TRIMETHYLENE TRINITROSAMINE ("TMTN")

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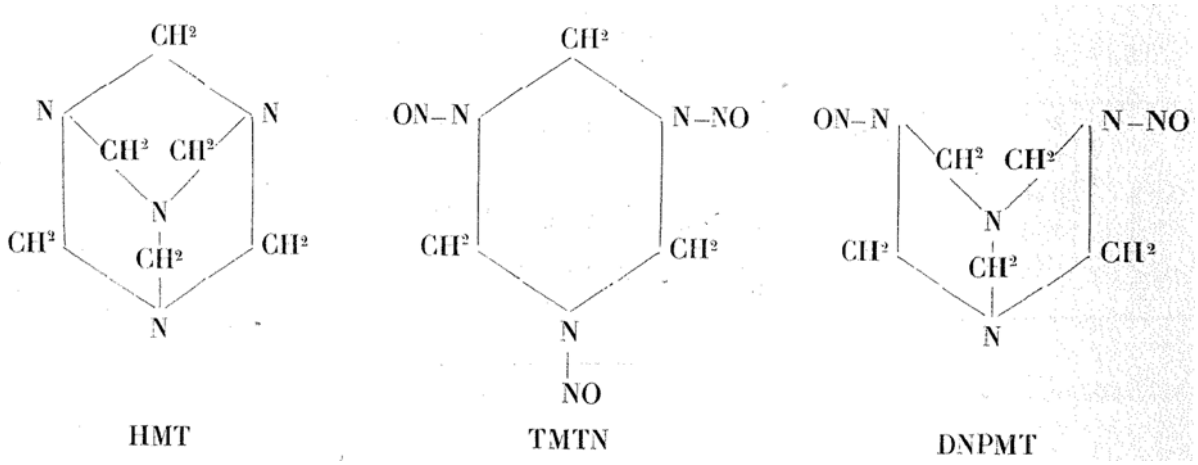
translation by pdb

Studies, suspended in 1935 because the product had been suspected to be somewhat unstable, were resumed in 1939, after it had been discovered that a TMTN sample had shown an excellent state of conservation after 3-year storage.

1. Preparation by quick mix

Nitrous acid reacts with hexamethylenetetramine ("HMT") in water solution to give TMTN or/and dinitrosopentamethylenetetramine ("DNPMT"), depending on the experimental conditions, and especially the acid used to generate nitrous acid from NaNO2.



Tests have been conducted, which consists in preparing water solutions of (1) HMT+NaNO2, (2) H2SO4, chilling these solutions with an ice-salt bath, and mixing them at once in a beaker with strong stirring ➔ a white-yellowish foam appears almost instantaneously. It is filtered after 20-30mns, washed with water until neutral and dried.

For 0,2 mol-gr of HMT :

Test #	NaNO2 (mol-gr)	Acid			Volume (ml)	°C	Crop	
		Nature	Total (mol-gr)	Excess (mol-gr)			Weight in gr	Nature
1	1	H2SO4	0,48		1200	2	32	DNPMT
2	1	H2SO4	0,55	0,05	1200	2	24,7	mix
3	1	H2SO4	0,60	0,10	1200	2	23	mix
4	1	H2SO4	0,70	0,20	1200	2	19,6	TMTN
5	1	H2SO4	0,80	0,30	1200	2	19	TMTN
6	1	CH3COOH	1,1		1200	2	18,	DNPMT
7	1	HCl	1,1		1200	2	16,6	TMTN
8	0,6	H2SO4	0,5	0,2	1200	2	16	TMTN
9	0,8	H2SO4	0,6	0,2	1200	2	17,7	TMTN
10	1,2	H2SO4	0,8	0,2	1200	2	20	TMTN
11	1	H2SO4	0,7	0,2	1200	18	16,8	TMTN
12	1	H2SO4	0,7	0,2	1200	40	3,2	TMTN
13	0,6	H2SO4	0,42	0,12	720	2	17	mix
14	0,6	H2SO4	0,52	0,22	720	2	16	TMTN

Effect of acid concentration (#1-5) :

Not enough acid ➔ DNPMT with good yield (86,5% of theory) (#1)
Small excess acid ➔ mix TMTN/DNPMT (#2-3)
More excess acid ➔ TMTN alone (#3-5)

If H2SO4 amount increases, the yield decreases due to decomposition (DNPMT more than TMTN) in acidic environment. Best H2SO4 concentration is 1,6%.

Effect of the nature of the acid used (#2, 6-7) :

Acetic ➔ DNPMT alone, whatever concentration
HCl ➔ TMTN alone
H2SO4 in same conditions than HCl ➔ mix, with better yield

To prepare TMTN alone, a strong acid is required, and H2SO4 gives the best result.

Effect of excess of nitrous acid (#4, 8-10) :

In theory, 0,6 mol-gr of nitrous acid matches 0,2 mol-gr of HMT. But in fact a huge excess is required because of the poor contact between liquid and gaz phases (foam). Best result obtained with 1 to 1,1 mol-gr HNO2 for 0,2 mol-gr HMT (i.e. excess of 70%).

Effect of temperature (#4, 11, 12) :

It is confirmed that the reaction must be conducted at low temperature. Yield in TMTN drops quickly with temperature, especially beyond 20°C (at 40°C, there is production of formaldehyde gas due to decomposition of TMTN by H2SO4). Better yields are likely possible under 0°C, but experiments have not been done because of the difficulty to carry such conditions on industrial scale.

Effect of time of contact :

Most of the crop (95%) is obtained in the first 10 minutes, and 5% during the following 20 minutes. Contact beyond 30 minutes should be avoided, because of the destruction speed, which tends to overpass the formation speed.

Effect of dilution (#2-4, 13, 14) :

With the procedure described earlier, there is no interest to use more concentrated solutions, due to the fact that then the precipitation is faster, but the gas production becomes tumultuous and the foam difficult to cope with. The temperature also rises too much. Thus there is no advantage to favour such a "brutal reaction".

2. Preparation by progressive mix

Non satisfactory attempts have been conducted with a continuous process, intended for industrial scale.

Better yields were obtained with a progressive mix:
- Separate aqueous solutions of HMT, NaNO2 and H2SO4 are prepared and chilled
- HMT and H2SO4 solutions are then mixed at once in a large beaker with strong stirring
- Then, the NaNO2 solution is poured in the mixture ➔ TMTN precipitates
- The whole solution is filtered 20 minutes later and the precipitate washed on filter

For 0,2 mol-gr of HMT :

Test #	NaNO2 (mol-gr)	H2SO4 (mol-gr)	Volume (ml)	Duration of NaNO2 addition	°C	TMTN crop (gr)
15	1	0,6	1200	10 mns	0	21,1
16	1	0,55	1200	10 mns	0	20,8
17	1	0,55	800	10 mns	6	22,2
18	1	0,7	800	10 mns	6	22,5
19	1	0,55	800	5 mns	6	22,6
20	1	0,55	800	20 mns	6	21,4
21	1	0,6	800	5 mns	19	21,2
22	1	0,55	800	5 mns	17	20,5

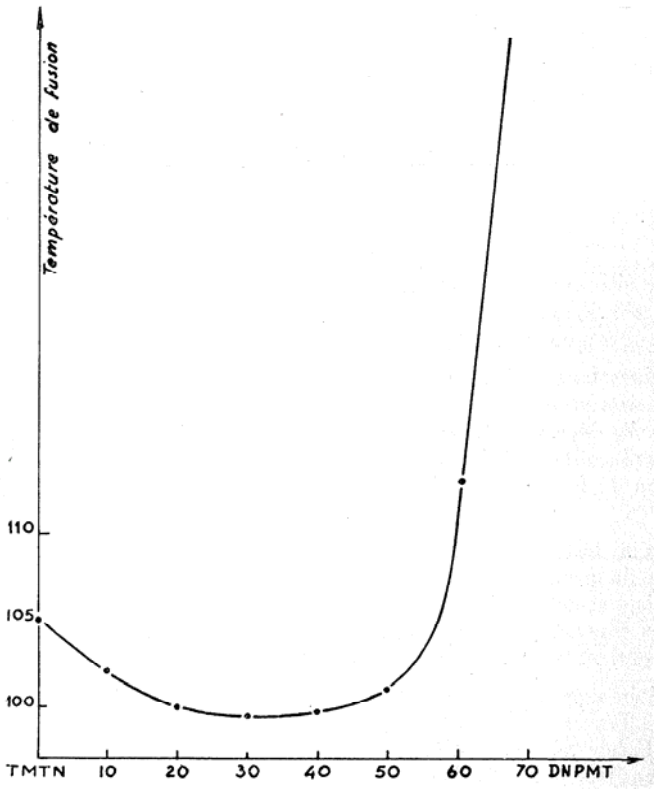
In this process, 0,55 mol-gr H2SO4 is sufficient to get pure TMTN (#16), while the earlier process gave a product rich in DNPMT (#2-3). This process allows a reduction in dilution, which allows a better yield (as shown in #16-17). The speed of addition is not of great importance; however, it should be of 5 mns at least (#17, 19-20). Also, the mixture of HMT with H2SO4 must be prepared at the last minute only, because the latter decomposes the former. The effect of temperature is by far less than in the earlier process; one can operate at 20°C with no significant loss in the yield (#21-22).

As a conclusion, this process must be preferred to the first one, and the best results are obtained by pouring within 5 mns a 1 mol-gr NaNO2 solution in an aqueous solution of 0,2 mol-gr HMT and 0,55 mol-gr H2SO4, the total volume being 800 ml and the temperature maintained under 20°C. Keep stirring for 5 more mns, filter and wash.

[the following part numbered II of the document is of less interest for us, as it refers to 1) HMT preparation from formaldehyde and NH4OH, 2) the theory of the reaction]

3. Properties of TMTN and DNPMT

Fusion temperatures of various TMTN/DNPMT mixtures are given on the graph below:



Very soluble in acetone: 33,4 gr of TMTN in 100 ml acetone at 15°C.

Both TMTN and DNPMT are both decomposed by acids, the latter violently with concentrated acids. A way to separate mixed products in to dissolve them in hot 25% acetic acid: DNPMT decomposes very rapidly, while TMTN is only slightly attacked. The high sensitivity of DNPMT to acids explains why spontaneous and violent decomposition of DNPMT+NH4NO3 mixtures have been observed.

4. Stabilization of TMT

TMTN becomes very stable after crystallisation from methylic alcohol, as shown by the Abel's test. However, TMTN decomposes in a few days under sunlight.

Crystallization from acetone is easier (far more soluble) and gives similar results.

In both cases, stability is obtained by elimination of traces of HNO2.

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