Experiment and Theory on methylformate and methylacetate kinetics at high temperatures: Rate constants for H-atom abstraction and thermal decomposition

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Biodiesel is a prevalent alternative that can be used as a neat fuel or in blends with conventional fuels. It offers substantial emissions advantages in compression ignition engines (1,2). Methyl ester combustion chemistry has therefore been the subject of experimental and modeling studies over the past few years (3,4). It is interesting to note though that little attention has been devoted to experimentally understanding the elementary kinetics of even the simplest methyl esters despite this intense activity aimed at understanding the combustion chemistry. This is the motivation for the present study on the title reactions.

The shock tube technique was used to study the high temperature thermal decomposition of methylformate (MF) and methylacetate (MA). The formation of H-atoms was measured behind reflected shock waves by using atomic resonance absorption spectrometry (ARAS). The experiments span a T-range of 1194 – 1371 K at pressures ~ 0.5 atm. The H-atom profiles were simulated using a detailed chemical kinetic mechanism for MF and MA thermal decomposition. The simulations were used to derive rate constants for sensitive decomposition and H-abstraction reactions in MF and MA. In methylformate, the most sensitive reactions that determine H-atom profiles are $CH_3OC(O)H \rightarrow HCO_2 + CH_3$ (A) and $CH_3OC(O)H + H \rightarrow CH_3OCO + H_2$ (B), where H is formed from $HCO_2 \rightarrow H + CO_2$. In methylacetate the most sensitive reactions affecting H-atom formation are $CH_3OC(O)CH_3 \rightarrow CH_3 + OC(O)CH_3$ (C) and $CH_3OC(O)CH_3 + H \rightarrow CH_2OC(O)CH_3 + H_2$ (D). Minor sensitivity was observed for the energetically higher lying bond fission, $CH_3OC(O)CH_3 \rightarrow CH_3 + CH_3OCO$ (E) and H-atom abstraction from MA by CH_3. In MA, H-atoms are formed from CH_3 radicals (through $CH_3 + CH_3 \rightarrow C_2H_4 + 2H$) generated primarily through the C-O bond fission channel (C) with minor contributions from (E). A master equation analysis was performed using CCSD(T)/cc-pv∞z//B3LYP/6-311++G(d,p) energetics and molecular properties for all thermal decomposition processes in MF and MA. The theoretical predictions were found to be in good agreement with the present experimentally derived rate constants for the bond fissions. TST calculations employing CCSD(T)/cc-pv∞z//MP2/aug-cc-pvtz energies and molecular properties for reactions (B) and (D), the only sensitive abstraction processes in MF and MA, are in good agreement with the experimental rate constants. To our knowledge this is the first study providing experimentally derived rate constant values for the primary bond fission and abstraction reactions in MF and MA.

References

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