LETTER

REPLY TO NEWLAND ET AL.:

The dominant phenolic pathway for atmospheric toluene oxidation

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Ji et al. (1) reassess the atmospheric oxidation mechanism of toluene: Their experimental work shows a larger-than-expected branching ratio for cresols but negligible formation of ring-opening products and is corroborated by theoretical calculations revealing that the phenolic pathway is kinetically and thermodynamically favored over the primary peroxy radical (RO_2) formation. Despite the compelling experimental and theoretical evidence, Newland et al. (2) question the atmospheric relevance of Ji et al.'s work, and their letter reflects a subjective view of the toluene chemistry. The authors state that "Their results challenge the mechanisms used in atmospheric chemical models...," without assessing the fundamental differences between the available studies. Experimental investigation of hydrocarbon chemistry is difficult (3, 4), since a product formation typically involves multiple possible steps and pathways and the product is subject to secondary reactions. Consequently, extrapolation of the kinetics and mechanism of hydrocarbon reactions from measured product yields is challenging. Current atmospheric chemical mechanism for the toluene oxidation has been developed mainly on the basis of product yields from the environmental chamber experiments (2). There exist additional intricate difficulties in the earlier chamber studies, further rendering the chamber approach to be unsuitable for application in developing detailed kinetics and mechanism of the toluene chemistry (1). Noticeably, these limitations included longer reaction times, higher reactant concentrations, wall loss, and lack of online detection and quantification of reactive reactants and products by advanced analytical instruments (1). In particular, the significance of wall loss for reactive and condensable species using the chamber method has been recently demonstrated (5). In contrast, the experimental methodology by Ji et al. is advantageous by effective elimination of wall loss and inhibition of secondary reactions, enabling elucidation of the initial steps of the OH-toluene reactions (Fig. 1A). Furthermore, Newland et al. (2) neglect the theoretical results of Ji et al., even though the theoretical method has been well established for studying many classes of atmospheric hydrocarbon reactions (6–9). Specifically, Ji et al. (1) demonstrate that the activation energy to form o-cresol is 3 kcal·mol^{-1} lower than that to form o-RO_2, and the o-cresol formation is 18 kcal·mol^{-1} more stable than that of o-RO_2 (Fig. 1B). The calculated rate constant for o-cresol formation is an order of magnitude faster than that for o-RO_2. The suggested interference of the OH-toluene adduct reaction with NO_2 by Newland et al. is speculative, since their simple model relies exclusively on kinetic data derived indirectly from the earlier chamber studies, but those are clearly inapplicable to the experimental conditions of Ji et al. Also, their equilibrium assumption contradicts the rapid exit channel for the OH-toluene adduct because of the OH-cresol reaction (1). While we agree with Newland et al. (2) that the uncertainties and limitations from the experimental studies of toluene oxidation need to be fully evaluated, the experimental and theoretical results by Ji et al. (1) provide important kinetic and mechanistic data for improving the toluene oxidation mechanism and accurately predicting its role in ozone formation and aerosol nucleation and growth (10, 11).

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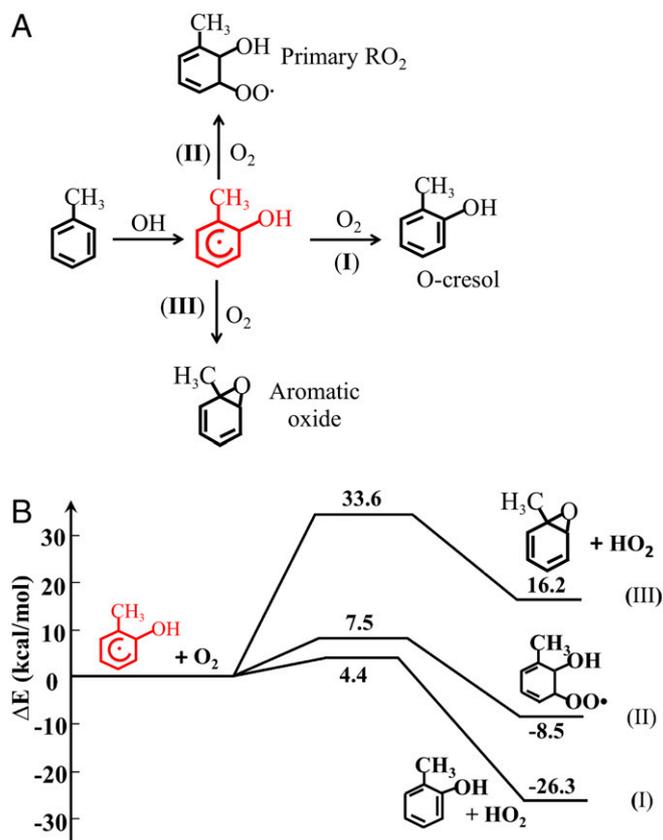
Fig. 1. Initial steps of the atmospheric chemistry of toluene oxidation. (*A*) The competing pathways for the reactions of the OH-toluene adduct (in red) with O₂ and (*B*) their corresponding potential energy surfaces (1).

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