by several persons, the differential thermal data are not in agreement. This is primarily the result of different conditions under which the data were obtained. Gordon and Campbell (3) used a heating rate of 15 degrees per minute, an air atmosphere, and no diluent in the sample cell. Stone (8)used N₂ and NH₃ atmospheres under dynamic conditions at various pressures. Alumina was used as reference material and sample diluent, but no heating rate was given. In addition, different samples of ammonium perchlorate have been found to show a marked difference in thermograms for which no satisfactory explanations are known to the authors.

Some difficulties present in the system include the increased vaporization of the sample due to the flowing gas and the occasional condensation of this vapor in the cooler exit tube. The vaporization of the sample below the

boiling point makes boiling point determinations difficult, and the condensation of sample before passage through the gas detector presents difficulties, as later the gas stream may become sufficiently hot to decompose the condensate. Neither of these conditions has been investigated thoroughly, but is believed to be less important than the data obtained.

The potentialities of the system when using other controlled conditions-i.e., the study of gas evolution under isothermal conditions, thermal behavior under atmospheres of different gases, and studies of compounds under various pressures-are readily apparent.

The small amount of modification necessary to include the gas profile system in a regular differential thermal analysis apparatus and the inexpensive equipment needed are far outweighed by the amount of additional information obtained from one sample.

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Use of Hydrazine to Accelerate the Rate of Hydrogen Sulfide Evolution from Thioacetamide Solutions

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The nature of the reaction between thioacetamide and hydrazine to give hydrogen sulfide has been determined. The rate of the reaction is first order with respect to both thioacetamide and hydrazine and displays both specific and general acid catalysis. Rapid precipitations of metal sulfides can be obtained in solutions of pH 4 to 6 with the thioacetamide-hydrazine combination. Rate constants have been determined from which the rate of precipitation of metal sulfides can be calculated.

WIFT and coworkers (4) have meas-Ured the rates of the acid- and basecatalyzed 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. At pH values between 4 and 8, however, both the acid- and base-catalyzed hydrolysis reactions proceed at rates which are too slow to achieve quantitative precipitations of metal sulfides in reasonable times.

Precipitations of metal sulfides with thioacetamide by a mechanism which does not involve the prior hydrolysis of the thioacetamide have been described

(1, 2), and in certain cases the rates of the reactions are rapid enough to achieve quantitative precipitations in reasonable time from solutions of pH 4 to 6. However, for many metals-e.g., nickel and zinc-prohibitively long times are required. It would be desirable to be able to precipitate homogeneously certain of these metals as sulfides from solutions having pH values of 4 to 6 because this might allow their separation from metals which do not form precipitates under these conditions-e.g., manganese(II) and chromium(III).

It was observed in these laboratories in 1952 that hydrazine accelerates the rate of formation of hydrogen sulfide from thioacetamide solutions having pH values of 4 to 6. For example, 100 ml. of a solution initially 1.0F (F represents gram formula weights per liter) in hydrazine hydrochloride, 1.0F in thioacetamide, and buffered at pH 5 with 0.10Facetic acid, and 0.17F 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.

This study was undertaken to elucidate the nature of the reaction which leads to hydrogen sulfide evolution from solu-

tions of thioacetamide and hydrazine, and to determine the analytical usefulness to 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 appropriate conditions can be selected for performing sulfide precipitations in solutions of pH 4 to 6.

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 a standard iodine solution (9).

Stock solutions of zinc sulfate were standardized volumetrically with EDTA (10)

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

All other stock solutions were prepared by weight.

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 (6). 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. TITRIMETRIC METHOD. The following method was used to follow the concentration of thioacetamide in the course of its reaction with hydrazine.

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 $50^{\circ} \pm 0.2^{\circ}$ 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 and in order to avoid any possible air oxidation of sulfide or hydrazine (11).

At appropriate times during the run aliquots of the reaction solution were pipetted into a 1F NaOH solution containing a measured excess of silver ion in the form of the thiosulfate complex. After the 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 (3).

Method. Polarographic This method was used to follow the total zinc concentration in a solution of hydrazine hydrochloride, zinc sulfate, sodium chloride, acetic acid-sodium acetate buffer, and thioacetamide.

The reaction solution was prepared in essentially the same manner as was used in the titrimetric method, 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 $50^{\circ} \pm 0.2^{\circ}$ 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 con-centration 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 $-1.1\overline{2}$ volts was continuously recorded, giving a plot of the formal zinc concentration in the reaction solution as a function of time.

RESULTS AND DISCUSSION

The first kinetic experiments were carried out by following the thioacetamide concentration in solutions containing an excess of hydrazine, according to the titrimetric procedure. Semilog plots of the concentration of thioacetamide vs. time showed that the reaction rate is first order with respect to thioacetamide. The pseudo firstorder rate constant obtained from the semilog plots was linearly dependent on the hydrazine concentration, indicating a first-order dependence on hydrazine as well. The average second-order rate constant, k'', measured in a solution buffered at pH 5.0 with 0.10F acetic acid and 0.175F sodium acetate, was 1.8×10^{-2} mole⁻¹ liter min.⁻¹ This method of studying the reaction was not continued, since the polarographic procedure proved to be much simpler and more rapid. However, the rate constant determined by the titrimetric procedure was used to check that the polarographic procedure could be relied upon to follow the disappearance of thioacetamide.

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 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. 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 imes 10⁻² and 1.8 imes 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 zeroorder rate constant, k', of variations of pH, temperature, and of the formal concentrations of thioacetamide, hvdrazine hydrochloride, and acetic acidacetate buffer.

Effect of Concentrations of Thioacetamide and Hydrazine Hydrochloride. The first-order dependence of the rate on thioacetamide and on hvdrazine hydrochloride are shown in Table I.

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

Table I. Thioacetamide and Hydrazine Hydrochloride Dependence

(0.129F)	NaOAc,	0.146F	$F HO_{I}$	Ac,	pH	4.5,
ionic	strength	= 1.0, 1	temp.	=	50°	±.
	0	0.2° Ć.)			

k', Mole	
Liter ⁻¹	k'/[Thio-
$Min.^{-1} \times$	acetamide]
105	$ imes 10^3$
	k', Mole Liter ⁻¹ Min. ⁻¹ \times 10^5

Thioacetamide^a

0.030	7.92	2.64
0.050	13.4	2.68
0.070	18.7	2.67

Hydrazine Hydrochloride^b

		k'/ [Hydra- zine Hydro- chloride] $ imes 10^4$
$\begin{array}{c} 0.089 \\ 0.178 \\ 0.222 \\ 0.310 \\ 0.355 \end{array}$	$\begin{array}{r} 4.91 \\ 10.9 \\ 13.4 \\ 19.3 \\ 22.4 \end{array}$	$5.52 \\ 6.12 \\ 6.04 \\ 6.23 \\ 6.30 \\$

^a Solution composition = 0.222F hydra-

zine hydrochloride. ^b Solution composition = 0.050F thioacetamide.



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

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

of k'' vs. the molal acetate concentration at various pH values are shown in Figure 1.

Effect of Temperature. An Arrhenius plot of the second-order rate constant, k'', is shown in Figure 2 for solutions in which the buffer concentration was 0.458F 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 (4).

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

Table	11.	Rate	Const	ants	for	H ₂ S	Evolu-
tion	from	n Thio	aceta	mide	϶-Ηγ	/dra	zine
			Solutio	one			

pН	ОАс-, М	k_1 , Mole Liter ⁻¹ Min. ⁻¹ $ imes 10^2$	k_2 , Mole- Liter ² Min. ⁻¹ $ imes 10^2$
4.5	$\begin{array}{c} 0.216 \\ 0.303 \\ 0.389 \\ 0.519 \end{array}$	1.1	$2.0 \\ 2.1 \\ 2.1 \\ 2.1 \\ 2.1$
5.0	$\begin{array}{c} 0.203 \\ 0.338 \\ 0.474 \\ 0.609 \end{array}$	0.9	$5.0 \\ 5.4 \\ 5.1 \\ 5.2$
5.5	$\begin{array}{c} 0.248 \\ 0.413 \\ 0.580 \\ 0.744 \end{array}$	1.0	$ \begin{array}{r} 6.3 \\ 6.0 \\ 6.2 \\ 6.0 \\ \end{array} $
6.0	$\begin{array}{c} 0.266\\ 0.442 \end{array}$	1.2	$\begin{array}{c} 5.9 \\ 6.1 \end{array}$

$$\frac{d[\mathrm{H}_2\mathrm{S}]}{dt} = k_1[\mathrm{N}_2\mathrm{H}_5^+][\mathrm{TAA}] + k_2[\mathrm{N}_2\mathrm{H}_5^+][\mathrm{TAA}][\mathrm{OAc}^-] \quad (1)$$

or equivalently,

 $\frac{d[\mathrm{H}_2\mathrm{S}]}{dt} = k_2[\mathrm{N}_2\mathrm{H}_4] [\mathrm{H}^+] [\mathrm{TAA}] + k_4[\mathrm{N}_2\mathrm{H}_4] [\mathrm{HOAc}] [\mathrm{TAA}] \quad (2)$

The common intercept of all the lines in Figure 1 corresponds to the first term in Equation 1. Values of k_1 and k_2 calculated at various pH values are given in Table II. 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 N₂H₅⁺ was equal to the formal hydrazine concentration.



Figure 2. Arrhenius plot of second-order rate constant,

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. 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 (7) suggests that a comparable mechanism might be involved. The mechanism would involve as the ratedetermining 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 hydrazidine:

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.

NHNH₂

Acetyl hydrazidine has been reported to condense to form a N-aminotriazole (δ) 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 liter² min.⁻¹).

Reaction Products. A measured amount of thioacetamide was allowed to react with excess hydrazine until no more hydrogen sulfide was evolved. The hydrogen sulfide evolved was collected and measured. The quantity of hydrogen sulfide formed corresponded to at least 90% of the theoretical amount based on complete conversion of the thioacetamide initially present to H₂S. Thus any side reactions that do not lead to the formation of hydrogen sulfide occur to an extent no greater than 10%.

In a similar experiment with an excess of thioacetamide over hydrazine, hydrogen sulfide evolution stopped when the hydrazine had been consumed but started again upon the addition of more hydrazine. Also within $\pm 10\%$ one mole of H₂S was formed per mole of 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 from the reaction solution.

The solution was evaporated under vacuum at 50° C. White crystals formed after the solution had been evaporated down to a few milliliters. On exposure to air the crystals slowly turned red. Upon recrystallization from ethyl alcohol long, thin crystals were obtained that appeared stable. The crystals melted at 199° to 201° C. Microanalysis and an approximate molecular weight determination indicated the formula C₄H₈N₄. Nuclear magnetic resonance measurements showed that the ratio of exchangeable to nonexchangeable hydrogens was 1 to 3.

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



Its reported melting point is 199° C. (8).

Qualitative experiments with hydroxylamine, urea, and N,N-dimethyl-hydrazine and thioacetamide showed that all of these substances lead to much slower rates of hydrogen sulfide evolution than is obtained with hydrazine.

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. The possibility that the thioacetamide-hydrazine combination could be used to effect separations, some of which are impossible with thioacetamide alone, is at present under investigation.

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Determination of Mixtures of Hydrazine and 1,1-Dimethyhydrazine

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► A method for determining mixtures of hydrazine and 1,1-dimethylhydrazine in a nonaqueous titration uses acetic acid as a solvent with perchloric acid in dioxane as the titrant. The method uses the selective action of salicylaldehyde which forms the neutral azine with hydrazine and a basic hydrazone with 1,1-dimethylhydrazine.

HYDRAZINE and 1,1-dimethylhydra-zine are both rocket fuels which when blended in certain proportions, possess certain properties superior to those of the individual fuels. The high specific impulse of hydrazine and lower

freezing point of 1,1-dimethylhydrazine are present in mixtures of these fuels. Since perchloric acid was first used by Conant and Hall (1) to titrate organic amines in acetic acid, many papers have been written on nonaqueous titrations. Of interest here are those of Fritz and Keen (3) and Riddick (5). Siggia and Stahl (6) determined 13 aldehydes including salicylaldehyde with 1,1-dimethylhydrazine by forming a neutral hydrazone in methanol. They (6) also state that "aromatic aldehydes yield hydrazones which exhibit no detectable basicity." This fact was verified by the author using methanol as the solvent system. However, when the sol-

vent system is changed to acetic acid, the hydrazone formed titrates basic. Whitnack et al. (8) studied the polarographic behavior of benzaldehyde derivatives of hydrazine, 1,1-dimethylhydrazine, and monomethylhydrazine. Wagner et al. (7) developed a procedure for determining secondary and tertiary amines using salicylaldehyde. Critchfield and Johnson (2) modified their procedure using salicylaldehyde for determining primary, secondary, and tertiary amines. Malone (4) analyzed mixtures of aniline, furfuryl alcohol, and hydrazine by separating the hydrazine from the mixture with salicylaldehvde.