BIMOLECULAR PYROLYSIS REACTIONS STUDIED BY CHIRPED-PULSE MILLIMETER-WAVE SPECTROSCOPY

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The feasibility of using Chirped-Pulse Millimeter-Wave (CPmmW) spectroscopy for studies of pyrolysis reactions is demonstrated. The molecules under investigation were mixed with a source of H-atoms (methyl nitrite) and put through a heated silicon carbide micro-reactor (2 cm x 1 mm). More efficient paths of thermal cracking of (i) acetaldehyde and (ii) acetone are demonstrated when using, as a catalyst, the free H-atoms released from methyl nitrite compared to cracking of neat acetaldehyde or acetone. CPmmW spectra of (i) formaldehyde and (ii) acetaldehyde were observed, suggesting that the following bimolecular reactions took place in the micro-reactor:
i) $CH_3CHO + H \rightarrow CH_3 + CH_2O$
ii) $CH_3COCH_3 + H \rightarrow CH_3 + CH_3CHO$.
The vibrational population distributions (VPDs) of the formaldehyde and acetaldehyde products of the pyrolysis reactions are measured using the broad bandwidth capability of the CPmmW technique. Although we found that the VPDs of the molecules convey little information about the pyrolysis reaction transition state(s), they provide insight to the vibrational collisional cooling mechanisms in different molecules. The relevance of the observed catalytic reactions to biomass decomposition is discussed and other bimolecular pyrolysis reactions are proposed for study by CPmmW spectroscopy. KP thanks the Petroleum Research Fund for support of this work.