Direct Synthesis in the Undergraduate Laboratory: Synthesis of Copper Complexes from Zero-Valent Metals as a Demonstration of Base-Catalyzed Direct Synthesis

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Abstract: Direct synthesis is an important and active research field for scientists and technologists involved with the use of elemental metals. An undergraduate laboratory demonstration is presented that exposes students to this important synthetic technique. The direct synthesis of $[Cu(NH_3)_4]^{2+}$ and $[Cu(en)_2]^{2+}$ complexes in aqueous solution from zero-valent Cu metal is employed as an experiment illustrating the oxidizing properties of alkaline hydrogen peroxide solutions. The experiment also shows the decomposition of hydrogen peroxide catalyzed by the copper complexes. Finally, students can learn that the direct oxidation of metallic copper by alkaline hydrogen peroxide solution is an efficient and novel alternative approach to synthesize these and other copper complexes.

Introduction

The direct synthesis of metal complexes starting from zero-valent metals [1] is an active research field that has demonstrated rapid progress over the last 25 years. Contributions to this field are of interest not only to chemists, but also to scientists and technologists involved in the use of elemental metals. Undergraduate inorganic courses utilize a wide variety of techniques and methodologies for the synthesis of inorganic compounds [2–4]; however, direct syntheses have been excluded from most courses even though this technique is well-established as a laboratory and commercial production method [5, 6]. The commercial synthesis of methylchlorosilanes (Rochow synthesis) is an example of an industrially important direct synthesis process [7]. Some isolated efforts have been made to introduce direct synthesis into the undergraduate curriculum [8–10], and several reviews of this method have been published [11–14].

In general, the direct synthesis of coordination compounds possesses several advantages over conventional ligand-displacement reactions. These include the use of metals as source of cations, the exclusion of all undesirable ions in the solution, higher product purity, and the use of metals, which can be purchased at lower cost that their salts. The interested reader is referred to other detailed work about the advantages of direct synthesis and its experimental details [13].

Direct synthesis, including mechanochemical synthesis, cryosynthesis, electrosynthesis, and oxidative dissolution of metals in non-aqueous media [5], can be used to introduce students to the topics of metal reactivity, surface chemistry, electrochemistry, sonochemistry, laser applications, matrix isolation, corrosion, and catalysis.

In this article the generation of copper(II) complexes, starting from Cu metal oxidized in situ by a solution of alkaline hydrogen peroxide, is demonstrated. This base-catalyzed direct synthesis shows students (1) that metal complexes can be prepared from the pure metal itself, (2) how the catalytic properties of ammonia–copper complexes contribute to the decomposition of hydrogen peroxide [15], and, (3) how the elevated oxidizing properties of alkaline hydrogen peroxide solutions can be used for direct synthesis.

Experimental

The reagents, concentrated HCl, concentrated NH_4OH, 30% H_2O_2 solution in water, copper foil, and ethylenediamine dihydrochloride, were obtained from Aldrich and used as received. All experiments should be carried out with the standard precautions related to the elevated reactivity of H_2O_2 in the presence of bases [19]. Concentrated H_2O_2 can cause severe burns in contact with skin, so the use of gloves is recommended. Eye protection must be used all times. Spectra were recorded in the 400–900 nm range using a Varian Cary-3 spectrophotometer.

Direct Synthesis of $[Cu(NH_3)_4]^{2+}$. Add 10 ml of concentrated NH_4OH to a test tube or small beaker (20-ml volume). Record the weight of a small piece of metallic copper, which has been previously treated with dilute HCl and cleaned in an ultrasonic bath, then add it to the beaker. Add two drops of aqueous 30% H_2O_2 (~0.5 ml) to the reaction system. Immediate evolution of oxygen is observed as the blue copper complex forms around the surface of the metal. After a few minutes, the solution turns a deep blue color. UV–vis spectra of this solution show a broad peak centered at 620 nm (λ_{max}), corresponding to the absorption peak for the complex ion $[Cu(NH_3)_4]^{2+}$ in aqueous solution. After 30 min of reaction, record the weight of the dried copper piece and calculate the mass dissolved in solution.

Direct Synthesis of $[Cu(en)_2]^{2+}$. Add 10 ml of NaOH (15.0 M) to a 25-ml Erlenmeyer flask. Next, add a total of 100 mg of ethylenediamine dihydrochloride, $en(HCl)_2$, to the solution and stir until complete dissolution. Record the weight of a small piece of metallic copper, which has been previously cleaned in an ultrasonic bath with dilute HCl, and add it to the beaker. Two drops of aqueous 30% H_2O_2 (~0.5 ml) are added to the reaction system. Immediate evolution of oxygen on the foil surface and the formation of a purple copper complex around the surface of the metal are observed. UV–vis spectra of this solution show a broad peak centered at 556 nm (λ_{max})

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corresponding to the absorption peak for the complex ion $[Cu(en)_2]^{2+}$ in aqueous solution. After 30 min of reaction, record the weigh of the dried copper piece and calculate the mass dissolved in solution.

Results and Discussion

It is a well-known fact that most direct syntheses using pure metals are notoriously sluggish, requiring acceleration by agitation, heating, or additional simultaneous use of ultrasonic treatment [16]. The velocity of metal dissolution depends on many factors [17]: the nature of the metal (structure, metal–metal bond energy), temperature, solvent, and the presence of oxygen or other oxidants or complex forming materials.

The oxidation of copper in aqueous ammonia solution is slow. In the case of this experiment, a strongly oxidizing solution of alkaline H_2O_2 (in which the hydroperoxyl (HO_2^-) species is present) catalyzes the oxidation of copper. The precise mechanism of oxidation is unknown but it seems likely that the hydroperoxyl ion attacks the metal surface as described by the following reactions [18].

$$H_2O_2 + OH^- \rightleftharpoons HOO^- + H_2O \tag{1}$$

$$HOO^- + Cu + OH^- \rightleftharpoons Cu^+ + O_2^- + H_2O \tag{2}$$

$$2O_2^- + Cu^+ + H_2O \rightleftharpoons HO_2^- + O_2 + Cu^{2+} + OH^- \tag{3}$$

$$Cu^+ + H_2O_2 \rightleftharpoons Cu^{2+} + OH^- + {\bullet}OH \tag{4}$$

$$Cu + {\bullet}OH \rightleftharpoons Cu^+ + OH^- \tag{5}$$

$$H_2O_2 + {\bullet}OH \rightleftharpoons HOO{\bullet} + H_2O \tag{6}$$

$$Cu^{2+} + HOO{\bullet} \rightleftharpoons Cu^+ + O_2 + H^+ \tag{7}$$

The formation of copper(I) and (II) complexes, and the catalytic decomposition of hydrogen peroxide by these complexes follow initial metal dissolution. The decomposition of hydrogen peroxide is associated with several processes, including chain reactions and heterogeneous and homogeneous catalysis, for which a complete understanding is only qualitative [8, 19].

$$Cu^+ + 2NH_3{\bullet}H_2O \rightleftharpoons [Cu(NH_3)_2]^+ + 2H_2O \tag{8}$$

$$[Cu(NH_3)_2]^+ + H_2O_2 \rightleftharpoons [Cu(NH_3)_2]^{2+} + \tfrac{1}{2}\, O_2^- + H_2O \tag{9}$$

$$[Cu(NH_3)_2]^{2+} + 2NH_3{\bullet}H_2O \rightleftharpoons [Cu(NH_3)_4]^{2+} + H_2O \tag{10}$$

$$[Cu(NH_3)_4]^{2+} + HOO^- \rightleftharpoons [Cu(NH_3)_4]^+ + HOO{\bullet} \tag{11}$$

Several equilibria are present in these simple redox reactions. Spectrophotometric determination of the copper complexes during the reaction time can be used to follow the reaction kinetics; we refer interested readers to some useful references about the spectrophotometric determination of amine–copper complexes [20, 21].

Copper(I) and copper(II) ions in solution also exhibit interesting interactions. A useful experiment involving the redox chemistry of copper in solution has been reported [23]. Using their reported [20, 22] molar absorptivity coefficients ($\varepsilon_{[Cu(NH_3)_4]} = 52$; $\varepsilon_{[Cu(en)_2]} = 85$), it is easy to determine the concentration of each complex in solution and the chemical efficiency of the synthesis reaction leading to them. Based in the amount of copper dissolved after 30 min, efficiencies in the range of 90–100% can be expected.

Conclusion

The base-catalyzed direct synthesis of copper(II) complexes with ammonia and ethylenediamine was demonstrated. In general, the facile oxidation of zero-valent copper to copper(II), avoiding the use of metallic salts or complexes [25], shows the main advantage of direct synthesis over traditional synthetic methods and also illustrates of the growing industrial interest in the use of elemental metals as starting materials.

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