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The combustion chemistry of the two butane isomers represents a subset in a comprehensive description of C₁?C₄ hydrocarbon and oxygenated fuels. A critical examination of combustion models and their capability to predict emissions from this class of fuels must rely on high-quality experimental data that address the respective chemical decomposition and oxidation pathways, including quantitative intermediate species mole fractions. Premixed flat low-pressure (40 mbar) flames of the two butane isomers were thus studied under identical, fuel-rich ($\phi=1.71$) conditions. Two independent molecular-beam mass spectrometer (MBMS) set-ups were used to provide quantitative species profiles. Both data sets, one from electron ionization (EI)-MBMS with high mass resolution and one from photoionization (PI)-MBMS with high energy resolution, are in overall good agreement. Simulations with a flame model were used to analyze the respective reaction pathways, and differences in the combustion behavior of the two isomers are discussed.

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