The oxidation dynamics of the well-defined CO adlayer phases on quasi-perfect Pt(111) facets have been examined in CO-saturated 0.1 M H2SO4 aqueous solutions via a combination of simultaneous, in situ, time-resolved, second harmonic generation (SHG, λinc = 590 nm), normalized differential reflectance spectroscopy (−ΔR / R, λinc = 633 nm), and potential step techniques. For both of these phases, the onset of oxidation of COads was found to be delayed with respect to the time at which the potential was stepped to values positive enough, Eox, to promote oxidation of the entire CO adlayers. This induction time, tind, was much longer for the (2 × 2)-3CO (few tens of milliseconds) compared to the √19 × √19 R23.4°-13CO phase (few milliseconds, and decreased monotonically for both of the phases as Eox was increased. Furthermore, for a fixed Eox, the oxidation rates, as measured by the optical techniques, were higher for the √19 × √19 R23.4°-13CO compared to the (2 × 2)-3CO phase. In the case of the (2 × 2)-3CO phase, the transient in situ optical data collected for Eox = 0.98 V vs RHE could be quantitatively accounted for by a model that assumes all sites on the surface are occupied either by CO or bisulfate. In fact, excellent statistical fits to the θCO transients for this latter phase derived from the SHG data could be obtained using Avrami’s nucleation and growth model. On this basis, the oxidation of the fully assembled (2 × 2)-3CO phase occurs at the edge of the domain and propagates through the entire island until the entire process is completed. Similar experiments involving CO adlayers on Pt(111) facets below saturation coverages (i.e., θCO < 0.75) formed by oxidative stripping of the fully assembled (2 × 2)-3CO phase yielded much longer tind values than surfaces with similar θCO prepared by dosing the otherwise bare Pt(111) surfaces. These findings strongly suggest that the rates of oxidation of COads increase with the number of non-CO-covered neighboring sites on the surface.