STUDIES ON THE "RASCHIG'S" HYDRAZINE SYNTHESIS

BY

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I.

I. Introduction.

In 1906 RASCHIG[1] discovered that hydrazine was formed in the reaction of ammonia with sodium hypochlorite, and that the hydrazine yield could be increased by increasing the excess of ammonia, by a rapid heating as soon as the agents were mixed, and especially by an addition of glue, or porteins in general, and by different sugars.

The reaction of ammonia with hypochlorite had been investigated previously by many authors[2], and it had been observed, that the main product of the reaction is nitrogen. But the mixed, cold solution of the agents also contained traces of a substance, which was able to liberate iodine from potassium iodide, while on heating traces of a powerfull reducing agent were formed.

RASCHIG (l. c.) assumed the oxidizing agent to be monochloroamine, and proved the reducing agent to be hydrazine. He did not, however, succeed in preparing monochloroamine in the pure state.

He has further investigated the reactions of monochloro-

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[1] C. B. 1908 I, 427, 1957; B. **40** (1907) 2065; Chem. Ztg. **31** (1907) 926; Z. angew. Chem. **20** (1907) 2065.

[2] SOUBEIRAN: Ann. Chim. Phys. **48** (1831) 141. SCHÖNBEIN: Jour. prakt. Chem. **84** (1861) 385. LUNGE & SCHOCH: B. **20** (1887) 1447. CROSS & BEVAN: Proc. Chem. Soc. 1890, 22. ARMSTRONG: Proc. Chem. Soc. 1890, 24. THIELE: Ann. **273** (1893) 160.

amine in aqueous solution with ammonia and with sodium hydroxide. With ammonia the main products of the reaction are nitrogen and ammonium chloride, but simultaneously some hydrazine and traces of azoimide are formed. In the reaction with sodium hydroxide nitrogen, sodium chloride, ammonia and traces of azoimide are formed. From these facts he assumes[1], that imide or triimide is formed as an intermediate product, and that the azoimide is a product of the reaction between monochloroamine and triimide.

MARCKWALD & WILLE[2] have in general confirmed these investigations on monochloroamine. They succeded in preparing monochloroamine in the pure state and were able to show, that in aqueous solution this substance is hydrolysed to some extend into ammonia and hypochlorous acid. This discovery, as it will be shown in the following, appears to be of much value for the understanding of the hydrazine synthesis.

When no glue, gelatine or sugar is present in the reaction of ammonia with hypochlorite, it appears, according to RASCHIG (l. c.), that the hydrazine yield is very varying. He discovers that the reaction, in which monochloramine is destroyed with evolution of nitrogen, is catalyzed by small quantities of such metals as iron, copper, lead, but especially cobalt. He illustrates this by adding a drop of a concentrated solution of a copper salt to the reaction mixture, which usually (in the presence of gelatine and no copper salt) gives hydrazine yields of 40—50 % of the hypochlorite.

Originally RASCHIG (l. c.) explained the activity of glue,

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[1] RASCHIG: Schwefel und Stickstoffstudien. Leipzig 1924, page 60. This will in the following be quoted as S & S.

[2] B. **56** (1923) 1322.

gelatine, sugar etc. due to the fact, that these substances increase the viscosity of the solution. This explanation was strongly criticised by LUTHER[1] and BREDIG[2]. In S & S (page 62 and the following) RASCHIG's point of view has changed, and he seems to believe, that these substances are able to increase the stability of the assumed, intermediate compound imide. He has further discovered that the presence of a strong base, such as sodium hydroxide, is necessary for the production of hydrazine from ammonia and hypochlorite, and now assumes the reaction to take place in such a manner, that one molecule of each of ammonia, hypochlorite and sodium hydroxide react to form hydrazine, sodium chloride and water.[3]

To prove the formation of imide as an intermediate product, RASCHIG[4] attempts to prepare this substance by other methods, but does not succeed.

SMITH[5] has obtained imide as an intermediate product in the decomposition of azoimide by the action of cool, conc. sulphuric acid. In aqueous solution, however, the imide unites with water forming hydroxylamine, and in solutions with organic solvents it generally reacts with these.

JOYNER[6] has investigated the variation of the hydrazine yield with variations in the concentrations of ammonia, hypochlorite and gelatine. The action of gelatine is proportional to its concentration to a certain limit, above which the action remains practically constant independent of a further increase. It is emphazised, that with no gelatine present

[1] Z. angew. Chem. **19** (1906) 2049.

[2] Z. angew. Chem. **19** (1906) 1985.

[3] S & S page 62 and following pages.

[4] S & S page 75 and following pages. See also RASCHIG: Z. angew. Chem. **23** (1910) 972 and THIELE: Ann. **271** (1882) 127.

[5] Z. angew. Chem. **36** (1923) 511. B. **57** (1923) 704.

[6] J. Chem. Soc. **123** (1923) 1114.

in the reaction mixture, the ammonia which is used must be very pure, and even then the hydrazine yield is very eratic, varying from 1 to 15 % of the hypochlorite. It is further proved that the action of glue is not due to a complex formation with monochloramine, and that the reaction mixture must contain hydroxyl ions within a certain range of concentrations.

Other authors[1] have investigated the hydrazine synthesis, but it should only be mentioned that, after this investigation was finished, BODENSTEIN[2] has published two papers dealing with monochloramine and hydrazine. The results are in all essential in agreement with the results of this investigation, and they will be taken up for discussion the in following.

II. Experimental.

1. Introduction.

From the results of RASCHIG and other authors one seems forced to assume, that the action of glue, gelatine, sugar etc. in the hydrazine synthesis must be due to a reaction in which these substances unite with or destroy a positive catalyst, i. e. a catalyst which accelerates reactions giving rise to the formation of nitrogen on the expence of monochloramine.

That the hydrazine yield may be fair, when the reaction mixture is heated immediately after the mixing of ammonia and hypochlorite, while it is very small if the reaction is allowed to take place at ordinary temperature, is a fact

[1] ORELKIN, CHLOPIN & TSCHERMAEV: J. Russ. Phys. Chem. Gess. 49 (1917) 82; C. B. 1923, III, 1544. PUTOCHIN: Arbeiten aus d. Inst. f. chem. reine Reagenzien (russ.) Lief. 2 (1923) 50; C. B. 1924, II, 1569.
[2] Z. phys. Chem., Abt. A, 139 (1928) 397; Z. phys. Chem., Abt. A, 137 (1928) 131.

which agrees very well with the theory of a positive catalyst. As a rule, catalytic reactions have a considerably smaller temperature coefficient than other reactions.

The reaction occurs in alkaline solution, and when the substances active in increasing the hydrazine yield are reviewed — glycerol, the sugars (glucose, mannite, cane sugar), the proteins (gelatine, glue, casein) — it seems very probable that the catalyticly active substance must be copper ions. All of the mentioned substances are able to unite with copper ions to form more or less stable complex compounds.

Copper ions are able to act as a powerful catalytic agent in many different reactions and especially in many redox-processes.

Titoff[1] has shown that copper ions catalyze the oxidation of sodium sulphite by the action of the atmospheric oxygen. A copper sulphate concentration of 10^{-12} molar is sufficient to effect a considerable increase in the oxidation velocity. He has also shown that mannite, ammonia, stannic chloride and potassium cyanide counteract copper ions, since these substances are able to unite with copper ions to form stable complex compounds.[2]

Raschig[3] has pointed out that small quantities of copper, lead, iron, nickel, mercury and especially cobalt have an unfavourable action, and he illustrates this by adding one drop of a concentrated solution of copper sulphate to a reaction mixture containing no gelatine. But Raschig has

[1] Z. phys. Chem. 45 (1903) 64.

[2] See also: Thatcher: Z. phys. Chem. 47 (1904) 64; Schönbein: J. prakt. Chem. 84 (1861) 385; Loew: J. prakt. Chem. (N. F.) 18 (1878) 298; Kappel: Arch. d. Pharm. (3), 20 (1882) 568; Traube & Biltz: B. 37 (1904) 3130; B. 39 (1906) 166; Meyer: B. 35 (1902) 3952.

[3] For instance S & S page 65.

not seen, that the action of glue is due to the fact that this substance unites with the positive catalyst.

The guiding idea of the first part of this experimental work has been, that the reason why the hydrazine yield is very varying and small (when no glue or gelatine has been added), is a trace of copper ions present in the ammonia, the sodium hydroxide and the distilled water which are used in the process. The first problem, therefore, would be to purify these substances for a presumed content of copper and apply the purified substances in RASCHIG's synthesis. Further, to observe the action of minute quantities of copper, and finally to investigate the action of a simultaneous addition of a copper salt and one of these substances which are able to increase the hydrazine yield.

2. Analytical Methods.

STOLLE's[1] method has been used in the titration of hydrazine. Here the hydrazine is titrated by means of an iodine solution in the precence of sodium bicarbonate. Starch is used as indicator and the addition of iodine must be continued until the solution is slightly purple and does not change its colour on shaking. The titration must take place immediately after the addition of sodium bicarbonate, since hydrazine in an alkaline solution is oxydized rapidly by the oxygen of the air. Ammonium salts do not effect the titration. The method has been recommended by many authors[2], and in the writers experience it is absolutely reli-

[1] J. prakt. Chem. **66** (1902) 332.

[2] SOMMER: Z. anorg. Chem. **83** (1913) 119; OLIVERI-MANDALA: Gazz. Chim. Ital. **51**, II (1921), 201; RASCHIG: l. c.; JOYNER: l. c.; BRAY & GUY: J. Amer. Chem. Soc. **46** (1924) 863; KOLTHOFF: J. Amer. Chem. Soc. **46** (1924), 2010.

able, when the titration is always made in the same volume of boiled water (50 ccs.), with the same quantity (3 grams) of sodium bicarbonate, and when the addition of iodine takes place rather slowly near the endpoint.

The iodine solution was standardized by means of a standardized sodium thiosulphate solution, the normality of which was determined from time to time by means of pure potassium dichromate.

The sodium hypochlorite solutions were titrated by means of a standardized solution of sodium arsenite[1]. Unfortunately this solution does not keep, but has to be standardized from time to time by means of the iodine solution.

The ammonia solutions were diluted, and a known fraction taken out for titration with a standardized solution of hydrochloric acid and methyl red as indicator.

3. Preliminary experiment.

The ammonia solution for these experiments was pure, commercial ammonia with a specific gravity $0._{91}$. The ammonia concentration is 13.23 N.

The sodium hypochlorite solution was prepared (by the method stated by RASCHIG (l. c.)) from MERCH's sodium hydroxide No. I (pure) and chlorine prepared from manganese dioxide, sodium chloride and sulphuric acid. The method is rather slow and the chlorine discharging tube, which dips down in the alkaline solution, often clogs up (NaCl).

A number of experiments were made with a 0.960 molar solution of sodium hypochlorite and the above mentioned

[1] LUNGE-BERL: Chemisch-technische Untersuchungsmethoden. Vol. I, 140, 508. (3 Aufl.)

ammonia solution; but with no gelatine in the reaction mixture no hydrazine was formed, even with ammonia in great excess. When a solution of 1 grame of gelatine in 10 ccs. of water was added to the ammonia before the addition of sodium hypochlorite, hydrazine yields of 40—41% (of the hypochlorite) could be obtained.

It appeared from these experiments that very pure solutions were necessary, if the reaction should be investigated in solutions which contained no gelatine.

4. Preparation of pure chemicals.

The water. Since a trace of alkali in the water is of no importance, the distilled water of the department was redistilled in a glass still of 3 litres capacity. The still and the receiver was steamed for a long time before the distillation and the first 3—400 ccs. were not collected.

The ammonia solution. This was prepared by saturation of redistilled water with pure ammonia obtained by heating a conc., commercial ammonia solution with potassium permanganate in a flask of 3 litres capacity fitted with reflux condenser. The current of ammonia was washed by passing through a pure, saturated ammonia solution.

The sodium hypochlorite solution. This solution is the weak point in the scheme, as it is very difficult to purify sodium hydroxide. To prepare the hypochlorite by electrolysis is not possible, since the concentration should be about 1 molar[1]. Metallic sodium could be distilled in vacuo and the hydroxide made from this, but this method was kept as the last refuge.

The solution, therefore, was made from redistilled water

[1] See Forster & Müller: Z. f. Elektrochem. 8 (1902) 8; Denso: Z. f. Elektrochem. 8 (1902) 147.

and MERCK's Natrium hydricum purissimum (e Natrio).
This is completely up to the standards given by MURRAY[1],
and the content of heavy metals, therefore, should be less
than 0.0004—0.0005 %. Chlorine, made from potassium
permanganate and hydrochloric acid[2] and carefully washed,
was passed into the ice-cold sodium hydroxide solution,
which was stirred rapidly by means of a glass stirring rod
rotating in bearings of paraffined cork (to avoid contam-
ination with metallic dust). The entire apparatus was
steamed before the preparation, and the sodium hydroxide
was cooled with ice during the process. In this manner
sodium hypochlorite solutions were made containing one
grammolecule of sodium hypochlorite and about 0.2 gram-
molecule of sodium hydroxide per litre. Such solutions
are very stable, and even at room temperature the hypo-
chlorite content does not decrease more than about 3 % per
month. Usually 6 litres were made in one operation, and
the solution was standardized as previously mentioned.

5. Experiments with pure substances.

The solutions were a 13.43 molar solution of ammonia
and a 0.775 molar solution of sodium hypochlorite. Five
different beakers of Jena resistance glass were used and
they were carefully cleaned, rinsed with ordinary distilled
water and finally with redistilled water. The volumes of
the solutions were measured by means of two measuring
cylinders, the same in the different experiments.

200 ccs. of the ammonia solution were placed in one of
the beakers and 200 ccs. of the hypochlorite solution added.

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[1] Standards and Tests for Reagent Chemicals, N. Y. 1920 page 320.
[2] GRAEBE: B. **35** (1902) 43.

The beaker was placed on an iron wire gauze and the content rapidly heated to boiling by means of a powerful Teclu burner. The boiling was continued until no odour of ammonia could be detected, and the reaction mixture was then cooled down to 15—16° by means of tap water. After acidifying the solution with sulphuric acid it was transferred to a measuring flask and made up to a known volume with boiled water. By means of a pipette a known volume of the solution was taken out and the hydrazine content titrated with iodine. The results of the first experiment in each one of the five beakers are given in table I. No gelatine was added in any of the experiments.

In table I and the following tables V is the volume of the entire solution before the titration. T is the volume taken out for titration. I_2 is the volume of standardized iodine solution (of the stated normality) which has been used in the titration of T ccs. of the hydrazine solution. The yield of hydrazine is calculated in percentage of the hypochlorite.

In some of the experiments the hydrazine yields are considerably higher than any obtained by Joyner (l. c.),

Table I.

0.775 M. NaOCl   13.4 M. NH_3

NaOCl	NH_3	V	T	I_2.0.08015 N.	$H_4 N_2$
c.cs	c.cs	c.cs	c.cs	c.cs	%
200	200	1000	50	94.86	25.0
200	200	500	10	11.78	7.6
200	200	500	10	43.95	28.4
200	200	1000	10	12.35	16.0
200	200	500	10	37.54	25.3

when no gelatine is added. The yields, however, are very eratic and seem to vary with some unknown property of

the beaker as the other experimental conditions are almost identical.

To observe the effect of gelatine experiments were made in the same manner as above, only 10 ccs. of a 10 % gelatine solution were added to the ammonia before the hypochlorite solution. The beakers were three new, never used Jena beakers, which has been washed and rinsed as above. The results are given in table II, and they are as constant as it might be expected, when it is difficult to produce exactly the same conditions in the different experiments.

Table II.

0.775 M. NaOCl   13.4 M. NH_3

NaOCl c.cs	NH_3 c.cs	G.10 % c.cs	V c.cs	T c.cs	I_2.0.08015 N. c.cs	N_2H_4 %
200	200	10	1000	10	33.94	44.0
200	200	10	1000	10	33.44	43.3
200	200	10	1000	10	34.20	44.2

Since the results in table I vary with, as it seems, some unknown properties of the beakers, a series of experiments was made with one and the same beaker and measuring cylinders. These vessels were carefully cleaned and steamed for about half an hour before each experiment, and these were made as above with no gelatine. The results are given in table III. In some of the experiments the ammonia solution was diluted with redistilled water before the addition of the hypochlorite solution. The volume of water added is stated in the table (column H_2O).

The result of the three first experiments are fairly constant. It appears that on dilution the hydrazine yield increases a little, and that an increase in the excess of ammonia produces an increase in the hydrazine yield.

Table III.

0.775 M. NaOCl   13.4 M. NH_3

NaOCl c.cs	NH_3 c.cs	H_2O c.cs	V c.cs	T c.cs	I_2.0.08015 N. c.cs	N_2H_4 %
200	200	0	1000	10	26.07	33.7
200	200	0	1000	10	26.40	34.2
200	200	0	1000	10	26.09	33.8
200	200	200	1000	10	30.24	39.1
100	200	100	1000	20	35.44	45.8

For comparison three experiments were made with the same vessels treated in the same manner, but with an addition of 10 ccs. of a 10 % gelatine solution. The results are given in table IV.

Table IV.

0.775 M. NaOCl   13.4 M. NH_3

NaOCl c.cs	NH_3 c.cs	G.10% c.cs	V c.cs	T c.cs	I_2.0.08015 N. c.cs	N_2H_4 %
200	200	10	1000	10	38.70	50.0
200	200	10	1000	10	36.80	46.7
200	200	10	1000	10	37.00	47.7

The results are fairly constant even if the yield in the first experiment of some unknown reason is slightly higher than the following.

It was of interest to see if it was possible to get better hydrazine yields in vessels of another material than glass, and a quartz flask, with a capacity of about 60 ccs. up to the beginning of the neck, was used in these experiments.

For the sake of comparison a series of experiments was made in a Jena flask of the same capacity. This flask, which had never been used, was boiled with hydrochloric acid, with redistilled water, rinsed several times with redistilled water and finally steamed for 20 min. The measuring cylinders and the flask were steamed as usual between

the experiments, which were made as usual. The result are given in table V.

Table V.

0.775 M. NaOCl   13.4 M. NH_3

NaOCl	NH_3	H_2O	V	T	$I_2.0.08015$ N.	N_2H_4
c.cs	c.cs	c.cs	c.cs	c.cs	c.cs	%
10	10	0	entire volume		1.40	0.29
10	10	0	200	25	15.45	31.9
10	10	0	200	25	15.85	32.8
10	10	0	200	25	16.40	33.9
10	10	0	200	25	16.30	33.5
10	10	10	200	25	16.50	34.3

It is obvious that a steaming is necessary, and that it must be very thorough, as the hydrazine yield is very poor even after a steaming for 20 min.

Corresponding experiments made in the quartz flask are given in the table VI. The flask was not steamed previous to the first experiment, but only boiled with hydrochloric acid and rinsed with redistilled water. Together with the measuring cylinders the flask was steamed for 20 min. between the experiments.

Table VI.

Experiments in a quartz flask.
0.775 M. NaOCl   13.4 M. NH_3

NaOCl	NH_3	V	T	$I_2.0.08015$ N.	N_2H_4
c.cs	c.cs	c.cs	c.cs	c.cs	%
11	11	entire vol.	titrated	70.78	17.1
10	10	100	10	13.68	35.4
10	10	200	25	17.20	35.6
10	10	200	25	18.50	38.2
10	10	200	25	18.00	37.2
10	10	200	25	18.20	37.6
10	10	200	25	15.85	33.0[1]

[1] In this experiment the flask had been placed for 24 hours under an inverted beaker after the steaming.

The table shows, that also when a quartz vessel is used, a steaming increases the hydrazine yield, and the agreement of the later experiments in the series is as good as it might be expected.

These yields of 37—38 % of hydrazine (and with a greater excess of ammonia about 46 %), obtained only by carefully purifying the reagents and the reaction vessels, show clearly, that it must be very small quantities of impurities which cause a catalytic decomposition of the monochloramine or an oxidation of the hydrazine, and it would now be of interest to find what substances are active.

After this had been written, Bodenstein (l. c.) has investigated the formation of hydrazine from monochloramine and ammonia. He states that a complete purification of the water does not change the hydrazine yield. The writer cannot agree with this (see also Joyner (l. c.)). In experiments with ordinary distilled water and no gelatine the hydrazine yields are very poor, while on purification of the water, the aqueous ammonia solution and by a very thorough steaming of the reaction vessel, hydrazine yields of 37—38 % of the hypochlorite are obtained. That the hydrazine yield, even when gelatine is added, does not approach 100 % is due to certain reactions, which should be discussed later.

6. Experiments with a cupric salt in the reaction mixture.

The copper sulphate solution was made by weighing out the pure, crystalline salt, and this was obtained by recrystallization of Kahlbaum's cupric sulphate for analysis. Exactly 0.2500 g. of the pure salt was weighed out and made up to 1000 ccs. with redistilled water in a steamed

volumetric flask. The solution is 1×10^{-3} molar. From this a 1×10^{-6} molar solution was prepared by making up 1 cc. to 1000 ccs. with redistilled water and, further, a 5×10^{-6} molar solution by making up 1 cc. to 200 ccs.

The experiments were made as follows: 10 ccs. of the ammonia solution were placed in the cleaned and steamed quartz flask, cupric salt solution and water (column H_2O in table VII) were added, making the volume up to 20 ccs., and finally the reaction was started by adding 10 ccs. of the hypochlorite solution. The mixture was heated to boiling as quickly as possible and kept boiling, until no odour of ammonia could be observed. The hydrazine yield was estimated as before.

The results are given in table VII, and they are made

Table VII.

$NaOCl = 0.768$ molar. $NH_3 = 13.2$ molar.

NaOCl ccs.	NH₃ ccs.	H₂O ccs.	CuSO₄ 10⁻³ molar ccs.	CuSO₄ 10⁻⁶ molar ccs.	Conc. of CuSO₄ molar	V	T	I₂. 0.08015 N. ccs.	Hydra-zine %
10	10	10	0	0	0	200	25	18.10	37.80
10	10	10	0	0	0	200	25	18.40	38.40
10	10	9	1	0	3.33×10^{-5}	200	25	0	0[1]
10	10	9	0	1	3.33×10^{-8}	200	25	13.20	27.25
10	10	10	0	0	0	200	25	16.32	34.26[2]
10	10	5	0	5	16.7×10^{-8}	200	25	9.95	20.76
10	10	0	0	10	33.3×10^{-8}	200	50	9.08	9.47
10	{ 10+10 ccs. of 5×10⁻⁶ molar CuSO₄ }				166×10^{-8}	200	50	1.94	2.02
10	10	10	0	0	0	200	25	15.22	31.73[2]
10	10	10	0	0	0	200	25	17.58	36.56[2]
10	10	10	0	0	0	200	25	18.50	38.61[2]

[1] Nitrite is formed in the solution.
[2] Control experiments.

in the stated order. As it may be seen from the table, the effect of the copper salt is considerable, even when the concentration is not more than 3.3×10^{-8} molar. The experiments, however, do not give a completely correct picture of the action, as the series has been started with a comparatively high copper salt concentration (3.3×10^{-5} molar), after which experiments with less copper have been made. But a cleaning and 20 minutes steaming of the quartz flask between the experiments are not enough to remove the last trace of copper. This may be seen from the control experiment in the middle and the three experiments in the end of the series. First in the last one of the experiments the hydrazine yield is the same, as the yields obtained in a perfectly clean quartz flask.

In the solution containing copper sulphate to a concentration of 3.3×10^{-5} molar considerable quantities of a nitrite are formed. The copper salt, therefore, must catalyze such reactions, in which ammonia is oxidized to nitrite by the action of a hypochlorite or monochloramine.

It appears that very minute traces of copper have an effect of decreasing the hydrazine yield strongly, and it is of interest to observe, if such substances, which produce an increase in the hydrazine yield, when ordinary chemicals are used, are able to prevent the hydrazine destruction, when they are added to the reaction mixture together with copper salts.

In such experiments, with copper salt and gelatine simultaneously in the reaction mixture, it appeared impossible to use the quartz flask, as the reaction mixture foamed out. A quartz beaker of 200 ccs. capacity was used, and it was cleaned and steamed carefully. The experiments were made as before, and the vessels cleaned and steamed carefully

between the experiments. The results are given in table VIII. The gelatine solution was made by dissolving 0.5 grams of gelatine in 100 ccs. of redistilled water, and column "G" in the table states, how much of this solution was added to the ammonia in the individual experiments. The copper sulphate solutions were the same as in the previous experiments. But, since such dilute copper salt solutions rapidly change their concentration (this fact was not clear to the writer, when the experiments were made), the experiments in table VIII cannot be compared with the experiments in table VII, but they may be compared mutually. The experiments are performed in the order of the table.

It may be seen from the table, that the hydrazine yields obtained in the quartz beaker are not as high, as the yields obtained in the quartz flask. This may be due to the

Table VIII.

$NaOCl = 0.750$ molar $NH_3 = 13.2$ molar

NaOCl ccs.	NH$_3$ ccs.	H$_2$O ccs.	CuSO$_4$ about 5×10^{-5} molar ccs.	CuSO$_4$ about 1×10^{-3} molar ccs.	G ccs.	V ccs.	T ccs.	I$_2$. 0.08015 N.	Hydra- zine %	CuSO$_4$ conc. about
10	10	0	0	0	10	200	25	20.40	43.6	0
10	10	0	0	0	10	200	25	20.20	43.2	0
10	10	10	0	0	0	200	25	14.1	30.1	0
10	10	5	0	0	5	200	25	20.90	44.7	0
10	10	0	5	0	5	200	25	21.24	45.4	8.3×10^{-7} m.
10	10	5	0	0	5	200	25	21.55	46.1	0
10	10	10	0	0	0	200	25	15.28	32.6	0
10	10	5	5	0	0	200	25	7.58	16.2	8.3×10^{-7} m.
10	10	4	0	1	5	200	25	17.15	36.6	3.33×10^{-5} m.
10	10	10	0	0	0	200	25	15.89	33.96	0
[1]10	10	9	0	1	0	200	25	0	0	3.33×10^{-5} m.

[1] Nitrite is here formed in large quantities.

easier admittance of the air to the reaction mixture in the beaker.[1]

The experiments show clearly how gelatine is able to "neutralize" the destructive action of the cupric salt. With no gelatine and a copper salt concentration of 3.33×10^{-5} molar not the slightest trace of hydrazine is formed, but the solution contains nitrite in large quantities. However, if the solution simultaneously contains 0.025 gram of gelatine in 30 ccs., a hydrazine yield of more than 36% of the hypochlorite is produced.

These experiments, therefore, confirm the hypothesis, that the catalytic action of minute traces of copper is the reason why the hydrazin yields are poor, when ordinary chemicals are used, and no gelatine is added.

It is not possible, however, to obtain a yield of almost 100% of the hypochlorite in form of hydrazine, even when pure chemicals are used, and even when gelatine is added, but this fact depends upon circumstances, which should be discussed later.

7. The variation of the hydrazine yield with the concentration of copper salt.

The copper salt solution was prepared as before by dissolving 0.2500 gram of copper sulphate (twice recrystallized from redistilled water) in redistilled water and making up the volume to 1000 ccs. in a steamed volumetric flask. From this solution more dilute solutions were made by dilution. However, as such dilute solutions are not stable, they were used immediately after the preparation.

In all these experiments a Jena beaker of 800 ccs.

[1] See Cuy & Bray: J. Amer. Chem. Soc. 46 (1924) 1786.

capacity was used. It was cleaned by boiling with nitric acid, with water, with pure, aqueous ammonia and finally with redistilled water, and after this it was steamed for an hour. Also the measuring cylinders were carefully cleaned and steamed for an hour.

100 ccs. of the ammonia solution were placed in the beaker together with 100 ccs. of a copper sulphate solution of the desired concentration. Finally 100 ccs. of the hypochlorite solution were added, the mixture rapidly heated to boiling and boiled, until no odour of ammonia could be observed. The results are stated in table IX and in the graph figure 1.

Table IX.

$NaOCl = 0.850$ molar. $NH_3 = 13.3$ N.

NaOCl ccs.	NH₃ ccs.	H₂O ccs.	CuSO₄ sol. 5×10^{-6} molar ccs.	Conc. of CuSO₄ molar	V	T	I₂. 0.1088 N. ccs.	Hydrazine %
100	100	100	0	0	1000	25	26.25	33.59
100	100	100	0	0	1000	25	27.13	34.70
100	100	100	0	0	1000	25	27.50	35.18
100	100	100	0	0	1000	25	28.01	35.84
100	100	100	0	0	1000	25	28.10	35.95
100	100	100	0	0	1000	25	28.00	35.83
100	100	97	3	0.5×10^{-7}	500	10	18.74	29.97
100	100	97	3	0.5×10^{-7}	500	10	19.00	30.39
100	100	94	6	1×10^{-7}	500	25	43.18	27.6
100	100	94	6	1×10^{-7}	500	25	42.80	27.2
100	100	88	12	2×10^{-7}	500	25	33.60	21.5
100	100	82	18	3×10^{-7}	500	25	25.70	16.4
100	100	82	18	3×10^{-7}	˙500	25	25.05	16.0
100	100	73	27	4.5×10^{-7}	500	25	16.80	10.8
100	100	64	36	6×10^{-7}	500	25	9.70	6.21
100	100	50	50	8.3×10^{-7}	500	25	4.80	3.71
100	100	0	100	16.6×10^{-7}	500	50	0.60	0.19
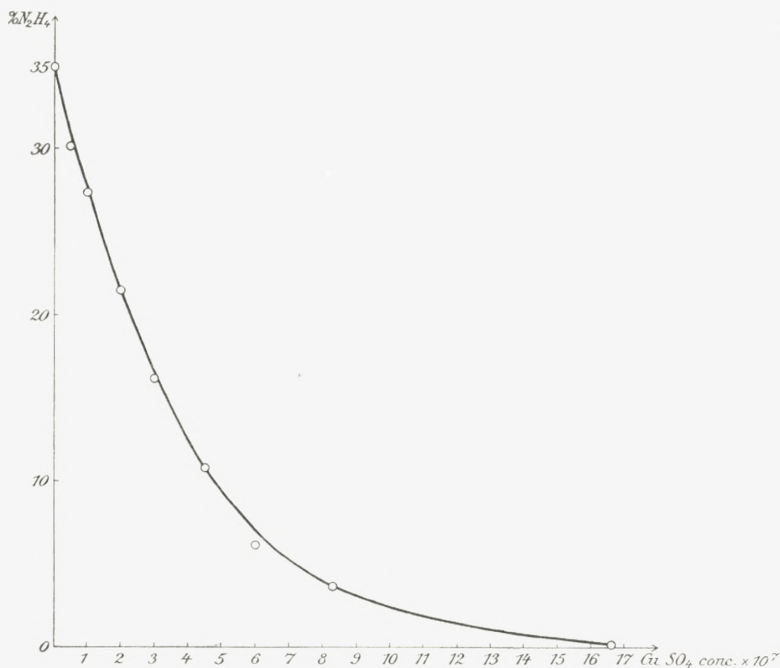
Fig. 1.

Table X.

c = 1×10^{-7}	k = 0.113×10^7	c = 6×10^{-7}	k = 0.127×10^7
2	0.106	8	0.118
3	0.113	12	0.104
4	0.116	16	0.127
5	0.123	Average of k =	0.116×10^7

It may be seen from the graph, that the action of the copper salt apparently is not proportional to its concentration. Now it must be assumed, that the catalytic action of copper salts is due to free copper ions. This seems obvious, as substances, which are able to form stable complex compounds with copper ions, are also able to "neutralize" the action of copper salts in RASCHIG's hydrazine synthesis.

Copper ions unite with ammonia to form complex ions

of the type $Cu(NH_3)_n^{++}$, with n having values from one to six [1] depending upon the concentrations, but, as the ammonia concentration in the experiments of table IX is great, immensily greater than the copper salt concentrations, and the same in all the experiments, an action, which is proportional to the copper ion concentration, should here also be proportional to the total concentration of the cupric salt, but this, apparently, is not the case.

However, it appears that the curve for the hydrazine yield at different copper salt concentrations may be expressed fairly well by the empirical equation:

$$k \cdot c = \log \frac{a}{a - x}.$$

In this equation c is the total copper salt concentration, a is the yield of hydrazine, when no copper salt is added, and x is the decrease in the hydrazine yield for the copper salt concentration c. Further, k is a constant, which is, on an average, $0.116 \cdot 10^7$.

When a is put equal to 35 %, the values of k have been calculated from the points of a smooth curve through the average position. They are given in table X.

Considering the difficulties in obtaining very accurate results, the values of k may be considered satisfactory.

The equation, as mentioned, is empirical, but it may be used to support a simple theoretical investigation.

If it may be assumed, that the hydrazine is formed in a reaction, which has a comparatively great reaction velocity (the ammonia concentration is very great), and that the velocity of the hydrazine decomposition is proportional to

[1] See JANNIK BJERRUM: Det Kgl. Danske Vidensk. Selsk. math.-fys. Medd. XI, 10.

the hydrazine concentration and to the copper ion concen-
tration in the solution at any moment, the equation for the
velocity of the hydrazine destruction may be written:

$$\frac{dx}{dt} = C \cdot c \cdot (a - x),$$

c being the copper ion concentration, a the maximum con-
centration of hydrazine, x the destroyed quantity and C a
constant. This equation gives on integration:

$$\ln \frac{a}{a - x} = C \cdot c \cdot t.$$

If it may be assumed, that the time expired, from the
start of the experiment to the moment the reaction mixture
is cooled, is the same in each experiment (this is true with
great approximation), then the value of t is the same for
the entire series of experiments in table IX, and the equa-
tion above, therefore, may be written:

$$\log \frac{a}{a - x} = K \cdot c.$$

Here K is a constant, and the other symbols indicate the
same as before. This equation, however, has exactly the
same form as the empirical equation, which has been found
from the experiments.

This fact seems to indicate, at least to a certain extent,
the assumptions are correct, but this will be discussed in
a following part of the paper.

7. Summary.

It has been shown:

1). That on using pure water, pure chemicals, and
carefully cleaned reaction vessels, it is possible to obtain
hydrazine yields up to about 46 % of the hypochlorite in

RASCHIG's hydrazine synthesis, even when no gelatine is added.

2). That copper salts, added to the reaction mixture, have a powerful ability to decrease the hydrazine yield. With a copper salt concentration of $1.66 \cdot 10^{-6}$ molar only a trace of hydrazine is observed. With more copper salt nitrite is formed.

3). That gelatine is able powerfully to reduce the catalytic action of copper salts, and that the role of gelatine in RASCHIG's hydrazine synthesis, therefore, seems to be to unite, forming complex compounds, with traces of copper ions present as impurities in the water and the chemicals, thus anihilating their action.

4). That hydrazine seems to be formed in a rapid but incomplete reaction from ammonia and sodium hypochlorite (or monochloramine), and that the hydrazine is then oxidized, more or less, by the remaining hypochlorite (or monochloramine). It is this oxidation, which is strongly catalyzed by copper salts.

II.

The Action of Salts of other Metals than Copper. The Action of other "Negative Catalysts" than Gelatine. The Azoimide Formation and the Gaseous Reaction Products.

1. Introduction.

In a previous part of this paper has been shown, that a minute trace of a copper salt is able to destroy the hydrazine yield in RASCHIG's hydrazine synthesis, when no gelatine has been added.

It is possible, however, that salts of other metals would

be able to act in the same manner, and RASCHIG[1] has stated, that a trace of a cobalt salt, added to the ammonia — hypochlorite mixture, produces a violent, catalytic decomposition, in which nitrogen is evolved. The action of salts of such ordinary metals, which are able to occur with two valencies, should, therefore, be investigated.

2. The action of salts of other metals than copper.

The experiments were made with very pure chemicals, prepared as mentioned in the previous part of the paper, and with the measuring cylinders and reaction vessels cleaned and steamed just before the experiment. The experiments were made in this manner, that 100 ccs. of the very pure ammonia (13.3 N.) were placed in a carefully cleaned and steamed beaker of 800 ccs. capacity, to this 100 ccs. of the salt solution of the desired concentration were added and finally 100 ccs. of the sodium hypochlorite solution (0.850 molar). The reaction mixture was now rapidly heated to boiling and boiled, until the excess of ammonia had been removed. The hydrazine yield was titrated in the same manner as before. From 100 ccs. of pure ammonia, 100 ccs. of pure water and 100 ccs. of sodium hypochlorite it is possible to obtain a hydrazine yield of from 34 % to 36 % of the hypochlorite.

In a series of experiments it appeared, that with a cobalt salt concentration of $3.3 \cdot 10^{-4}$ molar in the reaction mixture, the hydrazine yields which could be obtained were about 34 %. But it has been shown earlier, that with a copper salt concentration of this value not a trace of hydrazine is formed. The formation of a trace of hydrazine may just be observed, when

[1] B. **40** (1907) 2065.

the copper salt concentration is $1.66 \cdot 10^{-6}$ molar. The action of cobalt salts, therefore, is of no interest in this connection.

It also appeared, that manganese salts up to a concentration of $3.3 \cdot 10^{-4}$ molar had not the slightest influence with the hydrazine yield, and the same was the case on addition of lead salts (of divalent lead). In all cases hydrazine yields of about 35 % of the hypochlorite were obtained.

On addition of a nickel salt to a concentration of $3.3 \cdot 10^{-4}$ molar, the hydrazine yield dropped to 18 %. But after recrystallization of the nickel salt twice from redistilled water, the drop in the hydrazine yield was only from 35 % to 28,2 %. This seems to indicate, that the nickel salt contained an impurity (probably a trace of a copper salt), and this may not have been removed completely by two recrystallizations.

On addition of a ferric salt in various concentrations it appeared, that it had some effect in decreasing the hydrazine yield, but to a much smaller degree than copper salts. With a ferric salt concentration of $3.3 \cdot 10^{-4}$ molar the hydrazine yields were about 10 %, and the action of a copper salt, thus, is about 1000 times greater.

In certain cases it has appeared, that an iron salt may increase the catalytic action of a copper salt and vice versa[1]. But in a series of experiments, with simultaneous addition of copper sulphate and ferric chloride, it was found, that the catalytic action was approximately what might be expected by taking the sum of the action of the copper salt and action of the ferric salt.

From these experiments it must be concluded, that none of the investigated salts have an action, which can be compared with the action of a copper salt.

[1] See Traube: B. 17 (1884) 1062; Bahnson & Robertson: J. Amer. Chem. Soc. 45 (1923) 2512.

3. Experiments with a greater excess of ammonia.

In order to estimate the economy of Raschig's hydrazine synthesis it was of interest to investigate the variation of the hydrazine yield with the ammonia concentration.

Joyner[1] has investigated this by keeping a constant gelatine concentration, a constant hypochlorite concentration and a constant total volume with variable ammonia concentrations. But, on application of the synthesis in the laboratory, the volume of the reaction mixture would not be kept konstant. Various volumes of ammonia would be added to a certain quantity of sodium hypochlorite, until the most economic proportion was found.

A series of experiments were made with pure chemicals in a quartz beaker of 200 ccs. capacity (the same as mentioned in the previous part of this paper). This was cleaned carefully and steamed for an hour. 10 ccs. of a 0.850 molar solution of sodium hypochlorite (containing 0.2 molar sodium hydroxide) were placed in the beaker. To this a certain volume of conc., pure ammonia (13.5 molar) was added, the mixture rapidly heated to boiling and boiled, until no odour of ammonia could be observed. Now the reaction

Table XI.

NaOCl = 0.850 molar   NH$_3$ = 13.5 molar

NaOCl. ccs.	NH$_3$ ccs.	V ccs.	T ccs.	I$_2$. 0.1088 N ccs.	Hydrazine %
10	20	200	40	26.95	43.1
10	20	200	40	27.10	43.5
10	50	250	50	33.45	53.5
10	50	250	50	33.20	53.1
10	60	250	50	34.30	54.9
10	100	250	50	34.50	55.5

[1] Joyner: J. Chem. Soc. **123** (1923) 1114.

mixture was transferred to a measuring flask and made up to a definite volume (V in the table), a fraction of this (T in the table) was taken out and titrated with iodine as usual. The results of the experiments are given in table XI.

This table shows again, that it is possible to obtain fair yield of hydrazine with pure substances and a carefully cleaned reaction vessel, and, further, that the hydrazine yield increases with increasing ammonia concentration, but, above a certain ammonia concentration, the increase of the yield is small.

4. Experiments with other substances than gelatine as "negative catalysts".

These experiments have been made at different times in the course of the investigation (and therefore not with the same solutions), when the idea of testing the action of a certain substance occurred. These substances are, as a rule, such compounds, which are able to form complex compounds with copper ions.

The experiments were made with pure chemicals, carefully cleaned reaction vessels and in the usual manner. One of the first substances to be tested was cupferron[1]. But in a concentration of 0.2 gram in 400 ccs. reaction mixture it increased the hydrazine yield only from 33.7 to 37.4 %.

Gelatine unites with copper ions in the "biuret reaction", and one might expect, that all such substances, giving the biuret reaction[2], would be able to act as "negative catalysts" in RASCHIGS hydrazine synthesis. This, however,

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[1] BAUDISCH: Chem. Ztg. 1909, 1228.
[2] See SCHIFF: B. **29** (1896), 298. Ann. Chem. **299** (1897), 236.

is not at all the case. Such substances as biuret, tyrosin
and other amino-acids, on the contrary, decrease the hydra-
zine yields, when they are added to the reaction mixture.
This behaviour, probably, is due to the fact, that they are
very readily oxidized. [1]

The behaviour of gelatine shows that anhydrides of the
amino-acids are excellent "negative catalysts". Another an-
hydride of this type, casein (soluble), acts almost just as
well. When this is added in a quantity of 0.1 gram to
400 ccs. of a reaction mixture of ordinary chemicals (not
made from redistilled water), a yield of 46—48 % of hydra-
zine could be obtained, while, without casein, the yield
would be from 5—10 % of the hypochlorite.

From the experiments of Titoff[2] it is known, that
mannite is able to retard the oxidation velocity of sulphite
by the oxygen of the air, a reaction which is catalyzed
strongly by copper ions. It was, therefore, of interest to
investigate, if mannite is active in the hydrazine synthesis.

A series of experiments were made with pure substances,

Table XII.

0.850 molar NaOCl.   13.1 molar NH_3.

NaOCl ccs.	NH_3 ccs.	H_2O ccs.	$CuSO_4$ about 5×10^{-6} molar ccs.	Mannite grammes	V ccs.	T ccs.	I_2. 0.08015 N ccs.	Hydrazine %
100	100	73	27	0	500	25	18.03	11.54
100	100	73	27	1	500	25	45.10	28.87
100	100	50	50	0	500	25	5.1	3.27
100	100	50	50	1	500	10	14.82	23.70
100	100	100	0	1	500	10	25.10	40.17

[1] Loew: J. prakt. Chem. (2) **18** (1878), 298.
[2] Titoff: Z. Phys. Chem. **45** (1903) 64.

some with an addition of cupric sulphate and other with a simultaneous addition of cupric sulphate and mannite. The reaction was carried out in a carefully cleaned and steamed Jena beaker of 800 ccs. capacity. The results of the experiments are given in table XII. Here V is the volume, to which the reaction mixture is made up after the reaction, and T the volume taken out for titration with iodine.

It appears clearly from the table, that mannite is active also in this reaction, and that it, undoubtly, unite with copper ions to form very stable complexes.

Salicylic acid is also able to form complex compounds with copper ions in alkaline solutions[1], but it appears to have no action in the hydrazine synthesis.

As ordinary, pure, commercial ammonia gives poor hydrazine yields, when gelatine is not added, it was of interest to see, what role a content of pyridine bases played, inasmuch as the pyridine bases are also able to form complex compounds with copper[2]. It appeared in a series of experiments, that an addition of 1 cc. of pyridine to a reaction mixture of 20 cc. had practically no effect what so ever on the hydrazine yield.

Finally some experiments with flaxseed mucilage and carragen should be mentioned. The action of these substances was tested in order to show, that RASCHIG's original theory, concerning the viscosity of the medium, could not be right.

These substances were chosen, as their aqueous solution has a high viscosity. It was expected, that they would not be able to increase the hydrazine yield, but they did. It

[1] LEY & ERLER: Z. anorg. Chem. 56 (1908) 404.

[2] REITZENSTEIN: Z. anorg. Chem. 18 (1898) 253, 296; RENZ: Z. anorg. Chem. 36 (1903) 100; GROSSMANN & JÄGER: Z. anorg. Chem. 73 (1912) 48.

appeared, that the substances, which are formed from flax-seed mucilage in an alkaline hydrolysis, are able to form complex compounds with copper salts.

According to Hilger[1] flaxseed mucilage is probably a tetrasaccarose, which on hydrolysis gives d-glucose, d-galac-tose, l-arabinose, and l-xylose. It is not so strange, therefore, that it is able to act as a "negative catalyst" in the hydra-zine synthesis. The results of a series of experiments are given in table XIII.

Table XIII.

0.775 molar NaOCl.   13.4 molar NH_3.

NaOCl ccs.	NH_3 ccs.	Added	V	T	I_2.0.08015 N ccs.	Hydra-zine %	Rem.
200	200	10 ccs. 10 % gelatine	1000	10	37.0	42.7	In Jena beaker.
200	200	10 ccs. mucilage A	1000	10	40.09	51.8	
10	10	10 ccs. H_2O	200	25	17.2	35.6	In quartz beaker.
10	10	10 ccs. mucilage B	200	25	18.5	38.6	
10	10	10 ccs. mucilage C	200	25	22.1	46.2	

Mucilage A. 5 grammes of flaxseed boiled with 20 ccs. of redistilled water in a steamed flask. 10 ccs. of this liquid used.

Mucilage B. 0.5 gramme of flaxseed boiled with 25 ccs. of water. 10 ccs. used.

Mucilage C. 1 gramme of flaxseed boiled with 25 ccs. of water. 10 ccs. used.

Fairly good results may also be obtained by addition of carragen. On addition of a solution of 1 gram of carra-gen in 100 ccs. of water to 100 ccs. of an ordinary, conc., commercial ammonia, followed by an addition of 100 ccs. of an approximately 1 molar solution of sodium hypochlorite and by a rapid heating to boiling etc., hydrazine yields of 48—49 % of the hypochlorite could be obtained.

[1] B. **36** (1903) 3197.

5. The azoimide formation in Raschig's hydrazine synthesis.

In RASCHIG's hydrazine synthesis, when the solution is acidified with sulphuric acid, after the great excess of ammonia has been boiled out, a very characteristic odour is observed, the cause of which is a small quantity of azoimide. On distillation of the acidified reaction mixture a very dilute, aqueous solution of azoimide may be obtained. This solution gives a red colour-reaction with a ferric salt and a white precipitate with silver nitrate. The silver salt is insoluble in cool, dilute nitric acid, but soluble in the hot acid.

Traces of azoimide in the reaction of hypochlorites with ammonia has been discovered already by RASCHIG[1]. In his opinion it must be formed from triimide. In the reaction of alkalies with monochloroamine imide, NH, should be formed, which for a part polymerizes forming triimide, N_3H_3. When an excess of monochloroamine reacts with this substance, azoimide should be formed:

$$N_3H_3 + NH_2Cl = N_3H + NH_4Cl.$$
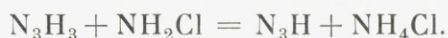
It appears, however, that in the different oxidation titrations of hydrazine which have been proposed[2], the smooth oxidation of hydrazine into water and nitrogen is very rare, ammonia and azoimide in varying quantities are formed simultaneously.

Thus azoimide seems to be formed ordinarily in the

[1] See for instance Schwefel und Stickstoffstudien page 76.

[2] For a critical review of all proposed titration methods of hydrazine see BROWNE & SHETTERLY: J. Amer. Chem. Soc. **31** (1909) 228, 782. CUY & BRAY: J. Amer. Chem. Soc. **46** (1924) 865, 1305, 1790. BROWNE & SHETTERLY: J. Amer. Chem. Soc. **30** (1908) 53. KURTENACKER & WAGNER: Z. anorg. Chem. **120** (1922) 261.

oxidation of hydrazine, and its presence among the reaction products in Raschig's hydrazine synthesis may be due to an oxidation of hydrazine, either by the action of sodium hypochlorite or by monochloroamine.

Many authors[1] have found that azoimide is formed in the reaction of nitrous acid with hydrazine.

From this fact Sommer[2] has drawn the conclusion, that the formation of azoimide, which is observed in so many different oxidations of hydrazine, is due to an intermediate formation of nitrous acid, produced in an oxidation of the primary product, ammonia, by the oxidizing agent in question. This conclusion of Sommer and his collaborators[3] is strongly attacked by Browne and his collaborators.[4] However, it seems to be likely, that nitrous acid is an intermediate product in the formation of azoimide, when hydrazine is oxidized.

It has been shown in an earlier part of this paper, that a nitrite is present in the reaction mixture, when ammonia is boiled with sodium hypochlorite in the precence of a minute trace of a copper salt (i. e. a copper salt catalyzes the oxidation of ammonia to a nitrite). As it is a catalytic reaction, it may be assumed to take place, even if no copper salt is present, only to a much slighter degree.

To solve the question of how azoimide is formed in Raschig's hydrazine synthesis, it would be of interest

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[1] See Curtius: B. **23** (1890) 3023. Angeli: Atti. accad. Lincei. [5] **2**, I, (1893) 569. C. B. 1893 II, 559, Dennstedt & Göhlich: Chem. Ztg. **21** (1897) 876. Sabanejeff, Dengin & Speransky: Z. anorg. Chem. **20** (1899) 21. Franke: B. **38** (1905) 4102. Dey & Sen: Z. anorg. Chem. **71** (1911) 236, Z. anorg. Chem. **74** (1912) 52. Sommer: Z. anorg. Chem. **83** (1913) 119.

[2] Sommer: Z. anorg. Chem. **86** (1914) 71.

[3] Sommer & Pincas: B. **49** (1916) 259, 1147. Sommer: Z. anorg. Chem. **96** (1916) 75.

[4] Browne & Overmann: J. Amer. Chem. Soc. **38** (1916) 285.

to investigate the variation of the azoimide concentration with the copper salt concentration.

The estimation of azoimide appeared to be difficult, as the quantities are small. The alkaline solution, obtained in the usual manner by mixing ammonia with hypochlorite (containing an excess of sodium hydroxide) and evaporating the mixture, until the free ammonia is removed, was placed in a flask for fractional distillation, the stopper of which was fitted with a separatory funnel and a glass tube connected with a boiler for steam production. The side tube of the distilling flask, the end of which was immersed in some water in the receiver, was fitted with a condenser. Dilute sulphuric acid from the separatory funnel was added to acid reaction, and the azoimide distilled off in a current of steam into a solution of silver nitrate. After the distillation the silver azide was transformed into silver chloride, which was dried and weighed.

It appeared, however, that on increasing the concentrations of copper salt in the reaction mixture, small quantities of chlorine passed over into the distillate. The chlorine must be formed in a reaction of hydrochloric acid with chloric acid in the acidified reaction mixture.

This must be due to a transformation of some of the hypochlorite into chlorate, and also this reaction seems to be catalyzed by copper salts. This formation of chlorine makes the estimation of azoimide very uncertain, as a part of it probably is destroyed by the chlorine.

To separate the silver azide from such quantities of silver chloride, which may be present, the distillate is filtered by means of a small filter and the precipitate washed with water, until the wash water does not give silver reaction. Only a small volume of water, the same in each one of

the estimations, was used for this washing, as silver azide is not completely insoluble in water[1]. The silver azide on the filter was then dissolved in hot, 4 N. nitric acid and the filtrate collected in a small, weighed glass basin[2]. On treatment with a mixture of nitric and hydrochloric acid the silver azide was transformed into silver chloride, which was weighed after drying to constant weight at 150°. The results of the experiment, with addition of gelatine, mannite and various quantities of copper sulphate to the reaction mixture, are given in table XIV. The yields of azoimide in percentage of hypochlorite have been calculated from the equation:

$$4\,NaOCl + 3\,NH_3 = N_3H + 4\,NaCl + 4\,H_2O.$$

When the content of azoimide had been removed from the solution by a steam distillation, the remainder was tranferred to a volumetric flask and made up to 500 ccs.

Table XIV.

0.850 molar NaOCl.   13 molar (approx.) NH_3.

NaOCl ccs.	NH₃ ccs.	H₂O ccs.	CuSO₄ approx. 5×10^{-6} molar ccs.	Added	V ccs.	T ccs.	I₂. 0.08015 N. ccs.	Hydrazine in % of NaOCl	AgCl grame	N₃H in % of NaOCl
100	100	100	0	{ 1 grame gelatine }	500	10	25.25	40.4	0.0092	0.30
100	100	100	0	{ 1 grame mannite }	500	10	22.70	36.3	0.0103	0.34
100	100	100	0	0	500	10	18.80	30.1	0.0117	0.38
100	100	90	10	0	500	10	15.85	24.4	0.0131	0.43
100	100	75	25	0	500	25	28.20	18.05	0.0143	0.45
100	100	50	50	0	500	25	4.80	3.7	0.0168	0.55
100	100	0	100	0 Nitrogen oxides are liberated on distillation.						

[1] Dennis & Browne: Z. anorg. Chem. 40 (1904) 94.
[2] Dennis & Isham: J. Amer. Chem. Soc. 29 (1917) 18.

From this solution a certain fraction (T in the table) was taken out for titration of the hydrazine content with iodine.

The experiments show an increase in the quantity of azoimide with an increasing copper salt concentration. But, as previously mentioned, the estimated values are not exact, since silver azide is not completely insoluble in water, and since some of the azoimide probably is destroyed by chlorine. Nevertheless, the course of these experimental results seems to agree with the point of view, which has been adopted by SOMMER (l. c.), that nitrous acid is an intermediate substance in the formation of azoimide in the oxidation of hydrazine. But, as far as the writer is able to see, this entire field requires a thorough experimental and theoretical investigation, before it may be stated with certainty, how azoimide is formed from hydrazine on oxidation.

6. A quantitative investigation of the hydrazine synthesis.

RASCHIG[1] has assumed that the formation of hydrazine takes place with imide, NH, as an intermediate product. Monochloroamine should, by the action of sodium hydroxide, give sodium chloride, water and imide, which then reacts with ammonia to form hydrazine.

If this is the case, it might be expected that a part of the imide, which certainly must be very unstable, would decompose into nitrogen and hydrogen, and that the gaseous reaction products would contain these elements, or that a part of the imide would react with water forming hydroxylamine.[2] In the alkaline solution, however, the hydroxylamine would decompose into ammonia, nitrogen, water

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[1] See Schwefel und Stickstoffstudien page 76.
[2] SMITH: Z. angew. Chem. **36** (1923) 511. B. **57** (1923) 704.

and some nitrous oxide, and this decomposition is accelerated by ammonia.[1]

It was therefore of interest to investigate the gaseous reaction products in the hydrazine synthesis, but this necessitates that the reaction takes place in a closed apparatus which does not contain nitrogen, hydrogen or oxygen.
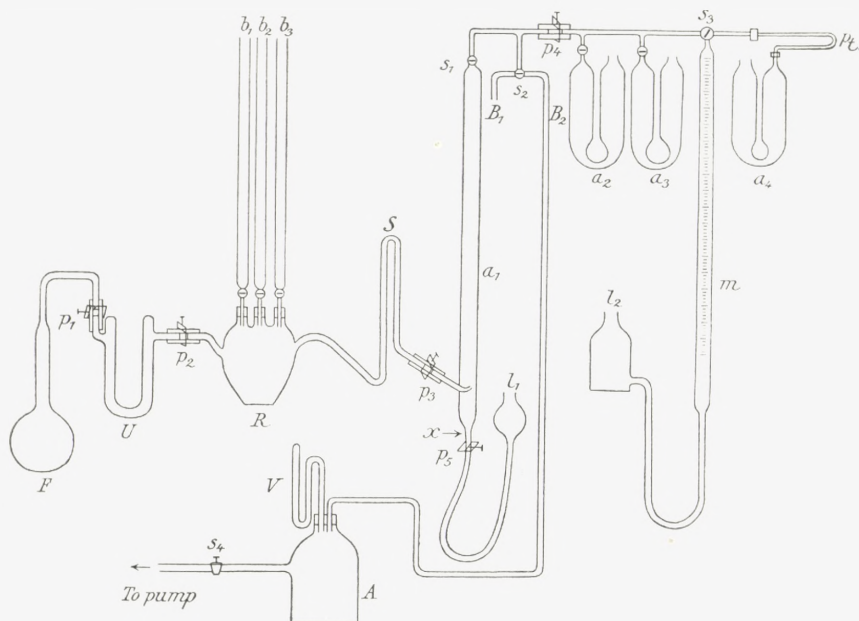

Fig. 2.

It is convenient, therefore, to have the reaction taking place in an atmosphere of ammonia.

The apparatus in fig. 2 was adopted for the investigation. Here F is the ammonia generator, U a u-tube with potassium hydroxide (to dry the ammonia). R is the three necked reaction flask. b_1, b_2 and b_3 are burettes (with capillary

[1] BERTHELOT: Comp. rend. **83** (1876) 473. BERTHELOT & ANDRE: Comp. rend. **110** (1890) 830. KOTOLOW: B. **26** (1893) 761. DUNSTAN & DYMOND: J. Chem. Soc. **51** (1887) 646.

tips) for sodium hypochlorite, ammonia and water, fitted into the reaction flask with rubber stoppers. S is a safety tube. a_1 is the ammonia absorption tube, which is about 90 cm long and 2.5 cm in diameter, this is connected with the leveling flask l_1 by means of which a solution of sulphuric acid may be brought into the absorption tube.

Through the capillary stopcock s_1 the ammonia absorption tupe a_1 is connected with an Orsat apparatus, having the absorption tube a_2 filled with strong sulphuric acid, and the tube a_3 with an alkaline solution of pyrogallic acid. Pt is a platinum capillary for hydrogen estimation. a_1 is also connected with the three way stopcock s_2 from which one branch, B_1, goes to the atmosphere and the other, B_2, is connected with a safety bottle A, a vacuum gauge V and a water jet filter pump. The single parts of the apparatus are connected with thick-walled rubber tubing, which may be closed by means of the pinchcocks p_1, p_2, etc.

When an experiment is started, the level of the sulphuric acid in a_1 is brought down to x, the pinchcocks p_1, p_4 and p_5 are closed and the apparatus evacuated. On opening of p_1 and heating the ammonia generator F, the apparatus is filled with ammonia, and this process of evacuating and passing ammonia into the apparatus is repeated, until all air has been removed, and the apparatus is filled with ammonia of one atmospheres pressure. The pinchcocks p_2 and p_3 are now closed, while p_5 is opened, and the sulphuric acid allowed to rise up in a_1. If no gas bubble remains in a_1 all the air has been removed, otherwise the evacuation and filling up with ammonia must be repeated. Measured volumes of ammonia, water and sodium hypochlorite are runned into the reaction flask, R, and the content rapidly heated to boiling. Pinchcock p_3 is opened with

care, but the rubber tubing is kept closed by the pressure of the fingers, until the pressure of the evolved gases is so high that they are able to pass over into the tube a_1. Here the main part of ammonia is absorbed. The reaction mixture in R is boiled for some time to carry the evolved gases by means of the steam into a_1, and the process is supported by passing ammonia from F through R. When no more gas bubbles pass up through a_1, the pinchcock p_3 is closed, and the gases in a_1 are now analysed in the Orsat apparatus. The remaining ammonia is absorbed in the pipette a_2, and the oxygen, nitrogen and hydrogen estimated in the usual manner. The reaction flask is detached from the apparatus, its content washed quantitatively into a measuring flask, and a known fraction titrated with iodine to estimate the hydrazine yield.

A great number of experiments were made, but in every one it appeared, that the gaseous reaction products contain neither hydrogen nor nitrous oxide in measurable quantities. Only a few of these experiments should be mentioned.

Experiment 1. An attempt to detect hydrogen.

The reaction mixture was: 10.0 ccs. of redistilled water, 10.0 ccs. of ammonia (13 molar) and 10.2 ccs. of sodium hypochlorite (0.8505 molar).

Volume of evolved gases...................... 60.70 ccs.
Volume after absorption of oxygen............ 59.80 ccs.
Volume after air has been taken in........... 72.40 ccs.
Volume after combustion...................... 72.30 ccs.

The evolved gas mixture thus contains 59.8 ccs. of nitrogen and 0.9 ccs. of oxygen at a pressure of 765 mm. and a temperatare of 21.5° C. The decrease in volume, on

heating the gas-air mixture, is less than the experimental error and does not indicate a content of hydrogen.

The remnant in the reaction flask was made up to 250 ccs., of which 50 ccs. were taken out for titration with iodine. The consumption was 8.70 ccs. of a 0.1088 N. iodine solution. The yield of hydrazine is 13.7 $\%$ of the hypochlorite.

If the evolved nitrogen is calculated from the equation:

(1) $3\,NaOCl + 2\,NH_3 = 3\,NaCl + 3\,H_2O + N_2$

85.73 $\%$ of the hypochlorite have reacted in this manner.

If the oxygen content of the gas is calculated from the equation:

(2) $2\,NaOCl = 2\,NaCl + O_2$

0.86 $\%$ of the hypochlorite has reacted in this manner. The hypochlorite has reacted, therefore, in the following manner:

> To form hydrazine . . . .   13.70 $\%$
> To form nitrogen . . . .   85.73 $\%$
> To form oxygen . . . .   0.86 $\%$
> Total . . . 100.29

The quantity of azoimide, which is formed simultaneously, has not been estimated or taken into consideration, as it is very small and would not change the result perceptibly.

The sulphuric acid in the absorption pipettes and the water in the gasburette m (see the figure) were boiled out before the experiment. The ammonia and the hypochlorite solutions were made from redistilled water. It might perhaps be assumed, therefore, that at least a part of the oxygen in the evolved gases has been formed in the reaction (2).

Experiment 2.

The reaction mixture was: 10.0 ccs. of sodium hypo-chlorite (0.8505 molar) and 20.08 ccs. of ammonia (13 molar), and gave the following results:

Volume of the evolved gases .... 52.8 ccs.
Volume after absorption of oxygen............. 52.0 ccs.
Volume after air has been admitted............ 70.0 ccs.
Volume after combustion....................... 69.9 ccs.

Thus the evolved gas contained 52.0 ccs. of nitrogen and 0.8 ccs. of oxygen measured at 761 mm. and 23° C.

The remnant in the reaction flask was made up 250 ccs., 50 ccs. of which were titrated with 14.16 ccs. of a 0.1088 N. iodine solution. The hypochlorite has reacted in the following manner:

To form hydrazine .... 22.64 %
To form nitrogen in the reaction (1) .... 75.67 %
To form oxygen in the reaction (2) .... 0.78 %
                                    Total... 99.09

Also here the agreement is fair. From all the experiments made in this manner, it appears that small quantities of oxygen are evolved, probably due to a decomposition of some of the hypochlorite. But with an excess of ammonia as large as applied in these experiments, it might be expected, that all the hypochlorite would be transformed into monochloramine, and in this case no oxygen should have been evolved. The fact that oxygen is evolved seems to indicate that the transformation of hypochlorite into monochloramine is not complete. Other observations suggest the same, and a further dicussion will be taken up in the following part of the paper.

In another series of experiments the gaseous reaction products were investigated for the presence of nitrous oxide, as this substance should be expected, if imide is formed as an intermediate reaction product.

After the absorption of ammonia and oxygen the remainder of the gaseous reaction products were mixed with hydrogen and passed through the heated platinum capillary. If nitrous oxide is present a decrease of the total volume should be observed, but no one of the experiments showed any such decrease. If hydrogen or nitrous oxide are present in the gaseous reaction products, it must be in quantities less than one percent of the total volume.

7. Summary.

It has been shown:

1). That salts of such metals as cobalt, manganese, nickel and lead, which are able to occilate between two valencies, and therefore might be able to act as oxygen carriers, have no ability to decrease the hydrazine yield in RASCHIG's hydrazine synthesis, even when they are present in concentrations very much exceeding the concentrations at which a copper salt destroys the hydrazine entirely.

2). That a ferric salt has a slight catalytic action, but this is about 1000 times weaker than the action of a copper salt.

3). With specially prepared solutions of great purity it is possible to obtain hydrazine yields of about 55 % of the hypochlorite, when the excess of ammonia is great. The hydrazine yield increases with increasing excess of ammonia, but to a certain limit only, when the yield becomes practically constant.

4). Mannite acts as a powerful "negative catalyst" and is able to nullify the action of comparatively large quantities of copper salts.

5). Other "negative catalysts" have been investigated, and the action of such substances as flaxseed mucilage and carragen may be compared with that of mannite.

6). The formation of azoimide in the hydrazine synthesis has been investigated, and it has been concluded, that azoimide probably is formed in an oxidation of hydrazine, and that it is likely that nitrous acid (or nitrite) is an intermediate product.

7). RASCHIG's hydrazine synthesis has been investigated in a special apparatus, and the reaction products estimated. It has been shown, that the gaseous products are nitrogen and small quantities of oxygen. If hydrogen or nitrous oxide are present, it must be in quantities less than one percent by volume. It is therefore unlikely, that imide is an intermediate product of the reaction. The presence of oxygen must be due to a decomposition of the hypochlorite, and this seems to indicate, that the reaction of ammonia with hypochlorite to form monochloramine is not complete, even when the excess of ammonia is very great.

III.

The Production of Hydrazine Sulphate in the Laboratory. Theoretical Discussion.

1. Introduction.

In previous parts of this paper the synthesis of hydrazine from very pure chemicals has been investigated, and further the action of certain metallic salts, the action of

certain "negative catalysts" and the combined action of these. From these experiments the conclusion may be drawn, that the reason why ordinary chemicals give a poor yield of hydrazine, when gelatine is not added, is the trace of copper compounds present in the chemicals and especially in the distilled water. In all these experiments the total yield of hydrazine has been estimated, but for a laboratory production of hydrazine it is not so much the total yield which is of interest, as the quantity it is possible to obtain in the form of hydrazine sulphate, together with the purity of the obtained product. This question has therefore been taken up for investigation.

2. The production of hydrazine in the laboratory.

To begin with a series of experiments were made to investigate the possibility of producing hydrazine by electrolysis of ammonia-sodium chloride solutions. This has previous been attempted[1], but with no sodium hydroxide in the solution and with platinum as electrodes. According to observations of RASCHIG[2] and JOYNER[3] a certain sodium hydroxide concentration is necessary for the formation of hydrazine from monochloramine and ammonia, and it has further been shown[4], that platinum catalyses the oxidation of hydrazine.

[1] TURRENTINE & OLIVI: J. Amer. Chem. Soc. 37 (1915) 1121. See also BREDIG: Z. f. Elektrochem. 18 (1912) 653.

[2] Schwefel und Stickstoffstudien page 64.

[3] J. Chem. Soc. 123 (1923) 1114.

[4] SABANIJEFF: Z. anorg. Chem. 17 (1898) 492; J. russ. phys. Ges. 31 (1899) 375; C. B. 1899 II, 32. See also: TANATAR: Z. phys. Chem. 40 (1902) 475; 41 (1902) 37; PURGOTTI & ZANICHELLI: Gazz. chim. ital. 34, I (1904) 57; GUTBIER & NEUNDLING: Z. phys. Chem. 84 (1913) 203; TURRENTINE & GIBBONS: J. Amer. chem. Soc. 34 (1912) 36.

In a series of experiments solutions containing sodium chloride (0.4 N.), sodium hydroxide (0.1 N.) and ammonia (6.5 N.) were electrolyzed with electrodes of Acheson graphite at 100° (about 0.3—0.4 Amp.), with constant replacement of the ammonia which evaporated. But only a trace of hydrazine could be obtained.

In the electrochemical oxidation of ammonia nitrite is formed[1], and this may be one of the reasons why the hydrazine yield is poor. No further attempts were made.

It has been observed by Thiele[2], that a reducing agent is formed, when sodium hypobromite reacts with a great excess of ammonia, but in quantities much smaller than in the corresponding reaction with a hypochlorite.

However, a sodium hypobromite solution, with a known excess of sodium hydroxyde, is more easily made from commercial, liquid bromine, than a corresponding solution of sodium hypochlorite from gaseous chlorine. In a series of experiments it was investigated, if it would be possible to obtain a fair yield of hydrazine by mixing sodium hypobromite and a large excess of ammonia at low temperature and rapidly heating the reaction mixture to boiling.

In the cool alkaline liquid it is possible to detect traces of hydrazine, but when the excess of ammonia is removed by boiling, and the mixture is acidified by sulphuric acid, elementary bromine is formed in large quantities. This, as a matter of course, must be due to a transformation of hypobromite into bromide and bromate.

That monobromoamine is formed intermediate is indicated by the precence of hydrazine in the cool alkaline solution.

[1] Oesterheld: Z. anorg. Chem. **86** (1914) 131.
[2] Ann. **273** (1893) 160.

After the experimental part of this paper has been finished, MOLDENHAUER & BURGER[1] have prepared mono-bromoamine in ethereal solution by mixing ethereal solutions of bromine and ammonia or by extracting an aqueous mixture with ether. This will be discussed further in the following.

RASCHIG[2] has published a laboratory method for the synthesis of hydrazine sulphate from sodium hypochlorite. But the yield is not more than 5—6 grms., and students in educational laboratories rarely obtain any yield at all.

Experiments were made, therefore, to find a modification of RASCHIG's method which would give satisfactory results. The original method was tested, and it was found that the quantity of sulphuric acid, which is used for the precipitation of hydrazine sulphate, is much to small. Precipitation with a quantity of sulphuric acid three times as large as stated by RASCHIG gave fair hydrazine yields (48—50 %) of the hypochlorite) in form of a very pure (99.2 %) hydrazine sulphate.

It is a rather troublesome procedure to make up small quantities of sodium hypochlorite solutions, containing a known excess of sodium hydroxide, from gaseous chlorine, as the amount of chlorine has to be measured fairly accurate. It would be much easier to use commercial, chlorinated lime. But this cannot be used directly, as the hydroxyl ion concentration of the solution obtained by extraction with water is too low.

It is easy, however, to transform chlorinated lime into chlorinated soda in a treatment with a solution of sodium carbonate. As a commercial, chlorinated lime contains cal-

[1] B. **62** (1929) 1615.
[2] B. **40** (1907) 2065.

cium hydroxide, this also reacts with sodium carbonate forming sodium hydroxide, which gives the solution the necessary alkalinity.

Experiments were made to find the most economic ratio between chlorinated lime and ammonia, and the following method is the result.

250 grms. of a good, dry, chlorinated lime (with 30—35 % of available chlorine) are placed in a porcelain basin and 300 ccs. of city-supply water added. The mass is stirred thoroughly and all lumps disintegrated by rubbing with a pistil. To 750 grms. of ordinary washing soda (Na_2CO_3, $10H_2O$) in a beaker 800 ccs. of city-supply water are added, and the soda dissolved on a water bath at 20°—25°. When the solution is saturated at this temperature, it is drained from the small quantity of soda, which may not have dissolved.

The soda solution is now added to the chlorinated lime with stirring. The mixture at first becomes a pasty mass, which on further stirring gradually becomes less viscid. When all lumps are disintegrated the mixture is filtered on a 15 cm. Büchner funnel with suction. The formation of cracks and chanals through the precipitate should be prevented by pressing and stamping the mass with a pistil.

A porcelain basin of 4 litres capacity is placed slightly sloping on a tripod, and a beaker is placed under the spout to take any overflow. 1 litre of commercial, aqueous ammonia (sp. gr. 0.91) is poured into the basin, and a solution of 10 grms. of gelatine in 100 ccs. of water is added and mixed with the ammonia. As many gasburners as it is possible to get room for are placed under the basin ready to lit. Now the above prepared sodium hypochlorite solution is added rapidly in one sweep into the center of the ammonia

in the basin, and all the burners are quickly lit. The mix-
ture foams and some may run out into the beaker; this
is poured back into the basin. The important point is to
heat the mixture to boiling as rapidly as possible. When
the boiling point has been reached, the boiling and evapo-
ration may be continued with a single burner, until no
odour of ammonia can be detected. The solution is now
poured into a beaker of two litres capacity, cooled some-
what by means of tap water, and filtered into a Griffin
beaker of 2 litres capacity, which has been marked with a
glass pencil line, up to which the volume is 600 ccs. The
solution is now made slightly acid by adding, little by little,
a small portion of a cool solution of 150 ccs. of conc.
sulphuric acid in 300 ccs. of water. (Test with litmus
paper and add the acid slowly, as the solution foams on
account of its carbonate content). The acidified solution is
evaporated in the Griffin beaker to a bulk of 600 ccs. (To
prevent bumbing add unglazed porcelain or pumic stone).
The solution is now cooled by means of tap water, the
remainder of the above mentioned sulphuric acid is added,
and the solution cooled again. The precipitation of hydra-
zine sulphate will be completed in about an hour. The
precipitate is filtered off on a Büchner funnel by suction and
brought completely from the beaker into the funnel by means
of 4 N. sulphuric acid, which is also used for washing. This
is done by stopping the pump and stirring up the precipitate
in a small volume of the acid, after which it is again
sucked dry. This is repeated 5—6 times, until the filtrate
does not foam on leaving the funnel tube. About 250 to
300 ccs. of the 4 N. acid are used. After the last washing
the precipitate is pressed slightly while the pump is working.
The filter pump flask is now cleaned, the funnel with the

hydrazine sulphate replaced, and this is washed twice with about 60 ccs. of methyl alcohol. The funnel is finally placed in a steam oven, and the hydrazine sulphate dried at 80 to 90°. The methyl alcohol from several syntheses may easily be regenerated.

The yield of hydrazine sulphate is about 45 grammes (ranging from 44 to 47 g.) of a very pure product, containing from 99.6 to 99.9 % of hydrazine sulphate. The hydrazine yield is about 42 % of the hypochlorite in the chlorinated lime, and from 53 to 55 % of the hypochlorite in the solution of chlorinated soda prepared from the chlorinated lime.

3. A Theoretical Discussion.

a. The formation of monochloroamine.

From Raschig's and Marckwald & Wille's [1] experiments it may be concluded, that in the reaction of ammonia with sodium hypochlorite monochloroamine is formed. To be able to explain the formation of chlorine monoxide, when monochloroamine is dried with calcium chloride, Marck-wald & Wille have to assume, that monochloroamine is hydrolyzed according to the equation:

$$NH_2Cl + HOH = NH_3 + HOCl.$$
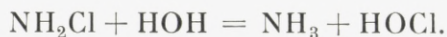
A similar hydrolysis has been known for a long time in the case of substituted chloroamines. [2]

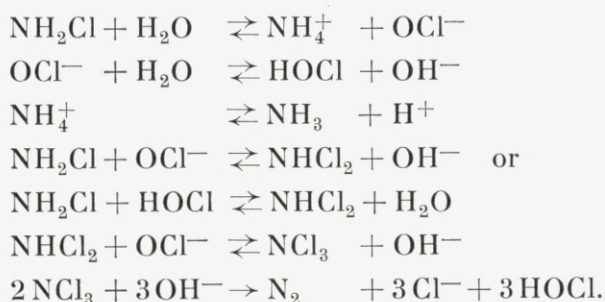Marckwald & Wille, however, do not apply this hydro-

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[1] l. c.

[2] See for instance: Berg: Comp. rend. **110** (1890) 862; ibid. **114** (1892) 3617; C. B. 1890 II 962; C. B. (1892) II 163. Seliwanov: B. **25** (1892) 3617. Chattaway: Chem. News **98** (1908) 166; C. B. 1908 II, 1504. J. Chem. Soc. **95** (1909) 129, 235, 464. Behal & Detoeuf: Comp. rend. **153** (1911) 681, 1229; C. B. 1911 II, 1521. Elliot: J. Chem. Soc. **123** (1923) 804.

lysis to explain the behaviour of monochloroamine in aqueous solutions. They have found, that an aqueous solution of mono-chloroamine decomposes according to the equation:

$$9\,NH_2Cl = 4\,NH_4Cl + 2\,N_2 + NCl_3 + 2\,HCl.$$

But this equation may be obtained as the sum of the following reactions:

$$NH_2Cl + H_2O \rightleftarrows NH_4^+ + OCl^-$$
$$OCl^- + H_2O \rightleftarrows HOCl + OH^-$$
$$NH_4^+ \rightleftarrows NH_3 + H^+$$
$$NH_2Cl + OCl^- \rightleftarrows NHCl_2 + OH^- \quad \text{or}$$
$$NH_2Cl + HOCl \rightleftarrows NHCl_2 + H_2O$$
$$NHCl_2 + OCl^- \rightleftarrows NCl_3 + OH^-$$
$$2\,NCl_3 + 3\,OH^- \rightarrow N_2 + 3\,Cl^- + 3\,HOCl.$$

Gradually, when the acidity of the solution increases, di-chloroamine, $NHCl_2$, becomes more stable[1], and finally, when the solution is distinctly acid, the trichloroamine, NCl_3, nitrogen chloride, is able to exist.

The observation of MARCKWALD & WILLE (l. c.), that a small quantity of ammonia is able to stabilize an aqueous solution of monochloroamine, is explained readily from the fact, that ammonia will displace the equilibrium in the monochloroamine hydrolysis.

In a slightly alkaline solution, buffered with sodium acetate, MARCKWALD & WILLE (l. c.) have found, that mono-chloroamine decomposes according to the equation:

$$3\,NH_2Cl = NH_4Cl + 2\,HCl + N_2 \,.$$

[1] CHAPIN: J. Amer. Chem. Soc. **51** (1929) 2112.

But this equation is readily obtained from the equations above, when it is taken into consideration, that in the alkaline solution nitrogen chloride is not stable.

These authors have found the same equation for the decomposition of monochloroamine by potassium hydroxide at ordinary temperature, but when the solution is hot, some potassium chlorate is formed. This, naturally, is due to a transformation of the hypochlorite, which is formed in the hydrolysis.

Also the reaction of monochloroamine with an acidified solution of potassium iodide may be explained as a result of a complete hydrolysis.

Raschig's[1] observation, that monochloroamine in a reaction with sodium bisulphite gives sodium sulphate, while in its reaction with sodium sulphite, a certain quantity of sodium amidosulphonate is formed, may be explained readily from the hydrolysis of monochloroamine and the different value of the hydrogen ion concentration in the two solutions.

After the experimental part of this paper had been finished, Bodenstein[2] has investigated the decomposition of monochloroamine in a slightly amoniacal solution. The process starts as an autocatalytic reaction, which after a while comes to a standstill, then again starts as an auto-catalytic reaction slowly dying out. This may be explained, qualitatively at least, by means of the equations given above. To begin with the hydrolysis is slight and the decompo-sition velocity slow, but when the hydrogen ion concen-tration increases, the decomposition takes speed. After a while such values of the hydrogen ion concentration are reached, at which dichloroamine is comparatively stable[3]

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[1] Schwefel und Stickstoffstudien. page 69.
[2] Z. phys. Chem. A. **139** (1928) 397.
[3] See Chapin (l. c.).

and the decomposition, therefore, is slow. When these values
of the hydrogen ion concentration have been exceeded, the
reaction again takes speed. Undoubtedly, it would be of
interest to investigate the reaction from this point of view,
but since the hydrolysis constants of mono- and dichloro-
amine are not known, it would be difficult to estimate the
velocity constants.

b. The formation of hydrazine from monochloro-amine and ammonia.

RASCHIG[1] has assumed, that the formation of hydrazine
from monochloroamine and ammonia takes place with an
intermediate formation of imide:

$$NH_2Cl + HO^- \rightarrow NH + Cl^- + H_2O$$
$$NH + NH_3 \rightarrow N_2H_4.$$
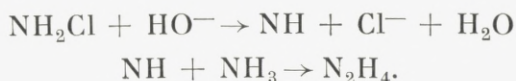
In recent years many papers have been published[2] on
the decomposition of ammonia by incandecent filaments,
by radiant energy in sensitized and non-sensitized reactions,
by low-voltage arcs, by silent discharges, or by cathode
rays, and in many of these reactions hydrazine has been
found as an ordinary product of the reaction. This is also
the case in the partial oxidation of ammonia with an oxy-
gen deficit, and when nitrogen is passed into the hydrogen-
oxygen flame.[3] In all these reactions the mechanism must
be, that either the imide group, NH, or the amide group,

[1] Schwefel und Stickstoffstudien page 71 and following pages. Page
213 and following pages.

[2] For literature see: HOWARD & BROWN: J. Amer. Chem. Soc. 55
(1933) 1968; WIIG & KISTIAKOWSKI: J. Amer. Chem. Soc. 54 (1932) 1806;
GEDYE & RIDEAL: J. Chem. Soc. 132 (1932) 1160, 1169.

[3] HOFMANN & KORPIUN: B. 62 B. (1929) 3000.

NH$_2$, is formed as an intermediate product, which then either decomposes or reacts to form hydrazine.

These reactions, however, take place either in gaseous systems or in heterogeneous systems (gaseous-solid or liquid-solid) on the surface of an activated catalyst, while Raschig's reaction takes place in a homogeneous system in aqueous solution. It is doubtful that the imide group should be able to exist in an aqueous solution, even for a very short time, without decomposing partially with the formation of nitrogen and hydrogen. But hydrogen has not been found in the gaseous reaction products.[1]

According to the investigation of Smith[2] it might also be expected, that the imide group would react with water forming hydroxylamine, which, in the alkaline solution, would decompose mainly with the formation of ammonia and nitrogen, but also with the formation of small quantities of nitrous oxide, and this has not been observed[1].

Raschig (l. c) and Joyner[3] have shown, that a certain hydroxyl ion concentration is necessary for the formation of hydrazine in the reaction of monochloroamine with ammonia, and that the reaction, therefore, might be:

$$NH_2 - \begin{array}{c} Cl \\ OH^- \end{array} + H - NH_2 = H_2N - NH_2 + Cl^- + H_2O.$$
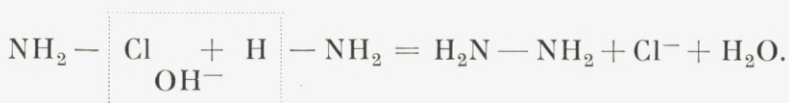
Hofmann & Korpiun (l. c.) have suggested, that in the catalytic oxidation of ammonia, by a catalyst consisting of sodalime activated with the oxides of copper, cobalt, nickel, iron etc., the stability of the intermediary formed imide might be due to a formation of the substance N-Na.

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[1] See page 40.

[2] Z. angew. Chem. **36** (1923) 511; B. **57** (1923) 704.

[3] J. Chem. Soc. **123** (1923) 1114.

The role of the sodium hydroxide in RASCHIG's synthesis might then be explained by the equations:

$$NH + Na^+ + OH^- \rightarrow N-Na + H_2O$$
$$N-Na + NH_4OH \rightarrow N_2H_4 + Na^+ + OH^-.$$
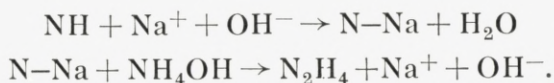
It is doubtful, however, that the substance N–Na should be more stable in aqueous solution than the imide itself.

The necessity of having a certain hydroxyl ion conc. in the solution may also be explained from the fact, that hydroxyl ions will prevent the formation of free hypo-chlorous acid in the hydrolysis of monochloroamine, since the very strong oxidizing agent hypochlorous acid will be transformed into the weaker oxidizing agent hypochlorite ions.

Without giving any details RASCHIG[1] has stated, that the reaction between monochloroamine and ammonia in aqueous solution proceeds exactly according to the following equation:

(a) $$NH_2Cl + NH_3 = N_2H_4 + HCl,$$

and that monochloroamine and hydrazine are present in the solution simultaneously. No intermediate product could be discovered, but, if the reaction is allowed to proceed to the end at ordinary temperature, the solution contains very little hydrazine.

That monochloroamine is able to exist simultaneously with hydrazine in an alkaline solution, where hydrazine is a strong reducing agent, shows that monochloroamine must be a very weak oxidizing agent. That the yield of hydrazine, nevertheless, is very small at ordinary temperature

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[1] Schwefel und Stickstoffstudien page 78.

must be due to the oxidation of hydrazine by the hypo-chlorite ions, which are formed in the hydrolysis of mono-chloroamine:

(b) $N_2H_4 + 2ClO^- = N_2 + 2Cl^- + 2H_2O.$

When the solution contains a large excess of ammonia, this reaction proceeds slowly, as the hypochlorite ion con-centration is small. Thus a large excess of ammonia simultaneously increases the velocity of the reaction (a) and decreases the oxidation of hydrazine in the reaction (b) by displacing the equilibrium of the monochloroamine hydro-lysis.

It seems probable, that it is the reaction (b), which is catalyzed by a trace of copper salts, and that it is due to this reaction, when little hydrazine is formed at ordinary temperature. If the reaction mixture is heated, the velocity of reaction (a) increases very strongly, while reaction (b), similar to the majority of other catalytic reactions, has a small temperature coefficient. As the result a considerable hydrazine yield may be obtained on heating.

Similar oxidations of hydrazine have been investigated by other authors, and it has been found, that a trace of copper has a very powerful action. Hodgkinson[1] has shown, that copper and copper salts catalyze the oxidation of hydrazine by potassium chlorate and the oxidation of hydrazine nitrate by hydrogen peroxide. Levi[2] has found, in the oxidation of hydrazine hydrate by the action of an alkali chlorite, that this reaction is catalyzed by traces of copper and iron compounds.

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[1] J. Soc. Chem. Ind. **33** (1913) 815; C. B. 1914 II 1340.
[2] Gazz. chim. ital. **53** (1923) I, 105; J. Chem. Soc. Abst. **124** (1923) 406.

After the experimental part of this investigation had been finished, BODENSTEIN (l. c.) has investigated the formation of hydrazine from monochloroamine and ammonia, and the decomposition of hydrazine by the action of monochloroamine. The two reactions are not investigated individually, but the total reaction is adjusted in such a manner, that no hydrazine is formed. The conclusion is, that the reactions are:

(a) $$NH_2Cl + NH_3 = N_2H_4 + HCl$$

(b_1) $$N_2H_4 + 2 NH_2Cl = N_2 + 2 NH_4Cl.$$

Reaction (a) is slow at ordinary temperature, but has a large temperature coefficient, while the reaction (b_1) is rapid, but has a negligible temperature coefficient and is catalyzed by copper salts. This agrees in so far with the conclusions which have been drawn by the writer, only, since monochloroamine and hydrazine are able to exist simultaneously in the solution, it is rather unlikely, that the monochloroamine itself is able to oxidize the strong reducing agent hydrazine. It seems much more likely, that the oxidation is due to the small quantities of hypochlorite, which are present in the solution in equilibrium with monochloroamine.

c. The formation of azoimide.

This has already been discussed in a previous part of this paper[1]. Since azoimide is a product ordinarily formed in the oxidation of hydrazine, it is most likely produced in an oxidation of hydrazine by the hypochlorite ions, which are formed in the hydrolysis of monochloroamine.

Since a nitrite is formed in the reaction of sodium

[1] See page 33.

hypochlorite with ammonia, when a copper salt of a certain low concentration has been added, the azoimide may also be formed in a reaction of hydrazine with nitrite. The mechanism of the hydrazine oxidation has not yet been solved, therefore, nothing very definite may be said with regard to the trace of azoimide which is formed in RASCHIG's hydrazine synthesis.

d. The reaction of other alkali hypohalogenites with ammonia.

It has been mentioned on a previous page, that small quantities of hydrazine are formed when a cool solution of sodium hypobromite reacts with a cool solution of ammonia. But when the reaction mixture is heated and boiled to remove the excess of ammonia and then acidified, bromine is liberated.

The formation of hydrazine at ordinary temperature indicates, that monobromoamine is formed, analogous with the formation of monochloroamine in the reaction of hypochlorite with ammonia[1].

That no hydrazine is obtained, when the reaction mixture is boiled, is due to the hydrolysis of monobromoamine. This, most likely, is considerably more hydrolysed than monochloroamine. The reactions, therefore, which are disastrous to the hydrazine yield, will proceed much more rapidly than in the case of monochloroamine, and the result will be a violent evolution of nitrogen.

The transformation of a hypobromite into a bromide and a bromate is also much faster than the corresponding trans-

[1] MOLDENHAUER & BURGER: B. **62** (1929) 1615; COLEMAN, SOROOS & YAGER: J. Amer. Chem. Soc. **55** (1933) 2075.

formation of a hypochlorite[1]. These properties, therefore, make sodium hypobromite quite unfit for the production of hydrazine.

In the reaction of a hypoiodite with ammonia the process is slightly different, as one of the iodoamines is slightly soluble and, therefore, more stable, when it is formed in a slightly alkaline solution, than the corresponding chlorine and bromine compounds. But the reaction of the hypoiodite and ammonia may be explained readily as a result of the hydrolysis of mono- and diiodoamine[2]. When a hypoiodite (or iodine) reacts with ammonia in excess, the first product of the reaction is probably monoiodoamine, NH_2I, but, as this is strongly hydrolysed, the reaction is not complete, and the hypoiodite in the solution will gradually transform the monoiodoamine into the diiodoamine, NHI_2, which is slightly soluble. The precipitate which is formed is the compound NHI_2, or the compound $N_2H_3I_3 = NH_2I, NHI_2$.[3] The reactions may be written:

$$NH_3 + IO^- \rightleftarrows NH_2I + OH^-$$
$$NH_2I + IO^- \rightleftarrows NHI_2 + OH^-.$$
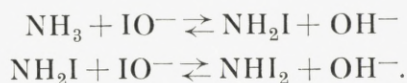
If the solution is too alkaline, these equilibria a displaced so far to the left hand side, that no precipitation occurs, and the hypoiodite is then rapidly transformed into an iodate.

[1] SKRABAL: Monatsh. f. Chem. 28 (1907) 319; CB. 1907 II 372.

[2] SELIVANOFF: B. 27. (1894) 443, 1012.

[3] BINEAU: Ann. Chim. Phys. (3) 15 (1845) 71; RASCHIG: Ann. 230 (1885) 221, S & S pag. 34; SZUHAY: B. 26 (1893) 1933; SELIVANOFF (l. c.); GLADSTONE: J. Chem. Soc. 4 (1851) 34; ibid. 7 (1854) 51; MILLON: Ann. Chim. Phys. (2) 69 (1838) 88; MARCHAND: Ann. Chim. Phys. (2) 73 (1840) 222; J. prakt. Chem. (1) 19 (1840) 1; GUYARD: Comp. rend. 75 (1872) 210; BUNSEN: Ann. 84 (1852) 1; MALLET: Amer. Chem. Jour. 1 (1880) 4; ibid. 10 (1888) 322; CHATTAWAY: J. Chem. Soc. 69 (1896) 1572; CHATTAWAY & ORTON: Amer. Chem. Jour. 23 (1900) 362, 369; ibid. 24 (1900) 159.

Guyard (l. c.) has observed, that the closer the compo-
sition of the "nitrogen iodide" approaches the formula
NHI_2, the less is it changed on washing with water. This
indicates, that the compound NH_2I is readily hydrolysed
on washing with water, while the slightly soluble compound,
NHI_2, is not effected so much. However, when nitrogen
iodide is treated with water for some time, it is transformed
into ammonium iodide, ammonium iodate and some ele-
mentary iodine. This reaction is readily explained as the
result of a hydrolysis, the transformation of the hypoiodite
into an iodide and an iodate, and a consecutive reaction
between some free hydriodic and iodic acid.[1]

Raschig (l. c.) has found, on treating nitrogen iodide with
sodium hydroxide, that sodium nitrite is found among the
reaction products. This is in agreement with the fact, that
a nitrite is formed in the reaction of sodium hypochlorite
with ammonia in the precense of a trace of a copper salt.
Undoubtedly, the reactions of nitrogen iodide (viz. NHI_2 or
NH_2I, NHI_2) may be explained readily as results of its
hydrolysis.

That no hydrazine is formed in the reaction of sodium
hypoiodite with ammonia must be due to the considerable
hydrolysis of the monoiodoamine. Such small quantities of
hydrazine, which may be produced in a slow reaction
between monoiodoamine and ammonia, are immediately
oxidized by the hypoiodite in the solution. A heating of
the reaction mixture to boiling does not help, as the velocity
of the transformation of a hypoiodite into an iodide and
an iodate is much greater than the corresponding trans-
formation of a hypobomite into a bromide and a bromate.

[1] Serullas: Ann. Chim. Phys. (2) **42** (1829) 200; Millon (l. c.); Stas:
Mem. Acad. Belg. **35** (1865) 3.

Summary.

1). It has been investigated, if it would be possible to produce hydrazine in an electrolysis, with graphite electrodes, of a solution containing sodium chloride, sodium hydroxide, ammonia and gelatine. Only a trace of hydrazine could be detected.

2). The hydrazine formation in the reaction of sodium hypobromite with ammonia has been investigated. A trace of hydrazine may be detected in the cool reaction mixture, but after boiling, to remove the excess ammonia, the hydrazine has been destroyed.

3). A laboratory method has been worked out for the production of hydrazine from chlorinated lime, soda, ammonia and gelatine. It has been used in an educational laboratory with good results.

4). The formation of monochloroamine, its decomposition and its reaction with ammonia has been discussed.

5). The reaction of other hypohalogenites with ammonia has been discussed.