present absolute measurements of reactions rates with the OH radical for a series of VOCs for different temperatures. An OH reactivity instrument previously used for field and chamber measurements was further developed to enable these accurate measurements of reaction rates. The OH reactivity (kOH) is the inverse lifetime of the OH radical expressed by the product of the OH reactant concentrations and its reaction coefficient with OH. In this instrument, OH reactivity is measured by the direct observation of the decay rate of OH that is produced in a flow tube by ozone laser flash photolysis at 266 nm. The decay of OH radicals is measured at a high time resolution of 1 ms. If a known concentration of an organic compound is added to the bath gas (humidified synthetic air) the decay time directly gives the rate coefficient. As the air temperature can be controlled, the Arrhenius expression of the rate coefficient can be determined.

VOC mixtures in synthetic air were prepared in canisters. The concentration was determined by the total organic carbon method, in which all carbon atoms are combusted to CO_2 on heated catalysts and the CO_2 concentration is measured by a commercial cavity ring-down instrument.

The method was validated with several alkanes for which reaction rates are well-known. Excellent agreement within a few percent with recommendations by IUPAC and NASA-JPL demonstrates the high accuracy of the new method. The Arrhenius expression of OH reaction rates was determined for several monoterpenes and aromatic hydrocarbons.