COMMENTS

Comment on "Primary Atmospheric Oxidation Mechanism for Toluene"

Michael E. Jenkin,*,† David R. Glowacki,‡
Andrew R. Rickard,§ and Michael J. Pilling‡

*Atmospheric Chemistry Services, Okehampton,
Devon EX20 1FB, U.K., School of Chemistry, University of
Leeds, Leeds LS2 9JT, U.K., and National Centre for
Atmospheric Science, University of Leeds,
Leeds LS2 9JT, U.K.*

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Baltaretu et al.[1] have recently published the results of a study of the initial OH-initiated oxidation sequence of toluene at short time scales, using turbulent flow chemical ionization mass spectrometry. The results of the study were used to challenge a number of aspects of the chemistry leading to first generation oxidized products that have been inferred from previous kinetics and product studies of toluene oxidation,[2−5] and that form the basis of the chemistry in detailed atmospheric chemistry mechanisms such as the Master Chemical Mechanism (MCM).[6,7] The main conclusions of the study were that the α-dicarbonyl products, glyoxal and methyl glyoxal, are not formed as primary (first generation) products of toluene oxidation, and that a major proportion of the primary oxidation sequence yields C_7 dienedial products, i.e., methyl-substituted muconaldehydes. Whereas it is readily accepted that many uncertainties remain in the details of aromatic oxidation chemistry, and its representation in the MCM and other mechanisms, the experiments reported by Baltaretu et al.[1] were performed under conditions that were somewhat different from those of the lower atmosphere and may not therefore yield results directly relevant to atmospheric chemistry. In particular, the combination of low concentrations of O_2 (a factor of about 100−500 lower than atmospheric) and high initial radical concentrations ($\geq 10^{11}$ molecules cm^{-3}) used in the study make it highly likely that there were interferences from radical−radical reactions that do not occur in the lower atmosphere, and that some key reactions involving O_2 were rendered uncompetitive. In addition, the experiments were necessarily performed at much lower than atmospheric pressure (about 100 Torr), which also influences certain aspects of the mechanism. An alternative interpretation of a mechanism that could account for their observations, while remaining generally consistent with previously reported studies, is illustrated in Figure 1 and now described.

The initial reaction mainly (90%) forms an OH−toluene adduct (R),[8] which, in the presence of O_2, is in rapid equilibrium with an associated peroxy radical (RO_2). The equilibrium constant for this reaction, and the rates of the forward and reverse reactions, have been characterized by Bohn;[9] and the analogous benzene system has been the subject of a number of studies (e.g., refs 10−12). At the concentrations of O_2 employed by Baltaretu et al.,[1] [RO_2]/[R] can be calculated to lie in the approximate range 0.02−0.003. At the radical concentrations used, it is probable that a substantial proportion of loss of R and RO_2 from this equilibrium system therefore initially results from "R + R" and "R + RO_2" reactions, the rate coefficient for the former reaction being 4.7×10^{-11} cm^3 molecule^{-1} s^{-1} (Bohn[9]), with a similar value estimated for the latter in the benzene system.[12] The products of these reactions have not been characterized, but both reactions can potentially form cresols, and (by analogy with the reaction of CH_3 with CH_3O_2[13,14]) the latter reaction is likely to have a major channel forming RO + RO. As shown in Figure 1, the subsequent chemistry of RO can lead to the formation of the dienedial products. At the radical concentrations in the side arm of the flow apparatus (inferred to be about 7×10^{11} molecules cm^{-3} from the information given), the radical−radical reactions are estimated to occur on the time scale of about 15−30 ms for the first 1/e folding. It is also noted that both R and RO_2 are likely to react to a certain extent with benzyl peroxy radicals, $C_6H_5CH_2O_2$, formed from the minor (10%) OH + toluene initiation channel (not shown in Figure 1), with formation of RO also likely from these reactions.

As the radical concentration decays, the unimolecular loss of the RO_2 radical to form cresol(s), or via ring closure to form the peroxide-bridged radical (see Figure 1) becomes more competitive. In the latter case, the mechanism is believed to proceed either via a further rearrangement to form an epoxy−oxy radical (I) or (more significantly under atmospheric conditions) via reaction with O_2 to form a peroxide-bridged peroxy radical (II). Evidence for the former in aromatic systems comes from the detection of epoxide products,[15,16] with direct evidence for the formation of peroxide-bridged intermediates reported recently by Wyche et al.[17] (for the 1,3,5-trimethylbenzene system). As shown in Figure 1, and discussed previously in numerous studies (e.g., refs 2−7, 15, and 18), the reactions of the peroxide-bridged peroxy radical are believed to lead to the formation of the α-dicarbonyl products, with their formation likely to be more efficient when NO is present. The theoretical studies of Suh et al.[19] (for the toluene system) and Glowacki et al.[20] (for the benzene system) provide support for the dominant formation of the peroxide-bridged peroxy radical (II) at atmospheric abundances of O_2, and therefore for the associated formation of the α-dicarbonyls as first generation products. At the much lower O_2 concentrations employed by Baltaretu et al.,[1] however, rearrangement of the peroxide-bridged radical to form the epoxy−oxy radical (I) can compete more effectively with its reaction with O_2. Furthermore, the recent study of Glowacki et al.[20] has shown that formation of the epoxy−oxy radical (in the benzene system) is further enhanced at lower pressures, owing to its prompt formation from the peroxide-bridged radical prior to stabilization. This is illustrated in Figure 2, which shows the estimated prompt yield of epoxy−oxy radicals from the OH-initiated oxidation of benzene as a function of pressure, based on the potential energy surface calculated by Glowacki et al.[20] By virtue of both lower pressures and much lower O_2 concentrations, therefore, Baltaretu et al.[1] were logically able to observe an epoxide product but did not detect any α-dicarbonyl products.

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* Corresponding author. E-mail address: atmos.chem@btinternet.com.
† Atmospheric Chemistry Services.
‡ School of Chemistry, University of Leeds.
§ National Centre for Atmospheric Science, University of Leeds.

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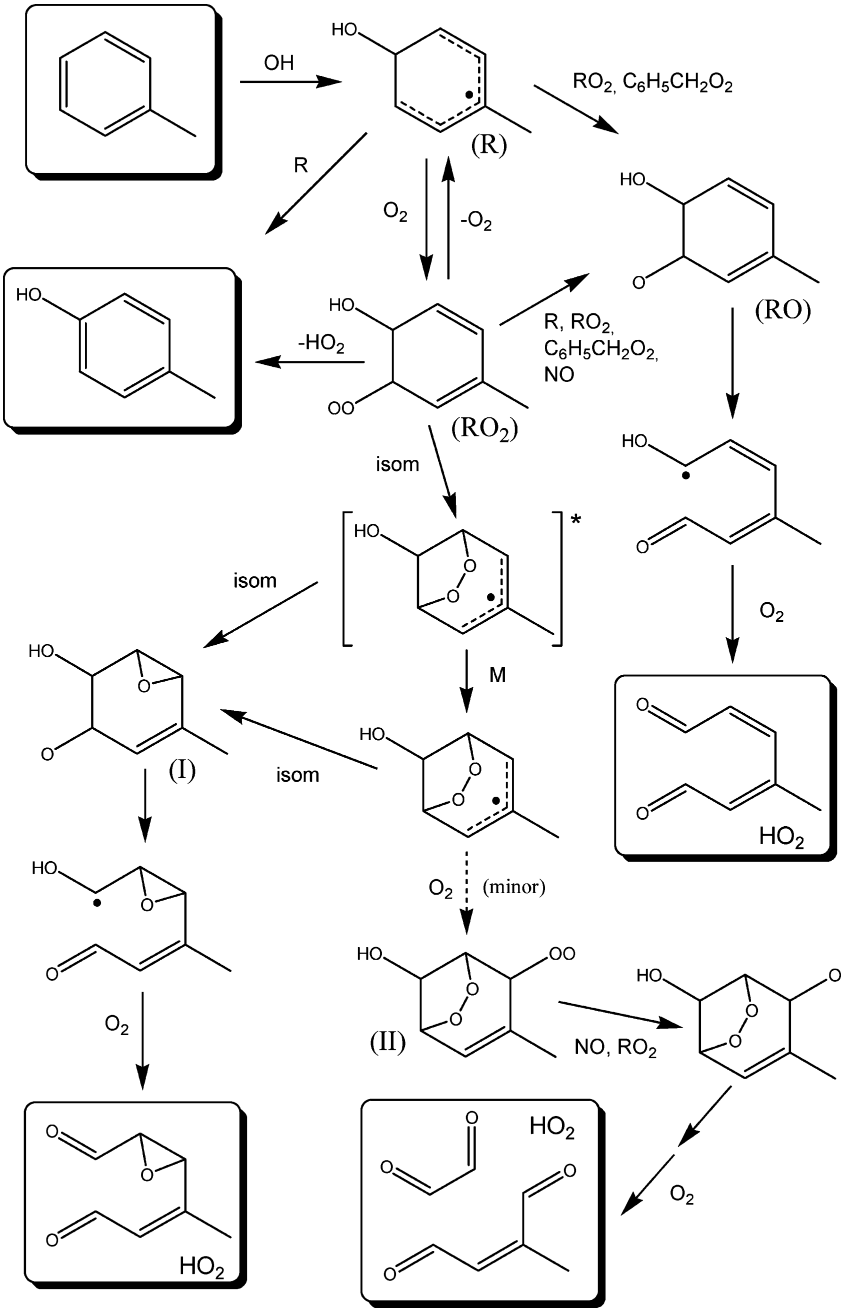

Figure 1. Possible interpretation of selected mechanistic routes occurring following the oxidation of toluene initiated by addition of OH, under the conditions employed by Baltaretu et al.[1] (see text). For clarity, only one isomeric form of the intermediates is shown.

The reported insensitivity of their results to addition of NO is also consistent with this explanation, as NO only impacts on the peroxide-bridged peroxy radical chemistry.

Finally, Baltaretu et al.[1] report (unquantified) formation of OH radicals in the system, which is implied to occur in conjunction with dienedial formation, following isomerization/decomposition of RO_2. It is noted, however, that no actual evidence for a mechanistic link between the formation of OH and the dienedial products is presented (e.g., from an equivalence in their yields, or a matched dependence on varying experimental conditions). This isomerization/decomposition process has actually been postulated previously, but has been ruled out on the basis of theoretical analyses of the analogous benzene system,[12,20] which showed that it cannot compete with ring-closure to form the peroxide-bridged radical. Given the probable importance of radical−radical reactions under the experimental conditions, it is possible that OH formation might

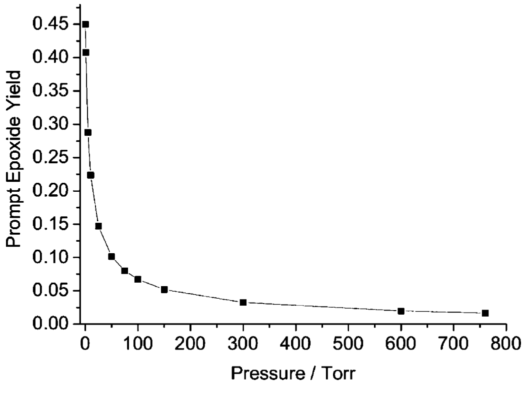

Figure 2. Prompt yield of epoxy−oxy radicals from the OH-initiated oxidation of benzene as a function of pressure, based on the potential energy surface calculated by Glowacki et al.[20]

result from the reactions of HO_2 with R, RO_2, or $C_6H_5CH_2O_2$, although further investigations would be required to confirm or refute this.

In conclusion, we feel that Baltaretu et al.[1] have presented an interesting and valuable study of the initial OH-initiated oxidation sequence of toluene at very low $[O_2]$ and moderately low pressure. While their results are not directly relevant to atmospheric conditions, their study provides a good example of how experiments over a range of temperatures and pressures may yield additional and potentially valuable information for elucidating complex atmospheric oxidation mechanisms. We hope that they will continue their studies on aromatic systems and look forward to seeing future results.

References and Notes

(1) Baltaretu, C. O.; Lichtman, E. I.; Hadler, A. B.; Elrod, M. J. *J. Phys. Chem. A* **2009**, *113*, 221.

(2) Calvert, J. G.; Atkinson, R.; Becker, K. H.; Kamens, R. M.; Seinfeld, J. H.; Wallington, T. J.; Yarwood, G. *The mechanisms of atmospheric oxidation of aromatic hydrocarbons*; Oxford University Press: Oxford, U.K., 2002.

(3) Volkamer, R.; Platt, U.; Wirtz, K. *J. Phys. Chem. A* **2001**, *105*, 7865.

(4) Gómez Alvarez, E.; Viidanoja, J.; Munõz, A.; Wirtz, K.; Hjorth, J. *Environ. Sci. Technol.* **2007**, *41*, 8362–8369.

(5) Arey, J.; Obermeyer, G.; Aschmann, S. M.; Chattopadhyay, S.; Cusick, R. D.; Atkinson, R. *Environ. Sci. Technol.* **2009**, *43* (3), 683.

(6) Jenkin, M. E.; Saunders, S. M.; Wagner, V.; Pilling, M. J. *Atmos. Chem. Phys.* **2003**, *3*, 181.

(7) Bloss, C.; Wagner, V.; Jenkin, M. E.; Volkamer, R.; Bloss, W. J.; Lee, J. D.; Heard, D. E.; Wirtz, K.; Martin-Reviejo, M.; Rea, G.; Wenger, J. C.; Pilling, M. J. *Atmos. Chem. Phys.* **2005**, *5*, 641.

(8) More strictly, a set of isomeric OH−toluene adducts is formed. For clarity, this is referred to in the singular in the present discussion, with the chemistry of a single representative isomer presented in Figure 1.

(9) Bohn, B. *J. Phys. Chem. A* **2001**, *105*, 6092.

(10) Bohn, B.; Zetzsch, C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5097.

(11) Johnson, D.; Raoult, S.; Rayez, M.-T.; Rayez, J.-C.; Lesclaux, R. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4678.

(12) Raoult, S.; Rayez, M.-T.; Rayez, J.-C.; Lesclaux, R. *Phys. Chem. Chem. Phys.* **2004**, *6*, 2245.

(13) Parkes, D. A. *Int. J. Chem. Kinet.* **1977**, *9*, 451.

(14) Pilling, M. J.; Smith, M. J. C. *J. Phys. Chem.* **1985**, *89*, 4713.

(15) Kwok, E. S. C.; Aschmann, S. M.; Akinson, R.; Arey, J. *J. Chem. Soc., Faraday Trans.* **1997**, *93* (16), 2847.

(16) Yu, J.; Jeffries, H. E. *Atmos. Environ.* **1997**, *31*, 2281.

(17) Wyche, K. P.; Monks, P. S.; Ellis, A. M.; Cordell, R. L.; Parker, A. E.; Whyte, C.; Metzger, A.; Dommen, J.; Duplissy, J.; Prevot, A. S. H.; Baltensperger, U.; Rickard, A. R.; Wulfert, F. *Atmos. Chem. Phys.* **2009**, *9*, 635.

(18) Atkinson, R.; Arey, J. *Chem. Rev.* **2003**, *103*, 4605.

(19) Suh, I.; Zhang, R.; Molina, L. T.; Molina, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 12655.

(20) Glowacki, D. R.; Wang, L.; Pilling, M. J. *J. Phys. Chem. A* **2009**, *113*, 5385.

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