

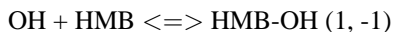


## What is the contribution of ipso-addition of OH in the reaction of methylated benzene-aromatics – first results on hexamethylbenzene

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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  $k \pm 2\sigma = (1.13 \pm 0.11) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for this reaction at 295K (Berndt and Böge, 2001), almost a factor of 2 larger than a value of  $0.64 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  obtained from current structure/reactivity relations of mono- and polysubstituted aromatics. Furthermore, hexamethyl-2,4-cyclcohexadienone was observed as a product, indicating ipso-addition. 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:



The Arrhenius expression  $k_1 = 2.8 \times 10^{-11} \exp(498 \text{ K}/T) \text{ cm}^3/\text{s}^{-1}$  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  $I_1/I_2 = K_1 [\text{HMB}]$  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, NO<sub>2</sub> and O<sub>2</sub>: benzene, naphthalene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline*, Atmos. Chem. Phys. 7, 2057-2071.