Reply to "Comment on 'Primary Atmospheric Oxidation Mechanism for Toluene'"

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In our article, we provided evidence for the formation of a dienedial product from our turbulent flow chemical ionization mass spectrometric (TF-CIMS) investigation of the OH-initiated oxidation of toluene and postulated that it arises from a unimolecular dissociation process involving a hydroxyperoxy radical intermediate (reaction O2f* → O2h in our Figure 1).[1] We also reported that we did not observe glyoxal and methylglyoxal (α-dicarbonyls) products, which have often been observed in atmospheric chamber measurements of the products of the OH-initiated oxidation of toluene. In their comment, Jenkin et al. have suggested alternative bimolecular pathways that could explain the observation of a dienedial product and the nonobservation of α-dicarbonyl products under our experimental conditions (the right-hand side of their Figure 1).[2]

Because of our long-standing interest in the kinetics of peroxy radical reactions, we were initially motivated to study the OH-initiated oxidation of toluene because of the postulated role of several different kinds of peroxy radicals in the oxidation mechanism (such as species O2f, O2j, and O3b in our Figure 1). Earlier work by Molina et al. using the TF-CIMS technique had identified a hydroxyperoxy radical intermediate (species O2f in our Figure 1) in the OH-initiated oxidation of toluene under the conditions of O_2 concentrations of about 1×10^{16} molecules cm^{-3} and at a total pressure of 7 Torr.[3] While we were aware of the subsequent work by Bohn,[4] we did not realize, as we planned our own experiments, that the Molina et al.[3] and Bohn results are contradictory. In particular, the Bohn experiments predict that the ratio of hydroxyperoxy radicals to toluene−OH radicals (defined as $[RO_2]/[R]$ by Jenkin et al.[2]) under the relatively low O_2 concentration conditions used in the experiments of Molina et al.[3] is about 0.003. This leads to a predicted absolute hydroxyperoxy radical concentration that is below the detection limits of the TF-CIMS instrument used by Molina et al.[3]

In our article, we reported experiments in which the O_2 concentration was held constant for all experiments ($[O_2]_{\text{side arm}} = 7 \times 10^{16}$ molecules cm^{-3} and $[O_2]_{\text{flowtube}} = 1 \times 10^{16}$ molecules cm^{-3}). Considering the alternative mechanism now proposed by Jenkin et al.,[2] it is unfortunate that we neglected to report an experiment in which much higher O_2 concentrations were achieved by adding a much higher flow of O_2 to the side arm ($[O_2]_{\text{side arm}} = 1.5 \times 10^{18}$ molecules cm^{-3} and $[O_2]_{\text{flowtube}} = 4.3 \times 10^{17}$ molecules cm^{-3}). Although we were not specifically concerned with the issues raised by Jenkin et al.,[2] we were motivated to try these higher O_2 concentration experiments simply because we had not succeeded in observing the peroxy radicals postulated to form from the OH-addition portion of the mechanism (species O2f and O3b in our Figure 1) under the lower O_2 conditions. However, we found that the stable products formed under these higher O_2 conditions were found to be roughly the same as under the lower O_2 conditions (in particular, the dienedial was a major product under both conditions) and no organic peroxy radicals arising from the OH-addition pathway were observed. Therefore, because the mechanism appeared to be unaffected by the higher O_2 levels, we used the lower O_2 conditions for our reported measurements. It is worth noting that, even at these higher O_2 concentrations, the Bohn results predict that the $[RO_2]/[R]$ ratio is 0.49 for the side arm and 0.14 for the main flowtube (under atmospheric conditions, the ratio is calculated to be 1.59). An additional complication, according to the standard MCM oxidation mechanism for toluene,[5] is that this equilibrium should be also affected by the isomerization of hydroxyperoxy radicals to bicyclic radicals (species O2g in our Figure 1) and eventual reaction with O_2 to form bicyclic peroxy radicals (species O3b). Therefore, even within the standard MCM scheme, it is difficult to predict the relative concentrations of toluene−OH (species O1b in our Figure 1), hydroxyperoxy (species O2f), bicylic (species O2g) and bicylic peroxy radicals (species O3b) under varying O_2 concentrations. In any case, we agree with Jenkin et al.[2] that this uncertainty suggests that measurements aimed at assessing atmospheric toluene oxidation processes should be carried out at or near atmospheric oxygen concentrations.

Specifically, Jenkin et al.[2] postulate that the self-reaction of toluene−OH radicals could lead to the observation of cresol products under our conditions. Specifically, given our initial OH concentration of 7×10^{11} molecules cm^{-3} in the side arm, the low $[RO_2]/[R]$ ratio predicted by Bohn at the lower O_2 concentrations in our experiments (leading to an upper limit estimate of $[R] = 7 \times 10^{11}$ molecules cm^{-3}), and the very fast rate constant for this reaction estimated by Bohn (4.7×10^{-11} cm^3 molecule^{-1} s^{-1}),[4] Jenkin et al.[2] point out that this upper limit estimate for the self-reaction is expected to have a 1/e folding time that is roughly equal to the residence time in the side arm.

Jenkin et al.[2] also propose that a bimolecular reaction of toluene−OH radicals with peroxy radicals (either species O2j or O2f in our Figure 1) could lead to the production of alkoxy radicals (species NO3a in our Figure 1 and denoted as RO in Figure 1 in Jenkin et al.[2]) via a mechanism similar to that observed for the reaction of CH_3O_2 with CH_3.[6,7] The fate of these alkoxy radicals is then postulated to involve a ring-opening process that leads to the dienedial product. Since the rate constants for these reactions have not been previously investigated, and the concentration of peroxy radicals is uncertain (especially given the earlier discussion of the O_2 effect) in our experiments, it is much more difficult to establish the potential kinetic relevance of these reactions.

While we were not specifically alerted to the potential cresol- and dienedial-forming side reactions suggested by Jenkin et al.,[2] our article reports additional experiments that were designed to establish whether bimolecular radical−radical side reactions were occurring under our experimental conditions (these experiments are not explicitly discussed in the Comment by Jenkin et al.[2]). In one set of experiments, the toluene oxidation events were initiated in the main flow tube, where the concentrations were 7 times lower than in the side arm. The point of these experiments was to slow down any bimolecular radical−radical processes (such as those proposed by Jenkin et al.[2]) that might be occurring at the higher radical concentrations present in the

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side arm experiments. We reported that while the benzaldehyde product yield was reduced under these conditions, the yields of the other major products (including cresol and dienedial) were largely unchanged. We also believe that our NO-dependence experiments provide strong evidence that secondary bimolecular radical−radical processes involving peroxy radicals are likely not responsible for the observation of the dienedial product. In these experiments, we specifically set the NO concentration to a level so that any RO_2 + NO reactions would have short lifetimes compared to any RO_2 + X secondary processes ([NO] $= 1 \times 10^{13}$ molecules cm^{-3}; assuming that $k_{RO_2+NO} \sim 1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} indicates that peroxy radicals should have a 1/e folding time of 10 ms under these conditions). Again, we reported that the major product yields were largely unaffected by the presence of NO. Although it is possible that our NO-free and high NO experiments could coincidentally lead to the same product distribution according to the proposal of Jenkin et al.[2] (specifically, the kinetics of the competing pathways for the fate of the hydroxyperoxy radical would have to remain the quantitatively the same, even though RO_2 pathways in the NO-free experiments are replaced by NO pathways in the high NO experiments), this seems unlikely.

Since the publication of our article, a similar TF-CIMS study of the OH-initiated oxidation of *m*-xylene has come to our attention.[8] These experiments were performed in a manner that was similar to our main flowtube oxidation experiments discussed in the preceding paragraph. These experiments were performed at 100 Torr total pressure and with similar radical concentrations as in our experiments and the effect of O_2 (ranging from 6×10^{16} to 4.5×10^{17} molecules cm^{-3}) and NO (ranging from 1×10^{12} to 1×10^{13} molecules cm^{-3}) concentrations on the observed products was directly tested. Interestingly, Zhao et al.[8] report the observation of both dienedials *and* methyglyoxal as major products under all conditions. They reported a modest increase in the yield of methylglyoxal and a modest decrease in the yield of the dienedials for the higher O_2 experiments. While the methylglyoxal yield was slightly higher at the high NO conditions, the yield of the dienedials was largely unaffected by NO.

In summary, we agree with Jenkin et al.[2] that additional TF-CIMS experiments using higher O_2 levels (and higher total pressures) are likely to provide additional insight on the toluene oxidation mechanism. Because we have previously operated our TF-CIMS instrument at pressures as high as 200 Torr[9] and with O_2 as the turbulent flow carrier gas,[10] we should be able to carry out additional experiments at atmospheric O_2 concentrations. In addition, given the very recent observation by Wyche et al. of stable oxidation products apparently arising from the reactions of bicyclic peroxy radicals formed in the oxidation of 1,3,5-trimethylbenzene,[11] we expect that TF-CIMS methods should be capable of detecting this apparently long-lived peroxy radical. Obviously, the direct detection of a bicyclic peroxy radical for any aromatic system and the kinetic association of its reaction with NO to produce α-dicarbonyl products would provide very strong support for the standard MCM mechanism.[5]

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