

***Interactive comment on* “Consecutive reactions of aromatic–OH adducts with NO, NO₂ and O₂: benzene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline” by R. Koch et al.**

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In Section 4.3 of the paper the authors cite Grebenkin and Krasnoperov (2004) who argue against an irreversible adduct loss in a reaction with O₂ by stating that a low value of the rate constant k_6 is inconsistent with its weak temperature dependence. I would like to note that in the presence of a fast equilibrium with a peroxy radical, the rate constant of adduct loss measured in the present work by Koch et al. most likely is

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an effective rate constant as outlined by Bohn and Zetzsch (1999):

$$k_6 = K_7 k_a + k_b$$

Here K_7 is the equilibrium constant of peroxy radical formation ($K_7 = k_7/k_{-7}$), k_a is the sum of first-order rate constants of unimolecular reactions possibly competing with peroxy radical dissociation back to the adduct and O_2 (e.g. formation of a bicyclic radical), and k_b is the sum of rate constant of O_2 reactions competing with formation of the peroxy radical (e.g. formation of HO_2 + phenol). Only in the case where $k_a = 0$, k_6 actually corresponds to the rate constant of an elementary reaction and the objection by Grebenkin and Krasnoperov (2004) is justified. The other extreme would be $k_b = 0$ where k_6 corresponds to the product $K_7 k_a$. In that case it can be shown that the effective activation energy of k_6 is the sum of the reaction enthalpy of peroxy radical formation ($\approx -50 \text{ kJ mol}^{-1}$) and the activation energy of k_a . Thus, there may be compensating effects and a complex temperature dependence of k_6 is therefore not surprising.

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