Elucidating the fate of the OH-adduct in toluene oxidation under tropospheric boundary layer conditions

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Ji et al. (1) published a study examining the mechanism of the initial stages of OH-initiated oxidation of toluene. Their results challenge the mechanisms used in atmospheric chemistry models [e.g., Master Chemical Mechanism (MCM) (2)] derived from chamber experiments at atmospheric conditions, and previous experimental (3, 4) and theoretical studies (5, 6). In these mechanisms, the main product (55–65%) of the O2 reaction with the OH-adduct is a peroxy-peroxide bridged radical (cyc-RO2, Scheme 1), the subsequent chemistry of which goes on to yield dienals and the dicarbonyls: glyoxal and methylglyoxal. The present study detected a negligible yield of these dicarbonyl products. From this, the authors conclude that the cyc-RO2 pathway is insignificant under atmospheric conditions.

The experiments use [O2] = 1 × 10^{15} \text{ cm}^{-3}, roughly 5,000 times lower than in the atmospheric boundary layer ([O2] = 5 × 10^{18} \text{ cm}^{-3}). The authors state that “the absolute O2 concentration had no effect for the competing reactions between the cresol and primary RO2 pathways (i.e., pathway I vs. pathway II in Fig. 1).” However, we believe this not to be the case, and their figure 1 to be an incomplete representation of the chemistry pertinent to the study. Crucially, it is missing the decomposition of RO2 back to the OH-adduct.

Reducing [O2] shifts the [RO2]/[OH-adduct] equilibrium toward the OH-adduct. While this alone has little effect on the relative contribution of pathway I vs. pathway II, it increases the importance of any other sinks of the OH-adduct. The authors have previously reported [NO2] = 3–7 × 10^{11} \text{ cm}^{-3} with a very similar experimental setup (7), presumably as a residual from the excess NO2 used in OH generation. The reaction rate of the OH-adduct with NO2 is a factor of 10^5 greater than with O2 (3, 8). Hence, for the present experimental setup, the NO2 reaction will become the dominant fate of the OH-adduct at [NO2] > 1 × 10^{10} \text{ cm}^{-3}. This reaction yields cresol (Y_{NO2}) (8) but not dicarbonyls (9).

From a simple model based on Scheme 1 [see the recent theoretical work of Wu et al. (6) and references therein for a more detailed description], at [O2] = 5 × 10^{18} \text{ cm}^{-3} the yield of products via pathway II is calculated to be 70%, while the yield of cresol is 23%, in good agreement with the MCM (2) and previous experimental studies (10). Reducing [O2] to 1 × 10^{15} \text{ cm}^{-3} (not including the OH-adduct + NO2 reaction), the cresol yield is 3% and products via pathway II yield is 6%, with 91% of the oxidized toluene present as the OH-adduct on the timescale of the experiments (~50 ms). Including the NO2 reaction in the model, assuming [NO2] = 5 × 10^{11} \text{ cm}^{-3} and Y_{NO2} = 0.5, we calculate a cresol yield of 32%.

Hence, while the present study provides an interesting exploration of the toluene system, its relevance to understanding the oxidation of toluene in the atmospheric boundary layer appears limited. We do not consider that the experimental results contradict the current understanding of the early stages of OH-initiated toluene oxidation. We would encourage the authors to repeat their experiments under a range of [O2] and [NO2] to elucidate the driving mechanisms behind their results.

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Scheme 1. Simplified representation of chemical mechanism of OH-initiated toluene oxidation. For clarity, only one isomeric form of the intermediates is shown.