I. A KINETIC STUDY OF THE REACTION BETWEEN THIOACETAMIDE AND HYDRAZINE

II. THE IODOMETRIC DETERMINATION OF PEROXYDISULFATE

III. EFFECT OF SURFACE OXIDATION AND PLATINIZATION ON THE BEHAVIOR OF PLATINUM ELECTRODES

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ABSTRACT

PART I

Hydrazine reacts with thioacetamide to produce hydrogen sulfide. This reaction is first order with respect to both thioacetamide and hydrazine and is both specific and general acid catalyzed. Rapid precipitation of metal sulfides can be obtained in solutions of pH 4-6 with the thioacetamide hydrazine combination.

PART II

Rate measurements were made of the catalytic effects of copper and iron salts on the rate of the peroxydisulfate iodide reaction. The optimum conditions for the iodometric determination of peroxydisulfate have been established on the basis of these measurements.

PART III

The electroreduction of vanadium (V) and iodate was investigated chronopotentiometrically with platinum electrodes subjected to a variety of pretreatment procedures. It was shown that platinization of the electrode resulting from the reduction of the platinum oxide film increases the reversibility of the electrode.

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PART I

A KINETIC STUDY OF THE REACTION BETWEEN THIOACETAMIDE AND HYDRAZINE

Introduction

Swift and coworkers (1) have measured the rates of the acid- and base-catalyzed hydrolyses of thioacetamide. The acid-catalyzed rate has a magnitude such that it is possible to precipitate certain metal sulfides quantitatively from solutions having pH values of 2 or less in a few minutes at 90°C. The base-catalyzed hydrolysis reaction can be similarly employed at pH values greater than 12.

It is often desirable, however, to perform sulfide precipitations at pH values between 4 and 8. For instance, H_2S can be used at pH 5 to separate nickel and zinc as sulfides from metals which do not form sulfide precipitates under these conditions - e.g., manganese (II) and chromium (III). However, the rate of the thioacetamide hydrolysis reaction is too slow at pH 5 even at 90°C to generate sufficient hydrogen sulfide to carry out the separation described.

Precipitations of metal sulfides with thioacetamide by a mechanism which does not involve the prior hydrolysis of the thioacetamide ("direct reaction") have been described by Swift and coworkers (2, 3). In certain cases these reactions are rapid enough to achieve quantitative precipitations in reasonable time from solutions of pH 4 to 6, but for many metals - e.g., nickel and zinc - prohibitively long times are required.

Data on the acid-catalyzed hydrolysis reaction and on the direct precipitation reaction for nickel and for zinc are shown in table 1-1. The rates of direct reactions have been shown to be dependent on the presence of traces of solid nuclei such as sulfur (4). The measurements shown in table 1-1 were made with reagent grade thioacetamide. Much slower direct reaction rates were obtained with thioacetamide solutions filtered through millipore filters (4) which effectively removes nuclei.

It was observed in 1952 by F. C. Anson that hydrazine accelerates the rate of hydrogen sulfide formation from thioacetamide solutions having pH values between 4 and 6. Subsequent experiments showed that 100 ml. of a solution initially 1.0 F in thioacetamide, 1.0 F in hydrazine hydrochloride, and buffered at pH 5 with 0.10 F acetic acid and 0.17 F sodium acetate produced 100 mmoles of hydrogen sulfide in 40 minutes at 50°C. Under the same conditions it would require 8×10^6 minutes to produce this amount of hydrogen sulfide by the hydrolysis of thioacetamide.

The present study was undertaken to elucidate the nature of the reaction which leads to hydrogen sulfide evolutions from solutions of thioacetamide and hydrazine and to determine the analytical usefulness of the reaction. Studies were made of both the rate at which thioacetamide and hydrazine react and the rate at which zinc sulfide is precipitated as a result of this reaction. From the data obtained

Table 1-1

1. Acid-Catalyzed Hydrolysis of Thioacetamide -

Rate Expression

$$\frac{d[H_2S]}{dt} = k[CH_3CSNH_2][H^+]$$

$k = 0.21 \pm 0.023$ liter mole^{-1}min^{-1} at 90°C.

Time required at 90°C to generate one millimole of H_2S from 100 ml. of a 1.0 F CH_2CSNH_2 solution

pH	minutes
4	6×10^2
5	6×10^3
6	6×10^4

2. Direct Reaction -

Rate Expression

$$-\frac{d[M(II)]}{dt} = k\frac{[M(II)][CH_3CSNH_2]}{[N^+]^{1/2}}$$

M(II)	k at 90°C
Zn	4.2×10^{-4} liter$^{1/2}$mole$^{1/2}$min^{-1}
Ni	2.2×10^{-4} " " "

Time required at 90°C to precipitate 99% of a metal from a solution 0.1 F thioacetamide and 0.01 F metal ion.

pH	Ni(II)	Zn(II)
4	1700 min	930 min
5	750 "	365 "
6	237 "	120 "

appropriate conditions can be selected for performing sulfide precipitations in solutions of pH 4 to 6.

Preliminary Observations and Reaction Products

The following experiment was undertaken to determine the percent conversion of thioacetamide to hydrogen sulfide upon reaction with an excess of hydrazine.

Twenty-five ml. of 1.19 F thioacetamide and 25 ml. of 2.26 F hydrazine were mixed with 50 ml. of water. The solution was placed in a flask designed so that the hydrogen sulfide gas resulting from the reaction could be swept from the solution with nitrogen and trapped in a solution of cadmium nitrate. The reaction solution was heated to 90°C and the hydrogen sulfide was collected for 18 hours. At this time the evolution of hydrogen sulfide had ceased. The amount of hydrogen sulfide was determined by titrating the cadmium solution with standard sodium hydroxide to determine the amount of hydrogen ion from the reaction,

$$H_2S + Cd^{++} \rightleftharpoons CdS + 2H^+ .$$

It was found that approximately 90% of the thioacetamide was converted to hydrogen sulfide. It was inferred that 10% of the original thioacetamide was consumed in a side reaction.

The side reaction product was found to have nearly the same ultraviolet spectrum as thioacetamide, both having maximum absorption at about 260 mμ.

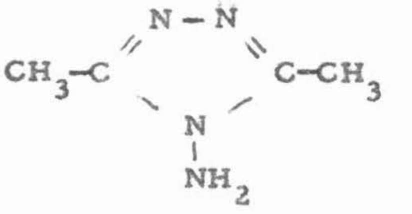
The above solution containing 10% of the original sulfur in the form of a side product was treated with cadmium nitrate. On prolonged heating no cadmium sulfide precipitate appeared.

Studies were made to determine the number of moles of hydrogen sulfide produced per mole of hydrazine when the hydrazine reacted with an excess of thioacetamide. It was found that within ± 10% one mole of hydrogen sulfide was formed per mole of hydrazine.

Several compounds related in structure to hydrazine were tested for their reactivity toward thioacetamide. It was found that hydroxylamine, urea, and N,N-dimethylhydrazine react much slower with thioacetamide (to produce hydrogen sulfide) than does hydrazine.

A product of the reaction between thioacetamide and hydrazine was isolated from the reaction mixture. The procedure consisted of allowing 25 grams of thioacetamide and 16 grams of hydrazine hydrate in 100 ml. of water to react at 50°C for several days. The solution was constantly purged with nitrogen to remove the hydrogen sulfide being generated and to remove any oxygen remaining in contact with the reaction solution. (An oxidation of hydrogen sulfide to sulfur can occur. This sulfur might react with hydrazine or it might react with ammonia provided that ammonia is one of the reaction products. The reaction between sulfur and pure hydrazine hydrate is known to produce $N_2H_4H_2S$ and N_2. The reaction between sulfur and liquid ammonia is known to produce N_4S_4 and $(NH_4)_2S$ (5).) The solution containing the products (aside from the hydrogen sulfide) of the thioacetamide hydrazine reaction was evaporated under vacuum at 50°C yielding white crystals. On exposure to air the crystals began to turn red. Upon recrystallization from ethyl alcohol, long, thin, white crystals were obtained that appeared stable in air. The crystals were found to melt at 199-201°C. NMR measurements by Dr. G. Fraenkel showed that the ratio of exchangeable to non-exchangeable hydrogens was approximately one to three. Microanalysis of this substance and an approximate determination of its molecular weight by freezing point depression indicated that it has the formula $C_4H_8N_4$.

A compound fitting the above data is the N-aminotriazole,



.

Its reported melting point is 199°C (6).

Rate Measurements of the Thioacetamide Hydrazine Reaction

The first kinetic experiments were made by following the decrease in the thioacetamide concentration in solutions containing an excess of hydrazine over thioacetamide. Solutions were buffered between pH 4 and 6 with acetic acid and sodium acetate. Some measurements were also made in solutions of pH 6 to 8 in the absence of a buffer.

Experimental

Reagents: All chemicals used were of reagent grade and were used without further purification. Stock solutions of hydrazine hydrochloride were prepared by neutralizing solutions of hydrazine hydrate (Matheson, Coleman, and Bell Chemical Co.) to pH 5 with hydrochloric acid. These solutions were standardized volumetrically with iodine (7).

Solutions of thioacetamide (Arapahoe Chemicals, Inc.) were prepared by weight and were not kept for more than a week.

Solutions of sodium thiosulfate were standardized against potassium iodate.

All other stock solutions were prepared by weight.

Procedure:

A reaction solution consisting of accurately measured aliquots of stock solutions of hydrazine hydrochloride, sodium perchlorate (to maintain the ionic strength at 1.5), and acetic acid-sodium acetate was heated to 50°C. The pH of the solution was adjusted at 50°C to the desired value with sodium hydroxide or hydrochloric acid with the aid of a pH meter. The solution was transferred to a large test tube supported in a constant temperature bath set at 50° ± 0.2° C, and an aliquot of a standard thioacetamide solution was added. Nitrogen was swept through the solution to remove hydrogen sulfide as it was formed in the reaction. The removal of hydrogen sulfide was necessary because of the analytical method. A diagram of the apparatus used is shown in figure 1-1.

At appropriate times during the run aliquots of the reaction solution were analyzed by one of the two following methods.

(1) Cadmium Sulfide Precipitation Method:

Aliquots of the reaction solution were pipetted into an ammoniacal cadmium nitrate solution. Sufficient time was allowed for cadmium and thioacetamide to react to form cadmium sulfide. Separate experiments had shown that under these conditions cadmium nitrate does not react with the side reaction products to form cadmium sulfide. The precipitate of cadmium sulfide was washed several times to remove the excess hydrazine and transferred quantitatively into a slightly alkaline solution containing KI and a measured excess of KIO_3. This solution was acidified with hydrochloric acid to dissolve the cadmium sulfide and liberate hydrogen sulfide and iodine. After the oxidation of hydrogen sulfide to sulfur by iodine, the excess iodine was back titrated with a standard sodium thiosulfate solution to a starch-iodine endpoint.

(2) Silver Sulfide Precipitation Method:

At appropriate times during the run aliquots of the reaction solution werepipetted into a 1 F NaOH solution containing a measured excess of silver ion in the form of the thiosulfate complex. After the

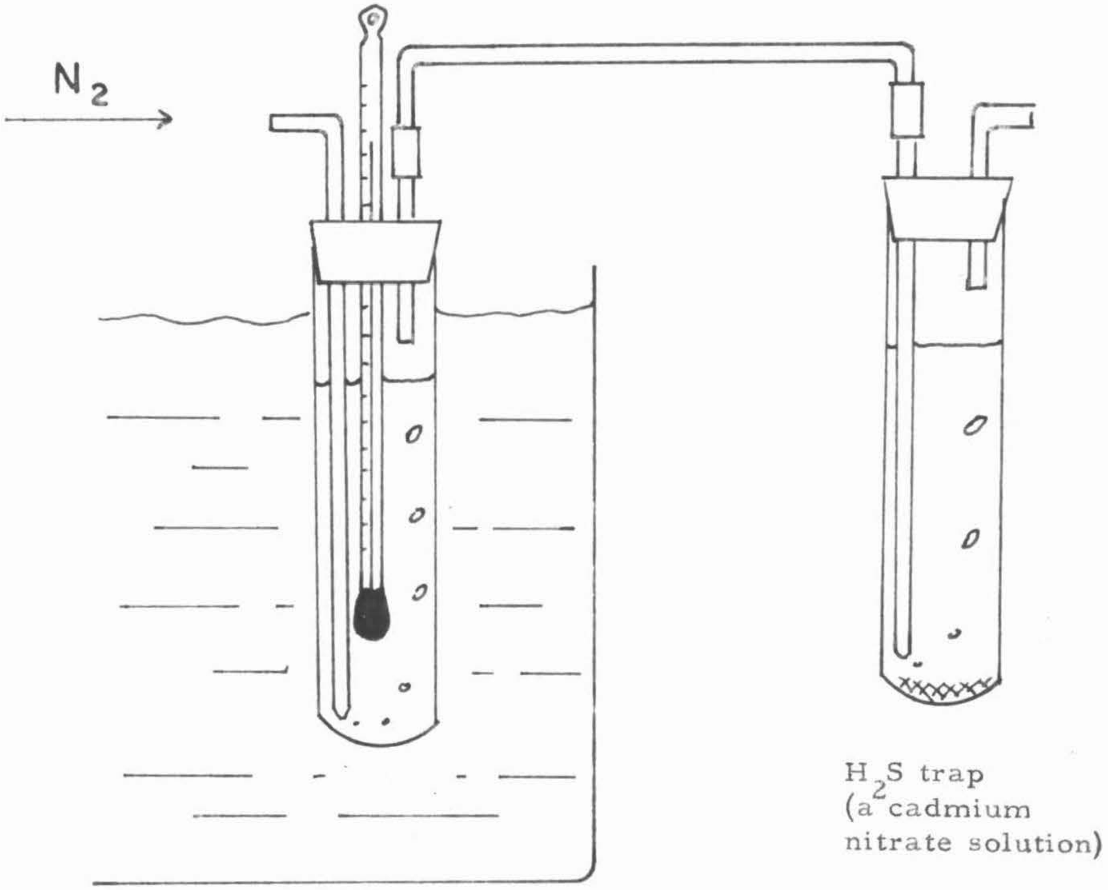


Figure 1-1. Apparatus

precipitation of silver sulfide (resulting from the reaction between the thioacetamide in the aliquot and the silver) was complete, the remaining silver was back-titrated with a standard thioacetamide solution. The end point was determined potentiometrically with a silver-silver sulfide electrode (8)

Results and Discussion

The rate of the reaction between thioacetamide and hydrazine was found to be first order with respect to both the formal thioacetamide concentration and the formal hydrazine concentration.

The first kinetic experiments were carried out by following the thioacetamide concentration in solutions containing an excess of hydrazine. Analyses were made by the cadmium sulfide precipitation method. Semilog plots of the concentration of thioacetamide versus time showed that the reaction rate is first order with respect to thioacetamide (see figure 1-2). The pseudo first-order rate constant, k', obtained from the semilog plots was linearly dependent on the formal hydrazine concentration, indicating a first-order dependence on hydrazine as well. A summary of the data is shown in table 1-2. The linear dependence of the first-order rate constant, k', on the hydrazine concentration is shown in figure 1-3.

The results obtained by the cadmium sulfide precipitation method were checked by repeating some of the above kinetic measurements

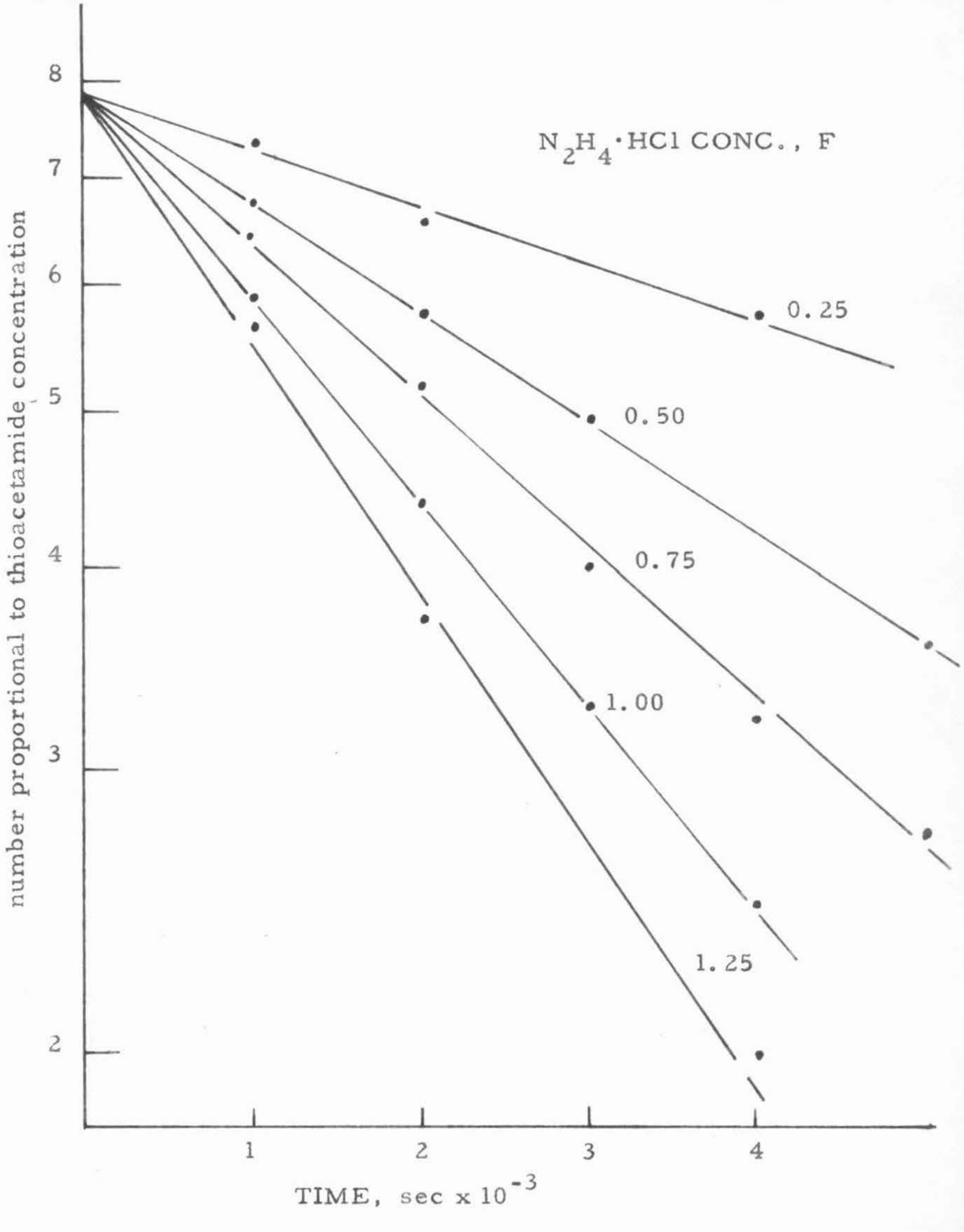


Figure 1-2. Rate of decrease of thioacetamide concentration at various hydrazine concentrations. Solutions buffered at pH 5 with 0.10 F $HC_2H_3O_2$ and 0.175 F $NaC_2H_3O_2$. Ionic strength = 1.50. Temperature = 50.0°C. Initial thioacetamide conc. in each case was 0.005 F.

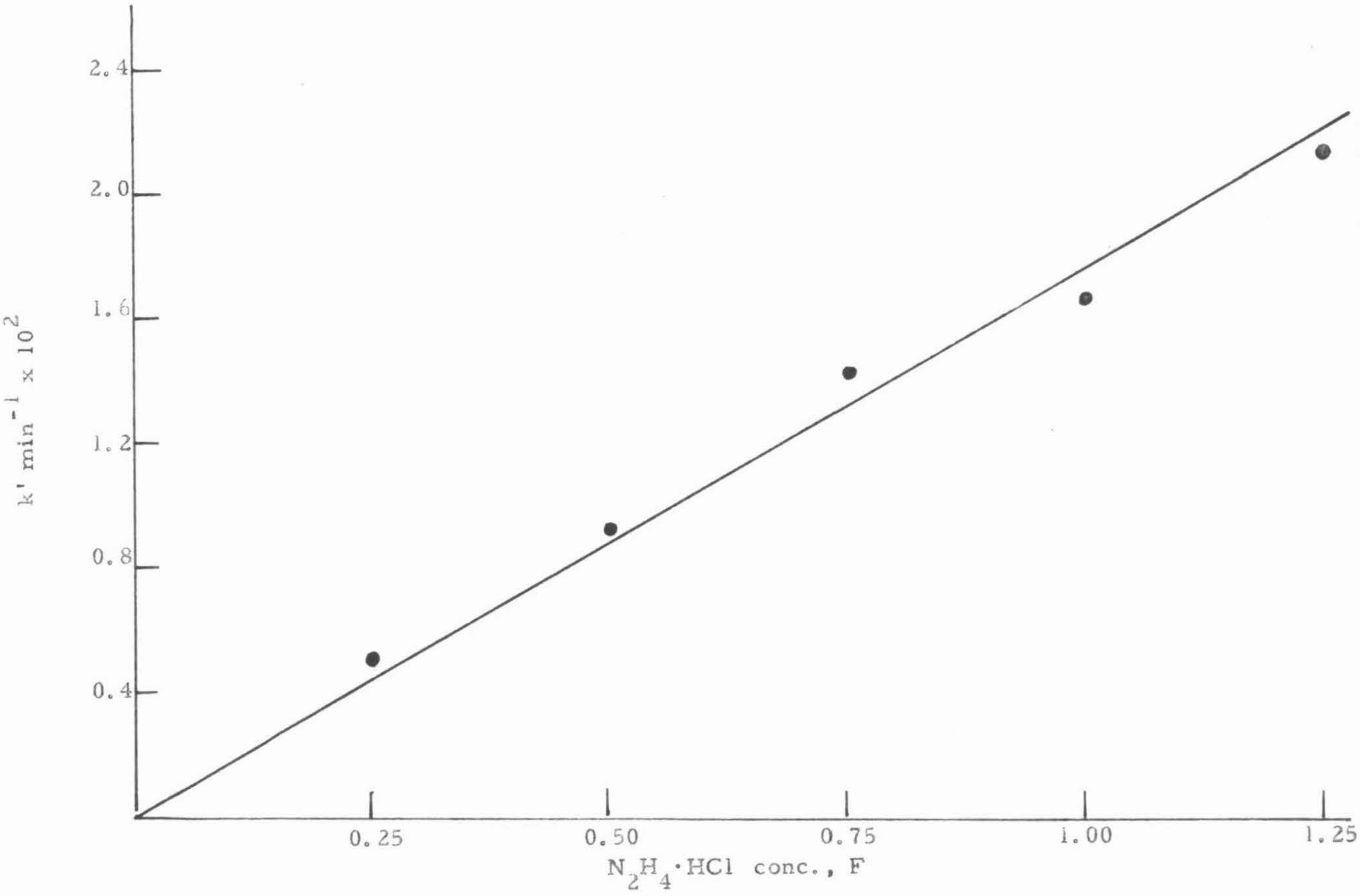


Figure 1-3. The effect of the formal hydrazine concentration on the pseudo first-order rate constant, k'.

Table 1-2

Effect of Formal Hydrazine Concentration on Rate of Disappearance of TAA.

μ = 1.50

temp. 50° ± 0.2°C

pH 5.0

0.10 F HAc

0.175 F NaAc

Method of analysis - CdS ppt.

$N_2H_4 \cdot HCl$	$k' min^{-1} x10^2$	$k' x10^2 / [N_2H_4 \cdot HCl]$
1.25 F	2.14	1.71
	2.14	1.71
1.00	1.73	1.73
	1.60	1.60
	1.67	1.67
0.75	1.48	1.97
	1.39	1.85
0.50	0.92	1.84
0.25	0.37	1.48
	0.73	2.92
	ave	1.84

using the silver sulfide precipitation method. The results were the same.

Additional rate studies in solutions buffered between pH 4 and 6 with sodium acetate and acetic acid showed that the rate is influenced by the total buffer concentration and by the pH of the reaction solution. These effects were investigated by means of a polarographic method to be discussed later.

Studies were made of the rate of the thioacetamide hydrazine reaction in solutions of pH 6 to 8 with no acetate-acetic acid buffer present. The results indicate that the reaction is initially first order in thioacetamide. However, the rate becomes faster after about 20 to 40% of the original thioacetamide has reacted. The reason for this increase is not known. The first order rate constants were difficult to determine because of this change in rate dependence. A summary of the data for the initial rates is presented in table 1-3. Again the reaction appears first order in the formal hydrazine concentration. The increase in the reaction rate with increasing pH (at constant formal hydrazine) indicates that the reaction probably involves the unprotonated hydrazine species which increases in concentration with increasing pH.

It is felt that the data are not sufficiently reliable to make any conclusions as to the reaction mechanism. It was found, however,

Table 1-3

Kinetic Studies of the Thioacetamide Hydrazine Reaction in the Absence of Acetate Buffer.

ionic strength = 1.0 temp. = 50.0°C

pH_∞	$N_2H_4 \cdot HCl$	k min^{-1}	Method of Analysis	$k' min^{-1}/N_2H_4 \cdot HCl$ F
6	1.25	3.96×10^{-2}	CdS ppt.	3.18×10^{-2}
6	1.00	3.18 "	" "	3.18 "
6	0.75	1.56 "	" "	2.09 "
6	0.50	1.59 "	" "	3.18 "
6	0.75	2.38 "	Ag_2S ppt.	3.16 "
7	1.00	23.7 "	" "	23.7 "
7	0.75	18.2 "	" "	24.3 "
7	0.50	13.0 "	" "	26.1 "
7	0.25	6.64 "	" "	26.6 "
5.94	1.00	1.38 "	" "	1.38 "
6.43	0.50	3.65 "	" "	7.30 "
6.90	0.25	6.83 "	" "	27.3 "
7.37	0.25	21.9 "	" "	87.6 "

that the last four rate measurements fit surprisingly close to the rate expression $-\frac{d[TAA]}{dt} = [TAA](k_1[N_2H_4] + k_2[N_2H_4][H^+])$, where k_2 is approximately 10^6 times larger than k_1.

Because of the deviation from first order dependence on thioacetamide, these studies were discontinued before firm conclusions as to the rate expression could be made.

Precipitation of Zn(II) from Solutions of Thioacetamide and Hydrazine

The following reaction rate studies were made of the rate at which Zn(II) is precipitated as zinc sulfide from solutions containing zinc sulfate, thioacetamide, hydrazine hydrochloride, and acetic acid-sodium acetate buffer.

Experimental

Reagents: All chemicals used were of reagent grade and were used without further purification.

Stock solutions of zinc sulfate were standardized volumetrically with EDTA (9)

Apparatus for Polarographic Method:

For the polarographic measurements a polarograph was constructed from a standard Moseley X-Y recorder, Model S-3 (F. L. Moseley Co., Pasadena, Calif.). The X-axis of the recorder was fed from the output of a high impedance, unit gain follower amplifier employing plug-in analog computer amplifiers (10). The scan voltage was supplied by a battery-powered Helipot driven with a synchronous motor. The current flowing between the dropping mercury electrode (d.m.e.) and a mercury pool electrode was measured with a resistor across the Y-axis input of the recorder. The voltage between the d.m.e. and a saturated calomel reference electrode (S.C.E.) was supplied to the input of the follower amplifier feeding the X-axis input. A standard d.m.e. was employed.

The reaction solution was contained in one half of a jacketed H-cell. The other half of the cell contained the S.C.E. and an agar-potassium chloride salt bridge. Constant-temperature water was circulated through the jacket of the H-cell.

Procedure:

The reaction solution was prepared in essentially the same manner as before except that zinc sulfate was also added; sodium chloride was used in place of sodium perchlorate, and pH adjustments were made at room temperature. The ionic strength was adjusted to 1.0 with the sodium chloride.

Prior to the addition of thioacetamide, the reaction solution was transferred to the polarographic cell. The solution was purged with a nitrogen stream for several minutes to remove dissolved oxygen. Water maintained at 50° ± 0.2°C was circulated through the jacket of the polarographic cell.

At 50°C the diffusion current was measured at -1.12 volts vs. the saturated calomel electrode. The diffusion current was proportional to the concentration of zinc.

The diffusion current at this potential was measured for the reaction solution. From this and from the known formal zinc sulfate concentration, the proportionality constant relating the diffusion current and formal zinc concentration was determined.

A measured aliquot of thioacetamide stock solution was added, and the solution was mixed by bubbling nitrogen through it. The diffusion current at -1.12 volts was continuously recorded, giving a plot of the formal zinc concentration in the reaction solution as a function of time.

Results and Discussion

In figure 1-4 are shown polarograms taken in a solution of zinc sulfate at pH 5. These were taken in the presence and absence of thioacetamide. It is seen that thioacetamide is without effect on the diffusion current or the half wave potential for the reduction of zinc. However, it appears to reduce the overvoltage of hydrogen.

Similar polarograms indicate that the zinc wave is not affected by hydrazine and that the zinc sulfide precipitate is not reduced.

The diffusion current for the zinc wave was measured at several formal zinc sulfate concentrations (see figure 1-5). The results show that at -1.12 volts vs. S.C.E. the diffusion current is directly proportional to the formal zinc sulfate concentration.

The polarographic measurements of the rate of precipitation of zinc sulfide were made from solutions containing much larger concentrations of thioacetamide and hydrazine hydrochloride than of zinc sulfate to assure that during the time required to precipitate all of the zinc there were no significant changes in the concentrations of the other

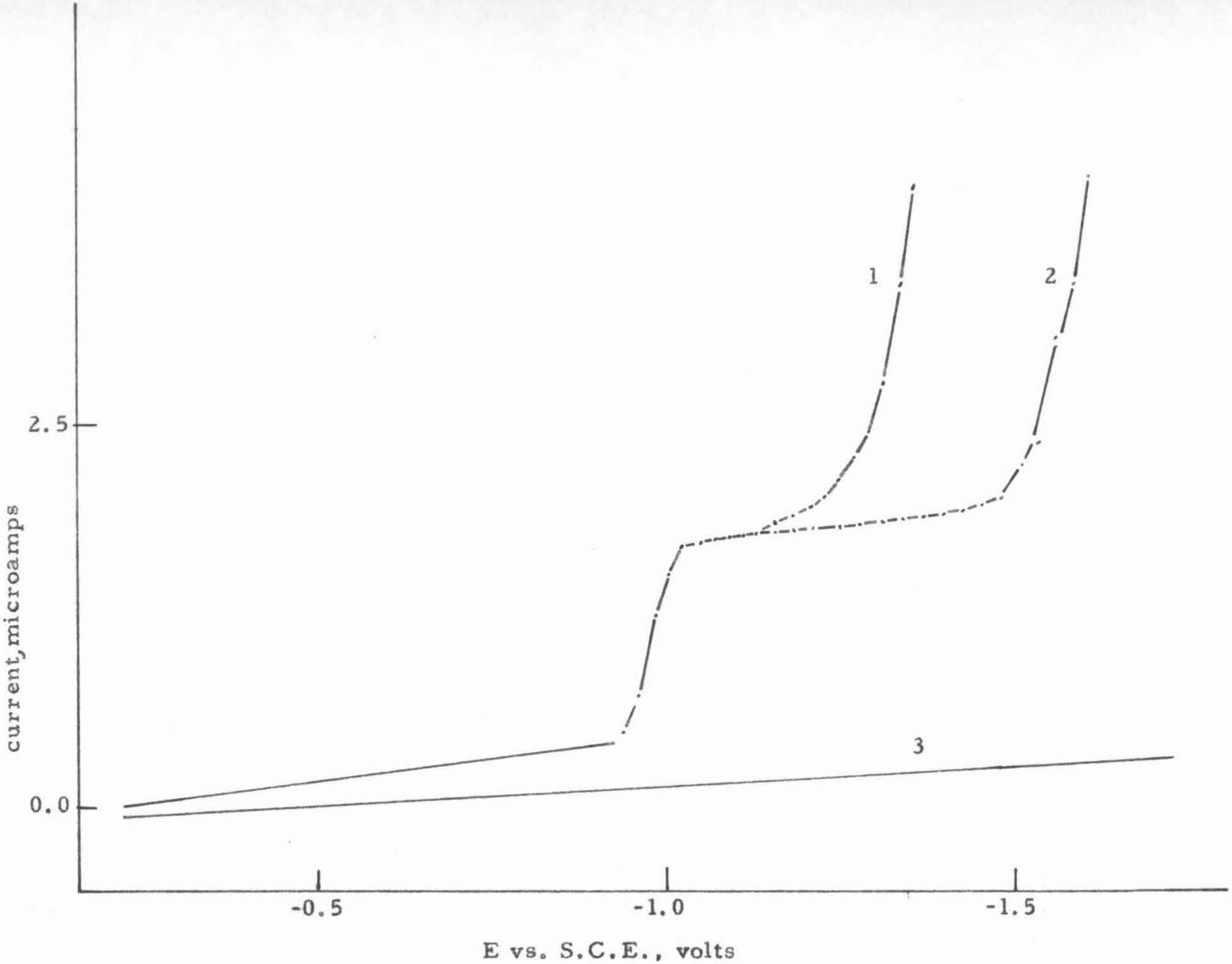


Figure 1-4. Effect of thioacetamide on the polarographic wave for the reduction of zinc: (1) zinc sulfate + thioacetamide, (2) zinc sulfate, (3) residual current.

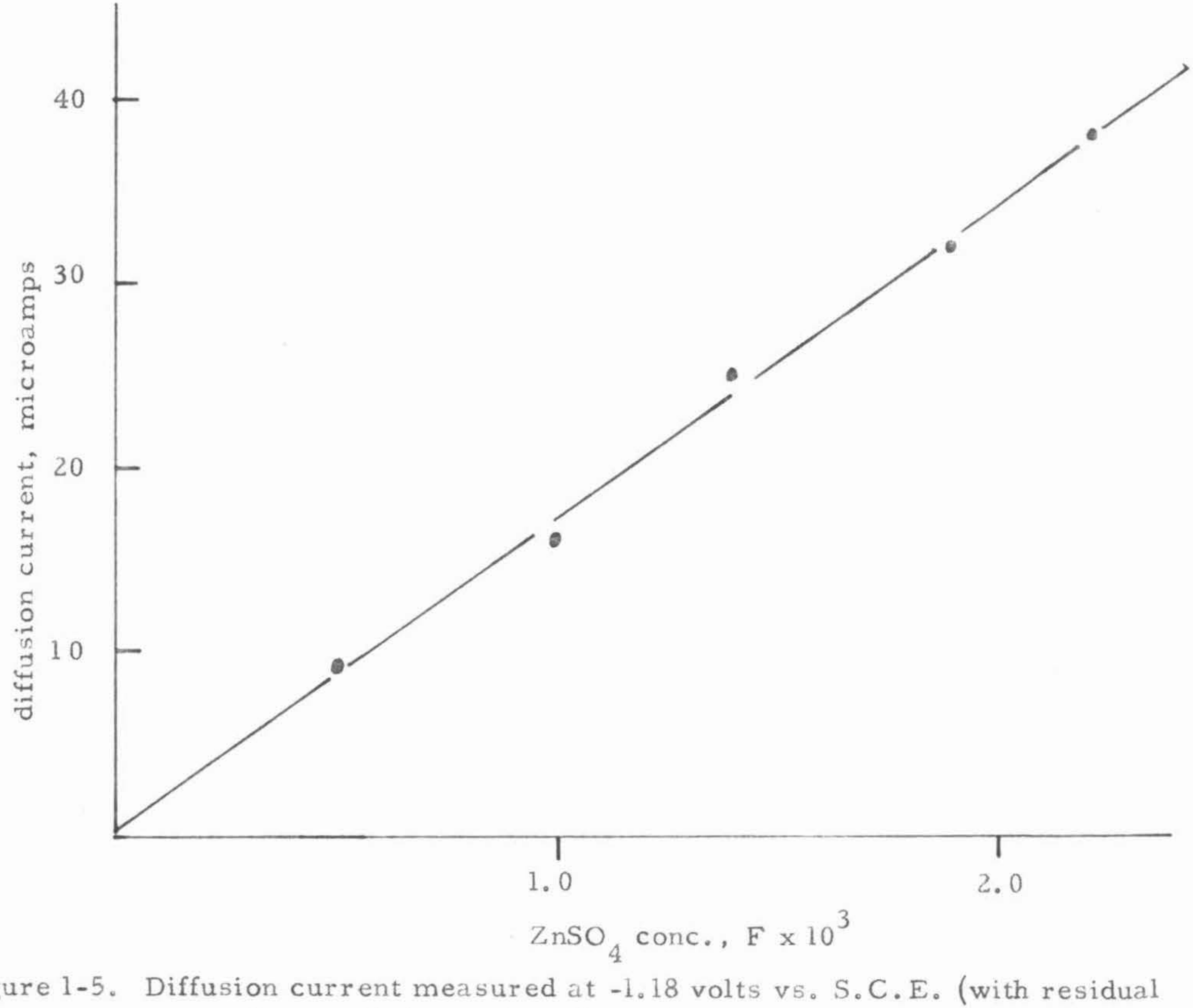


Figure 1-5. Diffusion current measured at -1.18 volts vs. S.C.E. (with residual current subtracted) for various formal zinc sulfate concentrations.

species present in the solution. Under these conditions the continuously recorded plots of diffusion current vs. time were essentially straight lines, indicating that the rate of decrease of the zinc concentration was zero order in zinc. In figure 1-6 is shown a typical kinetic run. To check that the rate of disappearance of zinc corresponded to the disappearance of thioacetamide, a run was made under conditions identical to those employed in the earlier experiments in which the thioacetamide concentration was followed titrimetrically. The second-order rate constants obtained by following the disappearance of zinc polarographically and by following the disappearance of thioacetamide titrimetrically were 1.9×10^{-2} and 1.8×10^{-2} mole^{-1} liter min^{-1}, respectively. Thus the rate of zinc sulfide precipitation is controlled by the rate of the reaction between thioacetamide and hydrazine.

A series of experiments was performed to determine the effects on the zero-order rate constant, k', of variations of pH, temperature, and of the formal concentrations of thioacetamide, hydrazine hydrochloride, and acetic acid-acetate buffer.

Effect of Concentrations of Thioacetamide and Hydrazine Hydrochloride.

The first-order dependence of the rate on thioacetamide and on hydrazine hydrochloride are shown in figures 1-7 and 1-8. The data are shown in table 1-4.

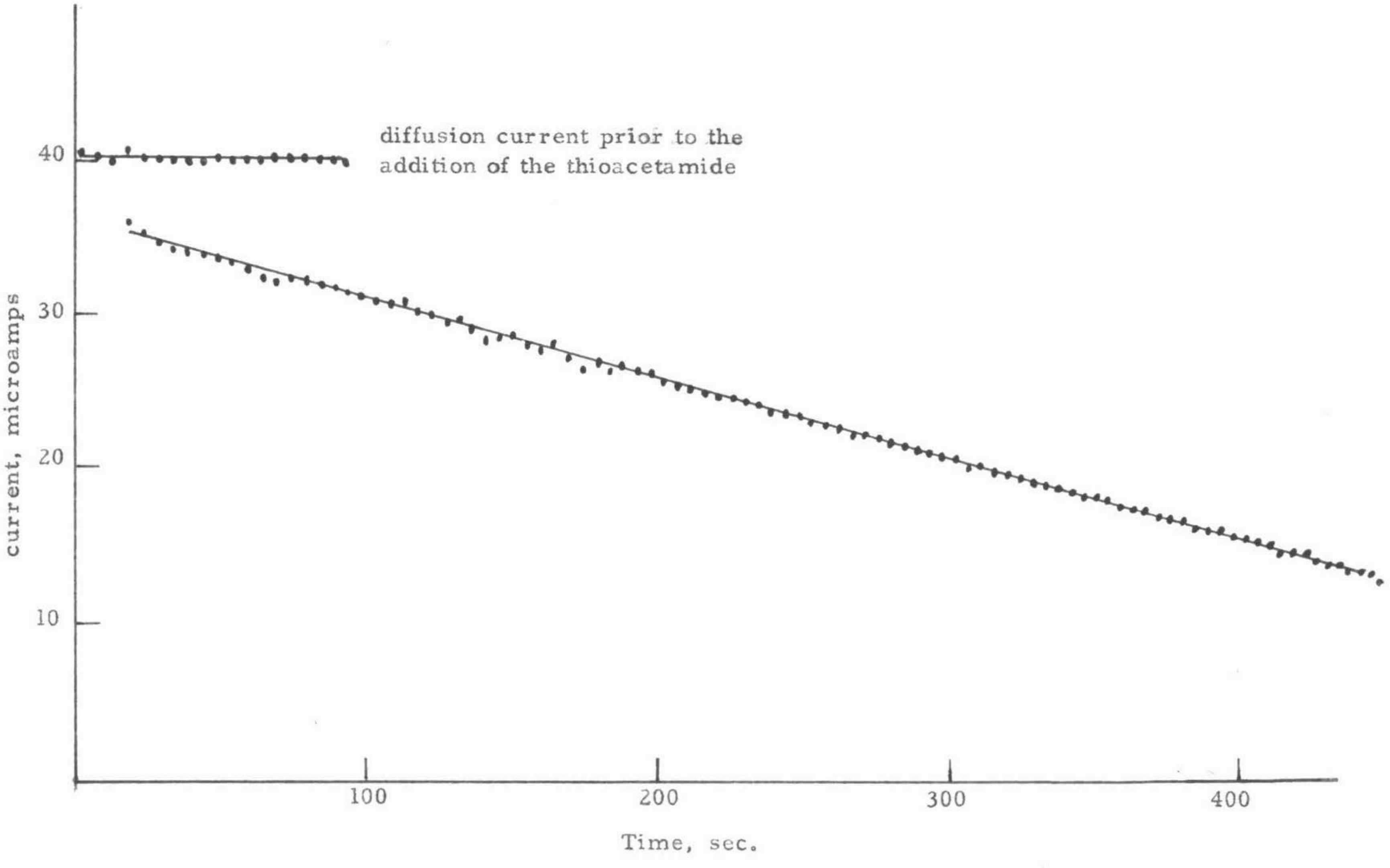


Figure 1-6. Typical kinetic run. Diffusion current measured at -1.12 volts vs. S.C.E. Solution contained 0.065 F $N_2H_4 \cdot HCl$, 0.033 F thioacetamide, and was buffered at pH 5.6 with 0.91 F total acetate. The initial $ZnSO_4$ concentration was 0.002 F.

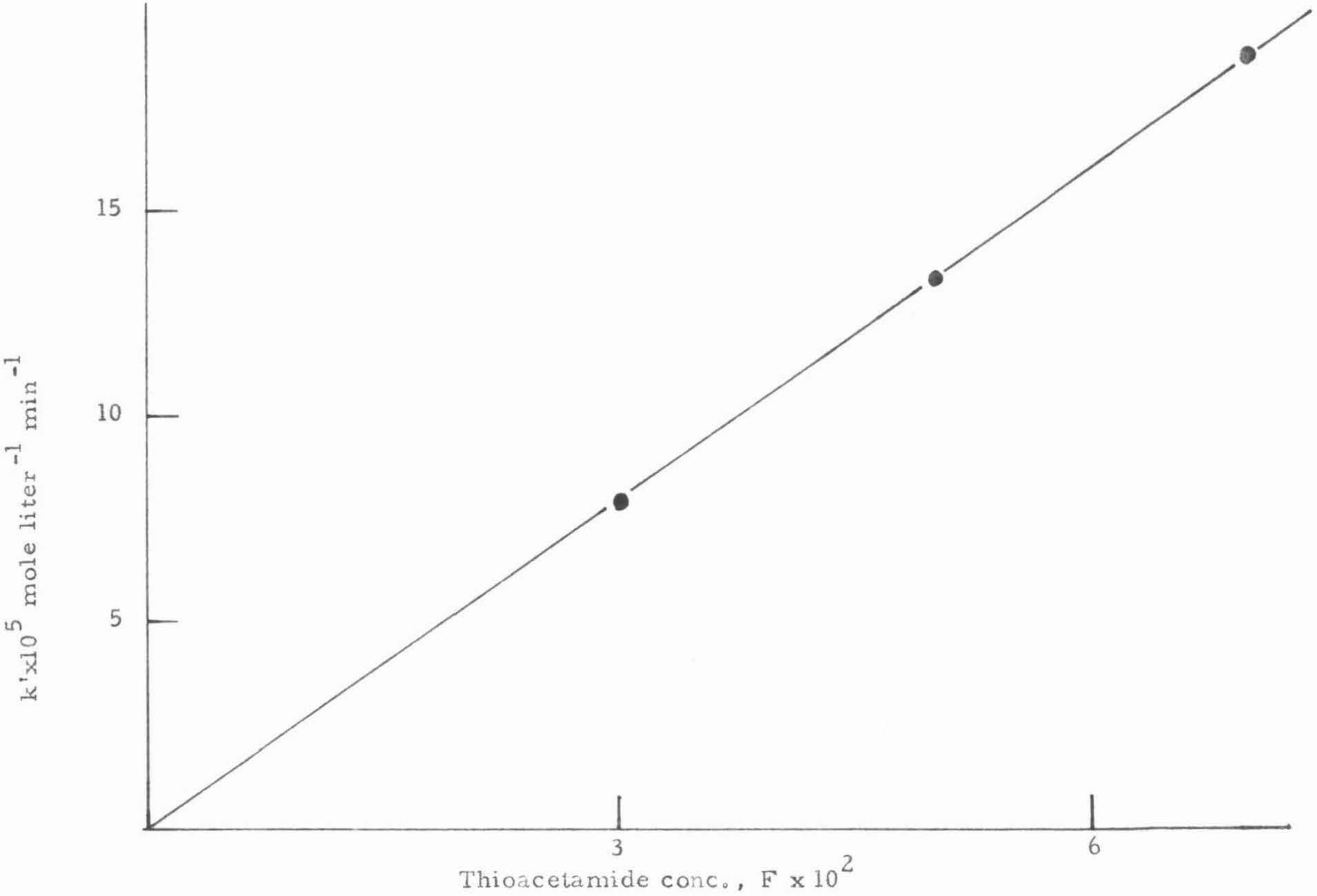


Figure 1-7. Dependence of the zero-order rate constant, k', on the formal thioacetamide concentration.

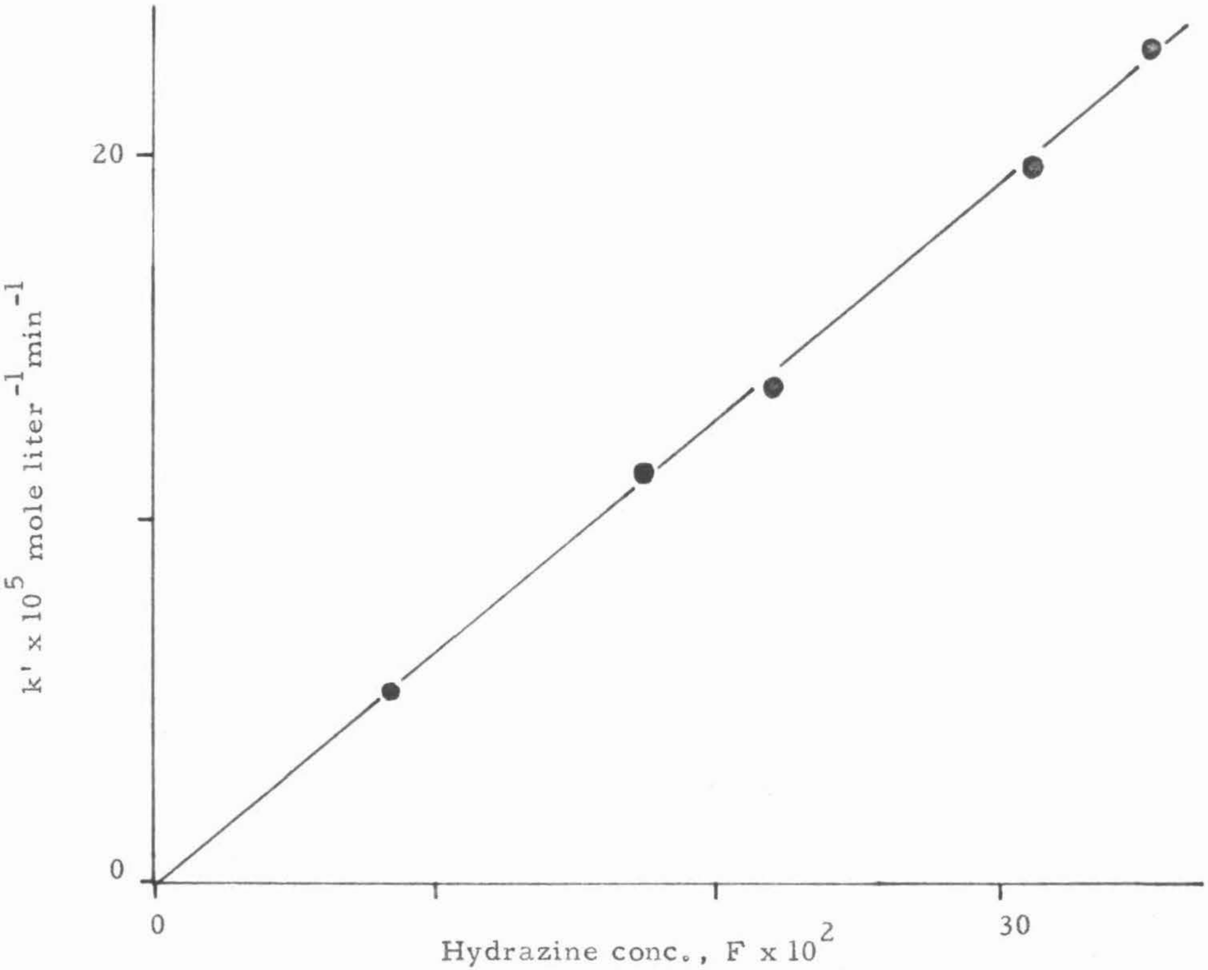


Figure 1-8. Dependence of the zero-order rate constant, k', on the formal concentration of hydrazine.

Table 1-4

Thioacetamide and Hydrazine Hydrochloride Dependence

(0.129 F NaOAc, 0.146 HOAc, pH 4.5, ionic strength = 1.0, temp. = 50° ± 0.2° C)

Concn., F	k' Mole Liter^{-1} Min.$^{-1}$ x 10^5	k'/[Thioacetamide] x 10^3
	Thioacetamide[a]	
0.030	7.92	2.64
0.050	13.4	2.68
0.070	18.7	2.67
	Hydrazine Hydrochloride[b]	
		k'/[Hydrazine Hydrochloride] x 10^4
0.089	4.91	5.52
0.178	10.9	6.12
0.222	13.4	6.04
0.310	19.3	6.23
0.355	22.4	6.30

[a] Solution composition = 0.222 F hydrazine hydrochloride.

[b] Solution composition = 0.050 F thioacetamide.

Effect of Buffer Concentration and pH.

Kinetic experiments were made at several concentrations of acetic acid-acetate buffer at pH values between 4.5 and 6.0. Since the reaction was first order in both thioacetamide and formal hydrazine, the second-order rate constant, k'', was calculated for each experiment. Plots of k'' vs. the molal acetate concentration at various pH values are shown in Figure 1-9.

Effect of Temperature.

An Arrhenius plot of the second-order rate constant, k'', is shown in Figure 1-10 for solutions in which the buffer concentration was 0.458 F and the pH was 5.0. The activation energy calculated from this plot is 17.7 kcal. per mole. For comparison the activation energies for both the acid- and base-catalyzed hydrolysis reactions are 19 kcal. per mole (1).

Rate Expression.

A rate expression that accounts fairly well for the various observed dependencies in acetate buffers is the following (TAA stands for thioacetamide):

$$\frac{d[H_2S]}{dt} = k_1[N_2H_5^+][TAA] + k_2[N_2H_5^+][TAA][OAc^-] \qquad (1)$$

or equivalently,

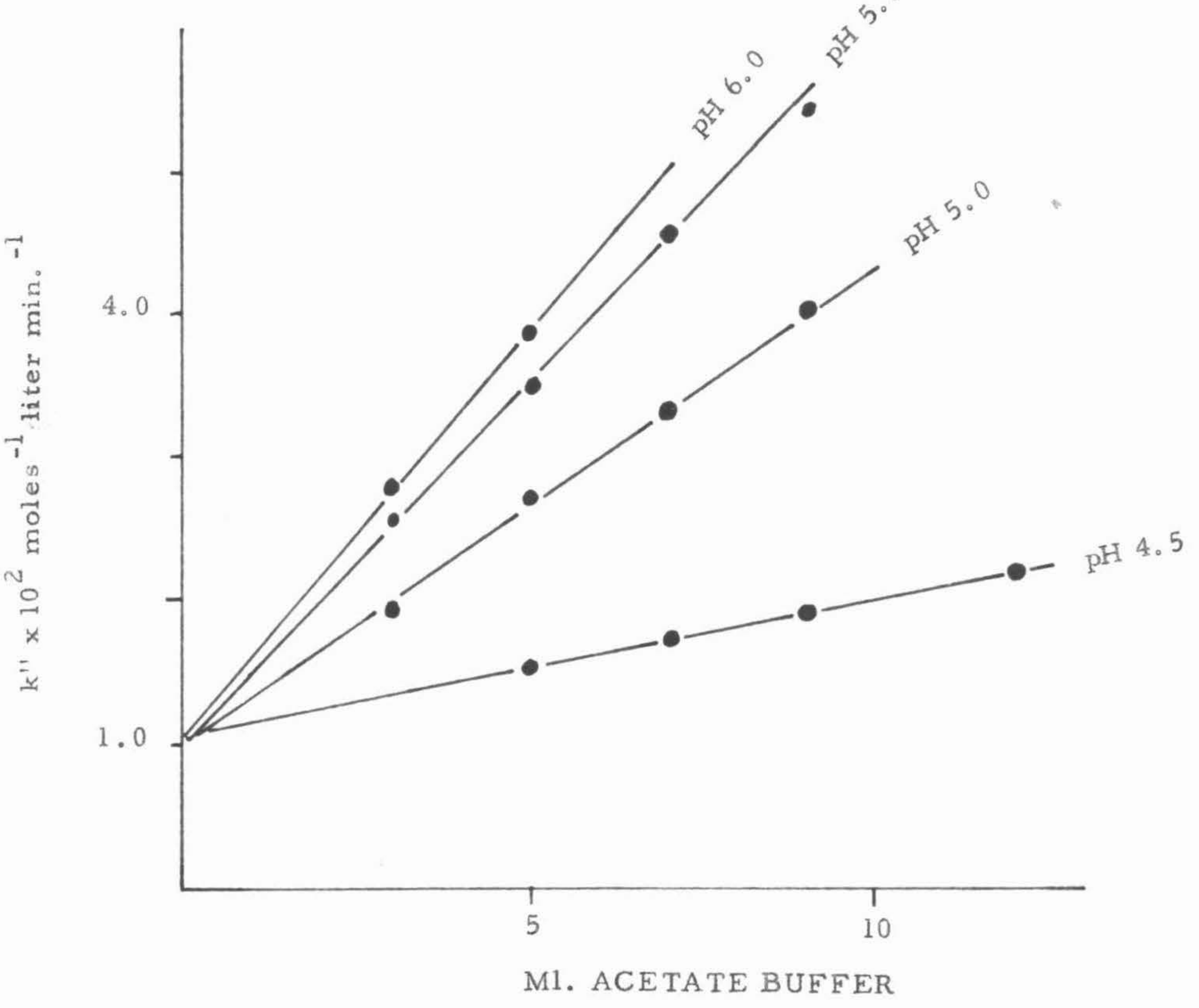


Figure 1-9. Dependence of second-order rate constant, k'', on concentration of acetate buffer.

Composition of buffer soln. 1.0 F HOAc and 1.75 NaOAc
Total soln. vol. 30.0 ml. in each case

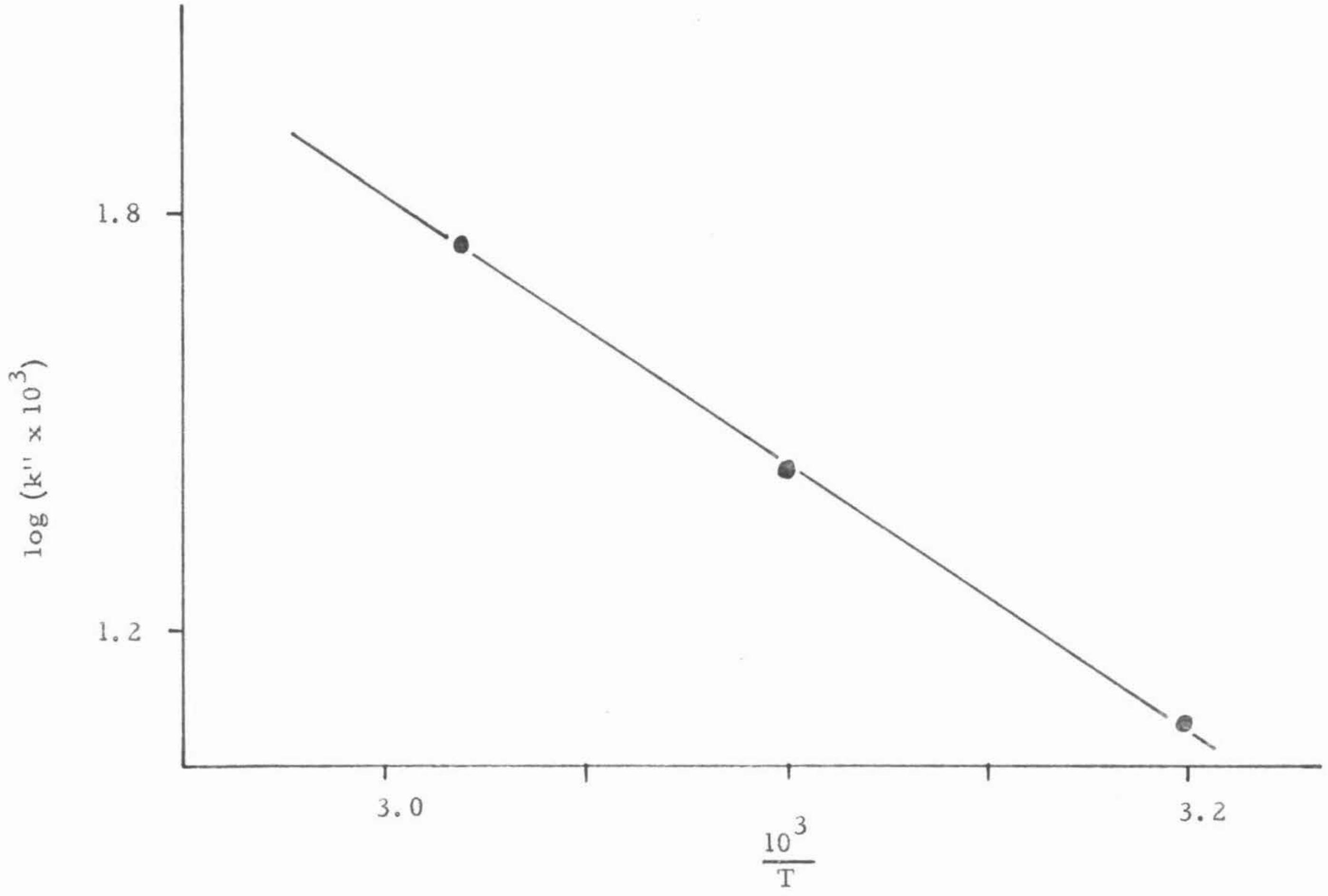


Figure 1-10. Arrhenius plot of second-order rate constant.

$$\frac{d[H_2S]}{dt} = k_3[N_2H_4][H^+][TAA] + k_4[N_2H_4][HOAc][TAA] \qquad (2)$$

The common intercept of all the lines in Figure 1-9 corresponds to the first term in equation 1. Values of k_1 and k_2 calculated at various pH values are given in Table 1-5. The value used for the ionization constant for acetic acid was 2.82×10^{-5}. This value was experimentally determined at an ionic strength of 1.0 and at a temperature of 50°C. In the range of pH values studied, the concentration of $N_2H_5^+$ was equal to the formal hydrazine concentration.

The relatively poorer precision in the values of k_2 compared with k_1 is a reflection of the strong dependence of k_2 on the value taken for the ionization constant for acetic acid. A small change in this constant causes a major change in k_2. At pH 5.5 and 6.0 the concentration of acetate ion is not so strongly affected by small errors in pH adjustment, so that the values for k_2 at these pH values are probably the most reliable.

The agreement of the data with this rate expression is sufficiently precise to enable the calculation of rates of precipitations of metal sulfides with the thioacetamide-hydrazine combination.

Reaction Mechanism.

The rate expression as written in equation 2 implies that a general as well as a specific acid catalysis contributes to the reaction.

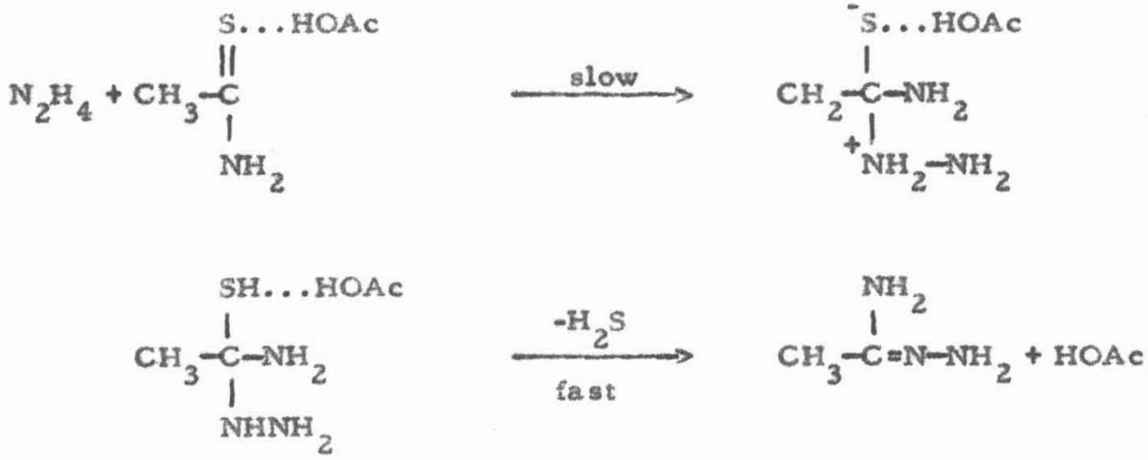
Table 1-5

Rate Constants for H_2S Evolution from Thioacetamide-Hydrazine Solutions

pH	OAc^-, M	k_1, Mole Liter^{-1} Min.$^{-1}$ x 10^2	k_2, Mole^{-2} Liter^{-2} Min.$^{-1}$ x 10^2
4.5	0.216	1.1	2.0
	0.303		2.1
	0.389		2.1
	0.519		2.1
5.0	0.203	0.9	5.0
	0.338		5.4
	0.474		5.1
	0.609		5.2
5.5	0.248	1.0	6.3
	0.413		6.0
	0.580		6.2
	0.744		6.0
6.0	0.266	1.2	5.9
	0.442		6.1

The general acid catalysis has also been observed with phthalate and phosphate buffers.

Comparison of equation 2 with that found for the addition reactions of substituted hydrazines with carbonyl compounds (11) suggests that a comparable mechanism might be involved. The mechanism would involve as the rate-determining step the addition of the unprotonated hydrazine to either the corresponding acid of the thiocarbonyl group or to the hydrogen-bonded complex of acetic acid and thioacetamide. The mechanism would lead to the formation of acetyl hydrazine:



$$N_2H_4 + CH_3-\underset{\underset{NH_2}{|}}{\overset{\overset{S...HOAc}{\|}}{C}} \xrightarrow{\text{slow}} CH_2-\underset{\underset{^{+}NH_2-NH_2}{|}}{\overset{\overset{^{-}S...HOAc}{|}}{C}}-NH_2$$

$$CH_3-\underset{\underset{NHNH_2}{|}}{\overset{\overset{SH...HOAc}{|}}{C}}-NH_2 \xrightarrow[\text{fast}]{-H_2S} CH_3-\overset{\overset{NH_2}{|}}{C}=N-NH_2 + HOAc$$

Acetyl hydrazine has been reported to condense to form a N-aminotriazole (12) which has been tentatively identified as one of the reaction products. A possible objection to this mechanism is that the value of k_3 would be unusually large (3×10^5 mole^{-2} liter^2 min.$^{-1}$).

Analytical Applications.

The application of the thioacetamide hydrazine system to the precipitation of metal sulfides should enable homogeneous precipitations to be made from weakly acid solutions. Preliminary experiments have shown that readily coagulated precipitates are obtained; even in the case of nickel the precipitate obtained under these conditions consists of large particles that are readily filtered. It is possible that the thioacetamide-hydrazine combination could be used to effect separations, some of which are impossible with thioacetamide alone.

PART II

THE IODOMETRIC DETERMINATION OF PEROXYDISULFATE

Various redox methods for the volumetric determination of peroxydisulfate have been proposed. Most numerous are methods involving the addition of an excess of a standard reducing agent, such as ferrous iron, arsenite, or oxalic acid, followed by titrations with standard oxidizing agents such as permanganate, dichromate, bromate, or quadripositive cerium. The iodometric determination of peroxydisulfate has also received repeated attention because of the slow rate of reaction between iodide and peroxydisulfate. Kolthoff and Carr (13) reviewed the above methods, and found that the iodometric and the ferrometric methods were the most satisfactory with regard to the times required and accuracies attainable.

The iodometric method is advantageous in that it requires only one standard solution, sodium thiosulfate, which is convenient to prepare and store. As mentioned above, peroxydisulfate reacts slowly with iodide and the stoichiometric equation is

$$S_2O_8^{=} + 3\,I^- = 2\,SO_4^{=} + I_3^- \ .$$

To insure quantitative reduction of peroxydisulfate in a convenient period of time, it is necessary to select conditions for which the rate of this reaction is made sufficiently rapid.

Kiss and Bruckner (14) found that an increase of ionic strength increases the rate of reaction. King and Jette (15) made use of this effect by providing a high concentration of potassium chloride.

Schwicker (16) found that the reaction is quantitative in a convenient time if a large excess of potassium iodide is added. This result was confirmed by Kolthoff and Carr (13) who also indicated that an excessive amount of electrolyte was objectionable since it tends to mask the starch-iodine endpoint.

A catalysis of the peroxydisulfate iodide reaction by both iron and copper salts was observed by Price in 1898 (17). Kinetic studies of this catalysis have been made by various workers and indicate that the catalyzed reaction proceeds many times faster than the uncatalyzed reaction.

Since the time of the first kinetic investigations various workers have sought to develop faster analytical procedures for the iodometric determination of peroxydisulfate by using the mentioned catalysts to increase the rate of the peroxydisulfate iodide reaction. Several have reported catalytic effects that are questionable. One worker has suggested that a suspension of cuprous iodide in water is an excellent catalyst (18). The combined use of ferrous ammonium sulfate and cupric sulfate has been reported to be more effective than either substance used separately (19). Ferric iron has been reported to have a greater specific catalytic effect than ferrous iron (20). This study was undertaken in part to reinvestigate these reports.

The primary purpose of this investigation was to study more quantitatively the catalytic effects of copper and iron salts on the rate of the peroxydisulfate iodide reaction under analytically desirable conditions and to establish the optimum conditions for the iodometric determination of peroxydisulfate. Rate measurements were made of the peroxydisulfate iodide reaction in the presence of various amounts of copper and iron salts. On the basis of these measurements, a procedure for the iodometric determination has been established and results of analyses by this method have been compared with those obtained by the ferrometric method.

Rate Measurements

Experimental: Except for the C. P. potassium peroxydisulfate, all chemicals used were of reagent grade. The potassium peroxydisulfate and other chemicals were used without further purification.

A series of reaction rate measurements were made at room temperature by the following procedure: Four grams of potassium iodide were dissolved in 10 ml. of H_2O and the solution was acidified with 0.1 ml. of 6 F (volume formal) HCl. A prescribed volume of 0.003 F $FeCL_3$ or 0.003 F $Cu(NO_3)_2$ was pipetted into the solution. Then 10 ml. of 0.05 F $K_2S_2O_8$ were added by means of a pipet and the resulting solution was diluted to 100 ml. At various time intervales this solution was titrated with standard 0.1 F $Na_2S_2O_3$ to a starch-iodine endpoint. The times at which successive endpoints were reached were recorded together with the total volumes of thiosulfate solution added at these times.

Discussion: Both the catalyzed and uncatalyzed peroxydisulfate iodide reactions have been shown to be first order with respect to the peroxydisulfate concentration (17). In the reaction rate determinations a large excess of iodide over peroxydisulfate was used. The pseudo first-order rate constants, k', for the decrease of peroxydisulfate concentration were calculated from the volumes of thiosulfate solution used and these rate constants are tabulated in Table 2-1, as are the concentrations of catalysts used.

Under the conditions of these experiments, the copper nitrate has a greater specific catalytic effect than does the ferric chloride.

In figure 2-1 are shown plots of the log of the peroxydisulfate concentration as a function of time for various formal copper nitrate concentrations. The pseudo first-order rate constants were determined from the slopes of these lines.

If one assumes that the catalyzed reaction and the uncatalyzed reaction proceed independently, the pseudo first-order rate constant, k, for the catalyzed reaction should equal the difference between the measured rate constant, k', for the combined reactions, and k' for the uncatalyzed reaction. Values for k calculated on the basis of this assumption are shown in Table 2-1.

Table 2-1

Catalysis Reaction Rate

c - volume formal metal salt concentration
k' - measured pseudo first-order rate constant
k - pseudo first-order rate constant for catalyzed reaction
$= (k'_{\text{combined rates}} - k'_{\text{uncatalyzed rates}})$

temp. - 23.5°C
μ - 0.25
initially
0.24 F KI
6×10^{-3} F HCl
0.005 F $K_2S_2O_8$

metal salt	$c \times 10^4$	$k' \times 10^3 \sec^{-1}$	$k \times 10^7 \sec^{-1}$	k/c
none		1.56		
		1.43		
		1.54		
$Cu(NO_3)_2$	0.15	2.2	0.7	47
	0.30	3.0	1.5	50
	0.60	4.1	2.6	43
	0.90	5.9	4.4	49
	1.20	7.3	5.8	48
	1.50	8.4	6.9	46
$FeCl_3$	0.85	2.1	0.6	7.1
	1.41	2.7	1.1	7.9
	2.82	3.6	2.1	7.4
	4.23	4.7	3.2	7.5

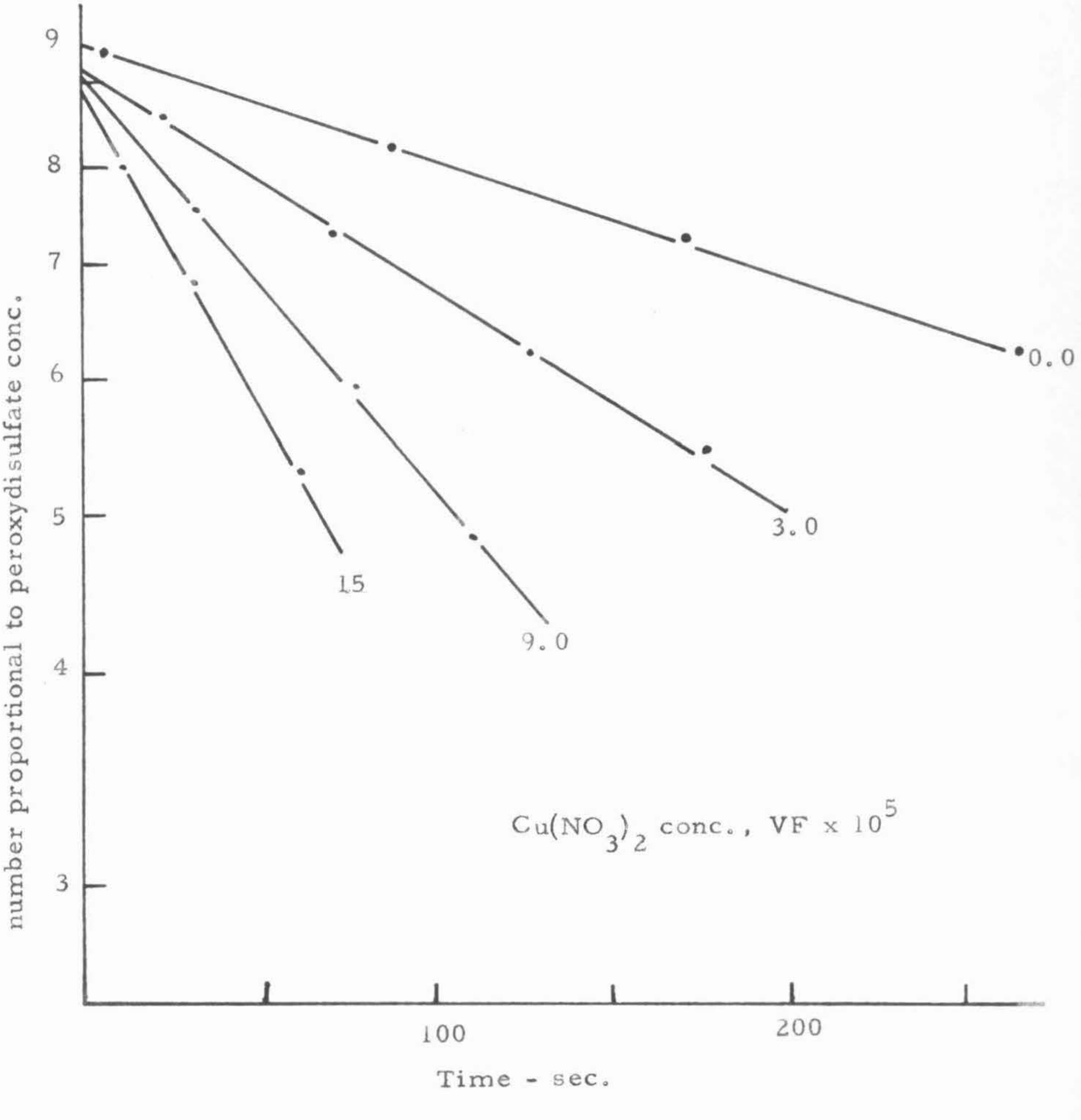


Figure 2-1. Concentration of peroxydisulfate as a function of time for various volume formal $Cu(NO_3)_2$ concentrations.

From the constancy of the ratios of the catalysis rate constant, k, and the formal catalyst concentrations, the catalyzed reaction appears to be first order with respect to the catalyst concentration. This first-order dependence is demonstrated in figure 2-2, in which the pseudo first-order rate constant for the catalyzed reaction, k, is plotted against the formal copper nitrate concentration.

No precipitate was observed in the reaction solutions indicating that the copper was present primarily as the cuprous iodide complex.

Measurements were made to determine the combined catalytic effect of iron and copper salts. The measured total rates indicate that only an additivity in the catalyzed rates was obtained. The k' was calculated by summing the k' for the uncatalyzed rate, the k for the copper nitrate catalyzed rate, and the k for the ferric chloride catalyzed rate at the concentrations prevailing. The data are summarized in Table 2-2.

The effect of solid cuprous iodide on the rate of the catalyzed reaction was also investigated. A series of rate measurements was made in which the formal copper nitrate concentration was increased up to that needed to precipitate cuprous iodide. It was found that the reaction rate increases in the expected manner to the point where cuprous iodide first precipitates. After adequate copper nitrate was added to cause rapid precipitation of the cuprous iodide, no further increase

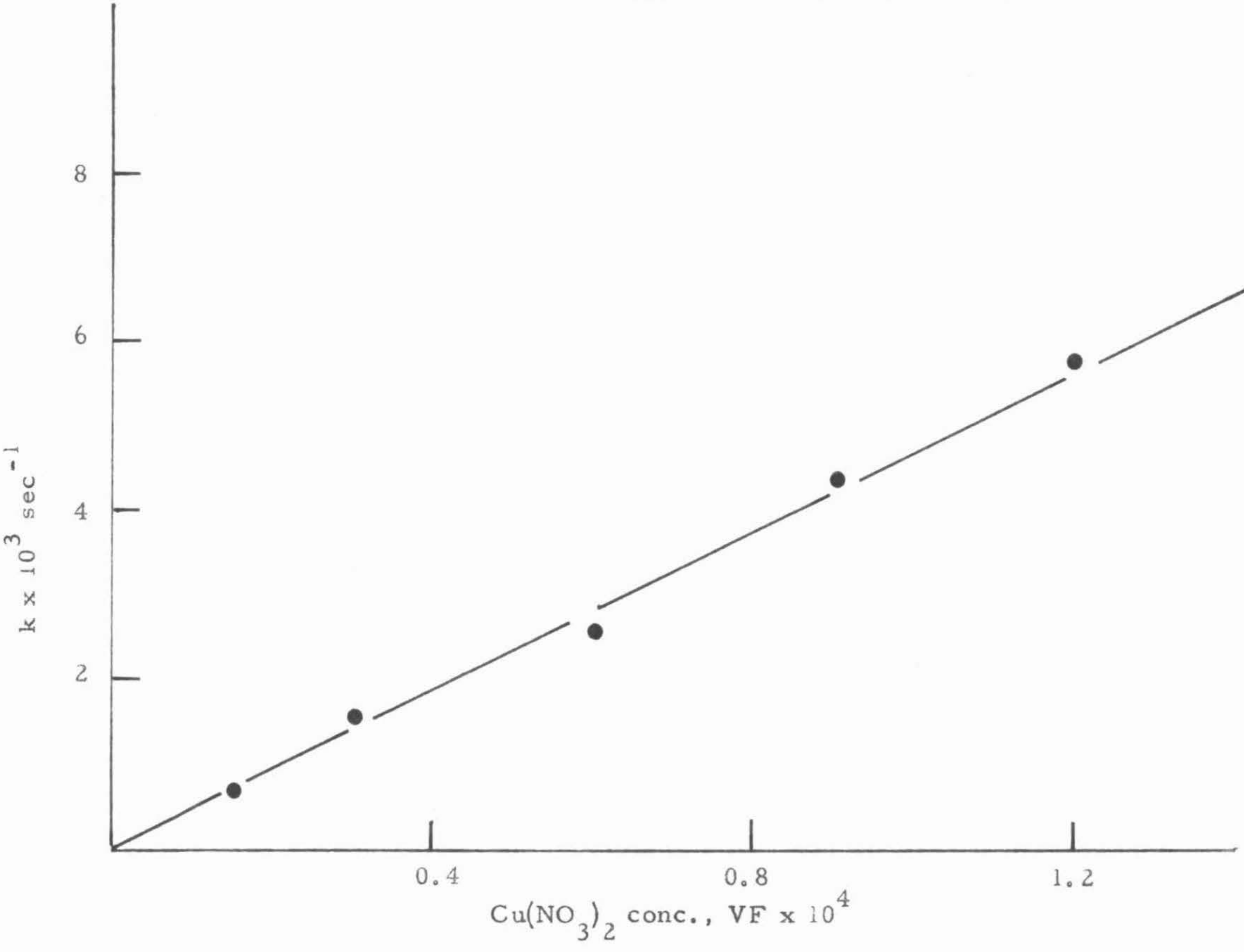


Figure 2-2. Effect of the copper nitrate concentration on the rate of the catalyzed reaction (k = pseudo first-order rate constant for the catalyzed reaction).

Table 2-2

Combined Catalytic Effect

temp. 23.5°C   0.24 F KI

μ 0.25 6×10^{-3} F HCl

initially 0.005 F $K_2S_2O_8$

$FeCl_3$	$Cu(NO_3)_2$	$k' \times 10^3$ experimental	$k' \times 10^3$ calculated
1.41×10^{-4} F	0.30×10^{-4} F	3.7 sec^{-1}	3.9 sec^{-1}
1.41 "	0.60 "	4.5 "	5.4 "
0.85 "	0.90 "	6.1 "	6.4 "
1.41 "	0.60 "	5.0 "	5.4 "
1.13 "	0.90 "	6.3 "	6.6 "

in the reaction rate was observed. Because of supersaturation effects these measurements were difficult to make. The slight decrease in rate after initial precipitation probably reflects a faster nucleation rate due to the presence of more precipitate. It was concluded that solid cuprous iodide has no catalytic effect. The data from these experiments are shown in Table 2-3.

It has been reported that ferric iron was a better catalyst than ferrous iron (20). To check this statement rate measurements were made in which both oxidation states of iron were tested for their catalytic effect. The iron catalysts were added to reaction solutions containing KI, HCl, and $K_2S_2O_8$, and the reaction rates were measured

Table 2-3

Effect of Solid Cuprous Iodide on Catalysis Reaction

temp. 1.5°C		0.12 F KI

μ 0.14		6×10^{-3} F HCl

initially 0.005 F $K_2S_2O_8$

C = formal concentration of $Cu(NO_3)_2$ neglecting precipitated CuI.

k'= measured pseudo first-order rate constant.

$C \times 10^4$	k' sec^{-1}
1.0	4.1×10^{-4}
2.0	8.2
3.0	Beginning of CuI precipitation
5.0	12.0
10.0	10.4
20.0	10.6

in the manner previously described. The same specific reaction rates were obtained with the two initially different oxidation states of iron, indicating that there is no difference in their catalytic effect.

The effect of the iodide concentration on the copper nitrate catalyzed reaction was determined. In a series of rate measurements, the iodide concentration was varied and with each variation both the uncatalyzed rate and the combined rate were determined. The data are shown in Table 2-4. The rate of the catalyzed reaction was found to be a rather complex function of the iodide concentration. Initially it appears to be approximately second order with respect to

Table 2-4

Effect of Iodide Concentration on Catalysis Reaction

temp. 23.5°C 1.5×10^{-4} F $Cu(NO_3)_2$
6×10^{-3} F HCl

initially 0.005 F $K_2S_2O_8$
ionic strength not maintained constant

KI	k' measured rate	k' uncatalyzed rate	k catalyzed rate
0.024	2.55×10^{-4} sec^{-1}	0.6×10^{-4} sec^{-1}	2.0×10^{-4} sec^{-1}
0.072	11.4 "	2.27 "	9.1 "
0.120	29.5 "	4.80 "	24.7 "
0.190	61.9 "	9.64 "	52.3 "
0.240	84.5 "	15.1 "	69.4 "
0.290	86.6 "	18.3 "	68.3 "
0.480	103.5 "	41.8 "	61.7 "

iodide, but this dependence vanishes at higher iodide concentrations.

The ionic strength was not held constant in this last series of measurements. However, experiments were made which showed that changes in ionic strength have little effect on the rate of the catalyzed reaction. This was done by varying the ionic strength with sodium perchlorate. Similar experiments showed that ionic strength changes do influence the uncatalyzed reaction. The data are shown in Table 2-5.

Table 2-5

Effect of Ionic Strength

(1) Uncatalyzed Reaction

temp. 23.5°C — 0.12 F KI

6×10^{-3} F HCl

initially 0.005 F $K_2S_2O_8$

k' = measured first-order rate constant

$NaClO_4$	Ionic strength	$k' sec^{-1} \times 10^4$
0.0 F	0.12	4.80
0.082	0.20	5.02
0.123	0.25	5.42
0.164	0.29	6.00

(2) Catalyzed Reaction

1.2×10^{-4} F $Cu(NO_3)_2$

other conditions the same

$NaClO_4$	Ionic strength	$k' sec^{-1} \times 10^3$
0.00	0.12	2.45
0.082	0.20	2.45
0.164	0.29	2.45

Recommended Procedure

A procedure for the iodometric determination of peroxydisulfate was tentatively formulated and tested. Copper nitrate was used as the catalyst. A sufficient amount is used to nearly saturate the solution with cuprous iodide. The reaction is carried out at pH 2. The rates of both the uncatalyzed and the copper catalyzed reactions were previously reported to be independent of pH in acid solution (17).

The sample is diluted prior to titration with sodium thiosulfate in order to eliminate possible decrease in sensitivity of the starch-iodine endpoint resulting from the presence of an excessive amount of electrolyte.

On the basis of the foregoing rate data and on the assumption that the uncatalyzed reaction is first order with respect to the iodide concentration, calculations were made which show that under the conditions of this formulated iodometric procedure, 470 mg. of $K_2S_2O_8$ will be 99.9% reduced in one minute. In the absence of catalyst, the calculated time for 99.9% completeness is 30 minutes. The actual rates are faster because the ionic strength used in this procedure is higher than that used in the rate measurements.

Procedure: Weigh into a 250 ml. flask sufficient peroxydisulfate sample to require from 35-45 ml. of 0.1 F $Na_2S_2O_3$. Dissolve the sample in 25 ml. of H_2O. Add 10 ml. of a solution containing 4 grams of KI and 0.1 ml. of 6 F HCl (the reaction solution had a pH of approximately 2). Add 1.00 ml. of 0.1 F $Cu(NO_3)_2$, swirl, and let the solution stand for three minutes. Dilute to 100 ml. and titrate with standard thiosulfate to a starch-iodine endpoint. Make a catalyst and reagent correction determination on a similar solution containing no peroxydisulfate.

Results of analyses obtained by this procedure of various weighed quantities of an undried C.P. $K_2S_2O_8$ are shown in Table 2-6. Also shown are the results of analyses obtained by the back titration of an excess of standard ferrous iron with quadripositive cerium (21). A 0.05 F $K_2S_2O_8$ solution was prepared and aliquots were analyzed by each of the above methods. Also a sample of the C.P. $K_2S_2O_8$ was recrystallized three times from distilled water and dried over sulfuric acid (22). Three weighed samples were analyzed by the iodometric method and the results are shown in Table 2-6.

The analytical results obtained by the iodometric procedure compare favorably with those obtained with the ferrometric method. The deviations in the analyses of the unpurified $K_2S_2O_8$ by both methods are probably caused in part by the non-uniformity of the C.P. $K_2S_2O_8$. Analyses of the 0.05 F $K_2S_2O_8$ solution and of the recrystallized $K_2S_2O_8$ showed smaller deviations.

Studies of the stability of $K_2S_2O_8$ solutions were made. A 0.05 F $K_2S_2O_8$ solution was prepared from the C.P. material and had

Table 2-6

Analysis of $K_2S_2O_8$

Analysis of Undried C.P. $K_2S_2O_8$

(1) Iodometric Method

mg. taken	mg. found	% $K_2S_2O_8$
165.5	164.1	99.15
328.6	326.0	99.21
572.0	567.1	99.14
463.1	459.5	99.22
285.7	284.7	99.65
225.7	224.3	99.37
355.3	352.3	99.16
521.9	518.8	99.41

average 99.29
s.d. 0.17

(2) Ferrous-Ceric Method

mg. taken	mg. found	% $K_2S_2O_8$
178.9	177.5	99.22
284.3	282.1	99.23
561.7	558.7	99.47
254.7	252.8	99.25

average 99.29
s.d. 0.10

Analysis of a 0.1 N $K_2S_2O_8$ Solution

method	no. of determinations	N ave	s.d.
iodometric	3	0.09328	0.01
ferrous-ceric	3	0.09323	0.02

Analysis of Recrystallized $K_2S_2O_8$ by Iodometric Method

mg. taken	mg. found	% $K_2S_2O_8$
226.3	225.9	99.84
453.8	453.2	99.87
501.8	500.7	99.79

average 99.83
s.d. 0.03

a pH of 2.2. This solution decreased in formality by 3% over a period of 20 days. A 0.05 F $K_2S_2O_8$ solution was prepared from the recrystallized material and was found to have a pH of 4.1. This solution was buffered at a pH of 7.0 by means of a bicarbonate-carbon dioxide system. It was found to decrease in formality by 3.6% over a period of 18 days.

Summary

It has been established that for a given concentration copper salts are better catalysts than iron salts. The peroxydisulfate iodide reaction is not catalyzed by solid cuprous iodide nor is there any synergistic effect on the combined catalytic effect of copper and iron salts.

The procedure proposed is believed to give results which are within the usual volumetric accuracy and permits more rapid analyses than do previous procedures.

PART III

EFFECT OF SURFACE OXIDATION AND PLATINIZATION ON THE BEHAVIOR OF PLATINUM ELECTRODES

Introduction

Anson and Lingane (23) showed that an electrolytically oxidized platinum electrode has a film of platinum oxide on its surface. Using the technique of chronopotentiometry they found that in an air-free sulfuric acid solution and at a current density of 0.2 milliamp. per cm^2, the electrode is oxidized at a potential of approximately +0.9 volts versus a saturated calomel electrode (S.C.E.). Under similar conditions the oxide film is reduced at a potential of +0.4 volts versus S.C.E. The maximum amount of oxide film produced on repeated oxidation and reduction was quite reproducible and corresponded if uniformly distributed over the electrode surface to a layer a few molecular diameters thick. Apparently this thin film inhibits further oxidation of the electrode.

This oxide film can be produced chemically as well as electrolytically. For example, silver (II) was reported to oxidize the electrode (24). Also the oxide film can be chemically reduced, for example, by ferrous iron in 1 M H_2SO_4 (25).

The presence of this oxide film greatly affects the voltametric behavior of the electrode. Certain electrolytic oxidations were found to proceed less reversibly at oxidized platinum electrodes. Anson and Lingane (23) found that the oxide film increased the overpotential for the oxidation of iodine and of oxalic acid to such an extent that their oxidations do not occur below the potential at which water is oxidized. However, at a reduced platinum electrode these oxidations do proceed at less oxidizing potentials and give sharply defined chronopotentiometric waves.

Various electrolytic reductions have been found to proceed more reversibly as a result of prior oxidation of the platinum electrode. Anson (26) found that the reduction of iodate proceeds much more reversibly at an oxidized than at a reduced electrode. Davis (24) reported this same effect for the reduction of vanadium (V), chromium (VI), arsenic (V), iodate, and oxygen.

The mechanism by which the oxide film affects the reversibility of electrode reactions at platinum electrodes has not been fully explained.

One mechanism invoked in the literature (26, 24, 27) is that the platinum oxide film facilitates electrolytic reductions by acting as an electron carrying bridge. Anson (26) suggested that the oxide film acts as an electron-carrying bridge at electrode potentials where the platinum oxide itself begins to be reduced.

Lingane (28, 29) and Sawyer (30, 31) in their investigations of the electrolytic reduction of oxygen found the oxide film to increase the reversibility of this electroreduction. They proposed that the platinum oxide film facilitates the electroreduction of oxygen catalytically according to schemes such as

$$\frac{1}{2}O_2 + Pt \longrightarrow PtO \qquad (1)$$

$$2H^+ + PtO + 2e^- \longrightarrow Pt + H_2O \text{ etc.} \qquad (2)$$

Lingane (29) has proposed that the potential of a platinum electrode is always governed by a platinum-platinum ion couple and that the primary electron-transfer step for any electrode reaction is always either the reduction of the platinum ion or the oxidation of platinum to platinum ion.

Anson (25) proposed an alternative mechanism to that of the oxide bridge. He suggested that reduction of the oxide film on an oxidized electrode results in a platinized electrode at which electrode reactions proceed more reversibly. He showed this hypothesis to be consonant with the behavior of the Fe(II) - Fe(III) couple at platinum electrodes.

As a result of the study of the Fe(II) - Fe(III) couple it seemed possible that the behavior of systems where prior electrode oxidation facilitates electroreduction might be explained more satisfactorily in terms of this platinization mechanism.

The behavior of vanadium (V) and iodate were investigated chronopotentiometrically with platinum electrodes subjected to a variety of pretreatment procedures. The experimental results are in accord with the platinization mechanism and can be adequately accounted for without resort to an oxide electron-bridge mechanism. The results are not sufficient, however, to rule out the catalytic mechanism proposed by Lingane and Sawyer.

Sufficient evidence to show that the indicated catalytic reactions occur has not been presented. In fact, Kolthoff and Tanaka (32) in an experiment designed to detect chemical oxidation of platinum electrodes in air-saturated solutions concluded that no oxidation of the electrode occurs. An unambiguous answer to the question as to whether oxygen chemically oxidizes platinum electrodes as indicated in the catalytic reaction 1 has yet to be provided.

Experimental

Reagents - All chemicals used were of reagent grade quality and were used without further purification. Stock solutions were prepared by weight and all measurements were made in oxygen free solutions.

Apparatus - The chronopotentiometric apparatus was conventional (33).

The potential between the working electrode and the S.C.E. reference electrode was fed through a unit gain follower amplifier employing Filbrick plug in unit follower amplifier units to a Mosely Autograph X-Y recorder.

The chronopotentiometric technique involves the constant current polarization of the working electrode. The potential of the working electrode versus S.C.E. is recorded as a function of time. The plot of potential versus time is referred to as a chronopotentiogram. An effect producing a decrease in the reversibility of a given electrolytic reduction will cause the potential at which the wave appears to be more reducing. In this study the electrode was subjected to a variety of pretreatments and the relative effects of these pretreatments on the reversibility of the reaction were noted. This was done by observing how the wave potential shifted on varying the pretreatment.

The length of the chronopotentiometric wave (referred to as the transition time) is generally a function of the bulk concentration of the electroactive species. In cases where the current is limited by the rate of mass transfer of electroactive species to the electrode, the transition time, τ , is proportional to the square of the concentration. The transition time bears a more complex relationship to concentration when other phenomena such as adsorption are involved.

The working electrode was a piece of platinum foil 0.9 cm^2 in area that had been spot welded to a short piece of platinum wire which was sealed in glass.

Electrode pre-treatment - In order to bring the electrode into a standard condition before treating it for use in an experiment, it was immersed in hot aqua regia for several minutes. This treatment resulted in dissolution of any finely divided platinum metal on the electrode. Next the electrode was conditioned according to one or more of the following procedures:

An oxidized electrode was prepared by recording an anodic chronopotentiogram in a solution of the supporting electrolyte (1$\underline{F}$ H_2SO_4 or pH 3 phosphate buffer). The current was interrupted just before the electrode potential reached the steady background potential.

A freshly reduced electrode was prepared by recording a cathodic chronopotentiogram with an oxidized electrode and interrupting the current when the potential was approximately one hundred millivolts less reducing than the steady reduction potential of the supporting electrolyte. The resulting electrode was then immediately used to record chronopotentiograms of the substances to be investigated.

An aged reduced electrode was a freshly reduced electrode that had been allowed to sit in a solution of supporting electrolyte for several hours prior to its use in recording chronopotentiograms.

A stripped electrode was prepared by dissolving the oxide film from an oxidized electrode with hot concentrated hydrochloric acid.

A platinized electrode was prepared by passing one to two milliamperes per cm^2 of cathodic current through the reduced electrode for 20-50 seconds in a $0.02\,\underline{F}$ K_2PtCl_4 solution. Comparison of transition times for the reduction of Fe(III) at both freshly reduced and platinized electrodes showed that this amount of platinization did not change the effective chronopotentiometric area for transitions times longer than 6 seconds.

According to the platinization mechanism, reduction of the oxide film produces a layer of finely divided platinum on the electrode surface and this layer has the same effect on the reversibility of electrode reactions as does a prior electrolytic deposition of platinum (platinization). It is well known that platinization of the platinum electrode increases the reversibility of the standard hydrogen electrode. It is not unreasonable to expect that the presence of finely divided platinum on the electrode will increase the reversibility of reactions carried out at the electrode. In fact, in 1924 Hammett (34) observed that oxidation and reduction of platinum electrodes increased their "activity" for the subsequent oxidation of molecular hydrogen and the reduction of hydrogen ion (23).

A clear-cut and direct demonstration of the effect of repeated oxidation and reduction of the electrode surface was obtained with the following experiment (experiment suggested by C. D. Russell): A new platinum electrode with a bright, lustrous surface was placed in a 1 $\underline{F}$ H_2SO_4 solution with an auxiliary electrode and the pair connected to a source of 60 cycle alternating current with the peak to peak voltage amplitude adjusted so that the electrode surface was oxidized and reduced during each cycle but no substantial gas evolution occurred. Within a few minutes after the A.C. was applied, the electrode surface had lost its luster and after 10 minutes, the electrode was quite dark and resembled the surface of electrodes which had been platinized by deposition from a chloroplatinate solution. This experiment leaves no doubt that platinization does in fact result from alternate oxidation and reduction of platinum electrodes.

Results and Discussion

Reduction of Vanadium(V). In Figure 3-1 are shown cathodic chronopotentiograms for a solution 0.01 F in NH_4VO_3 in 1 F H_2SO_4. Curves 1 through 4 correspond respectively to chronopotentiograms obtained with the oxidized electrode, the freshly reduced electrode, the stripped electrode, and the platinized electrode. Typically, two waves are obtained corresponding to the stepwise reduction of V(V) to V(IV) and V(III) (24). Because of the excessive length and lesser importance of the second wave only the first wave is shown in curves 1. 2, and 4.

Chronopotentiograms for the oxidation and reduction of the electrode in a solution free of vanadate are not shown but with a current density of 2.2 ma/cm^2 the transition times involved are negligible compared to those obtained for the reduction of the vanadium.

Curve 1 is similar to a chronopotentiogram obtained by Davis with an oxidized electrode. The unusual minimum in the curve was explained by him as resulting from a partial reduction of the platinum oxide film until the remaining oxide could provide electron bridges and allow the reaction to proceed at the more positive potentials. Curves 2 and 4 show, however, that vanadium(V) is even more readily reduced at freshly reduced or platinized electrodes where no such oxide bridges could be involved. Nevertheless if the oxide film is chemically stripped from the electrode with hot concentrated hydrochloric acid the reduction of vanadium(V) does proceed much less reversibly, as shown in curve 3.

Fig. 3-1. Chronopotentiograms for the reduction of 0.01 M V(V) in 1.0 M H_2SO_4: (1) at an oxidized electrode; (2) at a freshly reduced electrode; (3) at a stripped electrode; (4) at a platinized electrode; (5) at an oxidized electrode, solution stirred while recording the chronopotentiograms; (6) at a freshly reduced electrode, solution stirred. Current density was 2.2 milliamps./cm^2 throughout.

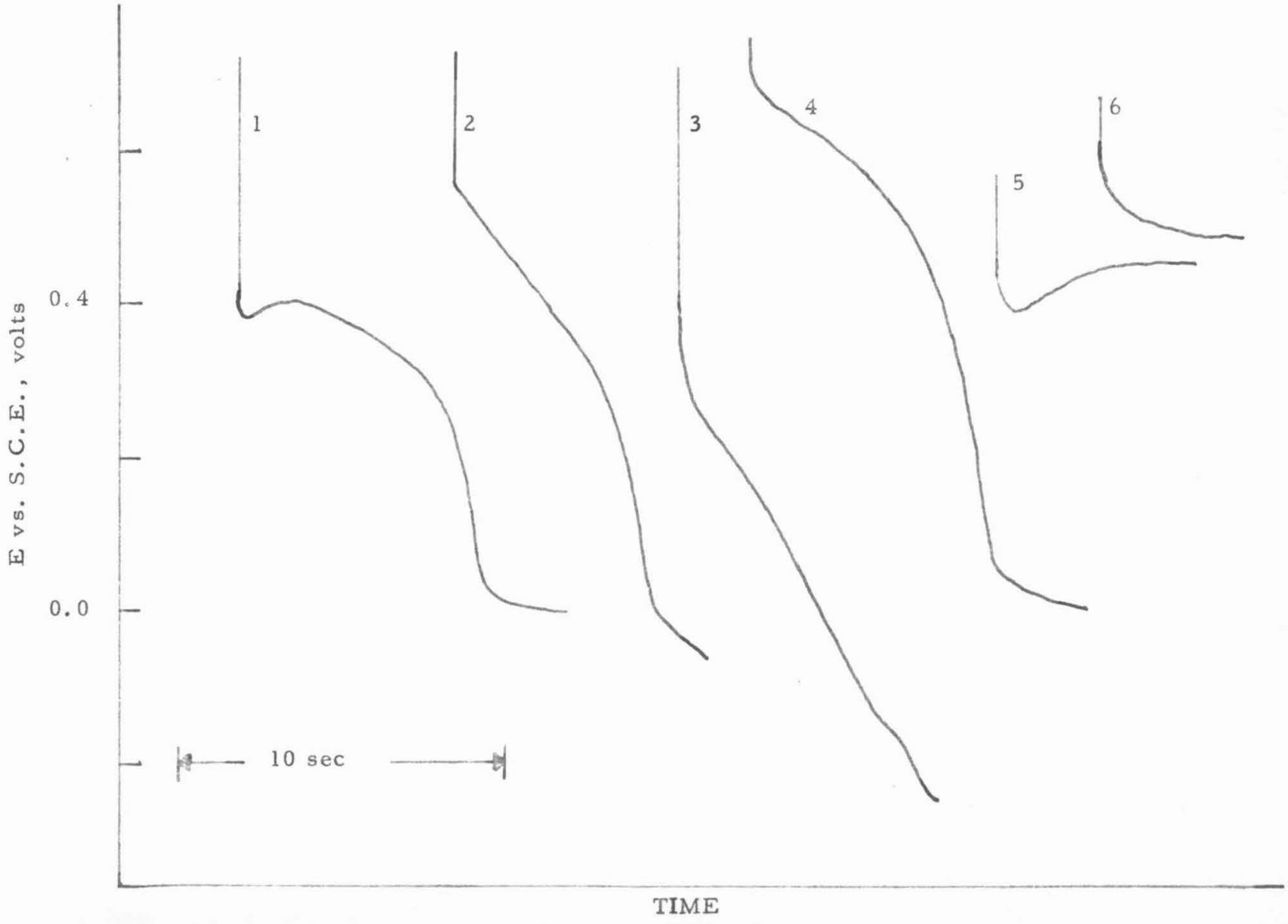


Figure 3-1

(Curve 2 gradually deteriorates into curve 3 as successive chronopotentiograms are recorded.)

This behavior is difficult to account for in terms of an oxide bridge mechanism but it is readily understood according to the electrode platinization idea as follows: It can be reasonably assumed that electrode reactions will display their greatest reversibility (i.e. least overvoltage) at platinum electrodes that have just been platinized. The standard hydrogen electrode is the best known example of this rule. The reason, then, that the reduction of vanadium(V) commences later in curve 1 than in curves 2 and 4 in Figure 3-1 is because oxidation of the electrode before curve 1 was recorded converted any finely divided platinum on its surface into platinum oxides thus effectively deplatinizing the electrode. The unusual minimum in curve 1 occurs at the potential where reduction of the platinum oxide takes place. This reduction produces a fresh layer of finely divided platinum metal on the electrode which renders the reduction of vanadium(V) more reversible so the potential climbs back to the value at which this more reversible reduction proceeds. No minima are observed in curves 2 or 4 because the electrode surface is already platinized and the reduction of vanadium(V) proceeds immediately at the more oxidizing potentials. To show that an initially oxidized electrode behaves identically with an initially reduced electrode once the oxide film is reduced, curves 5 and 6 were recorded while the solution was being stirred. The oxidized electrode (curve 5) still exhibits the minimum corresponding to the oxide film reduction but the potential then climbs back to the value at which vanadium(V) is reduced at an initially reduced electrode.

The small morphological differences in curves 2 and 4 result from the difference in the extent of platinization of the electrode in the two cases. The quantity of freshly formed platinum present on the electrode which had been plated in a chloroplatinite solution was about 50 times greater than when it was merely oxidized and reduced. This fact is doubtless responsible for the slightly earlier potential at which vanadium(V) reduction commences on the more heavily platinized electrode.

Curve 3 in Figure 3-1 corresponds to the reduction of vanadium(V) at an unplatinized electrode resulting from oxidation of the electrode followed by chemical stripping of the oxide film in hot, concentrated hydrochloric acid. The decrease in reversibility is so great that no separate wave for the reduction to V(III) is observed. Chronopotentiograms similar to curve 3 also result when freshly reduced electrodes are allowed to age before being used. This decrease in reversibility with time is presumably the result of the freshly formed platinum metal becoming deactivated either by adsorption of solution impurities or by gradual changes in the structure of the deposit (35).

The fact that the very irreversible curve 3 can be converted to the much more reversible curve 1 by oxidizing the electrode does not reflect participation by oxide bridges but only the well known fact that deactivated platinum can be reactivated by oxidation and reduction (34). The mechanism of this reactivation is simply that oxidation and reduction of the electrode platinizes its surface.

Reduction of Iodate. In Figure 3-2 are shown chronopotentiograms for the reduction of 0.002F KIO_3 in phosphate buffer solutions at pH 3. Curves 1 through 4 show, respectively, the reduction of iodate at an oxidized electrode, at a freshly reduced electrode prepared by reduction of the oxide film in the iodate solution, at a freshly reduced electrode prepared by reduction of the oxide film in an iodate-free pH 3 buffer solution, and at a platinized electrode.

All of these chronopotentiograms would show a second wave corresponding to complete concentration polarization of the iodate at much longer times but since these second waves are not affected by electrode pretreatments they were not important for this study.

The previously reported (26) effect of oxidation of the electrode on the reversibility of the reduction of iodate is apparent in the difference between curves 1 and 2. However, in curves 3 and 4 iodate reduction waves are obtained with unoxidized electrodes at potentials just as oxidizing as those in curve 1. This proves that the presence of a platinum oxide film on the electrode is not necessary in order for iodate to commence to be reduced at these less reducing potentials.

Figure 3-2. Chronopotentiograms for the reduction of 0.002 M IO_3^- in a phosphate buffer solution of pH 3: (1) at an oxidized electrode; (2) at an electrode reduced in an iodate solution prior to recording the chronopotentiogram; (3) at an electrode reduced in an iodate free solution prior to recording the chronopotentiogram; (4) at a platinized electrode. Current density was 1.1 milliamps./cm^2 throughout.

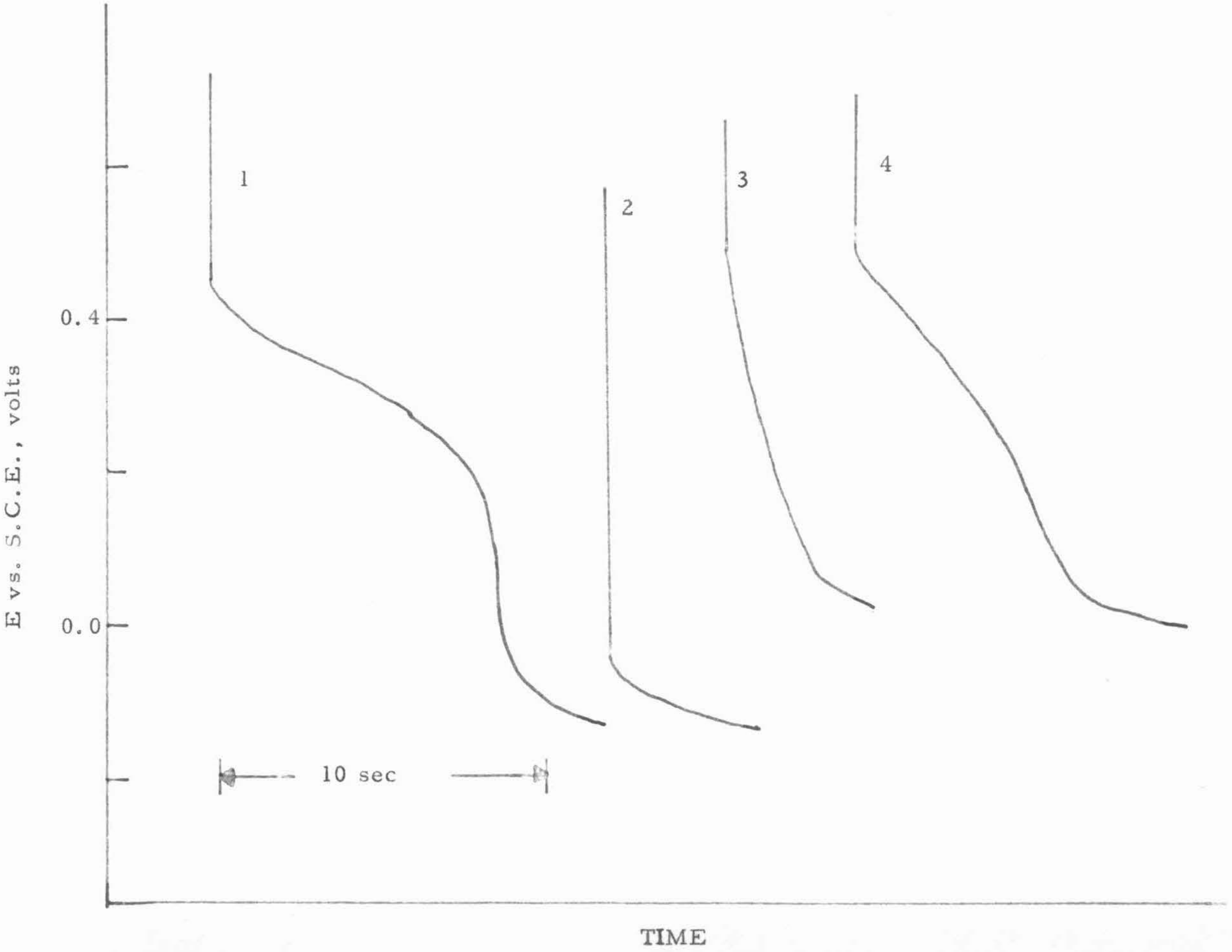


Figure 3-2

To understand the chronopotentiograms in Figure 3-2 it is necessary to inquire as to the source of the potential inflection in curves 1 and 4. As stated above and shown previously (26), complete concentration polarization of the iodate has not occurred at the time of the potential inflection in curves 1 and 4. According to the previously invoked oxide bridge mechanism (4), this potential inflection was assumed to occur when all of the platinum oxide had been reduced and no more electron bridges were available. However, curve 4 displays the same potential inflection at a platinized electrode even though no oxide was initially on the electrode.

The following experiment solved this riddle. A freshly platinized electrode which would have given rise to a curve such as 4 in Figure 3-2 if used immediately to record a chronopotentiogram in the iodate solution was instead dipped for about 60 seconds in a 2 millimolar solution of potassium iodide in pH 3 phosphate buffer. This solution corresponds to the environment experienced by the electrode near the end of an iodate chronopotentiogram (at all electrodes the reduction of iodate at pH 3 occurs at potentials more reducing than corresponds to the reduction of iodine to iodide so that iodide is the initial reduction product). When the electrode was washed free of iodide and used to record a cathodic iodate chronopotentiogram a curve such as curve 2 in Figure 3-2 resulted instead of curve 4. The increased reversibility of the iodate reduction resulting from platinization of the electrode was thus lost upon exposure of the electrode to iodide ion. It has been stablished (36) that iodide and iodine are strongly adsorbed on platinum electrodes and it has been previously observed (37) that adsorbed iodide and iodine render the Fe(II)-Fe(III) and ferro-ferricyanide couples much less reversible at platinum electrodes. This indicates that the adsorption of iodide on the electrode is responsible for the potential inflections in curve 4. When the concentration of iodide at the electrode surface has increased to the point where significant adsorption on the platinized platinum takes place the platinized surface loses its catalytic properties toward further iodate reduction and the potential inflects to values where iodate is reduced at unplatinized electrodes.

The behavior of the other curves in Figure 3-2 can now be understood. Iodate is reduced more reversibly at a previously oxidized electrode (curve 1) because upon reduction of the oxide a fresh deposit of finely divided platinum is formed at which iodate reduction proceeds most reversibly. This also explains why the potential at which iodate reduction commences at oxidized electrode is identical to the potential at which the platinum oxide reduction commences and displays the same pH dependence (26). No iodate reduction can commence before some platinum oxide is reduced to provide a platinized electrode surface. The potential inflection in curve 1 can arise in two ways: Iodide can be adsorbed on the freshly formed platinum and interfere with further iodate reduction as in curve 4. In addition, iodide ion in pH 3 buffer solution is capable of reacting chemically with the unreduced platinum oxides to give soluble iodoplatinum complexes. Experiments showed that 90 per cent of the platinum oxide was dissolved in 100 seconds in a 2 millimolar iodide solution at pH 3. Data for these experiments are given in table 3-1. In either case the electrode surface becomes deplatinized and loses its catalytic activity.

Curve 2 in Figure 3-2 results if a second chronopotentiogram is recorded after curve 1 with no pretreatment of the electrode. No iodate wave is observed because, even though the electrode surface has been freshly oxidized and reduced, the resulting platinized platinum is covered with adsorbed iodine (resulting from oxidation of adsorbed iodide by the dissolved iodate).

Curve 3 shows that a small iodate-reduction wave is obtained if the electrode is freshly oxidized and reduced in an iodate-free solution to ensure that no iodide adsorption occurs. However, the large difference in transition times for the waves in curves 1 and 3 is not expected if the oxide film present in curve 1 is only effective because it can be reduced to give a platinized surface.

The transition time for curve 1 of Figure 3-2 is expected to be longer because of the extra time required to reduce the oxide film. However, in the absence of iodate the time required to reduce the oxide at the current density corresponding to curve 1 in Figure 3-2 is only about one-sixth of the observed transition time. The reduction of the

Table 3-1

Effect of Iodide on Platinum Oxide Film

Electrode oxidized 10 seconds at 0.64 milliamps. in pH 3 phosphate buffer solution, then dipped in 2 mmolar KI (pH 3), rinsed, and used to record a cathodic chronopotentiogram at 0.64 ma.

Time dipped in 2 mmolar KI	Transition time
0 sec.	3.6 sec.
10	2.3
25	1.2
50	0.7
100	0.4

oxide will take more time in the presence of iodate because of the lower current efficiency for oxide reduction, but this effect would not be expected to be large enough to account for the difference in transition times in curves 1 and 3. It is also possible that the transition time is larger in curve 1 than in curve 3 because the iodide concentration requires a longer time to increase to the point where significant adsorption occurs due to the consumption of iodide in the chemical reaction with the platinum oxide.

The explanation offered to account for the potential inflection in curve 1 leads to the prediction that, as the iodate concentration is increased, a point should be reached beyond which the transition time for the wave should be independent of the iodate concentration. This is to be expected because once the concentration of iodide generated at the electrode surface reaches a value where the electrode is totally deactivated by adsorption or dissolution further increases in the generated iodide concentration should have no effect. Figure 3-3 shows the results of a set of experiments that confirmed this prediction. Above 0.016 M IO_3^- the transition time does in fact become essentially constant.

Reduction of $PtCl_6^=$. Several chronopotentiometric experiments were made of the electrolytic reduction of chloroplatinate in a solution buffered at pH 3 with phosphate. The results of these experiments are presented here without a definitive interpretation of either the electrode reactions or of the effect of various electrode pretreatments.

Fig. 3-3. Effect of iodate concentration on the transition time for the first cathodic iodate wave at an oxidized electrode. Prior to recording each cathodic chronopotentiogram the electrode was oxidized 10 sec at 0.9 milliamps. Current density was 2.4 milliamps./cm^2 throughout.

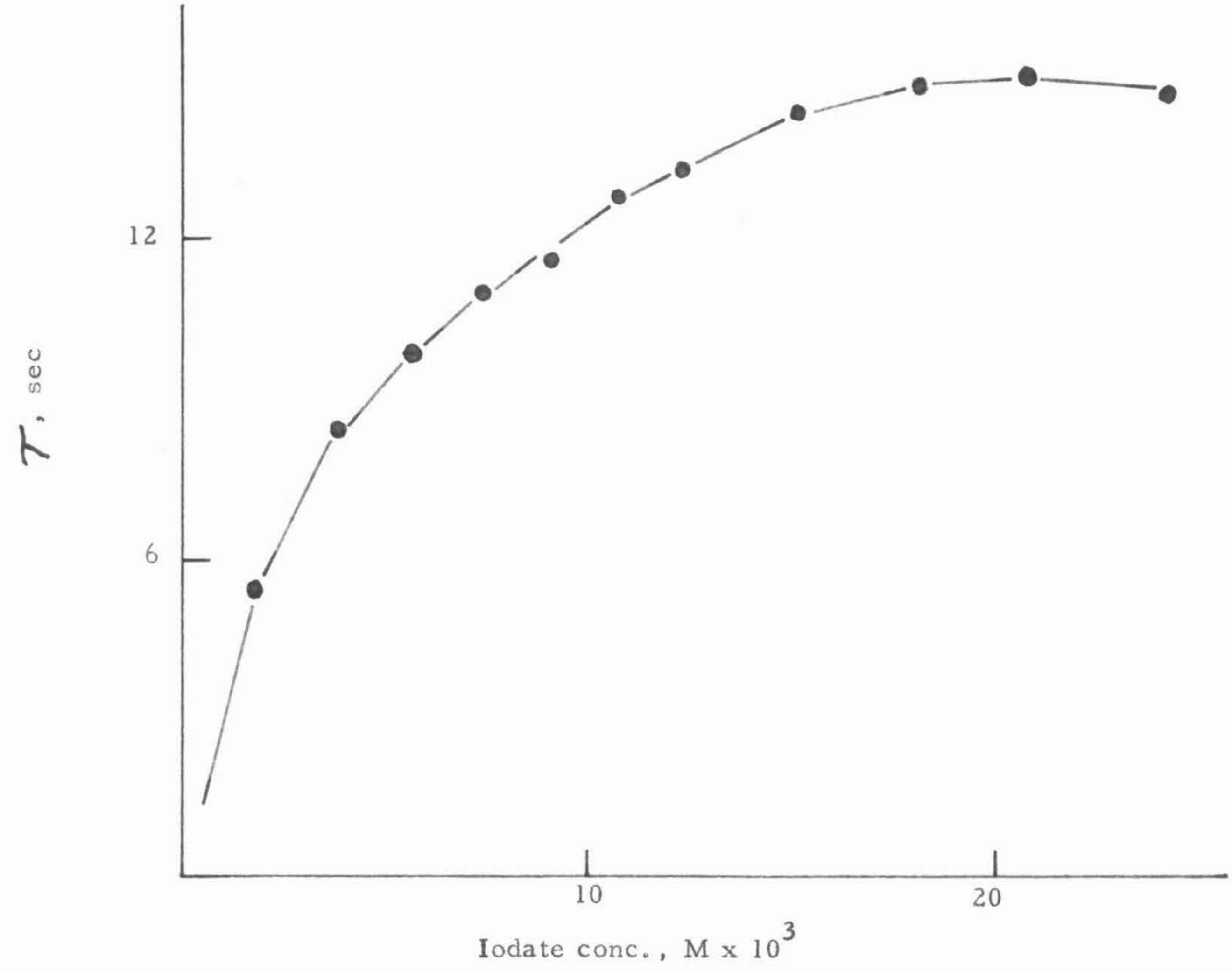


Figure 3-3

In Figure 3-4 are shown cathodic chronopotentiograms for the reduction of 0.02 M $PtCl_6^{=}$ in a solution buffered at pH 3 with 0.2 F total phosphate. Curves 1 through 4 correspond, respectively, to chronopotentiograms obtained with a stripped electrode, a freshly reduced electrode, an oxidized electrode, and a platinized electrode.

Reverse current studies were made to determine the product of the reduction of $PtCl_6^{=}$. Anodic chronopotentiograms were made of $PtCl_4^{=}$ and a wave was obtained corresponding to the oxidation of Pt(II) to Pt(IV). When the current was reversed after the first wave of curve 4, no wave for the oxidation of Pt(II) to Pt(IV) was obtained, indicating that $PtCl_6^{=}$ is reduced directly to platinum metal.

Curve 5 was taken with an aged reduced electrode in a stirred solution. It indicates that on a deplatinized electrode the reduction of $PtCl_6^{=}$ occurs at approximately -0.1 volts versus S.C.E. As a result of platinization the potential rises to approximately +0.25 volts versus S.C.E. This corresponds to the potential at which the first wave of curve 4 occurs at a platinized electrode. These results are in accord with the platinization mechanism. No oxide film was present on the electrode prior to recording curves 4 and 5.

No interpretation was made of the various inflections in curves 1, 2, and 3. The long potential pause at -0.1 volts in curve 1 presumably corresponds to the reduction of $PtCl_6^{=}$ since it occurs at the same potential at which $PtCl_6^{=}$ is first reduced in curve 5.

Figure 3-4. Chronopotentiograms for the reduction of 0.002 M $PtCl_6^{=}$ in a phosphate buffer solution at pH 3: (1) at a stripped electrode; (2) a freshly reduced electrode; (3) an oxidized electrode; (4) at a platinized electrode; (5) at an aged, reduced electrode, solution stirred. The current density was 1.6 milliamps./cm^2 throughout.

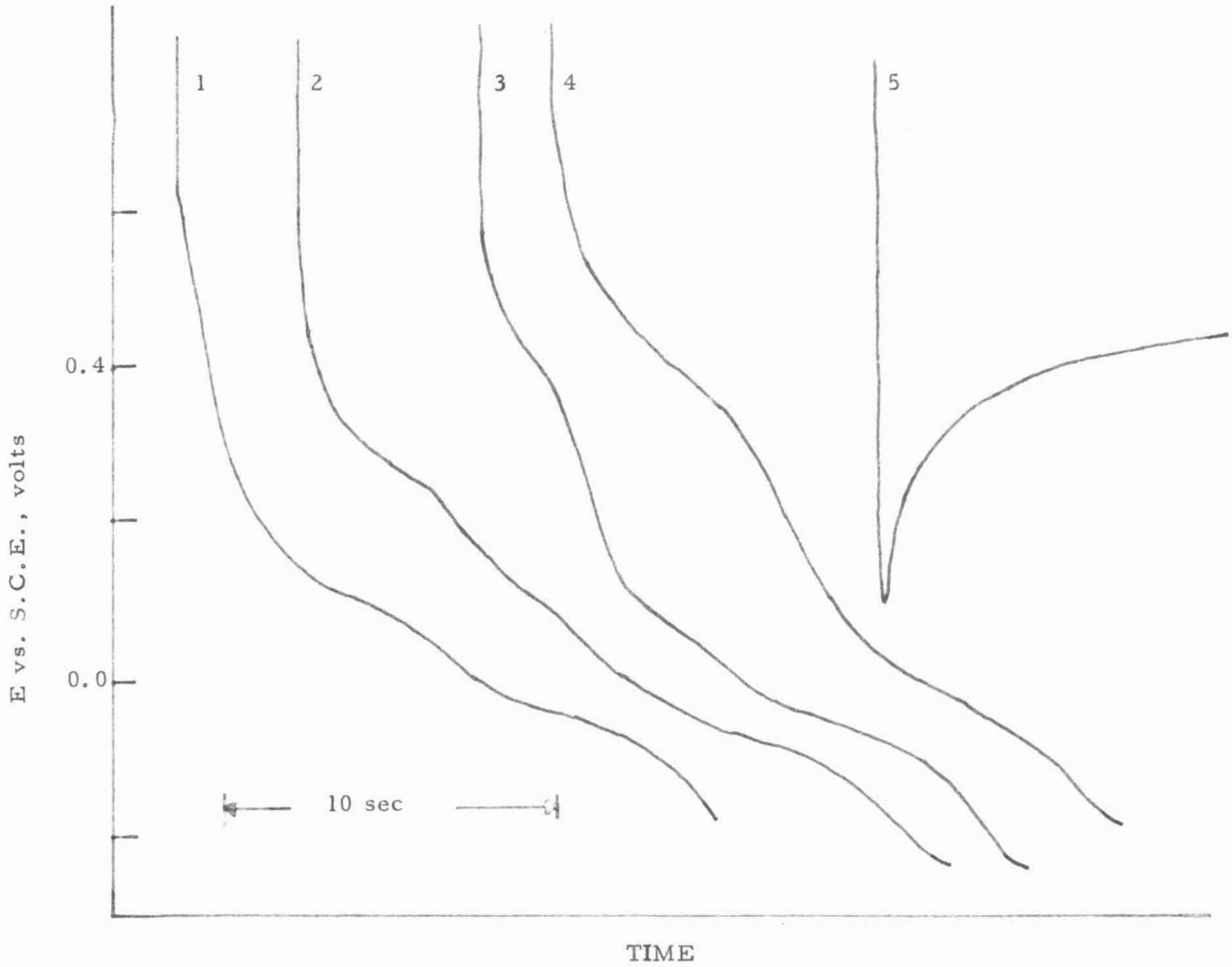


Figure 3-4

The reduction of $PtCl_6^{=}$ appears to be more reversible at a freshly reduced electrode (curve 2) than at a stripped electrode. The slight cathodic reaction beginning at +0.4 volts versus S.C.E. in curve 1 is not understood.

Conclusions

It was found that the enhanced reversibility of the electroreduction of vanadium(V) and iodate by prior oxidation of the platinum electrode could be explained by the platinization mechanism. This mechanism states that as a result of reduction of the oxide film the electrode acquires a coating of finely divided platinum and that this platinization is responsible for the observed enhanced reversibility.

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PROPOSITIONS

1. Karp and Meites (1) investigated the electrolytic oxidation of hydrazine. They found that in 0.5 F H_2SO_4 hydrazine is oxidized at +0.4 volts vs. S.C.E. (saturated calomel electrode) at a previously oxidized electrode. The predominant reaction products are nitrogen and hydrogen ion.

$$N_2H_5^+ \longrightarrow N_2 + 5H^+ + 4e^-$$

However it was found that an additional reaction occurs. By means of controlled potential coulometry it was shown that the number of moles of electrons transferred per mole of hydrazine oxidized is less than four. For a solution 0.01 F in hydrazine and 0.05 F in H_2SO_4 this number is 3.27 rather than 4.0. This number approaches 4.0 at higher sulfuric acid concentrations and at lower hydrazine concentrations. Karp and Meites (1) reported that ammonium ion is produced in this side reaction.

To account for the formation of ammonium ion Karp and Meites proposed the following mechanism. The initial electrode reaction is a two electron transfer producing diimide.

$$N_2H_5^+ \longrightarrow N_2H_3^+ + 2H^+ + 2e^-$$

$$N_2H_3^+ \rightleftharpoons N_2H_2 + H^+$$

The formation of nitrogen results from the subsequent oxidation of diimide.

$$N_2H_2 \longrightarrow N_2 + 2H^+ + 2e^-$$

In addition to this reaction, Karp and Meites (1) proposed that diimide dimerizes to form tetrazene

$$2N_2H_2 \longrightarrow N_4H_4$$

and that tetrazene decomposes into ammonium ion and azide ion.

$$N_4H_4 \longrightarrow NH_4^+ + N_3^-$$

No azide ion was found in the solution after electrolysis. They concluded that it is rapidly electroöxidized to nitrogen.

$$N_3^- \longrightarrow \frac{3}{2}N_2 + e^-$$

It is proposed that this mechanism is incorrect.

It involves as the initial step a two electron transfer. Studies of the chemical oxidation of hydrazine (2, 3, 4) indicate, however, that when the initial reaction step is a two electron transfer, hydrazine is completely oxidized to nitrogen. Only when the initial step is a one electron transfer can ammonium ion result as a product.

This mechanism involves the formation and subsequent electroöxidation of azide ion. However, it has been shown that the overvoltage for the oxidation of azide ion on platinum is very large (5). In order to oxidize azide ion at potentials used in the controlled potential coulometric studies of Karp and Meites, the current density can be no larger than approximately 10^{-7} amperes per cm^2. Controlled potential coulometric titrations are generally stopped at much larger currents. Since azide ion was not detected after electrolysis, it must not have been formed in this reaction.

Two alternative mechanisms are proposed. (a) Karp and Meites (1) concluded that the initial electrode reaction is a two electron transfer. They stated that an initial reaction step involving a one electron transfer is not possible since it necessitates a transfer coefficient of 0.98. Although this is an unusually large value, it is not impossibly large. For example, Stout (5) obtained a value of 1.0 for the transfer coefficient in the electrooxidation of azide ion at a platinum electrode.

It is proposed that the initial electrode reaction might be a one electron transfer. Subsequent reactions leading to the formation of ammonium ion can be written. These involve the formation and decomposition of tetrazane. These reactions are consistent with the mechanism for the chemical oxidation (2, 3, 4) of hydrazine by such oxidants as Fe(III).

$$N_2H_5^+ \longrightarrow N_2H_3 + 2\,H^+ + e^-$$

$$2\,N_2H_3 \longrightarrow N_4H_6$$

$$N_4H_6 \longrightarrow 2\,NH_3 + N_2$$

(b) Another mechanism which could account for the formation of ammonium ion is that hydrazine is catalytically decomposed by platinum into nitrogen and ammonia.

$$2\ N_2H_4 \longrightarrow N_2 + 4\ NH_3$$

It is well known that platinum catalyzes this reaction (6). The detailed mechanism for this process is not known. Audrieth (6) suggests that adsorbed hydrazine decomposes to nitrogen and hydrogen. Hydrogen then reduces hydrazine to ammonia.

It is believed that either of these proposed mechanisms is more consistent with prior chemical evidence than is the mechanism proposed by Karp and Meites.

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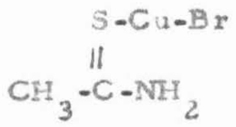
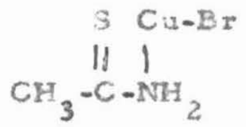
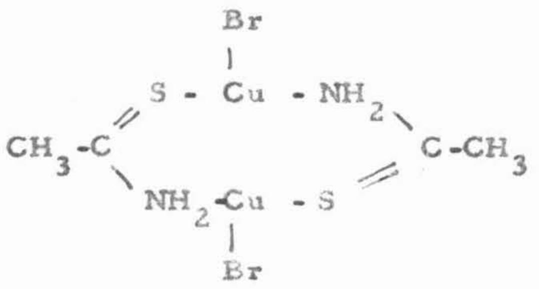
2. Rosenthal and Taylor (1) investigated the complexes of thioacetamide and copper(I). They demonstrated the existence of complexes containing thioacetamide, copper(I) and chloride ion (or bromide ion) in 1:1:1 proportions. They proposed such structures as



$CH_3\text{-}\overset{\overset{\text{S-Cu-Br}}{\|}}{C}\text{-}NH_2$,



$CH_3\text{-}\overset{\overset{\text{S Cu-Br}}{\|\ \ |}}{C}\text{-}NH_2$,



The complexed thioacetamide behaves differently than uncomplexed thioacetamide. In acid solution thioacetamide is readily hydrolyzed to acetamide and hydrogen sulfide (2). In the form of this complex, however, it is quite stable with respect to hydrolysis. Thioacetamide is stable in neutral solution. This complex, however, rapidly decomposes to precipitate cuprous sulfide.

Rosenthal and Taylor (1) found this complex to be unstable in the absence of excess halide ion. Apparently both hydrogen ion and halide ion are necessary to stabilize the complex with respect to decomposition into cuprous sulfide.

It is proposed that silver(I) forms analogous complexes with thioacetamide and halide ions. This proposition is based on the similarity of other complexes of silver(I) and copper(I) and on observations by Moore (3) in his study of the kinetics of the silver thioacetamide reaction.

The similarity in complexes of Cu(I) and Ag(I) is well known (4). These complexes have coordination numbers ranging from 2 to 4. Both form halide complexes, the iodo-complex being the most stable and the fluoro-complex the least stable. The polarizability of the ligand is an important factor in determining the stability of their complexes. Other similar complexes are formed with cyanide and ammonia.

Cu(I) and Ag(I) both form complexes with an excess of thioacetamide (3, 5). These complexes contain four thioacetamide molecules bonded to the metal ion. Moore (3) reported that the $Ag(\text{thioacetamide})_4^+$ complex is stable in aqueous solution but that the equilibrium $Ag(\text{thioacetamide})^+$ decomposes to silver sulfide. Analogous kinetic studies of the $Cu(\text{thioacetamide})_4^+$ complex have not been reported. It would presumably behave the same.

Moore (3) observed that anions present in solution had an unusual effect on the rate of precipitation of silver sulfide. He observed that an increase in the total buffer concentration decreased the rate of the silver thioacetamide reaction. The buffer ($HSO_4^- - SO_4^=$) appeared to stabilize the silver thioacetamide complex.

He found that freshly precipitated silver sulfide is dissolved by a solution of thioacetamide and sodium chloride and that the chloride is necessary in stabilizing this solution. He also reported that the complexed thioacetamide is not hydrolyzed in acid solution.

These observations seem to indicate silver forms thioacetamide complexes similar to those of copper(I).

It is proposed that studies be made of this complex. The potentiometric technique would be most convenient. The equilibrium silver ion concentration could be measured with a silver electrode. Previous potentiometric studies of the silver thioacetamide complex were attempted (6). Difficulties arose because of the precipitation of silver sulfide. It is proposed that these studies would be more successful if the solutions were first filtered through millipore filters. The direct reaction of thioacetamide and various cations has been shown to be catalyzed by traces of sulfur and other solids (7).

A knowledge of the existence and stability of such complexes is important.

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3. Thioacetamide is now extensively used as a substitute for hydrogen sulfide for the precipitation of metal sulfides (1). In addition to its applications in qualitative analysis, it has been shown to be of value as a titrant for precipitation titrations. Bush, Zuehlke, and Ballard (2) showed that silver(I) in the form of the thiosulfate complex in sodium hydroxide solution can be titrated with thioacetamide. In this titration silver (I) is rapidly precipitated as silver sulfide. The end-point is detected potentiometrically with a silver-silver sulfide electrode.

Swift and Anson (1) suggested that in addition to its application in metal sulfide precipitation titrations, thioacetamide should be of value in redox titrations. In these titrations the thio group would function as the reductant, itself being oxidized to sulfur.

Because of the potential value of thioacetamide as a titrant and because of its existing importance in gravimetric methods, accurate and rapid methods for its quantitative analysis are needed.

Anson (3) determined thioacetamide by titration with iodate. The thioacetamide is placed in a solution of potassium iodide and sulfuric acid. The iodate rapidly oxidizes iodide to tri-iodide. Tri-iodide and thioacetamide react to form iodide and sulfur. The temperature of the solution must be 70-80° in order for the tri-iodide thioacetamide reaction to be sufficiently rapid. The end-point can be detected either by the appearance of excess tri-iodide or amperometrically with two platinum electrodes across which 200 millivolts of potential difference is placed.

An alternative method (1) is to add an excess of standard iodine solution and back titrate with standard thiosulfate solution.

A method for the coulometric determination of thioacetamide is proposed. The method consists of generating iodine at a platinum electrode. The iodine will oxidize thioacetamide to sulfur. An amperometric method as employed by Anson (3) could be used to detect the endpoint of this titration.

The advantages of coulometric titrations have been described (4). The technique is applicable for quantities ranging from 100 milligrams to as little as a hundredth of a microgram.

Hydrogen sulfide has been analyzed by this technique (4). Coulometrically generated iodine was used. Tri-iodide and hydrogen sulfide react rapidly to form iodide and sulfur.

A difficulty in this proposed method is that the tri-iodide thioacetamide reaction proceeds rapidly only at high temperatures. The reaction solution would have to be heated prior and probably during the titration.

It may be possible to titrate thioacetamide with coulometrically generated bromine. The reaction might proceed at a sufficiently rapid rate at room temperature. Experiments would be necessary to determine the stoichiometry of the reaction.

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4. The oxidation of glycols with potassium dichromate has been the subject of repeated investigations (1, 2, 3, 4). The purpose of these investigations has been to develop rapid methods for their quantitative determination. The methods proposed generally involve the addition of excess dichromate to a sulfuric acid solution of the glycol. After the reaction has ceased, the excess dichromate can be determined iodometrically (1, 2), polarographically (3), or by titration with ferrous iron (4).

The method has been found to be satisfactory for the determination of ethylene glycol. Rapid and quantitative oxidation to carbon dioxide and water is achieved.

Diethylene glycol and triethylene glycol are not as rapidly and completely oxidized. Cardone and Compton (2) found that thirty minutes to an hour is required to completely oxidize 10-40 mg. of diethylene glycol in 50% by volume sulfuric acid at 100°C. They found that diethylene glycol is incompletely oxidized at lower sulfuric acid concentrations.

Whiteman, Roecker, and McNerney (1) investigated the oxidation of diethylene glycol and triethylene glycol at lower sulfuric acid concentrations. They found that although only partial oxidation was achieved, the reaction could be used for analysis over a limited range of reaction conditions.

Cardone and Compton (2) showed that the products of partial oxidation were not formic, oxalic, or glycolic acid. They suggested that partial oxidation resulted in the formation of a mixture of carbon monoxide and carbon dioxide.

Simon and coworkers (5) investigated the oxidation of a large number of organic compounds with dichromate in sulfuric acid solution. They found that the reaction products consisted generally of a mixture of CO and CO_2 under reaction conditions similar to those used by Cardone and Compton (2). They also found that oxidation is more complete if silver dichromate is used rather than potassium dichromate.

From these studies it appears that the incomplete oxidation of glycols and other organic compounds results from the inability of dichromate to oxidize carbon monoxide. Nakamura and Halpern (6) report that dichromate does not directly oxidize carbon monoxide in aqueous solution.

The effect of Ag(1) may be to catalyze this oxidation. This catalysis has not been reported. It is not likely that the mechanism for this catalysis would involve the reduction of Ag(1) by CO. This is known to be a slow reaction even at temperatures above 100°C.

Acidic solutions of Ag(1) are known to absorb carbon monoxide (7). Presumably a carbonyl type complex forms. The mechanism for the catalysis reaction might involve the oxidation of this carbonyl complex by dichromate. The products of this oxidation would be Ag(1) and CO_2. A kinetic study of this reaction should show if this mechanism is plausible.

Harkness and Halpern (8) observed that Ag(1) catalyzes the oxidation of CO by MnO_4^-. They studied the kinetics of this reaction. Their results can be interpreted by this same mechanism.

It is proposed that Ag(1) be used as a catalyst for the oxidation of glycols with dichromate.

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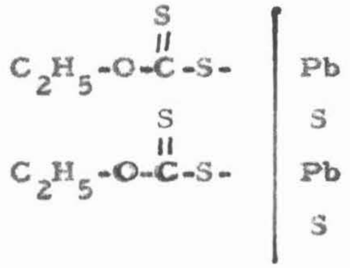
5. Infrared spectroscopy has been used to examine compounds adsorbed on various surfaces (1). The interpretation of the spectra of adsorbed species is generally based on an empirical comparison with the spectra of compounds of known structure. For example, a recent study (2) was made of the adsorption of ethyl xanthate on solid lead sulfide. It was found that under appropriate conditions a monolayer of adsorbed xanthate formed and that the infrared spectra of the monolayer was identical to that of lead xanthate. It was concluded that the monolayer had the following structure.



$$\begin{array}{l|l} C_2H_5\text{-}O\text{-}\overset{\overset{S}{\|}}{C}\text{-}S\text{-} & Pb \\ \qquad\quad\ \ S & S \\ C_2H_5\text{-}O\text{-}\overset{\|}{C}\text{-}S\text{-} & Pb \\ & S \end{array}$$

It is known that thioacetamide is adsorbed on the surface of sulfide precipitates (3). Klein (3) suggests that it is adsorbed thioacetamide that is involved in the "direct reaction" which leads to formation of metal sulfide precipitates. He proposes that metal ions diffuse to the surface of the sulfide particles and are incorporated into the precipitate by reaction with adsorbed thioacetamide.

The enhanced reactivity of adsorbed thioacetamide might result from some structural change produced by the adsorption process.

It is proposed that infrared spectroscopy be used to examine the structure of adsorbed thioacetamide. The procedure used by Greenler (2) for the study of the adsorption of xanthate on lead sulfide could be used. He prepared lead sulfide from lead acetate and thioacetamide in hot basic solution. Samples were pressed into KBr pellets for this study.

It is proposed that the infrared spectra of adsorbed thioacetamide will be similar to that of thioacetamide in complexes with Ag(I) and with Cu(I). Kurtzelnigg and Mecke (4) studied the infrared spectra of the Cu(I) complex and reported the following frequency shifts in absorption maxima.

TAA	$Cu(TAA)_4^+$
1482 cm^{-1}	1515 cm^{-1}
1307 cm^{-1}	1318 cm^{-1}

They believed that these shifts reflected the loss of double bond character in the thiocarbonyl group. This is the result of coordination through the sulfur atom to copper.

It is proposed that thioacetamide is similarly bonded to solid copper sulfide and that there will be a similar shift in the absorption maxima at 1482 and 1307 cm^{-1}.

This type of chemisorption may also occur on other metal sulfides. The enhanced reactivity of adsorbed thioacetamide may result from the weakening of the carbon sulfur bond.

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