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Methyl amines from carbinol and ammonium chloride

Arthur Mark Howald

METHYL AMINES FROM CARBINOL AND AMMONIUM CHLORIDE

BY

A. M. Howald

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THESIS

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During the spring of 1919 we undertook to prepare tri-methyl-amine for the Research Department of the Eastman Kodak Company in the Industrial Chemistry Laboratory of the Missouri School of Mines. According to V.Merz and K.Gasiorowski* the three methyl amines were qualitatively proven to be present in the reaction products obtained by heating methyl alcohol, ammonia and zinc chloride to 220°C. in a bomb for fourteen hours. As these raw materials are inexpensive we attempted to prepare the tri-methyl-amine by this reaction employing for the purpose a small industrial autoclave. Methyl amines were obtained but the yield especially of the tri- were very low (less than one percent) and the process was put aside until such time as smaller scale experimental work could be done upon it.

The researches to be described in this paper were undertaken to supply the need outlined above. The first necessary step was to devise or obtain from the literature a satisfactory method of analysis. The literature at hand up to this time spoke of six possible methods of separation as follows:

1- Reactions of the three classes of amines with HNO_2

2- Reactions of amines with di-ethyl-oxalic-ester.

*Berichte Vol. 17, page 623.

3-
Reactions of amines with formaldehyde.

4-
Reactions of amines with benzine-sulpho-chloride.

5-
Reactions of amines with carbon bi-sulphide.

6-
Differences in the soluabilities of the methyl-amine sulphates in absolute alcohol.

It was our intention to test each of these reactions as the possible basis of an analytical method and the first had been tried and found unsatisfactory when a method devised by Berthreume* was found in the literature. This method is based upon the fact that the hydrochlorides of di- and tri-methyl amine are soluable in pure dry chloroform while the hydrochlorides of ammonia and mono-methyl amine are not. The method as published is complete and satisfactory except from the standpoint of the time required which we were able to shorten from about thirty six to twelve hours. The method as finally used is as follows: when adapted so as to determine methyl alcohol also:

SOLUTIONS REQUIRED:

I-	I.000 normal	H Cl
2-	I.000 , , , ,	H_2SO_4
3-	I.000 , , , ,	Na OH
4-	0.1000 , , , ,	H Cl
5-	0.0500 , , , ,	H Cl
6-	0.0500 , , , ,	Na OH
7-	0.0500 , , , ,	Ag NO_3

*Comptes Rendus
Vol. I50 page I25I

8- iodine solution.
I27 gr. I_2 & I50 gr. KI per liter.

9- Na OH
30% solution.

IO- Na_2CO_3 20% solution.

II- Nessler's reagent

I2- saturated $HgCl_2$ solution or as an alternative yellow Hg O.

I3- Na_2SO_4, KI and other general reagents.

FLOW SHEET OF THE ANALYSIS:

reaction products from autoclave or bomb

-

Distill off CH_3OH after acidifying with H_2SO_4 Make basic with Na OH distill again and determine CH_3OH in distillate by Sp.G.

-

Distill bases into water & titrate with I normal H Cl

-

Evaporate .I5 to .30 mols in evap. dish with excess conc. H Cl. Add 20 gr. pure sand just before dryness & take just dry on water bath.

-

Dry 2 to 3 hours in vacuum dessicator over Na OH and $CaCl_2$

-

Extract 5 times with dry $CHCl_3$

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residue

-

evaporate $CHCl_3$. Dilute to 250 c.cm. after dissolving in water.

-

Titrate 25 c.cm. with $AgNO_3$ to get total bases.

-

Take sufficient to equal 50 c.cm. .5 N. soln. in I00 c.cm graduated cylinder.

extract

-

add H_2O, distill off $CHCl_3$, cool, dilute to 250 c.cm.

-

titrate 25 c.cm. with .05 N. $AgNO_3$ to get total bases.

-

Take .I00 mol. dilute to I00 c.cm., cool to 0^oC. & add 30 c.cm. of the iodine soln. also at 0^oC.

-

Add 3 c.cm. of 30% Na OH soln. 5 of 20% Na_2CO_3 and sufficient $HgCl_2$ soln. to give 2.5 gr. Hg O.*1

Agitate ½ hour

Filter thru gooch crucible into H_2SO_4.*2 Wash with same concentration of Na OH and Na_2CO_3.

precipitate	filtrate
Transfer to ammonia dist. flask. Add 30 gr. KI & a little Na OH	add Na OH and distill into .1 N. HCl and titrate
Distill into .1 N. HCl and titrate.	

Filter after one hour thru glass wool & wash with same iodine soln. diluted I:3

filtrate	precipitate
$N(CH_3)H \cdot HCl$	$N(CH_3)_3HCl$
dissolve I_2 in Na_2SO_3 soln.	Na_2SO_3 & NaOH
Add little Na OH, distill into .05 N. HCl & titrate.	Distill and titrate with .05 N. HCl.

Note:

Use Nessler's reagent to test for complete precipitation of NH_3. See page 162 in "Laboratory methods of Inorganic Chemistry" by Biltz, Hall & Blanchard.

*1-

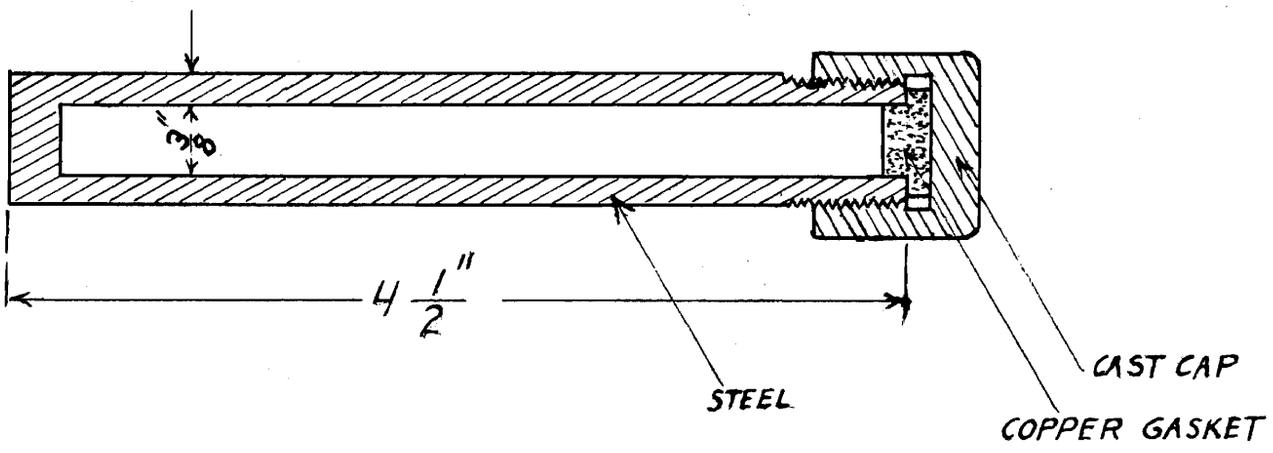
HgO can be used directly in place of $HgCl_2$ but the agitation must be longer (1 hour).

*2-

Attach a glass tube to the end of the Gooch funnel so that it projects below the surface of the H_2SO_4 thus preventing volitalization of the mono-methyl amine.

In the first experiments an attempt was made to heat solutions of ammonia or amines in methyl alcohol to equilibrium in glass bombs but they failed owing to the facts that the glass lacked tensile strength and was also attacked by the bases.*

In the second series steel bombs were used. Some trouble was found in designing a bomb that would not leak upon prolonged heating. For example in an ordinary ½ inch pipe capped at both ends the entire charge would leak out in one hour. The type of bomb finally used with success is shown in the accompanying diagram.



In this series the charges consisted of a solution of ammonia in methyl alcohol with and without the addition of fused zinc chloride. The temperature was maintained for varying lengths of time at 218°c. (B.P.of naphthalene). The naphthalene was boiled in a two liter

*Gelatinous silica was formed.

flask fitted with a reflux condenser and containing the experimental bomb suspended within it. The charges used ,the conditions of heating and an analysis of the products of reaction are given in the following tables.

Table one shows the charges of series one as they were before heating and also the loss on heating. It will be noticed that the losses were large due to the technique of closing the bombs not having been perfected

Time in Hrs	Temp. C.	Compound	Wt.	Mols.	Ratio to mols-NH_3
24	218	NH_3	1.03 gr	.0566	1.00
Charge No. one.		CH_3OH	5.83	.1520	3.00
		$ZnCl_2$	none	-------	-------
		loss on heating	1.56		
60	218	NH_3	1.30	.0623	1.00
Charge number two		CH_3OH	5.98	.1869	3.00
		$ZnCl_2$	none		
		loss	3.13		
2	218	NH_3	0.866	.0509	1.00
Charge number three		CH_3OH	4.89	.1518	3.00
		$ZnCl_2$	10.37		1.50
		loss	.18		

TABLE I.
CHARGES USED IN SERIES NUMBER ONE.

at this time. As shown by the table three experiments were run in this series;one for 24 hours without $ZnCl_2$ another for 60 hours without $ZnCl_2$ and a third for 2 hours with $ZnCl_2$. The yields in each case being so very low the series was discontinued. The yields as given in table 2 show however that ZnCl has a marked effect in increasing the yield of amines.

Time in Hrs	Temp. C.	Compound	Wt.	Mols.	Ratio to Mols.NH_3
24	218	NH_3	.751	.0442	I.00
Charge no. one		NCH_3H_2	.021	.00068	.021
		$N(CH_3)H_2$ $N(CH_3)_3$	trace		
		CH_3OH	4.200	.1313	2.97
		Undt.	.33		
60	218	NH_3	.576	.0339	I.oo
Charge number two		NCH_3H_2	.031	.0010	.029
		Trace of	di- & tri-		
		CH_3OH	3.31	.1034	3.05
		Undt.	,33		
2	218	NH_3	.834	.0453	I.00
Charge number three		NCH_3H_2	.132	.00359	.079
		Di-& Tri-		.00029	.0064
		CH_3OH	3.30	.1040	2.30
		Undt.	I.30		

TABLE No. 2.
PRODUCTS OF SERIES NUMBER ONE

CHARGES OF SERIES TWO

Time	Temp.	COMPOUND	WEIGHT	MOLS	ratio of mols NH_3-I
$5\frac{1}{2}$	218	NH_4Cl	2.862	.0535	I.00
Run number one.		CH_3OH	5.I40	.I606	3.00
		$ZnCl_2$	none		
		loss	I.3I		
5	218	NH_4Cl	3.30	.0598	I.00
Run number two.		CH_3OH	5.77	.I799	3.00
		$ZnCl_2$	I2.56		I.50
		loss	2.70		
5	218	NH_4Cl	I.00	.0I87	I.00
Run number three.		CH_3OH	5.42	.I684	9.00
		$ZnCl_2$	3.84		I.50
		loss	o.0I		
5	303	NH_4Cl	0.50	.00935	I.00
Run number four.		CH_3OH	3.67	.II46	I2.26
		$ZnCl_2$	I.9I		I.50
		loss	.02		
5	303	NH_4Cl	.50	.00935	I.00
Run number five.		CH_3OH	4.I2	.1288	I3.77
		$ZnCl_2$	0.00		
		loss	.00		
5	303	NH_4Cl	.50	.00935	I.00
Run number six.		CH_3OH	3.92	.I225	I3.06
		$ZnCl_2$	.95		.75
		loss	.05		
8	303	NH_4Cl	.50	.00935	I.00
Run number seven.		CH_3OH	3.74	.II69	I2.39
		$ZnCl_2$	I.9I		I.50
		loss	.04		

TABLE 3.

PRODUCTS OF SERIES TWO

TIME	TEMP.	Compound	Wt.	Mols	Ratio to mols NH_3
5½	218	NH_4Cl	2.587	.0525	I.00
Expt.number one.		NCH_3H_3Cl	.17I	.0026	.0525
		$N(CH_3)_2HCl$	.0469	.00057	.0II8
		$N(CH_3)_3HCl$	trace		
		CH_3OH	3.30	.103I	2.I3
		Undt.	.59	$ZnCl_2$	none
5	218	NH_4Cl	2.474	.0462	1.000
Expt.number two.		NCH_3H_3Cl	I.0I2	.0I50	0.325
		$N(CH_3)_2H_2Cl$	.0030	.000363	.0078
		$N(CH_3)_3HCl$	trace		
		CH_3OH	.720	.0225	.489
		Undt.	2.30	$ZnCl_2$	I.50
5	218	NH_4Cl	0.670	.0I253	1.000
Exptnumber three.		NCH_3H_2HCl	.368	.00540	.432
		$N(CH_3)_2H_2Cl$	.0458	.000558	.0454
		$N(CH_3)_3HCl$	.008I	.000084	.0067
		CH_3OH	2.05	.06406	5.II3
		Undt.	3.44	ZnCl	I.50
5	303	NH_4Cl	.279	.00522	I.00
Expt.number four.		NCH_3H_3Cl	.243	.00360	.689
		$N(CH_3)_2H_2Cl$	.0293	.00036	.069
		$N(CH_3)_3HCl$	.0II5	.00012	.023
		CH_3OH	I.696	.0530	I0.I5
		Undt.	2.00	$ZnCl_2$	I.50

This table is continued on next page.

5	303	NH_4Cl	.453	.00849	I.00
Expt.number five.		NCH_3H_3Cl	.0678	.000832	.098
		$N(CH_3)_2H_2Cl$	.0I20	.000I25	.oI47
		$N(CH_3)_3HCl$	.trace		
		CH_3OH	3.8I	.II$I	I4.04
		Undt.	.27	$ZnCl_2$	none
5	303	NH_4Cl	.396	.0074I	I.00
Expt. number six.		NCH_3H_3Cl	.II4	.$$I685	.227
		$N(CH_3)_2H_2Cl$	.0408	.00020	.0207
		$N(CH_3)_3HCl$	.0026	.000025	.00335
		CH_3OH	3.32	.I006	I3.57
		Undt.	.75	$ZnCl_2$	.75
8	303	NH_4Cl	.225	.00424	I.00
Expt. number seven.		NCH_3H_3Cl	.308	.00457	I.078
		$N(CH_3)_2H_2Cl$	.0600	.00074	.I62
		$N(CH_3)_3HCl$	.0II4	.000I2	.0262
		CH_3OH	------	lost	
		Undt.	.	$ZnCl_2$	I.50

TABLE 4

Tables three and four give the charges and the reaction products respectively of the second successful series in which ammonium chloride was used to replace the ammonia of the preceeding series. Again zinc chloride greatly increased the yields but it will be noticed that Expts. without zinc chloride in this series gave as large yields as those with zinc chloride in the preceeding series. Series two consists of experiments at two temperatures;one 218°C. (boiling point of naphthalene) the other 303°C. (the boiling point of acetanilide).

The important results of this series can be found in table four . Thus experiments two and three show that by multiplying the ratio of the mols of alcohol to the mols of ammonium chloride by 10 that the yield of mono-methyl-amine is multiplied by approximately I.5 while the yield of di-methyl-amine is increased to four times this degree or is multiplied by about 6. Experiments three and four show that while increasing the temperature has almost an equal effect in increasing the yields

of mono and di-methyl-amines but that it has three times this great an effect in increasing the yield of tri-methyl-amine. That is in raising the temperature of the experiments from 218°C. to 303°C. the yield of mono and di-methyl-amine is multiplied by approximately I.5 while the yield of tri-methyl-amine is multiplied by 4. Experiments four five and six show that decreasing the ratio of zinc chloride has a slightly greater effect in decreasing the yield of di-methyl-amine than of mono-methyl-amine and about 2.5 times this great an effect in decreasing the yield of tri-methyl-amine. Finally experiments four and seven show that while increasing the time of heating from five to eight hours practically doubles the yields of mono- and di-methyl-amines yet it has practically no effect on the yield of tri-methyl-amine.

It must be mentioned at this point that large quantities of gas was liberated in all bombs in which zinc chloride was used the amount of gas increasing with the time of heating. Upon analysis it proved to be hydrogen.

CONDITIONS		RATIOS OF MOLS AFTER HEATING NH_3=I					
Time	Temp	NH_3	NCH_3H_2	$N(CH_3)_2H$	$N(CH_3)_3$	CH_3OH	$ZnCl_2$
24	218	I.00	.0154			2.97	
60	218	I.00	.0290			3.05	
2	218	I.00	.0792	.0064		2.30	I.50
$5\frac{1}{2}$	218	I.00	.0550	.0121		2.17	
5	218	I.00	.3250	.0078		.49	I.50
5	218	I.00	.432	.0447	.0064	5.11	I.50
5	303	I.00	.689	.0690	.023	10.15	I.50
5	303	I.00	.098	.0147		14.04	
5	303	I.00	.227	.0207	.0034	13,57	.75
8	303	I.00	I.078	.162	.026	10-13	I.50

TABLE 5.

*H.I.Jones, J.A.C.S. Vol. 40- page 1411 f.f.

Table five sums up the important results of both series one and two and can advantageously be used in considering the conclusions stated in the following summary.

SUMMARY:

I-

Methyl amines are produced only in traces when NH_3 or NH_4Cl is heated below 305°C. without the addition of a dehydrating agent.

2-

Using $ZnCl_2$ as a dehydrating agent yields of mono-methyl-amine are obtained up to 55 % of the theoretical di-methyl-amine up to 7.5 % and tri-methyl-amine up to I.85 % of the theoretical in eight hours at 303°C.

3-

The yields increase* with increase in the amount of ZnCl or of CH_3OH present, with increase in temperature, and with increase in time of heating according to the following rules.

A-

Ratios of $ZnCl_2$ and CH_3OH to NH_3 and temperature of reaction have greatest effect on yield of tri, next

on di- and least effect on the yield of mono methyl amine.

B-

Time of heating has greater effect on the yield of di-methyl-amine than of mono-methyl-amine.

4-

Equilibrium cannot be reached in an iron vessel due to hydrolysis of the Zinc chloride and liberation of hydrogen from the HCl thus formed, by iron.

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