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# A Further Demonstration of Sulfite-Induced Redox Cycling of Metal Ions Initiated by Shaking

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Our group has done a series of studies on the metalcatalyzed autoxidation of sulfur(IV) oxides (H<sub>2</sub>SO<sub>3</sub>, HSO<sub>3</sub>, and  $SO_3^{2-}$ ) (1–5). In this process the interaction of the metal ion (Fe<sup>3+</sup>, Mn<sup>3+</sup>, Co<sup>3+</sup>, and Ni<sup>3+</sup>) with  $HSO_3^-$  or  $SO_3^{2-}$  (at low concentrations) results in the oxidation of sulfite to the •SO<sub>3</sub> radical and the reduction of the metal species to the +2 state. In the presence of oxygen, the metal ion is oxidized back to higher oxidation state to complete the catalytic cycle. Usually this spontaneous oxidation is very slow, but in the presence of sulfite the oxidation proceeds autocatalytically. Surprisingly, SO<sub>3</sub><sup>2-</sup>, the reducing agent, induces the autoxidation of the metal ion. It follows that a critical balance between the oxygen and sulfite concentration will control the overall reaction. In the presence of a large excess of sulfite over oxygen, all M(III) will be reduced to M(II), sulfite will be oxidized to sulfate, and oxygen is consumed.

This redox cycling demonstration was previously reported in this *Journal* with emphasis on the Co(II)/Co(III)/N<sub>3</sub>-, Mn(II)/Mn(III)/N<sub>3</sub>-, and Fe(II)/Fe(III)/H<sub>2</sub>O systems ( $\theta$ ). Changes in the oxidation state of the metal ion were indicated by changes in color of the complexes formed with azide ion (1, 2). Similar studies have been done in the Fe(II)/Fe(III)/H<sub>2</sub>O and Mn(II)/Mn(III)/H<sub>2</sub>O systems (3–5, 7, 8). In the present work, the color change in the Ni(II)/Ni(III) hydroxide system is used to demonstrate an induced reaction in a heterogeneous system, with sodium hydroxide replacing the toxic sodium azide solution.

A suspension of green  $Ni(OH)_2$  is very stable and there is no visible change due to the oxidation of Ni(II) by dissolved oxygen. When a sulfite solution of suitable concentration is added dropwise, precipitation of black  $Ni(OH)_3$  can be observed.

The overall reaction can be described as:

$$2Ni(OH)_2 + SO_3^{2-} + O_2 + H_2O \rightarrow 2Ni(OH)_3 + SO_4^{2-} \quad (1)$$
 green black

The black precipitate can be  $Ni(OH)_3$  or a mixture with  $NiO_2 \cdot H_2O$  (9), but the formula  $Ni(OH)_3$  is used herein for simplicity. This precipitate color change has been suggested as a spot test for qualitative analysis of S(IV) (10). Owing to the redox cycling of the nickel ion, when the concentration of S(IV) is too high compared to the oxygen concentration, the spot test fails, as the following paragraphs explain.

#### **Experimental Details**

Reagents

The working solutions were conveniently prepared from dilution of 1.0 M NiCl<sub>2</sub>, 1.0 M NaOH, 2.0 M Na<sub>2</sub>SO<sub>3</sub> (or 1.0 M Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>), 1.0 M HCl, 0.02 M KI, and starch solution. All reagents were AR or CP grade from Merck. All solutions were prepared with air-saturated distilled water.

Redox Cycling Conditions

The demonstration experiment exhibits clear color changes during the oxidation of S(IV) and  $Ni(OH)_2$  in the presence of dissolved oxygen. In the presence of a large excess of sulfite over oxygen, the redox cycling of the metal ion can be observed in the  $Ni(OH)_2/Ni(OH)_3/SO_3^{2-}$  system.

The following solution, mixture A, can be prepared in a 500-mL round flask. Add 1.5 mL of 1.0 M NiCl<sub>2</sub> solution to approximately 143 mL of distilled water, then add 6.0 mL of 1.0 M NaOH solution with stirring, so that colloidal green Ni(OH)<sub>2</sub> precipitates in the presence of excess hydroxide. When the concentration of OH $^-$  is stoichiometric relative to Ni<sup>2+</sup>, the reaction is less sensitive and much slower.

When one or two drops of 2.0 M  $Na_2SO_3$  solution are added to mixture A giving an initial S(IV) concentration of  $1.0 \times 10^{-3}$  M, a black precipitate forms but immediately decomposes, owing to the reduction of Ni(III) by S(IV) in large excess. The dissolved oxygen has been completely depleted, since in air-saturated solution the oxygen concentration is approximately  $2 \times 10^{-4}$  M. When the closed flask is shaken vigorously, oxygen is dissolved from the headspace and the formation of black precipitate is again observed. A new addition of approximately 0.6 mL or 12 drops of 2.0 M  $Na_2SO_3$  decomposes the black precipitate (i.e.,  $Ni(OH)_3$  is reduced to  $Ni(OH)_2$ ). At the solution surface, where there is some contact with oxygen from the air, some black precipitate is noted, and upon vigorous agitation, the formation of  $Ni(OH)_3$  takes place again.

When 0.15 mL (about 3 drops) of 2.0 M  $Na_2SO_3$  is added to 150 mL of mixture A to give an initial concentration of  $2 \times 10^{-3}$  M S(IV), the redox cycling can also be noted at least three times by alternately resting and shaking the solution. The flask can be opened to allow air to enter. At some stage all the sulfite will be oxidized to sulfate and addition of more

 $Na_2SO_3$  can start the experiment again. If the addition is done drop by drop with slow and careful agitation, the local formation of black precipitate can be seen with further decomposition.

### Verification of Ni(OH)<sub>3</sub> Formation As S(IV) Concentration Increases

A series of solutions can be prepared by adding freshly prepared 0.3 or 2.0 M Na<sub>2</sub>SO<sub>3</sub> solution to 150 mL of Ni(OH)<sub>2</sub> suspension (mixture A) so that their concentrations will range from  $0.2 \times 10^{-4}$  to  $5 \times 10^{-4}$  M. The addition of the S(IV) solution is done gradually, using a microliter syringe to deliver small volumes in order to avoid excessive dilution. As the S(IV) concentration increases, there is an increase in quantity of the black precipitate. At the smallest concentration  $(0.2 \times 10^{-4} \text{ M})$  the color change will occur within 5 to 10 minutes, but the reaction will be immediate at the highest concentration  $(5 \times 10^{-4} \text{ M})$ .

#### Quantification of Ni(III)

The amount of Ni(III) formed in the presence of  $0.5 \times 10^{-5}$  to  $7 \times 10^{-5}$  M S(IV) can be determined spectrophotometrically in a 5-cm path-length cell or 15-mL flask. A series of solutions can be prepared by adding, with vigorous agitation, 0.01-0.10 mL of freshly prepared  $5 \times 10^{-3}$  M Na<sub>2</sub>SO<sub>3</sub> to 10 mL of solution A. Allow 10 minutes for the complete oxidation of all S(IV) to S(VI), then add 1 mL of 0.02 M I<sup>-</sup>, 1 mL of 1.0 M HCl, and 3 drops of starch solution. The final volume is 12 mL.

All the precipitate will be dissolved with the acid addition and iodine is formed by eq 2 and detected by the blue color of the starch complex. The blue color intensity can be measured spectrophotometrically at 600 nm. As the reaction proceeds in a heterogeneous medium a linearity of the absorbance with initial S(IV) concentration is not very reproducible.

$$2Ni(OH)_3 + 6H^+ + 2I^- \rightarrow I_2 + 6H_2O + 2Ni^{2+}$$
 (2)

According to eq 1,  $Ni(OH)_3$  should be produced in the ratio 2:1 to the sulfite used. In fact this ratio is lower due to various side reactions related to the oxidation of sulfite (1).

This method to quantify Ni(III) can be used when the initial S(IV) concentration is in the range of  $0.5 \times 10^{-5}$  to  $5.0 \times 10^{-5}$  M, assuming that all S(IV) was oxidized to S(VI). At higher concentration, when there is still some S(IV) in solution, I<sub>2</sub> will react with it (eq 3) and the results will not be accurate, since the absorbance value will not be related to Ni(III) concentration.

When the initial concentration of S(IV) and dissolved oxygen are at  $10^{-4}$  M (air-saturated solution), the absorbance reaches an almost constant value because of the balance between the reduction and oxidation processes.

$$I_2 + HSO_3^- + H_2O \rightarrow 2I^- + SO_4^{2-} + 3H^+$$
 (3)

#### **Mechanistic Interpretation**

The S(IV) induced oxidation of  $Ni(OH)_2$  by oxygen can be explained on the basis of our previous work (1–5, 7), where we demonstrated that the presence of a very small amount of the metal ion at higher oxidation state is necessary to initiate the process. The main reactions of initiation and

autocatalysis are presented in eqs 4–11.

#### Initiation

$$SO_3^{2-} + O_2 \rightarrow SO_5^{2-}$$
 (4)

$$Ni(OH)_2 + SO_5^{2-} \rightarrow Ni(OH)_3 + SO_4^{2-}$$
 (5)

or some trace metal impurities (e.g., Fe(III) or Co(III))

#### Autocatalytic Process

$$Ni(OH)_3 + SO_3^{2-} \rightarrow Ni(OH)_2 + \cdot SO^{3-} + OH^{-}$$
 (6)

$$\cdot SO_3^- + O_2 \rightarrow \cdot SO_5^- \tag{7}$$

$$\cdot SO_5^- + SO_3^{2-} \to SO_5^{2-} + \cdot SO_3^-$$
 (8)

$$Ni(OH)_2 + \cdot SO_5^- + OH^- \rightarrow Ni(OH)_3 + SO_5^{2-}$$
 (9)

$$Ni(OH)_2 + SO_5^{2-} + H_2O \rightarrow Ni(OH)_3 + \cdot SO_4^- + OH^- (10)$$

$$Ni(OH)_2 + \cdot SO_4^- + OH^- \rightarrow Ni(OH)_3 + SO_4^{2-}$$
 (11)

Devuyst and coworkers (11) studied the oxidation of aqueous  $Na_2SO_3$  with air in the absence of  $Ni(OH)_2$  (eq 4). Analytical quantities of  $SO_5^{2-}$ , determined iodometrically, were indeed obtained only at pH higher than 8. At pH 13 they found the highest yield of  $SO_5^{2-}$  ( $\approx 30\%$ ). The oxidant  $SO_5^{2-}$  was also found to be stable over a period of several hours and produced  $Ni(OH)_3$  when added to a slurry of  $Ni(OH)_2$  under  $N_2$  (eqs 5 and 10). The spontaneous oxidation of  $Ni(OH)_2$  by the dissolved oxygen is not thermodynamically favorable.

According to Berglund et al. (8), the initiation of the oxidation of Ni(OH) $_2$  by  $\cdot$ SO $_5$ , in the absence of some initial Ni(III), is due to traces of Fe(III) or other metal ions present as impurities in the nickel salts. It is very difficult to exclude trace concentration of Fe(III), even in a highly purified water. Previous analysis showed that it may be present at concentrations of  $8 \times 10^{-9}$  to  $5 \times 10^{-8}$  M (8). If Fe(III) is present, it reacts with S(IV) and generates sulfite radical (as in eq 6), which rapidly forms peroxomonosulfate radical by reaction with oxygen (eq 7), which oxidizes Ni(OH) $_2$  to Ni(OH) $_3$  (eq 9). Subsequent reactions include the reduction of Ni(OH) $_3$  by SO $_3$ <sup>2-</sup>, with the formation of the radical  $\cdot$ SO $_3$ <sup>-</sup> (eq 6), which reacts with O $_2$  to form SO $_5$ <sup>2-</sup> (eq 7).

When all dissolved  $O_2$  is consumed and there is still some S(IV), the Ni(III) is reduced (eq 6). Shaking the solution causes  $O_2$  to dissolve, and Ni(III) is formed again. So the balance between the S(IV) and  $O_2$  concentration is important in order to observe the redox cycling. While the main sulfurcontaining product is  $SO_4^{2^-}$ , some  $S_2O_6^{2^-}$  can be formed by combination of  $\cdot SO_3^-$  radicals.

Other mechanisms have been proposed. For example, Feigel and Anger (10) suggested the oxidation of  $Ni_2(OH)_2SO_3$  by  $O_2$  with formation of  $Ni(OH)_4$ , while Bhargva et al. (12) suggested formation of  $NiO_2(OSO_2)$  on a  $Ni_2O_3$  surface followed by decomposition to  $HSO_5^-$ , in the pH range 4.5–5.8.

Redox cycling involving Ni(II)/Ni(III) ions in cyclam (1, 4, 8, 11-tetraazacyclotetradecane) complexes has been the subject of detailed kinetic studies. The redox cycling can be demonstrated very clearly when a spectrophotometer is available. As cyclam is an unusual ligand, the hydroxide is more adequate for this experimental demonstration (13).

The relevance of these studies to environmental (14, 15) and analytical (16, 17) interests has been reported in the literature.

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