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

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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.

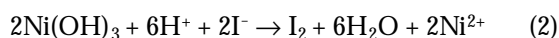
Verification of $\text{Ni}(\text{OH})_3$ Formation As S(IV) Concentration Increases

A series of solutions can be prepared by adding freshly prepared 0.3 or 2.0 M Na_2SO_3 solution to 150 mL of $\text{Ni}(\text{OH})_2$ suspension (mixture A) so that their concentrations will range from 0.2×10^{-4} to 5×10^{-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 (0.2×10^{-4} M) the color change will occur within 5 to 10 minutes, but the reaction will be immediate at the highest concentration (5×10^{-4} M).

Quantification of Ni(III)

The amount of Ni(III) formed in the presence of 0.5×10^{-5} to 7×10^{-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 5×10^{-3} M Na_2SO_3 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^- , 1 mL of 1.0 M HCl , and 3 drops of starch solution. The final volume is 12 mL.

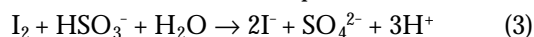
All the precipitate will be dissolved with the acid addition and iodine is formed by eq 2 and detected by the blue color of the starch complex. The blue color intensity can be measured spectrophotometrically at 600 nm. As the reaction proceeds in a heterogeneous medium a linearity of the absorbance with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



According to eq 1, $\text{Ni}(\text{OH})_3$ 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 0.5×10^{-5} to 5.0×10^{-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_2 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.

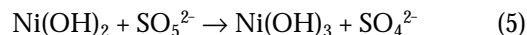
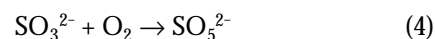


Mechanistic Interpretation

The S(IV) induced oxidation of $\text{Ni}(\text{OH})_2$ 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

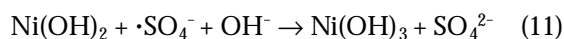
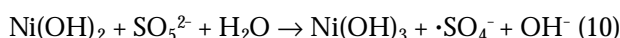
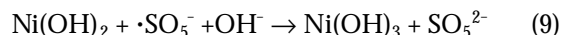
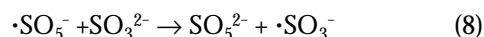
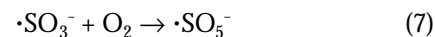
autocatalysis are presented in eqs 4–11.

Initiation



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

Autocatalytic Process



Devuyst and coworkers (11) studied the oxidation of aqueous Na_2SO_3 with air in the absence of $\text{Ni}(\text{OH})_2$ (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 $\text{Ni}(\text{OH})_3$ when added to a slurry of $\text{Ni}(\text{OH})_2$ under N_2 (eqs 5 and 10). The spontaneous oxidation of $\text{Ni}(\text{OH})_2$ by the dissolved oxygen is not thermodynamically favorable.

According to Berglund et al. (8), the initiation of the oxidation of $\text{Ni}(\text{OH})_2$ by $\cdot\text{SO}_5^-$, 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 8×10^{-9} to 5×10^{-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 $\text{Ni}(\text{OH})_2$ to $\text{Ni}(\text{OH})_3$ (eq 9). Subsequent reactions include the reduction of $\text{Ni}(\text{OH})_3$ by SO_3^{2-} , with the formation of the radical $\cdot\text{SO}_3^-$ (eq 6), which reacts with O_2 to form SO_5^{2-} (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 sulfur-containing product is SO_4^{2-} , some $\text{S}_2\text{O}_6^{2-}$ can be formed by combination of $\cdot\text{SO}_3^-$ radicals.

Other mechanisms have been proposed. For example, Feigel and Anger (10) suggested the oxidation of $\text{Ni}_2(\text{OH})_2\text{SO}_3$ by O_2 with formation of $\text{Ni}(\text{OH})_4$, while Bhargava et al. (12) suggested formation of $\text{NiO}_2(\text{OSO}_2)$ 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.

Acknowledgments

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