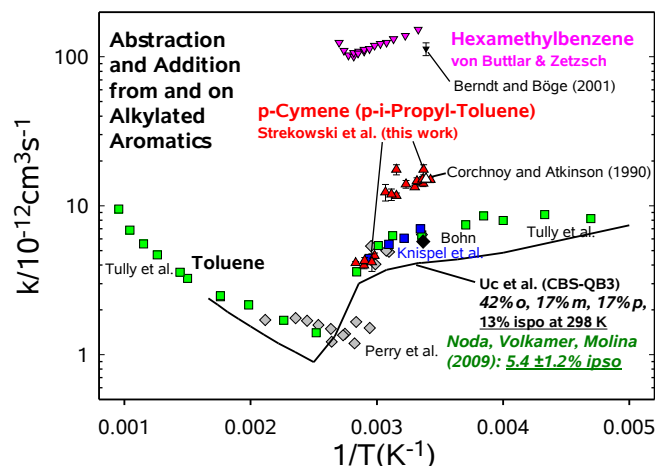


Rate constants and mechanisms for the reactions of OH with alkylated aromatics

R. Strekowski¹, M.-T. Rayez², J.-C. Rayez², P. Alarcon³, J. von Buttlar³, R. Koch³, M. Siese³,
and C. Zetzsch^{3,4}

Université de Provence, Marseille¹, Université Bordeaux 1, Talence², Universität Bayreuth³,
and Fraunhofer-Institut für Toxikologie und Experimentelle Medizin, Hannover⁴

The reaction of OH with alkylated aromatics is studied by pulsed vacuum-UV flash-photolysis of H₂O and time resolved resonance fluorescence. Initial concentrations of OH are around 10¹⁰ molecules/cm³ and are small against those of the aromatics, providing pseudo-first-order decays of the resonance fluorescence intensity (known to be strictly proportional to [OH]). The decay curves are exponential at room temperature, and biexponential decays are observed at only slightly higher temperatures of 40 °C and above. The biexponential decays indicate equilibration of OH with an OH-adduct and allow us to determine the reaction enthalpies from the temperature dependence of the equilibrium constants and the bond energies from the activation energies of the unimolecular decays. Temperature dependencies, observed for the loss of OH into abstraction and addition channels, are obtained for hexamethylbenzene and p-cymene and indicate a prereactive complex. They are displayed together with experimental literature data and calculations on toluene in the following Arrhenius plot.



The data for hexamethylbenzene indicate an extremely high rate constant for a reversible addition, that must be an ipso addition since hexamethylbenzene does not offer other opportunities. Above 80°C a curvature of the Arrhenius plots indicates a change of mechanism, possibly a loss of a methyl group from the ipso adduct. Similar behaviour of p-cymene (p-isopropyl toluene) is observed, with an equilibrium between 30 and 50 °C and a step-like change in rate constant (down by a factor of 3 at higher temperatures), continuing a similar temperature dependence. An interpretation of these observations with respect to formation of a less strongly bound adduct or a loss of the isopropyl group from the adduct is possible. Theoretical calculations by the density functional theory (DFT): B3LYP/6-31G(d, p) with an unrestricted description for open-shell structures are performed and compared with the experiments. On the other hand, a firm conclusion about the mechanism requires product analysis, e.g. accessible through flow reactor (Noda et al, 2009) and simulation chamber experiments with various analytical techniques.