ENCLOSURE (B) 9

SYNTHESIS OF HYDRAZINE FROM UREA

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LIST OF TABLES AND ILLUSTRATIONS

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SUMMARY

The synthesis of hydrazine from urea and sodium hypochlorite was studied. Solutions of urea and sodium hypochlorite were mixed and heated. After cooling, the hydrazine formed was precipitated by sulfuric acid, and hydrazine sulphate was separated and weighed. The necessary conditions to obtain high yields of hydrazine were as follows:

1. The mol ratio of urea to sodium hypochlorite was 1 : 1 or 1 : 0.8.

2. The concentration of the sodium hypochlorite was 1-1.25N.

3. Urea should be dissolved in a small amount of water prior to the addition of hypochlorite.

4. The temperature of mixing the raw materials must be below 5°C.

5. The temperature required to complete the reaction was 90°C.

6. In this reaction 3 mols of caustic soda to 1 mol of urea were required.

7. When 0.5 grams of glue per mol of sodium hypochlorite was added in the solution, the yield of hydrazine increased considerably.

8. The presence of rusty iron in the reaction vessel must be avoided.

I. INTRODUCTION

Hydrazine mixed with hydrogen peroxide was used for the energy source of the rocket. Although hydrazine is generally synthesized from ammonia and sodium hypochlorite, a large quantity of ammonia must be treated because of the small yield of hydrazine to ammonia used. The method using urea as the raw material was previously known, but since the exact conditions to obtain the maximum yield was not obvious, this method was studied. The experiments were begun in July 1944 and were finished in September 1944 by Chem. Eng. Lieut. Comdr. T. YAMAMOTO, Chem. Eng. Lieut. H. NAKAO, and Chem. Eng. Lieut. Comdr. Y. MOMOTARI.

II. DESCRIPTION OF APPARATUS AND PROCEDURE

A. A 3-necked flask with a glass stirrer was used as the reaction vessel.

B. Material Used

1. Sodium hypochlorite solution. 500 grams of bleaching powder were dissolved in 2.5 liters of water, and was added to 500 grams of sodium sulphate. After the calcium sulphate settled, the solution was filtered and the concentration of sodium hypochlorite was measured by iodometry. The concentration of sodium hypochlorite was adjusted to 1 N.

3. Glue Solution. A 1% solution of glue was made and 75cc per mol of sodium hypochlorite was used.

C. Details of Test Procedure and Conditions

Each solution was cooled to 5°C and mixed. The glue solution was added to the mixture of sodium hypochlorite and urea. The mixture was heated to 95°C and, after cooling, concentrated sulphuric acid was added until the concentration of sulphuric acid in the solution was 20%. The precipitated hydrazine sulphate was filtered, washed with alcohol, and dried at 100°C. The weight and purity were measured, and the percent yield was calculated.

III. EXPERIMENTAL RESULTS

A. The Effect of the Mol Ratio of Urea and Sodium Hypochlorite upon the Yield of Hydrazine

The results are tabulated in Table I(B)9, showing the ratio of urea to sodium hypochlorite should be 1 : 1-0.8.

B. The Effect of the Concentration of Sodium Hypochlorite upon the Yield of Hydrazine

The reaction was carried out using volumes of one mol sodium hypochlorite solution ranging from 600 - 2250cc and mol ratios of urea to sodium hypochlorite ranging from 1:0.8 to 1:1.35. The experimental results are tabulated in Table II(B)9, and show that the best conditions are a mol ratio of urea to hypochlorite of 1:0.8-0.9; and that the best volume for one mol of hypochlorite at this ratio is 1000-800cc. This corresponds to a 1.0 - 1.25 N solution of hypochlorite.

C. The Effect of Temperature on Mixing of the Raw Materials upon the Yield of Hydrazine

Using a mol ratio of urea to sodium hypochlorite of 1:0.8, and a concentration of 1 N sodium hypochlorite, yields were compared at various mixing temperatures.

The results are shown in Table III(B)9.

It is obvious that the temperature of mixing should be below 5°C.

D. The Effect of the Heating Temperature upon the Yield of Hydrazine

The mixture was heated to various temperatures and was maintained at that temperature for 20 minutes before treating as mentioned above. The experimental conditions were one mol of urea to 0.8 mols of hydrogen, the concentration of sodium hypochlorite was 1 mol of NaOCl per 800cc and the mixing temperature was 5°C. The results are shown in Table IV(B)9, and show that the temperature of heating must be higher than 90oC; but when the temperature is too high, hydrazine will be lost by evaporation.

E. The Effect of the Amount of Caustic Soda upon the Yield of Hydrazine

The effect of the amount of caustic soda on the yield of hydrazine was tested and it was found that the use of 3 mols of caustic soda to one mol of urea was sufficient as shown in Table V(B)9.

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F. The Effect of Glue on the Yield of Hydrazine

The results are tabulated in Table VI(B)9. The experimental conditions were as follows:

The mol ratio of urea to sodium hypochlorite was 1:0.8; the concentration of sodium hypochlorite was one mol of sodium hypochlorite in 800cc; the mol ratio of urea to caustic soda was 1:2.5; and the concentration of the glue was varied from 0 to 2.4 grams per mol of sodium hypochlorite.

From these data it appeared that the addition of 0.5 grams of glue per mol of sodium hypochlorite was sufficient to obtain a high yield of hydrazine.

G. The Effect of the Materials of the Reaction Vessel on the Yield of Hydrazine.

In order to clarify the effect of several materials on the reaction, various test pieces were put in the glass reaction vessel and the yield of hydrazine was measured. The results are shown in Table VII(B) 9. As indicated in Table VII(B)9, no yield was obtained when rusty steal was present in the reaction mixture.

This might be caused by the oxidation of hydrazine by Fe_2O_3 and the fact that glue is of no value in controlling this oxidation reaction.

III. CONCLUSIONS

From the experimental results described, it was ascertained that the best procedure for obtaining high yields of hydrazine from urea is as follows: one mol of urea and three mols of caustic soda are dissolved in a small amount of water. Separately, one litre of 1 N sodium hypochlorite solution and 50cc of 1% glue solution are prepared. These solutions are cooled to 5°C, mixed, and then heated to 95°C.

When cooled, an excess of sulphuric acid is added.

The precipitate of hydrazine sulphate produced is filtered and washed. The yield of the hydrazine will be higher than 50% based on the consumed urea.

No commercial application of this process has been made.

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Table I(B)9
EFFECT OF MCL RATIO OF UREA TO HYPOCHLORITE
ON YIELD OF HYDRAZINE

Raw Material (gm-mol)*	Yield (%)	
NaOCl	to Urea	to NaOCl
1.35	41.0	30.0
1.00	50.0	50.0
0.90	49.5	55.0
0.80	48.5	60.0
0.75	47.5	63.5
0.50	35.5	72.0

*In each NaOCl mixture were 1.0 gm-mol urea plus 2.5 gm-mols of NaOH.

Table II(B)9
THE EFFECT OF THE CONCENTRATION OF SODIUM HYPOCHLORITE
UPON THE YIELD OF HYDRAZINE

Raw Materials (gm-mol)* NaOCl	Vol. of Sol. Containing of NaOCl(cc)	Yield (%)	
		to Urea	to NaOCl
0.8	600	49.0	61.3
0.8	800	52.5	65.6
0.8	1150	48.0	60.0
0.8	1800	40.6	50.7
0.9	800	45.7	50.8
0.9	1000	51.8	57.6
0.9	1150	49.1	54.6
0.9	1800	45.7	50.8
1.0	800	44.4	44.4
1.0	1150	50.0	50.0
1.0	1800	38.5	38.5
1.0	2250	26.8	26.8
1.35	800	25.5	18.7
1.35	1150	41.4	30.7
1.35	1640	34.5	26.4
1.35	2140	9.5	7.4

*In each NaOCl mixture was 1.0 gm-mol urea.

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Table III(B)9
THE EFFECT OF THE TEMPERATURE OF MIXING OF THE RAW MATERIALS

Temp. of Mixing (°C)	Yield (%) to Urea
28	0
15	41
5	52
3	54
0	54
-5	53

Table IV(B)9
THE EFFECT OF THE HEATING TEMPERATURE UPON
THE YIELD OF HYDRAZINE

Heating Temp. (°C)	Heating Time (min)	Yield (%) to Urea
40	20	0
60	20	22
85	20	39
90	10	52
95	20	40

Table V(B)9
THE EFFECT OF THE AMOUNT OF CAUSTIC SODA
UPON THE YIELD OF HYDRAZINE

Raw Materials (gm-mol)*		Yield (%)	
Sodium hypochlorite	Caustic Soda	To Urea	to Sodium hypochlorite
0.8	2.0	31.4	39.3
0.8	2.5	54.0	67.5
0.8	3.0	58.8	73.5
0.8	5.0	58.4	73.0

*In each NaOCl was 1.0 gm-mol urea.

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Table VI(B)9
THE EFFECT OF GLUE ON THE YIELD OF HYDRAZINE

Glue used gm/mol. of NaOCl	Yield %	
	to Urea	to NaOCl
0	12.0	15.0
0.17	51.0	63.8
0.75	53.3	66.6
1.30	53.9	67.8
2.40	54.0	67.5

Table VII(B)9
THE EFFECT OF THE MATERIALS OF THE REACTION VESSEL

Test pieces	Yield of hydrazine %	Remark
none	52.0	
13-Cr-Steel	51.0	Polished before the test
18-8-Cr. Ni. Steel	41.0	
Rubber plate	49.0	
Lead	50.0	
Mild Steel	0	Rusty