

Precise determination of reference rate constants for reactions of OH with hydrocarbons in the Low-Temperature Aerosol Smog Chamber, LOTASC

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The degradation kinetics of 18 hydrocarbons (alkanes and aromatics) by OH-radicals was investigated at -25°C in the LOTASC. Rate constants for the reactions with OH were determined using toluene and hexane as reference compounds. The solar simulator, consisting of 16 fluorescent tubes (Osram Eversun Super, 80W each), irradiated the chamber from the bottom. OH-radicals were produced by photolysis of methyl nitrite, in this experiment the OH-concentration varied from $2 \cdot 10^7 \text{ cm}^{-3}$ at the beginning to $5 \cdot 10^6 \text{ cm}^{-3}$ after 6 hours of illumination. The decrease of the hydrocarbons was determined every 35 min from 30-ml gas samples using cryogenic trapping and GC-FID (using an alumina-coated capillary column Al203 PLOT) and is shown below.

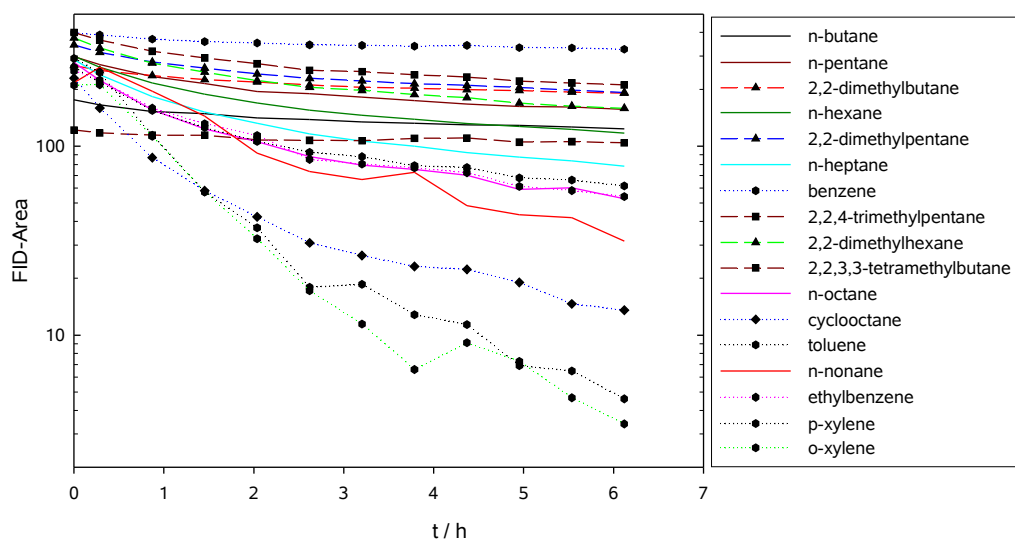


Figure 1: Decrease of the hydrocarbon concentration during a smog chamber run by reaction with OH at -25°C .

The relative rate constants are compared with extrapolated values from current recommendations and with measurements at room temperature from our own laboratory. Such data may help to diminish discrepancies caused by insufficient knowledge of temperature dependencies, existing mainly for aromatics. These must be resolved before the radical clock technique can be employed successfully for radical diagnostics for the presence of atomic Cl in halogen activation experiments at lowered temperatures.

