Degradation of hydrocarbons in the atmosphere by OH radicals: a kinetic study in the reaction chamber SAPHIR

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The decay of fast reacting hydrocarbons in reaction with OH radicals have been studied in the sunlit chamber under burdens of trace gases as they are typical for the moderately polluted planetary boundary layer. The chamber was filled with synthetic air with a mixture of the hydrocarbons and a few ppb of NO_2 added. To avoid significant degradation by ozonolysis the ozone mixing ratio was always smaller than 40 ppb. Under these circumstances the main OH source in SAPHIR is the photolytic decomposition of HONO that is emitted from the wall of the chamber. Time series of the hydrocarbon mixing ratios were measured by gas chromatography (n-octane, propene, m-xylene, isoprene) and by PTRMS [proton transfer spectroscopy] (isoprene and m-xylene). The OH concentrations, [OH], were determined with the DOAS (differential optical absorption spectroscopy) instrument of the ICG II. The degradation of the hydrocarbons is solely due to reaction with OH and can be described as a first order process. Small contributions of dilution due to the replenishment flow into the chamber were taken into account. The rate constant k_{new} was derived from a least squares fit (LSQ) for the negative time integral of $k_{ref} * [OH]$ and the logarithmic mixing ratios of the hydrocarbon. k_{ref} is a reference value for the rate constant taken from the Master Chemical Mechanism (MCM31). From the slope f from the LSQ we find $k_{new} = f * k_{ref}$. In all cases the deviation (f-1) was only a few percent and in most cases not significantly different from zero. Assuming no systematic uncertainty of the OH measurements these results confirm the literature data.