range of 10 to 80 μ. The crystallizations removed any pyrophosphate and other phosphates which were present as impurities in the commercial triphosphate. X-Ray powder diffraction patterns of the final product showed no crystalline phosphates present other than the hexahydrate; a similar result was obtained by tris-(ethylenediamine)-cobalt(III) method of Weiser.[11]

The hydration pressures of phase I and phase II at 25 and 50° were determined by measuring the gain in weight of samples of the anhydrous salt which were placed in a series of humidistats. Ten-gram samples of sodium triphosphate phase I and phase II were weighed into tared wide-mouth weighing bottles. The weighing bottles were placed in desiccators at a constant humidity maintained by saturated salt solutions or aqueous solutions of sulfuric acid held at the required temperature in a constant temperature air-bath. Equilibrium was determined by weighing the samples at suitable intervals until a constant weight was obtained.

The final hydration pressures for each phase at each temperature were obtained by gradually narrowing the range covered by each set of humidistats. Aqueous solutions of sulfuric acid were required to produce small differences between desiccators. The compositions of these solutions were checked after each weighing by density measurements, and any deviations from the required compositions were corrected before starting the next equilibrium time interval.

Results and Discussion

The hydration pressures determined in the manner described above are given in Table I.

TABLE I

HYDRATION PRESSURES OF SODIUM TRIPHOSPHATE (MM.), PHASES I AND II

Temp., °C.	Phase I	Phase II
25	10 ± 0.5	12 ± 0.5
50	41 ± 1.0	64 ± 1.0

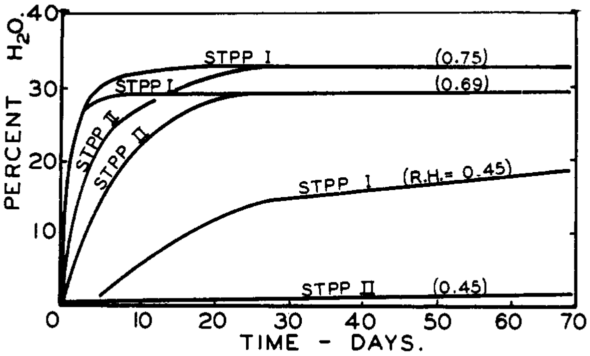

Fig. 1.—Rate of hydration at 50°.

Figure 1 shows the rate of hydration of phase I and phase II at 50° for three of the higher humidities. Phase I hydrates much more rapidly than phase II. At 75% humidity, phase I is completely hydrated in less than five days, while phase II requires twenty-five days. At 25°, on the other hand, the rates of hydration are very slow; complete hydration of phase I requires at least 10 months at 75% humidity and phase II requires a still greater time.

These hydration times are dependent to some extent on the conditions of the experiment. In this work, air was not removed from the desiccators. Therefore, these more practical hydration rates are slower than would be expected if the equilibrium with water vapor were carried out in the absence of air.

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BETHLEHEM, PENNSYLVANIA

[11] H. J. Weiser, Jr., Paper No. 2, Div. 4 Anal. Chem., 126th meeting, ACS, New York, September, 1954.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Monohalogen Derivatives of Sulfur Nitride

BY ALAN G. MACDIARMID

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The reaction of S_4N_4 with acetyl chloride is shown to produce diacetamide and sulfur dioxide in addition to S_4N_3Cl. The formation of S_4N_3Cl is shown to be caused by the presence of free hydrogen chloride in the acetyl chloride and not to any specific property of the reagent itself. It appears likely that the preparation of S_4N_3Cl from S_4N_4 and sulfur chlorides is due to a similar cause. Hydrogen chloride is shown to react with S_4N_4 under certain conditions to produce S_4N_3Cl, ammonium chloride and chlorine. Analogous reactions appear to take place with hydrogen bromide and hydrogen iodide.

One of the more interesting reactions displayed by sulfur nitride, S_4N_4, is its conversion to thiotrithiazyl "salts".[1-3] These compounds appear to contain an $(S_4N_3)^+$ cation, the nitrate, bisulfate, chloride and perchlorate of which are soluble in water. The bromide, iodide and thiocyanate are insoluble and may be formed by double decomposition reactions from the chloride. The compounds are highly colored and are decomposed by water at a measurable rate.[3]

Thiotrithiazyl chloride, S_4N_3Cl, may be prepared by refluxing sulfur nitride with sulfur chlorides[1,3] or acetyl chloride.[2] No other product of the latter reaction was reported except an unidentified white crystalline substance melting at 125°.

Dry hydrogen chloride gas reacts with sulfur nitride at room temperature to form a brown powder which does not change *in vacuo*. If treated with liquid hydrogen chloride at room temperature in a sealed tube, sulfur nitride completely decomposes to give ammonia, sulfur and chlorine.[4] A benzene solution of sulfur nitride, when treated with dry hydrogen chloride has been reported to form a bright yellow compound of unknown composition.[5]

[1] E. Demarcay, *Compt. rend.*, **91**, 1066 (1880).

[2] W. Muthmann and E. Seitter, *Ber.*, **30**, 627 (1897).

[3] A. Meuwsen and O. Jakob, *Z. anorg. Chem.*, **263**, 200 (1950).

[4] O. Ruff and E. Geisel, *Ber.*, **37**, 1573 (1904).

[5] A. Andreocci, *Z. anorg. Chem.*, **14**, 246 (1897).

In a previous note preliminary observations were given on the preparation of S_4N_3Cl from S_4N_4 and acetyl chloride.[6] The results of the completed study are presented in this paper.

Experimental

All experiments in this research were carried out several times in order to check their reproducibility.

Glass Apparatus.—All glass apparatus and reaction tubes were thoroughly cleaned and dried by washing with water, alcohol and ether, drying in an oven and cooling while a stream of dry nitrogen was passed through. Glass to glass joints in tubing were made with rubber tubing coated with paraffin wax. Ground glass joints of wash-bottles were also coated with paraffin wax.

Preparation and Purity of Chemicals and Reagents. i. **Sulfur Nitride.**—This was prepared from S_2Cl_2 and ammonia[7]; m.p. found 176°; lit. value 180°.[7]

ii. **Acetyl Chloride.**—Commercial acetyl chloride was refluxed with phosphorus pentachloride for several hours to remove traces of acetic acid and was then redistilled from an all-glass apparatus. The final product was collected over the range 50.0–51.5°.[8] It was difficult to prepare in a high state of purity, free from dissolved hydrogen chloride.

iii. **Carbon Tetrachloride.**—Commercial carbon tetrachloride was refluxed with phosphorus pentoxide for four hours to remove traces of moisture and was then redistilled. The fraction distilling at 76.4° was collected.[9]

iv. **Hydrogen Chloride.**—Hydrogen chloride was prepared from analytical reagent grade sodium chloride and sulfuric acid and was thoroughly dried by passage through analytical grade concentrated sulfuric acid.

Spot Test for S_4N_3Cl.—Many experiments involved determining the presence and the approximate amounts of S_4N_3Cl in precipitates. This was conveniently carried out by dissolving the precipitate in a small amount of water, (when a yellow solution would result if S_4N_3Cl were present), and then adding immediately a drop of potassium iodide solution. A dark red precipitate (of S_4N_3I)[2] confirmed the presence of the $S_4N_3^+$ radical and the amount present could be judged roughly from the bulk of the precipitate. Additional confirmatory evidence could be gained from the fact that S_4N_3Cl dissolved rapidly in aniline to give a dark green solution.

Nitrogen Analyses.—All nitrogen analyses were carried out by a micro-Kjeldahl method.

I. **The Reaction between Solid Sulfur Nitride and Acetyl Chloride.**—Sulfur nitride (1 g.) and acetyl chloride (4 g.) were refluxed in a semi-micro apparatus, the top of which was joined to a long capillary leading under water to a gas collection tube. Neither the S_4N_4 nor the S_4N_3Cl were appreciably soluble in the acetyl chloride. It was not difficult to note when the reaction was complete since the acetyl chloride began to "bump" vigorously, presumably due to the cessation of gas evolution. No water-insoluble gas (*e.g.*, nitrogen) was evolved, but the water gave strong positive tests for sulfur dioxide, which was, therefore, given off throughout the reaction.

The S_4N_3Cl, after filtration from excess acetyl chloride, was washed well with cold acetyl chloride and dried in a vacuum desiccator. Sulfur was determined by first oxidizing the compound with concentrated nitric acid and bromine and precipitating and weighing as barium sulfate. Chlorine was estimated by boiling the compound with dilute nitric acid and silver nitrate and weighing as silver chloride.

Anal. Calcd. for S_4N_3Cl: S, 62.38; N, 20.43; Cl, 17.28. Found: S, 60.0; N, 20.4; Cl, 17.5.

The dark brown acetyl chloride remaining from the reaction was connected to a trap immersed in liquid air and all volatile components were removed under vacuum. The condensate was distilled at atmospheric pressure and was found to consist almost entirely of unchanged acetyl chloride. When most of the acetyl chloride had distilled, the temperature rose rapidly and a few drops of a pale yellow liquid distilled. From its appearance, and from the fact that it was hydrolyzed by water with the liberation of a reducing agent, it was thought that this substance could have been a sulfur chloride.

A dark brown sticky solid remained after the removal of the acetyl chloride and sulfur chloride. This was extracted several times with boiling carbon tetrachloride. A small light-brown, putty-like residue remained which was insoluble in a wide variety of solvents. It was not investigated further. The yellow carbon tetrachloride extract was passed through an alumina chromatographic column and was extracted first with the solvent and then with ether. In addition to small amounts of two yellow oils which were not investigated further, 0.2 g. of diacetamide was recovered. This was identified by its melting point, found 78.0°; lit. value 78°.[10] Calcd.: N, 13.86. Found: N, 14.0, 13.9. No trace of the white compound (m.p. 125°) mentioned by the earlier authors[2] could be found.

II. **The Reaction between Sulfur Nitride and Acetyl Chloride in Carbon Tetrachloride Solution.**—In an endeavor to study the reaction between sulfur nitride and acetyl chloride under less drastic conditions, 5.0-ml. portions of sulfur nitride solutions in carbon tetrachloride (0.013 g. S_4N_4) were mixed with varying amounts (0.1 to 3.0 ml.) of pure acetyl chloride in glass tubes at room temperature, which were then sealed. In all cases, vigorous shaking was found to hasten the coagulation of precipitates which formed. The reaction could be carried out in the presence or absence of oxygen by first filling the glass reaction tubes with oxygen or nitrogen. When reaction was complete, the tubes were opened and the contents rapidly filtered through a sintered glass filter. Precipitates were washed well with carbon tetrachloride and dried in a vacuum desiccator.

When small amounts of acetyl chloride (0.2 ml. or less) were used, permanent orange-red curdy precipitates, which did not contain S_4N_3Cl, were always formed within one to two hours. With larger amounts of acetyl chloride, varying results, mostly non-reproducible, were obtained. The time in which a precipitate appeared varied from a few seconds to several hours and the color varied from pale yellow to red. Some precipitates contained S_4N_3Cl while others did not. The reproducibility of the results did not depend on whether the reaction was carried out in bright sunlight, in the dark, or in the presence or absence of oxygen.

When a drop of water was added to a mixture of 5 ml. of sulfur nitride solution and 1.5 ml. of acetyl chloride, an immediate cloudiness appeared, and an orange precipitate which rapidly turned pale yellow within ten minutes was formed. This contained a large amount of S_4N_3Cl. The reaction was reproducible. No appreciable change had taken place in a control tube even after half an hour. Consequently, the water itself, before it decomposed the acetyl chloride to give acetic and hydrochloric acids, or the acids so formed, play an essential part in the formation of S_4N_3Cl.

Acetic acid was shown to have no effect on the reaction by repeating the previous experiment, using a drop of glacial acetic acid in place of the water. S_4N_3Cl was not formed as in the experiment above. However, when 1 ml. of carbon tetrachloride saturated with hydrogen chloride was used in place of the drop of water or acetic acid, an orange precipitate again first appeared and then turned to a pale yellow color within 15 minutes. This contained large amounts of S_4N_3Cl. The reaction was reproducible.

It therefore appears that hydrogen chloride accelerates the reaction between sulfur nitride and acetyl chloride and causes it to become reproducible. These experiments do not indicate whether the hydrogen chloride acts purely as a catalyst or whether it is a major reactant.

III. **The Reaction between a Carbon Tetrachloride Solution of Sulfur Nitride and Hydrogen Chloride Gas.**—A hydrogen chloride stream was passed through 20 ml. of a carbon tetrachloride solution of sulfur nitride (0.0389 g. S_4N_4) in a wash bottle and then through a long thin capillary into a starch–iodide solution. The capillary was made especially long and thin so that no water vapor could diffuse back against the hydrogen chloride stream. The presence of an oxidizing agent (as shown by the color change of the starch–iodide reagent) presumably chlorine, was found to be present in the hydrogen chloride stream issuing from the reaction vessel.

After the hydrogen chloride had been passed for seven

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[6] A. G. MacDiarmid, *Nature*, **164**, 1131 (1949).

[7] M. H. Arnold, J. A. Huygill and J. M. Hutson, *J. Chem. Soc.*, **2**, 1648 (1936).

[8] Boiling point, 51–52°, "Handbook of Chemistry and Physics," 37th edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1955, p. 712–713.

[9] Boiling point 76.8°, ref. 8, p. 844–845.

[10] Ref. 8, p. 884–885.

minutes the solution began to appear cloudy and after 20 minutes a dark red, curdy precipitate (which did not contain S_4N_3Cl) started to form. This kept on growing rapidly for about half an hour and then, during the next 40 hours, it increased only slowly, lightening to a brownish-grey-colored precipitate which gave strong tests for S_4N_3Cl, was completely water soluble, and by analysis was deduced to contain an approximately equi-molecular mixture of S_4N_3Cl and NH_4Cl. *Anal.* Calcd. for 1 S_4N_3Cl + 1 NH_4Cl: N, 23.3. Found: N, 25.7, 25.3.

If the reaction bottle was filled with nitrogen saturated with water vapor before commencing the passage of hydrogen chloride, then an orange precipitate first appeared and then faded during a few minutes to a pale yellow exactly equi-molecular mixtures of S_4N_3Cl and NH_4Cl (yield 0.027 g.). *Anal.* Calcd. for 1 S_4N_3Cl + 1 NH_4Cl: N, 23.3. Found: N, 23.1, 23.3. The presence of S_4N_3Cl in the mixture was further confirmed by dissolving the mixture in ice-water, precipitating the red S_3N_3I with potassium iodide solution, rapidly washing with water, alcohol and ether and drying in a current of dry nitrogen. The resulting iodide was then analyzed. *Anal.* Calcd. for S_4N_3I: N, 14.14. Found: N, 14.4, 14.3, 14.5.

No unchanged sulfur nitride remained in solution, but the carbon tetrachloride was of a pale yellow color. On evaporation in a vacuum desiccator, a small amount of yellow powder was obtained which was not investigated further.

If a few ml. of nitrogen saturated with water vapor were bubbled through the reaction vessel at the stage where the initial red precipitate had appeared (*i.e.*, after about one hour's passage of hydrogen chloride), the red precipitate changed immediately (within 30 seconds) to a pale yellow equi-molecular mixture of S_4N_3Cl and NH_4Cl (yield 0.026 g.). *Anal.* Calcd. for 1 S_4N_3Cl + 1 NH_4Cl: N, 23.3. Found: N, 23.3. A portion of the red precipitate initially formed was removed from the reaction vessel. It began to decompose immediately in air and formed a black solid on the addition of a minute quantity of water. Hence, the red precipitate is decomposed by water in the absence of hydrogen chloride to give an unidentified substance and in the presence of hydrogen chloride to give S_4N_3Cl.

IV. The Reaction between Sulfur Nitride and Hydrogen Bromide and Hydrogen Iodide.—Preliminary experiments conducted with hydrogen bromide and hydrogen iodide indicate that the reaction is similar to that in which hydrogen chloride was used.

A saturated solution of hydrogen bromide in carbon tetrachloride was added to an equal quantity of the sulfur nitride solution. A precipitate, presumably containing thiotrithiazyl bromide, S_4N_3Br, was formed immediately, and on drying appeared as a stable orange powder.

A saturated solution of hydrogen iodide in carbon tetrachloride was added to an equal quantity of the sulfur nitride solution. A dark red precipitate, presumably containing thiotrithiazyl iodide, S_4N_3I, was formed immediately. At the same time, the carbon tetrachloride turned violet, thus indicating that free iodine probably had been formed. This would be equivalent to the release of chlorine in the S_4N_3Cl preparation.

Discussion

It appears that hydrogen chloride and sulfur nitride react directly under suitable conditions to form S_4N_3Cl. The over-all reaction is consistent with a process proceeding in the following steps

$$S_4N_4 + HCl \longrightarrow S_4N_4{\cdot}HCl \text{ (red precipitate)} \qquad \text{(i)}$$

$$S_4N_4{\cdot}HCl + 3HCl \xrightarrow{H^+} S_4N_3Cl + NH_4Cl + Cl_2 \qquad \text{(ii)}$$

i.e.

$$S_4N_4 + 4HCl \xrightarrow{H^+} S_4N_3Cl + NH_4Cl + Cl_2$$

The following side reactions would also be expected to occur.[11]

$$S_4N_4 + 2Cl_2 \longrightarrow S_4N_4Cl_4 \qquad \text{(iii)}$$

$$S_4N_4Cl_4 + 2S_4N_4 \longrightarrow (S_4N_4)_3Cl_4 \qquad \text{(iv)}$$

Reaction (i) is quite probable since sulfur nitride forms highly colored addition compounds with many covalent chlorides.[12,13] Reaction (ii) is greatly catalyzed by traces of hydrogen ion.

If the above four equations represent the over-all reaction then

Calcd. 0.0389 g. $S_4N_4 \longrightarrow$ 0.022 g. ($S_4N_3Cl + NH_4Cl$)
Expt. 0.0389 g. $S_4N_4 \longrightarrow$ (i) 0.026 g. ($S_4N_3Cl + NH_4Cl$)
(ii) 0.027 g. ($S_4N_3Cl + NH_4Cl$)

The somewhat high yields of product are to be expected since some of the chlorine is removed by the hydrogen chloride stream, thus leaving more sulfur nitride to react according to equations (i) and (ii).

Since it is possible for hydrogen chloride to react directly with sulfur nitride to form S_4N_3Cl it appears highly probable that the preparation of the latter compound from sulfur nitride and acetyl or sulfur chlorides is due only to the small amount of hydrogen chloride which is always present in these liquids and not to any special property of the reagents themselves.

The main reactions between sulfur nitride and acetyl chloride could take place as

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl \qquad \text{(a)}$$

$$S_4N_4 + 4HCl \xrightarrow{H^+} S_4N_3Cl + NH_4Cl + Cl_2 \qquad \text{(b)}$$

$$NH_4Cl + 2CH_3COCl \longrightarrow (CH_3CO)_2NH + 3HCl \qquad \text{(c)}$$

giving the over-all reaction

$$S_4N_4 + HCl + 2CH_3COCl \longrightarrow S_4N_3Cl + (CH_3CO)_2NH + Cl_2 \qquad \text{(d)}$$

A side reaction could also occur as

$$S_4N_4 + 4CH_3COOH + 4CH_3COCl \longrightarrow 4(CH_3CO)_2NH + 2SCl_2 + 2SO_2 \qquad \text{(e)}$$

Although neither free chlorine nor SO_2Cl_2 were identified in the sulfur dioxide evolved, it is probable that little of the chlorine would have reacted with the S_4N_4, according to equation (iii), since S_4N_4 is insoluble in acetyl chloride.

If equations (d) and (e) represent the over-all reaction between sulfur nitride and acetyl chloride, then

Calcd. 1.00 g. $S_4N_4 \longrightarrow$ 0.57 g. S_4N_3Cl
Expt. 1.00 g. $S_4N_4 \longrightarrow$ 0.56 g. S_4N_3Cl (av. of 4 expt.)

The hydrogen ion catalyst in equation (b) could be obtained from the acetic acid formed from the acetyl chloride and traces of moisture, or in the case where the reaction took place in carbon tetrachloride, more likely from water which did not react rapidly with the acetyl chloride because of its immiscibility in the solvent.

In the experiment where S_4N_4 was refluxed with acetyl chloride, the acetyl chloride used would need to absorb only 2.5% of its weight of water to provide sufficient hydrogen chloride for the reaction. This does not seem unlikely for such a hygroscopic substance unless the reaction was studied under conditions in which extreme precautions were taken to exclude traces of moisture.

The non-reproducibility of the reaction when carried out in carbon tetrachloride could be explained by the fact that the amount of hydrogen chloride and also hydrogen ion (either as acetic

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[11] E. Demarcay, *Compt. rend.*, **91**, 854 (1880).

[12] O. C. Davis, *J. Chem. Soc.*, **89**, 1575 (1906).

[13] H. Wolbling, *Z. anorg. Chem.*, **57**, 281 (1908).

acid or water) varied according to the amount of adsorbed moisture on the glass walls of the reaction tubes. The permanency of the intermediate red precipitate formed when only small amounts of acetyl chloride were used was probably caused by the consumption of all the available hydrogen chloride by reaction (i) thus leaving none for reaction (ii).

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY]

Reactions of Chloramine with Anhydrous Primary and Secondary Amines

BY GEORGE M. OMIETANSKI,[1] A. DONALD KELMERS,[2] RICHARD W. SHELLMAN[2] AND HARRY H. SISLER[3]

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Chloramine produced by the gas phase reaction of chlorine and ammonia will, in general, react with various anhydrous primary and secondary amines to form N-substituted hydrazines. It has been found that good yields of alkyl hydrazines are obtained in the absence of gelatin and permanent base. Preparation of the following compounds has been realized by this method: methyl-, ethyl-, isopropyl-, unsymmetrical dimethyl-, and unsymmetrical di-isopropylhydrazine and N-aminopiperidine. Various identifying derivatives have been prepared. The reaction with diethylamine yields monoethylhydrazine. The results have been discussed in terms of recently proposed reaction mechanisms.

Introduction

By means of a modification of the Raschig synthesis, Audrieth and others have shown that chloramine reacts with primary[4,5] and secondary[6,7] amines in aqueous solution to produce the corresponding alkyl hydrazines. As reported for the Raschig synthesis of hydrazine itself,[8,9] the production of monoalkyl hydrazines from the reaction of chloramine with primary amines in aqueous media is reported to proceed best in the presence of a permanent base and a metal deactivator such as gelatin.[4] In the reactions of chloramine with aqueous secondary amines, the role of permanent base (sodium hydroxide) has not been defined; however, the presence of an inhibitor such as gelatin does not appear to be necessary in order to obtain good yields of the corresponding unsymmetrical disubstituted hydrazines.[6]

The rather remarkable success achieved in this Laboratory in synthesizing hydrazine by the reaction of chloramine with ammonia in liquid ammonia solution[10,11] and in other solvents[12] in the absence of permanent base or other additive has led us to examine the reactions, under anhydrous conditions, of chloramine with alkyl-substituted ammonias, *viz.*, the amines. It has been found that chloramine reacts with anhydrous primary and secondary amines to form the corresponding alkyl hydrazines in good yield in the absence of permanent base or other additives. This work is reported in this paper.

As reported in a previous publication from this Laboratory, chloramine has also been found to react with anhydrous tertiary amines to form hydrazinium chlorides of the type $[R_3N-NH_2]^+Cl^-$,[13] clearly demonstrating its versatility as an N-aminating agent in anhydrous media.

Experimental[14]

Materials and Apparatus.—All of the amines were commercially available. The piperidine and diethylamine were dried over barium oxide and purified by fractionation through an efficient column packed with glass helices. Eastman Kodak Co. white label isopropyl- and di-isopropylamine and Matheson anhydrous methyl-, dimethyl- and ethylamine were used without further purification. The chloramine supply for study was produced by the gas phase reaction of ammonia and chlorine.[10] All of the other chemicals were of reagent grade and the apparatus has been previously described.[15]

Analytical Methods.—The reaction mixture was diluted to 500 ml. with CO_2-free distilled water and 50-ml. aliquots were taken. Separate aliquots were used for the chloramine and alkyl hydrazine determinations. The amount of chloramine originally added was obtained by determining the chloride present in the solution, using modified Volhard procedure for chloride analysis.[16] The alkyl hydrazines were determined as follows: the aliquot was neutralized with concentrated hydrochloric acid and sufficient excess acid was added so that the solution would be 7 *N* in hydrochloric acid at the end of the titration with potassium iodate: 15 ml. of chloroform was added and the solution was chilled to 0°. The standard potassium iodate (0.01667 *f*) was then added until the color of the chloroform layer changed from a dark brown to a light pink. At this point the iodate was added dropwise and the solution was shaken after the addition of each drop. Care was taken so that at no time did the temperature of the solution become greater than 5°. The end-point was the disappearance of the iodine color in the chloroform layer. This method is essentially that given by Hall and Kruse.[17]

Effect of Variables on the Yield of Alkyl Hydrazines.—In order to evaluate the effect of chloramine concentration on the yield of alkyl hydrazines, a standardized experimen-

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(1) Taken in part from the dissertation submitted for the degree of Doctor of Philosophy by George M. Omietanski.

(2) Taken in part from theses submitted for the degree Master of Science by A. Donald Kelmers and by Richard W. Shellman.

(3) Department of Chemistry, University of Florida, Gainesville, Florida.

(4) L. F. Audrieth and L. H. Diamond, THIS JOURNAL, **76**, 4869 (1954).

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(7) M. O. Forster, *J. Chem. Soc.*, **107**, 267 (1915).

(8) M. M. Jones, L. F. Audrieth and E. Colton, THIS JOURNAL, **77**, 2701 (1955).

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(10) R. Mattair and H. H. Sisler, *ibid.*, **73**, 1619 (1951).

(11) H. H. Sisler, F. T. Neth and F. R. Hyrley, *ibid.*, **76**, 3909 (1954).

(12) H. H. Sisler, C. E. Boatman, F. T. Neth, R. Smith, R. W. Shellman and D. Kelmers, *ibid.*, **76**, 3912 (1954).

(13) G. M. Omietanski and H. H. Sisler, *ibid.*, **78**, 1211 (1956).

(14) All melting points are uncorrected. The microanalyses are by Galbraith Laboratories, Knoxville, Tennessee.

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(16) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 38 (1935).

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