I. PRASEODYMIUM AND NEODYMIUM COMPLEXES WITH 8-QUINOLINOL-5-SULFONIC ACID.

II. SOME REACTIONS OF NITROSYL DISULFONATE ION.

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ABSTRACT

Stable complexes are formed between 8-quinolinol-5-sulfonic acid and praseodymium (III) and neodymium (III). There is no conclusive evidence for the existence, in solution, of complexes between that acid and praseodymium and neodymium in higher oxidation states than three.

Dry solid potassium nitrosyl disulfonate is stable indefinitely, but the moist solid decomposes quite rapidly. In acid solution, nitrosyl disulfonate ion undergoes autocatalytic decomposition. In the investigation of this decomposition it was discovered that the reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions is catalyzed by iron. The investigation of these two reactions, and particularly the kinetics of the latter reaction are described.

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I. PRASEODYMIUM AND NEODYMIUM COMPLEXES WITH 8-QUINOLINOL-5-SULFONIC ACID.

INTRODUCTION

In a recent paper by Nakatsuka and Chang(1), evidence is presented for the existence in aqueous solution of higher oxidation states than three for praseodymium and neodymium. They also present a method for separating these neighboring rare earth elements. Because their findings would be of interest and significance, it was deemed important to repeat some of their experiments. Although it has not been possible to confirm either the higher oxidation states or the separation method, there are constructive aspects of the chemistry involved which justify a description of our experiments.

Nakatsuka and Chang subjected ammoniacal solutions containing 8-quinolinol-5-sulfonic acid and nitrates of praseodymium and neodymium to oxidation by air and especially to anodic oxidation in a porous cup at a platinum electode. The solutions became a dark reddish-brown color; in the case of more complete anodic oxidation, the solutions became opaque. For the separation, the oxidized mixtures were treated with sodium carbonate and glucose (reducing agent) and then heated, whereupon, they reported, praseodymium (III) carbonate precipitated, while the neodymium remained in solution.

In our own experiments, an effort was made to confirm the separation method and to prepare, in solid form, the complex compounds that appear to exist in the mixtures indicated above.

EXPERIMENTAL

Reagents:

Samples of the light blue Nd_2O_3 and the jet black Pr_6O_{11}, each labeled 99% pure, were obtained from Research Chemicals, Incorporated, Burbank, California. Eastman Kodak Company "white label" 8-quinolinol-5-sulfonic acid, recrystalized from 5% hydrochloric acid, was used throughout. All other chemicals were of Reagent Grade.

Tests for Higher Oxidation States:

To 100 cc. of 0.5 VF (formula weights per liter of solution) ammonium hydroxide containing 1.5 g. of 8-quinolinol-5-sulfonic acid was added 20 ml. of a solution containing 0.08 g. of praseodymium as the nitrate; no precipitate formed. A similar blank solution containing no praseodymium was also prepared. On standing over night exposed to air, both solutions became reddish-brown in color to about the same degree. Anodic oxidation for twenty minutes in a porous cup at 6 volts, 0.2 ampere and 25 milliamperes per square centimeter of the platinum anode caused both mixtures to become darkened to the extent of being opaque. No precipitate formed in either the blank or test solution.

Tests of Separation Procedure:

Solutions containing praseodymium ion, neodymium ion, and mixtures of the two were prepared and treated as described above. To each such opaque solution were added 10 g. of sodium carbonate and 3 g. of glucose, and the resulting solution was heated for one and one half hours on a steam bath.

In the case of praseodymium alone, it was found that praseodymium (III) carbonate would not precipitate quantitatively as claimed; in different experiments from 10 to 50% of the praseodymium remained in solution. The amount which precipitated was determined by converting the carbonate to the oxalate, by igniting the oxalate in a muffle furnace to the black oxide, and by weighing this black oxide. Also it was not necessary to add glucose in order to precipitate a part of the praseodymium as the carbonate. In the case of neodymium alone, it partially precipitated as the carbonate under those conditions under which praseodymium was supposed to precipitate quantitatively. The neodymium was determined by the same method as that of Nakatsuka and Chang. After the treatment of the solution to remove praseodymium, it is made slightly acid, and a large excess of oxalic acid is added. The resulting precipitate of neodymium oxalate is filtered and washed, and ignited to the light blue sesquioxide. In the case of the mixture of praseodymium and neodymium, no even semi-quantitative separation was observed. The oxides obtained, which should have been the jet black Pr_6O_{11} and the light blue Nd_2O_3, where both the same shade of rust brown.

Preparation of Complex:

Efforts to prepare solid samples of the praseodymium (III) derivative of 8-quinolinol-5-sulfonic acid were fruitless. The attempt to prepare this substance was made by adding a concentrated solution of $PrCl_3$ to a concentrated solution of the ammonium salt of the sulfonic acid in an excess of ammonium hydroxide, and by further concentrating the resulting solution by evaporation with gentle heating in an atmosphere of nitrogen. The solid obtained, when analyzed for praseodymium, nitrogen, and sulfur, gave a composition which corresponded to no simple compound.

DISCUSSION

It is evident that the color changes which take place during the oxidation of the above solutions do not depend upon the presence of praseodymium and, therefore, no positive proof is provided that the praseodymium (III) was oxidized. Indeed it is well known that when compounds of the type of 8-quinolinol-5-sulfonic acid are oxidized, the products are highly colored substances. The reported procedure for the separation of neodymium and praseodymium is impracticable and, therefore, also constitutes no evidence for the existence, in solution, of higher oxidation states of these elements. Indeed in view of recent work by Popov and Glockler(2) on solid neodymium oxides, it appears that no stable compounds of neodymium in a higher oxidation state than three exist.

It is likely that the trouble encountered in the preparation of the solid praseodymium derivative of 8-quinolinol-5-sulfonic acid is the same as that encountered by Jackson at the University of Illinois(3) in his successful attempts to prepare the lanthanum derivate of 8-quinolinol, $La(C_9H_6NO)_3$. This difficulty was the partial hydrolysis and decomposition of the desired derivative either in concentrated solutions or by heating in the presence of water.

From the above observations it seems clear that Nakatsuka and Chang have found interesting complexes of praseodymium (III) and neodymium (III) which are stable in ammoniacal solutions without the precipitation of the hydroxides. However, their proposal of the existence, in solution, of oxidation states of praseodymium and neodymium greater than three does not appear tenable.

Very recently Nakatsuka and Kudo have published a paper(4) in which they state that they have prepared the 8-quinolinol derivative of neodymium (IV). Their procedure for this preparation is much the same as that described by Nakatsuka and Chang. An ammoniacal solution containing neodymium (III) and in this case, 8-quinolinol-7-sulfonic acid is subjected to anodic oxidation. The solution obtained is then heated with 8-quinolinol in a sealed tube. The analysis of the resulting solid product agreed, within a few percent, with that calculated for a compound with the formula, $Nd(C_9H_6NO)_4 \cdot H_2O$.

No further attempt has been made to repeat these later experiments, but work by Block, Bailar, and Pearce(5) may give a clue as to the nature of this neodymium compound. These investigators worked with a compound of silver reported by Nakatsuka(6) to be the 8-quinolinol derivative of silver (II), and they reported that, on the basis of the compound's chemical and magnetic properties, it was a derivative of silver (I), $Ag(C_9H_6NO)(C_9H_7NO)$. Therefore, there remains reasonable doubt about the existence of a stable compound of neodymium (IV). This doubt quite probably could be removed by a magnetic investigation of Nakatsuka's neodymium compound.

II. SOME REACTIONS OF NITROSYL DISULFONATE ION.

INTRODUCTION

There exists a very interesting family of compounds of sulfur, nitrogen, and oxygen whose properties have been discussed in two general texts on the subject(7,8). Also, the kinetics of some of the reactions of these compounds has been studied(9,10,11). This family of compounds consists of the sulfonate derivatives of ammonia and hydroxylamine. However, one should include in this family the salts of nitrosyl disulfonic acid, $ON(SO_3H)_2$, because it is so closely related by its reactions to the other members of the family.

Nitrosyl disulfonate ion is a moderately strong oxidizing agent, being capable of oxidizing iodide ion to iodine and ferrous ion to ferric ion under proper conditions. The principal product of the reduction of nitrosyl disulfonate ion is hydroxylamine disulfonate ion, $HON(SO_3)_2^{=}$, and hydroxylamine disulfonate ion may be oxidized to nitrosyl disulfonate ion by such strong oxidizing agents as lead dioxide, ozone, and potassium permanganate(12).

Potassium nitrosyl disulfonate is a golden orange solid which when dissolved in water produces a purple solution out of which may be recrystallized the orange solid. The solutions have been shown to be paramagnetic(13,14), while the solid is diamagnetic. Further, the anion in solution has been shown to have a minus two charge(15). These facts lead to the conclusion that the anion is of the form $ON(SO_3)_2^=$, and that in the solid state this ion is at least dimerized.

It is known that dry solid potassium nitrosyl disulfonate is indefinitely stable, while the moist solid decomposes very rapidly(16). In acid aqueous solution, nitrosyl disulfonate ion undergoes autocatalytic decomposition. On the basis of work carried out both in this laboratory and at the University of Washington(17), it is known that the principal products of the autodecomposition of nitrosyl disulfonate ion are initially hydroxylamine disulfonate ion, nitrous oxide, hydrogen ion, and sulfate ion:

$$4\ ON(SO_3)_2^= + 3\ H_2O \rightarrow N_2O + 2\ HON(SO_3)_2^= + 4\ SO_4^= + 4\ H^+. \quad (1)$$

Since the above reaction is autocatalytic, it was deemed desirable to investigate the reactions between nitrosyl disulfonate ion and the products of its own decomposition.

The reaction between nitrosyl disulfonate ion and hydroxylamine disulfonate ion in acid solution proved to be zero order with respect to nitrosyl disulfonate ion concentration when the hydroxylamine disulfonate ion was present in large excess. This indicated that the rate determining step in this particular reaction did not involve nitrosyl disulfonate ion. Also, the rate of disappearance of nitrosyl disulfonate ion corresponded to twice the rate of hydrolysis of the hydroxylamine disulfonate ion present. This latter rate was determined by using the value of the rate constant found by Naiditch and Yost(10) for the reaction:

$$HON(SO_3)_2^{=} + H_2O \rightarrow HONHSO_3^{-} + HSO_4^{-} . \qquad (2)$$

Thus it seemed that the reaction between nitrosyl disulfonate ion and hydroxylamine monosulfonate ion might be a relatively fast one.

In our investigation of the reaction between nitrosyl disulfonate ion and hydroxylamine monosulfonate ion, we found that the reaction was catalyzed by very small amounts of iron, and, in fact, would not take place in acid solution in the absence of iron. The details of these investigations and the conclusions drawn from them are given below.

EXPERIMENTAL

Reagents:

Potassium nitrosyl disulfonate was prepared by the method of Raschig(18). To 100 ml. of 5 VF (formula weights per liter of solution) sodium nitrite were added 200 g. of ice, and with stirring 100 ml. of 5 VF sodium bisulfite and 20 ml. of glacial acetic acid. The reaction mixture was continuously stirred. Every minute or so, a one milliliter test sample was withdrawn and diluted with 5 ml. of starch solution. When the first drop of a dilute iodine solution colored a test sample blue, 20 ml. of 15 VF ammonium hydroxide was added. This iodine test indicated the removal of bisulfite ion and therefore the completion of the reaction,

$$NO_2^- + 2\ HSO_3^- + H^+ \rightarrow HON(SO_3)_2^= + H_2O. \qquad (3)$$

To the reaction mixture was then added 400 ml. of 0.2 VF potassium permanganate. Manganese dioxide preciptitated quickly and was removed from the reaction mixture by filtration. The filtrate had the deep purple color of nitrosyl disulfonate ion. The filtrate was added to 1.6 liters of ice cold, saturated potassium chloride solution. The precipitated potassium nitrosyl disulfonate was filtered, washed with three portions of absolute alcohol and then with three portions of absolute ether, and dried and stored in a vacuum desiccator.

The potassium nitrosyl disulfonate was further purified by twice recrystallizing it from 0.1 *VF* potassium hydroxide. About 15 g. of the solid salt were dissolved in 400 ml. of 0.1 *VF* potassium hydroxide at 40°C. The solution was filtered and cooled slowly to 0°C. The precipitated salt was filtered, washed with absolute alcohol and then with absolute ether, and dried in a vacuum desiccator. The purity of the salt prepared in this way is greater than 99%(13,16,17).

Anhydrous potassium hydroxylamine disulfonate was prepared by the method of Rollefson and Oldershaw(19) as modifed by Naiditch and Yost(10). To 200 ml. of ice water were added 85 g. of potassium nitrite, 118 g. of potassium acetate, and 1500 g. of finely crushed ice. While the mixture was rapidly stirred, sulfur dioxide was bubbled through until its odor was just detectable above the mixture. During the addition of sulfur dioxide, potassium hydroxylamine disulfonate precipitated. After the addition of sulfur dioxide, the precipitated potassium hydroxylamine disulfonate was filtered and successively washed with three portions of ice water, three portions of absolute alcohol, and three portions of absolute ether. The preparation was dried and stored in a vacuum desiccator. Anhydrous potassium hydroxylamine disulfonate prepared in this way has a purity of greater than 99%(10).

Sodium hydroxylamine monosulfonate was prepared by the method of Raschig(20). To 1500 g. of finely crushed ice were added 200 ml. of 5 VF sodium bisulfite and 200 ml. of 5 VF sodium nitrite. Sulfur dioxide was bubbled through the mixture. The bubbling was stopped when the odor of sulfur dioxide was just detectable above the mixture. The resulting solution was allowed to stand over night and then was made neutral with sodium hydroxide. The neutral solution was evaporated by boiling until crystals of sodium sulfate appeared. The solution was cooled and after a short time a quantity of hydrated sodium sulfate crystallized out. The sodium sulfate crystals were removed by filtration. This evaporation, cooling, precipitation, and filtration procedure was repeated until a sirupy solution was obtained. The concentrated solution was placed in a desiccator and after about a week became a solid mass of crystals of sodium hydroxylamine monosulfonate. The crystals were dried by filtration and placed in a vacuum desiccator.

The sodium hydroxylamine monosulfonate prepared by this method was found by iodometric titration to be only about 75% pure; the principal impurity was sodium sulfate. Further purification was obtained by equilibrating the impure material with a 50-50 weight percent mixture of methanol and water. The excess solid material was filtered off, and the relatively pure (93-97%) product was precipitated by adding excess absolute methanol to the filtrate. Again the main impurity was sodium sulfate, as indicated by testing with barium chloride solution.

The purity of the sodium hydroxylamine monosulfonate preparation was determined by the following procedure: Ten grams of sodium acetate trihydrate were added to 25 ml. of distilled water. Into the resulting solution were pipetted exactly 25 ml. of standard triiodide solution. Then enough sodium hydroxylamine monosulfonate was weighted into the triiodide solution almost to decolorize it. The excess triiodide was back titrated with standard thiosulfate solution to a starch end point. The standard sodium thiosulfate solution was prepared and standardized against potassium dichromate, and the standard triiodide solution was prepared and standardized against the thiosulfate solution all by the methods of Swift(21).

Sodium perchlorate made by the G. Fredrick Smith Chemical Company was used to adjust ionic strengths until it was found that this reagent contained relatively large amounts of iron. Iron free potassium perchlorate was prepared in the following way: A ten percent excess of concentrated perchloric acid was added to a saturated solution of potassium chloride in water. The resulting precipitate was filtered, and washed several times with ice water. The well crystallized potassium perchlorate thus obtained was recrystallized from water.

Standard 0.0167 VF lanthanum perchorate was prepared by weighing out 5.43 gm. of lanthanum sesquioxide, just dissolving and neutralizing this solid with standard 0.100 VF perchloric acid, and diluting the solution obtained to 1.00 liter. The lanthanum sesquioxide used was labeled 99.9% pure, and was obtained from Research Chemicals, Incorporated, Burbank, California.

The water used in preparing all solutions was the tap distilled water redistilled from alkaline permanganate in an all-pyrex still. The water thus purified had a specific conductance of about 5×10^{-5} mho, and a pH value of about 6.5. The water was stored in a bottle fitted with a soda lime tube.

Solutions of ferric perchlorate were prepared in the following way: Reagent grade ferric chloride was twice resublimed. To the resulting solid was added a twenty percent excess of concentrated perchloric acid, and this mixture was fumed almost to dryness. More concentrated perchloric acid was added and the mixture again fumed almost to dryness. Excess perchloric acid was then filtered off. The precipitate was weighed, and dissolved in enough 0.1 VF perchloric acid to make the resulting solution 0.1 VF in ferric perchlorate. The stock solution gave a negative test for chloride when silver nitrate was added to a sample of it.

A dilute solution of ferric perchlorate was prepared by adding about one milliliter of the concentrated stock solution to a liter of 1.0×10^{-3} VF perchloric acid. The author is greatly indebted to Mr. J. K. Rowley who standardized the dilute stock solution by a coulometric procedure. This procedure involves the addition of iodide and excess standard thiosulfate and the coulometric back titration of the excess thiosulfate. An amperometric end point is used. The details of this procedure are to be published. The dilute stock solution underwent no physical or chemical change in three months as indicated by the constancy of rate measurements at the beginning and end of that period.

Standard solutions 0.0100 VF in perchloric acid were prepared by diluting concentrated, vacuum distilled perchloric acid with redistilled water. These solutions were standardized against recrystallized borax, using a Beckman Model H pH meter to determine the equivalence point, by the following procedure: A sample of recrystallized borax (approximately 0.10 gram) was accurately weighed into a 250 cc. beaker into which has been pipetted 50.00 ml. of the perchloric acid to be standardized. The borax sample was completely dissolved. While the solution was continuously stirred, small portions of the acid to be standardized were added from a buret, and the pH of the solution was determined after each addition. The data obtained were plotted to give a curve of pH vs. milliliters of acid added, and the inflection point on this curve was taken as the equivalence point of the titration. Results obtained by this method were reproducible within one half a percent.

Iron was tested for by the method of Appleman(22): The solution to be tested was acidified with sulfuric acid. A few drops of bromine water were added, and the excess bromine was removed by boiling. Small portions of an ethyl acetate solution saturated with water and with potassium thiocyanate were added to the solution to be tested until a second phase just appeared. A red color in the acetate-rich phase indicated the presence of at least one part per million of iron. Thus the test proved useful only when relatively large amounts of iron were present.

Versene Fe-3 Specific is the Bersworth Chemical Company's trade name for a very strong complexing agent for iron (III). The compound is sold as a 47% aqueous solution, the specific gravity of which is 1.21. The exact nature of the compound is not stated by the company. A 1.00 ml. sample of this preparation was diluted to one liter with redistilled water. A 25.00 ml. sample of this dilute solution was titrated with standard 0.0100 *VF* perchloric acid, a pH meter being used to determine an equivalence point. An inflection point occurred in the plot of pH *vs.* milliliters of standard acid solution added at a pH value of 5.75, at which point 6.53 ml. of the standard acid solution had been added.

The complete curve of pH *vs.* milliliters of added acid for the dilute solution of Versene Fe-3 Specific was valuable for two reasons. First, it gave information necessary for the calculation of the amount of acid to be added to dilute solutions of Versene Fe-3 Specific to adjust the pH to a desired value. Second, it gave an indication of the nature of the compound responsible for the complexing. The equivalent weight of this compound calculated from the data given above is 167 grams. So-called Regular Versene made by the same company is the "disodium salt of ethylene diamine tetra acetic acid", and it is of interest to note that the equivalent weights of the trisodium salts of 1, 2, 3, tris- [di(carboxymethyl) amino] propane and of tris- [di(carboxymethyl) aminomethyl] methane are 168 and 173 respectively. Thus, allowing for impurity in the original preparation, the complexing compound may well be one of these two "hexa acetic" acids.

Apparatus:

All rate runs were carried out in a Beckman Model DU spectrophotometer, in ten centimeter cells. The solutions to be used in any rate run were thermostated in a water bath whose temperature was controlled to within ± 0.03°C. The cell compartment of the spectrophotometer was thermostated by attaching to it brass plates to which had been soldered copper tubing, and by passing thermostated water through this tubing. The temperature control obtained in this way was within ± 0.05°C. provided that the temperature of the room was not more than a few degrees from the thermostating temperature.

The ten centimeter spectrophotometer cells themselves were constructed of pieces of twenty-two millimeter pyrex tubing, to each of which was attached a side arm, and to the ends of which optically flat quartz windows were attached by means of thermally aged glyptal. The two cells used were optically matched to the extent that when filled with water, their optical densities compared to air agreed within three tenths of a percent at a wave length of 245 mμ.

All glass ware, such as volumetric flasks, pipets, reaction vessels, etc., was cleaned in the following way: First, the object was rinsed with chromic acid cleaning solution, then with several portions of tap distilled water, then with concentrated hydrochloric acid, then with acidified Versene Fe-3 Specific, then with more tap distilled water, and finally with several portions of redistilled water. When working at very small iron concentrations, it was found desirable to rinse the reaction vessels with a solution of the same iron concentration as that to be used in a rate run before running that rate. This procedure largely eliminated any effects which may have been due to surface adsorbed iron.

Optical Properties of Solutions of Potassium Nitrosyl Disulfonate.

Determinations of the extinction coefficient of solutions of potassium nitrosyl disulfonate were carried out in the following way: A sample of the salt was weighed into a dry one liter volumetric flask. The sample was dissolved in 1.00 x 10^{-3} <u>VF</u> sodium hydroxide solution, and the resulting solution was diluted to the mark with the same sodium hydroxide solution. Samples of this stock solution were diluted with the 1.00 x 10^{-3} <u>VF</u> sodium hydroxide solution to an appropriate volume to give readily measurable optical densities.

In one group of experiments, the concentration of nitrosyl disulfonate ion was kept constant while the wave length of the adsorbed light was varied. The values obtained for the extinction coefficient as a function of wave length are shown graphically in Figure 1. There exists a maximum in the curve of extinction coefficient <u>vs.</u> wave length at about 5450 Å, where the extinction coefficient has the value 20.2 ± 0.2 lt.$\cdot$mole$^{-1}\cdot$cm.$^{-1}$, and there exists a minimum in this same curve at 2450 Å, where the extinction coefficient has the value 1690 ± 15 lt.$\cdot$mole$^{-1}\cdot$cm.$^{-1}$.

In another group of experiments, it was determined that the extinction coefficient at a wave length of 2450 Å of solutions containing nitrosyl disulfonate ion is independent of the concentration of that ion in the range of concentrations between 2 and 6 x 10^{-5} <u>VF</u>.

Since even in dilute sodium hydroxide, solutions of potassium nitrosyl disulfonate decompose slowly, checks were run at the beginning and end of each group of experiments to insure that the stock solution had not changed significantly during the course of the experiments.

The above two groups of experiments show that the spectrophotometric method is applicable to the accurate determination of concentrations of nitrosyl disulfonate ion on the order of 10^{-5} VF.

Procedure for Rate Runs:

In running any particular rate, all of the solutions to be used to establish the conditions of the run exclusive of that containing the potassium nitrosyl disulfonate were mixed in a reaction vessel, and the vessel was placed in the thermostat. The solution containing the potassium nitrosyl disulfonate was prepared separately and placed in the thermostat. A blank solution was prepared which was identical to the reaction mixture except that the quantity of potassium nitrosyl disulfonate solution to be used was replaced by redistilled water. The blank solution was placed in one of the ten centimeter cells. The same cell was always used for the blank solution. The cell which was to contain the reaction mixture was placed in the thermostated cell compartment for several minutes. An appropriate quantity of the potassium nitrosyl disulfonate solution was added to the rest of the reaction mixture, and the clock was started. The reaction mixture was rapidly stirred, and a sample of it was placed in the reaction cell. The first measurement of optical density was usually obtained one and one half minutes after the addition of the potassium nitrosyl disulfonate solution.

Readings of optical density were then made periodically, and the dark current and "zeroing" of the spectrophotometer were checked at appropriate intervals.

During the period of preparing for a run, and during the run itself, room temperature was kept within 2°C. of the temperature at which the run was to be carried out.

Solutions of potassium hydroxylamine disulfonate and potassium nitrosyl disulfonate are unstable with respect to reaction with water. Therefore, solutions of these compounds were used within one hour after their preparation.

The Autocatalytic Decomposition of Nitrosyl Disulfonate Ion:

When potassium nitrosyl disulfonate at moderate concentrations decomposes in dilute acid a gas is liberated which is a white solid at liquid air temperatures. The gas liberated from approximately 0.1 VF solutions contained small but undetermined amounts of sulfur dioxide and nitrogen dioxide, as detected by the odor and color of the gas, and had an average molecular weight of 44.9. The average molecular weight was determined by measuring the vapor density of the dry gas. The samples of gas obtained from more dilute solutions were colorless and odorless and had a molecular weight of 44.1 ± 0.2. This figure coupled with the physical properties of the gas prove it to be nitrous oxide.

The number of moles of nitrous oxide liberated per mole of nitrosyl disulfonate ion decomposing was determined by the following procedure: A sample of potassium nitrosyl disulfonate weighing 46.5 mg. was rinsed into the reaction chamber of a Van Slyke apparatus with just five milliliters of redistilled water. After about twenty minutes the color had disappeared from the solution, and after about forty more minutes the reaction had appearently reached completion. The pressure necessary to compress the evolved gas to a volume of 2 cc. was measured. A blank was run on the redistilled water alone. The amount of nitrous oxide liberated amounted to 0.250 ± 0.010 moles per mole of nitrosyl disulfonate ion decomposing.

That hydroxylamine disulfonate ion is one of the products of the decomposition of nitrosyl disulfonate ion is proved by the fact that the products of the decomposition are oxidized by small amounts of alkaline permanganate to give the characteristic purple color of nitrosyl disulfonate ion. The color of nitrosyl disulfonate ion is easily distinguished from that of dilute permanganate solutions. The only known ion which can be oxidized to form nitrosyl disulfonate ion is hydroxylamine disulfonate ion. Further, an iodometric titration of the products of the hydrolysis showed that one half mole of hydroxylamine monosulfonate ion was ultimately formed per mole of nitrosyl disulfonate ion decomposing. And since hydroxylamine disulfonate ion is known(10) readily to hydrolyze to form hydroxylamine monosulfonate ion, one half mole of hydroxylamine disulfonate ion must be initially produced by the decomposition of one mole of nitrosyl disulfonate ion.

The number of moles of hydrogen ion formed per mole of nitrosyl disulfonate ion decomposing was found to be 1.50 ± 0.03 by titrating the ultimate products of the decomposition with standard sodium hydroxide solution to a phenolphthalein end point.

If the products of the hydrolysis of nitrosyl disulfonate ion were allowed to stand over night, and the resulting solution treated with a twofold excess of barium chloride, 1.60 ± 0.01 moles of sulfate precipitate were formed per initial mole of nitrosyl disulfonate ion. If, however, the products of the hydrolysis were boiled with dilute hydrochloric acid, and the solution then treated with a twofold excess of barium chloride, 2.00 ± 0.02 moles of sulfate precipitate were formed per mole of decomposed nitrosyl disulfonate ion. These experiments were carried out upon solutions which were initially approximately 0.1 VF in potassium nitrosyl disulfonate.

The above experiments can be interpreted to mean that when the products of the hydrolysis were not boiled with acid, 1.50 moles of sulfate were produced per mole of decomposed salt, whereas, in the case of boiling with acid, the hydroxylamine monosulfonate ion formed in the decomposition reaction is further hydrolyzed forming hydroxylammonium and sulfate ions. The somewhat high value of 1.60 obtained in the first group of experiments may be said to be due to the coprecipitation of appreciable quantities of barium hydroxylamine monosulfonate.

Thus the stoichiometry of the decomposition of nitrosyl disulfonate ion in dilute acid solutions may be represented by the following three gross steps:

$$4\ ON(SO_3)_2^= + 3\ H_2O = N_2O + 2\ HON(SO_3)_2^= + 4\ SO_4^= + 4\ H^+ \qquad (1)$$

$$HON(SO_3)_2^= + H_2O = HONHSO_3^- + SO_4^= + H^+ \qquad (2)$$

$$HONHSO_3^- + H_2O = HONH_3^+ + SO_4^= \,. \qquad (4)$$

Reaction (2) was studied in detail by Naiditch and Yost(10), and further, these workers found that reaction (4) took place only in hot acid solutions.

That nitrosyl disulfonic acid is a strong acid was proved by the following experiment: The electrodes of a pH meter were immersed in 50 ml. of a freshly prepared 0.10 VF solution of potassium nitrosyl disulfonate. The pH of this solution was measured at intervals as one milliliter portions of 0.0100 VF perchloric acid were successively added. The pH of the solution decreased rapidly upon the addition of the first few portions of acid, and then decreased more slowly as more acid was added.

At no point in the curve of pH vs. milliliters of acid added was there any suggestion of an inflection point. The pH of the solution before the addition of any acid was 8.0. This is not to be taken to suggest that nitrosyl disulfonic acid is a weak acid; rather one would expect a small amount of basic impurity because the potassium nitrosyl disulfonate was recrystallized from potassium hydroxide solution. In fact, the pH value obtained indicates an impurity of potassium hydroxide on the order of only one part per million.

No complete investigation of the kinetics of the autocatalytic decomposition of nitrosyl disulfonate ion in acid solutions was carried out because after the stoichiometry of the reaction had been determined and some of the physical and chemical properties of solutions of that ion had been investigated, the author's attention was drawn to the thesis of J. Hamoodi Murib in which the kinetics of the decomposition reaction had been worked out(17).

The Reaction between Nitrosyl Disulfonate and Hydroxylamine Disulfonate Ions:

The first experiments carried out in order to establish the mechanism of the autocatalytic decomposition of nitrosyl disulfonate ion were measurements of the rate of reaction between nitrosyl disulfonate and hydroxylamine disulfonate ions. Freshly prepared anhydrous potassium hydroxylamine disulfonate was weighed into a one liter volumetric flask, and redistilled water was added to the mark. Approximately seventy milligrams of potassium nitrosyl disulfonate were dissolved in one liter of redistilled water. The water and vessels for these solutions had been thermostated at 30°C., and the solutions were placed in the thermostat. Samples of these two solutions were pipetted into a thermostated solution containing sodium perchlorate and perchloric acid in such concentrations that the conditions after the addition of the samples were as follows: Hydrogen ion concentration, 2.00 or 4.45 x 10^{-3} VF; sodium perchlorate concentration, 1.00 VF; potassium hydroxylamine disulfonate concentration, 10.9 or 2.60 x 10^{-4} VF; potassium nitrosyl disulfonate concentration, 2.53 x 10^{-5} VF, (determined spectrophotometrically).

The mixed solution was placed in a ten centimeter cell, and the cell was placed in the spectrophotometer. Readings of the optical density of the solution were taken periodically. The data obtained were plotted in such a way that the concentration of nitrosyl disulfonate ion was represented as a function of time. The curves thus obtained were linear, within the limits of experimental error, up to the point where as much as sixty percent of nitrosyl disulfonate ion had disappeared. This indicated that the rate determining step in the reaction between nitrosyl disulfonate and hydroxylamine disulfonate ions did not involve nitrosyl disulfonate ion. Also, the rate of disappearance of nitrosyl disulfonate ion was equal, within a few percent, to twice the rate of hydrolysis of hydroxylamine disulfonate as found by Naiditch and Yost(10). Therefore, it seemed reasonable that the rate determining step in the reaction between nitrosyl disulfonate and hydroxylamine disulfonate ions was the hydrolysis of the hydroxylamine disulfonate ion, which in turn was followed by a relatively rapid reaction between the hydroxylamine monosulfonate ion produced and nitrosyl disulfonate ion.

It must be noted that in the experiments described in the above section, no particular precautions were taken to remove small traces of iron from the reaction mixtures.

The Reaction between Nitrosyl Disulfonate and Hydroxylamine Monosulfonate Ions:

It was of interest to investigate the kinetics of the reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions. The rate of disappearance of nitrosyl disulfonate ion was measured under the following conditions: Sodium perchlorate, 0.250 VF; perchloric acid in the range between 0.50 and 2.00 x 10^{-3} VF; sodium hydroxylamine monosulfonate in range between 1.2 and 5.0 x 10^{-4} VF; potassium nitrosyl disulfonate on the order of 2.5 x 10^{-5} VF. The concentrations of hydroxylamine monosulfonate ion and of hydrogen ion were varied independently in the hope of determining the dependence of the rate of disappearance of nitrosyl disulfonate ion upon these two variables.

However, two facts came to light in this part of the investigation. First, the rate of disappearance of nitrosyl disulfonate ion did not depend on its concentration as indicated by the fact that plots of concentration of nitrosyl disulfonate ion vs. time had the same linear character as those in the case of the reaction between nitrosyl disulfonate ion and hydroxylamine disulfonate ion. Second, rates measured under as nearly identical conditions as possible were highly irreproducible. These two facts indicated that the rate determining step in the reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions does not involve nitrosyl disulfonate ion.

Since the rate determining step in the reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions does not involve nitrosyl disulfonate ion, one must consider the reactions which hydroxylamine monosulfonate ion may undergo. That the rate determining step is not the hydrolysis of the monosulfonate ion is proved by the fact that the only known hydrolysis of this ion takes place slowly in hot, acid solutions(23). It is possible that the rate determining step might be a tautomeric change like that which takes place when hypophosphorous acid is oxidized. However, this mechanism is ruled out because of the irreproducibility of results obtained under nearly identical conditions. The last probable mechanism, which will be shown to account well for the observations, is that in which the hydroxylamine monosulfonate is oxidized by a small amount of a catalyst at a measurable rate, the reduced state of the catalyst, in turn, being rapidly oxidized by the nitrosyl disulfonate ion. The catalyst will be shown to be iron.

If a 0.1 VF solution of nitrosyl disulfonate ion is added to a just acid, 0.1 VF solution of ferrous ion, decoloration of the nitrosyl disulfonate ion takes place as rapidly as the solutions mix.

$$Fe^{++} + ON(SO_3)_2^{=} + H_2O \rightarrow Fe(OH)^{++} + HON(SO_3)_2^{=}. \qquad (5)$$

The products of the reaction are ferric ion and hydroxylamine disulfonate ion.

If a 0.1 VF solution of hydroxylamine monosulfonate ion is added to a solution 0.1 VF in ferric ammonium sulfate and 0.1 VF in perchloric acid, decoloration of the ferric color takes place within a minute or so, the reaction being:

$$4\ Fe(OH)^{++} + 2\ HONHSO_3^{-} = N_2O + 4\ Fe^{++} + 2\ HSO_4^{-} + 3\ H_2O. \quad (6)$$

Reaction (6) is quite similar to the reaction used for the quantitative volumetric determination of hydroxylamine(24).

It was suspected that the source of iron contamination in the above rate measurements was the 1.00 VF sodium perchlorate used to adjust the ionic strength. A liter of this solution was filtered through a sintered glass filter of fine porosity, and though there was no turbidity in the original solution, a small amount of blackish precipitate was detected. This precipitate dissolved in a few milliliters of 6 VF hydrochloric acid to give a yellowish solution, which in turn gave a markedly positive test for iron upon the addition of potassium thiocyanate.

A rate run was carried out under conditions like those described on page 29 with the exception that a small amount of acidified Versene Fe-3 Specific was added to the reaction mixture. The result was that the initial rate of disappearance of nitrosyl disulfonate ion was very nearly zero.

Another rate run was carried out under condtions like those described on page 29 with the exception that the reaction mixture was made approximately 1×10^{-6} VF in ferric iron. The nitrosyl disulfonate ion had disappeared before a measurement could be made.

These experiments show that indeed it was iron that catalyzed the reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions, and therefore, it remained to investigate systematically the dependence of the rate of reaction between these two ions upon the amount of iron present.

The rate of disappearance of nitrosyl disulfonate ion was measured under the following conditions: Perchloric acid concentration, between 2.5×10^{-4} and 2.5×10^{-3} VF; ferric perchlorate concentration, as high as 1.46×10^{-6} VF; sodium hydroxylamine monosulfonate concentration, between 1.03 and 4.59×10^{-5} VF; potassium nitrosyl disulfonate concentration, between 4.7 and 1.4×10^{-5} VF, (determined spectrophotometrically); various concentrations of potassium perchlorate and lanthanum perchlorate to adjust the ionic strength; and the thermostating temperature of the bath and the cell compartment, $20.00 \pm 0.03^{\circ}$C. or $30.00 \pm 0.03^{\circ}$C. In Table 1 are presented the time-concentration data for two typical experiments.

A discussion of the results obtained from rate runs carried out under the above conditions, and an interpretation of those results appear below.

TABLE 1

Representative Time-Concentration Data for Rate Measurements at 20°C.

Experiment No. 56

Initial Conditions

$(H^+) = 5.0 \times 10^{-4}$ <u>VF</u>

$(HONHSO_3^-) = 4.60 \times 10^{-5}$ <u>VF</u>

$(\Sigma\ Fe^{+3})_a = 1.4_6 \times 10^{-7}$ <u>VF</u>

$(KClO_4) = 2.50 \times 10^{-2}$ <u>VF</u>

$(ON(SO_3)_2^=) = 1.83 \times 10^{-5}$ <u>VF</u>

Experiment No. 88

Initial Conditions

$(H^+) = 5.0 \times 10^{-4}$ <u>VF</u>

$(HONHSO_3^-) = 4.58 \times 10^{-5}$ <u>VF</u>

$(\Sigma\ Fe^{+3})_a = 3.6_5 \times 10^{-7}$ <u>VF</u>

$(KClO_4) = 2.50 \times 10^{-2}$ <u>VF</u>

$(ON(SO_3)_2^=) = 2.21 \times 10^{-5}$ <u>VF</u>

time(min.)	$(ON(SO_3)_2^=) \times 10^5$ <u>VF</u>	time(min.)	$(ON(SO_3)_2^= \times 10^5$ <u>VF</u>
1.50	1.71	1.50	1.85
2.00	1.65	2.00	1.72
2.50	1.60	2.50	1.60
3.00	1.54	3.00	1.49
3.50	1.49	3.50	1.37
4.00	1.43	4.00	1.26
4.50	1.37	4.50	1.14
5.00	1.32	5.00	1.05
5.50	1.26	5.50	0.93
6.00	1.20	6.00	0.82

DISCUSSION

The Autocatalytic Decomposition of Nitrosyl Disulfonate Ion:

As has been mentioned, the kinetics of the autocatalytic decomposition of nitrosyl disulfonate has been investigated in some detail by Murib at the University of Washington(17). Murib carried out his measurements in buffered solutions, and thus during any rate run, the hydrogen ion concentration remained essentially constant. He fitted his data to the following equation:

$$x_c = Ne^{\phi t} \qquad (7)$$

where N and ϕ are independent of time and t is the time. The quantity x_c is determined as follows. The logarithm of the concentration of nitrosyl disulfonate ion is plotted as a function of time. In the early stages of the reaction this plot is linear, while at later stages it deviates considerably from linearity. The quantity x_c is the deviation from linearity. When the logarithm of x_c is plotted against time, a straight line is obtained. The slope of this line is ϕ, and the intercept N.

Murib interpreted the above facts to mean that two reactions take place simultaneously, a reaction first order with respect to nitrosyl disulfonate ion concentration, and a chain reaction.

Because the chain reaction is inhibited by amine monosulfonate ion, because of the rate of appearance of hydrogen ion as compared to the rate of disappearance of nitrosyl disulfonate ion, and because nitrous acid reacts rapidly with nitrosyl disulfonate, Murib concluded that the species responsible for the chain reaction is nitrous acid.

In any investigation of the kinetics of an autocatalytic reaction, the possibility of the final products of the reaction being responsible for the catalysis must be recognized. Murib did not study the reactions between nitrosyl disulfonate ion and hydroxylamine disulfonate ion or hydroxylamine monosulfonate ion.

The studies carried out in this laboratory on the reactions between nitrosyl disulfonate ion and hydroxylamine disulfonate ion and between nitrosyl disulfonate ion and hydroxylamine monosulfonate ion are described below. It should be stated here that in acid solution no measurable reaction takes place between either hydroxylamine disulfonate ion or hydroxylamine monosulfonate ion and nitrosyl disulfonate ion in the absence of iron. Iron is removed from reaction solutions by adding 10^{-5} equivalents per liter of Versene Fe-3 Specific.

That the iron catalyzed reactions between the hydroxylamine sulfonate ions and nitrosyl disulfonate ion play no part in the autocatalytic decomposition of the latter is proved by the following fact. If, while nitrosyl disulfonate ion alone is rapidly decomposing, one adds 10^{-5} equivalents per liter of Versene Fe-3 Specific at the same pH as the reaction mixture, there is no change in the course of the reaction.

For the above reasons, Murib's conclusions regarding the kinetics of the autocatalytic decomposition of nitrosyl disulfonate ion are not challenged, but rather are made less open to doubt.

The Reaction between Nitrosyl Disulfonate and Hydroxylamine Disulfonate Ions:

Rate measurements were carried out on reaction mixtures in which the ratio of the concentrations of nitrosyl disulfonate ion to hydroxylamine disulfonate ion was large. The hydroxylamine disulfonate ion concentration was about 1×10^{-3} VF. In these reaction mixtures, the hydrogen ion concentration was on the order of 10^{-3} VF and the ionic strength was one. The ionic strength was adjusted with 3 VF sodium perchlorate which, it was then later determined, contained about 10^{-6} moles per liter of iron.

When the nitrosyl disulfonate ion concentration was plotted against time, the curve was linear until at least half of that ion had disappeared. The slope of the linear portion of the curve corresponded to about 10^{-6} moles per liter of nitrosyl disulfonate decomposing per minute.

Since the curve of nitrosyl disulfonate ion concentration *vs.* time was linear, until half of that ion had decomposed, the rate determining step in the reaction could not involve that ion. Further the rate of disappearance of nitrosyl disulfonate depended linearly upon the concentrations of hydrogen and hydroxylamine disulfonate ions.

In one experiment, the initial conditions were as follows: Sodium perchlorate concentrations, 1.00 *VF*; perchloric acid concentration 4.45×10^{-3} *VF*; potassium hydroxylamine disulfonate concentration, 1.09×10^{-3} *VF*; potassium nitrosyl disulfonate concentration, 2.50×10^{-5} *VF*, (determined spectrophotometrically). The temperature was 30°C. Until half of the nitrosyl disulfonate ion had reacted, its rate of disappearance was 1.06×10^{-6} moles per liter per minute.

Now, if it is assumed that the rate determining step in the reaction between nitrosyl disulfonate and hydroxylamine disulfonate ions is the hydrolysis of the latter ion, at least qualitative agreement would be expected between the rate of disappearance of nitrosyl disulfonate ion and the rate of hydrolysis of hydroxylamine disulfonate ion. Naiditch and Yost(10) in their investigation of the kinetics of the hydrolysis of hydroxylamine disulfonate ion,

$$HON(SO_3)_2^{=} + H_2O \rightarrow HONHSO_3^{-} + HSO_4^{-} , \qquad (2)$$

did not work with ionic strengths as great as one. However, if their values of the rate constant at various ionic strengths are extrapolated to unit ionic strength, the value obtained for the rate constant, k, is about 0.10 lt.$\cdot$mole$^{-1}\cdot$min.$^{-1}$ at 30°C.:

$$-\frac{d(HON(SO_3)_2^=)}{dt} = k(H^+)\ (HON(SO_3)_2^=) \qquad (8)$$

The extrapolated value is only qualitative since extrapolations to ionic strengths on the order of unity from ionic strengths on the order of one tenth may only be made on the basis of a smooth curve of k <u>vs</u>. $\sqrt{\mu}$, the square root of the ionic strength.

As will be shown later, nitrosyl disulfonate ion in acid solution reacts with hydroxylamine monosulfonate when small amounts of iron are present according to the equation:

$$4\ ON(SO_3)_2^= + 2\ HONHSO_3^- + H_2O = N_2O + 4\ HON(SO_3)_2^= + 2\ HSO_4^-. \qquad (9)$$

Therefore, in the case of the reaction between nitrosyl disulfonate and hydroxylamine disulfonate ions, the rate of disappearance of the former ion should be twice that of the latter, when, as in these experiments, small amounts of iron are present. Using the extrapolated value obtained for the k of equation (8), and the concentrations of hydrogen and hydroxylamine disulfonate ions, 4.45×10^{-3} and 1.09×10^{-3} VF, respectively, the calculated rate of decomposition of hydroxylamine disulfonate ion is 5×10^{-7} moles·lt.$^{-1}$·min.$^{-1}$. This value is very nearly half of the observed rate of disappearance of nitrosyl disulfonate ion, 10.6×10^{-7} moles·lt.$^{-1}$·min.$^{-1}$.

Versene Fe-3 Specific stops the reaction in acid solution between nitrosyl disulfonate and hydroxylamine monosulfonate ions by removing the catalyst, iron. No reaction takes place between hydroxylamine disulfonate and nitrosyl disulfonate ions in the presence of Versene Fe-3 Specific.

The above facts show that in acid solution and in the presence of small amounts of iron, the rate of the reaction between hydroxylamine disulfonate and nitrosyl disulfonate ions is determined by the rate of hydrolysis of the former ion. The hydroxylamine monosulfonate ion, formed by the hydrolysis, reacts relatively rapidly with nitrosyl disulfonate ion according to equation (9).

The Iron Catalyzed Reaction between Nitrosyl Disulfonate and Hydroxylamine Monosulfonate Ions:

When a preliminary investigation of the reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions was undertaken, it became evident that the reaction was catalyzed by iron. It was of interest to investigate this iron catalyzed reaction.

The dependence of the rate of disappearance of nitrosyl disulfonate ion upon hydrogen ion concentration, hydroxylamine monosulfonate ion concentration, nitrosyl disulfonate ion concentration, total iron concentration, ionic strength, and temperature was investigated.

In the majority of experiments, the initial rate of disappearance of nitrosyl disulfonate ion was measured. The value of the initial rate was determined by one of two methods. When the hydroxylamine monosulfonate ion concentration was greater than the nitrosyl disulfonate ion concentration the rate of disappearance was very nearly constant for the first three minutes of the reaction. Therefore, since spectrophotometric determinations of nitrosyl disulfonate ion concentration were made every half minute, the average amount decomposing in a half minute determined the rate. When the hydroxylamine monosulfonate concentration was not greater than the nitrosyl disulfonate ion concentration, a plot of concentration of nitrosyl disulfonate ion vs. time was constructed. The curve was extrapolated to zero time, and the slope at zero time was taken as the initial rate of the reaction. The symbol R denotes the initial rate of disappearance of nitrosyl disulfonate ion.

As long as the concentration of nitrosyl disulfonate ion was the same order of magnitude as that of hydroxylamine monosulfonate ion, the quantity R was independent of the former concentration. The first five and the twenty-sixth through the twenty-ninth entries in Table 2 demonstrate that independence.

The quantity R was found to be directly proportional to the initial hydroxylamine monosulfonate ion concentration. The initial concentration of that ion was determined by subtracting the amount of it oxidized according to equation (6) by the added ferric perchlorate from the amount added from the stock solution.

A new quantity R' is defined as R divided by the initial concentration of hydroxylamine monosulfonate ion.

The value of R' was determined for reaction mixtures of six different hydrogen ion concentrations, and four, or sometimes five, different total concentrations of added iron. The quantity $(\Sigma\ Fe^{+3})_a$ is defined as the total concentration of iron added, i.e., it is the formula weights of ferric perchlorate added per liter of reaction mixture, while $(\Sigma\ Fe^{+3})$ represents the total concentration of iron in the reaction mixture. The conditions under which the values of R' were obtained, and those values themselves are summarized in Table 2.

At each of the lower hydrogen ion concentrations, 2.5 and 5.0×10^{-4} VF, the values of R' are directly proportional to the total iron concentrations, as shown for the latter case in

TABLE 2

Values of R' at Various Concentrations of Reactants.
(Temperature 20°C.; Solutions 0.025 VF in $KClO_4$.)

	Initial Concentrations (VF)				
Experiment Number*	$(H^+) \times 10^3$	$(\Sigma Fe^{+3})_a \times 10^6$	$(HONHSO_3^-) \times 10^5$	$(ON(SO_3)_2^=) \times 10^5$	$R' \times 10^2$ (min.$^{-1}$)
1	2.45	1.46	1.08	2.68	14.2
2	2.45	1.46	1.08	3.41	14.5
3	2.45	1.46	1.08	3.04	14.2
4	2.45	1.46	2.21	2.55	14.0
5	2.45	1.46	2.21	3.10	14.2
40-43	2.45	0.73	1.15	3.42	9.5
9-12	2.45	0.73	2.27	1.88	9.2_4
13-16	2.45	0.36_5	2.28	2.96	5.12
36-39	2.45	0.36_5	4.58	3.78	5.04
17-19	2.45	0.14_6	2.30	1.93	2.32
28-31	2.45	0.14_6	4.60	2.88	2.26
20-23	2.45	0.00	2.31	1.42	0.24
194-195	1.94	1.46	2.21	3.94	15.0
192-193	1.94	0.73	2.27	4.14	9.7
184-187	1.94	0.36_5	4.58	3.32	5.44
180-183	1.94	0.14_6	4.60	2.07	2.30
188-191	1.94	0.00	4.61	3.43	0.24
162-163	1.55	1.46	2.21	3.31	15.6
160-161	1.55	0.73	2.27	3.37	10.5
168-171	1.55	0.36_5	4.58	2.80	5.76
164-167	1.55	0.14_6	4.60	2.07	2.36

TABLE 2 (cont'd)

Initial Concentrations (VF)

Experiment Number*	$(H^+) \times 10^3$	$(\Sigma\ Fe^{+3})_a \times 10^6$	$(HONHSO_3^-) \times 10^5$	$(ON(SO_3)_2^=) \times 10^5$	$R' \times 10^2$ $(min.^{-1})$
140-143	0.99	1.46	2.21	4.60	18.6
136-139	0.99	0.73	2.27	3.02	10.3
132-135	0.99	0.36_5	4.58	3.22	5.60
44-51	0.99	0.14_6	4.60	2.06	2.44
96-98	0.50	1.46	2.21	4.65	18.6
99	0.50	1.46	2.21	4.02	18.5
116-119	0.50	0.73	2.27	1.82	9.8
92-95	0.50	0.73	2.27	2.52	9.8
88-91	0.50	0.36_5	4.58	2.21	5.12
56-59	0.50	0.14_6	4.60	1.83	2.44
100-103	0.50	0.00	4.61	3.14	0.48
128-131	0.25	1.46	2.21	2.82	17.7
120-123	0.25	0.73	2.27	2.07	9.4
112-115	0.25	0.36_5	4.58	1.82	4.96
104-111	0.25	0.14_6	4.60	2.34	2.58

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* Where a series of experiments is indicated, the initial conditions were the same for the series, and the value of R' is the average for the series.

Figure 2. At higher hydrogen ion concentrations, plots of R' vs. $(\Sigma\ Fe^{+3})_a$ are not linear. At low total iron concentrations the plot is nearly linear, but at higher total iron concentrations it deviates considerably from linearity. An example of this behavior is shown in Figure 3. At these higher hydrogen ion concentrations, the slope of the curve of R' vs. $(\Sigma\ Fe^{+3})_a$ is measured at $(\Sigma\ Fe^{+3})_a$ equal to zero. This slope is defined to be equal to k_o. In the case of the linear plots of R' vs. $(\Sigma\ Fe^{+3})_a$, obtained at the lower hydrogen ion concentrations, the slope of the line is k_o.

The intercept of the extrapolated curve of R' vs. $(\Sigma\ Fe^{+3})_a$ on the ordinate axis is numerically equal to the amount of iron present in the reagents. That amount was, on the average, 3×10^{-8} VF.

That the rate determining step in the iron catalyzed reaction between nitrosyl disulfonate ion and hydroxylamine monosulfonate ion is the reaction between iron (III) and hydroxylamine monosulfonate ion is proved by the following facts. The rate is independent of nitrosyl disulfonate ion concentration. It is directly proportional to hydroxylamine monosulfonate ion concentration. And at small concentrations of added iron, it is directly proportional to those concentrations. Thus at a given hydrogen ion concentration, temperature, and ionic strength, and at total iron concentrations less than 3.5×10^{-7} VF, the rate of disappearance of nitrosyl disulfonate ion is well represented by the equation:

$$-\frac{d(ON(SO_3)_2^{=})}{dt} = k_o(\sum Fe^{+3})\ (HONHSO_3^-)\ . \qquad (10)$$

The dependence of k_o in equation (10) upon hydrogen ion concentration, shown graphically in Figure 4, indicates that predominantly one of the hydrolyzed species of ferric iron is responsible for the catalysis. Since k_o has a maximum value at a pH value of about three, $Fe(OH)^{++}$ must be the principal catalytic species.

The problem of the dependence of k_o upon hydrogen ion concentration may be treated mathematically in the following way: Let the three species Fe^{+3}, $Fe(OH)^{+2}$, and $Fe(OH)_2^+$ react with hydroxylamine monosulfonate ion with specific rate constants k_1, k_2, and k_3, respectively. Further let h_1 and h_2 be the equilibrium constants, respectively, for the two reactions:

$$Fe^{+3} + H_2O = Fe(OH)^{+2} + H^+ \qquad (11)$$

and

$$Fe(OH)^{+2} + H_2O = Fe(OH)_2^+ + H^+\ . \qquad (12)$$

Under the conditions of these experiments,

$$(\Sigma\ Fe^{+3}) = (Fe^{+++}) + (Fe(OH)^{+2}) + (Fe(OH)_2^+) \ . \qquad (13)$$

Making use of the equilibrium constants, and assuming that enough acid is present so that the hydrolysis of the iron does not change the hydrogen ion concentration significantly, the following are obtained for the concentrations of the various iron (III) species:

$$(Fe^{+3}) = \frac{(H^+)^2\ (\Sigma\ Fe^{+3})}{(H^+)^2 + h_1(H^+) + h_1h_2} \qquad (14)$$

$$(Fe(OH)^{+2}) = \frac{h_1(H^+)\ (\Sigma\ Fe^{+3})}{(H^+)^2 + h_1(H^+) + h_1h_2} \qquad (15)$$

$$(Fe(OH)_2^+) = \frac{h_1h_2(\Sigma\ Fe^{+3})}{(H^+)^2 + h_1(H^+) + h_1h_2} \ . \qquad (16)$$

As shown above, the rate determining step in the iron catalyzed reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions is the reaction between the various iron (III) species and hydroxylamine monosulfonate ion. Also, according to the stoichiometry of the over all reaction (equation (9)), two moles of nitrosyl disulfonate ion are reduced per mole of the monosulfonate reacting with iron (III). Therefore, the rate of disappearance of nitrosyl disulfonate ion will be twice the rate of reaction between iron (III) and hydroxylamine monosulfonate ion, and

$$\frac{1}{2}\, k_o(\Sigma\, Fe^{+3}) = k_1(Fe^{+3}) + k_2(Fe(OH)^{+2}) + k_3(Fe(OH)_2^{+}) \ . \quad (17)$$

By substituting equations (14), (15), and (16) into equation (17), and simplifying, k_o is related to the hydrogen ion concentrations by the following expression:

$$\frac{1}{2}\, k_o = \frac{k_1(H^+)^2 + k_2h_1(H^+) + k_3h_1h_2}{(H^+)^2 + h_1(H^+) + h_1h_2} \ . \qquad (18)$$

If it is assumed that both k_1 and k_3 are zero, k_o will have a maximum value when (H^+) is equal to $\sqrt{h_1h_2}$. The maximum value of k_o occurs when (H^+) equals 1.5×10^{-3} <u>VF</u>. Although there is general disagreement about the value of h_1 (25), a value of about 3×10^{-3} is reasonable for a temperature of 20°C., and an ionic strength of 0.025. Therefore, if k_1 and k_3 are zero, h_2 has the value, 7×10^{-4}.

Using the values determined above for h_1 and h_2, and the experimental values of k_o, a series of values of k_2 at various hydrogen ion concentrations may be calculated. These values are shown in the third columnof Table 3.

The fourth, fifth and sixth columns of Table 3 show the effect of assuming that $Fe(OH)_2^+$ enters into the catalysis to a significant extent. That $Fe(OH)_2^+$ does enter into the catalysis to a significant extent is indicated first by the variation in the values of k_2 at low hydrogen ion concentrations when k_3 is assumed to be equal to zero, and second by the constancy of the values of k_2 when a small but measurable value of k_3 is assumed. The most nearly constant values of k_2 are obtained if a value of $1.5 \pm 0.2 \times 10^4$ lt.•mole^{-1}•min.$^{-1}$ is assumed for k_3. The average value of k_2 is then $13.9 \pm 1.4 \times 10^4$ lt.•mole^{-1} •min.$^{-1}$. Thus k_3 is only one tenth as large as k_2.

The values of k_2 and k_3 obtained by the above calculations depend critically upon the value chosen for h_1. The value chosen for h_1 is taken from the work of Siddall and Vosburgh(25), and is the most recent value available. However, since there does exist disagreement about the value for h_1, the values of k_2 and k_3 must remain tentative. Further, in an equation with as many parameters as equation (18), it is difficult to determine some of those parameters accurately.

The choice of a value other than zero for the constant k_3, would be expected to change the value obtained for h_1h_2, and, therefore, change the value of k_2. However, when k_3 is

TABLE 3

Evaluation of the Rate Constants, k_2 and k_3.

$(H^+) \times 10^3$ <u>VF</u>	$k_o \times 10^{-4}$ *	$k_2 \times 10^{-4}$ $(k_3 = 0)$	$k_2 \times 10^{-4}$ $(k_3 = 1 \times 10^4)$	$k_2 \times 10^{-4}$ $(k_3 = 1.5 \times 10^4)$	$k_2 \times 10^{-4}$ $(k_3 = 2 \times 10^4)$
0.25	11.0	20.5	16.5	14.5	12.5
0.50	12.4	15.5	13.5	12.5	11.5
0.99	14.4	14.4	13.4	12.9	12.4
1.54	15.2	14.9	14.2	13.9	13.6
1.94	14.6	15.6	15.1	14.9	14.6
2.54	13.4	15.0	14.6	14.4	14.2

---

* The units of the rate constants k_o, k_2, and k_3 are $lt.\cdot mole^{-1}\cdot min.^{-1}$.

not zero the maximum of k_o occurs at

$$(H^+) = \sqrt{\frac{k_3^2\, h_2^2}{k_2^2} + \frac{h_1 h_2}{k_2}\,(k_2 - k_3)} - \frac{k_3 h_2}{k_2}\,. \qquad (19)$$

Using the values determined above for k_2, k_3, h_1, and h_2, k_o will have a maximum value when the hydrogen ion concentration is 1.4×10^{-3} <u>VF</u> which agrees with the experimental value, within the limits of experimental error.

The following mechanism is in accord with the experimental data:

$$Fe(OH)^{+2} + HONHSO_3^- \xrightarrow{k_2} \text{reactive products} + Fe^{+2} \qquad (20)$$

$$Fe(OH)_2^+ + HONHSO_3^- \xrightarrow{k_3} \text{reactive products} + Fe^{+2} \qquad (21)$$

$$\text{reactive products} + ON(SO_3)_2^= \rightarrow N_2O + HON(SO_3)_2^= \qquad (22)$$

$$\text{reactive products} + Fe(III) \rightarrow N_2O + Fe^{+2} \qquad (23)$$

$$Fe^{+2} + H_2O + ON(SO_3)_2^= \rightarrow Fe(OH)^{+2} + HON(SO_3)_2^= \,. \qquad (24)$$

Equation (23) summarizes the reactions which may take place between the various species of iron (III) and the reactive products of the initial oxidation of hydroxylamine monosulfonate ion. The reactions represented by equations (24) and either (22), (23), or both must be fast compared to those represented by equations (20) and (21). The rate of reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions in acid solutions, at total iron concentrations less than 3.5×10^{-7} VF, and at constant temperature and ionic strength is represented by the equation:

$$-\frac{d(ON(SO_3)_2^{=})}{dt} = 2 \left\{ \frac{k_2 h_1 (H^+) + k_3 h_1 h_2}{(H^+)^2 + h_1 (H^+) + h_1 h_2} \right\} (\Sigma\, Fe^{+3})(HONHSO_3^-). \tag{25}$$

There is at present no certain explanation of the curvature of the plots of R' vs. $(\Sigma\, Fe^{+3})_a$ for values of $(\Sigma\, Fe^{+3})_a$ greater than 3.5×10^{-7} VF. The curvature is not due to any slowness of the reaction between ferrous ion and nitrosyl disulfonate ion because the rate of the disappearance of the latter ion is independent of its own concentration. Also the curvature is not due to complex formation between iron (III) species and hydroxylamine monosulfonate ion because the values of R' were independent of the concentration of the latter ion. The curvature would seem to be due to the removal of ferric ion, Fe^{+3}, because the curvature increases with increasing hydrogen ion concentration, and indeed, vanishes at low hydrogen ion concentrations.

The deviations from linearity of the plots of R' vs. $(\Sigma\ Fe^{+3})_a$ are, at a given hydrogen ion concentration, approximately proportional to $(\Sigma\ Fe^{+3})_a^2$. There are two ways by which this dependence of the deviations could be explained. The first, and least probable, is that a binuclear complex between ferric ion and one of the species present in the reaction mixture is formed. The second depends upon the fact that iron was added to the reaction mixtures as iron (III) which in turn reacted almost completely with the large excess of hydroxylamine monosulfonate ion before the solution containing nitrosyl disulfonate ion was added. Thus if an unreactive complex of the form Fe(III)X could form, and if X were a product of the reaction between hydroxylamine monosulfonate ion and iron (III), then at a given hydrogen ion concentration the amount of iron removed from the catalytic reaction would depend upon $(\Sigma\ Fe^{+3})_a^2$.

The effect of ionic strength upon the rate of the iron catalyzed reaction between nitrosyl disulfonate and hydroxylamine monosulfonate ions would be expected to be complex because of the nature of k_o. Further, there is disagreement about the quantitative effect of added "inert" electrolytes upon the hydrolysis of ferric ion(25,26) and upon ionic reactions in general(27). Therefore, the experimental results, summarized in Table 4, are useful primarily in determining the magnitude of any errors resulting from small changes in ionic strength. From the values shown, it is evident that a change in ionic strength of ten percent would cause at most a one percent change in the value of k_o.

On the basis of the data shown in Table 4, the following two qualitative statements may be made. First, a plot of log k_o vs. $\sqrt{\mu}$ for either of the two hydrogen ion concentrations has a slope of about minus one and one half, and therefore, changes in ionic strength effect the rate determining reactions more than the hydrolysis constants. Second, there is no change in the value of k_o if lanthanum perchlorate is substituted for potassium perchlorate to fix the ionic strength.

The effect of changes in temperature upon the rate of the iron catalyzed reaction between hydroxylamine monosulfonate and nitrosyl disulfonate ions would be expected to be complex again because of the nature of k_o. The effect of a ten degree change in temperature upon the values of k_o obtained at hydrogen ion concentrations of 1.94 and 0.50 x 10^{-3} VF, are shown in Table 5. Also, an apparent activation energy, ΔE_a, has been calculated by use of the equation:

TABLE 4

The Effect of Ionic Strength on k_o.

$(H^+) \times 10^3$ <u>VF</u>	$\mu \times 10^2$	$k_o \times 10^{-4}$ lt.·mole^{-1}·min.$^{-1}$
1.94	2.70 ($KClO_4$, 2.5×10^{-2} <u>VF</u>)	14.6
1.94	2.70 ($La(ClO_4)_3$, 4.17×10^{-3} <u>VF</u>)	14.4
1.94	0.20	13.7
0.50	2.55 ($KClO_4$, 2.5×10^{-2} <u>VF</u>)	12.5
0.50	2.55 ($La(ClO_4)_3$, 4.17×10^{-3} <u>VF</u>)	12.5
0.50	0.06	19.80

TABLE 5

The Effect of Temperature on k_o.

($KClO_4 = 2.5 \times 10^{-2}$ <u>VF</u>)

$(H^+) \times 10^3$ <u>VF</u>	t^o C.	$k_o \times 10^{-4}$ lt. mole^{-1} min.$^{-1}$	$\Delta E_a \left(= \frac{-R \, \Delta \log_\epsilon k_o}{\Delta \frac{1}{T}} \right)$
1.94	20.0	14.6	
1.94	30.0	48.6	21.4 kcal.
0.50	20.0	12.5	
0.50	30.0	41.7	21.4

$$\Delta E_a = \frac{-R\,\Delta \log_\epsilon k_o}{\Delta \frac{1}{T}}\,, \qquad (26)$$

where T is the absolute temperature and R the gas constant. That ΔE_a has the same value for the two hydrogen ion concentrations is quite probably fortuitous.

An approximate value of the activation energy of the reaction with specific rate constant k_2 may be calculated if the following assumptions are made. The reaction with specific rate constant k_3 has the same activation energy as that with specific rate constant k_2. The value of the constant h_2 changes with temperature in the same way as that of h_1. Making the above assumptions, and using the value 4.6 kcal.(25) for the ΔH of the first hydrolysis of ferric ion, the value calculated for the activation energy is 20.6 kcal.

An estimate of the possible error due to incomplete control of the temperature shows that a 0.08°C. error in temperature gives rise to an error of one percent in the value of k_o.

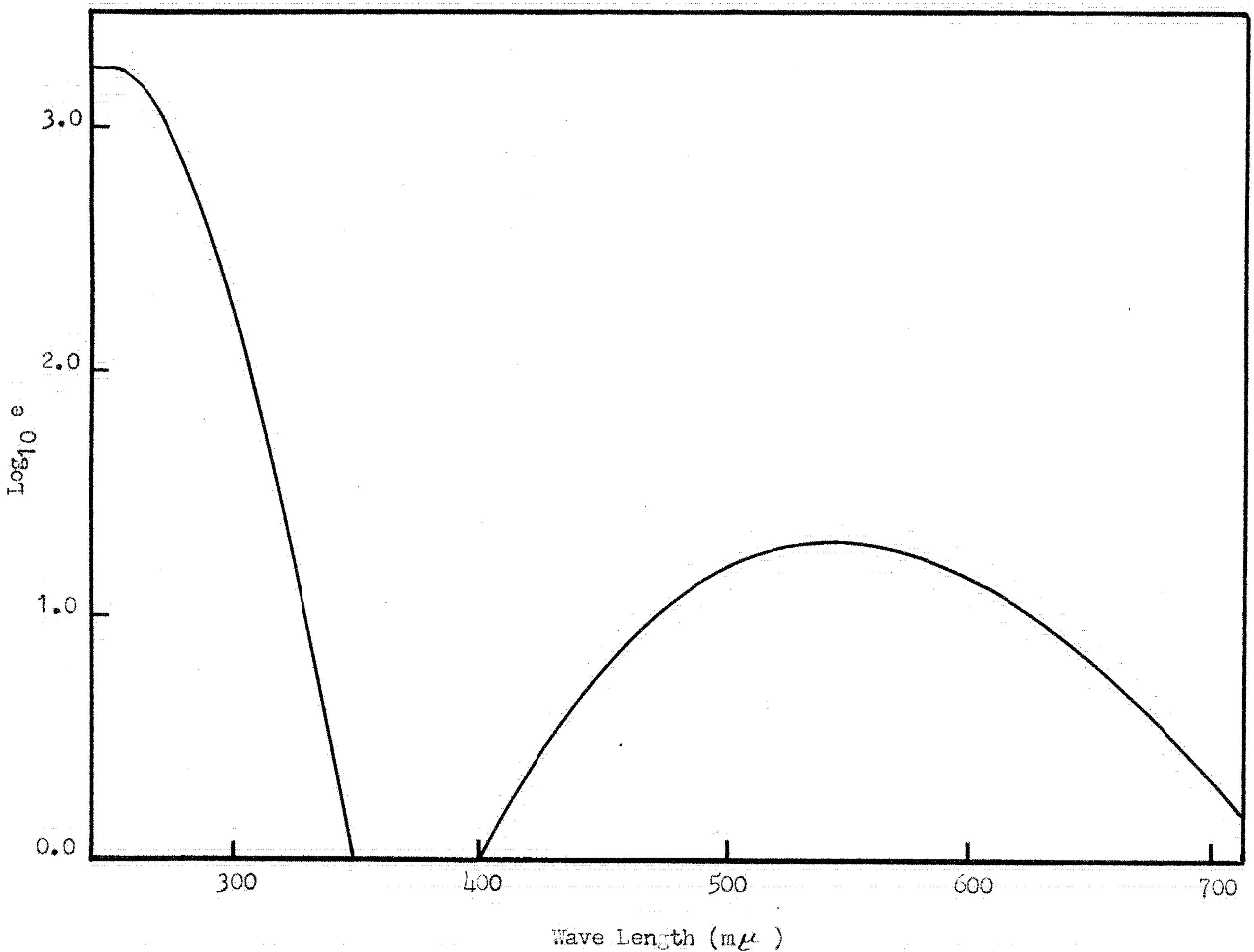

Figure 1: Logarithm of the Extinction Coefficient (lt.$\cdot$mole$^{-1}\cdot$cm.$^{-1}$) of Nitrosyl Disulfonate Ion *vs.* Wave Length (mμ).

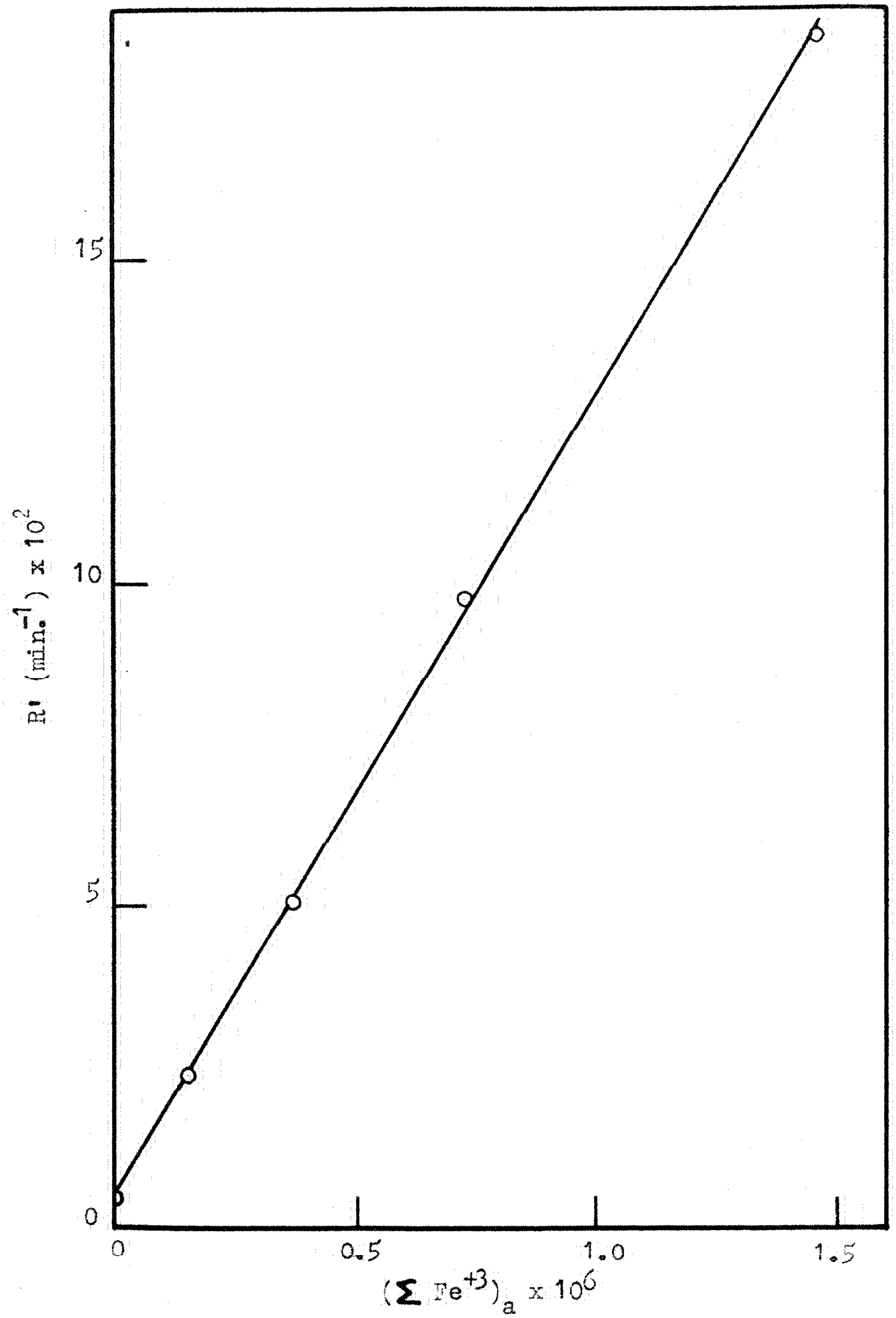

Figure 2: R' vs. $(\Sigma \mathrm{Fe}^{+3})_a$, slope equals k_o.
$((\mathrm{H}^+) = 0.50 \times 10^{-3}$ VF; $(\mathrm{KClO}_4) = 0.0250$ VF; t = 20°C.)

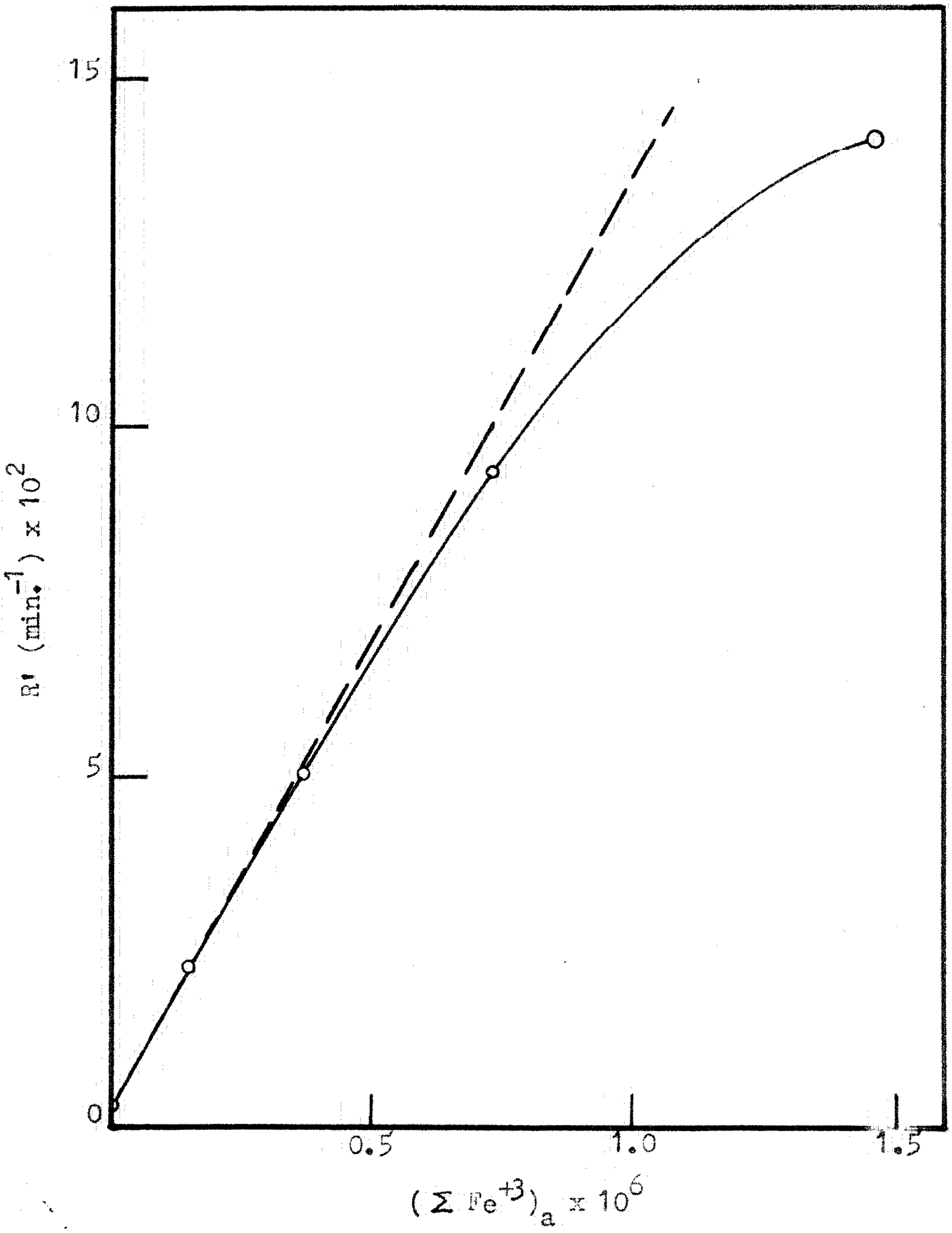

Figure 3: R' vs. (Σ Fe^{+3})$_a$, slope of dashed line equals k_o.
((H^+) = 2.54 x 10^{-3} VF; ($KClO_4$) = 0.0250; t = 20°C.)

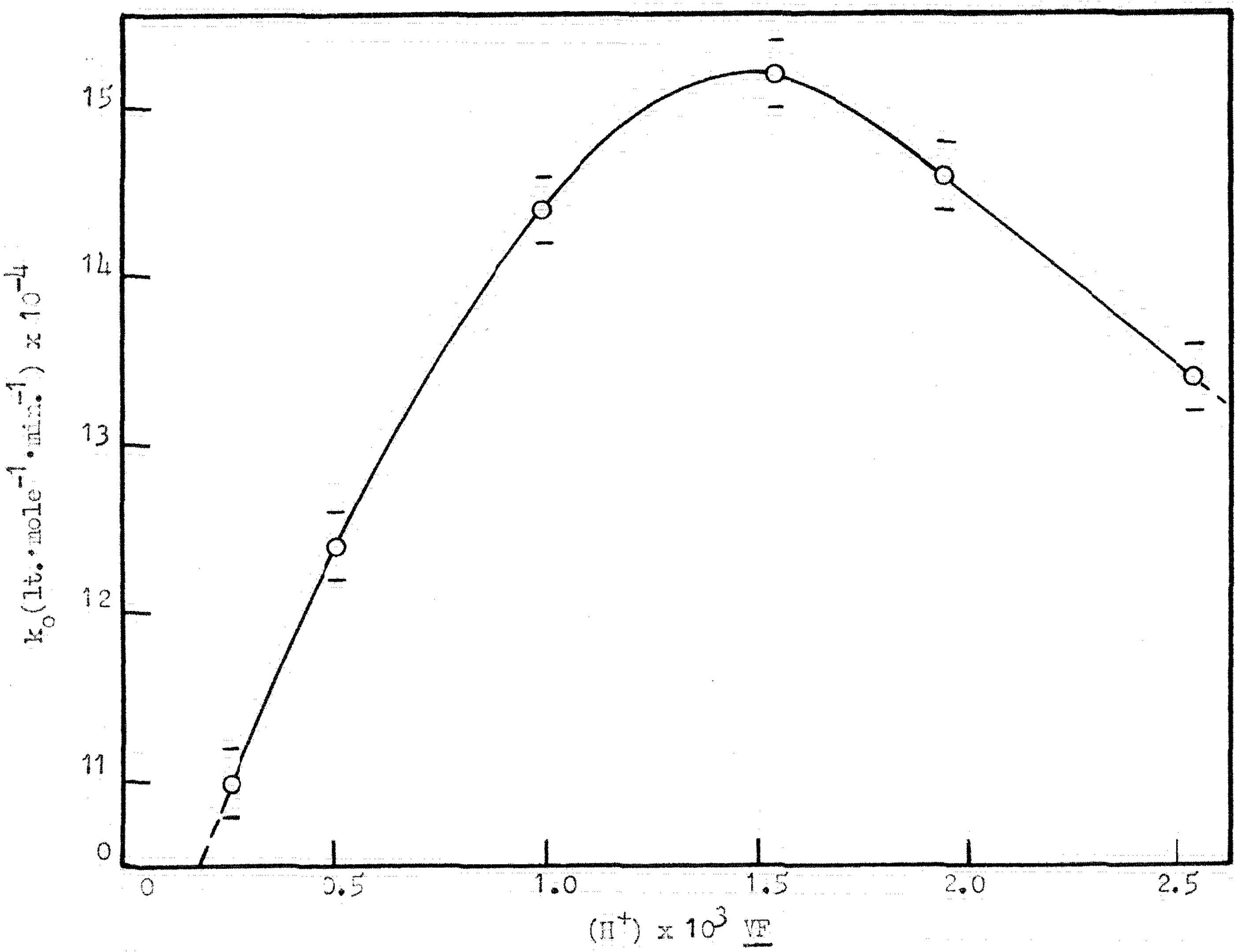

Figure 4: k_o vs. (H$^+$), bars above and below point are equivalent to ± 2% error in k_o.

((KClO$_4$) = 0.0250 VF; t = 20°C.)

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PROPOSITIONS

1. Nakatsuka and Kudo(1) claim to have prepared a stable compound of neodymium (IV) and 8-quinolinol. Work by Block, Bailer, and Pearce(2) on a compound claimed by Nakatsuka(3) to be one of silver (II) and 8-quinolinol showed it to be a compound of silver (I). An investigation of the magnetic properties of Nakatsuka's neodymium compound is recommended.

2a. The reaction between ferrous and nitrosyl disulfonate ions probably proceeds according to the equation,

$$Fe(OH_2)^{++} + ON(SO_3)_2^{=} \rightarrow Fe(OH)^{++} + HON(SO_3)_2^{=}.$$

Only the transfer of a hydrogen atom from one of the water molecules in the sphere of hydration of the ferrous ion to the nitrosyl disulfonate ion is involved.

b. If the reaction between nitrosyl disulfonate and ferrous ions is a second order one, the rate constant is greater than or equal to 2×10^6 lt.•mole^{-1}•min.$^{-1}$ at 20°C. and an ionic strength of 2.5×10^{-2}.

c. Using a fifty centimeter optical cell, concentrations of nitrosyl disulfonate ion on the order of 10^{-6} VF can be determined spectrophotometrically. Concentrations of ferrous iron on the order of 10^{-5} VF may be determined coulometrically. Therefore, an attempt should be made to measure the rate of reaction between nitrosyl disulfonate and ferrous ions at these low concentrations, at an ionic strength of one, and at 0°C.

3a. Qualitative measurements show that the rate of hydrolysis of iodine in basic solutions may be measured amperometrically(4). A quantitative investigation of the hydrolysis of iodine should be undertaken using coulometrically generated, and amperometrically determined, iodine.

b. The reaction between ammonia and iodine also may be investigated at low concentrations by the above method.

4. The "least squares" method of fitting a straight line to a group of data is sometimes used where a method of minimizing the absolute value of the relative error would be more sound.

If the group of data consists of values of y_i and their associated values of x_i, the values of m and b in the equation $y = mx + b$ which minimize the relative error in y are,

$$m = \frac{\sum_i \frac{x_i}{y_i} \sum_i \frac{1}{y_i^2} - \sum_i \frac{1}{y_i} \sum_i \frac{x_i}{y_i^2}}{\sum_i \frac{x_i^2}{y_i^2} \sum_i \frac{1}{y_i^2} - \left(\sum_i \frac{x_i}{y_i^2}\right)^2} ,$$

and

$$b = \frac{\sum_i \frac{x_i^2}{y_i^2} \sum_i \frac{1}{y_i} - \sum_i \frac{x_i}{y_i^2} \sum_i \frac{x_i}{y_i}}{\sum_i \frac{x_i^2}{y_i^2} \sum_i \frac{1}{y_i^2} - \left(\sum_i \frac{x_i}{y_i^2}\right)^2} .$$

5. H. S. Johnston(5) has proposed mechanisms for several reactions involving N_2O_5 which depend upon the equilibrium,

$$N_2O_5 \rightleftarrows NO_3 + NO_2 .$$

In demonstrating the validity of his mechanisms, an independently measured value of the equilibrium constant for that reaction would be desirable. I propose that such a value be obtained from paramagnetic resonance measurements.

6. The possibility of carrying out coulometric titrations in liquid ammonia should be investigated with particular attention to the possibility of determining metal ions.

7. Many proposals have been put forth for the production of pure water from ocean water by evaporation. I propose that an economical process would utilize a "heat pump"; pure water would be obtained in the forms of ice and steam.

8. There exists a class of autocatalytic reactions of the general type,

$$A + B \xrightarrow{k_1} C + \text{ unreactive products,}$$

$$A + B + C \xrightarrow{k_2} 2C + \text{ unreactive products.}$$

Such a reaction is the hydrolysis of hydroxylamine disulfonate ion$^{(6)}$, in which case A is water, B is hydroxylamine disulfonate ion, and C is hydrogen ion. If it is assumed that $(C)_o = 0$, $(A)_o k_2 \gg k_1$ and $(A)_o \gg (B)_o$, where the subscript, o, refers to initial concentrations, then,

$$\frac{(B)}{(B)_o} = \frac{1 + \dfrac{k_1}{(B)_o k_2}}{1 + \dfrac{k_1}{B_o k_2} e^{(A)_o (k_1 + (B)_o k_2) t}} .$$

The concentration of B at time t is represented by (B).

The rate constants, k_1 and k_2, can be determined in the following way: Two times, t_1 and t_2, are chosen such that t_1 is twice t_2. Let x_1 and x_2 be the values of $(B)/(B)_o$ at the times t_1 and t_2, respectively. The quantity, Q, is defined by the equation,

$$Q = \frac{1}{2(1 - x_2)^2 x_1} \left\{ (1 - x_1)x_2^2 - 2(1 - x_2)x_1 + \sqrt{\left[(1 - x_1)x_2^2 - 2(1 - x_2)\right]^2 - 4x_1(1 - x_2)^2(x_1 - x_2^2)} \right\}.$$

The value of k_1 is then determined by the relation,

$$k_1 = \frac{1}{(A)_o\ (1 + Q)\ t_1} \log_\epsilon \frac{Q(1 - x_1) + 1}{x_1},$$

or

$$k_1 = \frac{1}{(A)_o\ (1 + Q)\ t_2} \log_\epsilon \frac{Q(1 - x_2) + 1}{x_2}.$$

The value of k_2 is simply,

$$k_2 = \frac{Qk_1}{(B)_o}.$$

These kinetic equations are applicable to the hydrolysis of any compound which liberates hydrogen ion, which takes place in neutral solution, and which is catalyzed by hydrogen ion.

9. I propose that the kinetics of the reaction between nitrosyl disulfonate and iodide ions be investigated because the reaction is rapid in neutral or just acid solutions, because concentrations of the reactants on the order of 10^{-5} VF may be determined quantitatively by coulometric(7) and spectrophotometric means, and because the reaction is between two negatively charged ions. Therefore, a check on the conclusions of Olson and Simonson(8) concerning reaction between ions of like charge may be made.

10. Some inorganic preparations should be included in the second year chemistry course at this Institute.

11. I propose that an attempt be made to prepare a soluble salt of the acid $ON(SeO_3H)_2$, because this salt and its solutions might be even more beautiful than those of potassium nitrosyl disulfonate.

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