Synchrotron Product Detection Studies of Ortho and Meta Methylphenyl + O_2

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Conventional combustion chemistry is predominantly driven by reactions of hydrocarbon radicals with O_2. In the case of the aromatic-fuel archetype toluene ($C_6H_5CH_3$), its corresponding radical benzyl ($C_6H_5CH_2$) is relatively resilient to molecular oxygen and this underpins toluene's resistance to autoignition. It is emerging however, that the reactive methylphenyl ($C_6H_4CH_3$) isomers of benzyl, formed in low levels through the initial attack of OH on toluene, warrant consideration. Recent kinetic modeling of toluene oxidation in a flow reactor finds that the methylphenyl channel accounts for 15% of the initial destruction of toluene.[1] To date there have been few experimental studies of these methylphenyl oxidation reactions. To address this, we utilize synchrotron photoionisation mass spectrometry (PIMS) performed at the Chemical Dynamics Beamline of the Advanced Light Source (Berkeley, USA) to examine the products of the *ortho*-methylphenyl + O_2 reaction. Comparisons are made to the *meta*-methylphenyl + O_2. These reactions are first studied at room temperature and 4 Torr.

Oxidation products are detected on several mass channels for both the *ortho* and *meta*-methylphenyl isomers; the *ortho* case contains two additional significant products. In both cases, O-atom loss is a major product channel. For *o*-methylphenyl + O_2, the presence of the methyl group at the *ortho* position provides additional pathways for the peroxyl radical intermediate to rearrange. Ultimately, this leads to two unique product channels, corresponding to OH elimination and CH_3CO elimination. For both reactions we discuss the likely chemical pathways to these products drawing on computationally derived potential energy diagrams. This enables us to explain some of the underlying chemistry leading to the observed products.

References

(1) Metcalfe, W. K.; Dooley, S.; Dryer, F. L. *Energy Fuels* **2011**, *25*, 4915.