Tetrahydrofuran (THF) is a prototype biofuel and a common intermediate in combustion of alkanes and alkenes. Photolytic Cl atom-initiated oxidation of THF was studied with multiplexed photoionization mass spectrometry (MPIMS) technique at temperatures 400-650 K and pressures 0.005-2 bar. Photoionization spectra and kinetic time traces were recorded simultaneously for all mass channels. Photoionization spectra, recorded with tunable VUV synchrotron radiation, were used to separate and identify isomers with the same nominal molecular formula, providing mechanistic insight into the underlying kinetics. Our study suggests that formation of alkylperoxy radicals and their subsequent isomerization to hydroperoxyalkyl radicals plays an important role in low temperature oxidation of THF, while ring opening of THF–H radical (which dominates THF oxidation at T>800 K) is less important at our conditions.