The chemical kinetics of the OH+CO reaction plays important roles in combustion and atmospheric processes. OH+CO has two product channels, H+CO₂ and the stabilized HOCO intermediate, with a branching ratio that is highly pressure dependent. Therefore, establishing an accurate kinetic model for this chemical system requires knowledge of the reaction rates and product yields, and the lifetimes of all molecules along a particular reaction pathway. We report the application of time-resolved frequency comb spectroscopy (TRFCS) in the mid-infrared (3.7 μm) spectral region to address the complex reaction kinetics of OD+CO at room temperature. We use the deuterated forms to avoid atmospheric water interference. This technique allows us to detect the lowest energy conformer trans-DOCO intermediate with high time-resolution and sensitivity while also permitting the direct determination of rotational state distributions of all relevant molecules. We simultaneously observe the time-dependent concentrations of trans-DOCO, OD, and D₂O which are used in conjunction with kinetics modeling to obtain the pressure- and collision partner-dependent branching ratio of OD+CO.