

Experimental and Modeling Study on the Formation of Oxygenated Polycyclic Aromatic Hydrocarbons (PAHs) and Nitrogen-containing PAHs in the Oxidation of Hydrocarbons

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[Abstract]

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Understanding the formation mechanism of not only polycyclic aromatic hydrocarbons (PAHs) but also PAHs with functional groups, such as oxygenated PAHs (OPAHs) and nitrogen-containing PAHs (NPAHs), during combustion is necessary because they have high detrimental characteristics and become a precursor of particulate matter. Although a number of studies on PAH formation have been carried out, there are still limited fundamental studies that investigate formation processes of OPAHs and NPAHs. Because practical fuels contain a variety of hydrocarbon components, it is highly important to investigate the dependence of hydrocarbon molecular structure on PAHs, OPAHs and NPAHs formation to understand their reaction mechanism during combustion properly. In this study, experimental investigation of fuel-rich oxidation in a flow reactor at atmospheric pressure, mean gas temperatures from 1050 to 1350 K, residence times from 0.2 to 1.5 s, and equivalence ratios from 3.0 to 12.0 was performed. Ethylene, toluene, and n-decane were used as fuels. 21 kinds of PAHs, 9 kinds of OPAHs, and 1 kind of NPAH were quantitatively measured using a direct sampling method of reacted gas by gas chromatography mass spectrometry. The results showed that PAH/OPAH/NPAH production was strongly affected by the hydrocarbon molecular structure, providing the order of their formation, ethylene < n-decane < toluene. A chemical kinetic model was developed to describe PAH/OPAH/NPAH formation during combustion. The calculated results using the model were in reasonable agreement with the measured concentration profiles of PAHs and OPAHs under the current experimental conditions. Although there is still a lot of room for improvement in the model performance of NPAH, this study was the first attempt to model the NPAH formation. The reaction pathway and sensitivity analyses on not only PAHs but also OPAHs and NPAHs were conducted using the kinetic model. Main formation pathways toward PAHs and NPAHs were affected by initial fuels, while those for OPAHs were not dependent so much. According to sensitivity analysis, reactions involving light species showed large coefficients in ethylene and n-decane oxidation, while those involving aromatic species had high sensitivity in toluene oxidation. From experiments and modeling, this study succeeded in clarifying the conditions and reaction mechanism toward the formation of OPAHs and NPAHs for the first time.

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