[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Reduction of Sulfate to Sulfide in Acid Solutions by Divalent Chromium[1]

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Acid solutions of Cr(II) are shown to reduce sulfate to sulfide. The reaction is relatively slow but is catalyzed by certain halides and by phosphate. In order that measurable rates of H_2S evolution may be observed temperatures up to 55° were used. Moreover, the concentrations of the various substances involved in the H_2S-forming reaction were high because of the slowness of the reaction at lesser concentrations. The concentrations made use of were of the order of magnitude indicated: Cr(II) 1.25 M, $SO_4^=$ 3.5 M, H^+ 8 M and for the catalysts such as Cl^-, 5 M. The relative catalytic effect as compared to chloride is indicated by the numbers in the parentheses: iodide (340), bromide (27), phosphate (14) and chloride (1)

Divalent chromium has long been known as one of the most powerful and rapid reducing agents available for use in aqueous solutions. Its usefulness has been restricted because of the uncertainties regarding the rate at which it liberates hydrogen from acid solution.

Berthelot[2] observed that divalent chromium slowly liberated hydrogen from the acid necessary for oxygen absorption. Twenty-nine years later, in 1927, Asmanow[3] pointed out that if sulfuric acid was used, and chloride was absent, the divalent chromium did not react with sulfuric acid up to 10 M concentration. He believed that chloride catalyzed the reduction of hydrogen ion by Cr(II). Stone and Skavinsky[4] and Stone[5] have shown that this reduction of acid hydrogen is extremely slow or absent above a pH of 3. Pecsok, in this Laboratory, has shown that 0.1 N $CrCl_2$, in 0.05 N HCl, after being stored in the absence of molecular oxygen for more than five years, had decreased in Cr(II) titer only 0.05%, an almost negligible reduction of acid hydrogen by the chromium reagent. This was in the presence of 0.35 M chloride ion which Asmanow[3] had regarded as a catalyst for the liberation of H_2 by this reagent.

Branham's[6] report of similar possible reduction of sulfate to sulfide in acid solution by Cr(II) has remained unchallenged and uncorroborated in the chemical literature since 1938. The present study was undertaken with the hope of obtaining sufficient facts concerning sulfate reduction by divalent chromium to prevent the uncertainties and controversial statements such as have appeared concerning the acid hydrogen reduction.

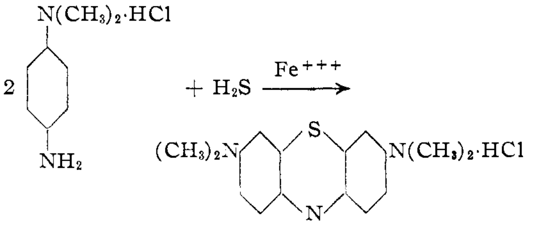
Hydrogen sulfide formation by the action of divalent chromium on acid sulfate solutions was studied by mixing the desired components in an oxygen-free, thermostated reactor vessel, and removing the hydrogen sulfide gas which was formed by an absorbing solution of $N/100$ sodium hydroxide. The hydrogen sulfide was swept from the reactor to the absorbing solution by a rapid stream of oxygen-free nitrogen. The absorbed sulfide was then determined colorimetrically by an improved methylene blue method.

Apparatus and Method

The apparatus included a water jacketed reactor vessel in which the temperature was controlled thermostatically. This vessel was equipped with a thermometer, a reagent addition tube, a spray trap and a means of introducing a stream of oxygen-free nitrogen. A three-way stopcock, for by-passing the stream of N_2, was placed in the line connecting the reaction vessel with the absorber. The gas containing the H_2S was introduced into the $M/100$ sodium hydroxide solution in the absorber through a sintered glass gas diffusion tube. A flow meter, to permit regulation of the gas flow, was included in the system.

The desired quantities of reagents other than chromous solutions were added to the reactor vessel and dissolved oxygen was removed by bubbling nitrogen through the solution. The tip of the chromous storage buret was inserted into the opening provided and a measured quantity of the reagent was added. A copious flow of nitrogen from the addition opening assured exclusion of air during this step. The opening was then closed with a rubber policeman. After sufficient time had elapsed for the attainment of thermal equilibrium and of a steady state between the hydrogen sulfide generated and that swept out, the gas stream was diverted into the absorber vessel for a specified period. Precautions were taken to prevent access of air to the oxygen-free absorbing solution which was analyzed by the methylene blue method.

The methylene blue method was developed from the one given by Snell,[7] which is based on the formation of methylene blue by the reaction



(1)

It was found that by using twice the concentration of reagents recommended by Snell, in a smaller volume, both the range and the sensitivity were materially increased.

A 25-ml. volume of solution containing the sulfide to be measured was poured into a graduated cylinder. The container and bubbler were then rinsed once with distilled water which in turn was added to the graduate. The solution in the cylinder was then diluted to 40 ml. and poured into a 125-ml. glass stoppered erlenmeyer flask; 10.0 ml. of distilled water was then added to the graduate as a rinse and poured into the flask. Then 5.0 ml. of p-aminodimethylaniline reagent (0.8 g. per liter of 6 N HCl) and 1.0 ml. of ferric chloride reagent (27 g. per liter of 6 N HCl) were added rapidly and in that order with swirling. The flask was stoppered immediately to prevent loss of hydrogen sulfide. After standing one-half hour the solution was ready to be observed in the spectrophotometer.

Test showed that although the time necessary to reach the peak optical density varied with the quantity of hydrogen sulfide present, all solutions containing quantities of sulfide within the capacity of the test solutions were within 1% of

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(1) Presented before the Physical and Inorganic Section of the American Chemical Society at the XIIth International Congress, New York City, N. Y., September 10, 1951.

(2) M. Berthelot, *Compt. rend.*, **127**, 24 (1898)

(3) A. Asmanow, *Z. anorg. allgem. Chem.*, **160**, 209 (1927).

(4) H. W. Stone and E. R. Skavinski, *Anal. Ed., Ind. Eng. Chem.*, **17**, 495 (1945).

(5) H. W. Stone, *Anal. Chem.*, **20**, 747 (1948).

(6) J. R. Branham, *J. Research Natl. Bur. Standards*, **21**, 45 (1938).

(7) F. D. Snell, "Colorimetric Methods of Analysis," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1936, p. 593.

this peak in less than 30 minutes and maintained that value with that accuracy for more than 15 hours.

The instrument used for all measurements was a Beckman quartz spectrophotometer, Model DU. The cells were Corex and 1.00 cm. in thickness. The calibration data and all readings were taken at 665 mμ and with the instrument set so that the slit width was always 0.10 mm., the zero adjustment being made with the sensitivity control knob. Reference liquid for all measurements was distilled water since several blank test solutions run against water all gave an optical density of less than 0.01.

TABLE I

CALIBRATION DATA FOR METHYLENE BLUE SULFIDE DETERMINATION

H_2S, μg.	Optical density
23.0	0.297
46.0	.604
57.5	.743
69.0	.883
86.2	1.10
115.0	1.41

The hydrogen sulfide was transferred by "sweeping out" with a stream of nitrogen from which the last trace of oxygen had been removed by bubbling through an acid solution of chromous chloride.

It may be assumed that, on bubbling nitrogen through an acid solution in which hydrogen sulfide is being generated at a constant rate, an equilibrium will be established whereby the quantity swept out will equal the quantity generated during the same interval. Successive determinations on the same solution indicated that 15 minutes was sufficient to establish the equilibrium under the nitrogen flow conditions employed, *i.e.*, 60 ml./min. Reproducibility of determinations was within the ±10% generally observed for measurements of different aliquots of the same solution. No increasing or decreasing trend was observed. The quantities of hydrogen sulfide formed were not sufficient to alter the concentrations of the reactants materially over the time intervals employed.

Reduction of Sulfate by Divalent Chromium.—Duplication of Branham's[6] experiments using lead acetate paper to detect hydrogen sulfide in a stream of inert gas bubbling through a chromous chloride solution showed no sulfide until sulfate had been added in the form of sodium sulfate or sulfuric acid. It was established also that an increase in temperature increased the rate of sulfide generation.

To study the sulfide production, solutions of chromous chloride or chromous sulfate, prepared by the zinc amalgam reduction method, and diluted sulfuric and hydrochloric acids were added to the reactor vessel together with any other substances whose effect upon the reaction was to be studied. It was found necessary to work at elevated temperatures and fairly high concentrations to avoid lengthy adsorption periods and still obtain amounts of hydrogen sulfide which could be measured on the accurate portion of the calibration curve.

Data and Discussion

The *effect of temperature* on the rate of production of hydrogen sulfide was measured at 5° intervals, from 25 to 55° in a solution which was 1.0 M in Cr(II), 8.45 M in H^+, 3.6 M in $SO_4^=$ and 4.25 M in Cl^-. The hydrogen sulfide evolved from 50 ml. of solution ranged from 8 micrograms per hour at 25° to 400 micrograms per hour at 55°. When the yield of hydrogen sulfide was plotted against the temperature a straight line was obtained with the points fitting closely.

The initial rate of production of hydrogen sulfide was also shown to be a function of the concentration of the various substances taking part in the reaction

$$8\mathrm{Cr(II)} + SO_4^= + 10H^+ \longrightarrow 8\mathrm{Cr(III)} + H_2S + 4H_2O \quad (2)$$

In certain experiments some of these substances were replaced by others assumed to have no effect upon the sulfide formation. For example, hydrogen ion was replaced by sodium or ammonium ion. In other instances variations were introduced by reducing the quantity of reagent added to the solution. This procedure necessarily caused changes in the concentration of other ions and in the ionic strength, thus complicating the effects. Unless otherwise noted, all temperatures were at 50°.

A study of the effect of varying the molar concentration *of the sulfate* on the micrograms of H_2S, evolved per hour, from 50 ml. of solution at 50° was made. When the concentration of the sulfate was 1.4 M, 6 micrograms of H_2S was evolved per hour, while at a sulfate concentration of 3.6, 275 micrograms of H_2S was evolved. When six different sulfate concentrations within the above limits were plotted against the weight of H_2S evolved, a straight line was obtained, with five of the points falling closely on the line and the sixth deviating by about 15 micrograms of H_2S out of 100 at 2.8 M sulfate concentration.

Variations in the *chromous* concentration on the micrograms of H_2S evolved from 50 ml. of solution at 50° was also observed. Two different solutions were used. One was 3.6 M in sulfate, 8.45 M in hydrogen ion and 1.25 M in chloride, exclusive of the chromous chloride added. The other solution was 3.6 M in sulfate, 7.8 M in hydrogen ion and 0.6 M in chloride exclusive of the chromous chloride added.

When the weight of H_2S produced per hour was plotted against the square root of the Cr(II) concentration in moles per liter straight parallel lines were obtained for these solutions. All of the nine points used in the plotting fell closely on the curves. The micrograms of H_2S produced varied from approximately 15 micrograms at the lower Cr(II) concentration to over 200 micrograms per hour per 50 ml. at 50° at the higher Cr(II) concentration.

Figure 1 is a graphic presentation of data obtained from a study of the effect of varying the *hydrogen ion* concentration on the rate of evolution of H_2S by the reaction of Cr(II) on sulfate. The term hydrogen ion concentration is not satisfactory for solutions of such high ion concentrations but is used to represent the molar hydrogen ion concentration based on the assumption that the strong acids present are completely dissociated. The line labeled A represents the addition of hydrochloric acid to a solution 1.13 M in Cr(II), 3.6 M in sulfate and 3.75 M in chloride, exclusive of the hydrochloric acid added. B represents the replacement of hydrogen ion with sodium ion; C represents a solution 1.0 in Cr(II), 3.6 M in sulfate and 4.84 M in chloride; D represents a solution 1.13 M in Cr(II), 3.6 M in sulfate and 4.2 M in chloride.

The *catalytic effect* of certain anions have been studied by comparison with the effect exhibited by chloride ion. Chloride ion does not take a direct part in reaction 2 but it was present in high concentration because chromous chloride was used as the source of Cr(II) and HCl was used as a source of H^+. It has been shown by Asmanow[3] that chloride is catalytic in the reaction

$$2H^+ + 2\mathrm{Cr(II)} \longrightarrow 2\mathrm{Cr(III)} + H_2 \quad (3)$$

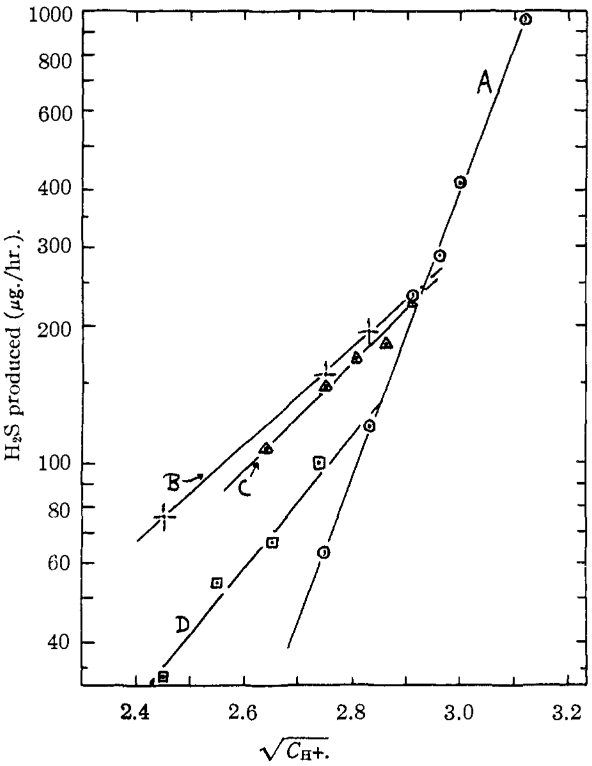

Fig. 1.

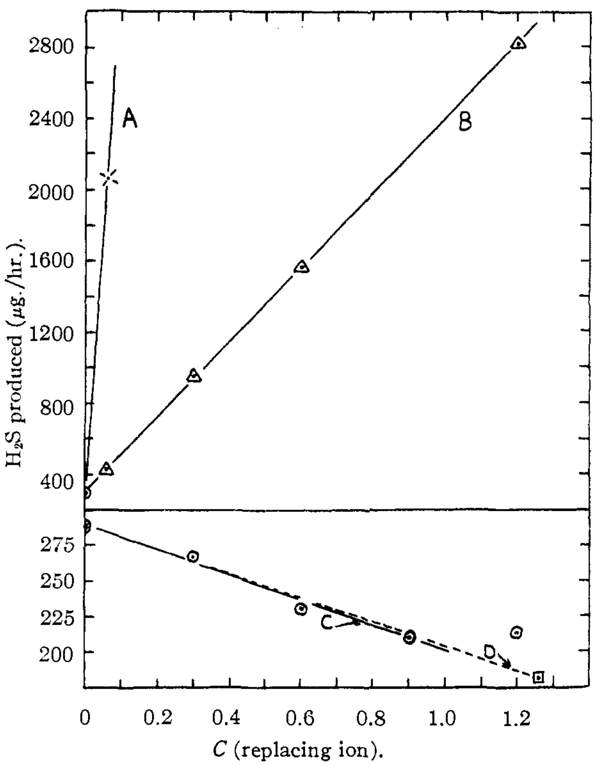

Fig. 2.

Replacement of a portion of the chloride by other halogens in reaction 2 led to a startling increase in sulfide production. A search for a non-catalytic anion of a strong acid which was not appreciably reduced by chromous ion led to the use of perchlorate and fluoroborate ions. Fluoroboric acid solution, according to Wamser,[8] is an equilibrium mixture with a number of components but was assumed to be largely in the fluoroborate form due to the high hydrogen ion concentration. Dilute perchloric acid (less than 0.5 *M*) showed surprising stability to chromous ion even at the temperatures used in these experiments but as the concentrations were increased, the reduction proceeded at an appreciable rate, a green coloration becoming visible in the reactor in a very few minutes.

Figure 2 shows the catalytic effect of chloride, bromide and iodide on the evolution of H_2S by the action of Cr(II) on sulfate in acid solution. It also indicates that perchlorate and fluoroborate ions are not catalysts for this reaction. The curves are all for a solution 1.13 *M* in Cr(II), 3.6 *M* in sulfate and 4.93 in chloride before replacement with other ions. The replacements were A, iodide; B, bromide; C, perchlorate; D fluoroborate.

The fact that the replacement of a portion of the chloride by perchlorate and fluoroborate ions gives lines of essentially the same slope indicates that these ions have no appreciable effect upon the sulfide generation. The inverse of this slope may be considered to be the effect of increasing chloride concentration and so may be compared with the slopes of the lines produced by replacement of chloride by bromide and iodide. The ratio of these slopes is $I^-:Br^-:Cl^- = 340:27:1$.

Since chloride is catalytic in reaction 2, chloride-free chromous reagents were prepared by the reduction of chromium aluminum sulfate solutions. The rates observed were of the order of magnitude expected for the ionic concentrations employed. The presence of chloride or a halide is not necessary for the reduction of sulfate, as it appears to be in the reduction of hydrogen ions.

A chloride-free chromous sulfate solution that might be used in gas analysis was investigated in order to estimate the production of H_2S in solutions of this type at room temperatures. The run was made at 50° and the temperature factor applied to find the sulfide production at 25°. The solution was 0.4 *M* in chromium alum and 0.5 *M* in sulfuric acid before reduction. Hydrogen sulfide production from 50 ml. of this solution was 0.47 μg./hr. at 50.0° which becomes 1.3×10^{-2} μg./hr. at 25°. Since 1 μg. of hydrogen sulfide occupies only 6.6×10^{-4} ml., the quantities indicated here would be immeasurable by conventional gas analysis methods over long periods of time but would probably foul the small area of mercury surface.

Because of the well known stability of anions containing four oxygen atoms as contrasted with any lower state of oxidation of the same element, the rate-controlling step is most probably the initial one or two electron reduction of the sulfate ion.

Attempts to determine a rate constant met with failure for several reasons. It was necessary to increase the hydrogen sulfide production to a rate of 1000 μg./hr. or better to obtain a significant change in the concentration of the chromous ion in

[8] C. A. Wamser, This Journal, **70**, 1209 (1948).

a reasonable time and to do this without the use of highly catalytic substances like bromide ion or iodide ion required concentrations so high that trouble with insolubility of some salts, probably chromous sulfate, was encountered. On one rate run which ran for 24 hours with an initial rate of 835 μg./hr., analysis of the solution for divalent chromium at the end of the run showed a 12.5% reduction in concentration while calculations based on the sulfide production would indicate about 7.5% reduction. This would indicate that 40% of the reduction in chromous ion concentration was due to oxidation by hydrogen ions. Consequently any rate constant so derived would be a composite of the two reactions and would not be valid for the reaction under consideration.

The determination of the order of the rate-controlling reaction from consideration of the initial rates also failed. Use of the formula

$$n_A = \frac{\log\left(-\frac{dA_1}{dt}\right) - \log\left(-\frac{dA_2}{dt}\right)}{\log A_1 - \log A_2}$$

where n_A is the order with respect to A, A_1 and A_2 the initial concentrations of A in two runs, and dA_1/dt and dA_2/dt the initial rates in the same two runs, gave values of 2, 4 and 4 for Cr^{+2}, SO_2^{-2} and H^+, respectively. It is felt that the formulas developed for dilute solution kinetics would not be applicable to solutions with ionic strengths on the order of 15–20 in any event.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORIES, HARVARD UNIVERSITY]

Conductance Studies of Organometallic Chlorides of Group IVB and of Hydrogen Chloride in N,N-Dimethylformamide. Some Observations About the Purification of the Solvent

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Solutions of organometallic chlorides of the elements of Group IVB in N,N-dimethylformamide have been investigated conductimetrically, and have been found not to dissociate into organometallic cations and chloride ions. Since N,N-dimethylformamide is difficult to purify, appreciable amounts of water may remain in it after purification, so that easily solvolyzed solutes, such as triphenylchlorosilane, produce large amounts of hydrogen chloride in solution. The problem of purifying N,N-dimethylformamide is discussed, and a means of detecting the amount of proton-releasing impurity is described. Data are presented on the conductance of hydrogen chloride in N,N-dimethylformamide.

Introduction

In recent years there has been increasing interest in N,N-dimethylformamide as an electrolytic solvent. Most of this interest has been concerned with conductances of ionophoric[1] compounds such as alkali metal and quaternary ammonium salts[2–5]; however, some attention has been given to conductances of ionogenic[1] compounds such as hydrogen chloride,[6] acyl halides,[7] and organosilicon and organogermanium chlorides.[8,9] This paper presents a study of the conductimetric behavior of organometallic chlorides of the elements of Group IVB and of hydrogen chloride in N,N-dimethylformamide, and includes some observations of general utility concerning the purification of the solvent.

The observation that organochlorosilanes give conducting solutions in N,N-dimethylformamide[8,9] is the first reported instance of possible electrolytic properties for organosilicon compounds. It would be desirable to determine the identity of the ionic species present, especially in view of the observed reaction between organochlorosilanes and N,N-dimethylformamide at high temperatures[10] to form dimethylamine hydrochloride, and also because minute traces of proton-releasing impurities can solvolyze organochlorosilanes to produce hydrogen chloride. The electrolytic behavior of organohalostannanes in water[11] and in various non-aqueous solvents[12,13] also makes the electrolytic properties of such compounds in N,N-dimethylformamide of interest, and measurements have been extended to the entire group.

Experimental

Purification of the Solvent.—N,N-Dimethylformamide (hereafter called DMF) is very difficult to purify. Trace amounts of proton-releasing impurities have a profound effect on the observed conductimetric behavior of any solute which yields a hydrogen halide as a solvolysis product, and every effort must be made to eliminate such impurities or to estimate their concentration so that their effects can be taken into account in the interpretation of the results. Impurities of importance in this respect include water, alcohols and primary and secondary amines.

DMF decomposes slightly at its normal boiling point to give small amounts of dimethylamine and carbon monoxide.

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[1] R. M. Fuoss, *J. Chem. Ed.*, **32**, 527 (1955). Prof. Fuoss makes a valuable distinction between those electrolytes which are discretely ionic in the crystal lattice (ionophores), and those which exist as molecular entities in the original compound to become electrolytes only by virtue of acid–base reaction with appropriate solvents (ionogens).

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