A Base Induced Oxidation-Reduction Reaction of Bis(salicylaldimine)copper(II)

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It seems interesting to determine what kind of effects an external base has on the internal oxidation-reduction reactions of complexes. We studied this in connection with our study of the role of an existing base in an oxidation reaction by a metal ion. We investigated the oxidation reactions of imines,1) and so, naturally, have been interested in the internal oxidation-reduction reaction of bis(salicylaldimine)copper(II). This complex decomposes through an internal oxidation-reduction reaction at a higher temperature (for thermal-induced oxidation-reduction reactions, *cf.* Ref. 2); at the same time, the central copper(II) ion is reduced to metallic copper and some of the ligands are oxidized to the corresponding nitrile.3) At room temperature, however, this complex is very stable in the solid state and also in a pyridine solution. Oxygen oxidizes this complex in a pyridine solution at relatively high temperatures, thus yielding coordinated salicylonitrile, according to Shinra *et al.*4)

The present authors found that this complex decomposed easily in a pyridine solution when treated with a strong base such as sodium amide, sodium hydroxide, and sodium methoxide.

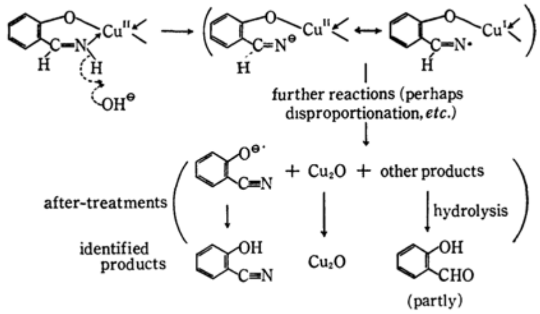
When this complex and a base was stirred in pyridine under a nitrogen atmosphere at room temperature, the color of the mixture changed from green to a final yellow-brown in several steps. After the resulting mixture had been treated by adequate methods, copper(I) oxide, salicylonitrile, and salicylaldehyde were found. These products and their relative amounts (the starting complex: Cu_2O : salicylonitrile$\fallingdotseq$2 : 1 : 1) suggest the following stoichiometric reaction:

$$2\ \mathrm{Cu(HN{=}CH{-}C_6H_4{-}O)_2} + 4\ \mathrm{NaOH} \xrightarrow[\text{after-treatments}]{\text{reaction and}} \mathrm{Cu_2O} + 3\mathrm{H_2O} + \text{salicylonitrile}$$

$+$ other products such as salicylaldehyde
(products obtained through no electron transfer)

When the copper complex was not stirred with a strong base in pyridine, no salicylonitrile was detected.

The existing base may abstract the imine hydrogen of the complex dissolved in pyridine, and then an oxidation-reduction reaction may occur between the deprotonated ligand and the central ion. The deprotonated ligand may be more easily oxidized than the undeprotonated one. This supposition may also be supported by the fact that a similar mechanism has been suggested for other oxidation reactions by the copper(II) ion.5)



This reaction should also be compared to the deprotonation reaction of cobalt(III) complexes with amines by an amide ion in liquid ammonia, which is followed by no internal electron transfer from the deprotonated ligand to the central ion.6) The redox potential of the central ion of the resulting complex after the deprotonation reaction may mainly decide whether a successive electron transfer reaction proceeds or not.

The reaction mechanism is now being examined in detail.

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