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# Mechanism of Reduction of Cadmium by Aminoiminomethanesulfinic Acid in Alkaline Media

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Aminoiminomethanesulfinic acid, formamidinesulfinic acid, or thiourea dioxide is the compound made by the reaction of thiourea and hydrogen peroxide. This compound is remarkable in that it readily reduces cadmium to the metal from aqueous solutions. Zinc metal does not precipitate. Dithionite,  $S_2O_4^{2-}$ , occurs in alkaline solutions of aminoiminomethanesulfinic acid. Solutions of dithionite do not reduce cadmium to the metallic state and finding carbon in the precipitated cadmium indicated that the species responsible for the strong reducing properties of the compound is a radical ion formed by a homolytic cleavage of the carbon–sulfur bond. A scheme to explain the above observations is presented.

Aminoiminomethanesulfinic acid, known also as formamidinesulfinic acid and thiourea dioxide, was first prepared in 1910 by de Barry Barnett (1) by the oxidation of thiourea with aqueous solutions of hydrogen peroxide. The fact that alkaline solutions of this compound exhibit strong reducing properties, reducing cadmium and those elements less electropositive than cadmium to the metallic state, was reported in 1936 by Böeseken (2). Since this discovery there have been numerous commercial applications of this reducing property, especially in the textile industry.

In addition to the commercial use, this compound has been utilized to a limited extent in chemical analysis. In acid media where it is reported to act as a complexing ligand rather than as a strong reducer (3), it has been used for the quantitative separation of platinum from solution (4), for the precipitation of palladium (5), for the determination of rhodium (6), and for the separation of rhodium and iridium (7). In neutral solution with boiling and in alkaline solution with heating, it has been used to reduce uranium(VI) to uranium(IV) (8), and also in alkaline media for the microdetermination of tin by precipitating tin(II) sulfide (9), and the reduction of iron(III) hydroxide (10).

The decomposition of aminoiminomethanesulfinic acid in alkaline media is apparently quite complex. Some workers have attributed the fact that alkaline solutions of this compound possess greater reducing properties than dithionite to the formation of sulfoxalate ion (2, 11, 12) by hydrolysis of aminoiminomethanesulfinic acid while others attribute these properties to the compound itself (13, 14).

Golovnya and Bolotova (3) studied the reducing properties and the decomposition products of aminoiminomethanesulfinic acid in various media. They reported that the magnitude and rate of change of potential was greatly influenced by the

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media, concentration, and temperature. Potentiometric studies showed that this compound was not a strong reducing agent in acid media and in neutral solution and that the acid itself reacted with strong oxidizing agents, the number of equivalents of oxygen consumed depending on the medium and the oxidizing agent. In alkaline media the acid and its decomposition products, which were more readily oxidized than the acid, reacted with oxidizing agents in freshly prepared solutions. Alkaline solutions were reported to decompose rapidly. The strong reducing properties in alkaline media were attributed to the decomposition products, chiefly to sulfoxylic acid and its salts.

The ease and low cost with which aminoiminomethanesulfinic acid can be prepared and purified make it a very attractive analytical reagent. Its greatest potential usefulness as an analytical reagent is apparently due to the strong reducing properties exhibited in alkaline solution. Cadmium and those elements less electropositive are reduced to the metallic state while zinc, for example, is not reduced. This suggests that a better understanding of the mechanism of reduction in alkaline media could possibly lead to conditions that would make this separation and similar ones possible, thereby greatly enhancing the usefulness of this compound as an analytical reagent.

#### EXPERIMENTAL

Apparatus and Material. Ultraviolet spectra were recorded using a Perkin-Elmer Model 4000-A UV/Visible Spectrophotometer and a Cary Model 14 Recording Spectrophotometer. Infrared spectra were made with a Perkin-Elmer Model 137 Spectrophotometer and electron paramagnetic resonance (EPR) studies were conducted on a Varian Model E-3 EPR Spectrometer. A Leeds & Northrup Model 62200 Electro-Chemograph was used for polarographic studies and measurements of pH were made with a Leeds & Northrup Model 7405 pH Indicator which had been previously standardized using appropriate National Bureau of Standards reference buffers. Measurements of potential were made with a Leeds & Northrup Model 7401 pH Indicator equipped with a platinum indicator electrode. X-ray diffraction patterns were recorded with a Norelco Automatic Recording X-ray Diffractometer.

Allied Chemical special high-purity 59-Grade Cadmium "D" Metal, 99.999% pure, was used for preparation of stock solutions of cadmium. Technical grade thiourea was purified by recrystallization from ethanol prior to use. Practical grade sodium dithionite was purified using the procedure of Jellinek (15) with modifications suggested by Christiansen and Norton (16) with the exception that a nitrogen atmosphere was used instead of carbon dioxide. The water used was distilled and deionized by passage through an ion-exchange column charged with Bio-Rex RG-501-X8 mixed-bed resin. All other chemicals were of reagent grade unless otherwise noted.

Stock solutions of cadmium were prepared by dissolving the metal with the appropriate inorganic acid, diluting to volume with water, and standardizing by titration with EDTA at pH 10 using Calmagite as indicator. A cross check of the standardization procedure was made using the gravimetric cadmium sulfate procedure (17). Aminoimi-

#### Table I. Mole Ratio of Reducing Agent to Metal

Mole ratio, reducing agent to metal	Cd taken, mg	Cd found, mg	Reduction, %	
A. In S	3 M aqueous a	mmonia at 85 °	РС	
1:1	48.3	27.2	56.3	
2:1	48.3	43.9	90.9	
3:1	<b>48.3</b>	47.2	97.7	
5:1	48.3	47.9	99.2	
9:1	48.3	48.1	99.6	
B. In 3 M aqueo pre	us ammonia wi sent at ambier	ith 0.3 g potass at temperature	ium chlorate	
1:1	47.9	17.2	. 35.8	
2:1	47.9	41.2	86.1	
5:1	47.9	45.7	95.5	
10:1	47.9	46.3	96.7	

nomethanesulfinic acid was prepared as required by the oxidation of thiourea with 6% aqueous hydrogen peroxide solution according to the procedure of de Barry Barnett (1).

**Procedure.** For the reduction of cadmium, an accurately measured volume of the standard cadmium solution was placed in a beaker, the appropriate solvent added, the temperature adjusted to the desired value, and the solid reducing agent added. After standing for a prescribed period of time, the precipitate was collected using a tared medium-prosity fritted-glass crucible with aid of suction, washed thoroughly with water, dried in an oven at 105 °C for 1.5 h, cooled in a desiccator, and weighed. To determine the amount of cadmium present, the precipitate was dissolved with one and one hydrochloric acid and a few drops of 30% hydrogen peroxide, neutralized with potassium hydroxide, adjusted to pH 10 with ammonia–ammonium chloride buffer, and titrated with EDTA using Calmagite as indicator.

All ultraviolet spectra were recorded using 1.00-cm matched quartz cells with water as the reference and were made at ambient temperature. Electron paramagnetic resonance (EPR) measurements were made in 2-mm o.d. fused-quartz sample tubes and were scanned in the region from 7800 to 5700 gauss with a fixed frequency of about 9.53  $\times$  10<sup>9</sup> hertz.

#### **RESULTS AND DISCUSSION**

**Study of Precipitated Cadmium.** It was noted that the weight of precipitate obtained from a cadmium reduction in 3 M aqueous ammonia at 85 °C was greater than the amount of cadmium taken. When 96.6 mg of cadmium was taken, a precipitate weighing 99.4 mg was obtained. Extraction with carbon disulfide failed to decrease the weight of the precipitate indicating the absence of elemental sulfur. The odor of hydrogen sulfide was noted when the precipitate obtained under the above conditions was dissolved with hydrochloric acid. Determination of the sulfur present as sulfide by the ASTM Sulfur by the Evolution Method (18) failed to account for all the weight. A 99.4 mg precipitate with 96.6 mg of cadmium present gave 1.1 mg of sulfur present as sulfide by this method. This suggested the presence of some species other than cadmium metal and cadmium sulfide.

X-ray diffraction patterns of the precipitate failed to show sharp peaks. After digestion of a sample of precipitated cadmium for approximately 30 h on a steam bath, broad, rounded peaks were obtained at the spacing corresponding to the three most intense bands of cadmium metal. Because of the poorly defined crystalline structure of the precipitate, x-ray diffraction patterns were of little value in establishing the identity of the species present.

The precipitate from a reduction in 3 M aqueous ammonia at 85 °C was placed in a muffle furnace and heated to approximately 300 °C and the weight monitored as a function of time. An increase in weight was noted and the color of the precipitate changed from a gray metallic luster to a brownish



Figure 1. Ultraviolet spectrum of 0.01 g/100 ml of aminoiminomethanesulfinic acid in 3 M aqueous ammonia in 1.00-cm quartz cells

(A) After 1 min. (B) After 5 min. (C) After 10 min

color. An x-ray diffraction pattern of this material showed bands corresponding to cadmium metal, cadmium oxide, and cadmium sulfate. Because of the apparent ease of oxidation of the precipitate probably due to its finely divided nature, this procedure was not helpful in detecting the presence of any volatile organic material.

A reduction was carried out in 5 M aqueous ammonia/0.2 M sodium hydroxide with 0.5 g of potassium chlorate present at ambient temperature in order to minimize the formation of sulfide. Again the weight of the precipitate exceeded the weight of cadmium taken for the reduction. A sample of precipitated cadmium obtained using the above conditions was sent to a commercial laboratory for determination of carbon and hydrogen. This resulted in a report of 0.74% carbon and 0.59% hydrogen. A repeat of this analysis on another sample resulted in a report of 0.17% carbon, 0.50% hydrogen, 0.03% nitrogen, and 0.006% sulfur.

Establishment of the presence of carbon in the precipitate plus the fact that the sulfur content was greatly reduced by conditions which minimized the formation of sulfide gave strong support to an active reducing agent which contained carbon.

Study of Species Present under Reducing Conditions. An attempt was made to determine whether or not a clear relationship existed between the number of moles of reducing agent and cadmium metal. Reductions were carried out in 3 M aqueous ammonia at 85 °C and in 3 M aqueous ammonia with 0.3 g of potassium chlorate present at ambient temperature. Results are given in Table I.

As shown by these results, no apparent clear stoichiometric relationship exists between the reducing agent and the cadmium ion. Although it is therefore not possible to establish unequivocally the number of electrons involved in the half-cell reaction of the reducing species based on these results, there is indication that two moles of reducing agent are required for each mole of cadmium ion.

The ultraviolet spectrum of a solution of aminoiminomethanesulfinic acid in 3 M aqueous ammonia was recorded as a function of time. The spectrum is shown in Figure 1. The absorption band at 269 nm, attributed to aminoiminomethanesulfinic acid (19), decreased in intensity with time and a band appeared at 316 nm which increased in intensity with time. The ultraviolet spectrum of sodium dithionite exhibited an absorption band at 316 nm.

A solution of aminoiminomethanesulfinic acid in 3 M aqueous ammonia was tested for the presence of dithionite with Naphthol Yellow S, a specific reagent for dithionite (20). The results were positive. A polarogram of aminoiminomethanesulfinic acid in 0.5 M diammonium hydrogen phosphate/1 ammonium hydroxide/0.01% gelatine supporting electrolyte also gave a positive indication of the presence of dithionite (21).

Electron paramagnetic resonance (EPR) measurements were made on solid sodium dithionite powder, sodium dithionite in 0.5 M sodium hydroxide, solid aminoiminomethanesulfinic acid, aminoiminomethanesulfinic acid in 0.5 M sodium hydroxide, and aminoiminomethanesulfinic acid in 3 M aqueous ammonia. A strong paramagnetic signal, g =2.004, was obtained for solid sodium dithionite confirming reports of earlier workers (22). A strong paramagnetic signal, g = 2.006, which persisted longer than an hour was obtained for solutions of sodium dithionite in 0.5 M sodium hydroxide. This confirmed reports of earlier workers (23, 24) that basic solutions of sodium dithionite may contain the  $SO_2^-$  radical ion. Solid aminoiminomethanesulfinic acid did not exhibit paramagnetism under these conditions. However, strong paramagnetic signals, g = 2.006 and g = 2.007, were obtained for solutions of aminoiminomethanesulfinic acid in 0.5 M sodium hydroxide and 3 M aqueous ammonia. These EPR observations are consistent with the presence of dithionite and strongly indicate the presence of  $SO_2^-$  radical ions in basic solutions of aminoiminomethanesulfinic acid.

The filtrate from a cadmium reduction in 3 M aqueous ammonia at 85 °C with a 10-fold excess of the reducing agent was taken to dryness on a steam bath using a rotary evaporator under aspirator vacuum. A yellow-white solid was obtained. A portion of this solid was dissolved in water, passed through a mixed-bed ion exchange column, and the effluent again taken to dryness. An odorless white powder, mp 129–130 °C, was obtained. Its infrared spectrum was identical to that of urea. This confirmed reports that basic solutions of aminoiminomethanesulfinic acid yielded urea (2, 10-12) and proved that urea was the only non-ionic species present.

Sodium dithionite was added to water that had been boiled for approximately 30 min and then cooled to ambient temperature with a stream of nitrogen gas bubbling through it. A platinum electrolysis electrode was then placed in the solution. No bubbles of gas were visible around the electrode. Cadmium was introduced into a solution of dithionite prepared in this manner. The solution remained clear for about 10 min and began to turn yellow. There was no cadmium metal visible in the solution. Apparently, sodium dithionite does not liberate hydrogen from water and does not reduce cadmium to the metallic state.

A platinum electrolysis electrode was placed in a solution of aminoiminomethanesulfinic acid in 3 M aqueous ammonia and bubbles of gas were noted around the electrode. This supports reports that aminoiminomethanesulfinic acid liberates hydrogen from ammonical solutions with a catalyst present (3).

The increase in absorbance at 316 nm was measured as a function of time at varying pH values and aminoiminomethanesulfinic acid concentrations. Approximately 500 ml of water was adjusted to pH 11 with sodium hydroxide. Four 50-ml portions were taken, 0.05, 0.10, 0.25, and 0.50 g of aminoiminomethanesulfinic acid were added, and the absorbance of each solution at 316 nm measured as a function of time. In each case a straight line relationship with the same slope was found between the natural logarithm of absorbance and time. This procedure was repeated with the pH being adjusted to pH 12 prior to the addition of aminoiminomethanesulfinic acid. A plot of both the natural logarithm and the reciprocal of absorbance vs. time failed to give a straight line.

These observations do not permit establishment of the order of the reaction in basic solutions by monitoring the absorbance at 316 nm. The first-order relationship with a rate independent of the concentration of aminoiminomethanesulfinic acid indicates that the rate depends on the hydroxide ion at very low concentrations of this ion. This relationship does not hold true as the hydroxide ion concentration increases.

The fact that alkaline solutions of aminoiminomethanesulfinic acid reduce cadmium to the metallic state and liberate a gas from water in the presence of a catalyst and alkaline solutions of dithionite apparently do not, leads to the conclusion that alkaline solutions of aminoiminomethanesulfinic acid contain a more powerful reducing agent. Establishment of the presence of carbon in the precipitated cadmium metal plus the reduction in its sulfur content by addition of chlorate to minimize the formation of sulfide without loss of the ability to reduce cadmium to the metallic state supports a carbon-containing reducing agent.

The presence of the  $SO_2^-$  radical ion in alkaline solutions of aminoiminomethanesulfinic acid supports a homolytic cleavage of the carbon-sulfur bond. A heterolytic cleavage of this bond to form the  $SO_2^{2-}$  anion with subsequent loss of an electron to form the  $SO_2^-$  radical ion seems unlikely in light of the above observations. The following equations give a proposed reaction sequence to explain these observations:



It is proposed that the  $H_2N(=NH)CSO_2^-$  anion reacts with hydroxide to produce a cleavage of the carbon–sulfur bond to form the  $SO_2^-$  radical ion and the  $H_2N(=NH)COH^-$  radical ion with the latter being the species responsible for the strong reducing properties of aminoiminomethanesulfinic acid in alkaline solutions.

At low pH values, reaction 1 is apparently the slow step of the sequence due to the low hydroxide ion concentration. As the pH increases, this no longer holds true. A possible explanation for the fact that monitoring the absorbance at 316 nm does not permit elucidation of the order of the reaction is the reaction of the  $SO_2^-$  radical ion or dithionite or both with water to form species with different absorptivities than dithionite at 316 nm. This is consistent with the known lack of stability of aqueous solutions of dithionite.

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## Determination of Hydrogen Ion Concentrations in Seawater from 5 to 40 °C: Standard Potentials at Salinities from 20 to 45%

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Evidence has been presented to show that seawater behaves as a "constant ionic medium", stabilizing the activity coefficients of solutes present in small concentrations and reducing or eliminating the residual liquid-junction potential encountered in measuring the pH of seawater systems. Under these conditions, an experimental scale of hydrogen ion concentration becomes a practical possibility. The standard emf of the H<sub>2</sub>/Ag;AgCl cell, needed to establish standard reference buffer solutions in seawater, has been determined in synthetic seawater at salinities from 20 to 45% and temperatures from 5 to 40 °C. Supplementary measurements in seawater to which HCl has been added lead to values of  $\beta_{\text{HSO}_{4}}$ , the formation constant of HSO4<sup>-</sup>, in this range of salinity and temperature.

In earlier contributions (1-3), we have examined the possibility of determining experimentally, by electrometric methods, the hydrogen ion concentration of natural seawater. It was concluded that seawater of 35‰ salinity possesses the favorable characteristics of a "constant ionic medium". Thus, the liquid-junction potential between seawater and the customary concentrated potassium chloride solution of the reference electrode is nearly constant when small changes in the composition of the seawater solution occur. Furthermore, the activity coefficients of solutes present in relatively small amounts in the seawater medium are stabilized, changing but little as the concentrations of these substances are altered. As a consequence of these favorable conditions, it appears feasible to standardize a scale of pH, defined as  $-\log c_{\rm H}$ , for seawater that can be experimentally realized through measurements with the electrometric assembly of the usual glass-calomel type. The practical advantage of such a scale derives both from the utility of the quantity  $c_{\rm H}$  and from the greater simplicity

of the concept of hydrogen ion concentration as compared with that of the hydrogen ion activity.

In practice, the pH of an "unknown" solution (X) is derived from the emf  $(E_X)$  of the cell

Glass electrode | Soln X || KCl, Reference electrode (A)

and from the corresponding emf  $(E_S)$  for the same cell in which a standard solution (S) of known or assigned pH [pH(S)] replaces Solution X. Use is made of the operational definition

$$pH(X) = pH(S) + \frac{(E_X - E_S)F}{RT \ln 10}$$
(1)

When the ionic strengths and compositions with respect to the preponderant electrolytes are the same in the solutions X and S, Equation 1 yields an experimental measure of  $pm_{\rm H}({\rm X})$  if  $pm_{\rm H}({\rm S})$  is known ( $m = {\rm molality}$ ).

In order to establish hydrogen ion concentrations or molalities for buffer solutions in synthetic seawater (sw) in the pH range close to that of natural seawater, we have chosen to study the emf of cells without liquid junction, in a manner similar to that used to derive pH(S) for the NBS standard reference solutions (4). Hydrogen electrodes and silver-silver chloride electrodes are used in this method. The standard potentials required for studies in seawater have now been derived from emf measurements of cells of the type

$$Pt;H_2(g,1 atm) \mid HCl(m) in sw \mid AgCl;Ag$$
 (B)

The compositions of the solutions in synthetic seawater were adjusted in such a manner as to keep both the ionic strength and the molality of chloride ion constant in all of the cells. The synthetic seawater was composed of NaCl, KCl, CaCl<sub>2</sub>, and MgCl<sub>2</sub>; the only major component of natural seawater missing from this formulation is sulfate ion. In a supplementary series of measurements, HCl solutions in synthetic seawater containing sulfate ion were studied in cell B. These data, interpreted with the aid of the standard potentials, yield values for  $\beta_{\rm HSO_4}$ , the equilibrium constant for the ion association process

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