

The Preparation of Prussian Blue in a Mortar: An Example to Teach Sustainable Chemistry with Mechanochemical Reactions

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Abstract: Solvent-free mechanochemical reactions represent an important path towards sustainable chemistry. The preparation of Prussian blue from solid iron and hexacyanoferrate compounds by the simple use of a mortar and pestle is an easy, inexpensive, and fast method to teach mechanochemical reactions. The course of the reaction can be followed very well visually via the color change of the solid mixture towards blue. With this communication, earlier publications on Prussian blue and mechanochemistry in the field of chemical education are updated and extended.

Keywords: Prussian blue; mechanochemistry; green chemistry; solvent-free synthesis; general public; demonstrations; hands-on learning

1. Introduction

Mechanochemistry, also known as tribochemistry or mechanical alloying [1], is the application of mechanical force to influence chemical reactions. Mechanical actions, such as ball milling, grinding, sliding, or plastic deformation can lead to chemical reactions due to intimate mixing, heating, compression, shear, and/or friction of compounds or mixtures of compounds.

“Mechanically induced solid-state chemical reactions can be performed completely without solvents. Ideally, by-products disappear via the gaseous phase. As a consequence, solid-state mechanochemistry is an attractive alternative to classical, solvent-based syntheses routes and can be regarded as green chemistry” [2].

The beginnings of mechanochemistry “fade into prehistory” because grinding with a mortar and pestle “was already used in the stone age” [3].

Mechanochemical reactions hold great promise to provide environmentally friendly, solvent-free, cleaner, safer, and more efficient chemical reactions for a sustainable chemical industry [4]. To be considered sustainable, the production of chemicals should meet as many of the 12 principles of green chemistry as possible [5]. It has been shown convincingly in several examples that mechanochemical reactions can meet all of these 12 principles [6]. Therefore, it is necessary and useful to introduce chemistry students to mechanochemistry.

Several experiments have been proposed for this purpose in recent years, such as the reaction of palladium(II) chloride with a bidentate phosphine resulting in a catalyst for the Suzuki coupling reaction [7], the synthesis of tetrathiafulvalene–chloranil charge transfer salt, a functional organic electronic material [8] or the preparation of the antidiabetic drug tolbutamide [9]. However, the formation of the deep blue compound Prussian blue by simply grinding together two more or less unattractive yellowish-brownish or (more attractive) reddish solids in a mortar can be a much more impressive way to show a mechanochemical reaction in an undergraduate chemistry teaching laboratory. The impressive color change of this reaction eliminates the need for any additional chemical analysis to be performed before, during, or after the experiment to prove that a mechanochemical reaction took place.

Prussian blue, iron(III) hexacyanoferrate(II), is a deep blue pigment [10] that can be reduced to Prussian white, iron(II) hexacyanoferrate(II), or oxidized to Prussian yellow,



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iron(III) hexacyanoferrate(II). Prussian blue was discovered in 1706 in Berlin by Johann Jacob von Diesbach (ca. 1670–1748) and Johann Conrad Dippel (1673–1734) [11]. As Berlin was at that time the capital of the newly founded Kingdom of Prussia, this new compound was named Prussian blue in the English-speaking world. Because of its impressive formation by deep blue precipitation upon mixing two yellowish aqueous solutions and the remarkable color change during oxidation or reduction, Prussian blue and its reactions are long-time companions of chemistry teachers [12–20]. Figure 1 shows a roughly 200-year-old teaching example with Prussian blue: a chemistry teacher demonstrating to his student the formation of a Prussian blue precipitate.



Figure 1. The painting “Chemist and Assistant in Laboratory” from 1827 depicts a teacher demonstrating the precipitation of Prussian blue to his student (source: Inv. 56577, © History of Science Museum, University of Oxford).

In recent years [21–24], discussions and detailed analyses of the wealth of research results of the last two decades led to the conclusion that Prussian blue, if slowly and carefully prepared, has a structure that was already described by James F. Keggin (1905–1993) and Frank D. Miles (1885–1968) in 1936 [25]. According to the Keggin and Miles model, Prussian blue $KFe^{III}[Fe^{II}(CN)_6]$ crystallizes in a cubic lattice in which Fe(II) and Fe(III) alternately occupy the corners of a cube. Fe(II) and Fe(III) are each connected to one another by cyanide groups located on the edges of the cube. The low-spin iron(II) is always bound to the carbon and the high-spin iron(III) to the nitrogen atom of these cyanide groups. The result is an edge length of the cube of about 5.1 Å and a wide-meshed framework with large cavities. The lattice constant for Prussian blue made out of eight such cubes is therefore about 10.2 Å, but a more exact value of 10.16 Å is often reported [26]. Figure 2 shows this Prussian blue lattice.

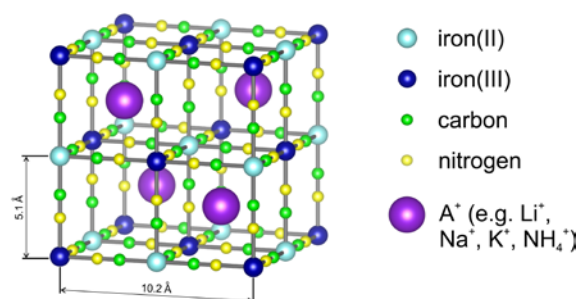
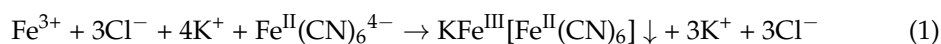


Figure 2. Structure of the defect-free Prussian blue lattice according to the Keggin and Miles model from 1936 with four alkali ions in alternate octants.

The Prussian blue lattice according to the still-popular Ludi model [27] from the 1970s with 25% hexacyanoferrate(II) vacancies is only formed by excessively fast precipitation,

e.g., by precipitation upon mixing aqueous solutions of iron(III) salts, such as ferric chloride, and potassium hexacyanoferrate(II) as shown in Figure 1 and described in Reaction (1) [24].



For more than 300 years, Prussian blue has been in use as a blue pigment [10]. However, today, applications in such diverse fields as biomedicine; catalysis; energy storage technologies; environmental protection, especially for radioactive caesium decontamination and sea water desalination; poison antidotes; electrochromism; and sensor technology make Prussian blue one of the most versatile materials for use in a multitude of modern cutting-edge technologies [28].

The mechanochemical or tribochemical way to prepare Prussian blue without solvents from solid precursors only is not new [29,30], but is also not widely known and has not been proposed for teaching mechanochemical reactions in a publication before. This preparation method has recently regained the interest of researchers and has been proposed to produce battery-grade Prussian blue [31–33] and/or Prussian blue for more efficient caesium ion adsorption [34].

2. Materials and Methods

For these simple experiments, it is advantageous to use a mortar and pestle made of porcelain or other white ceramic materials. In this way, the solid-state reaction can be most easily followed visually. The chemicals used were ferrous sulfate $\text{Fe}^{\text{II}}\text{SO}_4 \cdot 7\text{H}_2\text{O}$, ferric chloride $\text{Fe}^{\text{III}}\text{Cl}_3 \cdot x\text{H}_2\text{O}$, potassium hexacyanoferrate(III) $\text{K}_3[\text{Fe}^{\text{III}}(\text{CN})_6]$, and potassium hexacyanoferrate(II) $\text{K}_4[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$, all purchased from Sigma Aldrich. Three different mechanochemical Prussian blue preparations were followed: (i) grinding together ferric chloride and potassium hexacyanoferrate(II)—Reaction (2), (ii) ferrous sulfate and potassium hexacyanoferrate(III)—Reaction (3), and (iii) ferrous sulfate and potassium hexacyanoferrate(II)—Reactions (4) and (5). The reactions were performed by manually grinding equimolar amounts (0.01 mol) at room temperature in air with a 43% relative humidity. Humidity measurements were performed using a Testo 623 hygrometer device. If the water content of the compounds was not stated by the supplier, $(x\text{H}_2\text{O}) \times 5$ was used for calculations. Photographs were taken during certain time intervals. It should be noted that the reaction rate strongly depends on the speed and force applied during the manual grinding operations. However, as a rule of thumb, a dark blue Prussian blue color can always be seen after less than 5 min of grinding.

Care must be taken in handling all chemicals. Personal protective equipment (goggles, gloves, and a laboratory coat) must always be worn. The chemicals used (ferrous sulfate, ferric chloride, potassium hexacyanoferrate(III), potassium hexacyanoferrate(II)) or produced in the experiments (Prussian blue, potassium sulfate, potassium chloride) need to be treated according to the safety measures given by the corresponding safety data sheets. Waste disposal should follow the appropriate steps including consolidation, labeling, and delivery to the proper location in the laboratory.

3. Results and Discussion

Figure 3 shows a sequence of 10 photographs of the mechanochemical Prussian blue formation by grinding together $\text{Fe}^{\text{III}}\text{Cl}_3 \cdot x\text{H}_2\text{O}$ and $\text{K}_4[\text{Fe}^{\text{II}}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. First, ferric chloride is placed into the mortar, followed by the addition of potassium hexacyanoferrate(II). During grinding together, the process of these two compounds forming the blue-colored Prussian blue can easily be followed. The reaction follows the equation





Figure 3. Mechanochemical preparation of Prussian blue from ferric chloride and potassium hexacyanoferrate(II).

The blue powdery product we see in the last photograph of the series in Figure 3 is a mixture of Prussian blue, white potassium chloride, and perhaps some unreacted starting materials. It was shown by Gong et al. that “a certain amount of the crystal water in raw materials is indispensable” for the formation of Prussian blue [32].

The mechanochemical formation of Prussian blue is also possible by using ferrous sulfate and potassium hexacyanoferrate(III) as starting materials. Figure 4 shows the corresponding sequence of 10 photographs for this reaction, which can be described by

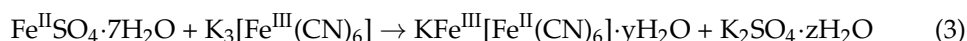


Figure 4. Mechanochemical preparation of Prussian blue from ferrous sulfate and potassium hexacyanoferrate(III).

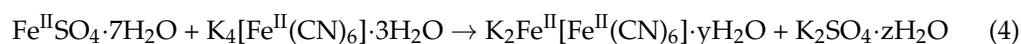
The product mixture in the last photograph in Figure 4 consists of dark blue Prussian blue and white potassium sulfate.

Prussian blue is a mixed-valence compound that contains iron in two different oxidation states: iron(II) and iron(III). In the first two experiments, we also used iron compounds with these two different oxidation states for Prussian blue preparation. In the third experiment, it is shown that Prussian blue is also formed if two iron compounds in the iron(II) oxidation state are used: ferrous sulfate and potassium hexacyanoferrate(II). Figure 5 shows how this reaction develops.

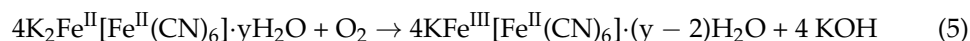


Figure 5. Mechanochemical preparation of Prussian blue from ferrous sulfate and potassium hexacyanoferrate(II).

This Prussian blue formation can be described by the next two equations. First, $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ is formed, also called Prussian white or Everitt's salt [35].



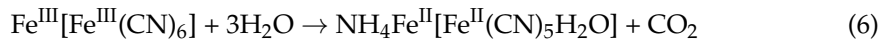
Prussian white is an uncolored compound that is easily oxidized to Prussian blue by oxygen (from air). Water is necessary for this reaction, as can be seen from Reaction (5) [36]. This can be crystal water in the solid reaction mixture and/or water from the humidity of the air.



This Prussian blue formation from two Fe(II) salts is slower compared to its formation from iron compounds in different oxidation states. Therefore, in the last picture of Figure 5, the reaction mixture is not as deeply colored as in the reactions according to Reactions (2) and (3). After several hours standing in the open air, the reaction mixture was as deeply blue colored as the other two.

To further slow down the oxidation of Fe(II) to Fe(III), Reguera et al. added solid hydrazine hydrochloride, a reducing agent, to the solid mixture [30]. Using this method, they could produce Prussian white, which was stable for some time before it was eventually oxidized to Prussian blue.

Finally, I want to remark that if ferric chloride and potassium hexacyanoferrate(III), i.e., the two iron(III) compounds, are ground together, brown Prussian Yellow, iron(III) hexacyanoferrate(III), is produced. This will also eventually react to Prussian blue. The first step is the formation of Prussian white according to Reaction (6) as described by de Wet and Rolle [37].



This is followed by its oxidation to Prussian blue according to Reaction (5). However, because this reaction is much slower compared with the oxidation of Prussian white only by oxygen, according to Reaction (5), it is not useful for the demonstration of the mechanochemical preparation of Prussian blue.

Such a mechanochemical Prussian blue preparation experiment could be part of a lecture in inorganic chemistry courses, which deal with coordination chemistry and the transition elements. Here, it could be demonstrated by the lecturer perhaps in comparison to the precipitation reaction for Prussian blue formation from aqueous precursor solutions as shown in Figure 1. However, these experiments could also be performed by undergraduate chemistry students by themselves during the preparative methods in inorganic chemistry laboratory courses.

4. Conclusions

A simple mortar-and-pestle experiment for teaching green, solvent-free mechanochemical reactions to undergraduate chemistry students was presented. The color change from brownish-yellowish and/or reddish to dark blue allows an easy assessment of the reaction progress. This communication updates and extends the topics of Prussian blue formation and mechanochemistry that were published earlier in chemical education journals independently of each other. The reaction described in this communication can be included by chemistry teachers in their programs for teaching sustainable chemistry.

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