PYROLYSIS OF ACETALDEHYDE: A FLEETING GLIMPSE OF VINYLIDENE

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The thermal decomposition of acetaldehyde has been studied in a heated silicon carbide "microtubular reactor", with products monitored by both photoionization mass spectrometry and matrix-isolation Fourier transform infrared spectroscopy. A well-known, and observed, route of decomposition occurs when the weakest C-C bond is broken; this process leads to methyl and formyl radicals. In addition to this, we find evidence for two additional channels: $CH_3CHO + \Delta \rightarrow H_2CCO$ (ketene) and $CH_3CHO + \Delta \rightarrow C_2H_2$ (acetylene), reactions that also generate molecular hydrogen and water, respectively. This talk focuses on the last pathway, which proceeds via vinyl alcohol. Evidence is presented that the high temperature unimolecular dehydration of vinyl alcohol proceeds by two mechanisms; one of these is a (1,2) elimination that directly yields acetylene, and the other is a (1,1) elimination that necessarily accesses the vinylidene isomer of C_2H_2 as an intermediate.