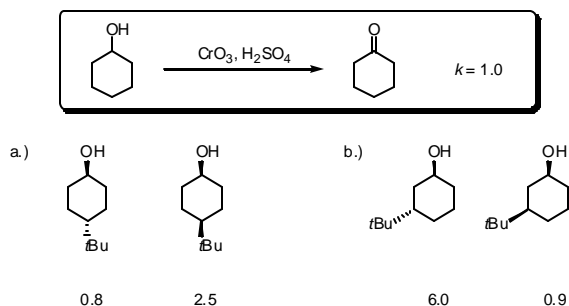


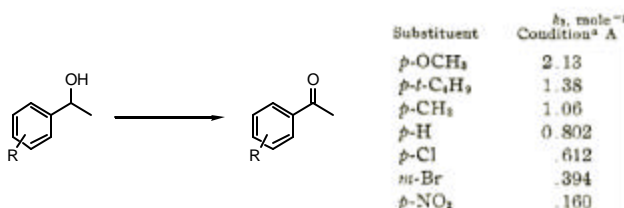
## Alcohol Oxidation by Stoichiometric Metals

### 1. Chromium Oxidations

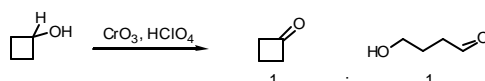
- a.) The first example of a chromium induced oxidation of primary alcohols was reported in 1859 by Herr G. Stadeler using chromium trioxide in aqueous sulfuric acid. He observed that the final inorganic product of the reaction was chromium(III) sulfate. Please provide a balanced equation for the oxidation and note the stoichiometry.
- b.) The following data have been used to argue that the first step in chromic acid oxidations is formation of a chromate ester. How might these relative rates support such an argument?



- c.) An isotope effect of  $k_H/k_D = 7$  has been observed for the reaction of 2-propanol vs 2-*d*<sub>1</sub>-2-propanol. What does this suggest about the mechanism of oxidation?
- d.) Plot and interpret the following linear free energy relationship data:



- e.) Oxidation of an alcohol is a two electron process. As such, the immediate inorganic product of a Cr(VI) oxidation must be a Cr(IV) species (such an intermediate has been observed). However, the final product of Cr(VI) oxidations is always Cr(III). Given the stoichiometry from part (a), propose several ways in which Cr(III) might be formed. How would you determine experimentally whether your proposals are viable?
- f.) Account for the following observation regarding the oxidation of cyclobutanol. What does this experiment tell you about the mechanism of Cr(VI) oxidations generally?



## 2. Permanganate Oxidations

a.) Interpret the following Hammett plot data:

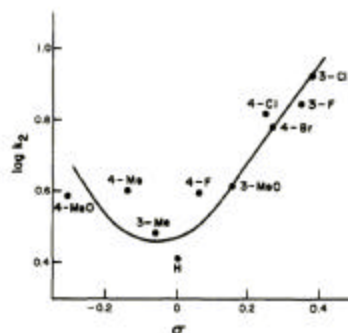


Figure 4. Hammett plot for the oxidation of substituted mandelate ions by permanganate in 1.0 M KOH solutions at 25.0 °C.

- b.) When corrected for statistical factors, the rate of permanganate oxidation is roughly equivalent for both isopropanol and diisopropyl ether. What does this suggest about the mechanism?
- c.) The rate law for the  $\text{KMnO}_4$  oxidation of secondary alcohols has been determined to be:

$$\text{Rate} = k[\text{R}_2\text{CHOH}][\text{MnO}_4^-][\text{OH}^-]$$

Given what you know for part (b), what do you think is the function of the hydroxide?

## 3. Synthetic Applications

a.) Corey did this to make a prostaglandin precursor.

