

Reversible reactions of OH with methylated benzenes and contributions of ipso addition

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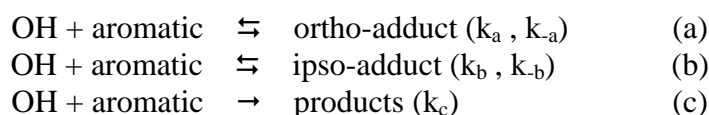
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The reversible addition of OH radicals to the methylated benzenes toluene, p-xylene, all three trimethylbenzenes, 1,2,4,5-tetramethylbenzene, pentamethylbenzene, and hexamethylbenzene has been studied by VUV flash photolysis of H₂O in the presence of the aromatic at various temperatures in inert buffer gas, monitoring OH by time resolved resonance fluorescence. A reversible reaction of OH with hexamethylbenzene, observed by the same technique by Koch et al. [1] and von Buttler et al. [2], implies that ipso addition to a fully substituted aromatic can be a rapid process in the gas phase.

In general, addition in competition with abstraction leads to biexponential decays of OH as soon as it becomes reversible on the time scale of the observation. The decays may become triexponential if only two types of reversible addition (ortho and ipso) exist by symmetry. This has been shown for trimethylbenzene (1,3,5-) by Bohn and Zetzsch [3], where the other isomers (1,2,3- and 1,2,4-) follow a similar behavior with two predominating adducts. Meanwhile we observed such behavior of OH with 1,2,4,5-tetramethylbenzene (only ortho and ipso available, see *Alarcon et al., this conference*) and a similar behavior with pentamethylbenzene according to the mechanism



where isomerizations of the adducts cannot be excluded. We present determinations of Arrhenius parameters for the reversible additions.

References

- (1) Koch, R.; Knispel, R.; Elend, M.; Siese, M.; Zetzsch, C. *Atmos. Chem. Phys.* **2007**, *7*, 2057-2071.
- (2) von Buttler, J.; Koch, R.; Siese, M.; Zetzsch, C. *Geophys. Abstr.* **2008**, *10*, EGU2008 – 10576.
- (3) Bohn, B.; Zetzsch, C. *J. Phys. Chem. A* **2012** (submitted for publication).