

Pyrolysis of Oxalates, a Convenient Method To Synthesize Powdered Cobalt and Nickel with Catalytic Activity: A Laboratory for General or Inorganic Chemistry Laboratory

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S Supporting Information

ABSTRACT: A laboratory experiment for the synthesis of cobalt and nickel oxalates and their subsequent pyrolysis to their respective elementary metals is described. The oxalates are obtained by a metathesis reaction and the pyrolysis products (especially cobalt) show remarkable catalytic activity in the decomposition of hydrogen peroxide.

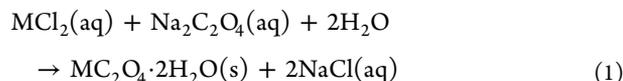


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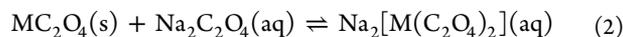
Powdered metals show remarkable chemical activity.¹ For example, they can spontaneously ignite in air² and they can show catalytic activity in a variety of valuable reactions.³ Thus, they are interesting and exciting for students to study. Many authors obtain pyrophoric cobalt and nickel by decomposing their respective carboxylates: oxalates^{4,5} or formates.^{2–4} Oxalates were chosen for this experiment due to their insolubility and because they are easily obtained by metathesis reaction. Literature offers two sources for the oxalate ions for this approach: sodium oxalate and oxalic acid.⁶ Equilibrium considerations, however, make sodium oxalate the only possible choice in this student experiment (vide infra).

■ EXPERIMENT OVERVIEW

In this experiment, the students synthesize solid cobalt or nickel oxalate from solutions containing sodium oxalate and cobalt or nickel chloride:⁷

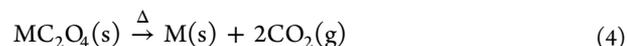
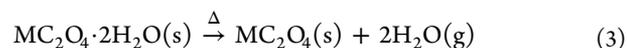


It is important for the student to use the reactants in the exact stoichiometric ratios. Any excess metal chloride will remain dissolved in solution and any excess oxalate will result in the formation of soluble oxalate complex:



With either metal, the supernatant solution will be colored (pink for cobalt and green for nickel), allowing the visualization of the students' inaccuracies in weighing the reactants.

The students then dehydrate hydrated oxalates (eq 3) and subsequently decompose anhydrous oxalates to yield powdered metal (eq 4).



During the reductive decomposition at elevated temperatures, the metal oxalate should be protected from exposure to air, due to its high reactivity toward oxygen. However, under standard laboratory conditions, the student is not able to avoid the presence of some oxide impurities in the final metal product. The students investigate the products to (a) confirm that they have isolated the desired metals, (b) demonstrate their catalytic activity in the decomposition of hydrogen peroxide, and (c) observe their smoldering upon exposure to air.

The experiment is divided into two parts. In the first part, synthesis of oxalates requires knowledge of the following concepts: stoichiometry, metathesis reactions, and complexation. It involves the demonstration of skills in (a) stoichiometric calculations, (b) solubility calculations, (c) weighing, (d) dissolving, and (e) filtering and drying of precipitates. In the second part, the decomposition of oxalates and the investigation of the products require knowledge of decomposition, hydrated salts, oxidation and reduction, metals, heterogeneous catalysis, and the role of a surface. The necessary skills involve (a) pyrolysis of substances, (b) air-free handling of

chemicals and reactions, and (c) establishing the chemical nature of a product based on its chemical properties. The main goal of this laboratory experiment is to link multiple concepts and skills that the student should have previously acquired.

Each of the two parts requires about 1–1.5 h (excluding the necessary calculations), with a break of several days to allow the precipitates to dry. If the experiment is to be carried out in a single laboratory session, the precipitates may be dried at elevated temperatures and the time required for the entire experiment will be three hours.

CHEMICAL BACKGROUND

In general, oxalates of bivalent transition metals exist as dihydrates and are insoluble.¹ The solid oxalates of cobalt and nickel are able to coordinatively bind an additional oxalate ion, resulting in the formation of soluble complexes⁸ (eq 2; Table 1). Consequently, ensuring a precise stoichiometric ratio during the precipitation of the solid oxalates (eq 1) becomes important to ensure quantitative yield.

Table 1. Metal–Oxalate Binding Constants, β , for Cobalt and Nickel

Metal	$\log \beta_1$ (for MC_2O_4)	$\log \beta_2$ (for $[\text{M}(\text{C}_2\text{O}_4)_2]^{2-}$)
Co^{2+}	3.5 ^a	6.7 ^b ; 6.4 ^a
Ni^{2+}	4.3 ^c	6.5 ^b ; 7.5 ^c

^aData from ref 9. ^bData from ref 8. ^cData from ref 10.

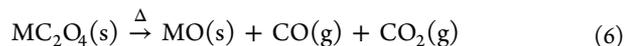
Literature suggests using either a soluble oxalate salt or oxalic acid as the source of the oxalate ion for the precipitation. This experimental procedure uses sodium oxalate because the relatively weak oxalic acid could prevent the metal oxalate from quantitative precipitation due to an equilibrium:



Although the acid equilibrium constant for the second proton of the oxalic acid is small and the association constants for the metal and oxalate are large, there is a significant concentration of protons present in solution from the first acid ionization of the diprotic acid. The latter will prevent the equilibrium in eq 5 from proceeding far to the right, reducing the yield of metal oxalate as a result.

Upon heating, cobalt and nickel oxalates first lose the crystal water and then totally decompose. In an inert atmosphere, that is, in the absence of oxygen, both steps are endothermic.^{5,6,11–17} With gradually increasing temperatures, these steps can be safely performed by the students under standard laboratory condition. Dehydration in an inert atmosphere (eq 3) occurs at temperatures ~ 150 – 220 °C and ~ 200 – 280 °C for cobalt and nickel, respectively.^{1,6,11,12} At higher temperatures, temperatures greater than 220 and 280 °C for cobalt and nickel, respectively, in the presence of oxygen or air, oxides are

formed.^{1,4,6,7,11,13} However, increasing the temperatures (in vacuo or inert atmosphere) to ~ 320 – 450 °C and ~ 320 – 375 °C for cobalt and nickel, respectively, decomposes the oxalates (eq 4) to yield mainly pyrophoric metals.^{4,5,12} In the presence of H_2 , the particle size was reported to be about 0.1–1 μm .¹⁴ Possible side reaction^{1,8,13,15} or the presence of residual traces of water^{16,17} during this second step of the pyrolysis leads to the presence of metal oxides that cannot be removed from the final metal powder:



To prevent the formation of oxides (eq 6), one needs to ensure the complete dehydration of the oxalates before the decomposition step and to perform the dehydration and decomposition under an inert atmosphere, for example, N_2 or CO_2 . The easiest way to protect the products is to use self-generated atmosphere of CO_2 during the decomposition.

EXPERIMENTAL PROCEDURE

Preliminary Calculations

Before the hands-on laboratory procedures, the students calculated the masses of sodium oxalate and metal chloride hexahydrate needed to obtain 1 g of the metal; the volumes of water needed to dissolve the respective oxalates and metal chlorides; and the theoretical yields of oxalates. The calculated values are presented in Table 2.

Synthesis of Oxalate Dihydrates

To obtain metal oxalate dihydrates, students dissolved 4.55 g of $\text{Na}_2\text{C}_2\text{O}_4$ in 80 mL of water. If necessary, students heated the mixture slightly for about 15–20 min until a homogeneous solution was observed. In another vessel, 4.05 g of metal chloride hexahydrate was dissolved in 10 mL of water. Slowly, while stirring, the solution of metal salt was added to the oxalate solution. Pale pink precipitate formed for cobalt and pale green for nickel.

The excess supernatant was decanted and the precipitated collected by standard filtration or using vacuum and a Buchner funnel. The isolated precipitates were either dried in air at room temperature for seven days or by heating at temperatures below ~ 200 °C using a porcelain dish on a sand bath for 20–30 min.

Dehydration of Oxalates

The oxalate dihydrate was placed in a porcelain dish and heated while stirring for 20–30 min at 200–250 °C, using a heater or sand bath, until the cobalt oxalate changed color from pink to lilac or the nickel oxalate turned from bluish green into greenish yellow. If a black color was observed, the temperature was too high. The anhydrous substances were transferred to a test tube while they were hot because they are hygroscopic.

Pyrolysis of Oxalates

The anhydrous oxalate was placed in a test tube and capped using a cork with a narrow right-angled glass tube. This allowed

Table 2. Calculated Data for a Yield of 1 g of the Respective Metal

Metal	$\text{Na}_2\text{C}_2\text{O}_4$			$\text{MCl}_2 \cdot 6\text{H}_2\text{O}$			$\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
	Mass/g	Solubility ^a /(g/100 g)	Volume of H_2O ^b /mL	Mass/g	Solubility ^a /(g/100 g)	Volume of H_2O ^c /mL	Theor. Yield/g
Co	2.28	3.7	62	4.04	55	2.2	3.11
Ni	2.28	3.7	62	4.05	53	2.3	3.11

^aSolubility given for 20 °C. ^bRecommended: 80 mL. ^cRecommended: 10 mL.

the gaseous products out but impeded the back mixing in of air, thus providing an easy way to protect the excessive oxidation of the products. With the use of a test tube holder, the test tube was heated over a flame while continuously maintaining a circular movement. If water condensed on the walls of the test tube, the walls were gently heated until the water evaporated. If the vapor condensed in the glass tube, the students let it drip out into a small beaker. Water condensation was usually observed as the result of incomplete dehydration in the previous step. The pyrolysis was complete when the mixture in the test tube turned black. The reaction mixture was cooled down while still utilizing the cork to cover the tube. This stage usually required 10–15 min.

Investigation of the Products

A small quantity of the black product was placed into an aqueous solution of 3% H_2O_2 and another small quantity into an aqueous solution of 10–12% HCl . In both cases, the evolution of gas was observed. The gas evolved from aqueous H_2O_2 was tested for oxygen using a glowing or smoldering match. The gas released from HCl was tested for hydrogen by using a burning match to ignite it. To demonstrate the combustible nature of the powders, a flame from a butane gas torch was directed over a small sample of powder in a porcelain dish for a few seconds. The powder smoldered. This investigative stage usually required about 10 min.

HAZARDS

Safety goggles, an apron, and gloves should be worn throughout this experiment. Students should be cautioned not to touch hot objects and should immediately place burns under cool running water. Sodium oxalate, nickel chloride, and cobalt chloride are toxic and skin irritants. As always, students should avoid swallowing and inhalation. In case of skin contact, these chemicals should be washed off using cold water without soap. The particular hazards for cobalt chloride are describes elsewhere.¹⁸

While decomposing well-dried anhydrous oxalates in the second step of the pyrolysis, fine powder can be carried out of the test tube with the gas flow. Furthermore, carbon monoxide may also be formed. Therefore, this stage should be conducted in a fume hood. If there are residues of oxalate hydrates, water condensate may drop onto the hot glass surface and crack it. Students should avoid heating the whole test tube.

The obtained powders can be pyrophoric. Students should avoid using flammable materials in the fume hood while handling the metal powders. Also, these metal powders can be irritating. Therefore, students should not inhale and should avoid exposure in general. The powders should not be stored. To dispose of them properly, they need to be covered with water, which prevents evaporation.

DISCUSSION

This laboratory (without the dehydration part) has been conducted in accelerated classes in our school with eighth grade students. When the students carried out this experiment, they had been studying chemistry for at least 1.5 years with 4 lessons (45 min) a week and had learned about metathesis reactions, decomposition, stoichiometric calculations, and calculations of solubility. They also had carried out tasks involving stoichiometric calculations and calculations with solutions and had performed several laboratory experiments developing the skills involved in metathesis reactions, weighing, filtration, and

heating of substances (first as individual steps and later in a sequence involving several different steps). The total number of students that successfully completed this laboratory experiment exceeds 60. The experiment required two periods of 1.5 h in addition to the time necessary for calculations (about 45 min in total, under the guidance of a teacher).

Synthesis of Oxalates

While adding a solution of a metal salt to oxalate solution, initially an intensively colored solution is formed (purple for cobalt and green for nickel). This can be easily explained by complex formation. Upon continued addition, precipitation is observed. When isolating the precipitate, the decanted solution is almost colorless both for cobalt and for nickel.

Pyrolysis of Oxalates

Commonly observed challenges encountered by the students were incomplete pyrolysis and water condensing in the bent tube, often dropping down into a beaker. It helped to continuously move or gently shake the tube; otherwise, some of the crystals on the inside would not decompose.

Properties of the Decomposition Products

We sometimes observed several sparks when exposing the hot product of the cobalt oxalate decomposition to air; however, we did not observe this in the case of nickel or with either decomposition products when cooled to room temperature. However, when directing a jet of a gas flame onto both powders, they begin to smolder and continue smoldering after the flame has been removed.

Both powders catalyzed the decomposition of 3% aqueous hydrogen peroxide: a smoldering match test for gaseous product, O_2 , was positive. The catalytic properties of cobalt are remarkable: the powder is not able to sink to the bottom of the solution but floats on the gas bubbles that are produced. The catalytic properties of nickel powder are less pronounced. Therefore, cobalt is more suitable for demonstrating the catalytic effect.

Both powders react with 10% aqueous HCl with gas evolution being observed; however, the cobalt powder reacts more vigorously. The hydrogen gas may be ignited, producing a “wooshing” sound. Hence, the powder contains a significant portion of metal capable of reducing the hydrogen cations. The gas formed from nickel powder does not produce this unique sound upon ignition, mainly because the metal is less reactive, producing hydrogen at a lesser rate or because the powder contains higher portion of nickel oxide.

CONCLUSIONS

The synthesis of powdered cobalt and nickel via pyrolysis of their oxalates is a beautiful laboratory exercise, linking different concepts and skills. It is easy to visualize students' mistakes during this procedure.

ASSOCIATED CONTENT

Supporting Information

Student handout; instructor notes; spreadsheet showing calculation for the synthesis; movie. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

- (1) Rochfort, G. L.; Rieke, R. D. Preparation, Characterization, and Chemistry of Activated Cobalt. *Inorg. Chem.* **1986**, *25*, 348–355 and references therein.
- (2) Viter V. N. Synthesis of Pyroforic Metals. *Chemistry and Chemists*, [Online] **2010**, 183–230 ff; http://chemistry-chemists.com/N6_2010/183-230.pdf (accessed Nov 2013) (in Russian).
- (3) Grosse, E.; Weissmantel, C. *Chemie selbst erlebt*; Urania Verlag: Leipzig-Jena-Berlin, 1974, and references therein.
- (4) Dollimore, D. The Thermal Decomposition of Oxalates. A Review. *Thermochim. Acta* **1987**, *117*, 331–363.
- (5) Gorrie, T. M.; Kopf, P. W.; Toby, S. The Kinetics of the Reaction of Some Pyrophoric Metals with Oxygen. *J. Phys. Chem.* **1967**, *71*, 3842–3845.
- (6) Vannatta, M. W.; Richards-Babb, M.; Sweeney, R. Oxalate Synthesis and Pyrolysis: A Colorful Introduction to Stoichiometry. *J. Chem. Educ.* **2010**, *87*, 1225–1229.
- (7) Mohamed, M. A.; Galwey, A. K.; Halawy, S. A. A Comparative Study of the Thermal Reactivities of Some Transition Metal Oxalates in Selected Atmospheres. *Thermochim. Acta* **2005**, *429*, 57–72.
- (8) Barney, E.; Argersinger, W. J.; Reynolds, C. A. A Study of Some Complex Chlorides and Oxalates by Solubility Measurements. *J. Am. Chem. Soc.* **1951**, *73*, 3785–3788.
- (9) Urbańska, J.; Biernat, J. Evaluation of Stability Constants of Complexes Based on Irreversible Polarographic Waves with Variable Electrode Mechanism: Part I. The Co^{2+} - $\text{C}_2\text{O}_4^{2-}$ System. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *130*, 123–140.
- (10) Urbańska, J.; Biernat, J. Evaluation of Stability Constants of Complexes Based on Irreversible Polarographic Waves with Variable Electrode Mechanism: Part II. The Ni^{2+} - $\text{C}_2\text{O}_4^{2-}$ System. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *130*, 141–151.
- (11) Macklen, E. D. Influence of Atmosphere on the Thermal Decomposition of Some Transition Metal Oxalates. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2689–2695.
- (12) Broadbent, D.; Dollimore, D.; Dollimore, J. The Thermal Decomposition of Oxalates. Part VII. The Effect of Prior Dehydration Conditions upon the Subsequent Decomposition of Cobalt Oxalate. *J. Chem. Soc. A* **1966**, 1491–1493.
- (13) Nikumbh, A. K.; Athare, A. E.; Raut, V. B. A Study of The Thermal Decomposition of Cobalt (II) And Nickel (II) Oxalate Dihydrate Using Direct Current Electrical Conductivity Measurements. *Thermochim. Acta* **1991**, *186*, 217–233.
- (14) Majumdar, S.; Sharma, I. G.; Bidaye, A. C.; Suri, A. K. A Study on Isothermal Kinetics of Thermal Decomposition of Cobalt Oxalate to Cobalt. *Thermochim. Acta* **2008**, *473*, 45–49.
- (15) Małecka, B.; Drozd-Cieśla, E.; Małecki, A. Non-Isothermal Studies on Mechanism and Kinetics of Thermal Decomposition of Cobalt (II) Oxalate Dihydrate. *J. Therm. Anal. Calorim.* **2002**, *68*, 819–831.
- (16) Małecka, B.; Małecki, A.; Drozd-Cieśla, E.; Tortet, L.; Llewellyn, P.; Rouquerol, F. Some Aspects of Thermal Decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. *Thermochim. Acta* **2007**, *466*, 57–62.
- (17) Garn, P. D.; Kessler, J. E. Thermogravimetry in Self-Generated Atmospheres. *Anal. Chem.* **1960**, *32*, 1563–1565.
- (18) Young, J. A. Cobalt(II) Chloride Hexahydrate. *J. Chem. Educ.* **2003**, *80*, 610.