THERMAL DECOMPOSITION OF METHYL ACETATE (CH_3COOCH_3) IN A FLASH-PYROLYSIS MICRO-REACTOR

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The thermal decomposition of methyl acetate (CH_3COOCH_3) has been studied in a set of flash pyrolysis micro-reactors. Samples were diluted to (0.06 – 0.13%) in carrier gases (He, Ar) and subjected to temperatures of 300 - 1600 K at roughly 20 Torr. After residence times of approximately 25 – 150 μseconds, the unimolecular pyrolysis products were detected by vacuum ultraviolet photoionization mass spectrometry at 10.487 eV (118.2 nm). Complementary product identification was provided by matrix isolation infrared spectroscopy. Decomposition began at 1000 K with the observation of (CH_2=C=O, CH_3OH), products of a four centered rearrangement with a $\Delta_{rxn}H_{298}$ = 39.1 $\pm$ 0.2 kcal mol^{-1}. As the micro-reactor was heated to 1300 K, a mixture of (CH_2=C=O, CH_3OH, CH_3, CH_2=O, H, CO, CO_2) appeared. A new novel pathway is calculated in which both methyl groups leave behind CO_2 simultaneously, $\Delta_{rxn}H_{298}$ = 74.5 $\pm$ 0.4 kcal mol^{-1}. This pathway is in contrast to step-wise loss of methyl radical, which can go in two ways: $\Delta_{rxn}H_{298}$ ($CH_3COOCH_3 \rightarrow CH_3$ + $COOCH_3$) = 95.4 $\pm$ 0.4 kcal mol^{-1}, $\Delta_{rxn}H_{298}$ ($CH_3COOCH_3 \rightarrow CH_3COO$ + CH_3) = 88.0 $\pm$ 0.3 kcal mol^{-1}.