AN ABSTRACT OF THE THESIS OF

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Title: NUCLEOPHILIC SUBSTITUTION AT NITROGEN.

MECHANISMS AND INTERMEDIATES INVOLVED IN

SUBSTITUTION REACTIONS OF THE HYDROXYLAMINE-O-

SULFONATE ION.

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Abstract approved: _____
                        James H. Krueger
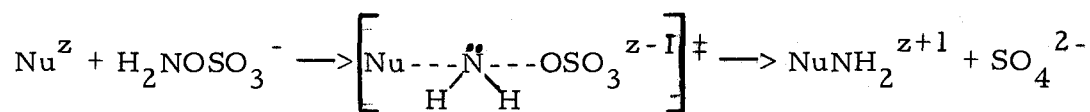
The kinetics of reactions between various nucleophiles and

hydroxylamine-O-sulfonate ion, $H_2NOSO_3^-$, have been studied

spectrophotometrically in water and in 50 wt % water-methanol. The

objective of the study was to make a quantitative evaluation of nucleo-

philic reactivity at the trivalent nitrogen center in $H_2NOSO_3^-$.

Reactions of the various nucleophiles (Nu) with $H_2NOSO_3^-$ show first-

order behavior in both reactants, leading to the general rate law

$-d[H_2NOSO_3^-]/dt = k_2[H_2NOSO_3^-][Nu^z]$. From the kinetic studies the

following results were obtained:

Nucleophile	k_2 $M^{-1}sec^{-1}$	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ eu	k_H/k_D	pH range
$(C_6H_5)_3P$	2.0 ± 0.1	7.4 ± 0.1	-32 ± 1	1.6 ± 0.1	$5-7$
I^-	0.069 ± 0.06	11.6 ± 0.3	-24.4 ± 1	1.3 ± 0.1	$3-8$
$S_2O_3^{2-}$	0.550 ± 0.015	10.8 ± 0.1	-22.8 ± 0.5	1.1 ± 0.05	$3-9$
$(H_2N)_2C=S$	1.63 ± 0.07	7.4 ± 0.2	-32.3 ± 1.5	1.1 ± 0.1	$3-11$

For the reactions of $(C_6H_5)_3P$, $(H_2N)_2C=S$, and I^-, the second-order

rate constants decrease below pH 3 and, in the case of Nu = I^-, it was

possible to obtain the rate constant for reaction with molecular

H_3NOSO_3, $k_{HOS} = 0.023 \ M^{-1}sec^{-1}$.

A general mechanism is proposed in which the nucleophile

attacks the nitrogen atom of $H_2NOSO_3^-$ in a typical S_N2 process.

$$Nu^z + H_2NOSO_3^- \longrightarrow \left[Nu\text{---}\overset{\cdot\cdot}{\underset{H^{\diagup} \diagdown H}{N}}\text{---}OSO_3^{z-1} \right]^{\ddagger} \longrightarrow NuNH_2^{z+1} + SO_4^{2-}$$

The mechanism is strongly supported by identification of an

$NuNH_2^{z+1}$ species, either as an intermediate, or as the product in

each of the reactions, except that involving iodide. Deuterium isotope

effect studies, steric effects, and the observed pH dependence strongly

suggest that nitrogen attack takes place in the iodide reaction as well.

The three $NuNH_2^{z+1}$ species detected are the well-known

$(C_6H_5)_3PNH_2^+$ ion, the previously reported $H_2NSSO_3^-$ ion, and the

novel cation, $(H_2N)_2CSNH_2^+$, isolated as the sulfate salt. Infra-red

spectra of the latter two are reported and the properties and several

reactions of $(H_2N)_2CSNH_2^+$ are described.

From the results, the trivalent nitrogen atom in hydroxyl-amine-O-sulfonate ion is characterized as a fairly soft acid center in terms of the hard and soft acid and base (HSAB) principle. Polariz-ability and ease of oxidation of the nucleophile clearly are more important than proton basicity in determining reactivity of the nucleophile.

Attempts to study the reactions of N-methyl and N-benzoyl substituted hydroxylamine-O-sulfonate with the same nucleophiles are reported. Because the reactions are very slow, only qualitative results are reported.

Nucleophilic Substitution at Nitrogen.   Mechanisms and
Intermediates Involved in Substitution Reactions of
the Hydroxylamine-O-sulfonate Ion

by

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A Hélène et à Sophia.

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I. INTRODUCTION

Hydroxylamine-O-sulfonic acid, $H_3N^+OSO_3^-$, has been known

since the beginning of the century. Until the last 15 years, very little

had been done to study its properties. Since then, some work has

been done to try to understand its structure, its aminating properties,

and its stability in water. Reports of kinetic studies involving

hydroxylamine-O-sulfonic acid are rare and incomplete. It is the pur-

pose of this work to report the first detailed kinetic study of hydroxyl-

amine-O-sulfonic acid, in particular, kinetics of reactions where

hydroxylamine-O-sulfonic acid is used as an oxidizing agent.

Synthesis and Properties of Hydroxylamine-O-sulfonic Acid

Hydroxylamine-O-sulfonic acid can be prepared by two different

methods. In 1914, Sommer and Templin (1) reported that the reaction

between hydroxylammonium sulfate and fuming sulfuric acid at room

temperature gave a good yield of hydroxylamine-O-sulfonic acid. In

1925, Sommer and co-workers (2) obtained the same product by

replacing the fuming sulfuric acid with chlorosulfonic acid. The pro-

duct obtained by these methods is not 100% pure. Higher purity can

be achieved, as mentioned by Smith and co-workers (3), either by recrystallization from cold absolute ethanol, or by repetition of the chlorosulfonic acid treatment of the product, followed by addition of dry ether. The latter method gave better results and was used in this work after modification of the first step of the synthesis, as outlined in the Experimental Section.

Hydroxylamine-O-sulfonic acid is a white, hygroscopic solid and is soluble in water, methanol, and ethanol (3,4). In water it is a fairly strong acid. The ionization constants reported are 1.7×10^{-2} at 55-85° (5) and 3.3×10^{-2} at 45° (6). In the solid form, hydroxylamine-O-sulfonic acid is believed to exist as a zwitter-ion according to an x-ray study (7), an ir study (8), and also an nmr study (9). The hydroxylamine-O-sulfonic acid crystal structure, determined by Baenziger and co-workers (7) from the Weissenberg and precision single crystal x-ray diffraction pattern, shows four molecules of the acid arranged in one unit cell. Each molecule contains a distorted tetrahedron of four oxygen atoms at the corners around the central sulfur atom. The nitrogen atom is bonded to the oxygen atom farthest from the sulfur atom. It has not as yet been determined if hydroxylamine-O-sulfonic acid exists as a zwitter-ion, of the form shown below, in aqueous solution.
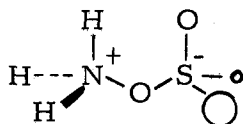
Syntheses Involving Hydroxylamine-O-sulfonic Acid

Over the years, hydroxylamine-O-sulfonic acid has been used

predominantly as an aminating agent for organic and inorganic com-

pounds. Direct aminations of aromatic compounds, using $AlCl_3$ as a

catalyst, have been reported (10). The reaction is described by Equa-

tion 1, where the interaction of hydroxylamine-O-sulfonic acid with

the catalyst is believed to occur according to Equation 2.

(1) $$ArH + H_2NOSO_3H \xrightarrow{AlCl_3} ArNH_2 + H_2SO_4$$

(2) $$H_2NOSO_3H + AlCl_3 \longrightarrow H_2NOSO_2OAlCl_2 + HCl$$
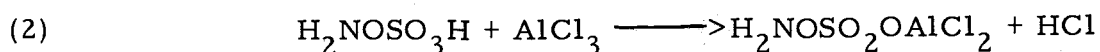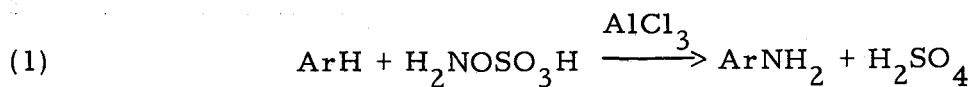
The formation of diimide, H_2N_2, _in situ_, has also been reported (11).

In basic solution, diimide is formed by the reaction of hydroxylamine

and hydroxylamine-O-sulfonic acid according to a proposed mechan-

ism indicated by Equations 3 and 4. Diimide thus formed is used as

(3) $$H_2NOH + H_2NOSO_3^- + OH^- \longrightarrow H_2NNHOH + SO_4^{2-} + H_2O$$

(4) $$H_2NNHOH \longrightarrow NH=NH + H_2O$$
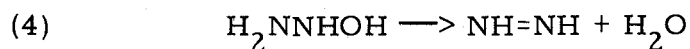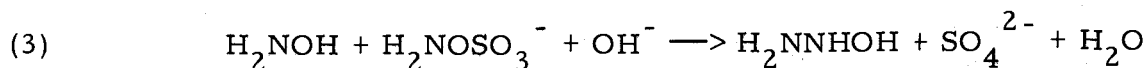
a hydrogenating agent with unsaturated hydrocarbons. Sisler and

co-workers (12) have used hydroxylamine-O-sulfonic acid to prepare

compounds similar to the compounds they obtained using chloramine

and substituted chloramine. Using R_2NCl, they were able to prepare

hydrazine derivatives according to Equation 5. Using hydroxylamine-O-sulfonic acid they were also able to prepare similar hydrazine derivatives according to Equation 6. They have shown that compounds containing P-N bonds could likewise be prepared according to Equations 6 and 7. Preparation of $(C_6H_5)_3PNH_2^+HSO_4^-$, as described by Equation 8, has been proposed independently by Appel and co-workers (13). The mechanisms proposed by Sisler and co-workers were not based on kinetic studies.

(5) $\qquad R_2NCl + R'NH_2 \longrightarrow R_2NNHR' + HCl$

(6) $\qquad (CH_3CH_2)_3N + H_2NOSO_3H \longrightarrow (CH_3CH_2)_3NNH_2^+HSO_4^-$

(7) $\qquad R_2NCl + Ar_3P \longrightarrow Ar_3P-NR_2^+Cl^-$

(8) $\qquad H_2NOSO_3H + (C_6H_5)_3P \longrightarrow (C_6H_5)_3P-NH_2^+HSO_4^-$
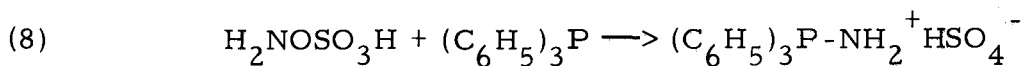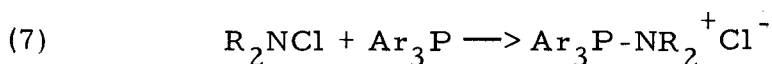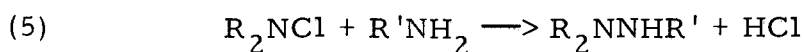
Recently, in our laboratories, hydroxylamine-O-sulfonic acid was used to prepare S-methyl-S-phenylsulfiminium perchlorate (14) according to the method of Appel and Büchner (15).

(9) $\qquad 2Me(Ph)S + 2H_2NOSO_3H + 2NaOCH_3 \xrightarrow[25°]{CH_3OH}$

$$[Me(Ph)SNH_2]SO_4 + Na_2SO_4 + 2CH_3OH$$

(10) $\qquad [Me(Ph)SNH_2]_2SO_4 + 2NaClO_4 \longrightarrow$

$$2[Me(Ph)SNH_2]ClO_4 + Na_2SO_4$$
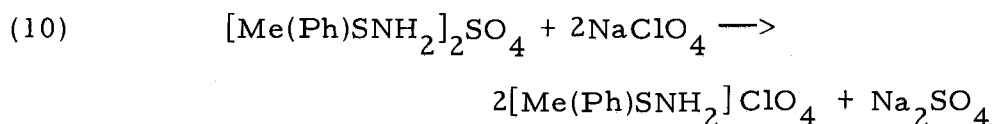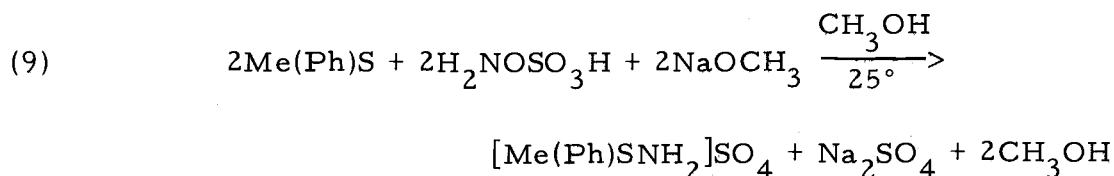
Many interesting reactions of hydroxylamine-O-sulfonic acid have been described in a paper by Wannagat (8) and also in a chapter of "Inorganic Sulfur Chemistry" (52).

Previous Kinetic Studies

Reports of kinetic studies involving hydroxylamine-O-sulfonic acid are not abundant. In 1959, Audrieth (5) was the first to report the stability of hydroxylamine-O-sulfonic acid in water. He found that the acid can decompose to yield hydroxylammonium ion in an acid-catalyzed reaction. He also observed that in basic solution, a self-oxidation-reduction reaction could occur to produce nitrogen and ammonia. In 1965 Candlin and Wilkins (6) reported the acid-catalyzed hydrolysis of hydroxylamine-O-sulfonic acid. The mechanism, described by Equations 11 and 12, is supported by $H_2^{18}O$ labeling experiments which show that S-O cleavage occurs.

$$(11) \qquad H_3N^+OSO_3^- + H^+ \xrightarrow{\text{slow}} NH_3OH^+ + SO_3$$

$$(12) \qquad SO_3 + H_2O \xrightarrow{\text{fast}} HSO_4^- + H^+$$
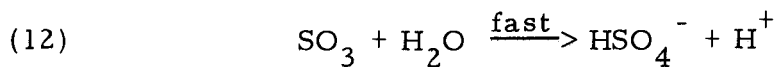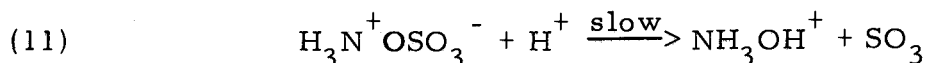
In more basic solutions, evidence of N-O cleavage was obtained with experiments in $H_2^{18}O$, implying that the reaction could take place by a mechanism described by the following equation.

(13) $$H_2{}^{18}O + H_2NOSO_3{}^- \longrightarrow H^{18}O-NH_2 + HSO_4{}^-$$
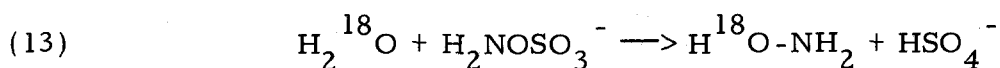
In 1964, Smith and co-workers (3) reported the simultaneous

hydrolysis and iodide-ion reduction of many hydroxylamine-O-sulfonic

acid derivatives of the form $R_1R_2NOSO_3H$. They found that the rate of

hydrolysis is more or less independent of the nature of R_1 and R_2.

Their study was done at pH < 1 using fairly high concentrations of the

acids. The mechanism proposed for the hydroxylamine-O-sulfonic

acid-iodide reaction, which involves attack on nitrogen by iodide, was

based on the following rate law derived from their kinetic data:

(14) $$\text{Rate} = k_a[H_2NOSO_3H][I^-]$$

More recently Durckheimer (11), in a very superficial study,

has proposed a mechanism for the reaction of hydroxylamine and

hydroxylamine-O-sulfonic acid in water. It is not clear that he was

justified in reaching his conclusion using the sparing kinetic data he

had gathered.

In our laboratories, Lee (16) has reported preliminary work on

the nucleophilic displacement reactions involving hydroxylamine-O-

sulfonic acid with triphenylphosphine and sodium thiosulfate in 50 wt %

methanol-water solution. The results will be discussed later.

Concurrently, in our laboratories, Sudbury (17) is studying

nucleophilic displacement reactions involving hydroxylamine-O-sulfonic

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acid with more basic nucleophiles. Solvent effects and leaving group

effects are also under investigation in the same work.

Purpose of the Work

Reactions at some inorganic centers, such as platinum in

Pt(II)-complexes, and oxygen in H_2O_2, have been studied extensively.

The numerous investigations of nucleophilic displacement involving

these molecules have brought about a good understanding of the

mechanisms involved. Furthermore, a good characterization of these

centers, according to the Hard and Soft Acids and Bases (HSAB)

principle, has been obtained. The HSAB principle is described below.

Studies involving nitrogen as an inorganic center are scarce,

except for a report on the hydrolysis of R_2NCl (18) and an interesting

study involving oxidation of several nucleophiles by HNF_2 (19). In the

latter report it was shown that the reactions were first-order in

difluoramine and first-order in each nucleophile. Nucleophilic sub-

stitution at nitrogen was proposed and, in the case of azide as the

nucleophile, direct evidence for attack on nitrogen was obtained. The

rate-determining step of the mechanism proposed is described by

Equation 15.

(15) $\quad Nu + HNF_2 \longrightarrow \left[Nu\text{---}\overset{\overset{H}{|}}{\underset{\underset{F}{|}}{N}}\text{---}F^- \right]^{\ddagger} \longrightarrow Nu\text{-}NHF + F^-$
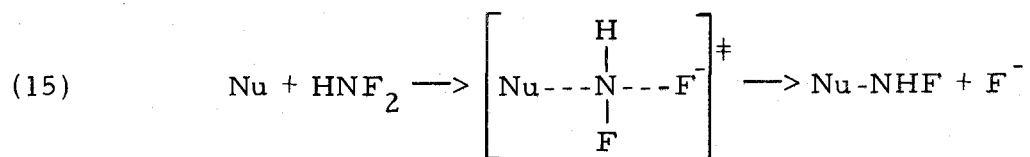
As can be seen, more work involving nitrogen as the center of attack should be done in order to better understand the mechanisms involved, and to characterize nitrogen according to the HSAB principle. Hydroxylamine-O-sulfonic acid is a useful molecule to study in order to achieve the goals outlined above. Primarily we were interested in studying nucleophilic displacement reactions involving hydroxylamine-O-sulfonate ion for the reason that three sites of attack are possible, as shown in 16.

(16)

$$H \underset{H}{\overset{}{\diagdown}} N - O - \overset{\overset{O}{|}}{\underset{\underset{O}{|}}{S}} - O^-$$

It can be seen that attack by a nucleophile is possible on sulfur, or oxygen, or nitrogen. S-attack can be ruled out as most unlikely, because of the steric hindrance created by the four oxygen atoms surrounding the sulfur atom. Attack on either oxygen or nitrogen is equally likely to occur under the right conditions. It appeared that the site of attack could be distinguished experimentally. If S_N2 attack occurs on the nitrogen, sulfate should be the leaving group as shown in Equation 17. On the other hand, if S_N2 attack occurs at the oxygen center, the bond broken could be either N-O or S-O, according to Equations 18 and 19.

(17) $$Nu + H_2NOSO_3^- \longrightarrow NuNH_2^+ + SO_4^{2-}$$

(18) $$Nu + H_2NOSO_3^- + H^+ \longrightarrow NuOSO_3 + NH_3$$

(19) $$Nu + H_2NOSO_3^- \longrightarrow NuONH_2^+ + SO_3^{2-}$$
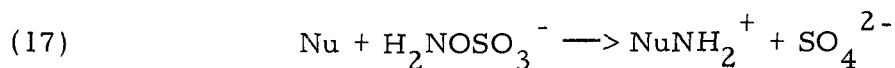
Simultaneous formation of a strong oxidizing agent and a strong reducing agent is very unlikely. This is what would happen if attack on the oxygen could occur giving an O-S breakage as shown in Equation 19. On the other hand, attack at the oxygen with N-O bond breakage could occur in a process that should be acid-dependent. NH_2^- is a very poor leaving group and has to be protonated in order to leave as NH_3. Having this idea in mind, it was decided to investigate the reactions of triphenylphosphine, potassium iodide, potassium thiosulfate, and thiourea in water and 50 wt % methanol-water solution with hydroxyl-amine-O-sulfonic acid and substituted hydroxylamine-O-sulfonic acid.

As will be seen in the Results and Discussion sections, good evidence that the reactions outlined above, occur exclusively via an S_N2 attack at nitrogen has been obtained. With the range of nucleophiles used in this study, it is our intention to characterize the nitrogen center according to the HSAB principle.

HSAB Principle

The HSAB principle states that soft nucleophiles will react faster with soft acid centers and that hard nucleophiles will react faster with hard acid centers. Many papers have described in detail

the HSAB principle (20, 21, 22). An understanding of what is meant by hard and soft will be sufficient to visualize the reasons why the HSAB principle was used in this work. S_N2 reactions can be thought of as being Lewis acid-base reactions. The nucleophile, being a Lewis base, leads one to expect that the more basic the nucleophile, the faster the reaction would occur. Some nucleophiles react at an appreciable rate, even if their proton basicity is very low. Polarizability is used in such cases to explain the reactivity. A molecule is said to be polarizable when empty, low-energy orbitals are available as the molecule is undergoing reaction. Basic nucleophiles are qualified as hard because in general, they lack low-energy empty orbitals, are highly electronegative, are difficult to oxidize, and their charge-size ratios are high. On the other hand, polarizable nucleophiles are qualified as soft because they have available, low-energy orbitals, undergo oxidation easily, have low electronegativities and have a low charge-size ratio. It is our intention to use these principles in trying to characterize nitrogen according to the HSAB principle which has been derived from the results of many kinetic studies like ours.

II. EXPERIMENTAL

Reagents

Hydroxylamine-O-sulfonic acid was prepared by the reaction of

chlorosulfonic acid with hydroxylammonium sulfate. The method used

was a modification of one first used by Sommer and co-workers (2).

After 25 ml of chlorosulfonic acid (Matheson, Coleman, and Bell,

99+ %) were added slowly to 13 g of hydroxylammonium sulfate

(Matheson, Coleman, and Bell, iron free), the resulting mixture was

heated to 100° for 5 minutes and then stirred vigorously until a homo-

geneous suspension was obtained. Usually, all the lumps of hydroxyl-

ammonium sulfate disappeared within one-half hour. After the sus-

pension was cooled using ice, 500 ml of anhydrous ether were added

slowly and a white precipitate was obtained. The precipitate was

washed with 1 liter of anhydrous ether and filtered, using a sintered

glass funnel. The precipitate was dried under vacuum and stored in a

desiccator over P_2O_5. Using this procedure, the hydroxylamine-O-

sulfonic acid obtained had a purity of 96-98% without further treatment

with chlorosulfonic acid or recrystallization. Periodic purity checks

showed that hydroxylamine-O-sulfonic acid, prepared by this method,

remained suitable for kinetic study (>94%) for a period of 3-6 months,

depending on the ambient temperature.

The purity of the hydroxylamine-O-sulfonic acid was determined

by an iodometric method. To a large excess of potassium iodide dis-

solved in a minimum amount of water, a weighed sample of hydroxyl-

amine-O-sulfonic acid (0.025 g) and 25 ml of 1 M sulfuric acid were

added. The iodine produced was immediately titrated using standard-

ized sodium thiosulfate. A blank was used to correct for air oxidation.

Identical results were obtained using glacial acetic acid or an acetate

buffer instead of the sulfuric acid.

The preparation of N-methylhydroxylamine-O-sulfonic acid was

similar to the preparation of hydroxylamine-O-sulfonic acid. The

N-methylhydroxylamine hydrochloride (Aldrich, 98%) had a yellow

coloration and a characteristic odor. It was dissolved in a minimum

amount of methanol and the solution was treated with activated char-

coal until a colorless solution was obtained. The N-methylhydroxyl-

amine hydrochloride was then precipitated using an excess of anhy-

drous ether. After filtration, the precipitate was dried under vacuum

over phosphorus pentoxide. In a typical synthesis, 25 ml of chlorosul-

fonic acid were added to 10 g of recrystallized N-methylhydroxylamine

hydrochloride.

Because the reaction of N-methylhydroxylamine-O-sulfonic acid

with iodide ion is very slow, an iodometric method could not be used

to check the purity of the compound. Instead, the purity of the

N-methylhydroxylamine-O-sulfonic acid was determined by titration

with standardized sodium hydroxide to find its equivalent weight. A

weighed sample of N-methylhydroxylamine-O-sulfonic acid (0.05 g) was titrated using methyl red as the indicator. The equivalent weight of N-methylhydroxylamine-O-sulfonic acid is 127. The titration of our sample gave values in the range 123-125. Elemental analysis, which was performed by Galbraith Laboratories, Knoxville, Tenn., gave the following results for CH_3NHOSO_3H. Calculated: C, 9.45; H, 3.95; S, 25.2. Found: C, 9.36; H, 4.09; S, 25.5.

Pyridinium N-benzoylhydroxylamine-O-sulfonate was prepared by the reaction of benzohydroxamic acid (Aldrich) with pyridine-sulfur trioxide (23) according to the procedure of Daniher (24). The melting point of this product was 140-142°. The value given by Daniher is 140-141°.

Triphenylphosphine (Matheson, Coleman, and Bell reagent) was dissolved in hot cyclohexane or in hot octane. Any undissolved impurities were filtered from the hot solution, which was then slowly evaporated until the first crystal of triphenylphosphine appeared. The solution was cooled in ice water and the solid was filtered and washed with water. The crystals were powdered and dried under vacuum over P_2O_5 for 24 hours. The melting point of triphenylphosphine was 80.0-80.6°. The literature value is 80.0° (25).

A special technique was used to dissolve triphenylphosphine in 50 wt % methanol-water. The amount needed was dissolved with reagent grade methanol in a 50 ml volumetric flask. A 5 ml aliquot

was pipetted into a 50 ml volumetric flask to which 20 ml of reagent grade methanol had already been added. With stirring, 19.8 ml of water were added from a 50 ml buret. The dilution was completed using 50 wt % methanol-water.

Potassium iodide (B & A reagent) and potassium thiosulfate (B & A reagent) were powdered, and dried at 110° for 2-4 hours before use in the kinetic experiments.

Thiourea (Matheson, Coleman, and Bell reagent) was dissolved in a minimum amount of boiling water, any undissolved impurities filtered off, and the water slowly evaporated until the first crystal of thiourea appeared. Then the solution was cooled in ice water. Thiourea was filtered, powdered, and dried at 110° for 24 hours before use in the kinetic experiments.

The chemicals used for buffer solutions were reagent grade. They were powdered, and dried at 110° for 24 hours before use in the kinetic experiments. The chemicals used as buffers were the following: potassium hydrogen phthalate, potassium acetate, sodium acetate, potassium hydrogen phosphate, sodium hydrogen phosphate, potassium dihydrogen phosphate, sodium dihydrogen phosphate, boric acid, tris(hydroxymethyl)aminomethane also known as THAM (Fisher Certified), perchloric acid (Mallinckrodt 70% Analytical reagent), and sodium hydroxide standard volumetric solution (Anachemia Chemicals Ltd). The concentrations of the salts and the concentrations of

perchloric acid, used in making the buffers, were at least 10^{-2} M

in all the reactions studied, except in the iodide study where, the

concentrations used were 10^{-3} M. In order to calculate the pH at

μ = 0.1 M and 20°, the following pK_A values were used: pK_A = 4.748

for CH_3COOH, pK_A = 6.988 for $H_2PO_4^-$, pK_A = 8.46 for THAM (31).

The salts used to achieve proper ionic strength were potassium

perchlorate (B & A reagent) and sodium perchlorate (Fisher Certi-

fied). Both were powdered and dried at 110° for 24 hours before use

in the kinetic experiments.

Miscellaneous chemicals were used at one time or another dur-

ing the course of this research. Mention of their uses will be made

in the proper paragraphs. All the reagents used during the course

of this research were stored over P_2O_5 in order to keep them mois-

ture free.

<h2 style="text-align:center">Solvents</h2>

The solvents used in this project, were water or 50 wt %

methanol-water. Doubly distilled water was stored in a polyethylene

container and used as such in the kinetic experiments. When needed,

deoxygenated water was prepared by boiling the water and bubbling

prepurified nitrogen through it.

Methanol (B & A reagent) was used with doubly distilled water in

making the 50 wt % solvent. A typical batch consisted of 504 ml of

methanol and 400 ml of water. Each batch was prepared under the same conditions, to get the same composition. Reproducible data were obtained from similar kinetic runs, using different batches of the solvent.

Deuterium effect studies were done using D_2O or 50 wt % MeOD-D_2O. Deuterium oxide 99.8% D (Stohler Isotope Chemicals) was used as received in the kinetic experiments. Methanol-d_1 99.0% D (Stohler Isotope Chemicals) was used with the deuterium oxide in preparing the 50 wt % deuterated solution. A ratio of 1.36:1.00 methanol-d_1:deuterium oxide, was used.

Instrumentation and Temperature Control

The kinetics of the iodide reaction with hydroxylamine-O-sulfonate ion were followed with a Beckman Model DU Spectrophotometer equipped with a thermostated cell holder. The temperature control of the DU cell holder has been described (26). The kinetics of all the other reactions were followed with a Cary Model 16 Spectrophotometer equipped with a thermostated cell holder, multi-speed recorder, and automatic sample changer. Built-in options of the Cary 16 permitted absorbance readings in the range of 0.01 to 2.00. All absorbance readings were taken automatically. Temperature control of the Cary 16 cell holder was achieved using a Haake temperature control apparatus.

Temperature Calibration

The temperature calibration of the DU has been determined

(26). The temperature inside the cell holder of the Cary 16 was

determined by using a calibrated thermistor. It was found that the

temperatures inside the cell holder were 10.38°, 20.34°, 29.74° when

the settings on the thermoregulator were 10°, 20°, and 30°, respec-

tively. The same settings on the DU thermoregulator gave tempera-

tures of 10.37°, 20.34°, and 29.67° respectively. For each run at a

specific temperature, the stock solutions were thermostated. An

insulated bath was equipped with cooling coils, thermoregulator,

heater, and a stirrer. In order to achieve the equilibrium tempera-

ture the solutions were suspended in the water bath, set at the proper

temperature, for 20 to 30 minutes. The temperature of the bath was

always 0.5 to 1.0 degree lower or higher than the temperature of the

cell compartment, so that by handling the solutions, the temperature

would be raised or lowered to the temperature of the cell compart-

ment. The room temperature and the temperature at which a particu-

lar run was carried out were taken into account in setting the tempera-

ture of the water bath.

Typical Kinetic Run

The Cary 16 or the Beckman DU was set up so that it would

function properly at the desired wavelength and the right temperature in the cell holder. After the cell in each position had been balanced using solvent, each cell was rinsed and dried before being put back into the cell holder, and allowed to come to equilibrium.

Total volume for the reactions was always 30 ml except for deuterated solvents, in this case a volume of 20 ml was used. The amount of salts needed to achieve proper pH and ionic strength were weighed into a 50 ml glass-stoppered Erlenmeyer flask. The salts were dissolved in the amount of solvent required to bring the total volume to 30 ml. The perchloric acid was prepared in a volumetric flask and its concentration checked by titration to the phenolphthalein end point, of a sample of the solution using standardized sodium hydroxide. The other reagents were prepared by weighing out the proper amount in a volumetric flask and dissolving in the solvent. The solutions were brought to the desired temperature in the water bath. The reagents were added to the reaction flask with a pipet. The moment when the pipet containing the last reagent to be added to the solution was half empty was taken to be time t = 0. The solutions were thoroughly mixed, and a small volume was transferred to a silica cell using a dropper. After the cell was inserted into its position in the cell holder, readings were taken manually or automatically at time intervals such that enough data points would be available to get a rate constant. As a general rule infinite-time absorbances were

taken after 5 to 10 half-lives.

Intermediates and Products

Proof of the mechanisms of some of our reactions was achieved either by interception of the intermediate involved, or by positive identification of the product of the reaction (see Discussion Section). The compounds assumed to be involved in the reaction were synthesized in order to compare their properties with the properties of the products of the reactions in question. The preparations of these compounds are discussed below.

Preparation of Potassium Thiohydroxylamine-S-sulfonate

Potassium thiohydroxylamine-S-sulfonate was prepared by the method of Gösl and Meuwsen (27) with the following modifications. Hydroxylamine-O-sulfonic acid (12.5 g) was dissolved in 20 ml of water plus 10 ml of methanol at 0° and the resulting solution was neutralized with 22 ml of 5 M KOH, using methyl red as the indicator. A solution of 20 g of anhydrous potassium thiosulfate in 40 ml of water was added in small increments over a period of 5-10 minutes, keeping the temperature of the solution around 0° using a salt-ice bath. After addition, the solution was kept at 0° for 20 minutes with vigorous stirring. Methanol (170 ml) was added slowly, so that the temperature of the solution was always below 10°. Potassium sulfate, which

precipitated, was filtered out with suction and the remaining solution

was poured with stirring into 250 ml of isopropanol at -20° using a

carbon tetrachloride-dry ice bath. The solid was filtered, washed

with ether, and recrystallized by dissolving in methanol at 60° fol-

lowed by addition of excess anhydrous ether.

The purity of H_2NSSO_3K was determined, using the same method

described for H_2NOSO_3H except that the use of acetic acid was

required. The purity determinated on several samples was in the

range 92-96%, we were never able to get the fantastic yield reported

by the authors mentioned above. Elemental analysis (Galbraith

Laboratories), gave the following results for H_2NSSO_3K. Calculated:

S, 38.34; N, 8.37. Found: S, 38.17; N, 8.25. An ir spectrum was

taken, and is described and discussed in Appendix II.

Preparation of S-aminoisothiouronium Sulfate

Hydroxylamine-O-sulfonic acid (0.010 mole) was dissolved in

30 ml of absolute ethanol. Triethylamine (0.010 mole) was added to

neutralize the acid. Thiourea (0.010 mole), dissolved in 30 ml of

absolute ethanol, was added dropwise, with stirring. A white cloudi-

ness first appeared. After 5 minutes of mild stirring, a white pre-

cipitate settled and the reaction seemed to be completed. The solid

was filtered with suction and washed thoroughly with absolute ethanol.

The solid was kept out of the contact of air and moisture as much as

possible. The precipitate was dried under vacuum over P_2O_5 for

one-half hour. The product obtained is very sensitive to air and

moisture; thus, handling of the compound has to be done as fast as

possible to avoid contact with the atmosphere. The compound was

divided into smaller portions to avoid unnecessary contamination and

each portion was stored over P_2O_5.

The purity of $[(NH_2)_2CSNH_2]_2SO_4$ was determined, using the

method described for H_2NOSO_3H. Acid was necessary for the reac-

tion to occur and results obtained, using acetic acid, were satisfac-

tory. The compound obtained was 96% pure. Elemental analysis

(Galbraith Laboratories) gave the following results for

$[(H_2N)_2C-S-NH_2)]_2SO_4$. Calculated: N, 29.97; C, 8.56; H, 4.31.

Found: N, 29.84; C, 8.57; H, 4.14. An ir spectrum was taken and

is described and discussed in Appendix II.

Preparation of Formamidinedisulfide Dichloride

Formamidinedisulfide dichloride had to be synthesized because

a good value of the molar extinction coefficient was not found in the

literature. The compound can be made using several oxidizing agents

(28). But most of these methods do not give the highest purity and

evidence of some unreacted thiourea is found. Since we anticipated

the separation of thiourea and formamidinedisulfide dichloride to be

very difficult, a method where the amount of unreacted thiourea would

be at a minimum had to be found. We chose a method in which chlorine was used as the oxidizing agent (29).

Necessary precautions were taken to prevent the reaction from becoming too violent. Behind an explosion-proof shield, 0.1 mole of thiourea (7.61 g) was dissolved in a minimum amount of ice-cold absolute ethanol. Slowly, chlorine gas was bubbled through a gas dispersion tube into the gently stirred solution. After 2-3 minutes a white precipitate started to appear. The bubbling of the chlorine gas was continued for 5 minutes, after which time, the reaction seemed to be complete. Then nitrogen gas was bubbled through the solution to get rid of any excess chlorine gas. The precipitate was filtered with suction, washed with absolute ethanol, and dried under vacuum over P_2O_5.

A purity check, using the same method as described for hydroxylamine-O-sulfonic acid gave misleading results. The purity found by this method was never higher than 85%, due to the fact that an equilibrium (30) as described by Equation 20 was reached instead of a complete reaction. Therefore, it was concluded that the iodometric

$$(20) \qquad 2(H_2N)_2C=S + I_2 \rightleftharpoons (H_2N)_2C-S-S-C(NH_2)_2^{2+} + 2I^-$$
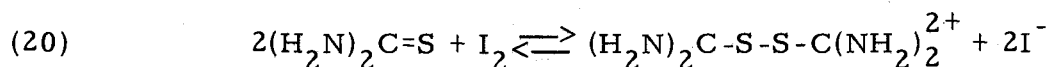
method for the determination of the purity was giving us inaccurate results. A melting point determination gave a melting point of 155-157° with decomposition, compared with the literature value of 155°

(30). Elemental analysis (Galbraith Laboratories) gave the following

results for $[(H_2N)_2C-S]_2Cl_2$. Calculated: C, 10.76; H, 3.61;

N, 25.10; Cl, 31.77. Found: C, 10.87; H, 3.58; N, 24.93; Cl, 31.65.

Instrumentation Used

Nuclear magnetic resonance spectra were obtained using a

Varian H.A. -100 Spectrometer. Infra-red spectra were obtained

using a Perkin-Elmer Model 180 Spectrometer. The KBr-pellet

technique, using potassium bromide (Mallinckrodt, infra-red grade),

was used for all the spectra. Ultra-violet and visible spectra were

obtained on the Cary Model 16 spectrophotometer equipped with a

servo-slit, a two-speed wave length drive, and a multi-speed auto-

matic recorder.

III. RESULTS

Triphenylphosphine-hydroxylamine-O-sulfonate Reaction

The reaction was studied following the change in absorbance of triphenylphosphine at 260 nm, $\mu = 0.075$ M, T $= 20.34°$ in a 50 wt % solution of methanol-water. The solutions were buffered and the pH range was calculated to be 5.03-6.72, using pK_A 5.64 (31) for acetic acid in 50 wt % solution of methanol-water. Hydroxylamine-O-sulfonate ion was the reactant in excess, 5.0-20.0 x 10^{-4} M, with triphenylphosphine concentration of 4.0 x 10^{-5} M.

Determination of the Rate Law

A $\ln(A_t - A_\infty)$ versus time plot where A_∞ = infinite-time absorbance and A_t = absorbance at time t is shown in Figure 1. The relationship observed indicates that the reaction is pseudo-first-order.

$$(21) \qquad Rate = -d[(C_6H_5)_3P]/dt = k_1[(C_6H_5)_3P]$$

Values of k_1 were obtained for a series of different concentrations of hydroxylamine-O-sulfonate ion, which did not change during the course of the reaction. The reaction was then assumed to be first-order in hydroxylamine-O-sulfonate ion and the rate law formulated as follows
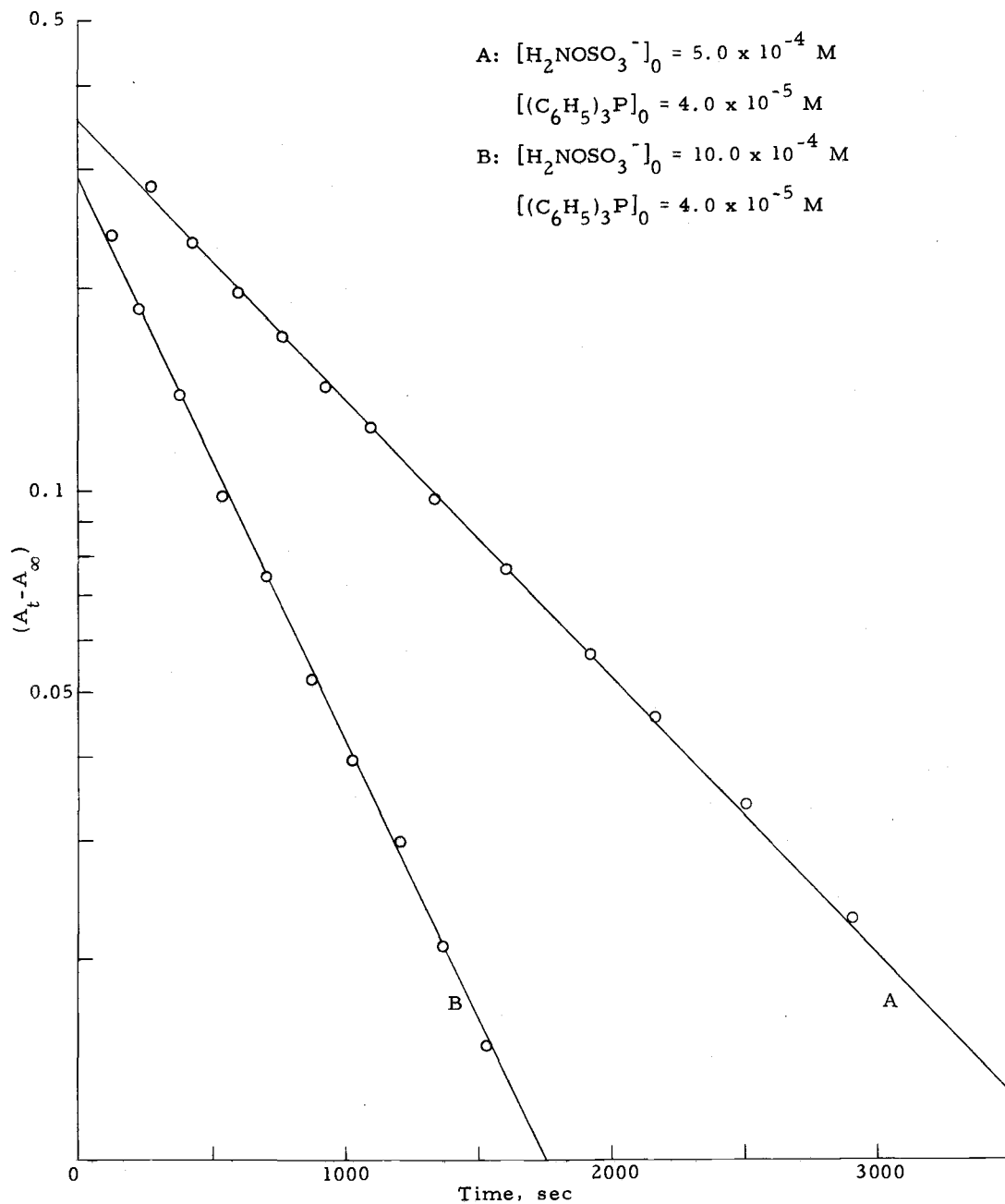
Figure 1. Pseudo-first-order plots for the triphenylphosphine-hydroxylamine-O-sulfonate ion reaction at $\mu = 0.075$ M at 20.34° and at pH 5.75 in 50 wt % methanol-water solvent.

(22) $$\text{Rate} = k_2[H_2NOSO_3^-][(C_6H_5)_3P]$$

From the kinetic data summarized in Table 1, the rate constant was

calculated to be $k_2 = 2.0 \pm 0.1 \ M^{-1}sec^{-1}$. In the runs, where the

difference in the concentration was small, the concentration of

hydroxylamine-O-sulfonate, at one half-life was taken for the calcula-

tion of the rate constant, k_2.

Stoichiometry

Two possible products for the reaction could be expected accord-

ing to the following equations.

(23) $$(C_6H_5)_3P + H_2NOSO_3^- \xrightarrow{\text{r.d.}} (C_6H_5)_3PNH_2^+ + SO_4^{2-}$$

(24) $$(C_6H_5)_3PNH_2^+ + H_2O \longrightarrow (C_6H_5)_3P=O + NH_4^+$$
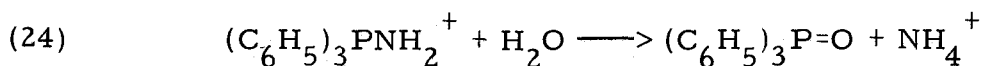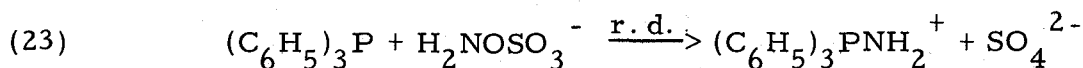
The only species absorbing at 260 nm are $(C_6H_5)_3P=O$, $(C_6H_5)_3P$, and

$(C_6H_5)_3PNH_2^+$. Both compounds were prepared and their uv spectra

scanned between 300-220 nm (16). Their molar absorption coeffi-

cients were determined. The difference in the ε_{260} values of the

compounds was a good criterion for deciding which of the two was the

product of the reaction. It was found that $(C_6H_5)_3PNH_2^+$ is the pro-

duct of the reaction by comparing the value of the infinite-time

absorbance at 260 nm for the reaction and the value of the absorbance

Table 1. Kinetic data for the triphenylphosphine-hydroxylamine-O-sulfonate ion reaction at μ = 0.075 M and 20.34° in 50 wt % methanol-water solvent.

$10^4[H_2NOSO_3^-]_0$, M	$10^5[(C_6H_5)_3P]_0$, M	pH^a	k_2, $M^{-1}sec^{-1}$
5.0	4.0	5.75	2.09
5.0	4.0	5.75	2.11
10.0	4.0	5.75	2.13
10.0	4.0	5.75	2.01
10.0	4.0	5.75	2.08
15.0	4.0	5.75	1.98
5.0	4.0	6.72	2.07
10.0	4.0	6.72	2.04
5.0	4.0	5.03	2.03
10.0	4.0	5.03	2.00
10.0	4.0	5.75	1.12[b]
10.0	4.0	5.75	1.27[b]
20.0	4.0	5.75	1.14[b]
20.0	4.0	5.75	1.29[b]
10.0	4.0	3.30	1.84
10.0	4.0	3.00	1.75
10.0	4.0	2.83	1.64

[a]Using acetic acid-acetate buffer where pK_A = 5.64 (31).

[b]Runs in MeOD-D_2O.

at 260 nm for the product prepared independently. The first step of

the reaction, described by Equation 23, is the rate-determining step.

The absorbance of the solution remained stable for a period of 2-3

hours, indicating that step 2, described by Equation 24, if it does

occur, is too slow to affect the kinetics of the reaction.

The observed molar absorption coefficients $(M^{-1}cm^{-1})$ at

260 nm for $(C_6H_5)_3P$, $(C_6H_5)_3PNH_2^+$ and $(C_6H_5)_3P=O$ in 50 wt %

methanol-water solutions are:

$(C_6H_5)_3P$	$(C_6H_5)_3PNH_2^+$	$(C_6H_5)_3P=O$	Ref.
11,500	1,970	1,420	(16)
--	2,270	---	(17)
11,460	2,320[a]	---	this work
11,000	---	1,260	(32)

[a]Product of the reaction

Furthermore, during all the runs, the absorbance of a blank contain-

ing triphenylphosphine under the reaction conditions was found to be

stable for as long as it took to reach the infinity readings for the runs.

Temperature Effect

In order to obtain activation parameters, kinetic runs were made

at 12.38°, 20.34°, and 29.74°. The temperature dependence of the

second-order rate constant is summarized in Table 2. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$

were calculated from data listed in Table 2 using Equation 25 from

Table 2. Temperature dependence of the triphenylphosphine-hydroxyl-amine-O-sulfonate ion at $\mu = 0.075$ M and pH 5.75.

Temp (°C)	$10^4[H_2NOSO_3^-]_0$, M	$10^5[(C_6H_5)_3P]_0$, M	k_2, $M^{-1}sec^{-1}$
12.38	9.8	4.04	1.37
	19.7	4.04	1.39
	10.1	4.04	1.40
	20.3	4.04	1.42
20.34	10.0	4.00	2.04[a]
29.67	5.5	4.25	3.18
	10.9	4.25	3.06
	5.1	4.25	3.14
	10.0	4.25	3.10

[a]This value is an average and was entered four times in the least-squares calculation to give the data at each temperature equal weight.

transition-state theory (33).

(25) $\qquad \ln(k_2/T) = \ln(k_b/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$

Figure 2 shows the temperature dependence of the second-order rate

constant.

$$\Delta H^{\ddagger} = 7.4 \pm 0.1 \text{ kcal/mole}$$

$$\Delta S^{\ddagger} = -32 \pm 1 \text{ eu}$$

The above values were calculated using a least-squares computer

program described in Appendix I.

Deuterium Isotope Effect

In order to help elucidate the mechanism of nucleophilic substi-

tutions on hydroxylamine-O-sulfonic acid a deuterium effect study was

undertaken with the four nucleophiles (see Discussion Section). The

reaction was studied using a 50 wt % solution of methanol-d_1 and

deuterium oxide. Evidence that the hydrogen atoms on nitrogen

exchange very rapidly with the deuterium atoms of the solvent was

obtained from [1]H n.m.r. This conclusion was reached when no peak

for the NH_2 protons was observed in a solution containing hydroxyl-

amine-O-sulfonic acid (0.50 M) and sodium acetate (1.0 M) in 99.8%

D_2O. Although a strong absorbance for the methyl proton of the

acetate was observed, there was no trace of any peak other than that
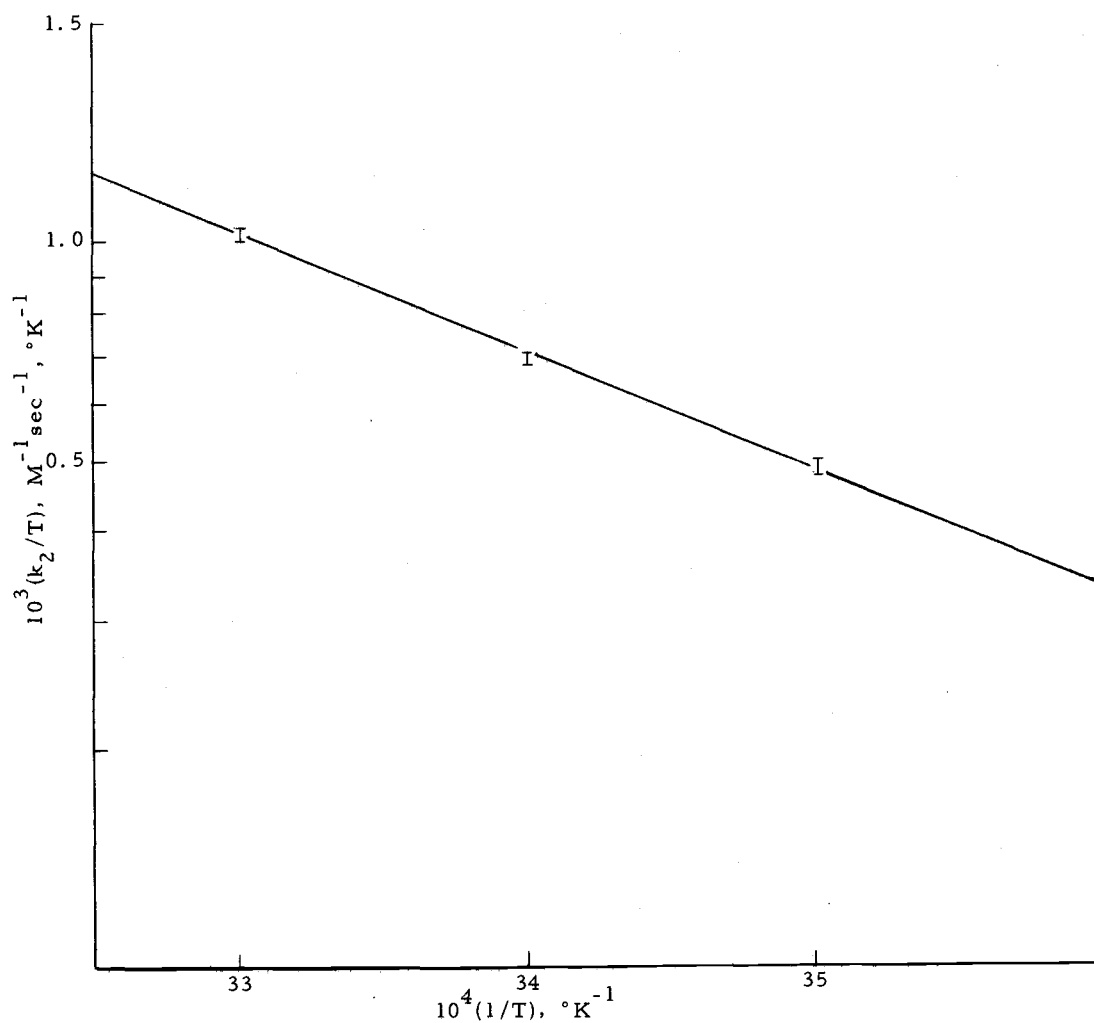
Figure 2. Temperature dependence of the second-order rate constant for the triphenylphosphine-hydroxylamine-O-sulfonate ion reaction.

due to residual water. The average rate constant calculated from data listed in Table 1 was found to be:

$$k_2(D_2O-CH_3OD) = 1.2 \pm 0.1 \ M^{-1}sec^{-1}$$

The ratio of the second-order rate constants found in non-deuterated and deuterated solvent was found to be:

$$\frac{k_2(H_2O-CH_3OH)}{k_2(D_2O-CH_3OD)} = 1.6 \pm 0.1$$

Reaction with Added Formaldehyde

Difficulties occurred when runs in deuteromethanol were done. An n.m.r. spectrum of methanol-d_1 showed that an impurity was present and was affecting the reaction. This impurity was believed to be formaldehyde and was found only in one particular batch of the methanol-d_1. In order to erase the doubt that formaldehyde could have been present to a certain extent in the other batch of methanol-d_1 or in the regular methanol solvents, tests were made to prove that the solvents were free of any impurities.

Formaldehyde reacts with hydroxylamine-O-sulfonate ion to give an oxime according to the following reaction (2).

(26) $\qquad H_2C=O + H_2NOSO_3^- \longrightarrow H_2C=NOSO_3^- + H_2O$

This oxime is unreactive toward triphenylphosphine; thus, if the $H_2C{=}O$ concentration is high enough, one should not be able to observe any reaction between hydroxylamine-O-sulfonate ion and triphenylphosphine. To prove this, known concentrations of formaldehyde were added to the reaction and the following results were observed. By checking the infinite time absorbance of the reactions it was found that the amount of unreacted triphenylphosphine depended upon the initial concentration of the formaldehyde and also on the time lapse between the addition of the formaldehyde and the start of the reaction.

Regular methanol with added formaldehyde, and regular methanol with no formaldehyde added were treated as follows. To 500 ml of methanol, 0.1×10^{-3} mole of formaldehyde, 0.3×10^{-3} mole of iodine, and 3.0×10^{-2} mole of sodium methoxide were added. The solution was allowed to stand for 12 hours. Solid sodium thiosulfate $(0.3 \times 10^{-3}$ mole) was then added to remove the unreacted iodine and the solution was distilled collecting the middle fraction. The resulting formaldehyde-free methanol was then used to prepare the 50 wt % solvent for the kinetic runs. The same results were obtained using either the treated methanol or the untreated methanol. The same procedure was used on a smaller scale to purify the methanol-d_1 and the same results were obtained.

Runs at Lower pH

Determination of a rate constant for the system at lower pH was attempted. Hydroxylamine-O-sulfonate ion can be protonated (see results of the iodide study) and so can triphenylphosphine (34). From data listed in Table 1, it was observed that the rate constant for the reaction was decreasing as the pH was decreasing. Many combinations of reactants can be used to account for the rate constant observed. The problem is complex but can be resolved. It was decided not to pursue the investigation further, when it was clear that the information that could be obtained would not help to better understand the mechanisms.

Potassium Iodide-hydroxylamine-O-sulfonate Ion Reaction

The reaction was studied by following the change in absorbance of the triiodide produced at $\lambda = 400$ nm, T = 20.34° and in water. The pH range 1.0-7.76, was achieved by using different buffers. Potassium iodide was the reagent in excess ($[0.075-9.0] \times 10^{-2}$ M) over hydroxylamine-O-sulfonic acid (1.0×10^{-4} M). The kinetic data for the reaction are summarized in Table 3 and in Table 4. The rate constants were determined over a wide range of pH. From pH 3.0 to 8.0, the rate constant, $k_{2(OS^-)} = 0.069 \pm 0.006$ M^{-1}sec^{-1}, is independent of the pH. As the H$^+$ concentration increases above

Table 3. Kinetic data for the iodide-hydroxylamine-O-sulfonate ion
reaction at μ = 0.1 M and 20.34° in water.

$10^4[H_2NOSO_3^-]_0$, M	$10^2[I^-]_0$, M	pH	k_2, $M^{-1}sec^{-1}$
1.00	0.75	4.75	0.0681
1.02	1.00	4.75	0.0632
1.00	1.50	4.75	0.0675
1.00	1.50	4.75	0.0673
1.00	1.50	4.75	0.0655
1.00	1.50	4.75	0.0686
1.00	1.50	4.75	0.0660
1.01	2.00	4.75	0.0651
0.97	2.00	4.75	0.0605
1.00	3.00	4.75	0.0705
1.02	3.01	4.75	0.0647
1.02	3.00	4.75	0.0624
1.01	4.01	4.75	0.0665
0.97	4.01	4.75	0.0660
1.02	6.00	4.75	0.0675
1.04	6.00	4.75	0.0704
1.02	9.00	4.75	0.0745
1.04	9.00	4.75	0.0704
1.00	1.50	5.35	0.0682
1.00	1.50	5.35	0.0727
1.00	1.50	5.35	0.0714
1.01	2.01	5.65	0.0659
1.01	4.01	5.65	0.0697
1.00	1.50	6.41	0.0713
1.00	1.50	7.21	0.0762
1.00	1.50	7.21	0.0725
1.00	1.50	7.21	0.0743
0.97	2.00	7.76	0.0690
0.97	4.01	7.76	0.0748
1.00	1.50	4.75	0.0516[a]
1.00	1.50	4.75	0.0535[a]
1.00	4.70	5.75	0.0356[b]
1.00	4.70	5.75	0.0375[b]
1.00	1.5	4.75	0.0533[c]
1.00	1.5	4.75	0.0795[d]

[a]Runs in D_2O.
[b]CH_3OH/H_2O run.
[c]μ = 0.021 M.
[d]μ = 0.3 M.

Table 4. Kinetic data for the iodide-hydroxylamine-O-sulfonate ion reaction at $\mu = 0.1$ M at 20.34° and at pH lower than 3 in water.

$10^4[H_2NOSO_3H]_0$, M	$10^2[I^-]_0$, M	pH	k_2, $M^{-1}sec^{-1}$
1.00	1.50	2.00	0.0629
1.00	1.50	2.00	0.0611
1.00	1.50	1.70	0.0574
1.00	1.50	1.70	0.0549
1.00	1.50	1.60	0.0547
1.00	2.00	1.52	0.0528
1.00	1.50	1.52	0.0522
1.00	3.00	1.52	0.0513
1.00	1.50	1.37	0.0503
1.00	1.50	1.37	0.0489
1.00	1.50	1.30	0.0481
1.00	1.50	1.30	0.0443
1.00	1.50	1.07	0.0411
1.00	1.50	1.00	0.0399
1.00	1.50	1.30	0.0309[a]
1.00	1.50	1.30	0.0312[a]

[a] Runs in D_2O.

10^{-3} M, the rate decreases. Iodide does not protonate but the hydroxylamine-O-sulfonate ion does (3,6). Thus, the rate constant observed, as shown in Figure 3, below pH 3 is a combination of the rate of the protonated and non-protonated forms that exist simultaneously under the conditions of the reaction.

Determination of the Rate Law

A $\ln(A_\infty - A_t)$ versus time plot is shown in Figure 4. The linear relationship observed indicates that the reaction is pseudo-first-order. In order to facilitate the presentation and understanding of the following equations, the following notations will be used:

$$H_2NOSO_3^- = OS^- \quad \text{and} \quad H_2NOSO_3H = HOS.$$
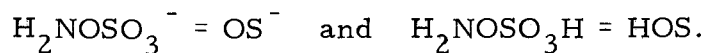
$$3 < pH < 8$$

(27) $$\frac{-d[OS^-]}{dt} = k_{1(OS^-)}[OS^-]$$

(28) $$k_{2(OS^-)} = \frac{k_{1(OS^-)}}{[I^-]}$$

Since $k_{2(OS^-)}$ is independent of the iodide concentration, the reaction is first-order in each reactant and the following rate law can be written:

(29) $$\text{Rate} = k_{2(OS^-)}[I^-][OS^-]$$

$$1 < pH < 3$$
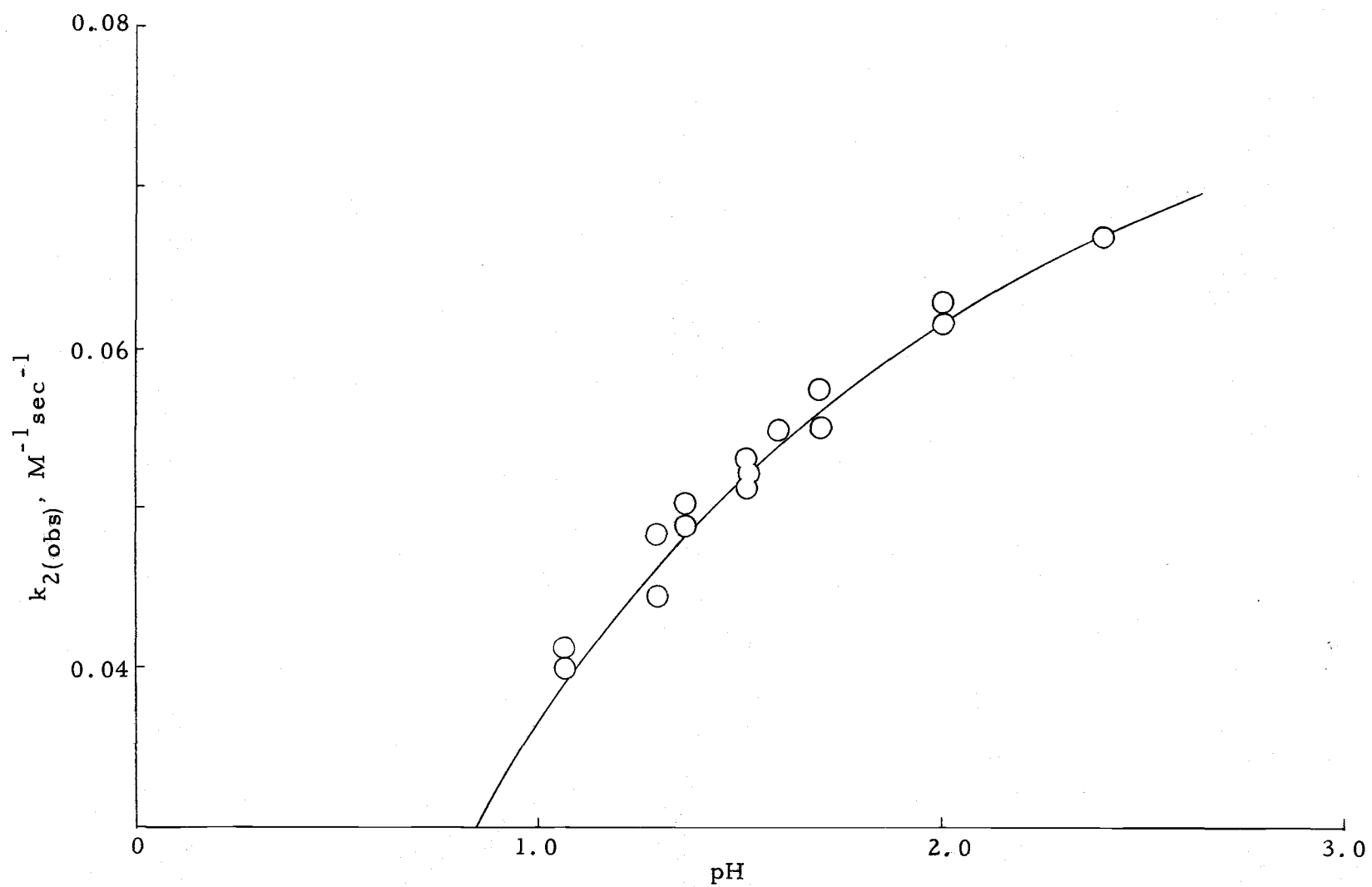
Figure 3. Second-order rate constant versus pH for the iodide-hydroxylamine-O-sulfonate ion reaction at 20.34° and μ = 0.1 M.
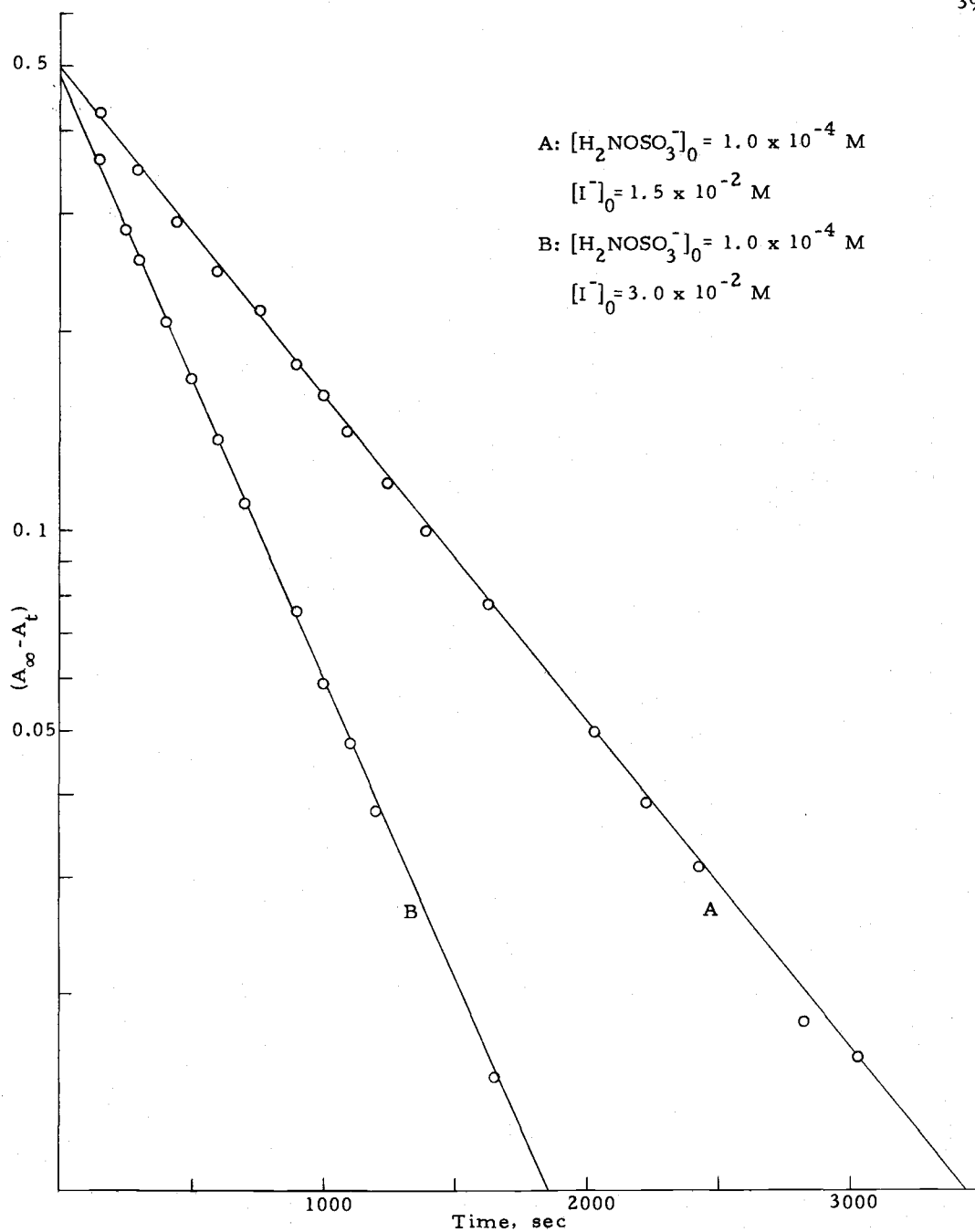
Figure 4. Pseudo-first-order plots for the iodide-hydroxylamine-O-sulfonate ion reaction at μ = 0.1 M, at 20.34° and pH 4.75 in water.

In this pH range there is a mixture of HOS and OS$^-$ and a rate law

of the form shown in Equation 30 is assumed.

(30) $\dfrac{-d\Sigma[HOS]}{dt} = (k_{2(HOS)}[HOS] + k_{2(OS^-)}[OS^-])[I^-]$

(31) $HOS \rightleftharpoons H^+ + OS^-$

(32) $K_A = \dfrac{[H^+][OS^-]}{[HOS]}$

Combining 32 and 30 with $\Sigma HOS = [HOS] + [OS^-]$ we get

(33) $\dfrac{-d\Sigma[HOS]}{dt} = k_{2(HOS)}[\dfrac{\Sigma[HOS]}{1+K_A/[H^+]} + k_{2(OS^-)}\dfrac{\Sigma[HOS]}{1+[H^+]/K_A}][I^-]$

Rearranging Equation 33 we finally get:

(34) $k_{1(obs)}/[I^-] = k_{2(obs)} = k_{2(HOS)} + K_A(k_{2(OS^-)} - k_{2(obs)})/[H^+]$

K_A and $k_{2(HOS)}$ being constants, it is easy to relate Equation 34 to

a linear equation of the type $y = a + bx$. Thus, by using the data in

Table 4, a value of $K_A = 0.055 \pm 0.01$ and a value of

$k_{2(HOS)} = 0.023 \pm 0.003 \ M^{-1}sec^{-1}$ were calculated. The above values

were obtained using a least-squares program, described in Appendix

I. The K_A value compares favorably with the literature value

$K_A = 0.033$ at 45° (6). Due to ionic strength limitations, it was not

possible to directly measure $k_{2(HOS)}$ in solutions in which

hydroxylamine-O-sulfonate is entirely in the protonated form. There is strong reason to believe that the value of the rate constant observed will become constant when the hydroxylamine-O-sulfonic acid is completely protonated in solution (3).

Stoichiometry

The reaction is believed to occur according to Equations 35 and 36. Experimental results are such that the same stoichiometry was observed for the protonated and non-protonated forms.

$$(35) \qquad H_2NOSO_3^- + 3I^- + 2H^+ \longrightarrow NH_4^+ + SO_4^{2-} + I_3^-$$

$$(36) \qquad H_3N^+OSO_3^- + 3I^- + H^+ \longrightarrow NH_4^+ + SO_4^{2-} + I_3^-$$
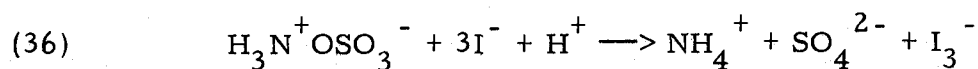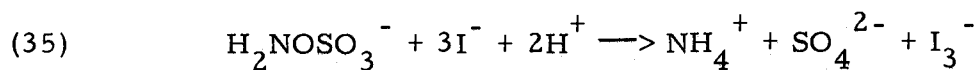
From the above equations, it can be seen that for each mole of hydroxylamine-O-sulfonate ion used, 1 mole of iodine is produced and 2 moles of acid are consumed. The stoichiometry was determined by titration and by spectrophotometry.

Determination of the Stoichiometry by Titration. The amount of

iodine produced was found by titration with standardized sodium thiosulfate (0.1 M). The amount of acid present before and after the reaction was found by titration with standardized sodium hydroxide (0.1 M), recording the pH with a Heath Model EUW-301 pH Recording Electrometer. The end point was determined by plotting pH versus ml

of sodium hydroxide added. Since the iodine-thiosulfate reaction does not consume acid, the iodine produced was titrated before the acid

$$(37) \qquad 2S_2O_3^{2-} + I_2 \longrightarrow 2I^- + S_4O_6^{2-}$$
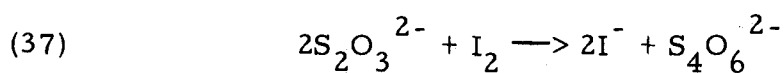
concentration was determined. In order to check that NH_4^+, which is a product of the reaction, had no influence whatsoever on the determination of the acid concentration, an equivalent amount of ammonium sulfate was added to the hydroxylamine-O-sulfonic acid-perchloric acid blank solutions. Reproducible data were obtained in all cases. The ratio of the number of moles of acid consumed to the number of moles of iodine produced was obtained in the buffered solution (pH 4.75) and in the non-buffered solution (pH 2.00).

A) pH 2.00	Calculated	Found
Total acid	91.2×10^{-5} M	91.7×10^{-5} M
Acid left after reaction	28.65×10^{-5} M	28.59×10^{-5} M
Iodine produced	31.29×10^{-5} M	31.43×10^{-5} M
Ratio	2.000	2.007

B) pH 4.75		
Total acid	20.29×10^{-5} M	20.21×10^{-5} M
Acid left after reaction	5.15×10^{-5} M	5.71×10^{-5} M
Iodine produced	7.57×10^{-5} M	7.28×10^{-5} M
Ratio	2.000	1.991

Spectrophotometric Determination of the Stoichiometry. The

concentration of triiodide in solutions depends on the following

equilibrium (38):

(38) $I_3^- \rightleftharpoons I_2 + I^-$ (K_{diss})

This equilibrium can be shifted depending on the concentration of

iodide. In our study the maximum concentration of I_3^- produced is

1.0×10^{-4} M.

In order to find out if hydroxylamine-O-sulfonate ion reacted

completely, the following experiment was done. A Beer's law plot,

using solutions containing different concentrations of I_2 in 4.0×10^{-2} M

potassium iodide, was obtained at 400 nm. From the straight line

obtained, $\varepsilon_{(400)} = 5790$ $M^{-1} cm^{-1}$ at $[I^-] = 0.04$ M was found. In

order to check the stoichiometry a value of $\varepsilon_{(400)}$ at infinite concen-

tration of iodide had to be determined. From the equilibrium

described by Equation 38 the concentration of I_3^- can be expressed

as

(39) $[I_3^-] = \Sigma[I_2] \dfrac{[I^-]}{K_{(diss)} + [I^-]}$

where $K_{(diss)} = 1.15 \times 10^{-3}$ at 20° and $\mu = 0.1$ (35). At concentration

lower than infinity, the ratio $[I^-]/(K_{(diss)} + [I^-])$ is less than one. By

multiplying the ε value obtained from the Beer's law plot by

$$\frac{(K_{(diss)}+[I^-])}{[I^-]}$$ it is possible to obtain the corresponding value of ε

at infinite concentration of I^-. The value obtained by this calculation

is: $\varepsilon_{(400)}$ = 5950($[I^-] = \infty$). Thus, the infinite-time absorbances

obtained from the kinetic runs can be compared to the ones expected

from Equation 40.

$$(40) \qquad A_{(calc)} = (5,950) \frac{[I^-]}{K_{(diss)}+[I^-]} \Sigma[H_2NOSO_3^-]_0$$

This calculation was repeated for typical runs at different iodide con-

centrations and the calculated infinite-time absorbances agreed

within the experimental error (2-3%) with the observed infinite-time

absorbances.

Temperature Effect

In order to obtain activation parameters, kinetics runs were

made at 10.37°, 20.34°, and 29.67°. The temperature dependence of

the second-order rate constant is summarized in Table 5. $\Delta H^{\ddagger}$ and

$\Delta S^{\ddagger}$ were calculated from data listed in Table 5, using Equation 41

from transition state theory (33).

$$(41) \qquad \ln(k_2/T) = \ln(k_b/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$$

Figure 5 shows the temperature dependence of the second-order rate

constant.

Table 5. Temperature dependence of the iodide-hydroxylamine-O-sulfonate ion reaction at μ = 0.1 M and at pH 4.75.

Temp (°C)	$10^4 [H_2NOSO_3^-]_0$, M	$10^2 [I^-]_0$, M	k_2, $M^{-1}sec^{-1}$
10.37	1.00	3.00	0.029
	1.00	3.00	0.032
	1.00	3.00	0.032
20.34[a]	1.00	1.50	0.069
29.67	1.00	1.50	0.123
	1.00	1.50	0.121
	1.00	1.50	0.124

[a]This value is an average and was entered four times in the least-squares calculation to give the data at each temperature equal weight.

$$\Delta H^{\ddagger} = 11.6 \pm 0.3 \text{ kcal/mole}$$

$$\Delta S^{\ddagger} = -24.4 \ (\pm 1.0) \text{ eu}$$

The above values were calculated using a least-squares computer

program described in Appendix I.

Deuterium Isotope Effect

The reactions were studied in 99.8% deuterium oxide. Both

buffered and non-buffered solutions were used. The average rate

constants, calculated from data in Tables 3 and 4 were found to be:

$$k_2(D_2O) = 0.0525(\pm 0.001) \text{ M}^{-1}\text{sec}^{-1} \quad \text{pH } 4.75$$

$$k_2(D_2O) = 0.0310(\pm 0.001) \text{ M}^{-1}\text{sec}^{-1} \quad \text{pH } 2.00$$

The ratios of the second-order rate constants found in non-deuterated

and deuterated solvent are:

$$k_2(H_2O)/k_2(D_2O) = 1.3 \pm 0.1 \qquad \text{pH } 4.75$$

$$k_2(H_2O)/k_2(D_2O) \sim 1.6 \text{ (uncertain)} \quad \text{pH } 2.00$$

Solvent Effect

The reaction was also studied in 50 wt % methanol-water to get

a rate constant in that solvent for comparison with the rate found in

water under the same conditions. The average rate constant calculated
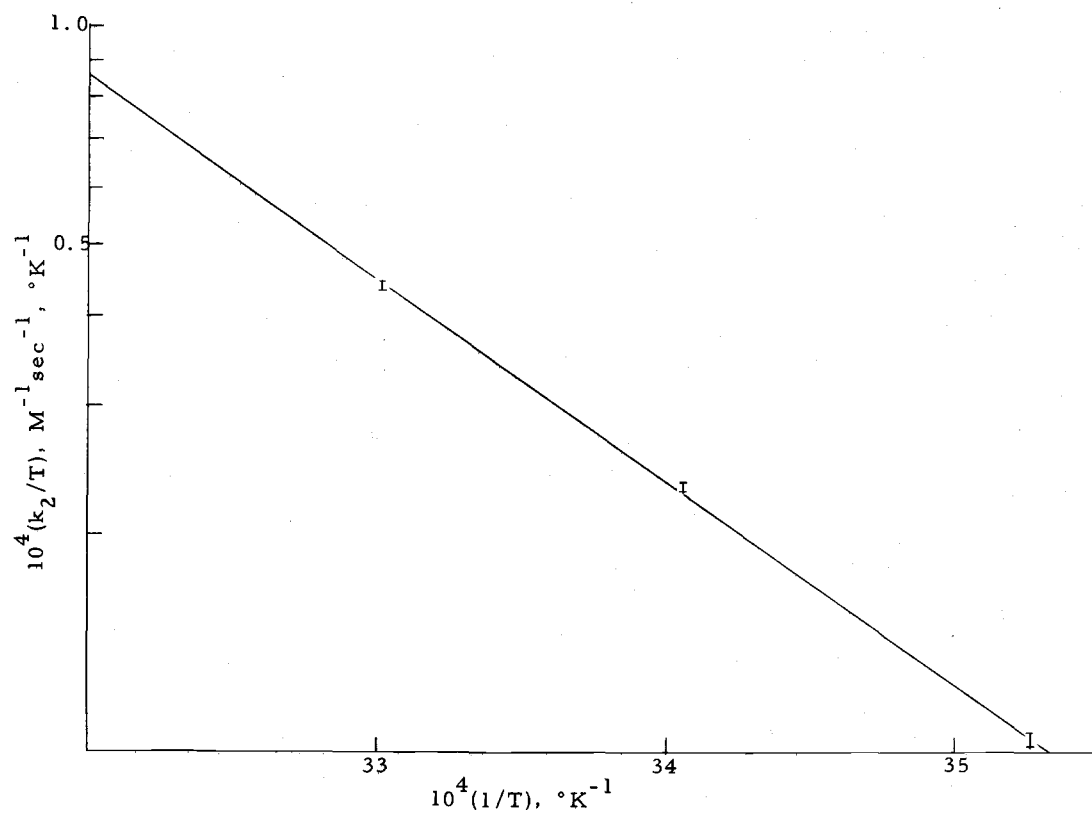
Figure 5. Temperature dependence of the second-order rate constant for the iodide-hydroxylamine-O-sulfonate ion reaction.

from data in Table 3 was found to be:

$$k_2(H_2O/CH_3OH) = 0.0365(\pm 0.001) \ M^{-1}sec^{-1}$$

Reactions with Added Chloride and Bromide

Since chlorosulfonic acid was used for the synthesis of hydroxyl-amine-O-sulfonic acid, hydrochloric acid is a possible impurity in the product. In order to check if chloride had any catalytic effect on the reaction, potassium chloride was added to the reaction mixture. The same rate constant was found in the reactions containing chloride (1.5×10^{-2} M) as in the reactions without chloride. It was concluded that, within the concentration limits of this study, the chloride ion is unreactive toward hydroxylamine-O-sulfonate ion. The possibility of a catalytic effect of bromide ion was also tested with a 5-fold excess of bromide, compared with iodide, added to the reaction mixture. Even with $[Br^-] = 5.0 \times 10^{-2}$ M, the rate constant remains the same. It is concluded that, within the concentration limits of this study, bromide ion is at least 50 times less reactive toward hydroxylamine-O-sulfonate ion than is iodide ion. However, in very concentrated solutions of bromide and hydroxylamine-O-sulfonic acid a reaction was observed. This conclusion was reached after observations of a yellowish coloration and evolution of an odorless gas (nitrogen). A study of this reaction was finally forsaken when it was found that

solutions that were too concentrated were necessary to observe a
reaction that would be comparable to the iodide reaction. Further-
more, it was also found that at concentrations higher than 0.1 M,
hydroxylamine-O-sulfonic acid undergoes a self oxidation-reduction
reaction that leads to its decomposition. This conclusion was reached
when bubbles of nitrogen gas were observed in a solution which was
left standing for as little as 15 minutes.

Potassium Thiosulfate-hydroxylamine-O-sulfonate Ion Reaction

The reaction was studied by following the change in absorbance
of the tetrathionate produced at 270 nm, μ = 0.1 M, and T = 20.34°
in water. The pH range was calculated to be 2.7-9.5 using the
appropriate buffers. The reaction was studied in a second-order
fashion because of the small differences in absorbances of the species
involved. The rate law was found to be valid for the following range
of concentrations: $(1.0-4.0) \times 10^{-3}$ M for hydroxylamine-O-sulfonic
acid and $(2.0-6.0) \times 10^{-3}$ M for thiosulfate. From the kinetics data
summarized in Table 6, the rate constant was calculated to be:
k_2 = $0.550(\pm 0.015)$ $M^{-1} sec^{-1}$, and was found to be independent of the
pH.

Table 6. Kinetic data for the thiosulfate-hydroxylamine-O-sulfonate ion reaction at μ = 0.1 M at 20.34° and in water.

$10^3[H_2NOSO_3^-]_0$, M	$10^3[S_2O_3^{2-}]_0$, M	pH	k_2, $M^{-1}sec^{-1}$
1.00	3.00	4.73	0.548
1.00	3.02	4.79	0.540
1.00	3.00	4.73	0.544
1.00	3.01	4.73	0.550
1.00	6.00	4.73	0.549
2.00	2.00	4.71	0.552
1.98	2.00	4.71	0.568
3.05	2.03	4.71	0.553
4.00	2.00	4.71	0.552
6.10	2.03	4.71	0.526
1.00	3.00	5.04	0.549
1.00	3.00	5.04	0.532
1.00	3.00	5.26	0.547
1.00	3.00	5.26	0.560
1.00	3.00	5.26	0.551
1.00	3.00	5.33	0.546
1.00	3.00	5.33	0.547
1.00	6.00	5.26	0.552
2.00	2.00	5.26	0.565
1.00	3.03	6.19	0.565
1.00	3.03	7.03	0.549
1.00	3.01	4.74	0.493[a]
1.00	3.01	4.74	0.489[a]
1.00	3.00	4.73	0.455[b]
1.00	3.01	4.73	0.452[b]
1.00	3.00	4.73	0.501[c]
1.00	6.00	4.73	0.502[c]
4.99	3.00	~9.3	0.537[d]
8.02	3.00	~9.3	0.559[d]
9.98	3.00	~9.3	0.526[d]

[a]Runs in D_2O.

[b]μ = 0.06 M.

[c]μ = 0.08 M.

[d]Infinite-time absorbance adjusted.

Determination of the Rate Law

In order to find the second-order rate constant, the absorbance data had to be transformed as a function of the concentration using the following formulas:

$$(42) \qquad y = [R]_0 \frac{[A_\infty - A_t]}{[A_\infty - A_0]}$$

$$(43) \qquad x = [R]_0 - y$$

where R_0 is the initial concentration of the limiting reagent, y is the concentration of R_0 left after time t, and x is the concentration of R_0 that has reacted. The calculations of the rate constant according to Equation 44 were performed using a special computer program,

$$(44) \qquad kt = \frac{1}{b_0 - 2a_0} \ln \frac{a_0}{b_0} \frac{(b_0 - 2x)}{(a_0 - x)}$$

the features of which will be discussed in Appendix I. Typical plots for the reactions are shown in Figure 6. The linear relationships observed indicate that the reaction is second order overall and first order in each reactant; thus, the following rate law is valid.

$$(45) \qquad Rate = k_2 [H_2NOSO_3^-][S_2O_3^{2-}]$$
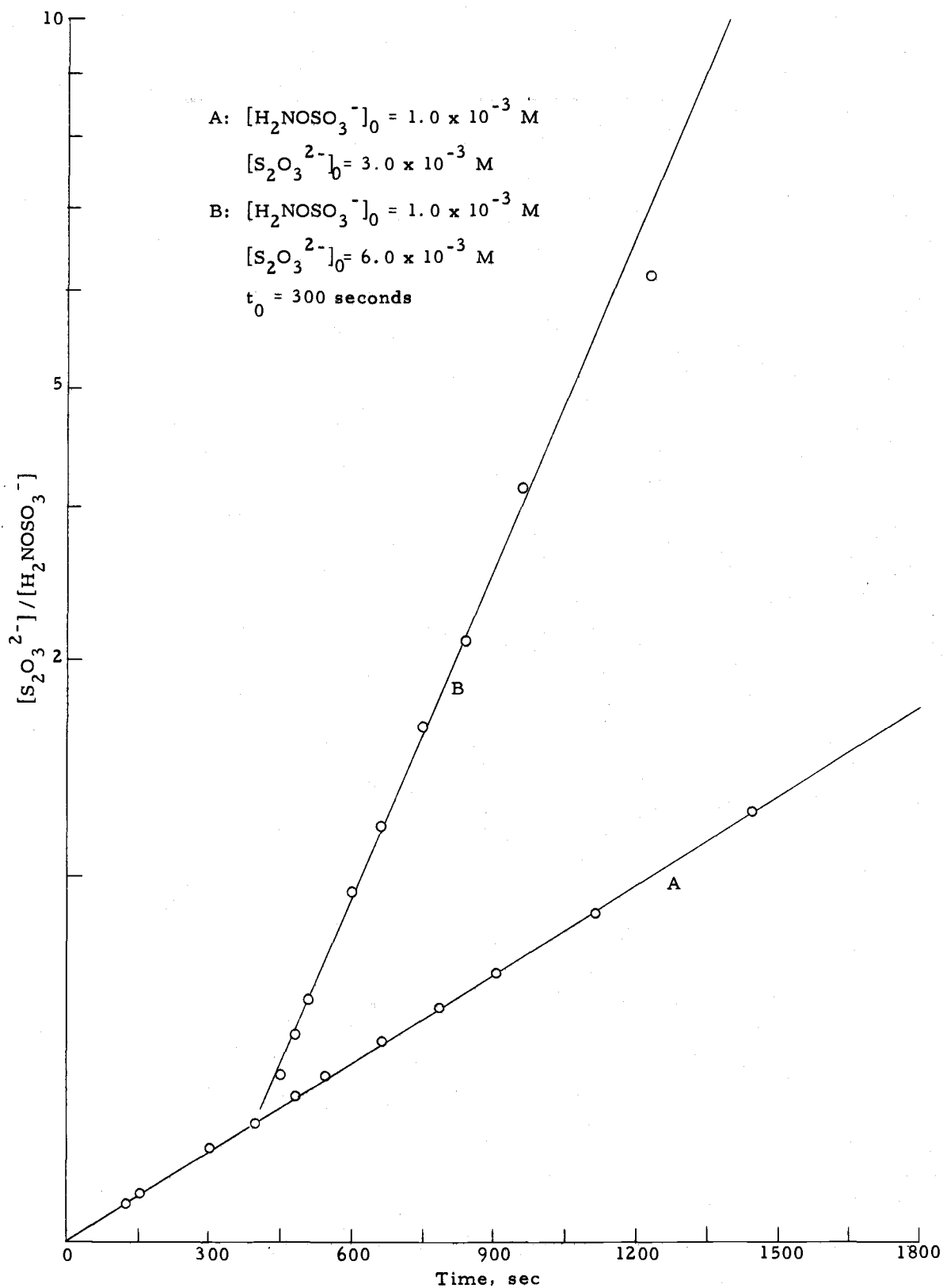
Figure 6. Second-order plots for the thiosulfate-hydroxylamine-O-sulfonate ion
reaction at μ = 0.1 M at 20.34°. and at pH 4.75 in water.

Stoichiometry

The reaction is believed to occur according to the following

equations:

(46) $\qquad S_2O_3^{2-} + H_2NOSO_3^- \xrightarrow{\text{r. d.}} H_2NSSO_3^- + SO_4^{2-}$

(47) $\qquad S_2O_3^{2-} + H_2NSSO_3^- + H^+ \xrightarrow{\text{fast}} S_4O_6^{2-} + NH_3$
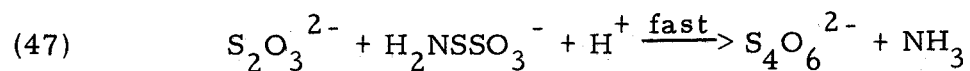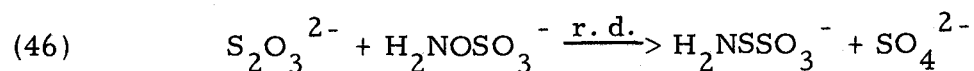
In order to provide evidence in support of the above equations, the

intermediate thiohydroxylamine-S-sulfonate was prepared as described

in the Experimental Section. It was also shown that reaction 47 was

retarded by decreasing the H^+ concentration and, eventually, the

reaction could be stopped after the rate-determining step at pH higher

than 9. The uv spectrum of thiohydroxylamine-S-sulfonate, which is

shown in Figure 7, was scanned from 320 nm to 240 nm and ε_{270} was

calculated to be 55 $M^{-1}cm^{-1}$. For tetrathionate, ε_{270} was calculated

to be 316 $M^{-1}cm^{-1}$ (36) and ε_{270} for thiosulfate was calculated to be

16 $M^{-1}cm^{-1}$.

The stoichiometry was further proved by the following spectro-

photometric study. Initial absorbances A_0 for thiosulfate and thio-

hydroxylamine S-sulfonate were calculated using ε_{270} values obtained

from the uv spectrum and compared with the values obtained experi-

mentally in the kinetic runs. Final absorbance, A_∞, was also
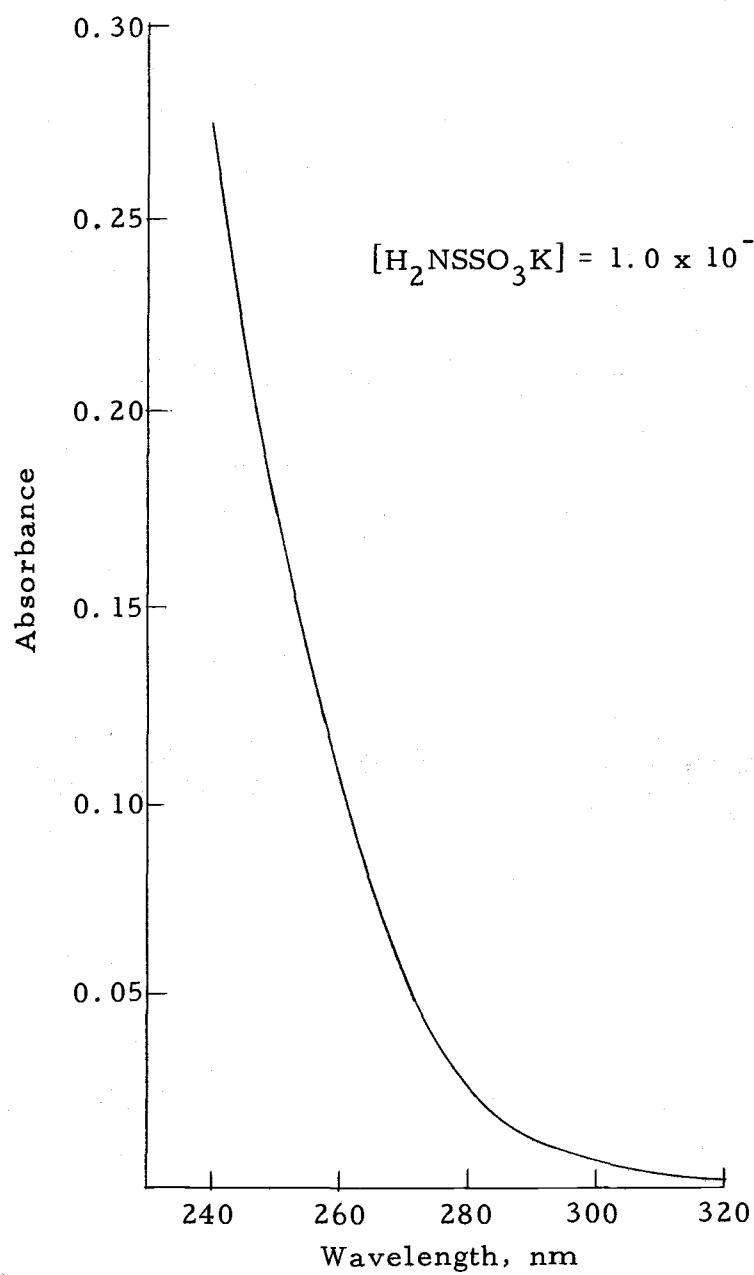
Figure 7. Uv spectrum of potassium thiohydroxylamine-S-sulfonate in water.

calculated and compared with the values found experimentally

in the kinetic runs of either hydroxylamine-O-sulfonate

ion and thiosulfate or thiohydroxylamine-S-sulfonate and thiosulfate.

The results are summarized below:

Abs (calc)	Abs (obs)	$10^3[H_2NOSO_3^-]_0$, M	$10^3[S_2O_3^{2-}]$ M	pH
$A_0 = 0.048$	$A_0 = 0.049$	1.0	3.0	<7
$A_\infty = 0.332$	A_∞ 0.327			
$A_0 = 0.048$	$A_0 = 0.049$	5.0	3.0	>9
$A_\infty = 0.165$	$A_\infty = 0.175$			
$A_0 = 0.032$	$A_0 = 0.036$	6.0	2.0	<7
$A_\infty = 0.316$	$A_\infty = 0.314$			
		$10^3[H_2NSSO_3^-]_0$, M		6 < pH < 7
$A_0 = 0.103$	$A_0 = 0.113$	1.0	3.0	
$A_\infty = 0.348$	$A_\infty = 0.345$			

The discrepancy between A_∞(calc) and A_∞(obs) for the reaction at

pH >9 of hydroxylamine-O-sulfonate and thiosulfate was found to be

larger in slower reactions. Small production of tetrathionate in the

reaction is believed to be causing the differences in absorbances.

At higher concentration of thiosulfate (6.0 x 10^{-3} M), the reac-

tion never seems to reach a stable infinity reading. After carefully

examining the data, it was found that, in fact, a stable infinity reading

was reached but that it was not stable for more than 30-60 min. After

that time, the absorbance started to increase because of the reaction

of thiosulfate and tetrathionate which, under the conditions of the experiment, is catalyzed by H^+ to form the more highly absorbing species $S_5O_6^{2-}$. This conclusion was reached after a description of that reaction was found in the literature (37, 38). The rate constant for the above reaction is very small compared to the one found in our study and cannot by any means, affect our results. Reproducible data at lower concentrations of thiosulfate reinforce this conclusion. Except under the conditions described above, thiosulfate and tetra-thionate were found to be stable in solution for as long as 3-4 hours.

Temperature Effect

In order to obtain the activation parameters, kinetic runs were made at 10.38°, 20.34°, and 29.74°. The temperature dependence of the second order rate constant is summarized in Table 7. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from data listed in Table 7 using Equation 48 from transition state theory (33).

(48) $\qquad \ln(k_2/T) = \ln(k_b/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$

Figure 8 shows the temperature dependence of the second-order rate constant

$$\Delta H^{\ddagger} = 10.8(\pm 0.1) \text{ kcal/mole}$$

$$\Delta S^{\ddagger} = -22.8(\pm 0.5) \text{ eu}$$

Table 7. Temperature dependence of the thiosulfate-hydroxylamine-
O-sulfonate ion reaction at $\mu = 0.1$ M and at pH 4.75 in
water.

Temp (°C)	$10^3[H_2NOSO_3^-]_0$, M	$10^3[S_2O_3^{2-}]_0$, M	k_2, $M^{-1}sec^{-1}$
10.38	1.01	3.02	0.266
	1.01	6.04	0.277
	1.08	3.01	0.269
	1.08	3.01	0.275
20.34	1.00	3.00	0.550[a]
29.74	1.00	3.02	0.986
	1.12	3.00	0.984
	1.12	3.00	1.001

[a]This value is an average and was entered four times in the least-
squares calculation to give the data at each temperature equal weight.
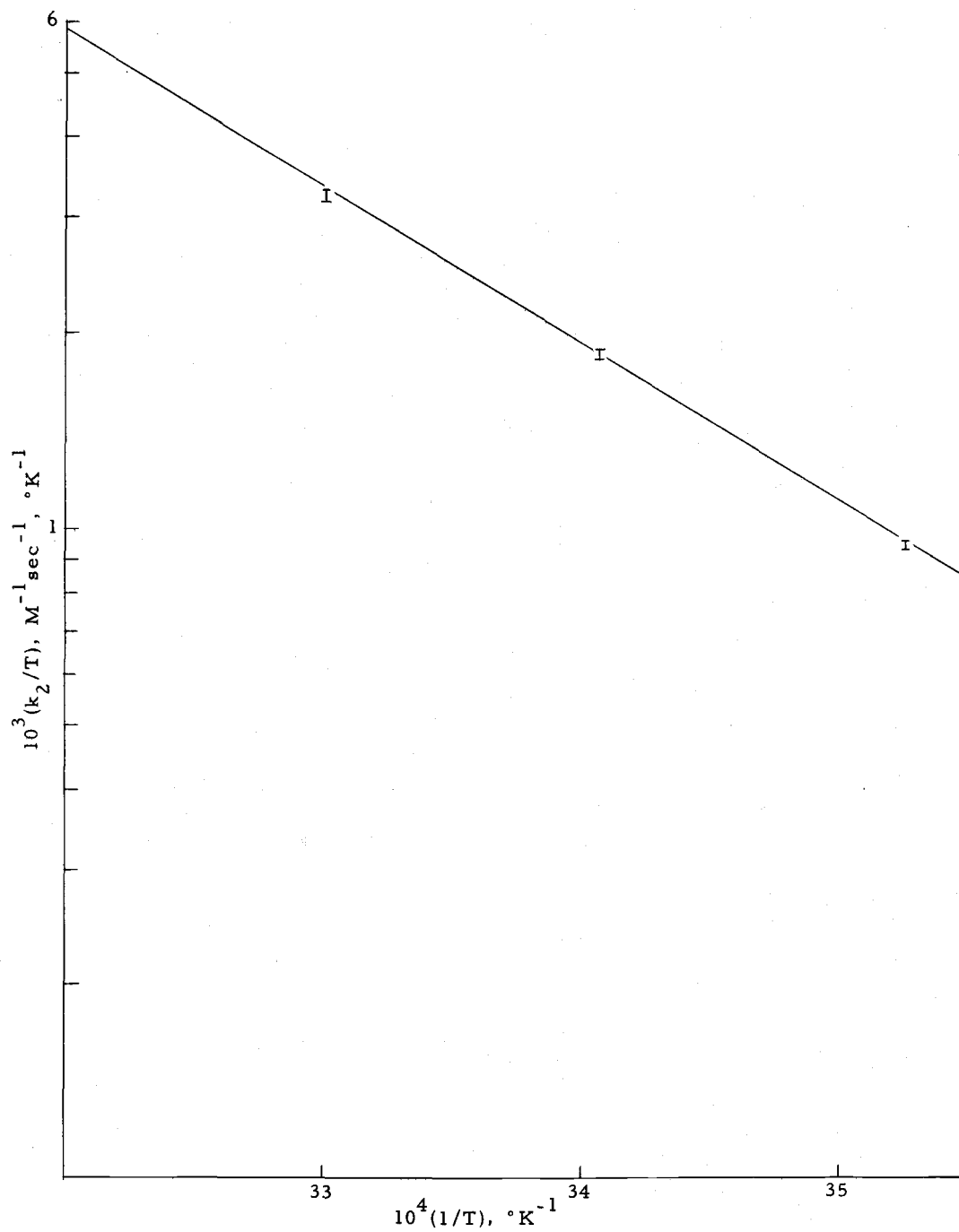
Figure 8. Temperature dependence of the second-order rate constant for the thiosulfate-hydroxylamine-O-sulfonate ion reaction.

The above values were calculated using a least-squares computer

program described in Appendix I.

Deuterium Isotope Effect

The reaction was studied in 99.8% deuterium oxide. The aver-

age rate constant calculated from data in Table 6 was found to be:

$$k_2(D_2O) = 0.491(\pm 0.002) \ M^{-1} sec^{-1}$$

The ratio of the second-order rate constants in non-deuterated and

deuterated solvent was found to be:

$$k_2(H_2O)/k_2(D_2O) = 1.1(\pm 0.05)$$

Hydrogen-Ion Dependence of the Thiohydroxylamine-S-sulfonate-
thiosulfate Reaction

As stated before, the reaction of hydroxylamine-O-sulfonate ion

and thiosulfate occurs in two steps. The first step, represented by

Equation 46, is the rate-determining step which yields the intermedi-

ate. The intermediate, as seen from Equation 47, will undergo

attack by another thiosulfate, if hydrogen ions are present to give the

expected product, tetrathionate. During the kinetics runs, it was

found that, at pH higher than 7, the reaction is greatly retarded and

that, at pH higher than 9, the second step did not occur at all. The

intermediate having been isolated, it was decided to try to show that,

in fact, the second step was acid dependent and, furthermore, that

this dependency was first order. Fortunately, it was found that rate

constants for this process could be determined in the very narrow

range of pH 6.87-7.84 using the proper buffers. Data for these

experiments are summarized in Table 8.

Assuming the following rate law;

$$(49) \qquad \frac{Rate}{[H_2NSSO_3^-][S_2O_3^{2-}]} = k_{(obs)} = k_r K_A^{-1}[H^+] + k_{(H_2NSSO_3^-)}$$

where K_A is the dissociation constant of $H_3N^+SSO_3^-$ and k_r is the

rate constant for $H_2NSSO_3^- + S_2O_3^{2-} + H^+$ reaction. Furthermore, if the

reaction is first order in $[H^+]$ one can see that a plot of $k_{(obs)}$ versus

$[H^+]$ should be linear. The intercept should be very near zero

assuming $k_{(H_2NSSO_3^-)} = 0.0$ because of the fact that it was shown that

reaction was stopped at the intermediate at pH higher than 9. Further-

more a plot of log $k_{(obs)}$ versus pH should give a value $|1.0|$, for the

slope, if the reaction is first order in H^+ concentration. Calculations

using the SIMLIN program, described in Appendix I, were done using

data summarized in Table 8. From Figure 9 it can be seen that the

intercept value found is equal to -0.152 ± 0.110. Furthermore a

value of $|1.007 ± 0.028|$ was found for the slope when log $k_{(obs)}$ was

plotted versus pH. Within the experimental error, the above results

proved without doubt that the thiosulfate-thiohydroxylamine-S-sulfonate

Table 8. Kinetic data for the thiosulfate-thiohydroxylamine-S-
sulfonate reaction at $\mu = 0.1$ M and at 20.34° in water.

$10^3[S_2O_3^{2-}]_0$, M	$10^3[H_2NSSO_3^-]_0$, M	pH	k_2, $M^{-1}sec^{-1}$
2.00	0.849	6.87	10.04
2.00	0.849	6.87	9.39
2.00	0.849	7.42	2.49
3.02	1.00	7.43	2.39
3.01	1.00	7.43	2.47
3.00	1.00	7.40	2.56
3.02	1.00	7.87	0.997
3.01	1.00	7.87	0.975
3.00	1.00	7.84	0.928
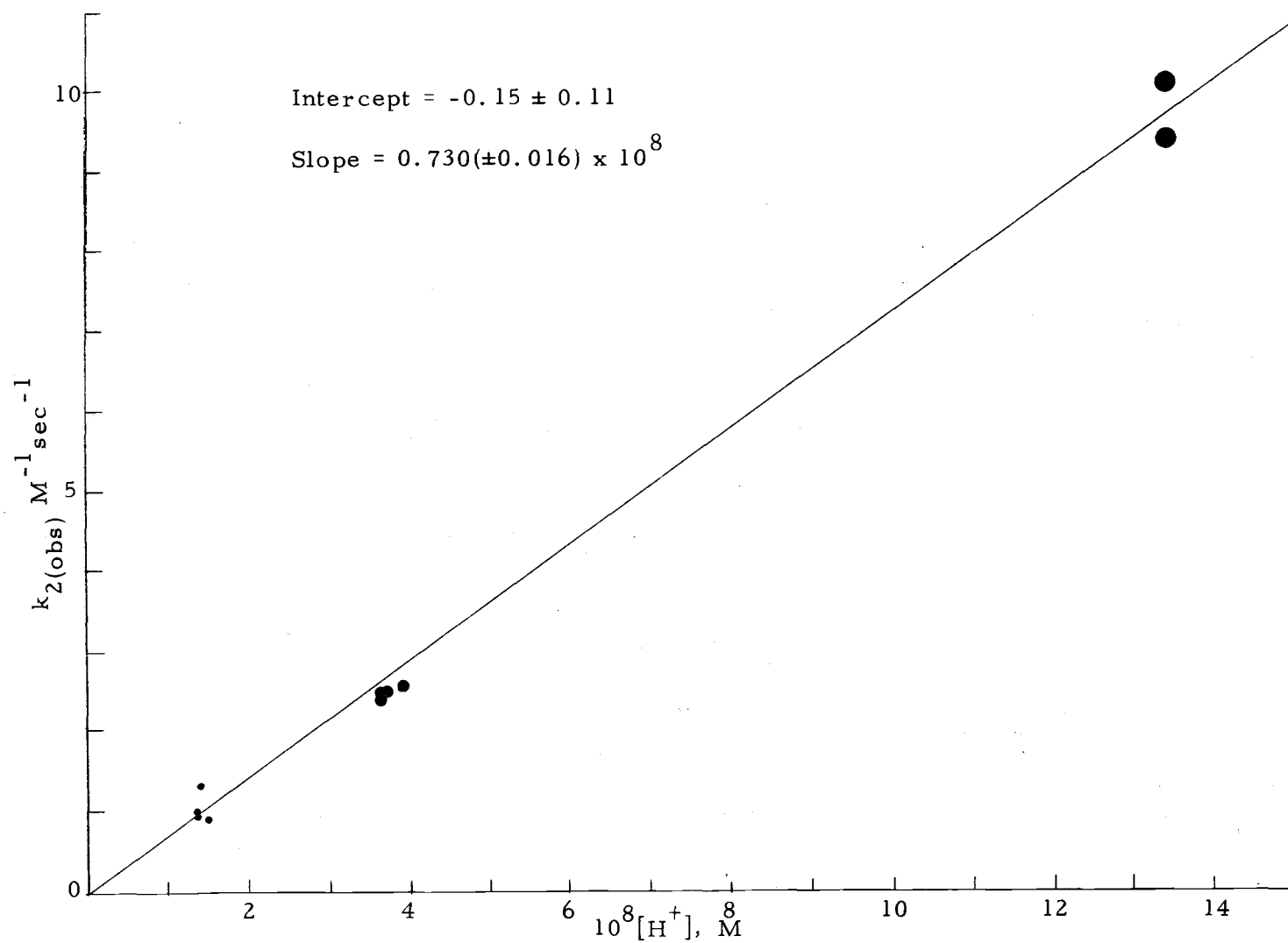
Figure 9. $k_{2(obs)}$ for the thiosulfate-thiohydroxylamine-S-sulfonate reaction as a function of H^+ concentration.

reaction is first order in $[H^+]$.

Determination of the pK_A of Thiohydroxylamine-S-sulfonic Acid

From the same rate law and the results of the above calculations, it would be possible to find the value of k_r if K_A were known. The K_A for the following equilibrium was determined by measuring the pH of a solution containing 0.0200 M H_2NSSO_3K and 0.0104 M $HClO_4$.

$$(50) \qquad H_2NSSO_3H \rightleftharpoons H^+ + H_2NSSO_3^-$$

A value of $K_A = 8.2(\pm 0.1) \times 10^{-2}$ was determined from the observed pH equal to 2.10. Using Equation 51, and substituting the K_A value found and the value of the slope $= 0.730(\pm 0.016) \times 10^8$ from Figure 9,

$$(51) \qquad slope = k_r K_A^{-1}$$

k_r was found to be $k_r = 0.59(\pm 0.03) \times 10^7 M^{-1} sec^{-1}$, so the rate of the attack of thiosulfate at the sulfur of $H_3N^+SSO_3^-$ is 10^7 times faster than the attack of the same nucleophile at the nitrogen center of $H_2NOSO_3^-$.

Ion-Pair Effects in the Reaction of Hydroxylamine-O-sulfonate to Form Tetrathionate

It is known that ion pairing occurs when potassium thiosulfate is dissolved in water,

(52) $$S_2O_3K^- \rightleftharpoons K^+ + S_2O_3^{2-}$$
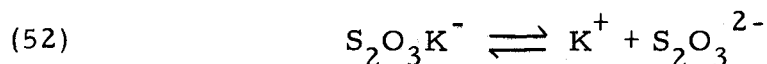
A dissociation constant, $K = 0.12$, was found from a spectrophotometric study (39) of the above equilibrium in water. This value of 0.12 was obtained under temperature and ionic strength conditions similar to those in our study. Because of the difference of charge on $S_2O_3K^-$ and $S_2O_3^{2-}$, it was expected that their reactivity toward $H_2NOSO_3^-$ would be different and that the rate constant for the system would be a combination of $k_{2(S_2O_3^{2-})}$ and $k_{2(S_2O_3K^-)}$. The following experiments at pH 4.75 were made in order to break the rate constant into its components. The reactions were carried out as usual, using different ratios of $[K^+]$ to $[(C_2H_5)_4N^+]$ in solution. It was assumed that $(C_2H_5)_4N^+$ does not ion-pair with thiosulfate. $(C_2H_5)_4NClO_4$ was made but was found to be of no use to us because of its insolubility under the conditions of the experiments. An attempt was made to prepare $(C_2H_5)_4NOOCCH_3$ but the product obtained, which was of unknown purity, again was not soluble under the experimental conditions. It was decided to use $(C_2H_5)_4NCl$ as the salt, knowing that chloride does

Table 9. Kinetic data for the ion-pairing effect in the thiosulfate-hydroxylamine-O-sulfonate ion reaction at μ = 0.1 M at 20.34° and at pH 4.75 in water.

$10^3[S_2O_3^{2-}]_0$, M	$10^3[H_2NOSO_3^-]_0$, M	$10^2[KClO_4]$, M	$10^2[(C_2H_5)_4NCl]$, M	k_2, $M^{-1}sec^{-1}$
3.00	1.01	7.0	---	0.549
3.00	1.01	---	7.0	0.452
3.00	1.01	---	4.1	0.501
2.99	0.992	4.1	---	0.524
2.99	0.992	---	4.1	0.503
2.99	0.992	---	7.0	0.452
2.98	1.01	8.9	---	0.557[a]
2.98	1.01	---	8.9	0.444[a]
3.00	1.01	8.9	---	0.552[a]
3.00	1.01	---	8.9	0.445[a]

[a]pH 2.7

not react with hydroxylamine-O-sulfonate ion. (See Results of the

Iodide Study).

Determination of $k_{2(S_2O_3{}^{2-})}$ and $k_{2(S_2O_3K^-)}$ was carried out

using the modified rate law,

$$(53) \qquad \frac{Rate}{[H_2NOSO_3{}^-]} = k_1[S_2O_3{}^{2-}] + k_2[S_2O_3K^-]$$

where $k_1 = k_{2(S_2O_3{}^{2-})}$ and $k_2 = k_{2(S_2O_3K^-)}$ was assumed. The

total concentration of thiosulfate in solution can be expressed as

$$(54) \qquad \Sigma[K_2S_2O_3] = [S_2O_3{}^{2-}] + [S_2O_3K^-]$$

Rearranging the above equations in the following way,

$$(55) \qquad [S_2O_3{}^{2-}] = \Sigma[K_2S_2O_3]/(K_1+1/K_1)$$

$$(56) \qquad [S_2O_3K^-] = \Sigma[K_2S_2O_3]/(1+K_1)$$

where

$$(57) \qquad K_1 = \frac{K}{[K^+]} = \frac{[S_2O_3{}^{2-}]}{[S_2O_3K^-]}$$

$$(58) \qquad \frac{Rate}{\Sigma[K_2S_2O_3][H_2NOSO_3{}^-]} = k_{(obs)} = \frac{k_1}{(K_1+1)/K_1} + \frac{k_2}{K_1+1}$$

we obtain Equation 59 which has the form $y = mx + a$ where m, the

slope, $= k_1$ and a, the intercept, $= k2$.

(59) $$(K_1+1)k_{2(obs)} = k_1K_1 + k_2$$

Using the data from Table 9 the values of $k_{2(S_2O_3^{2-})}$ and $k_{2(S_2O_3K^-)}$ were found, using SIMLIN to calculate the least-squares fit of the data plotted in Figure 10. The values of the rate constants are:

$k_{2(S_2O_3^{2-})} = 0.433(\pm0.008)$ $M^{-1}sec^{-1}$ and

$k_{2(S_2O_3K^-)} = 0.653(\pm0.027)$ $M^{-1}sec^{-1}$.

Using the equilibrium constant, $K = 0.12$ and Equation 53, the concentration of $S_2O_3^{2-}$ and $S_2O_3K^-$ were determined in a random sample of our regular runs. The rate constant, thus calculated was compared with that observed and they were found to agree within experimental error. Because of the charges involved the lower value for the rate constant $k_{2(S_2O_3^{2-})}$ for the non ion-pair thiosulfate was expected.

Reactions at Lower pH

Unfortunately thiosulfate undergoes a self oxidation-reduction reaction at lower pH, which leads to the production of sulfur, so runs in more acidic solutions were impossible to perform to the extent that they were in the iodide study. However, hydroxylamine-O-sulfonic acid, being a fairly strong acid, a few runs where the
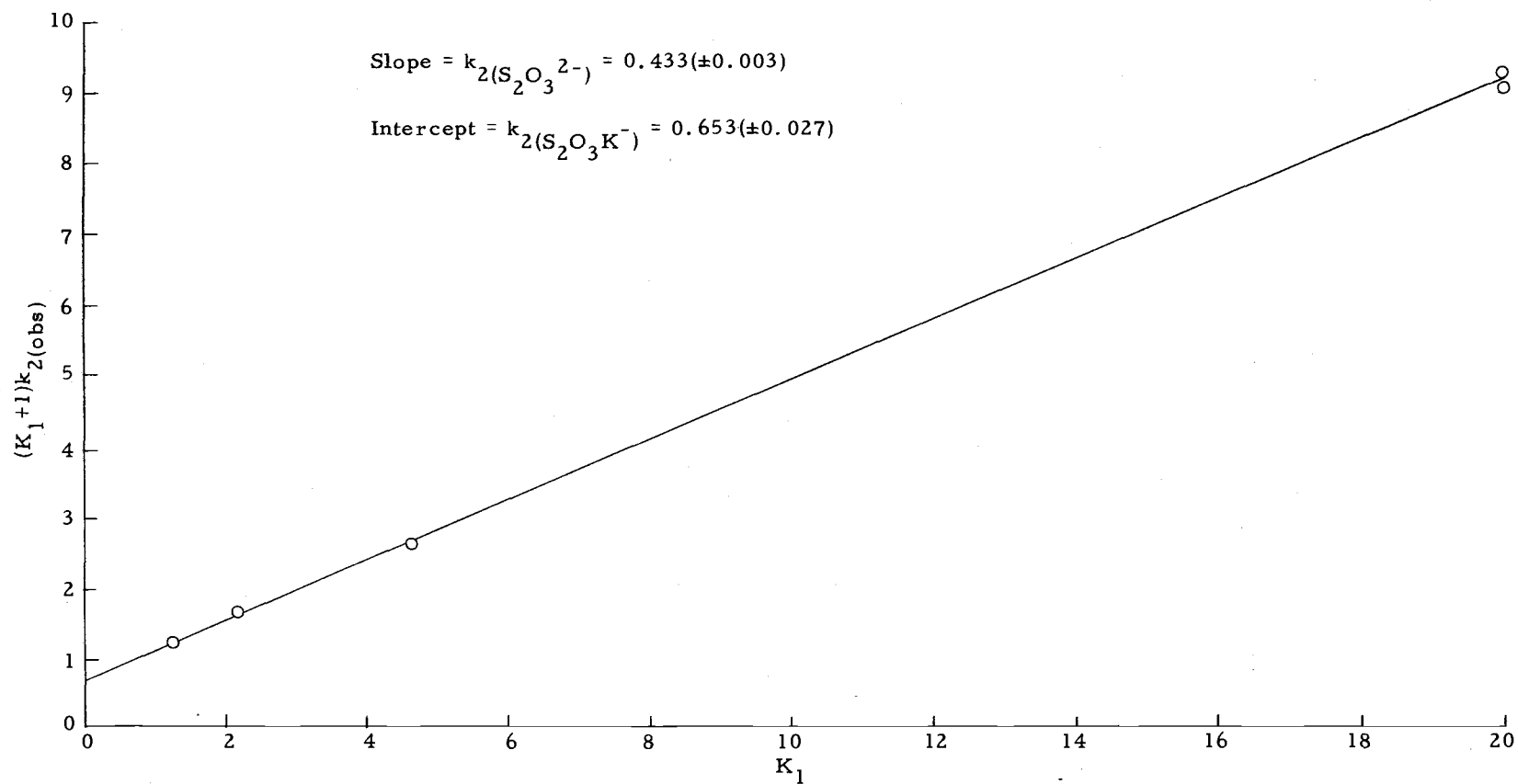
Figure 10. Plot to determine the ion-pairing effect on the thiosulfate-hydroxylamine-sulfonate ion reaction at $\mu = 0.1$ M, 20.34° and at pH 4.75 in water

hydroxylamine-O-sulfonic acid concentration was fairly high

(1.0×10^{-2} M) were made to observe the behavior of the reaction at

lower pH. The reactions observed were very fast and the thiosulfate

in solution was consumed by $H_2NOSO_3^-$ before it underwent the self

oxidation-reduction described above. The accuracy of the data was

less than in the regular runs because the reaction had to be carried out

too fast. The rates ($\pm 10\%$) were obtained in a pH range too small and

too near pH 3, to be able to conclude that the rate constant changes in

one direction or the other at pH < 3.

Thiourea-hydroxylamine-O-sulfonic Acid Reaction

The reaction was studied by following the change in absorbance

of thiourea at 235 nm, $\mu = 0.1$ M and T = 20.34° in water. In order to

check the stoichiometry, a few runs under the same conditions were

studied as a second-order reaction. The pH range was calculated to

be 1.00-11.0 using the appropriate buffers or added acid to achieve

the desired pH. In all the runs thiourea was always the limiting

reagent. The rate law was found valid in the pseudo-first-order reac-

tion for the following range of concentrations;

$[H_2NOSO_3^-] = (1.0-6.0) \times 10^{-3}$ M and $[(H_2N)_2C=S] = (2.0-6.0) \times 10^{-5}$ M.

In the second-order reaction, the rate law was found valid for the fol-

lowing range of concentrations: $[H_2NOSO_3^-] = (1.0-4.0) \times 10^{-4}$ M and

$[(H_2N)_2C=S] = 6.0 \times 10^{-5}$ M.

Table 10. Kinetic data for the thiourea-hydroxylamine-O-sulfonate ion reaction at μ = 0.1 M at 20.34° and at different pH values in water.

$10^3[H_2NOSO_3^-]_0$, M	$10^5[(H_2N)_2C{=}S]_0$, M	pH	k_2, $M^{-1}sec^{-1}$
0.99	2.01	4.75	1.67
1.05	3.00	4.75	1.68
0.99	4.03	4.75	1.70
1.03	4.01	4.75	1.60
0.99	4.01	4.75	1.58
1.00	3.94	4.75	1.64
1.05	6.00	4.75	1.64
2.00	3.94	4.75	1.67
2.07	4.01	4.75	1.67
3.03	2.00	4.75	1.62
6.06	2.00	4.75	1.64
1.03	4.01	4.05	1.67
0.99	4.01	4.05	1.56
2.07	4.01	4.05	1.64
1.99	4.01	4.05	1.62
0.99	4.01	5.35	1.57
1.99	4.01	5.35	1.63
1.01	4.16	6.41	1.64
1.06	4.14	6.41	1.65
1.06	4.14	7.21	1.63
1.01	4.16	7.21	1.64
1.06	4.14	7.76	1.61
1.01	4.16	7.76	1.63
1.01	3.98	8.46	1.65
2.02	3.98	8.46	1.69
1.06	4.14	8.46	1.61
1.01	4.16	8.46	1.64
1.06	4.14	9.06	1.56
1.01	4.16	9.06	1.63
0.98	4.09	11.0	1.66
0.98	4.09	11.7	1.62

Table 10.   Continued.

$10^3[H_2NOSO_3^-]_0$, M	$10^5[(H_2N)_2C{=}S]_0$, M	pH	k_2, $M^{-1}sec^{-1}$
0.125	5.93	8.46	1.62[a]
0.184	5.93	4.75	1.66[a]
0.249	5.93	8.46	1.61[a]
0.368	5.93	4.75	1.68[a]
0.355	5.78	8.46	1.68[a]
0.98	4.00	5.75	0.74[b]
1.07	4.00	5.75	0.74[b]
1.97	4.00	5.75	0.76[b]
0.97	4.01	4.75	1.48[c]
1.66	4.01	4.75	1.57[c]
1.70	4.01	4.75	1.53[c]

[a]Found from a second-order rate law.

[b]Runs in 50 wt % methanol-water.

[c]Runs in D_2O.

Determination of the Rate Law

A $\ln(A_t - A_\infty)$ versus time plot is shown in Figure 11. The linear relationship observed indicates that the reaction is pseudo-first-order.

(60) $$\text{Rate} = k_1[(H_2N)_2C=S]$$

From the kinetics data summarized in Table 10 a constant value of $k_2 = 1.63 \pm 0.07 \, M^{-1}sec^{-1}$ was obtained with different concentrations of hydroxylamine-O-sulfonate ion, which remained constant during the course of the reaction. The reaction was then assumed to be first order in hydroxylamine-O-sulfonate ion and the rate law was formulated as follows:

(61) $$\text{Rate} = k_2[H_2NOSO_3^-][(H_2N)_2C=S]$$

Stoichiometry

The reaction is believed to occur according to the following equation:

(62) $$(H_2N)_2C=S + H_2NOSO_3^- \xrightarrow{\text{r.d.}} (H_2N)_2CSNH_2^+ + SO_4^{2-}$$
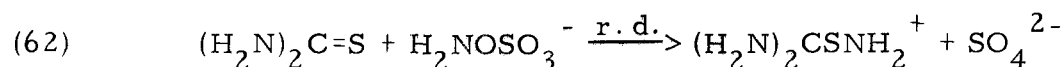
A second step, which would give the more stable product formamidine-disulfide ion is described by Equation 63. The reasons why this

A: $[H_2NOSO_3^-]_0 = 1.04 \times 10^{-3}$ M

$[(H_2N)_2C=S]_0 = 4.0 \times 10^{-5}$ M

B: $[H_2NOSO_3^-]_0 = 2.08 \times 10^{-3}$ M

$[(H_2N)_2C=S]_0 = 4.0 \times 10^{-5}$ M
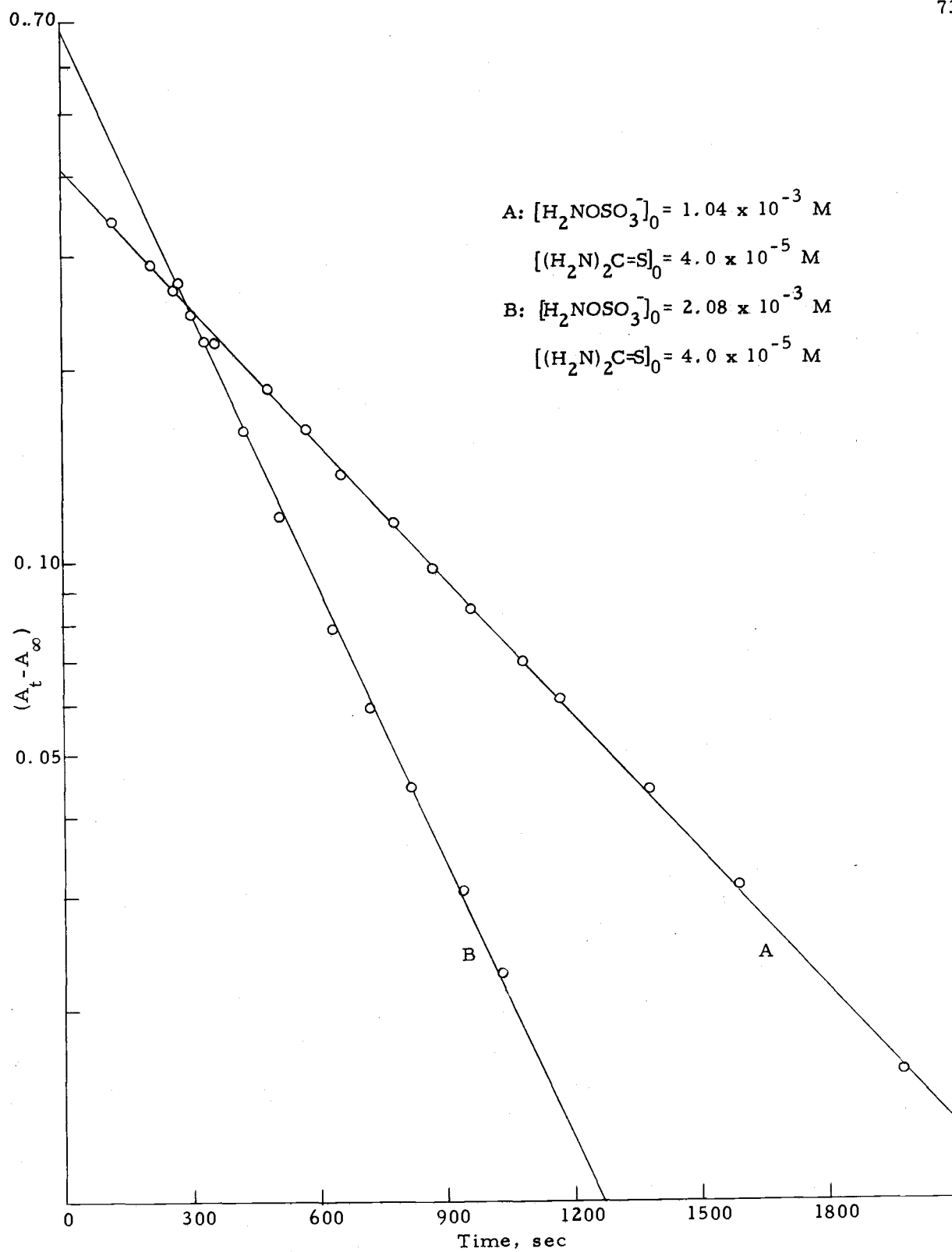
Figure 11. Pseudo-first-order plots for the thiourea-hydroxylamine-O-sulfonate ion
reaction at μ = 0.1 M, at 20.34°, and at pH 4.75 in water.
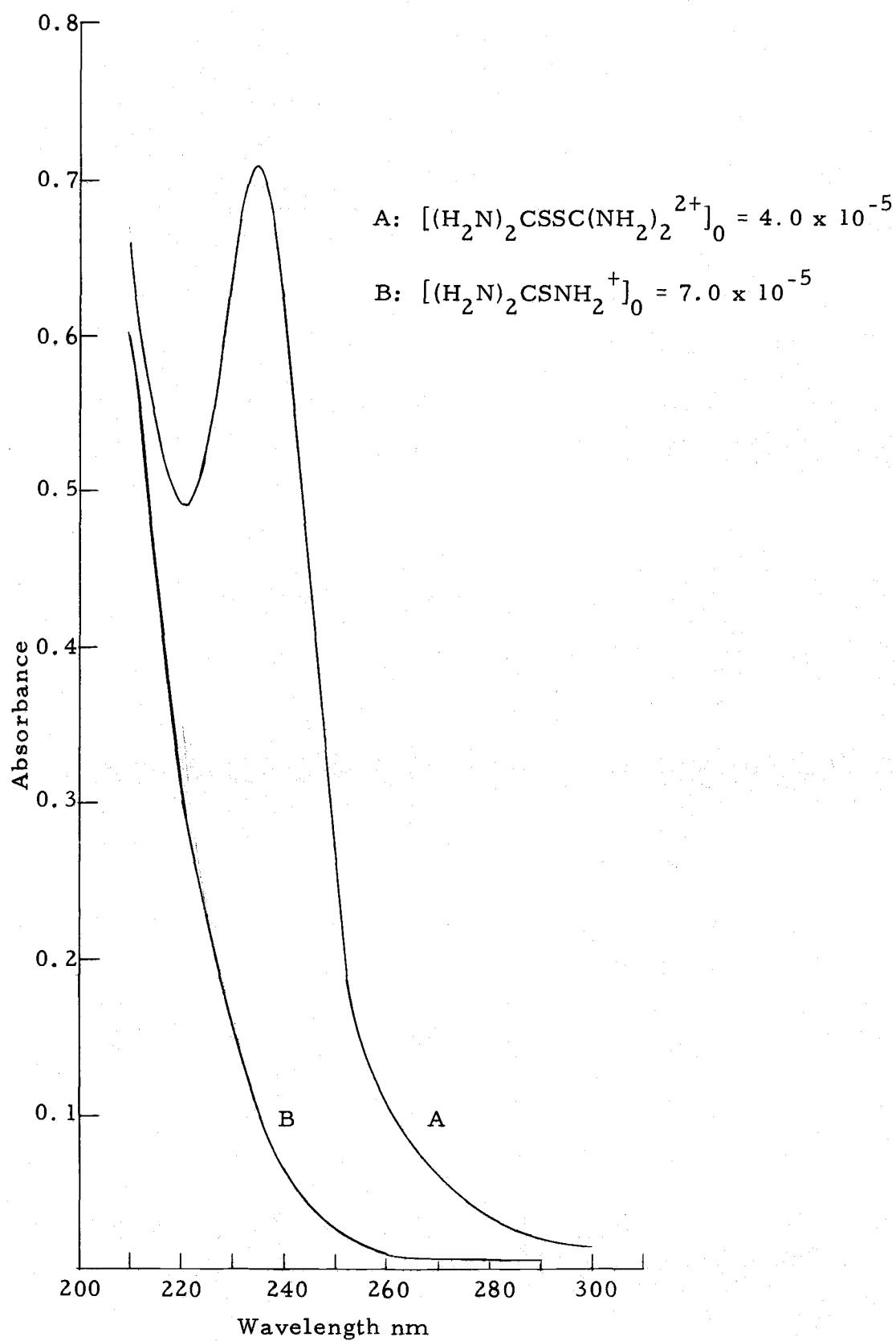
Figure 12. Uv spectrum of (A) formamidinedisulfide dichloride and of (B) S-aminoisothiouronium sulfate in water.

second step does not occur will be explained in the Discussion Section.

(63) $(H_2N)_2CSNH_2^+ + (H_2N)_2C=S + H^+ \longrightarrow (H_2N)_2CSSC(NH_2)_2^{2+} + NH_3$
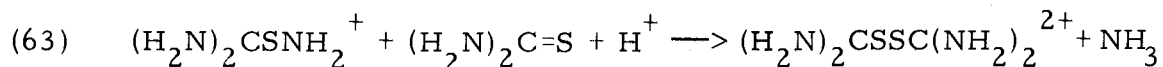
By analogy with the thiosulfate reaction, one more thiourea should

attack the intermediate and produce the well-characterized species

formamidinedisulfide cation (28). No evidence was found that the step

described by Equation 63 was occurring, when thiourea was the limit-

ing reagent. This conclusion was reached by the results of the follow-

ing experiment.

At 235 nm many species absorb to a certain extent including the

salts used in our system to achieve proper buffer and ionic strength.

The absorbance of the salts did not affect kinetics because their con-

centrations, and thus their absorbances, remained constant during the

course of the reaction. The kinetics experiments were designed such

that all the thiourea was consumed so that the only absorbing species

at the end of the reaction, other than the added salts, would be

$(H_2N)_2CSNH_2^+$ or the formamidinedisulfide cation. As expected, the

two products postulated have different molar extinction coefficients at

235 nm. In the abundant literature on formamidinedisulfide (28) no

uv spectrum was found; $(H_2N)_2CSNH_2^+$ is, we believe, a new species.

For these reasons it was decided to synthesize both compounds

in order to compare their molar extinction coefficients with the ones

calculated for the product of our reaction. The syntheses of the two

$[H_2NOSO_3^-]_0 = 1.8 \times 10^{-4}$ M

$[(H_2N)_2C=S]_0 = 5.9 \times 10^{-5}$ M
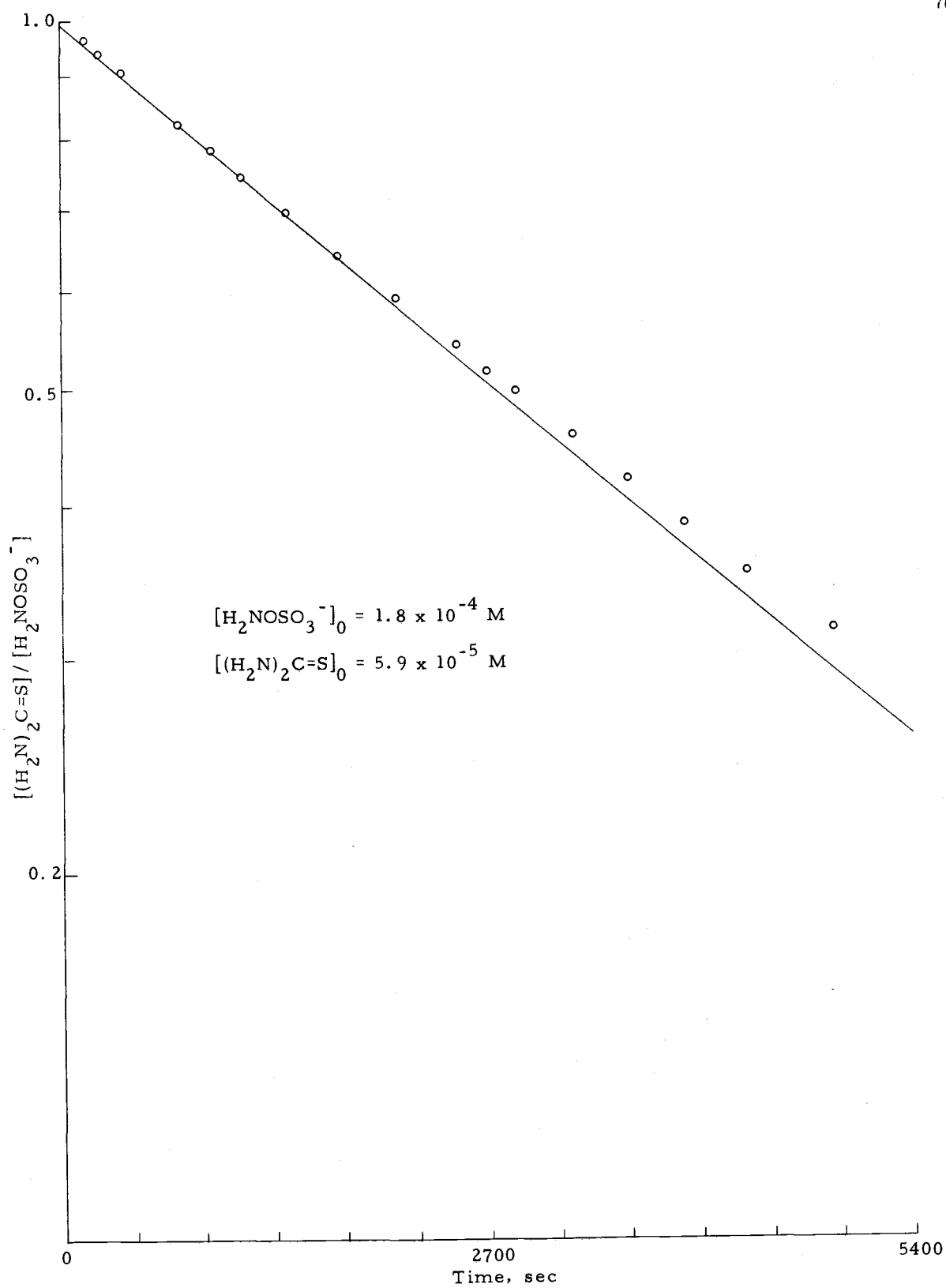
Figure 13. Second-order plot for the thiourea-hydroxylamine-O-sulfonate ion reaction at μ = 0.1 M at 20.34° and at pH 4.75 in water.

compounds have been described in the Experimental section.

Both products were scanned in the uv in order to determine their molar extinction coefficients. The traces obtained are shown in Figure 12 and the ε_{235} values obtained are summarized below:

	Conc. (M)	abs	ε_{235} $(M^{-1}cm^{-1})$
$(H_2N)_2CSNH_2^+$	7.05×10^{-5}	0.105	1,490
$[(H_2N)_2CS]_2^{2+}$	4.0×10^{-5}	0.710	17,800
Product of the reaction[1]	3.94×10^{-5}	0.060	1,520

From the above results, and from the ε value calculated for the product of the reaction it can be assumed that $(H_2N)_2CSSC(NH_2)_2^{2+}$ is not the product of the reaction. This fact can further be proved by arranging the initial concentrations so that both reactants are consumed in a second-order process. It should be possible to distinguish between a reaction where only one mole of thiourea per mole of hydroxylamine-O-sulfonate ion is used up instead of two. This may be better understood by comparing stoichiometric Equations 64 and 65.

(64)   A + 2B ——> product

(65)   A + B ——> product

The integrated forms of the rate laws for the above stoichimetries

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[1] Obtained by following a reaction where the absorbances of the salts were cancelled out.

are, respectively,

(66) $\quad (b_0-2a_0)^{-1} \ln(a_0/b_0)(b_0-2x)/(a_0-x) = kt$

(67) $\quad (b_0-a_0)^{-1} \ln(a_0/b_0)(b_0-x)/(a_0-x) = kt$

From Figure 13 it can be seen, as expected, that the plot of the data

for the second-order reaction, where two moles of thiourea were

assumed to be consumed, deviates from linearity. However, the plot,

which is not shown, for which only one mole of thiourea was assumed

to be consumed is perfectly linear. This result eliminated the

formamidinedisulfide cation as the product of the reaction.

Temperature Effect.

In order to obtain activation parameters, kinetics runs were

made at $10.37°$, $20.34°$, and $29.67°$. The temperature dependence of

the second-order rate constant is summarized in Table 11. $\Delta H^{\ddagger}$ and

$\Delta S^{\ddagger}$ were calculated from data listed in Table 11 using Equation 68

from transition state theory (33).

(68) $\quad \ln(k_2/T) = \ln(k_b/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$

Figure 14 shows the temperature dependence of the second-order rate

constant.

$$\Delta H^{\ddagger} = 7.4(\pm 0.2) \text{ kcal/mole}$$

$$\Delta S^{\ddagger} = -32.3(\pm 1.5) \text{ eu}$$

Table 11. Temperature dependence of the thiourea-hydroxylamine-O-sulfonate ion reaction at $\mu = 0.1$ M and at pH 4.75 in water.

Temp (°C)	$10^3[H_2NOSO_3^-]_0$, M	$10^5[(H_2N)_2C{=}S]_0$, M	k_2, $M^{-1}sec^{-1}$
10.38	2.01	4.03	0.977
	2.07	4.03	0.979
	4.01	4.03	1.04
	4.13	4.03	1.07
20.34	2.00	4.00	1.64[a]
29.74	0.36	4.03	2.50
	0.53	4.03	2.42
	0.72	4.03	2.42
	1.07	4.03	2.42

[a]This value is an average and was entered four times in the least-squares calculation to give the data at each temperature equal weight.
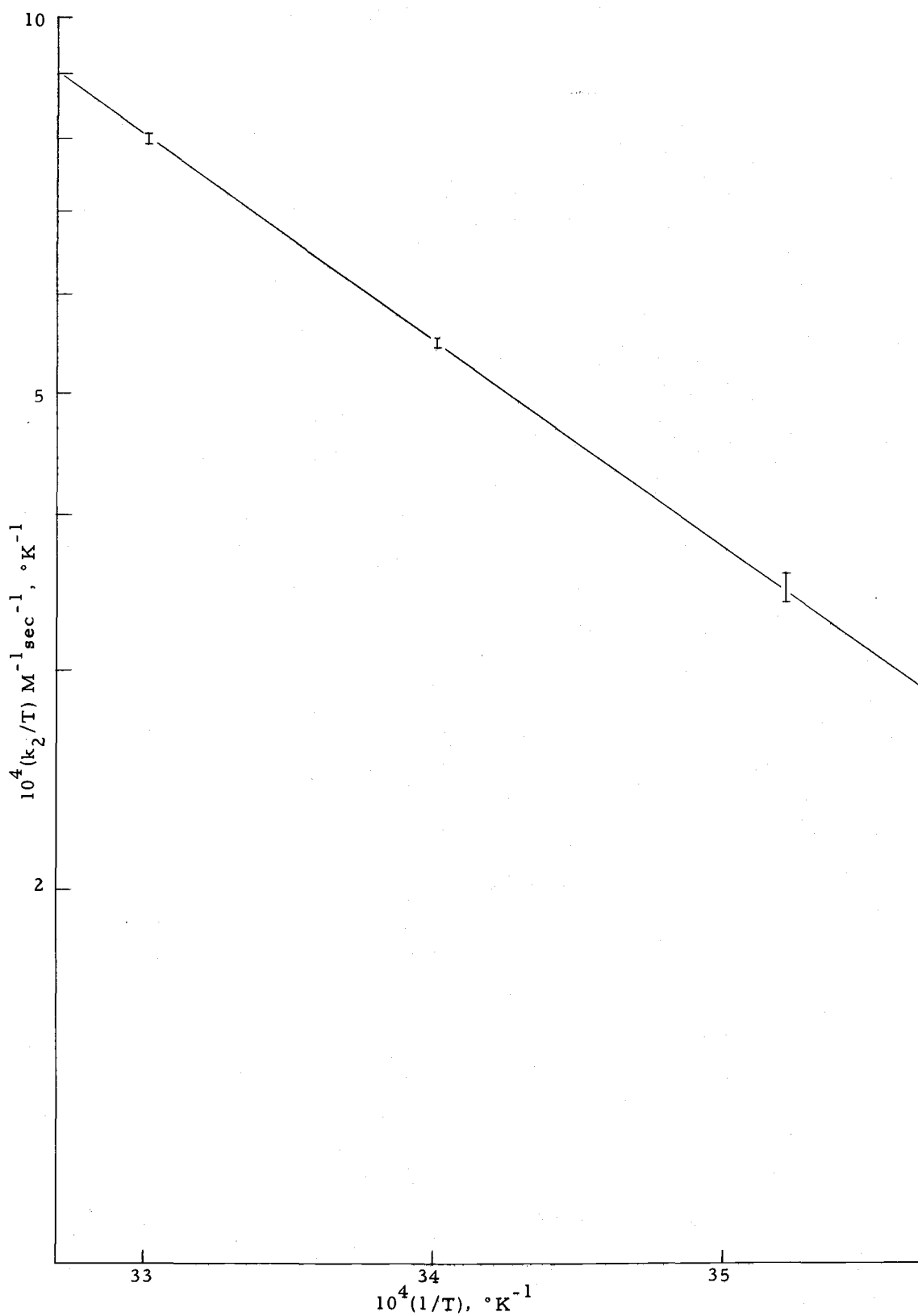
Figure 14. Temperature dependence of the second-order rate constant for the thiourea-
hydroxylamine-O-sulfonate ion reaction.

The above values were calculated using a least-squares computer

program described in Appendix I.

Deuterium Isotope Effect

The reactions were studied in 99.8% deuterium oxide. The

average rate constant calculated from data in Table 10 was found to be:

$$k_{2(D_2O)} = 1.53(\pm 0.05) \ M^{-1} sec^{-1}$$

The ratio of the second-order rate constants in non-deuterated and

deuterated solvent was found to be $k_2(H_2O)/(D_2O) = 1.1(\pm 0.1)$.

Solvent Effect

The reaction was also studied in 50 wt % methanol-water solu-

tion. The average rate constant calculated from data in Table 10 was

found to be: $k_2(H_2O-CH_3OH) = 0.75(\pm 0.01) \ M^{-1} sec^{-1}$.

Reactions at Lower pH

Because of the low proton basicity of thiourea (40), acid concen-

trations around pH 1.0 should not protonate the molecule. As in the

iodide study, it was expected that increasing concentration of H^+

would protonate the hydroxylamine-O-sulfonate ion only, and leave the

thiourea molecule unaffected so that a possible change of the rate

observed could be attributed to protonation of the

hydroxylamine-O-sulfonate ion only. Runs at lower pH were carried out. The rate constants calculated from data summarized in Table 12 were found to first increase, reach a plateau, and then decrease with a decrease in pH. Because of this unexpected behavior it was impossible to make calculations like those in the iodide study to find $k_{2(H_2NOSO_3H)}$ and K_A for hydroxylamine-O-sulfonic acid. We believe that changing the nucleophile from iodide to thiourea should not affect the protonation of hydroxylamine-O-sulfonate ion at lower pH. Surprisingly, the decrease in the rate observed, occurred at a lower pH than for the iodide.

Second-Order Reaction with Thiourea in Excess

Determination of the rate constant using the second-order rate law gave results in agreement with those obtained when the reaction was run in a pseudo-first-order manner only when thiourea was the limiting reagent. When hydroxylamine-O-sulfonate ion was the limiting reagent, it was impossible to get a rate constant. In order to observe a reaction, the thiourea concentration had to be increased. Because of the high molar extinction coefficient of thiourea at 235 nm, the reaction was followed at 260 nm. At first, a decrease in absorbance was observed but, after a while, the absorbance started to increase and in fact became larger than the initial absorbance. The rate at which the absorbance increased was found to depend on the

Table 12. Kinetic data for the thiourea-hydroxylamine-O-sulfonate ion reaction at $\mu = 0.1$ M at 20.34° and at pH lower than 3.0 in water.

$10^3[H_2NOSO_3^-]_0$, M	$10^5[(H_2N)_2C=S]_0$, M	pH	k_2, $M^{-1}sec^{-1}$
1.00	4.01	2.96	1.92
1.00	4.01	2.66	1.94
1.00	4.01	2.48	2.18
1.00	4.01	2.36	2.18
1.01	4.01	2.30	2.21
1.01	4.01	2.00	2.26
1.00	4.01	2.00	2.19
1.01	4.01	1.82	2.08
1.01	4.03	1.70	1.96
1.00	4.01	1.70	2.00
1.03	4.03	1.75	2.10
1.00	4.03	1.52	1.78
1.03	4.03	1.45	1.77
1.00	4.03	1.40	1.56
1.03	4.03	1.28	1.44
1.03	4.03	1.15	1.21

concentration of thiourea in solution. The higher the concentration of

thiourea, the faster the absorbance was found to increase. This

increase in absorbance was due to the reaction of thiourea with the

intermediate, $(H_2N)_2CSNH_2^+$.

This was shown by adding $(NH_2)_2C=S$ to a solution of

$(NH_2)_2CSNH_2^+$ and observing a slow increase of the absorbance. Even

in acidic solution the reaction is slow compared to the same type

observed in the thiosulfate study. This fact can account for the sec-

ond step, described by Equation 63, not occurring in the regular

kinetic runs. An interesting question can be raised at this point. Why

is it that the second step in this system, presumably occurring by the

same mechanism, is so slow compared to the second step of the

thiosulfate system?

Nucleophilic Reactions Involving Substituted Hydroxylamine-O-sulfonate Ion

Attempts to study the kinetics of two substituted hydroxylamine-

O-sulfonate ions were made. Kinetic studies were performed on

N-methylhydroxylamine-O-sulfonate ion and on pyridinium N-benzoyl-

hydroxylamine-O-sulfonate. Preparations are described in the

Experimental Section. We were partly successful with the former,

but no evidence of any reaction was observed with the latter.

Reactions of N-methylhydroxylamine-O-sulfonate with iodide,

triphenylphosphine and thiourea are extremely slow compared to the reaction of the same nucleophiles with the parent compound. The amount of data available in these experiments being very small, and the difficulties encountered being similar for each reaction, the results will be summarized in the same table.

Determination of the Rate Law

The reactions were studied in water at pH 4.75 (5.6 for the triphenylphosphine reaction) and μ = 0.1 M (0.5 M for the iodide reaction) using the initial rate method. The rate constant was obtained by calculating the slope of the first 2-5% of the reaction. The ε values used in the calculations were, respectively:

$\varepsilon_{(353)}$ = 26,400 $M^{-1}cm^{-1}$ for I_3^-, $\varepsilon_{(290)}$ = 3,550 $M^{-1}cm^{-1}$ for $(C_6H_5)_3P$, and $\varepsilon_{(250)}$ = 3,190 $M^{-1}cm^{-1}$ for $(H_2N)_2C=S$. The concentration ranges were (10-30) x 10^{-3} M, (3-12) x 10^{-3} M, and (5-10) x 10^{-3} M for N-methylhydroxylamine-O-sulfonate when the concentrations of the nucleophiles were respectively, 2.4 x 10^{-4} M for triphenylphosphine, 3.6 x 10^{-4} M for thiourea and (5-10) x 10^{-2} M for iodide. From data summarized in Table 13 the reactions seem to be first order in each reactant and thus follow the rate law:

(69) $$\text{Rate} = k_2[CH_3NHOSO_3^-][Nu]$$

where Nu is the nucleophile.

Table 13. Kinetic data for the reactions involving N-methylhydroxyl-amine-O-sulfonate with triphenylphosphine[1] and thiourea.[2]

$10^3[CH_3NHOSO_3^-]_0$, M	$10^4[(C_6H_5)_3P]_0$, M	pH	10^3k_2, $M^{-1}sec^{-1}$
9.120	2.48	5.75	1.76
9.984	2.48	5.75	1.76
10.04	2.38	5.75	1.38
10.04	2.38	5.75	1.58[a]
14.95	2.37	5.75	1.76
14.95	1.19	5.75	1.49
15.03	2.40	5.75	1.66
15.03	2.40	5.75	1.52[a]
15.03	1.19	5.75	1.39
19.97	2.48	5.75	1.72
20.09	2.38	5.75	1.72
20.09	2.38	5.75	1.72[a]
22.81	2.48	5.75	1.72
30.07	2.40	5.75	1.63
30.07	1.20	5.75	2.16[a]
30.07	1.19	5.75	1.87

	$10^4[(NH_2)_2C=S]_0$, M		
3.00	3.58	4.75	1.51
6.00	3.58	4.75	1.57
6.02	3.58	4.75	1.70
12.04	3.58	4.75	1.49

[1] In 50 wt % methanol-water at 20°, μ = 0.1 M where ε_{290} = 3550.

[2] In water at 20°, μ = 0.1 M where ε_{250} = 3187.

[a] Delay experiment. 1 hour wait before adding $(C_6H_5)_3P$.

Determination of the Rate Constants

In the case of the iodide reaction, only an upper limit on the rate constant could be determined. This upper limit was found to be: $k_2 = 1 \times 10^{-4}$ $M^{-1}sec^{-1}$. The reaction is at least 10^5 times slower than that with hydroxylamine-O-sulfonate ion. A difficulty encountered in this reaction was first, an induction period in which production of I_3^- could not be observed, presumably because of the presence of a trace amount of N-methylhydroxylamine hydrochloride which consumes I_2. Addition of I_2 at the beginning of the reaction eliminated this problem. After the induction period was over, the absorbance started to increase very rapidly ($t_{1/2} \sim$ 2 minutes), as if a small amount of impurity was causing a pseudo-first-order reaction. After that fast jump in the absorbance, the absorbance continued to increase slowly. The slope was not constant but decreased with time. After many attempts to eliminate the difficulty, it was decided that the system was unsatisfactory for an accurate study. From average values obtained in several experiments, the upper limit on the rate was determined.

Reaction with triphenylphosphine gave a rate constant, $k_2 = 1.7(\pm 0.2) \times 10^{-3}$ $M^{-1}sec^{-1}$. The rate constant observed is 10^3 lower than that for the parent compound. Reaction with thiourea gave a rate constant $k_2 = 1.6(\pm 0.1) \times 10^{-3}$ $M^{-1}sec^{-1}$. The rate constant observed is 10^3 times lower than that for the parent compound. The

above rate constants were determined using data from Table 13.

Those data are the best available and were gathered from reactions

where the mixing time was the same as much as possible, and the

slopes for each run were calculated from data collected during the

first 1800 seconds. In these systems, the difficulties were not as

great as with the iodide system, but again, the slopes decreased with

time. It is possible that impurities, which we were unable to remove,

were causing an initial, more rapid reaction that was affecting the

data. In experiments in the absence of N-methylhydroxylamine-O-

sulfonate, there was no evidence that N-methylhydroxylamine reacts

with either thiourea or triphenylphosphine. Although the reactions

were too slow to determine the stoichiometry, there is no reason to

believe that it should be different than that of hydroxylamine-O-

sulfonate systems.

IV. DISCUSSION

General Mechanism

Since it turns out that the mechanisms proposed for all the systems studied are the same, the general aspects of the mechanisms will be discussed here. The general rate law obtained from the different kinetic studies involving hydroxylamine-O-sulfonate ion, was found to be first-order in the hydroxylamine-O-sulfonate ion and first-order in the nucleophile. A mechanism involving an S_N2 displacement in the rate-determining step by the nucleophile is proposed.

$$(70) \qquad Nu^z + H_2NOSO_3^- \longrightarrow [Nu\text{---}\overset{\cdot\cdot}{N}\text{---}OSO_3^{z-1}]^{\ddagger} \longrightarrow NuNH_2^{z+1}$$
$$\underset{H}{\diagup}\underset{H}{\diagdown}$$
$$+ SO_4^{2-}$$
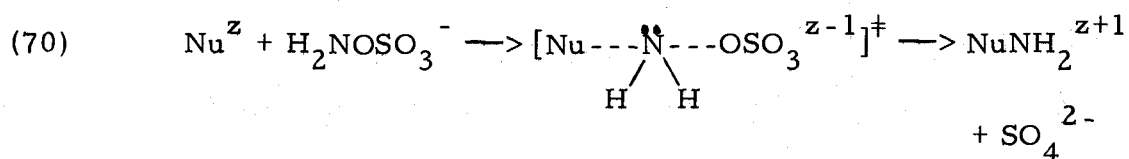
In some of the systems addition of a second step, involving the nucleophile, is required by the experimental results. The above mechanism is supported by the rate laws which were found to be:

$$(71) \qquad Rate = k_2[H_2NOSO_3^-][Nu^z]$$

Also, $\Delta S^{\ddagger}$'s of reactions involving S_N2-type mechanisms are expected to be in the range -10 to -40 eu (41). As it can be seen from Table 14, the $\Delta S^{\ddagger}$ values found in our study fall in the range expected.

In this study, the concentration of hydroxylamine-O-sulfonic

acid used was always very small compared to the concentrations used in the hydrolysis studies discussed in the Introduction section. Furthermore, the temperature range used in the present study was lower than the temperature range used in the hydrolysis studies (3, 5, 6). Evidence of hydrolysis in our systems, which could have affected our kinetic results, has never been found. The fact that the same rate constants were obtained in delay experiments, where hydroxylamine-O-sulfonic acid was left in solution for one or two hours before the start of the reaction, is a good indication that hydrolysis does not affect our systems in any way.

An alternative $S_N 1$ dissociative type mechanism is possible in our systems.

$$(72) \qquad H_2NOSO_3^- \rightleftharpoons NH_2^+ + SO_4^{2-}$$

$$(73) \qquad Nu^z + NH_2^+ \longrightarrow NuNH_2^{z+1}$$

$$(74) \qquad NH_2^+ + H_2O \longrightarrow NH_3OH^+$$
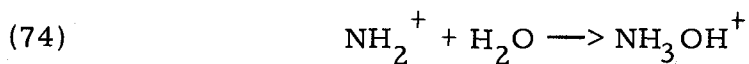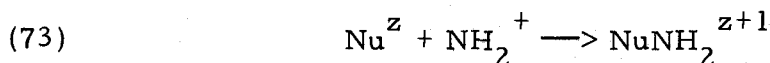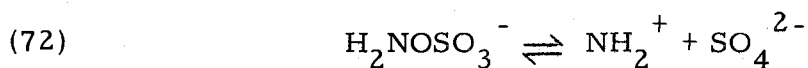
It is believed that, if reactions were occurring totally, or partially, by such a mechanism, the two steps described by Equations 73 and 74 would become competitive. The results of that competition would be to get two different products for the reactions, NH_3OH^+, and $NuNH_2^{z+1}$. Within experimental error, 100% of the expected product

was observed, with no evidence whatsoever for NH_3OH^+, the product

of hydrolysis.

Site of Attack

The site of attack of the nucleophile is believed to be the nitrogen

atom for numerous reasons that will be discussed here. Attack on the

bridge oxygen of hydroxylamine-O-sulfonate ion, according to an S_N2

type reaction where N-O bond breakage occurs, is ruled out because

of the fact that all the reactions involving hydroxylamine-O-sulfonate

ion are pH independent.

(75) $$H_2NOSO_3^- + H^+ \rightleftharpoons H_3N^+OSO_3^- \quad (K_A^{-1})$$

(76) $$Nu^z + H_3N^+OSO_3^- \longrightarrow \left[Nu---O---NH_3^z \underset{\displaystyle |}{\overset{\displaystyle SO_3}{}} \right]^{\ddagger}$$

$$\longrightarrow NuOSO_3^z + NH_3$$
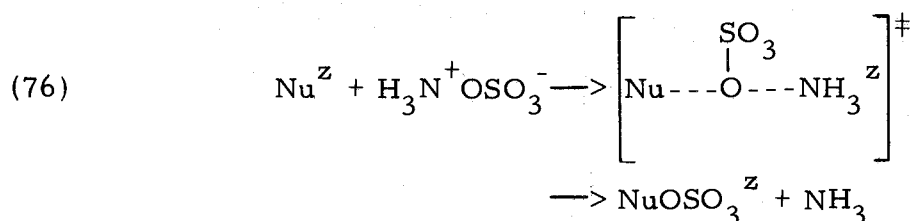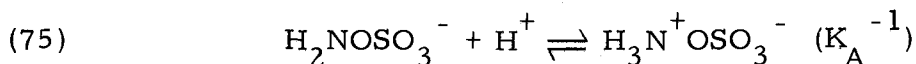
According to the mechanism described by Equation 76, protonation of

the NH_2 group is required to get NH_3 as the leaving group. The rate

law for such a reaction should contain an $[H^+]$ term, which is not

observed. Attack on the oxygen of hydroxylamine-O-sulfonate ion,

according to an S_N2 process where O-S bond breakage occurs, has

already been ruled out for reasons given in detail in the Introduction

Section. The key positive evidence for nitrogen attack is the fact that,

for all the systems studied, except iodide, it was possible to either intercept as an intermediate or to identify as the product of the reaction, a compound containing a Nu-N bond. The similarity of the results obtained in the deuterium effect studies (see following paragraph) also suggests strongly that the mechanism involved in our systems is the same for all the systems and involves nucleophilic attack on the nitrogen. The fact that the reaction involving iodide is also pH independent, and has the same behavior as the others in the deuterated solvent, strongly suggests that the attack occurs on the nitrogen.

Deuterium Isotope Effects

The similarity of $k_{2(H)}/k_{2(D)}$ values in our systems seems to confirm that the mechanism for each reaction involves attack on nitrogen. The ratio $k_{2(H)}/k_{2(D)}$ being larger than one, and the fact that no bond involving a deuterated atom is broken, suggest that the effect is a normal, secondary effect (33). The purpose of this study in deuterated solvent was to differentiate between different possible sites of attack. As it turns out, the site of attack involved is the same for each system. The results of the isotopic study can be used to support the previous conclusions. The rate constants obtained in deuterated solvent are smaller than the rate constants obtained in the normal solvent. Many factors have to be taken into account in order

to explain this behavior, for example, the change in the activation

energy arising from changes in zero-point energies of stretching and

bending modes, and the solvation effect. The weighing of all these

possible factors in trying to explain the rate decrease is a tremendous

task. According to Laidler (33), one has to be careful to include all

possible effects in his discussion. The amount of information gathered

from these experiments does not seem to be sufficient to justify a

discussion of the decrease in rate in the deuterated solvents.

<div align="center">Specific Mechanisms</div>

Triphenylphosphine

According to the rate law observed,

$$\text{Rate} = k_2[(C_6H_5)_3P][H_2NOSO_3^-] \, ,$$

and the stoichiometry of the reaction (77), a mechanism is proposed

which involves a nucleophilic attack on the nitrogen of

(77) $\qquad (C_6H_5)_3P + H_2NOSO_3^- \longrightarrow (C_6H_5)_3PNH_2^+ + SO_4^{2-}$

hydroxylamine-O-sulfonate ion according to an S_N2 type reaction to

give $(C_6H_5)_3PNH_2^+$ as the product.

(78) $\quad (C_6H_5)_3P + H_2NOSO_3^- \longrightarrow [(C_6H_5)_3P \text{---} \overset{\cdot\cdot}{\underset{H \diagup \diagdown H}{N}} \text{---} OSO_3^-]^{\ddagger}$

$$\longrightarrow (C_6H_5)_3PNH_2^+ + SO_4^{2-}$$
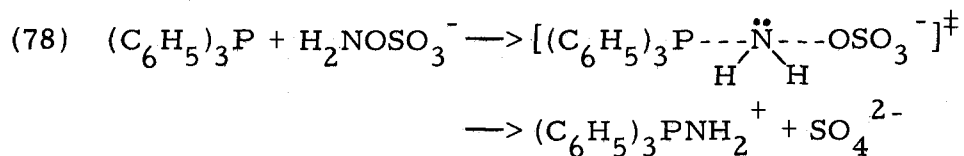
As outlined in the Results section, the absorbance of the product at infinite time is in accordance with the value found for the compound prepared independently, and also the absorbance value given in the literature (32) at 260 nm. The final absorbance of the product of the reaction being constant for at least 1 hour after the reaction is over, we can eliminate a possible second step for the system as described by Equation 79 in which triphenylphosphine oxide would be the product

$$(79) \qquad (C_6H_5)_3PNH_2^+ + H_2O \longrightarrow (C_6H_5)_3P=O + NH_4^+$$
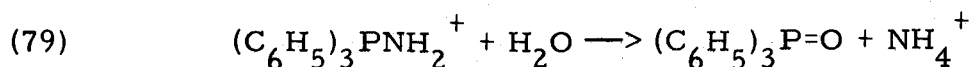
of the reaction. The results obtained strongly support attack at nitrogen.

Iodide

According to the rate law observed, Rate $= k_2[I^-][H_2NOSO_3^-]$ and the stoichiometry of the reaction 80, we propose a mechanism that involves a nucleophilic attack by iodide on the nitrogen of

$$(80) \qquad H_2NOSO_3^- + 3I^- + 2H^+ \longrightarrow NH_4^+ + SO_4^{2-} + I_3^-$$
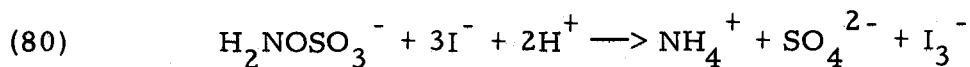
hydroxylamine-O-sulfonate ion according to an S_N2 type reaction to produce NH_2I, which then reacts with one more iodide in a fast step to produce I_3^-.

(81) $I^- + H_2NOSO_3^- \longrightarrow [I\text{---}\overset{H}{\underset{H}{N}}\text{---}OSO_3{}^{2-}]^{\ddagger} \longrightarrow NH_2I + SO_4{}^{2-}$

(82) $NH_2I + H^+ + I^- \xrightarrow{\text{fast}} NH_3 + I_2$
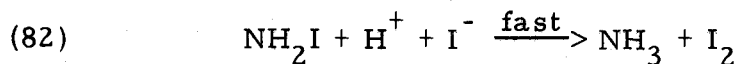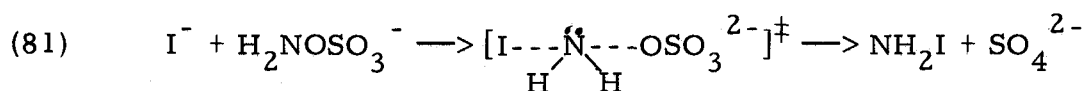
NH_2I is the proposed intermediate for this reaction. No attempts were

made to isolate it due to the expected great instability. For reasons

discussed in the section "General Mechanism" NH_2I is the only pos-

sible intermediate because, in order to propose the highly reactive

$IOSO_3^-$ species as the intermediate, the rate-determining step would

have to be pH dependent, which is not the case.

As can be seen from Figure 3 in the Results section, the rate

constant starts to decrease with decreasing pH at about pH 3. This is

due, we believe, to protonation of the hydroxylamine-O-sulfonate ion

below pH 3. The rate constants observed result from a combination

of the rates due to the protonated and non-protonated forms reacting

simultaneously. Using the rate constant $k_2 = 0.069 \ M^{-1}sec^{-1}$ obtained

for $H_2NOSO_3^-$ and Equation 34 from the Results section it was pos-

sible to estimate $k_2 = 0.023 \ M^{-1}sec^{-1}$ and $K_A = 0.055$ for $H_3N^+OSO_3^-$.

The values obtained for the rate constant and the K_A of the acid are

within a factor of 2 of those found in the literature (3,6).

Before the experiments were carried out, there were no reasons

to suspect that the protonated form would react more slowly than the

non-protonated form. After all, the methods outlined in the literature

on the determination of the purity of hydroxylamine-O-sulfonic acid by the iodometric method state unequivocally that the reaction goes faster in an acid medium (3, 5, 6, 8). From kinetic theory (33) one would expect that a reaction involving a neutral and a 1- charged species would react faster than a 2- species. The reactions of $H_3N^+OSO_3^-$ and $H_2NOSO_3^-$, respectively, are of these charge types. Furthermore, if protonation occurs on the nitrogen, this center will be more positive and more likely to undergo attack by a negatively charged nucleophile. One can also argue that in the non-protonated form, the lone pair of electrons on nitrogen is causing some hindrance to nucleophilic attack which could be relieved by protonation. Even with all these good arguments in favor of a greater reactivity of the protonated form, the actual rate observed is smaller. This is due, we believe, to the fact that protonation of nitrogen makes the electron pair unavailable for a good overlap with the low-lying empty orbitals of the iodide ion. This protonation causes more energy to be needed in achieving the activated complex, thus causing the rate to be lower. If protonation were to occur on oxygen instead, the only difference, besides the charge involved, would be in the leaving group. HSO_4^- would have to be a poorer leaving group than SO_4^{2-} in order to explain the decrease in the rate constant. This requirement is unreasonable when the reaction occurs in water.

I_3^- is not stable in basic solution. At pH 8 some of the rate

constants are a little higher than expected. This is due, we believe,

to some loss of I_3^- which has the effect of making the calculated rate

constant larger. By analogies with the results of the other studies it

seems very unlikely that the rate constant would change with increas-

ing pH.

From our study, we can conclude that the reaction of hydroxyl-

amine-O-sulfonate ion and bromide ion is at least 50 times slower

than the reaction of the former with iodide. Reaction of hydroxylamine-

O-sulfonate ion with chloride does not occur at all under our reaction

conditions. However, it was found that at very high concentrations of

hydroxylamine-O-sulfonate ion and bromide a yellowish coloration due

to the production of Br_3^- was observed, as well as bubbles of nitrogen

gas. We therefore believe that the oxidation of bromide is possible,

but the conditions under which it occurs are improper for kinetic

study. The appearance of N_2 might be a sign that the reaction occurs

by another mechanism, but this is most unlikely and we believe that

the N_2 production most likely comes from the self-oxidation-reduction

reaction of hydroxylamine-O-sulfonic acid as proposed by Audrieth

(5).

Thiosulfate

According to the rate law observed, rate = $k_2[S_2O_3^{2-}][H_2NOSO_3^-]$,

and the stoichiometry of the reaction 83, we propose a mechanism

which involves a nucleophilic attack by $S_2O_3^{2-}$ on the nitrogen of

(83) $\quad H_2NOSO_3^- + 2S_2O_3^{2-} + H^+ \longrightarrow NH_3 + S_4O_6^{2-} + SO_4^{2-}$
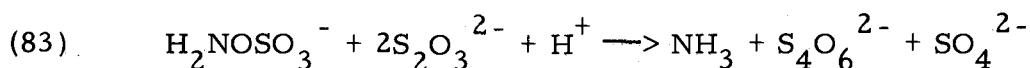
hydroxylamine-O-sulfonate ion according to an S_N2 type reaction to

produce $H_2NSSO_3^-$ as the intermediate, which then reacts further in a

fast step with one more $S_2O_3^{2-}$ to give the final product, $S_4O_6^{2-}$.

(84) $\quad S_2O_3^{2-} + H_2NOSO_3^- \longrightarrow [O_3SS\text{---}\overset{..}{N}\text{---}OSO_3^{3-}]^{\ddagger}$
$$\underset{H \quad H}{}$$

$$\longrightarrow H_2NSSO_3^- + SO_4^{2-}$$

(85) $\quad H_2NSSO_3^- + SSO_3^{2-} + H^+ \longrightarrow S_4O_6^{2-} + NH_3$
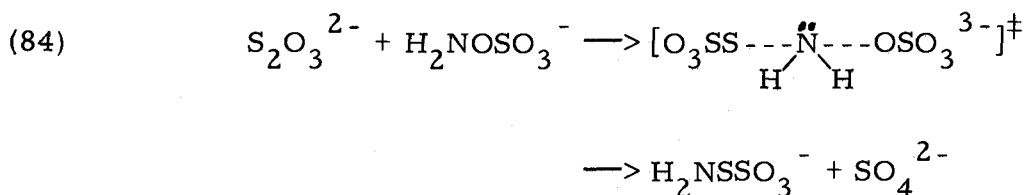
It was falsely reported before (16) that this reaction occurs by an

attack of $S_2O_3^{2-}$ on the oxygen of the hydroxylamine-O-sulfonate ion

according to an S_N2 type reaction, followed by a fast step in which one

more $S_2O_3^{2-}$ would react with the intermediate to give as the final

product $S_4O_6^{2-}$.

(86) $\quad S_2O_3^{2-} + H_2NOSO_3^- \longrightarrow \left[O_3SS\text{---}\underset{\underset{SO_3}{|}}{O}\text{---}\overset{\overset{H\text{---}OH}{|}}{NH_2}^{3-} \right]^{\ddagger}$

$$\longrightarrow NH_3 + OH^- + {}^-O_3SS\text{-}O\text{-}SO_3^-$$

(87) $\quad$ $^-O_3SS\text{-}O\text{-}SO_3^- + S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + SO_4^{2-}$
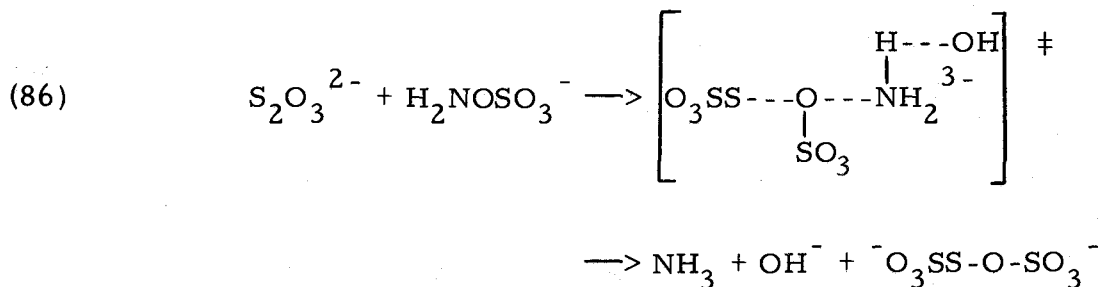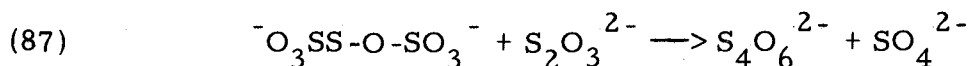
It is possible to rule out the mechanism which involves attack on the oxygen for two reasons. First, as explained under the "General Mechanism" paragraph, the rate-determining step is not pH dependent. Second, we were able to prepare the intermediate proposed (see Experimental section) and were able to stop the reaction after the first step showing that the final absorbance observed compared adequately with the absorbance of the prepared product.

In order to understand better, let us separate the reaction steps as follows:

Step A

(88) $\quad$ $S_2O_3^{2-} + H_2NOSO_3^- \xrightarrow{\text{r.d.}} H_2NSSO_3^- + SO_4^{2-}$

Step B

(89) $\quad$ $S_2O_3^{2-} + H_2NSSO_3^- + H^+ \longrightarrow S_4O_6^{2-} + NH_3$
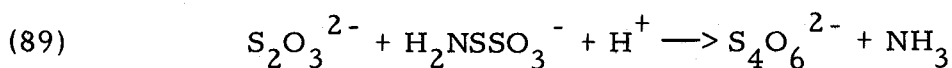
At pH <7, Step A is rate determining and Step B is very fast and the product of the reaction is $S_4O_6^{2-}$. At 7 < pH < 9, Step B is greatly retarded by decreasing H^+ concentration and the rate constants were not determined experimentally because both steps apparently become competitive. At pH >9, Step A is still the rate-determining step, but Step B does not occur at all and $H_2NSSO_3^-$ is the product of the reaction. The values

of the rate constants, obtained for Step A and Step B as a function of

pH, are shown in Figure 15.

At pH > 9, the infinite-time absorbance observed is close to,

but somewhat higher than the expected absorbance if the product were

100% $H_2NSSO_3^-$. The deviation becomes smaller as the reaction

takes place more rapidly. This seems to suggest that a small amount

of $S_4O_6^{2-}$ is produced in the solutions. Using the observed infinite-

time absorbances in the calculations of the rate constants, one finds

that the curves deviate from linearity and that the rate constants

obtained are lower than expected. Faster runs were designed in order

to minimize the production of $S_4O_6^{2-}$ and the calculated infinite-time

absorbance for 100% production of $H_2NSSO_3^-$ was used in the calcula-

tion of the rate constant. The results were that the plots were linear

and the rate constants calculated, even if the uncertainty was greater,

were comparable with the rate constants obtained at lower pH (see

Results section). Since in the $(H_2N)_2C=S$, $H_2NOSO_3^-$ system, the rate

constant remains constant for reactions occurring at pH as high as 11,

(see Results section) there is no reason to believe that the rate con-

stant should change with increasing pH.

Another point that supports the mechanism proposed is the fact

that we were able to show that Step B was first order in H^+ concentra-

tion. According to the plot shown in Figure 9, it can be seen that the

intercept being (0, 0) within the experimental error, the second term,
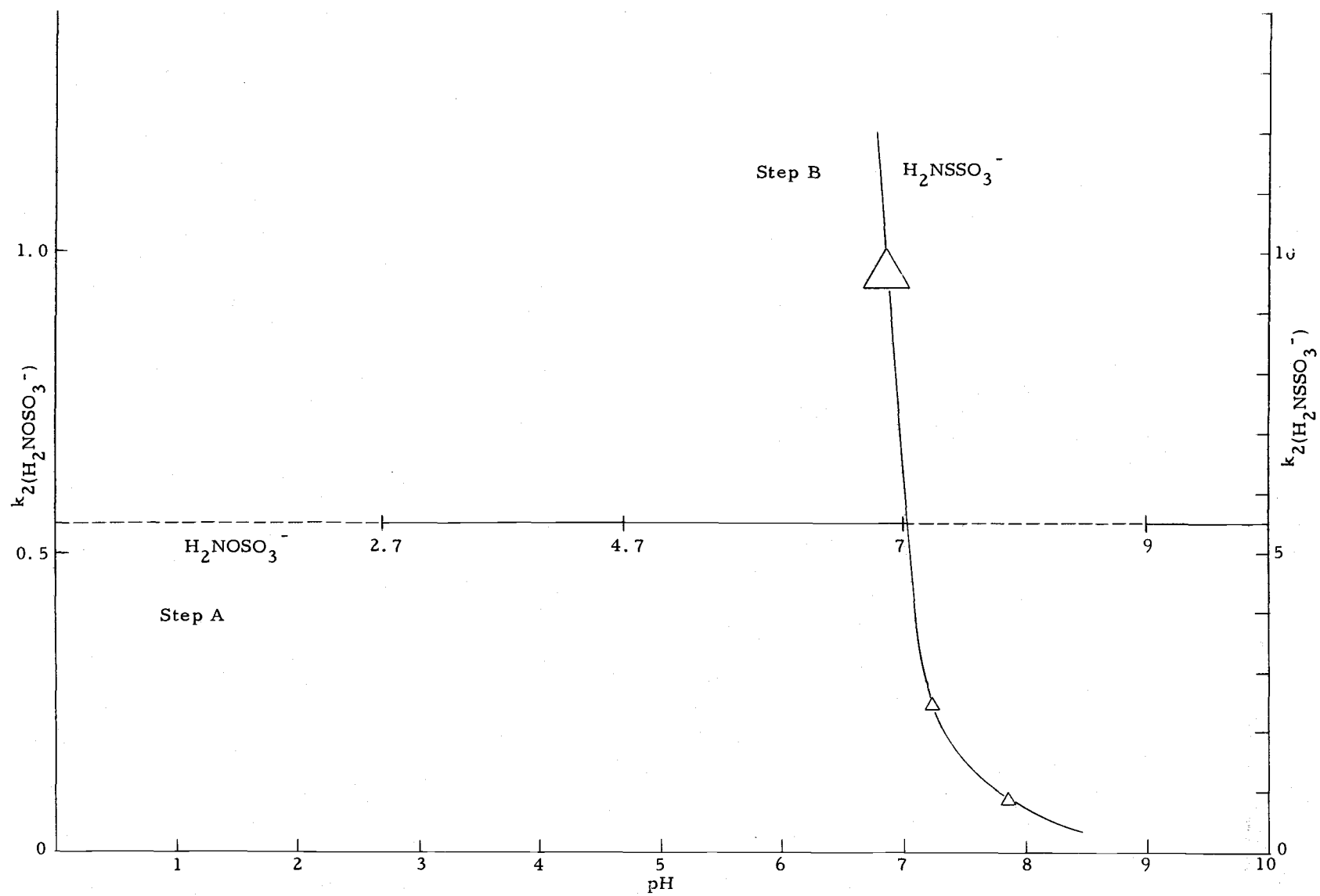
Figure 15. $k_{2(obs)}$ for the reaction of hydroxylamine-O-sulfonate ion and thiohydroxylamine-S-sulfonate with thiosulfate as a function of pH.

$k_{2(H_2NSSO_3^-)}$, from Equation 49 has to be zero. This, unequivocally, proves that Step B and the formation of $S_4O_6^{2-}$ will happen if and only if there is some H^+ in large enough concentration to allow the reaction to proceed.

The rate constant found for the nucleophilic attack of thiosulfate on the sulfur center of $H_3N^+SSO_3^-$ is 10^7 times greater than the attack of the same nucleophile on the nitrogen center of $H_2NOSO_3^-$. A very interesting question can be raised at this point. Why is it that, if the reaction by an attack on the sulfur is so fast, no evidence of attack on the oxygen, which is just above sulfur in the periodic table, has been found? There is no experimental evidence that can provide an answer to this question but the availability of d-orbitals gives the sulfur atom characteristics rather different from those of oxygen.

In Step B, in order to get $S_4O_6^{2-}$ as the product, there is no doubt that the attack by the nucleophile has to be on the sulfur, but we have not investigated the possibility that there could be a preferential attack on the nitrogen as in Step A. If this preferential attack takes place, the effect would be a simple exchange according to the following equation:

$$(90) \quad SSO_3^{2-} + H_2NSSO_3^- \longrightarrow \left[O_3SS \cdots \overset{\cdot\cdot}{\underset{H \quad H}{N}} \cdots SSO_3^{3-} \right]^\ddagger$$

$$\longrightarrow SSO_3^{2-} + H_2NSSO_3^-$$
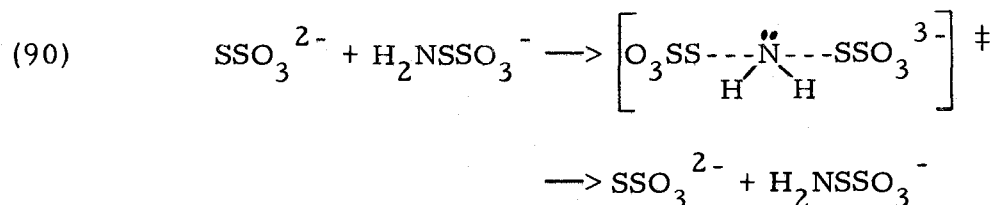
The extent of this exchange could be measured using ^{35}S and isotopic techniques. It would be a good extension of this work if one were able to determine if exchange occurs and if so, to measure its rate.

Thiourea

According to the rate law observed,

$$Rate = k_2[(NH_2)_2C{=}S][H_2NOSO_3^-]$$

and the stoichiometry of the reaction 91 we propose a mechanism that involves a nucleophilic attack by thiourea on the nitrogen of

(91) $(NH_2)_2C{=}S + H_2NOSO_3^- \longrightarrow (NH_2)_2CSNH_2^+ + SO_4^{2-}$
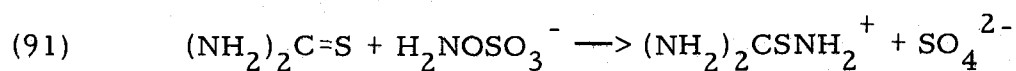
hydroxylamine-O-sulfonate ion according to an S_N2 type reaction to give $(NH_2)_2CSNH_2^+$ as the product.

(92) $(NH_2)_2C{=}S + H_2NOSO_3^- \longrightarrow [(NH_2)_2C{=}S\text{---}\overset{..}{N}\text{---}OSO_3^-]^{\ddagger}$
$H \diagup \diagdown H$
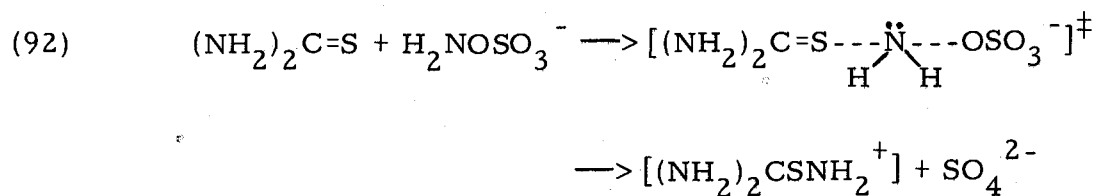
$$\longrightarrow [(NH_2)_2CSNH_2^+] + SO_4^{2-}$$

It would not be surprising if the species $(NH_2)_2CSNH_2^+$ would be short-lived and that thiourea would react with it to give the more stable and well-known compound $(NH_2)_2CSSC(NH_2)_2^{2+}$ according to Equation 93.

(93) $(NH_2)_2CSNH_2^+ + (NH_2)_2C{=}S + H^+ \longrightarrow (NH_2)_2CSSC(NH_2)_2^{++} + NH_3$
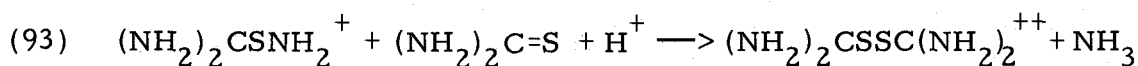
However, we have proved without any doubt that the reaction is over after the step described by Equation 92 and that the product of the reaction is not formamidinedisulfide cation (see Results section).

As outlined in the Experimental section, S-aminoisothiouronium sulfate is very unstable. Within an hour after contact with air, decomposition is noticed by the change in the color of the solid from white to yellow, due to the formation of sulfur. From the above facts, some doubts about the products of the reaction are introduced. It is conceivable that if decomposition occurs in water, a possible mechanism would be the following.

(94) $(NH_2)_2CSNH_2^+ + H_2O \longrightarrow (NH_2)_2C{=}O + NH_2SH_2^+$

(95) $NH_2SH_2^+ \longrightarrow NH_4^+ + S$
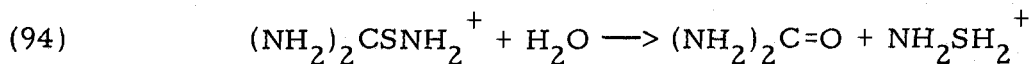
Thiohydroxylamine has never been isolated, and many attempts to do so have given a product that decomposed to give sulfur. At any rate, if decomposition occurs, the suspected products do not have any oxidizing power. It is known, from the Experimental section that $(NH_2)_2CSNH_2^+$ can oxidize iodide in acidic solution, so an experiment was attempted to show that the product solution has oxidizing power. A second-order reaction was designed to get the same 1:3 ratio of

thiourea:hydroxylamine-O-sulfonate ion as in the kinetic runs. If the reaction is allowed to go to completion, one can see that 33% of the hydroxylamine-O-sulfonic acid has reacted and the oxidizing capacity of the solution should decrease accordingly if the product S-aminoiso-thiouronium cation has undergone hydrolysis. A blank containing the same initial concentration of $H_2NOSO_3^-$ was used to find the maximum amount of I_3^- expected, at 400 nm by adding 0.5 M iodide to the solution. After the reaction was started, checks for the oxidizing capacity remaining were made at the first half-life, at the third half-life, at the end of the reaction, and at one hour after the completion of the reaction. The absorbances observed in each case corresponded, within the experimental error, to the absorbance of the blank. The results of the above experiment suggest strongly that indeed the product of the thiourea-hydroxylamine-O-sulfonate ion is the S-aminoiso-thiouronium cation.

S-aminoisothiouronium cation has been isolated only as the sulfate salt, $((NH_2)_2CSNH_2)_2SO_4$, for reasons obvious from the description of the synthesis in the Experimental section. There does not seem to be any previous report of this compound in the literature. The name chosen for the compound has been derived by analogy from well-known S-alkylisothiouronium salts. A compound (I), for which the S-aminoisothiouronium cation could be thought of as the parent com-pound, has been reported in the literature (42). It is prepared by the

(I)

$$Ph-N \diagdown$$
$$C-S-N(CH_3)_2$$
$$(CH_3)_2-N \diagup$$

reaction of $(CH_3)_2NH$ and $(PhNH)[(CH_3)_2N]C=S$ in presence of NaClO as the oxidizing agent in water at 30°. The name given to that compound is a derivative of isothiourea. The known properties of S-aminoisothiouronium sulfate are small in number at this point and have been mentioned at one point or another throughout this thesis. The most important are as follows: The solid partially decomposes to yield sulfur, within one hour after it has been prepared. In solution at a concentration as low as 10^{-3} M, it partially decomposes to give sulfur; on the other hand if the concentration is not higher than 10^{-5} M, it seems to be stable for about 3 hours. It reacts rapidly with iodide in presence of H^+ to produce I_3^-. In a reaction which does not seem to be affected by the concentration of H^+, it produces the formamidinedisulfide cation when allowed to react with thiourea.

Reactions Involving Substituted Hydroxylamine-O-sulfonate Ion

Reactions involving N-methylhydroxylamine-O-sulfonate ion are extremely slow, and reactions involving pyridinium N-benzoylhydroxylamine-O-sulfonate do not occur under the experimental conditions. It was not possible to determine a precise rate law, or a clear mechanism for the reactions with the limited amount of data available.

The effect of substituting a methyl group for hydrogen on a carbon atom has been widely investigated in numerous kinetic studies of organic reactions. The substitution has the effect of decreasing the rate of the reactions occurring by an S_N2 type mechanism. This effect has been attributed to steric hindrance. The decrease in the rate, usually one or two orders of magnitude, is not as drastic as the decrease observed in this study for the same kind of substitution on nitrogen. In order to investigate the extent of the suspected electronic effect, it was decided to try a study where a benzoyl group would be attached to nitrogen instead of a methyl group. The methyl group is generally considered to be an electron-donating group, whereas the benzoyl group is an electron-withdrawing group. Electron withdrawal might be expected to increase the rate, however, no reaction was observed using the N-benzoyl compound, suggesting very strongly that the steric effect dominates over any electronic effect. It seems, according to the facts mentioned above, that the rates for the N-substituted reactants can be attributed to a very large steric hindrance created by a substitution on nitrogen. This is in agreement with the conclusion reached by Smith and co-workers (3). The steric effect seems to be much more important when nitrogen is involved than when carbon is involved. Furthermore, according to Smith (3), hydrolysis becomes a more important pathway as the bulkiness of the substituted group increases. It was shown that the suspected product of the

hydrolysis reaction interfers greatly with a determination of the expected product of the substitution. It is a very clear fact that substitution on the nitrogen decreases its reactivity. To better understand reaction of the N-substituted reactants more work needs to be done and apparently different conditions need to be found in order to obtain a decent rate constant, which is the primary condition to satisfy in order to determine the exact mechanism of a reaction.

Relative Reactivity of the Nucleophiles

According to Edwards and Pearson (20), nucleophilic reactivities can be attributed to a combination of three principal factors: basicity, polarizability and the alpha effect. Results obtained in this study, which are summarized in Table 15, seem to indicate that the reactivities of the nucleophiles involved are more or less the same. The small differences observed in the rate constants, plus the fact that the nucleophiles involved are easily polarizable, lead to the conclusion that the principal factor contributing to the reactivity is polarizability. The proton-basicity of the nucleophiles involved does not seem to be of great importance. Since none of the nucleophiles studied has a lone-pair of electrons on the atom adjacent (alpha) to the attacking atom, the alpha effect cannot be evaluated.

Triphenylphosphine, thiosulfate, and thiourea are large, easily polarizable species. The small differences observed in their

reactivities toward hydroxylamine-O-sulfonate ion are not large enough to distinguish their ability to be polarized. The small differences in their reactivity can be attributed to the differences in their size, charge, geometry and ability to be solvated. The rate constant observed for the iodide reaction seems to be small compared to the others. According to the charge involved, iodide should react faster than thiosulfate. According to the rate constants in Table 14, this is not the case. Thiosulfate is more readily oxidized than iodide and according to Edwards (43), the ease of oxidation is a measure of polarizability. Thus, the rate of the reaction involving iodide is slower probably because iodide is less polarizable. All the nucleophiles involved being equally poor bases, basicity is not a factor in the reactivity, so the order of reactivity of the nucleophiles involved in this study is as follows:

$$(C_6H_5)_3P \sim (NH_2)_2C=S \sim S_2O_3^{2-} > I^- \gg Br^- \sim Cl^- \sim OH^- .$$
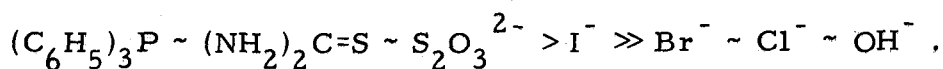
Evidence of reactions involving the very basic and very hard nucleophiles like OH^-, PO_4^{3-}, and CH_3COO^- was never found. This conclusion was reached when it was observed that different concentrations of the above, used in our buffer systems, did not affect the rate constants. It was then concluded that proton basicity is not a significant contributing factor in the determination of the reactivity at the nitrogen

center of hydroxylamine-O-sulfonate. With the Nu involved, the only

contributing factor is the polarizability. This seems to suggest that

the nitrogen of hydroxylamine-O-sulfonate ion is a fairly soft center.

Table 14. Nucleophilic reactivity toward hydroxylamine-O-sulfonate ion in H_2O at 20.4°.

Nucleophile	k_2, $M^{-1}sec^{-1}$	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (eu)
$(C_6H_5)_3P$	4.0 ± 0.1[a] 2.0 ± 0.1	7.4 ± 0.1	-32 ± 1
I^-	0.069 ± 0.06	11.6 ± 0.3	-24.4 ± 1
$S_2O_3^{2-}$	0.550 ± 0.015	10.8 ± 0.1	-22.8 ± 0.5
$(NH_2)_2C=S$	1.63 ± 0.07	7.4 ± 0.2	-32.3 ± 1.5

[a]Estimated for reaction in H_2O from the rate obtained with the other nucleophiles in 50 wt % methanol-water solution.

BIBLIOGRAPHY

1. F. Sommer and H. G. Templin, *Chem. Ber.*, 47, 1221 (1914)

2. F. Sommer, O. F. Schulz and M. Nassau, *Z. Anorg. Allg. Chem.*, 147, 142 (1925)

3. P. A. S. Smith, H. R. Alul, and R. L. Baumgarten, *J. Am. Chem. Soc.*, 86, 1139 (1963)

4. H. J. Matsuguma and L. F. Audrieth, *Inorganic Synthesis*, 5, 122 (1957)

5. H. J. Matsuguma and L. F. Audrieth, *J. Inorg. Nucl. Chem.*, 12, 186 (1959)

6. J. P. Candlin and R. G. Wilkins, *J. Am. Chem. Soc.*, 87, 1490 (1965)

7. N. C. Baenziger, R. F. Belt, and C. V. Goebel, *Inorg. Chem.*, 6, 511 (1967)

8. V. U. Wannagat and R. Pfeiffen-Schneider, *Z. Anorg. Allg. Chem.*, 297, 151 (1958)

9. R. E. Richards and R. W. Yorke, *J. Chem. Soc.*, 2821 (1959)

10. P. Kovacic and R. P. Bennett, *J. Am. Chem. Soc.*, 83, 221 (1961)

11. W. Durckheimer, *Justus Liebigs Ann. Chem.*, 721, 240 (1969)

12. H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, 81, 2982 (1959)

13. R. Appel, W. Büchner, and E. Guth, *Justus Liebigs Ann. Chem.*, 618, 53 (1958)

14. R. J. Kiyokane, Master Thesis, Oregon State University, Corvallis, Oregon, 1972.

15. R. Appel and W. Büchner, *Chem. Ber.*, 95, 849 (1962)

16. A.P. Lee, Master Thesis, Oregon State University, Corvallis, Oregon, 1970.

17. B.A. Sudbury, Ph.D. Thesis, (work in progress), Oregon State University, Corvallis, Oregon, 1973.

18. W.J. le Noble, Tetrahedron Lett., 7, 727 (1966)

19. W.T. Yap, A.D. Craig, and G.A. Ward, J. Am. Chem. Soc., 89, 3442 (1967)

20. J.O. Edwards and R.G. Pearson, J. Am. Chem. Soc., 84, 16 (1962)

21. R.G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963)

22. R.G. Pearson and J. Songstad, J. Am. Chem. Soc., 89, 1827 (1967)

23. P. Baumgarten, Chem. Ber., 59, 1976 (1926)

24. F.A. Daniher, J. Or. Chem., 34, 2908 (1969)

25. "Handbook of Chemistry and Physics," 49th Edition, p. C-473, (1968-69), The Chemical Rubber Co.

26. R.D. Ritter, Ph.D. Thesis, Oregon State University, Corvallis, Oregon, 1970

27. R. Gösl and A. Meuwsen, Z. Anorg. Allg. Chem., 92, 2521 (1959)

28. O. Foss, J. Johnsen, and O. Tvedten, Acta Chem. Scand., 12, 1782 (1958)

29. L.C. Leitch, B.E. Baker, and L. Brickman, Canadian Journal of Research, 23, Sec. B 139, (1945)

30. E.A. Werner, J. Chem. Soc., 101, 2166 (1912)

31. R.G. Bates, "Determination of pH: Theory and Practice," John Wiley, Inc., New York, N.Y., (1964).

32. H.H. Jaffe and L.D. Freedman, J. Am. Chem. Soc., 74, 1069 (1952)

33. K. J. Laidler, "Chemical Kinetics, " McGraw-Hill, New York, 1965.

34. C. A. Streuli, Anal. Chem. , 32, 985 (1960)

35. L. I. Katzin and E. Gebert, J. Am. Chem. Soc. , 77, 5814 (1955)

36. A. D. Awtrey and R. E. Connick, J. Am. Chem. Soc. , 73, 1842 (1951)

37. O. Foss, Acta Chem. Scand. , 15, 1610 (1961)

38. O. Foss, Acta Chem. Scand. , 15, 1608 (1961)

39. F. G. R. Gimblett and C. B. Monk, Trans. Faraday Soc. , 51, 783 (1955)

40. D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution, " Butterworths London, p. 449, (1965).

41. L. L. Schaleger and F. A. Long, "Advances in Physical Organic Chemistry, " Vol. 1. V. Gold, (ed), Academic Press, London & New York.

42. K. Ley, and U. Eholzer, Angew. Chem. (Int. Ed.), 5, 674 (1966)

43. J. O. Edwards, J. Am. Chem. Soc. 76, 1540 (1954)

44. R. C. Williams and J. W. Taylor, J. Chem. Educ. , 47, 129 (1970)

45. A. M. Vuagnat and E. L. Wagner, J. Chem. Phys. , 26, 77 (1957)

46. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds, " John Wiley and Sons, Inc. , New York, N. Y. , p. 118, (1970).

47. J. E. Stewart, J. Chem. Phys. , 26, 248 (1956)

48. R. Mecke and W. Kutzelnigg, Spectrochim. Acta, 16, 1225 (1960)

49. E. R. Lippincott and M. C. Tobin, J. Am. Chem. Soc. , 73, 4990 (1951)

50. E.R. Lippincott and M.C. Tobin, J. Chem. Phys., 21, 1559 (1953)

51. R.J. Philippe and H. Moore, Spectrochim. Acta, 17, 1004 (1961)

52. "Inorganic Sulphur Chemistry" edited by G. Nickless, American Elsevier Publishing Co. Inc. New York, N.Y.

53. J.R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N.J., p. 38, (1965).

APPENDICES

APPENDIX I

In this work all the calculations have been made using different
computer programs which have a least-squares calculation subroutine
available. Before the data were fed into the computer, enough evi-
dence of reasonable linearity had been obtained, so that the purpose
of using the computer was to obtain the best fit and not to find out if
the data were linear or not.

SIMLIN

SIMLIN is a least square calculation program written by Oregon
State Computer Center staff members and is available through the
Computer Center library. We used the program to get the slopes,
the intercepts, the deviations and the correlation coefficients of our
data points. It was used with satisfactory results in the determination
of the activation parameters, second-order rate constants and in some
miscellaneous calculations mentioned in the Results section.

KINDAT

This program was written by Williams and Taylor (44) and
modified for its use on Oregon State University's computer by M.
Gilbert. The program is designed to calculate rate constants of first-
order type reactions. Many subroutines are available through the

program and are well described in the above reference. We will

describe in more details some of the features of the program that

were widely used in our calculations.

We chose to use the automatic weighing subroutine, which gives

a weight of one to each data point entered unless otherwise specified.

When there was a certain amount of doubt on the points obtained in the

first 100-200 seconds of certain reactions, especially in very fast

reactions or reactions at lower or higher temperatures, where more

time was needed to achieve thermal equilibrium, fractions of one were

entered, the magnitude of which depended on the uncertainty of the

data points. The program gives you the liberty of putting 90, 95 or

99% confidence limits on data. We chose the 95% confidence limit on

our data with satisfactory results. Within that 95% confidence limit

any points with excessive deviation were automatically rejected, as

points beyond the 4th half-life. By far the most important feature of

the program was the infinite-time absorbance adjustment. Based

on the value of the infinite-time absorbance entered, the program

tried to find a better value within 0.010 abs unit in order to get

the best possible fit for the least-squares calculations. Most

of the time the value used by the computer was within the experi-

mental error of the observed value. Thus, the rate constants,

obtained were more precise and the error limit of the average

was minimized. When the computer was not able

to find a better value of the infinite time absorbance reading, it used the value entered.

PIERRE and SOPHIA

These programs were written by the author to calculate the rate constants of second-order type reactions. The programs are essentially the same except that SOPHIA has a least-squares sub-routine whereas PIERRE does not. PIERRE was used mostly to get the concentration data from the absorbance data. The values obtained were then plotted to see if the resulting curve was a straight line. When assurance that the data were following the second-order rate law was obtained, a least-squares calculation was done on the stored data, using SIMLIN. When there were no reasons to believe that the data were not following a second-order rate law, SOPHIA was used in order to get the second-order rate constant directly. All the rate constants reported in this work that have been calculated using either SOPHIA or PIERRE, were all checked for linearity by plotting on graph paper. SOPHIA and PIERRE were used mostly to save time in the calculations for the transformation of absorbance data into concentration data, and also to get the best possible value for the rate constants after we were assured that the data were linear.

All the programs mentioned above, except SIMLIN, are available on tape or cards for future use at Oregon State University. All information necessary will be given by Dr. J.H. Krueger, Chemistry Dept., Oregon State University.

APPENDIX II

Infra-red Spectrum of Potassium Thiohydroxylamine-S-sulfonate

The ir spectrum of H_2NSSO_3K was scanned from 4000 cm^{-1} to 400 cm^{-1}, using the KBr pellet technique, in order to observe absorption bands due to S-S and S-N bonds. To help in making the assignments, the spectrum of H_2NOSO_3H will be used as a reference. The ir spectra of the compounds are shown in Figures 16 and 17. The ir spectrum of H_2NOSO_3H is in good agreement with a spectrum published earlier (8) in the 4000-700 cm^{-1} range, except for the fact that moisture is present in our sample and has broadened the N-H stretch in NH_2 at 3400 cm^{-1}.

For H_2NSSO_3K, as expected for an N-H stretch, a nice doublet, centered on 3300 cm^{-1}, is observed. Between 1500 cm^{-1} and 1600 cm^{-1}, a triplet is observed for $H_3N^+OSO_3^-$ but not for H_2NSSO_3K where a singlet is observed at 1600 cm^{-1}. This absorbtion band at 1600 cm^{-1} is due to an NH_2 bending mode. The triplet has been assigned to an NH_3^+ bending mode by Wannagat (8) and by Wagner (45) for the same type of zwitter-ion in sulfamic acid. In the ir spectrum of the potassium sulfamate the triplet is replaced by a singlet.

For potassium sulfamate, the absorbtion band at 805 cm^{-1} has been assigned to an S-N stretch (45). According to Nakamoto (46) stretching and bending absorption bands for S-O, S=O, and O-S-O
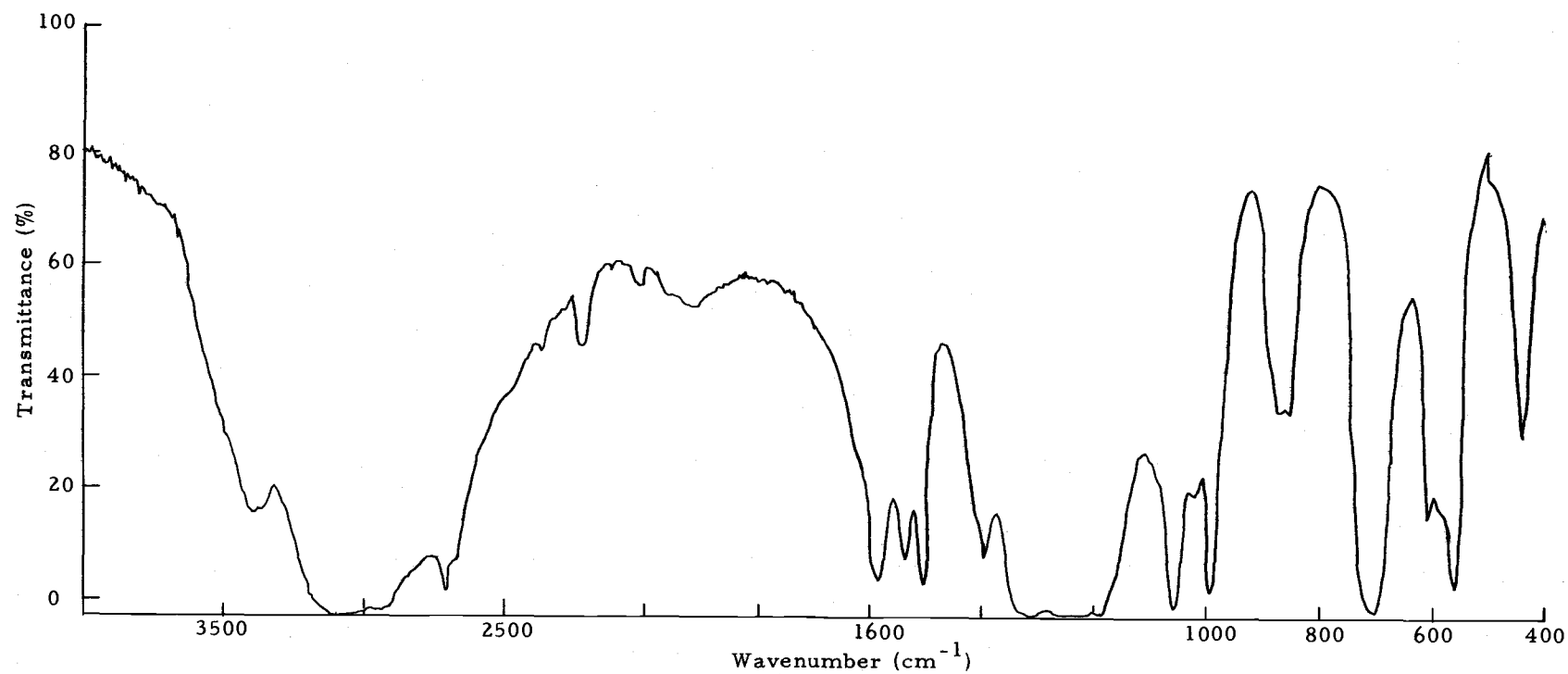
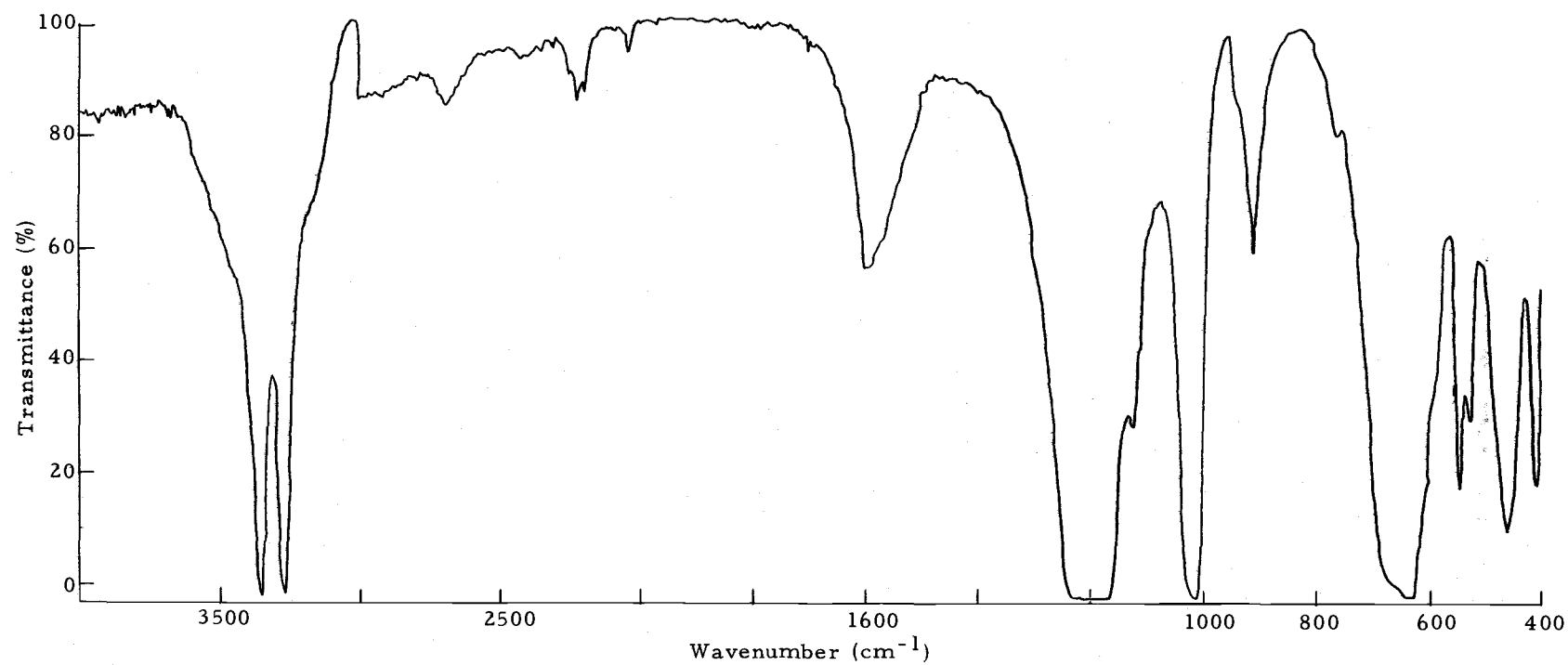Figure 16. Infra-red spectrum of hydroxylamine-O-sulfonic acid using KBr pellet technique.

Figure 17.   Infra-red spectrum of potassium thiohydroxylamine-S-sulfonate using KBr pellet technique.

bonds can be found anywhere from 1500 cm^{-1} to 900 cm^{-1} and from 750 cm^{-1} to 400 cm^{-1}. From the same reference, absorption bands due to S-S bond stretching are expected in the range 500-400 cm^{-1}. From the above facts and by comparing the spectra in Figure 17, it seems that the stronger signal of the S-O bonds observed does not allow for a clear-cut assignment of the S-S and S-N stretching absorption bands. The weak shoulder observed at 765 cm^{-1} could be due to a S-N stretch. Other experimental evidence strongly suggests that the proposed structure is valid.(see Experimental and Results sections). The only positive result from the ir study is the confirmation of the existence of the NH_2 in the intermediate. Direct evidence for the NH_2 group was not obtained from other experiments.

Infra-red Spectrum of S-aminoisothiouronium Sulfate

The ir spectrum of $[(NH_2)_2CSNH_2]_2SO_4$ was scanned from 4000 cm^{-1} to 400 cm^{-1}, using the KBr-pellet technique. Because of the unstable nature of the compound, the spectrum was obtained within one-half hour after its preparation. Pressure applied to make the pellet and time taken to scanned the spectrum did not cause the decomposition of the sample, based on the fact that no yellow coloration due to sulfur was observed.

In order to help make the assignment, the absorption bands of the spectrum shown in Figure 18 were compared to the absorption
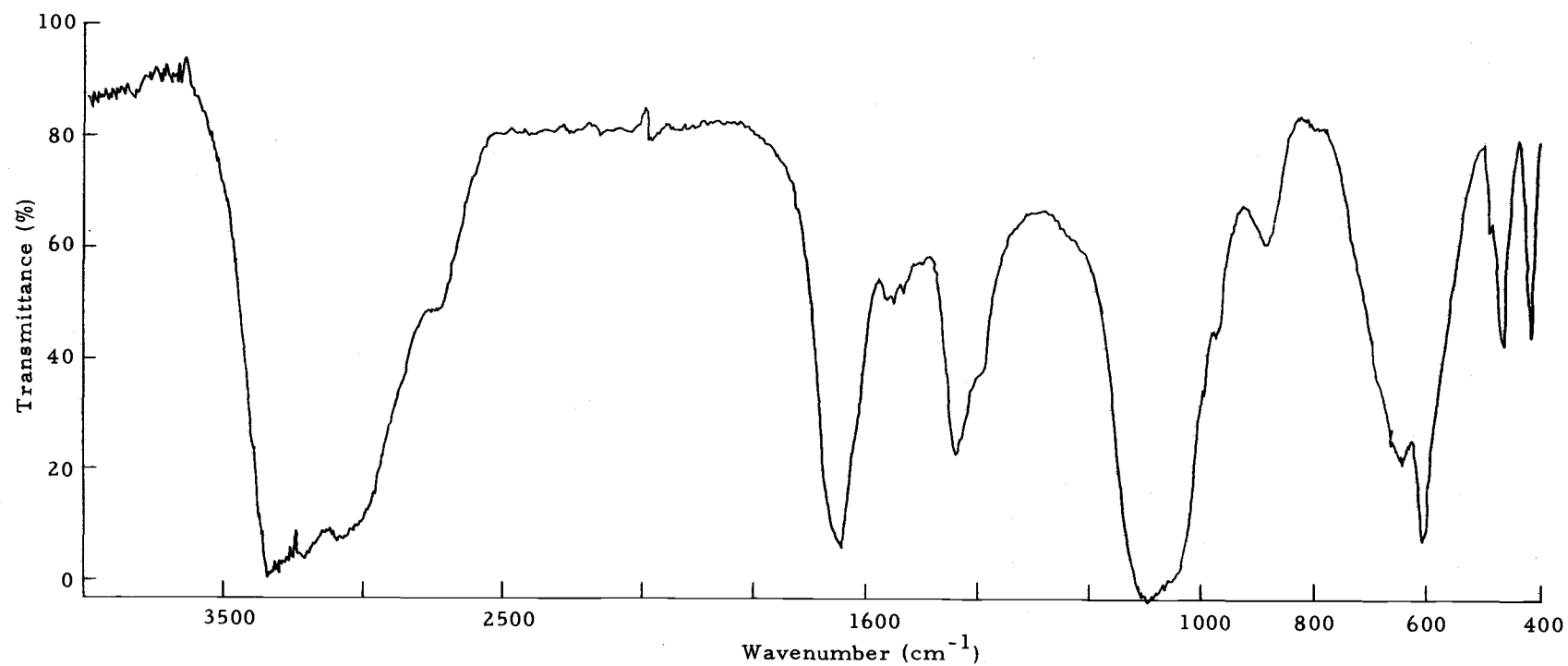
Figure 18. Infra-red spectrum of S-amino isothiouronium sulfate using KBr pellet technique.

bands of a spectrum of thiourea (47) and guanidinium nitrate (48).

From the assignments in the above references, the following assign-ments were made for the spectrum of our compound. The N-H stretch in NH_2, the NH_2 bending absorption and the C-N stretching absorption are observed, respectively, at 3400-3000 cm^{-1}, 1650 cm^{-1}, and at 1450-1400 cm^{-1}.

S-N stretching frequencies are expected in the range 840-700 cm^{-1} (49, 50). C=S stretching frequencies are expected anywhere from 1200 cm^{-1} to 1050 cm^{-1} (51, 53) and C-S anywhere from 700 cm^{-1} to 600 cm^{-1} (51). Because of the uncertainty of the bond order for C-S in our compound, the range of possible C-S stretching frequencies is very large. The shoulders observed at 890 cm^{-1} and at 650 cm^{-1} could be due to either the S-N or C-S stretch. The apparent overlap of N-H stretch absorption bands observed at 3300-3000 cm^{-1} suggests that more than one type of NH_2 is involved. The spectrum shows definitely that the compound is not thiourea or guanidinium nitrate but, unfortunately, the features observed are not sufficient to confirm the proposed structure for the compound.