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What is the contribution of ipso-addition of OH in the reaction of methylated benzene-aromatics – first results on hexamethylbenzene

J. von Buttlar (1), R. Koch (1), M. Siese (1), C. Zetzsch (1,2)

(1) Atmospheric Chemistry Research Laboratory, University of Bayreuth, Germany, (2) Fraunhofer-Institute for Toxicology and Experimental Medicine, Hannover, Germany (cornelius.zetzsch@uni-bayreuth.de / Fax: +49-921-555726)

Addition of OH is well-known to be the predominating primary step in the tropospheric transformation of aromatic hydrocarbons. The addition occurs preferably at a non-occupied position. The low OH-reactivities of hexafluorobenzene and hexachlorobenzene imply that the ipso addition is typically very slow. On the other hand, a recent study on hexamethylbenzene reported a very large rate constant of $k\pm 2\sigma =$ $(1.13\pm0.11) \times 10^{-10} \text{ cm}^3 \text{s}^{-1}$ for this reaction at 295K (Berndt and Böge, 2001), almost a factor of 2 larger than a value of 0.64 x $10^{-10} \text{ cm}^3 \text{s}^{-1}$ obtained from current structure/reactivity relations of mono- and polysubstituted aromatics. Furthermore, hexamethyl-2,4-cyclcohexadienone was observed as a product, indicating ipsoaddition. We used the flash-photolysis/resonance fluorescence technique to investigate the reaction in the range between 300 and 370 K. The biexponential decays of the resonance fluorescence signal clearly indicate a reversible addition of OH according to:

 $OH + HMB \le HMB-OH(1, -1)$

The Arrhenius expression $k_1 = 2.8 \times 10^{-11} \exp (498 \text{ K})/\text{T cm}^3/\text{s}^{-1}$ confirms the large reactivity and yields a value of $1.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 295 K in reasonable agreement with the value of Berndt and Böge. Abstraction of H atoms from the methyl groups of HMB can be estimated to contribute a very minor channel only. Extrapolating the respective abstraction channels of toluene and the xylenes to six methyl substituents yields $k_{abs} = 4.0 \times 10^{-11} \exp (-709 \text{ K/T}) \text{ cm}^3 \text{ s}^{-1}$. This amounts to less than 5% of k_1 in the total temperature range and can almost be neglected within the experimental

uncertainty.

Evaluating the equilibrium constant from the linear dependence of the amplitude ratio I_1/I_2 on the concentration of HMB according to the equation $I_1/I_2 = K_1$ [HMB] leads to $K = 2.0 \times 10^{-25} \exp(11407 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1}$. Combining the abstraction-corrected addition with the equilibrium constant leads to $k_{uni} = 1.0 \times 10^{14} \exp(-10500 \text{ K/T}) \text{ s}^{-1}$ and a value of $k_{uni} = 0.063 \text{ s}^{-1}$ at 300 K. The large stability of HMB-OH implies that ipso-addition may be an important reaction channel with other methylated benzenes, and a careful inspection of the decays of OH in the presence of 1,3,5-trimethylbenzene revealed triexponential behaviour, indicating a significant contribution of an ipso-adduct in this case.

Thus, ipso-addition may be more important than thought before, and it may play an increasing role in the phenolic ring-retaining products of the later oxidation stages, including the oligomers from gas-to-particle conversion.

Berndt, T. and Böge, O. (2001) *Rate constants for the gas-phase reaction of hexamethylbenzene with OH radicals and H atoms and of 1,3,5-trimethylbenzene with H atoms*, Int. J. Chem. Kinet., 33, 124-129.

Koch, R., Knispel, R. Elend, M., Siese, M., Zetzsch, C. (2007) *Consecutive reactions* of aromatic-OH adducts with NO, NO₂ and O₂: benzene, naphthalene, toluene, m-and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline, Atmos. Chem. Phys. 7, 2057-2071.