ing is the failure to obtain hydrazine in ethyl ether ($C_2H_5OC_2H_5$) whereas considerable yields are obtained in ethyl cellosolve ($C_2H_5OCH_2CH_2OH$) and in ethyl alcohol (C_2H_5OH). We suspect that the reaction mechanism may depend in some manner upon the H-bonding characteristics of the solvent. This and other pertinent aspects of the chloramine–ammonia reaction are being subjected to further study.

Though we have confirmed Wiberg's observation that no hydrazine is obtained from the reaction of chloramine with ammonia in diethyl ether, we certainly do not accept his conclusion that this proves that chloramine is not an intermediate in the Raschig hydrazine synthesis. Our work in other anhydrous solvents (ammonia, cellosolve and absolute ethyl alcohol) is sufficient to refute his arguments.

Acknowledgment.—The authors acknowledge with pleasure the generous support of much of this work by the Davison Chemical Corporation through the Ohio State University Research Foundation. Suggestions and advice by members of the research staff of that corporation have contributed much to the progress of this study.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

Preparation of Anhydrous Hydrazine from Mixtures of Hydrazine Monohydrohalides and Ammonium Chloride

BY HARRY H. SISLER, FLOYD T. NETH, CLAUDE E. BOATMAN AND RICHARD W. SHELLMAN

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It has been shown that anhydrous hydrazine can be recovered from hydrazine hydrochloride or from mixtures of hydrazine hydrochloride and ammonium chloride, by treatment with (a) an equivalent amount of sodium dissolved in liquid ammonia, (b) an equivalent amount of sodium methylate in methanol, (c) an excess of solid alkali hydroxide or alkaline earth metal oxide, or (d) a high-boiling amine. A portion of the NH_4Cl–N_2H_5Cl system (0–23 mole % NH_4Cl) has been studied. It has been shown that mixtures of hydrazine hydrochloride and ammonium chloride can be enriched with respect to the former component by centrifugation of the molten mixture as it undergoes crystallization.

In the Sisler–Mattair process for the synthesis of hydrazine,[1] the hydrazine is formed along with ammonium chloride in liquid ammonia solution. After the liquid ammonia is allowed to evaporate, the hydrazine, because of its considerably lower volatility than ammonia, displaces ammonia from the ammonium chloride in accordance with the equation

$$N_2H_4 + NH_4Cl \longrightarrow N_2H_5Cl + NH_3$$

There results, therefore, a solid mixture of hydrazine monohydrochloride and excess ammonium chloride. We were interested in examining various procedures by which anhydrous hydrazine could be obtained from this solid mixture. The present report is concerned with the results of some of the experiments carried out for this purpose, *viz.*, (a) treatment with sodium in liquid ammonia solution, (b) treatment with sodium methylate in methanol solution, (c) treatment with alkali metal hydroxides or alkaline earth metal oxides, and (d) treatment with a non-volatile amine.

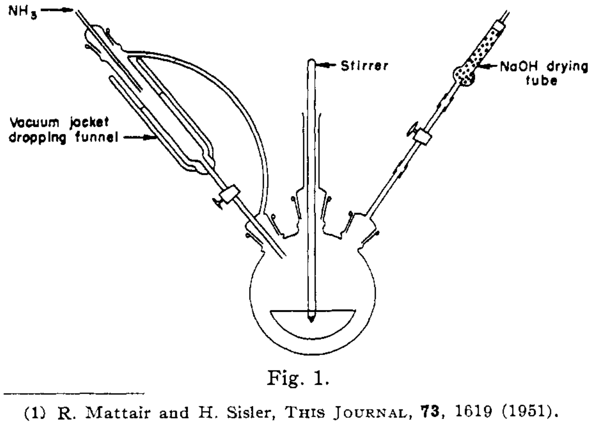

Fig. 1.

Separation with Sodium in Liquid Ammonia.—The separation of anhydrous hydrazine from the mixture formed by the reaction of chloramine with liquid ammonia could be accomplished by destroying the ammonium ion before allowing the ammonia to evaporate. We have found that this can be accomplished very satisfactorily by treating the liquid ammonia solution of hydrazine and ammonium chloride with a liquid ammonia solution of metallic sodium equivalent to the chloride in the hydrazine solution.

The following is a typical experiment. Using the apparatus shown in Fig. 1, one mole of metallic sodium was dissolved in sufficient liquid ammonia to yield a blue solution, and was added dropwise with continuous stirring to a solution containing one-half mole of hydrazine and one mole of ammonium chloride in 400 ml. of liquid ammonia. Both solutions were kept chilled in a Dry Ice-bath. The reaction of the sodium was immediate and the blue color instantly disappeared and sodium chloride precipitated.

$$Na + NH_4^+ + Cl^- \longrightarrow NaCl(s) + NH_3 + {}^1/_2H_2(g)$$

The precipitated sodium chloride was separated by inverse filtration under nitrogen pressure and was washed with additional portions of liquid ammonia. The combined filtrate and washings were distilled. After most of the ammonia had come off, the pressure in the system was reduced to 14–16 mm. and the distillation continued through a fractionating column. Approximately 75% of the theoretical quantity of hydrazine was obtained with about 99% purity. Washing the still pot solid residue (sodium chloride) and the distillation column with liquid ammonia produced enough additional hydrazine to give a recovery of about 95%. Similar results have been obtained in several such experiments separately carried out by two of the authors.

It should be noted that the use of an excess of sodium in this process is not permissible for the excess would react with hydrazine to give the treacherously explosive sodium hydrazide.

Separation with Sodium Methylate.—DeBruyn[2] reported the preparation of anhydrous hydrazine by the reaction of sodium methylate with hydrazine monohydrochloride in

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[1] R. Mattair and H. Sisler, THIS JOURNAL, **73**, 1619 (1951).

[2] L. deBruyn, *Ber.*, **28**, 3085 (1895).

methanol but the yields calculated from his results are low. We decided to try a similar procedure in which the methanol solution of the hydrazine hydrohalide is treated with ammonia gas to set free the hydrazine before the solution is reacted with sodium methylate.

A typical experiment was carried out as follows: One-half mole of hydrazine dihydrochloride was dissolved in 100 ml. of anhydrous methanol and the resulting solution saturated with ammonia gas. This results in a solution containing one-half mole of free hydrazine and one mole of ammonium ion.

$$N_2H_6^{++} + 2NH_3 \longrightarrow N_2H_4 + 2NH_4^+$$

A solution containing one mole of sodium methylate in 500 ml. of absolute methanol made by dissolving one mole of sodium in the alcohol was then added from a dropping funnel while the solution was constantly stirred. A rapid stream of ammonia gas was maintained during the addition of the sodium methylate solution. As the sodium methylate was added precipitation of sodium chloride occurred.

$$NH_4^+ + Cl^- + Na^+ + OCH_3^- \longrightarrow NH_3 + CH_3OH + NaCl(s)$$

This sodium chloride was removed by inverse filtration and was washed twice with absolute methanol. The combined filtrate and washings were fractionated, first at atmospheric pressure, and later, after most of the methanol had been removed, under reduced pressure (14–16 mm.). Approximately 50% of the hydrazine was thus obtained with a purity of 92%. Much of the impurity was methanol. Recovery of hydrazine held up in the fractionating column and remaining in the still pot was sufficient to give a total recovery of approximately 90%. There is no question that, with somewhat modified distillation equipment and, on a continuous basis, good recoveries of hydrazine of high purity could be obtained by this method.

Separation with Alkalies.—Mixtures of hydrazine monohydrochloride (prepared by heating Mathieson hydrazine dihydrochloride and recrystallizing the product from water) and ammonium chloride (C.P. grade) were placed in a single distilling flask attached to a Liebig condenser, with a receiver attached in such a way that the ammonia vapor produced could be withdrawn with or without reducing the pressure inside the apparatus, as might be desired. The desired amount of alkali metal hyroxide (C.P. grade) or alkaline earth metal oxide (Analytical or C.P. grade) was then added to the solid mixture, the apparatus closed, and the flask slowly heated by means of a heating mantle until no further distillate could be obtained. The distillate was then analyzed for hydrazine. The summary of a series of such experiments using sodium hydroxide is presented below in Table I. Listed in each case is the nature of the product as determined from the boiling point and hydrazine analysis.

TABLE I

Wt. N_2H_4Cl, g.	Wt. NH_4Cl, g.	Wt. NaOH, g.	Mole ratio, base/salt	Yield of N_2H_4, %	Nature of product
20	20	150	5.64	82.5	N_2H_4
20	20	130	4.90	91.4	N_2H_4
20	20	120	4.50	83.8	$N_2H_4 + N_2H_4 \cdot H_2O$
20	20	110	4.13	79.6	$N_2H_4 + N_2H_4 \cdot H_2O$
20	20	90	3.38	92.8	$N_2H_4 + N_2H_4 \cdot H_2O$
20	20	80	3.00	86.4	$N_2H_4 + N_2H_4 \cdot H_2O$
20	20	60	2.26	93.3	$N_2H_4 + N_2H_4 \cdot H_2O$
20	20	40	1.49	77.2	$N_2H_4 \cdot H_2O$
15	10	20	1.23	67.8	$N_2H_4 \cdot H_2O$

The results show that, by the use of sodium hydroxide, hydrazine may be recovered from mixtures of its hydrohalides with ammonium halides. Furthermore, if sufficient excess base is used (approximately 5 moles per mole of salt) the hydrazine is obtained in the anhydrous form. It is, moreover, reasonable to believe that by careful design of equipment and procedure the recovery could be made almost quantitative. With the simple procedures and equipment used here recovery was commonly in the range of 85 to 95%. Our results give quantitative confirmation to the qualitative statements concerning the use of alkali for hydrazine recovery in a recent note by Bulgozdy and Wagner.[3] We have carried out similar experiments with potassium hydroxide and found similar results. A similar series of experiments was carried out with mixtures of hydrazine monohydrobromide and ammonium chloride. The results obtained are in close agreement with those listed in Table I.

A few experiments in which mixtures of hydrazine monohydrochloride (or hydrobromide) and ammonium chloride were heated with slightly more than equimolar portions of barium oxide were carried out. Very little hydrazine distilled out of such mixtures at atmospheric pressure. However, under reduced pressures a major portion (60–80%) of the hydrazine distilled out as hydrazine hydrate. We believe that the hydrazine is tied up as a barium complex and that this complex breaks down under reduced pressure.

With calcium oxide no hydrazine was obtained even under reduced pressure.

Separation with Cyclohexylamine.—In a recent patent[4] Schwarcz states that hydrazine or hydrazine hydrate can be formed from hydrazine salts by treatment of the salts with a high-boiling amine. Before this patent appeared we had already carried out a series of experiments in which a mixture of hydrazine monohydrobromide and ammonium chloride was treated with an excess of cyclohexylamine and the liquid mixture distilled and had found it to be possible in this way to obtain anhydrous hydrazine in very high yields.

Separation of Ammonium Chloride and Hydrazine Monohydrochloride by Fractional Crystallization.—Qualitative observations had indicated that ammonium chloride has only a limited solubility in molten hydrazine monohydrochloride. This suggested to us that at least a partial separation of ammonium chloride from hydrazine hydrochloride should be obtainable by fractional crystallization procedures. In order to establish the theoretical limits of such procedures a cryoscopic study of a portion of the binary system N_2H_5Cl–NH_4Cl was carried out. The hydrazine monohydrochloride was prepared by heating the dihydrochloride and recrystallizing the product from water. The melting point of the resulting product was 92.5°. C.P. grade ammonium chloride was used. Synthetic mixtures of the two components were melted together, ground and then placed in Pyrex test-tubes and slowly heated in an oil-bath with constant stirring until solution was complete. The samples were then allowed to cool slowly, with stirring, and the freezing point carefully observed. Mixtures in the composition range 0–23 mole % ammonium chloride were studied. The data obtained are presented in Table II and Fig. 2, and indicate that as ammonium chloride is added to pure hydrazine monohydrochloride, the freezing point drops from 92.5° for the pure hydrazine salt to a eutectic temperature of approximately 84° at 10.6 mole per cent. of ammonium chloride. Thus, the theoretical limit of this method for removing ammonium chloride is about 10 mole per cent. ammonium chloride. Partial separation would be useful, however, in that less alkali, sodium, or sodium methylate would be required to free the hydrazine base from the concentrate by one of the methods described above, than would be the case if all the ammonium chloride were allowed to remain in the mixture.

TABLE II

FREEZING POINTS IN THE BINARY SYSTEM HYDRAZINE MONOHYDROCHLORIDE–AMMONIUM CHLORIDE

NH_4Cl, %	M.p., °C.	NH_4Cl, %	M.p., °C.	NH_4Cl, %	M.p., °C.
0.00	92.5	8.64	85.3	17.10	130.0
1.00	91.0	9.50	85.0	17.50	135.0
2.00	90.5	10.00	84.2	18.00	139.0
3.32	89.0	10.65	85.0	19.00	145.0
4.50	88.3	11.50	91.0	20.00	152.5
4.96	87.0	12.45	96.0	21.00	158.0
6.30	86.6	13.00	99.5	22.00	166.0
6.73	86.3	15.00	120.0	23.00	174.0
7.50	86.0	15.60	121.0		

A convenient method which should produce a partial separation of ammonium chloride and hydrazine hydrochloride by crystallization from the fused mixture would

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[3] E. Bulgozdy and E. Wagner, THIS JOURNAL, **73**, 5866 (1951).

[4] M. Schwarcz, U. S. Patent 2,537,791 (Jan. 9, 1951).

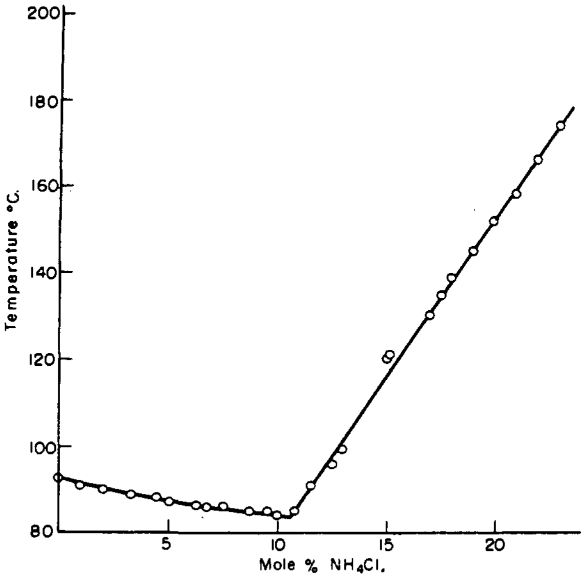

Fig. 2.—Part of the system NH_4Cl–N_2H_5Cl.

consist in placing the molten mixture in a test-tube which is whirled in a centrifuge during crystallization. The crystals of ammonium chloride being heavier than the melt should sink to the bottom of the tube during the centrifugation. Thus, when the melt is completely solidified there should be a gradation in composition from top to bottom, the bottom section being richer in ammonium chloride and the top section in hydrazine hydrochloride. Some simple experiments to test this procedure were carried out as follows.

Mixtures of hydrazine hydrochloride and ammonium chloride were melted, thoroughly mixed and then centrifuged until solidification was complete. The glass tube container was then carefully broken and the solidified mass carefully divided into four segments which were analyzed for hydrazine hydrochloride. The results of three such experiments are listed in Table III.

TABLE III

	N_2H_5Cl, %		
	Expt. 1	Expt. 2	Expt. 3
Top quarter	76.0	84.0	88.8
Third quarter	45.3	43.4	39.4
Second quarter	40.6	40.7	39.3
Bottom quarter	37.5	48.2	38.8

These results show that separation does occur. In fact, in expt. 3 the composition of the top quarter approaches the theoretical limit indicated by the eutectic composition. It is also apparent that by controlling the rate of cooling and increasing the force of centrifugation, the separation could be improved.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Spectrophotometric Study of Phosphorus Pentabromide in Various Solvents[1,2]

BY ALEXANDER I. POPOV AND NORMAN E. SKELLY

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Spectrophotometric studies of phosphorus pentabromide and bromine solutions in carbon tetrachloride, ethylene dichloride and carbon disulfide have shown that in the 300–600 mμ region a large fraction of the absorption can be ascribed to the undissociated "complex" $PBr_3 \cdot Br_2$. This observation invalidates the usually accepted value of the dissociation constant of PBr_5 in these solvents, which was determined colorimetrically, on the assumption that bromine is the only absorbing species. An approximate value for the molar absorbancy index of $PBr_3 \cdot Br_2$ "complex" has been determined and the correspondingly approximate values of the dissociation constant of this compound have been calculated for carbon tetrachloride and ethylene dichloride solutions. Similar study on phosphorus pentachloride shows that it does not undergo appreciable dissociation in the solvents used.

Introduction

The degree of dissociation of phosphorus pentabromide in carbon tetrachloride and in carbon disulfide was determined colorimetrically in 1899.[3] It was at that time assumed that the color of the solution was due entirely to the free bromine present as a dissociation product. A 90% dissociation was reported in the carbon tetrachloride and 100% dissociation in carbon disulfide; however, it was observed that the addition of an excess of phosphorus tribromide to the carbon disulfide solutions decreased the color intensity. If this was due to the repression of the dissociation, the observation was obviously incompatible with a 100% dissociation.

Popov and Schmorr[4] reported that the absorption spectrum of phosphorus pentabromide solution in carbon tetrachloride was identical to that of bromine in the same solvent, but with a somewhat lower molar absorbancy index[5]; thus the results of previous investigators were apparently confirmed.

However, it was observed that additions of excess of phosphorus tribromide resulted in a dissociation suppression which was usually greater than the one calculated on the assumption of a 90% dissociation. Likewise, the absorbancy variations on dilution were incompatible with the predicted ones. It seemed that a more detailed investigation of this problem was needed.

Experimental Part

The absorption curves reported in this investigation were obtained with a Cary recording spectrophotometer model 11. When the measurements involved determinations of absorbance at a single wave length, a Beckman DU spectrophotometer was used.

The absorbance scales of both spectrophotometers were calibrated against standardized filters supplied by the National Bureau of Standards and appropriate corrections were applied whenever necessary. Corex, stoppered cells with path length of 1.00 ± 0.01 cm. were used and all measurements were made at the room temperature of approximately 25°.

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(1) Presented before the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September 14, 1952.

(2) Abstracted in part from the M.S. thesis of Norman E. Skelly, S.U.I., February, 1953.

(3) J. H. Kastle and L. O. Beatty, *Am. Chem. J.*, **21**, 392 (1899).

(4) A. I. Popov and E. H. Schmorr, THIS JOURNAL, **74**, 4672 (1952).

(5) Symbols and nomenclature used in this paper follow the recommendations of the National Bureau of Standards, Letter Circular LC-857 (1947).