



Experimental and theoretical study of the reaction of OH with the aromatic molecule p-cymene, proceeding via two adducts.

Paulo Alarcon (1), Cornelius Zetzsch (1,4), Birger Bohn (2), Marie-Thérèse Rayez (3), and Jean-Claude Rayez (3)
(1) University of Bayreuth, Bayreuth, Germany (paulo.alarcon@uni-bayreuth.de), (4) Fraunhofer Institut of Toxicology and Experimental Medicine, Hannover, Germany (cornelius.zetzsch@uni-bayreuth.de), (2) Institute of Energy and Climate Research. IEK-8: Troposphere.FZJ, Jülich, Germany (b.bohn@fz-juelich.de), (3) Institut des Sciences Moléculaires, groupe ISM-THEO, University Bordeaux 1, France (mt.rayez@ism.u-bordeaux1.fr)

Nonmethane volatile organic compounds (NMVOCs) play a major role in the photochemical formation of ozone and secondary aerosols, and both processes are initiated by OH radicals, which are important in combustion as well. We studied the reaction of the biogenic p-cymene with OH radicals at Bayreuth in the temperature range between 300 and 413 K at a total pressure of 195 mbar in He by vacuum UV flash photolysis of H₂O and time resolved resonance fluorescence of OH. The addition of OH predominates at room temperature and we can distinguish two adducts being formed. The observed decays of the OH signal are triexponential at elevated temperatures and consistent with the mechanism:

OH + p-cymene \leftrightarrow adduct 1 (1, -1)

OH + p-cymene \leftrightarrow adduct 2 (2,-2)

OH + p-cymene \leftrightarrow products (3)

The sum ($k_1 + k_2 + k_3$) was found to be $(1.50 \pm 0.05) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, in very good agreement with a value of $1.51 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ determined by Corchnoy and Atkinson (1990) in a chamber study at $T=295\text{K}$, and decrease slightly with increasing temperature up to $T=330\text{K}$, where it starts to fall to around $4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Assuming that abstraction (k_3) is negligible against addition, the equilibrium constant K_1 of the loosest adduct (k_1/k_{-1}) can be estimated from the expression:

$$K_1 = (k_1 + k_2 + k_3)^2 / (k_{-1} \times k_{-2}) \sim k_{12} / (k_{-1} \times k_{-2})$$

DFT calculations performed at Bordeaux using the M06-2X functional shows a prereactive complex (PRC), 6.2 kcal/mol below the entrance channel followed by a transition state between -0.5 and 0.6 kcal/mol according to the addition site. If entropy is taken into account by calculating the activation free energy, we have found that the ortho and meta sites with respect to the CH₃ substituted site are the most reactive. More theoretical studies are in progress.