Atmos. Chem. Phys. Discuss., 2, S794–S797, 2002
www.atmos-chem-phys.org/acpd/2/S794/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds" *by* M. E. Jenkin et al.

Anonymous Referee #1

Received and published: 28 December 2002

This article provides an overview of the updated version of the Master Chemical Mechanism for aromatic hydrocarbons, and as such is a valuable addition to the literature. Use is made of the literature data concerning the kinetics, products and mechanism of the atmospheric reactions of aromatic hydrocarbons and their reaction products. I have a few relatively minor comments concerning this article, as follows:

(1) Page 1907, line 5. While mention is made here of secondary organic aerosol formation from aromatic atmospheric degradations, there is little discussion further in the manuscript concerning which products are likely to partition into the aerosol phase. Do the authors believe that the first-generation products formed from the aromatic

Full Screen / Esc

Print Version

Interactive Discussion

Original Paper

hydrocarbons undergo gas-to-particle conversion, or rather that it is the second- (or later-) generation products which end up in the aerosol phase? (2) Page 1908, line 15. Because some of the reaction products undergo gas-to-particle conversion, degradation to CO2 and water does not happen for all products. (3) Page 1915, line 23. The study of Bethel et al. (2000) also showed that 3-hexene-2,5-dione and/or biacetyl are first-generation products of the reactions of OH radicals with p-xylene and 1,2,3- and 1,2,4-trimethylbenzene, thereby ruling out their formation from secondary reactions of (for example) 1,6-di-unsaturated dicarbonyls. (4) Page 1916, lines 13-18, and page 1917, lines 1-12. Bethel et al. (2000) obtained yields of 3-hexene-2,5-dione at low NO2 concentrations (32% molar yield) which are in reasonable agreement with the glyoxal yields obtained by Smith et al. (1999) [39.4 +/- 11%] and Volkamer et al. (2001) [40.4 +/- 10.6%] at low NOx levels, consistent with glyoxal and 3-hexene-2,5-dione being co-products. From the literature product yields of Smith et al. (1999), Bethel et al. (2000) and Volkamer et al. (2001) for the formation of p-tolualdehyde, 2,5-dimethylphenol, glyoxal + 3-hexene-2,5-dione, and methylglyoxal (+ its expected co-product HC(O)C(CH3)=CHCHO) from the OH radical-initiated oxidation of p-xylene, 70% of the products can be accounted for. The remainder are then presumably the epoxydicarbonylene discussed in this article and observed (qualitatively) by Yu and Jeffries (1997) and Kwok et al. (1997), and by the 1,6-di-unsaturated dicarbonyls observed (but not quantified) by Yu et al. (1997) and Kwok et al. (1997). (5) Page 1918, lines 5-17. Olariu et al. (2002) have shown that 1,2-dihydroxybenzenes (or 1,2-dihydroxy-methylbenzenes) are formed in high yield from the OH radical-initiated reactions of phenol and the cresols, and rate constants for the reactions of OH radicals with selected 1,2-dihydroxybenzenes have been measured by Olariu et al. (2000). (6) Page 1921, lines 13-19. The recent product study of Bethel et al. (2001) suggested that formation of CH3C(O)CH(OH)CHO + CH3CO from OH + 3-hexene-2,5-dione dominates. The organic nitrate CH3C(O)CH(OH)CH(ONO2)C(O)CH3 formed from reaction of the initial RO2 radical with NO was also observed. (7) Page 1923, lines 16-21. No mention is made of the potential formation of 1,6-di-unsaturated dicarbonyls, which could also

Interactive Comment

account, at least in part, for the products not presently quantified (see Comment #5 above).

References.

Bethel, H. L., Atkinson, R., Arey, J.: Products of the gas-phase reactions of OH radicals with p-xylene and 1,2,3-and 1,2,4-trimethylbenzene: effect of NO2 concentration, Journal of Physical Chemistry A, 104, 8922-8929, 2000.

Bethel, H. L., Arey, J., Atkinson, R.: Products of the OH radical-initiated reaction of 3-hexene-2,5-dione, Environmental Science and Technology, 35, 4477-4480, 2001.

Kwok, E. S. C., Aschmann, S. M., Atkinson, R., Arey, J.: Products of the gas-phase reactions of o-, m- and p-xylene with the OH radical in the presence and absence of NOx, Journal of the Chemical Society Faraday Transactions, 93, 2847-2854, 1997.

Olariu, R. I., Barnes, I., Becker, K. H., Klotz, B.: Rate coefficients for the gas-phase reactions of OH radicals with selected dihydroxybenzenes and benzoquinones, International Journal of Chemical Kinetics, 32, 696-702, 2000.

Olariu, R. I., Klotz, B., Barnes, I., Becker, K. H., Mocanu, R.: FT-IR study of the ring-retaining products from the reaction of OH radicals with phenol, o-, m-, and p-cresol, Atmospheric Environment, 36, 3685-3697, 2002.

Smith, D. F., Kleindienst, T. E., McIver, C. D.: Primary product distributions from the reaction of OH with m-, p-xylene, 1,2,4- and 1,3,5-trimethylbenzene, Journal of Atmospheric Chemistry, 34, 339-364, 1999.

Volkamer, R., Platt, U., Wirtz, K.: Primary and secondary glyoxal formation from aromatics: experimental evidence for the bicycloalkyl-radical pathway from benzene, toluene, and p-xylene, Journal of Physical Chemistry A, 105, 7865-7874, 2001.

Yu, J., Jeffries, H. E., Sexton, K. G.: Atmospheric photooxidation of alkylbenzenes I. Carbonyl product analyses, Atmospheric Environment, 31, 2261-2280, 1997.

Full Screen / Esc

Print Version

Interactive Discussion

Original Paper

Yu, J., Jeffries, H. E.: Atmospheric photooxidation of alkylbenzenes II. Evidence of formation of epoxide intermediates, Atmospheric Environment, 31, 2281-2287, 1997.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 1905, 2002.