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Synthesis of Cyclotetramethylene Tetranitramine by Three Stage Method

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Abstract. A three stage method has been developed for the preparation of cyclotetramethylene tetranitramine (HMX) at 45 ± 3°C. Hexamine was nitrated to 1,5 methylene-3,7 dinitro-1,3,5,7 tetra aza cyclo octane (DPT) in acetic anhydride and acetic acid with ammonium nitrate–nitric acid mixture in presence of BF_3 as catalyst, DPT along with reaction mixture was further treated with excess of nitric acid and acetic anhydride in the second stage. The product so obtained was converted into HMX in third stage treating with ammonium nitrate-nitric acid mixture and acetic anhydride. Effect of various concentration of ammonium nitrate, nitric acid and acetic anhydride was also studied on the yield of HMX in final stage.

1. Introduction

Cyclotetramethylene tetranitramine (1,3,5,7 tetranitro-1,3,5,7 tetrazacyclo-octane) also known as octogen is one of the most powerful modern high explosives. It is used in propellants, heat stable compounds, plastic bonded explosives and in gelled slurry explosives. The production of HMX was started in UK during the world War II but the procedure was kept secret. After the War several workers[1–4] carried out nitration of hexamine using acetic anhydride, ammonium nitrate and nitric acid and isolated HMX along with many other nitro compounds i.e. RDX, DPT, PHX, and QDX, etc. Aristoff *et al.*[4] in 1949, isolated 1, aceto-3,5,7 trinitro-1,3,5,7-tetra aza cyclo octane (QDX) along with RDX in the nitrolysis of hexamine. They further converted QDX into HMX with 98 per cent HNO_3 and obtained HMX yield (25 per cent). Bachmann *et al.*[5–6] in 1951 also carried out nitrolysis of hexamine and prepared DPT. DPT was converted into PHX, which was finally nitrated to HMX with 28 per cent yield.

Esptein and Winkler[7] studied the effect of proportion of reactants, temperature and concentration of the ingredients on the yield of HMX and came to the conclusion that concentration of ammonium nitrate had profound effect on the yield of HMX. They found that 2–3 moles of ammonium nitrate to 1 mole of hexamine was optimum for good yield of HMX. To get good yield of HMX, many workers[8–11] carried out nitration of hexamine with ammonium nitrate in nitric acid and acetic anhydride under different set of reaction conditions and reported the yield of HMX upto 60–70 per cent.

A good yield of HMX (85–90 per cent) was reported[12–13] by using three feed two stage methods but the cost of synthesis is high. To reduce the cost, several experiments were conducted keeping in view the concentration of ammonium nitrate. Finally a modified process has been developed using almost stoichiometric proportion of ammonium nitrate (2.2 mole to 1 mole of hexamine).

2. Experimental Procedure

Into a stainless steel beaker provided with stirrer, acetic acid (110 ml), acetic anhydride (15 ml) and borontrifluoride diethyletherate (2 ml) were added. The three ingredients, (i) hexamine (20 g) in glacial acetic acid (40 ml), (ii) ammonium nitrate (18 g) in 98 per cent nitric acid (11 ml) and (iii) acetic anhydride (45 ml) were taken in three graduated separating funnels. The hexamine and nitric acid solution were added continuously and proportionally in 15 minutes. At the end of 5 minutes, 15 ml acetic anhydride was added maintaining the temperature 45 ± 3°C with constant stirring. The reaction mixture was aged for 15 minutes. After aging, nitric acid (10 ml) and acetic anhydride (30 ml) were added in 10 minutes at 45 ± 3°C and the mixture was again aged for 10 minutes. After aging, ammonium nitrate (8 g) in nitric acid (11 ml) and acetic anhydride (60 ml) were added continuously and proportionally in 15 minutes at 45 ± 3°C. The mixture was aged for 60 minutes and afterward, 70 ml hot water was added to it. The whole reaction mixture was refluxed for 30 minutes to decompose the undesirable product and convert acetic anhydride to acetic acid. It

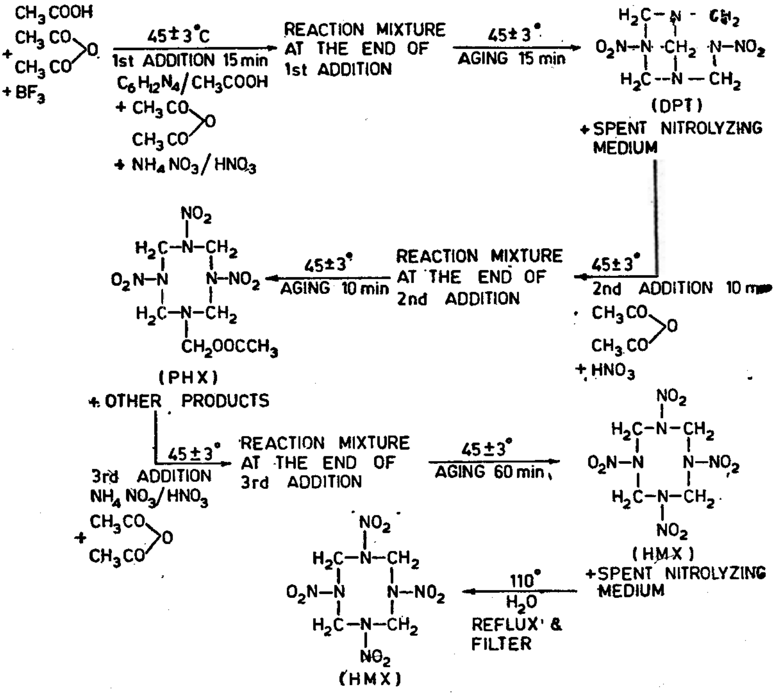


Figure 1. Flow diagram for the nitrolysis of hexamine.

was cooled with ice to 20°C, filtered, and washed with cold water till it was free from acid.

Such experiments were repeated by taking various concentration of ammonium nitrate—nitric acid solution and proportions of acetic anhydride in the third stage of the process (Table 1).

Table 1. Effect of variation of concentration of ammonium nitrate, nitric acid, and acetic anhydride on the yield of HMX in third stage

Set	NH_4NO_3(g)/ HNO_3(ml) ratio	Acetic anhydride (ml)	Yield* of HMX (g)
A	22:11	60	28.5
	20:11	60	30.5
	18:11	60	31.5
	16:11	60	32.5
	14:11	60	33.0
	12:11	60	34 0
	10:11	60	34.8
	8:11	60	36.0
	6:11	60	28.5
	4:11	60	27.0
B	8:15	60	26.0
	8:13	60	31.0
	8:11	60	36.0
	8: 9	60	30.0
	8: 7	60	24.5
C	8:11	80	29.0
	8:11	70	34.0
	8:11	60	36.0
	8.11	50	27.5
	8:11	40	25.0

*Yield is based on 20 g Hexamine.

3. Analysis and Purification of HMX

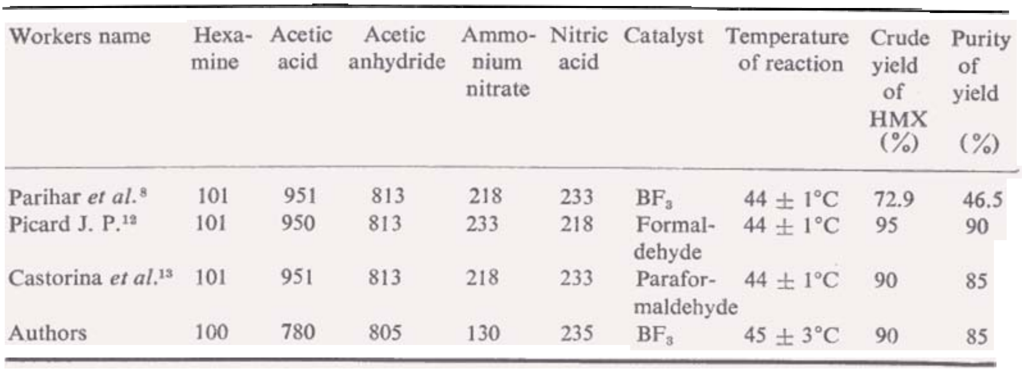
The analysis was carried out by the reported method[14] which showed the presence of RDX to extent of 12–14 per cent in HMX. It was purified by destroying the RDX chemically by refluxing it with 10 per cent solution of sodium carbonate as reported by Singh *et al.*[15]. The HMX was recrystalised with acetone and melting point was found to be 280°C.

4. Results and Discussion

Table 2 reveals that earlier workers have taken ingredients in the same ratio with little change in their mode of addition in the nitration process. Although good yield of

HMX was reported by Picard[12] and Castorina *et al.*[13] yet they have taken the same ingredients almost in the same ratio. They did not optimise the reaction parameters such as reaction temperature, amount of reagent and quantities of solvents, etc. To reduce the cost, attempt has been made here to optimize the quantity and proportion of ingredients which may help in getting good yield at lower cost of synthesis. Though the yield (95 per cent) obtained by Picard is of 90 per cent purity but it contains mostly α HMX which is metastable and very sensitive, so the process involves hazard. Table 2 further shows that the three stage method described here gives good yield of HMX (90 per cent) of 85 per cent purity although quantity of ammonium nitrate and acetic acid used is 45 per cent and 20 per cent less respectively as compared to the quantity used by other workers (Table 2). Quantity of ammonium nitrate used is as small as possible, just in stoichiometric ratio because increase of it, decreases the yield of HMX.

Table 2. Reaction parameters of various workers in the synthesis of HMX (all ingredients are taken in grams).



Workers name	Hexamine	Acetic acid	Acetic anhydride	Ammonium nitrate	Nitric acid	Catalyst	Temperature of reaction	Crude yield of HMX (%)	Purity of yield (%)
Parihar *et al.*[8]	101	951	813	218	233	BF_3	44 ± 1°C	72.9	46.5
Picard J. P.[12]	101	950	813	233	218	Formaldehyde	44 ± 1°C	95	90
Castorina *et al.*[13]	101	951	813	218	233	Paraformaldehyde	44 ± 1°C	90	85
Authors	100	780	805	130	235	BF_3	45 ± 3°C	90	85

It is also evident from the Table 1 that yield of HMX depend upon the appropriate quantity of reactants, i.e., ammonium nitrate, nitric acid and acetic anhydride, etc. Effect of various concentration of ammonium nitrate, nitric acid and acetic anhydride was studied in third stage which showed that increase or decrease of reactants have profound effect on the yield of HMX. Maximum yield of HMX was obtained when ammonium nitrate (8 gm) in nitric acid (11 ml). and acetic anhydride (60 ml) had been used.

This modified process of preparation of HMX is simple and less costly.

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