Controlled Synthesis of Two Copper Oxalate Hydrate Complexes: Kinetic versus Thermodynamic Factors

A Laboratory Experiment for Undergraduates

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This undergraduate laboratory experiment is used as an introduction for students interested in research. The experiment develops a student's reasoning and experimental skills. The primary goal of this experiment is to synthesize two different crystals by controlling the experimental conditions. The synthesis of \( \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\cdot2\text{H}_2\text{O} \), 1, is a traditional experiment in the teaching curriculum (1). However, there is a tetrahydrate analog \( \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\cdot4\text{H}_2\text{O} \), 2, that has also been prepared (2).

Results and Discussion

Students are required to discuss the reactions with respect to the literature that they have studied and to calculate the yield and the water content of the products (see the online material for details). An instructor-modified example is presented based on one group of typical students’ data and integration of the students’ discussion.

An aqueous solution of \( \text{KHC}_2\text{O}_4 \) (which is synthesized from \( \text{H}_2\text{C}_2\text{O}_4 \) and \( \text{K}_2\text{CO}_3 \)) and \( \text{CuO} \) was heated at 80 °C. After complete dissolution of \( \text{CuO} \), the solution was filtered while hot. From the blue filtrate, complexes 1 and 2 of different crystal shapes can be separated by carefully controlling the concentration of the \( \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2] \) solutions. The reactions involved are as follows:

\[
2\text{H}_2\text{C}_2\text{O}_4 + \text{K}_2\text{CO}_3 \rightarrow 2\text{KHC}_2\text{O}_4 + \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{CuO} + 2\text{KHC}_2\text{O}_4 \rightarrow \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2](\text{aq}) + \text{H}_2\text{O}
\]

When a dilute solution of \( \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2] \) at 80 °C was allowed to cool on the bench to room temperature, dark blue needle crystals were obtained (Figure 1A). Alternatively, when a concentrated solution at 80 °C was cooled on the bench to room temperature, light blue flat crystals were obtained (Figure 1B).

Water content analyses (by heating the freshly prepared crystals to 200 °C for 30 min) show that the dark blue needle crystals are the tetrahydrate compound while the light blue flat crystals are the dihydrate.

\[
\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\text{[conc. solution]} \xrightarrow{\text{cooling}} \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\cdot2\text{H}_2\text{O} \text{(flat crystal)}
\]

\[
\text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\text{[dilute solution]} \xrightarrow{\text{cooling}} \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\cdot4\text{H}_2\text{O} \text{(needle crystal)}
\]

Interestingly, when the needle crystals of compound 2 were immersed in the mother liquid for more than 1.5 h, the needles slowly converted to flat crystals of compound 1. The conversion can be accelerated by shaking. On this basis, we conclude that product crystallization proceeds via two routes (Figure 2). \( \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\cdot4\text{H}_2\text{O} \), 2, is the kinetic product with a lower activation energy but with less stabilization energy, while \( \text{K}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]\cdot2\text{H}_2\text{O} \), 1, is the thermodynamic product with a higher activation energy but with more stabilization energy.

Experimental Overview

Freshly prepared copper oxide was used to react with \( \text{KHC}_2\text{O}_4 \). Therefore, the experiment first involves the synthesis of \( \text{CuO} \) and \( \text{KHC}_2\text{O}_4 \). Then, the reaction of \( \text{CuO} \) with \( \text{KHC}_2\text{O}_4 \) in hot water gives blue solutions from which needle or flat crystals can be obtained by evaporation of a concentrated or dilute solution. The time required for the experiment is about 3–4 h. Water content determination can be made if time permits. This experiment is suitable for first-year students (second semester). All chemicals are of analytical grade and are commercially available. The experiments are conducted in air. Other relevant information is available in the online material.

![Figure 1. The shapes of crystals: (A) needle crystals (dark blue) 2 and (B) flat crystals (light blue) 1. (Shown in color on p 533.)](image-url)
Hazards

CuSO$_4$·5H$_2$O and K$_2$CO$_3$ are harmful if swallowed and can cause irritation to skin, eyes, and respiratory tract. NaOH is corrosive and may be fatal if swallowed. It causes burns to any area of contact. H$_2$C$_2$O$_4$ is corrosive and can cause severe irritation and burns to skin, eyes, and respiratory tract.

Conclusion

This experiment clearly demonstrates that the concentration of the solutions is a key factor in the formation of different compounds during crystallization. The concept of thermodynamic and kinetic products can sometimes be difficult for students to understand. This experiment is a good example of the concept. It shows physically that different products can be understood with chemical principles. Thus, this complicated process of crystallization will help students to understand some factors that determine the formation of different complexes.

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Literature Cited