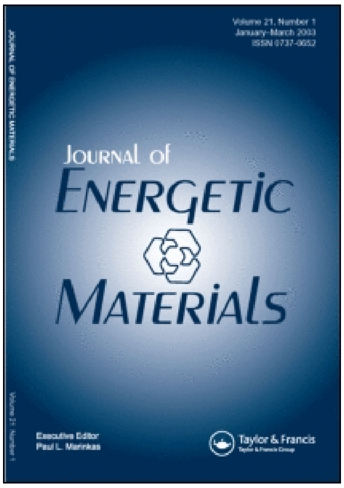

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ALTERNATIVE EXOTHERM SUPPRESSANTS FOR THE NITROLYSIS OF DAPT

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Abstract. Various potential exotherm suppressants for use in the nitrolysis of DAPT have been assessed both in a synthetic spent acid medium and in actual nitrolysis reactions. Formamide and acetamide have been identified as suitable additives for controlling the exotherm which occurs in the absence of an exotherm suppressant. The DADN which is isolated when these additives are used is somewhat purer than that which is obtained in the presence of urea, the normal exotherm suppressant.

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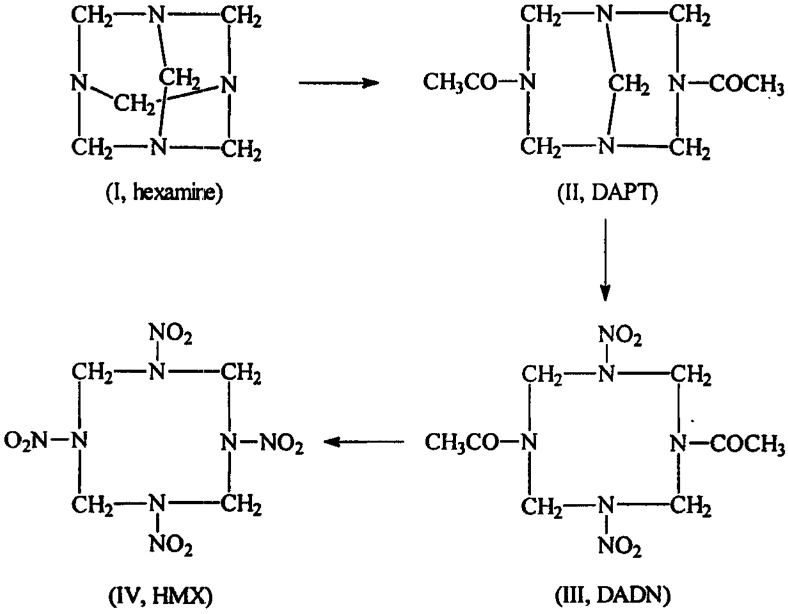
INTRODUCTION

One of the newer synthetic routes for preparing HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane, IV) involves the acetylation of hexamethylenetetraamine (hexamine, I) to DAPT (diacetylpentamethylenetetraamine, 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane, II), nitrolysis of DAPT to DADN 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane, III), and finally nitrolysis of DADN to HMX[1] (see Scheme).

Scheme



(I, hexamine)

(II, DAPT)

(IV, HMX)

(III, DADN)

It was found[2] that the original three-step process could be reduced to a two-step process by combining the first two steps into a one-pot reaction. Thus a solution of DAPT was prepared by treating hexamine with acetic anhydride and ammonium acetate in the presence of water, and the DAPT solution was then added to the nitrolysis medium (nitric acid/sulphuric acid) at 20°C to give DADN as the first isolated intermediate. The initial report[2] used five-times (10 equivalents) the required amount of nitric acid and obtained DADN in 96% yield (based on hexamine). In order to make the process economically viable Coburn and Benziger[3,4] investigated the possibility of reducing the amount of nitric acid to 3.3 equivalents and increasing the temperature. Under these conditions, a violent exotherm (30 → 70°C) is observed, accompanied by gas evolution and foaming, at the end of the nitrolysis of DAPT and a reduced yield of DADN is obtained. This does not occur with the larger excess of nitric acid. It was suggested[3,4] that the exotherm is caused by the oxidation of formaldehyde, released by the nitrolysis of DAPT, with concomitant reduction of the remaining HNO_3 to HNO_2. This was supported by analysis of the reaction solution for HCHO and HNO_2,[3,4] and identification of the evolved gas as CO.[4] Coburn and Benziger[3,4] found that adding urea to the DAPT feed solution caused the exotherm to be considerably reduced or even eliminated, depending upon the amount of urea added. At the same time the reaction temperature could be increased to 30 or 40°C, giving a reduced reaction time (30 and 10 minutes respectively), and the yield was restored to the levels observed when a large excess of nitric acid was used. Roughly stoichiometric amounts of urea (0.5-1.0 equivalents vs hexamine) are required to eliminate the exotherm. The role of the urea is not entirely clear, since urea reacts with both HCHO[5a] and HNO_2[5b], but the authors appear to favour condensation of HCHO with urea to form an adduct eg dimethylol urea $HOCH_2NHCONHCH_2OH$, which protects the HCHO from oxidation. In any case, analysis of reactions which contained urea demonstrated that concentrations of both HCHO and HNO_3 remained essentially constant after DADN formation was complete, and that HNO_2 was essentially absent.

If urea were functioning as a trap for HCHO, then we reasoned that there might be other additives which would function in a similar manner ie suppress the exotherm without interfering with the production of DADN. Those which we selected for testing were compounds which are known to react with HCHO and/or HNO_2[5c] viz semicarbazide salts, hydroxylamine salts, dimedone, thiourea, formamide and acetamide. However before running DAPT nitrolysis reactions in the presence of these, their stability in a spent acid medium approximating to that obtained in a real nitrolysis was tested as described below.

RESULTS AND DISCUSSION

Selection of Potential Exotherm Suppressants

The formation of DAPT in the presence of acetic anhydride and ammonium acetate is represented by the following equation[4]:

$$C_6H_{12}N_4 \text{ (hexamine)} + 2.4(CH_3CO)_2O + 0.8CH_3COONH_4 \rightarrow 1.2C_9H_{16}N_4O_2 \text{ (DAPT)} + 3.2CH_3COOH$$

and the nitration of DAPT to DADN may be represented by:

$$\text{DAPT} + 2HNO_3 \rightarrow \text{DADN} + CH_2O + H_2O$$

However when a solution of DAPT is prepared by adding acetic anhydride (0.25mol) to a slurry of hexamine (0.1mol) and ammonium acetate (0.082mol) in water (0.14mol), the overall equation for the formation of DAPT becomes:

$$0.1C_6H_{12}N_4 \text{ (hexamine)} + 0.25(CH_3CO)_2O + 0.082CH_3COONH_4 + 0.14H_2O \rightarrow 0.12C_9H_{16}N_4O_2 \text{ (DAPT)} + 0.34CH_3COOH + 0.13H_2O$$

If approximately 90% of the DAPT formed above were converted to DADN (typical yield of DADN) using 90% HNO_3 (0.33mol) and 98%H_2SO_4 (2.25mol) then the nitration may be written as:

$$0.11C_9H_{16}N_4O_2 \text{ (DAPT)} + 0.22HNO_3 \rightarrow 0.11C_8H_{14}N_4O_6 \text{ (DADN)} + 0.11CH_2O + 0.11H_2O$$

Assuming that the remaining 0.01mol DAPT is completely hydrolysed to 0.05mol formaldehyde:

$$0.01C_9H_{16}N_4O_2 + 0.05H_2O \rightarrow 0.05CH_2O$$

then the composition of a typical spent acid (before any further decomposition) would be:

H_2SO_4	2.25mol
HNO_3	0.11mol (0.33 - 0.22)
H_2O	0.19mol (0.13 + 0.11 - 0.05; plus H_2O from H_2SO_4 and HNO_3)
CH_3COOH	0.34mol
CH_2O	0.16mol (0.11 + 0.05)

A synthetic spent acid with the above composition was prepared by mixing the components in the order shown (see Experimental). Both paraformaldehyde and trioxan were tested as the source of formaldehyde. When paraformaldehyde (4.8g ≡ 0.16mol formaldehyde) was added to the other components at 30°C, the temperature rose to 64°C , 18min after the addition. With trioxan (4.8g, 0.053mol ≡ 0.16mol formaldehyde) the temperature rose to 52°C after 34min. In both cases there was considerable foaming. In non-synthetic systems involving the nitration of DAPT with 3.3 equivalents of HNO_3 and in the absence of an exotherm suppressant, the temperature rose to 66-70°C after 22min. Using synthetic spent acid in the presence of urea (0.1mol) as the exotherm suppressant, the addition of paraformaldehyde did not cause an exotherm whereas the addition of trioxan did produce a small exotherm (2.5K) after 5min. It was therefore concluded that paraformaldehyde was preferable to trioxan in attempts to simulate the spent acid from a DAPT nitration. [The addition of formic acid (0.16mol), instead of a source of formaldehyde, did not produce an exotherm, supporting the view that the source of the exotherm is oxidation of formaldehyde and is not due to dehydration of the resultant formic acid to give CO.]

Further experiments with the synthetic spent acid involved adding a potential exotherm suppressant (0.05-0.2mol) to the acid mixture before adding paraformaldehyde and observing the resultant behaviour (see Table 1). Many of the additives caused obvious chemical reaction when the paraformaldehyde was added, with gas evolution and exothermic behaviour, and were clearly unsuitable as exotherm suppressants. In the case of semicarbazide salts, reaction occurred even before the addition of paraformaldehyde. Only two additives, formamide and acetamide, largely suppressed the exotherm which would normally occur in the absence of an exotherm suppressant and showed no other evidence of chemical reaction. In the case of acetamide, the magnitude of the exotherm decreased as the amount of acetamide was increased and 2 equivalents were required to almost totally suppress the exotherm; with formamide the same effect was observed with only 1 equivalent. When trioxan instead of paraformaldehyde was used in conjunction with formamide there was a vigorous reaction. This also supports the conclusion made above that paraformaldehyde is preferable to trioxan as a source of formaldehyde in a simulated spent acid. Formamide and acetamide were subsequently selected for testing in real DAPT nitrations as possible alternatives to urea.

TABLE 1. Assessment of Potential Exotherm Suppressants

	mol	formaldehyde source	mol	exotherm time^a (min)	 temp.^{b} (°C)	evidenc chemica
	-	paraformaldehyde	0.16	18	64	y
	-	trioxan	0.053	34	52	y
	0.1	paraformaldehyde	0.16	-	-	n
	0.1	trioxan	0.053	5	32.5	n
	0.1	paraformaldehyde	0.16	0	33.5	y
	0.1	paraformaldehyde	0.16	22	34.5	n
	0.1	trioxan	0.1	11.5	$>45^c$	y
	0.05	paraformaldehyde	0.16	21	45.5	n
	0.1	paraformaldehyde	0.16	21	36.5	n
	0.2	paraformaldehyde	0.16	17	33.5	n
ide ide	0.1	none	-	c	c	y
ide	0.05	none	-	<0	55	y
ide	0.05	paraformaldehyde	trace	0	$>48^c$	y
monium	0.1	paraformaldehyde	trace	0	$>33.5^c$	y
	0.05	paraformaldehyde	0.16	5	55	y

ter the addition of the formaldehyde source   b: reaction was performed at 30
n terminated

Nitrolysis of DAPT in the Presence of Potential Exotherm Suppressants

Nitrolysis with 10 equivalents of HNO_3 without an exotherm suppressant behaved as described[2] although the yields were somewhat lower (Table 2, runs 1 and 2). Nitrolysis with 3.3 equivalents of HNO_3, again without an exotherm suppressant, also behaved as described,[3,4] the time before the exotherm and the severity of the exotherm being dependant upon the reaction temperature (Table 2, runs 3-5). Nitrolysis with 3.3 equivalents of HNO_3 in the presence of 1 equivalent of urea behaved as described by Coburn and Benziger[3,4] ie no exotherm was observed. The isolated yield of DADN was however significantly lower than reported.[3,4]

When the nitrolysis was performed with 3.3 equivalents of HNO_3 in the presence of the two potential exotherm suppressants formamide and acetamide (1 equivalent, Table 2, runs 8 and 9 respectively), small, easily controllable exotherms were observed (30 → 39 and 30 → 37°C respectively) and the yields of DADN were comparable to those obtained in the presence of urea. Both formamide and acetamide therefore passed the second selection procedure for alternative exotherm suppressants in the DAPT nitrolysis.

The quality of the DADN produced by the above nitrolyses was then assessed (Table 3). Analysis by HPLC of the DADN from all 9 runs showed that DADN was the predominant 'visible' component (>98% in all cases). However when the results were analysed using

TABLE 2. Nitration of DAPT: Reaction Conditions

conc.	HNO_3/hexamine molar ratio	reaction temp. (°C)	reaction time[a] (min)	additive[b]	exothe (°C)
	10	18-20	70	none	none
	10	18-20	70	none	none
	3.3	20	81.5	none	35
	3.3	30	21.5	none	66[c]
	3.3	30	28.5	none	70[c]
	3.3	30	23	urea	none
	3.3	30	22.5	urea	none
	3.3	30	32	formamide	39
	3.3	30	34.5	acetamide	37

n time plus time to exotherm (if any) b: 1 molar equivalent

m with gassing and foaming

TABLE 3. Nitration of DAPT - Product Data

purity by HPLC (%) % of all peaks	external standard[a]	m.p.[b] (°C)	onset of melting [c] (°C
99.4	96.3	259.6-260.3	274.4
99.5	96.5	259.3-260.3	276.8
99.6	98.0	264.4-264.9	277.6
99.6	101.1	264.1-264.4	277.1
99.6	98.8	263.1-263.6	277.2
99.1	89.0	259.4-260.2	275.4
98.4	88.0	258.9-260.0	275.6
99.6	99.0	261.0-261.5	276.2
99.7	96.4	261.4-261.7	277.9

using recrystallised DADN as an external standard

3°C/min; recrystallised DADN had m.p. 263.0-263.8°C

20°C/min; onset defined as temperature when melting endotherm reached 1W/g; recrystallised DADN had onset temperature 278.7°C recrystallised DADN as an external standard, it became apparent that the DADN-content of the products from runs 6 and 7 (with urea added) was considerably lower than this (<90%). By contrast, the DADN-content of the other products, including those from reactions where formamide or acetamide had been present, was high (>95%).

This difference in purity was also reflected in the onset of melting as measured by DSC (20K/min), and in the melting point (capillary tube), although the latter is less reliable due to the amount of decomposition which occurs before melting at the slow rate of heating involved (3K/min). The products from runs 6 and 7 (urea addition) exhibited lower melting onset temperatures than those from runs 8 and 9 (formamide and acetamide addition respectively). Furthermore, recrystallisation of the product from run 6 gave a lower recovery of DADN than that from run 9. The recrystallised material from run 9 was again purer than that from run 6 according to DSC analysis.

The recrystallised DADN from run 9, on treatment with N_2O_5/HNO_3, gave HMX in good yield.[6] Depending upon the exact reaction conditions, the HMX could be obtained in either the β or the α crystal form, as previously observed in the nitrolysis of TAT (1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane).[6,7]

CONCLUSIONS

The use of formamide and acetamide as exotherm suppressants in the nitrolysis of DAPT was found to be almost as effective as urea, and the resultant DADN was found to be purer than that when urea was used. The yields with all three additives were comparable. Any small unsuppressed exothermic behaviour encountered when formamide and acetamide are used should not be a problem in scale up.

EXPERIMENTAL

Assessment of Potential Exotherm Suppressants

A mixed acid consisting of H_2SO_4 (221g, 2.25mol), HNO_3 (6.93g, 0.11mol) and H_2O (4.7g, 0.26mol) was transferred to a 500ml r.b. flask fitted with a thermometer and mechanical stirrer. Acetic acid (20.4g, 0.34mol) was added at 10-20°C, followed by the potential exotherm suppressant (0.05-0.2mol). The flask was then placed in a water bath at 30°C and allowed to equilibrate. Whilst still in the water bath, paraformaldehyde (4.8g ≡ 0.16mol formaldehyde; in some experiments trioxan instead of paraformaldehyde was used) was added and the temperature of the solution was recorded against time. Any physical changes were also noted. When no exotherm suppressant was added, the temperature rose to 64°C after 18min.

The following potential exotherm suppressants were tested: urea, thiourea, formamide, acetamide, semicarbazide hydrochloride and acetate, hydroxylammonium acetate, dimedone. The results are given in Table 1. Of the compounds tested only urea, formamide and acetamide showed potential as exotherm suppressants.

DAPT Nitration

The nitration procedures were adaptations of those used previously.[2,3,4]

(i) With an Excess of Nitrating Agent

Hexamine (14.0g, 0.1mol) and ammonium acetate (6.2g, 0.081mol) were stirred into water (7.0g, 0.39mol) contained in a 50ml r.b. flask held at 5-10°C. Acetic anhydride (30.6g, 0.3mol) was added dropwise with stirring during 60min whilst maintaining the temperature at 5-10°C. The resultant clear solution of DAPT was stirred for a further 30min and then transferred to a dropping funnel and added dropwise, with mechanical stirring, during 80min to a mixture of 99% HNO_3 (63g, 1.00mol) and 96% H_2SO_4 (221g, 2.25mol) maintained at 18-20°C. After the addition the solution was maintained at 20°C for a further 20min and then poured onto ice (1000g) with vigorous stirring. The mixture was diluted with cold water (1500ml), the product was filtered off and washed thoroughly with water, and then dried. For results see Table 2, runs 1 and 2.

(ii) With a Near-Stoichiometric Amount of Nitrating Agent

Hexamine (14.0g, 0.1mol) and ammonium acetate (6.2g, 0.081mol) were stirred into water (2.5g, 0.139mol) contained in a 50ml r.b. flask held at 5-10°C. Acetic anhydride (25.5g, 0.25mol) was added dropwise with stirring during 60min whilst maintaining the temperature at 5-10°C. If required, an exotherm suppressant was added to the resultant clear solution of DAPT at this stage and then the solution was transferred to a dropping funnel. It was then added dropwise, with mechanical stirring, during 6min to a mixture of 90% HNO_3 (23.1g, 0.33mol) and 98% H_2SO_4 (221g, 2.25mol) maintained at 30-35°C by cooling in an ice/water bath. After the addition the solution was maintained at 30°C for the remainder of the reaction period (see Table 2) and then poured onto ice (1000g) with vigorous stirring. The mixture was diluted with cold water (1500ml), the product was filtered off and washed thoroughly with water (5x250ml), and then dried. For results see Table 2, runs 3-9.

The products from runs 6 and 9 were purified by recrystallisation from nitromethane (5.0g/350ml); the product from run 6 (urea addition) gave some undissolved material which was filtered off to leave a light brown solution; the product from run 9 (acetamide addition) gave only a slight amount of undissolved material which was filtered off to leave an almost colourless solution. The recrystallised material was filtered off and washed with nitromethane (3x10ml). Yield: 84% from run 6, 89% from run 9.

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