The oxidation of hydrocarbons in combustion or in atmospheric chemistry involves a complicated web of chemical transformations, passing through multiple unstable intermediates. Modeling the oxidation process requires understanding how these intermediates react. However it is unsettlingly common that critical intermediate species cannot be readily interrogated, and that the kinetics of key reactions must be inferred from indirect measurements. I will discuss recent experiments that employ tunable synchrotron valence photoionization to enable a look inside the “black box” of two important oxidation processes, ozonolysis and autoignition, and directly measure kinetics of some elusive intermediate species. I will also briefly discuss prospects for other future experiments that could employ synchrotron or next-generation light sources for combustion studies.