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NITROSATION CLEAVAGE OF HEXAMETHYLENETETRAMINE IN SLIGHTLY ACID MEDIUM FROM THE ASPECT OF THE THERMOCHEMISTRY OF THE NITROSATION AGENT FORMATION

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ABSTRACT

Various sources of nitrosation agent (i.e. dinitrogen trioxide) were used to carry out nitrosation cleavage of hexamethylenetetramine (HMTA) to give 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (DNPT). The sources used were combinations of an acid with alkali metal or calcium nitrites. Relationships were found to exist between the enthalpies of nitrosation agent formation on the one hand and reaction yields and DNPT thermostability on the other. It is inferred that the enthalpy of gaseous dinitrogen trioxide formation from separate combinations of acid with nitrite is the scale of the nitrosation agent activity; taking this enthalpy into consideration, theories on the thermal reactivity of DNPT, also partially involving mechanisms of HMTA nitrosation cleavage , are presented.

INTRODUCTION

Hexamethylenetetramine (HMTA), as an *N*-Mannich base, exhibits a relatively high reactivity (a survey of the significant reactions in technological practice is given in ref. 1). During electrophilic attack on sp^3 nitrogen electrons within its molecule, derivatives of 1,3,5,7-tetraazacyclooctane, 1,3,5-triazacyclohexane, linear systems with a methylene amine grouping within the molecule, or even formaldehyde, possibly methylene glycol and ammonia ions, result, depending upon the agent, reaction temperature and polarity of the medium. The extent of HMTA cleavage in the compounds in the enumerated sequence increases as the agent activity increases, reaction temperature increases or as a result of an increase in the polarity of the medium.

From among the electrophilic substitutions ranging from HMTA to 1,3,5,7-tetraazacyclooctane, or 1,3,5-triazacyclohexane derivatives, nitrolysis has so far been studied [2–4] from the point of view of both reaction mechanism and reaction conditions. Nitrosation cleavage (nitrosolysis) of HMTA has, on the other hand, only been described from the point of view of reaction conditions [5]; depending upon the acidity of the medium, 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (DNPT) or 1,3,5-trinitroso-1,3,5-triazacyclohexane (R-salt) results. The former is the nitrosolysis product in slightly acid medium (pH ≥ 3) [5], while the latter predominates or is the only product of nitrosation cleavage of HMTA at pH ≤ 2 [5].

It is a well-known fact that dinitrogen trioxide is a nitrosation agent in slightly acid medium [6,7]; this oxide acts as an agent in the case of nitrosolysis of HMTA down to DNPT [8]. The most convenient source of dinitrogen trioxide, in the technology of HMTA nitrosation cleavage, is provided by the combination of a mineral acid and an alkali metal nitrite [5,8–31] or calcium nitrite [9,29]. An excess of nitrite is used, this excess acting as a catalyst for nitrosolysis [8,9,18] and, at the same time, as a buffer [8,9].

In much the same way as the nitrating HMTA cleavage, its nitrosolysis is complex, consisting of both simultaneous and consecutive reactions [8,9], viz.

(a) nitrosation cleavage leading to DNPT, R-salt, methylol derivatives, or formaldehyde;

(b) hydrolytic reactions leading to secondary and primary amines, or possibly even ammonia, methylol derivatives and formaldehyde. These processes are preferred in media possessing high water activity and a higher concentration of protons;

(c) neutralization reactions whose final products are ammonium ions;

(d) oxidation reactions always taking place in a reaction mixture: they are conditioned by the instability of the $CH_2O–HNO_2$ [8,9,32] and $NH_4^+–NO_2^-$ [8,33] systems producing CO_2, HCOOH, NO, N_2 and H_2O.

The above survey does not include secondary reactions of the final products of separate types of reaction e.g. disintegration of *N*-methylolnitrosamines. Also the disproportionation reactions of nitrous acid [34,35], or dinitrogen trioxide [34,35] have not been mentioned.

To the above secondary reactions, DNPT degradation in the reaction mixture is also added. During nitrosolysis, DNPT forms a suspension due to its very low solubility in the reaction medium. Its nucleation is influenced by the presence of ions and some organic compounds in the reaction mixture [8,9]. Being a typical *N*-Mannich base, DNPT is easily liable to acidolysis, particularly in solution [36]; its decomposition by water occurs readily under normal conditions [36]. On the other hand, due to the stabilizing effect of the crystal lattice, in the solid state DNPT exhibits a higher chemical stability than that corresponding to its molecular structure [8]. Therefore the yield of the HMTA nitrosolysis procedure is largely dependent upon the DNPT nucleation rate from the reaction mixture; a decisive role in this process is played by macrokinetic factors, in particular the method of mixing the reaction mixture [22].

It is well known that some anions exhibit a catalytic influence upon nitrosation of secondary and tertiary amines [6,8,37]. The influence exercised by ions upon hydrolysis, or HMTA acidolysis, respectively, is also known [38]; this influence has already been described in the case of DNPT acidolysis [36] and R-salt acidolysis [39]. The influence exercised by ions upon the course of such a complicated nitrosation process from the point of view of secondary reactions as HMTA nitrosolysis has not yet been studied.

Taking thermochemical evaluation of HMTA nitrosation cleavage [8] into account, standard enthalpies (ΔH^0_{298}) of gaseous dinitrogen trioxide formation have been applied within the framework of the present paper to specify the influence of ions upon the yield of the process and quality of DNPT; the calculations of the said enthalpy are based upon the reaction

$$2\,NO_2^- + 2\,H^+ \rightarrow H_2O + N_2O_3 \qquad (I)$$

They were carried out using tabulated standard enthalpies of formation [40,41].

The results of the present work show the influence exercised by nitrosation agent sources upon HMTA nitrosolysis in a slightly acid medium under prevailing constant reaction conditions. The practical application of the reaction discussed above under technologically optimum conditions is the subject of a series of papers [17,19,21–29,31].

EXPERIMENTAL

Nitrosolysis

Nitrosation cleavage of HMTA was carried out in a 750 ml sulfonating flask equipped with a propeller agitator, thermometer and jacket cooler. HMTA (28 g, 0.2 mole) and 140 ml 7.78 mole water were introduced into the flask. Sodium, potassium, or calcium nitrite was added to the solution so obtained. The contents of the flask were then cooled to −10°C and an aqueous solution of the acid added with vigorous stirring in small amounts over a period not exceeding 3 sec (after 4 or 5 sec, DNPT began to separate from the reaction mixture). During the introduction of the acid, the temperature of the reaction mixture was maintained below 10°C by means of cooling.

The amounts of the nitrite and acid were selected so as to make the original molar relationships, related to 1 mole HMTA, form the following ratios: 2.5 mole NO_2^-, 2.3 mole H^+, 38.9 mole of water introduced together with HMTA and NO_2^- and 33.3 mole of water dosed in the form of acid solution.

After introducing all the acid, reaction was allowed to proceed for 10 min at between 9 and 10°C. The acid reaction mixture was then filtered. The DNPT on the filter was washed with 40 ml of water, then with 60 ml of 4% water ammonia and, finally, three times with 40 ml of water. The product was dried in a thin layer for between 32 and 36 h at 40–45°C.

Analogously, nitrosolysis with liquid dinitrogen trioxide was carried out: only 38.9 mole of water and 1.25 mole of dinitrogen trioxide, related to 1 mole HMTA, were introduced into the reaction.

Differential thermal analysis

In order to specify the quality of DNPT from separate nitrosolysis experiments, DTA was used in the manner described by Zeman [42]: the weighed amounts of sample varied by about 0.1 g and the rate of linear temperature increase was 6°C min^{-1}. In this way, the initial T_D values of the exotherms of DNPT and the R-salt content (the method according to Tall [43]) were determined.

RESULTS AND DISCUSSION

The results of HMTA nitrosolyses, based upon the use of various sources of nitrosation agent, are summarized in Table 1. By analysis of the mutual relationship of ΔH^0_{298} values (of gaseous dinitrogen trioxide formation according to reaction I) and values of α, the degree of conversion of HMTA to DNPT, linear dependences were obtained (see Fig. 1) which are expressed generally by

$$\Delta H^0_{298} = b\alpha + a \tag{1}$$

From Fig. 1, it is obvious that the form of eqn. (1) for the use of acetic acid in nitrosolysis is relatively well correlated with the data obtained from HMTA nitrosation cleavage by means of liquid N_2O_3 (Table 1, nitrosolysis No. 12); ΔH^0_{298} is, in this case, represented by the heat of evaporation of the dinitrogen trioxide.

As seen from Fig. 1, eqn. (1) exhibits separate forms for nitrosolyses using (a) mineral acids and (b) acetic acid. Outside the two separate forms of eqn. (1) are the data for nitrosolysis 16 (see Table 1 and Fig. 1), i.e. the data for the use of formic acid. These differences are due to different strengths of the acids: the acids with

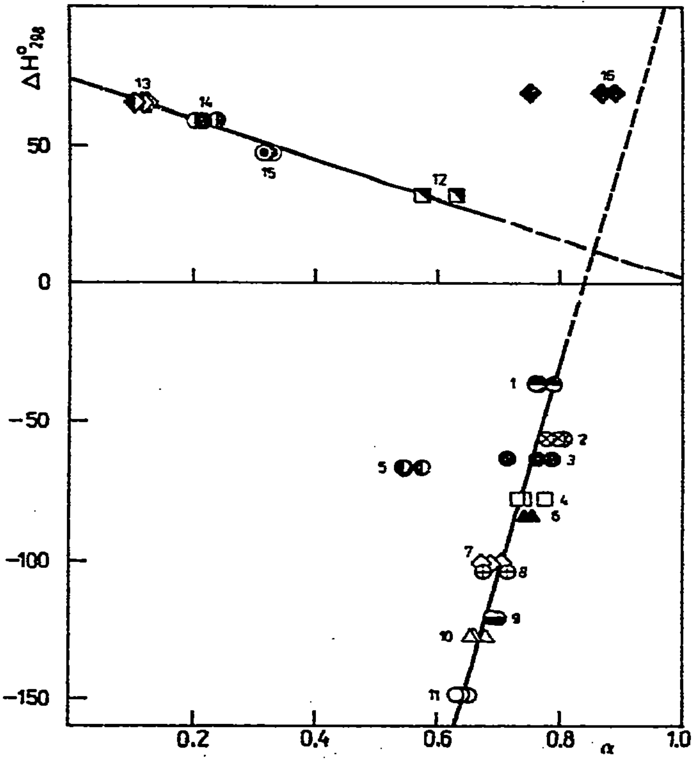

Fig. 1. Graphic representation of eqn. (1). The numbers refer to the nitrosolysis numbers given in Table 1.

TABLE 1

Survey of results

Nitrosolysis no.	Source of nitrosation agent			ΔH^0_{298} [a] (kJ mole^{-1})	Degree of conversion of HMTA (α)	Quality of DNPT	
	Acid	Nitrite	By-product			R-salt content (%.wt)	Initial of exotherm T_D (°C)
1	Phosphoric	Potassium	KH_2PO_4	−35.79	0.7605	2.90	115.7
					0.7657	3.20	117.8
					0.7926	3.05	118.6
2	Sulfuric	Sodium	Na_2SO_4	−56.26	0.8069	1.85	120.0
					0.7773	1.60	122.0
					0.7961	1.50	121.3
3	Perchloric	Potassium	$KClO_4$	−63.38	0.7142 [b]		
					0.7629 [b]		
					0.7873 [b]		
4	Nitric	Sodium	$NaNO_3$	-70.79	0.7396	1.85	127.7
					0.7746	1.60	130.0
					0.7316	1.50	128.4
5	Phosphoric	Sodium	Na_2HPO_4	−68.8	0.5433	0.0	148.1
					0.5460	0.0	148.9
					0.5729	0.0	151.0
6	Sulfuric	Potassium	K_2SO_4	−83.48	0.7423	1.68	125.2
					0.7423	1.20	129.5
					0.7558	1.30	128.3
7	Nitric	Potassium	KNO_3	−100.77	0.6727	0.80	133.8
					0.6885	0.90	133.1
					0.7047	1.10	134.0
8	Nitric	Calcium	$Ca(NO_3)_2$	−102.59	0.6751	1.00	124.8
					0.7154	1.00	124.1
					0.7154	0.80	123.5
9	Hydrochloric	Sodium	NaCl	−120.74	0.6993	0.15	133.1
					0.6966	0.10	137.0
					0.6939	0.13	134.2
10	Hydrochloric	Calcium	$CaCl_2$	−125.54	0.6778	2.00	123.2
					0.6610	1.90	124.8
					0.6562	2.10	122.1
11	Hydrochloric	Potassium	KCl	−148.54	0.6320	3.60	125.8
					0.6401	3.00	126.6
					0.6509	3.45	124.1
12	Liquid N_2O_3		HNO_2	32.40 [c]	0.6331	4.10	125.0
					0.5763	4.30	123.7
13	Acetic	Sodium	CH_3COONa	65.39	0.1051	0.0	149.1
					0.1251	0.0	149.9
					0.1201	0.0	148.0

TABLE I (continued)

Nitrosolysis no.	Source of nitrosation agent			ΔH^0_{298} [a] (kJ mole^{-1})	Degree of conversion of HMTA (α)	Quality of DNPT	
	Acid	Nitrite	By-product			R-salt content (% wt)	Initial of exotherm T_D (°C)
14	Acetic	Potassium	CH_3COOK	59.20	0.2402	0.0	151.0
					0.2052	0.0	151.9
					0.2177	0.0	150.2
15	Acetic	Calcium	$(CH_3COO)_2Ca$	47.80	0.3178	0.0	144.3
					0.3203	0.0	145.0
					0.3328	0.0	142.4
16	Formic	Sodium	HCOONa	68.90	0.8902	0.0	148.2
					0.8685	0.0	149.0
					0.7522	0.0	147.9

[a] Standard enthalpy of gaseous nitrosating agent (N_2O_3) formation calculated using tabulated standard enthalpies of formation [40,41] of acids and nitrites.

[b] Determined in a mixture of $KClO_4$ with DNPT, which resulted from nitrosolysis, on the basis of extraction by dimethylsulfoxide.

[c] Evaporation heat of dinitrogen trioxide.

dissociation constants close to that of nitrous acid or slightly lower produce the nitrosation agent slowly by means of equilibrium reactions. This means that the difference between the rates of formation, on the one hand, and consumption of dinitrogen trioxide in the reaction, on the other, is essentially lower than in the case of the use of mineral acids. This is also why the datum obtained from nitrosolysis No. 5 does not correlate with the form of eqn. (1) for inorganic acids (the second dissociation constant of phosphoric acid at 0°C is 4.85×10^{-8} [44] compared with the value of 3.20×10^{-4} [44] for nitrous acid). The slower production of the nitrosation agent can result in a higher HMTA consumption in secondary reactions, particularly in hydrolytic reactions.

Equation (1) involves the influence exercised by ions in the reaction mixture not only upon the nitrosation cleavage itself, but also upon the undesirable HMTA hydrolysis and oxidation reactions of dinitrogen trioxide, or nitrous acid, respectively. Nevertheless, it can be concluded that ΔH^0_{298} can, in terms of this relationship and for the use of acids which are stronger than nitrous acid, be taken as the activity scale for nitrosation agents (in general, electrophilic agents).

Linear relationships were also found between the values of ΔH^0_{298} and the R-salt content of DNPT. These relationships are represented in Fig. 2. The dependences mentioned above suggest various points related to the mechanism of R-salt formation: the secondary inorganic products of the reaction in terms of reaction I, namely NaCl, KNO_3, $NaNO_3$, Na_2SO_4 and KH_2PO_4, most probably influence R-salt

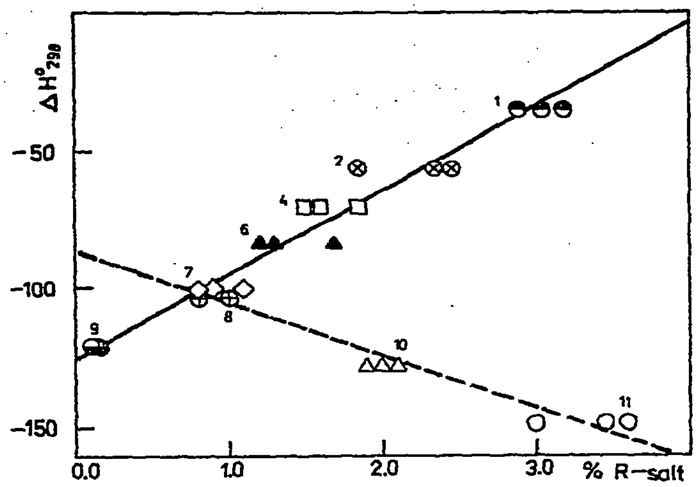

Fig. 2. Graphic representation of the relationship between the enthalpy of nitrosation agent formation (ΔH^0_{298}) and the R-salt mass content within DNPT (% R-salt). The numbers refer to the nitrosolysis numbers given in Table 1.

formation from HMTA largely via their influence upon the polarisation of dinitrogen trioxide, i.e. via parallel secondary cleavage processes. Calcium salts, KCl and HNO_2 (see also Figs. 3 and 4) exercise a negative influence upon the kinetics of DNPT nucleation in the reaction mixture; thus conditions for R-salt formation are also provided by reactions of DNPT.

The presence of the R-salt in DNPT increases its thermal reactivity [8,45,46]. This is quite logical as in this case, the R-salt acts principally as a solvent, i.e. it disturbs the stabilising effect of the DNPT crystal lattice. This destabilisation manifests itself in the DTA traces in the form of shifts in the start of exothermic decomposition (T_D) in DNPT towards lower values. It was found that the R-salt content was inversely proportional to T_D [8,45,46].

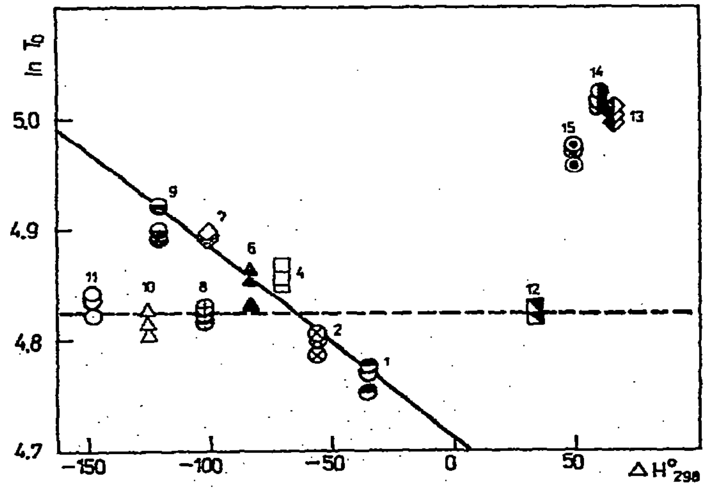

Fig. 3. Graphic representation of eqn. (2). The numbers refer to the nitrosolysis numbers given in Table 1.

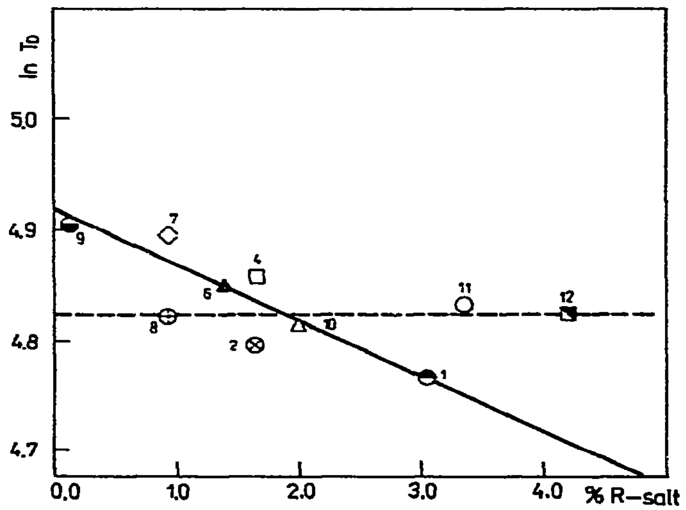

Fig. 4. Graphic representation of the relationship between the initial T_D of the exotherm and the mass content of the R-salt (% R-salt) within DNPT (averaged data are used). The numbers refer to the nitrosolysis numbers given in Table 1.

Within the scope of this work, relationships of general shape were found between the T_D values from non-isothermal DTA and ΔH^0_{298} of nitrosation agent formation.

$$\ln T_D = b_1 \Delta H^0_{298} + a_1 \qquad (2)$$

These relationships are represented in Fig. 3. The shape of Fig. 4 indicates an analogous dependence between the T_D values and the mass content of the R-salt in DNPT.

It follows from Figs. 3 and 4 that the DNPT stability is influenced by another factor in addition to the R-salt content. In view of the spatial arrangement of the DNPT molecule [47–50] (particularly with regard to *syn-* and *anti-* orientation of the nitroso groups [48–50]), this factor is most probably represented by a disturbance of the crystal lattice (i.e. dislocations). What has been stated so far can be supported by the following known facts.

In nitrosolyses with acetic acid, the DNPT separation from the reaction mixture is relatively slow and results in a product in the form of small, but well-developed, crystals. On the other hand, in the case where mineral acids are used, DNPT separation is essentially quicker, the resulting product being reminiscent of an amorphous mass. It can therefore be deduced that DNPT stability from nitrosolyses 13–15 and also from nitrosolyses 5 and 16, is unambiguously the highest (see Fig. 3). Similarly, in nitrosation cleavages 8 and 10–12 where there is a negative influence of DNPT nucleation kinetics in the reaction mixture, the reduced occurrence of dislocations probably compensates for the negative influence of the R-salt on the thermostability of the product (see Figs. 3 and 4).

The relationships arrived at within the framework of the present paper cannot be fully used to assess the influence of the substituted source of the nitrosation agent upon the economy of the process and the quality of the DNPT. The relative representation of secondary reactions during nitrosolysis in the general HMTA consumption, i.e. in the yield of the process, depends upon

(a) temperature (a trivial factor);

(b) the amount of water in the reaction mixture [8,31];

(c) the source of nitrosation agent (see above and refs. 9,22,23 and 29) and, at the same time, upon the excess (contrary to the theory) of the nitrite used [8,9,18,22];

(d) the presence of HMTA hydrolysis products in the reaction as early as at the beginning of the nitrosation cleavage [8,25,28], i.e. on the way the reaction is run under conditions which are reminiscent of the Bachmann conditions of HMTA nitrolysis [2–4,5];

(e) the method of mixing [8,9] or adding [8,19] the raw materials;

(f) the size, shape and degree of filling of the nitrosation unit [8,9,22]; and

(g) the presence in the reaction mixture of surface active substances (i.e. tensides [8,20,52], polyols [8,52] and others);

The above factors can also be influenced separately so as to reduce the secondary nitrosolysis reactions, particularly HMTA hydrolysis, to a minimum. This is also why optimization of the nitrosation HMTA cleavage for different sources of the nitrosation agent [53] results in a somewhat different sequence of corresponding yields [9] than is the case for eqn. (1).

CONCLUSIONS

In nitrosation cleavage of hexamethylenetetramine (HMTA) to 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane (DNPT), the nitrosation agent is dinitrogen trioxide. The scale of the activity of this agent in the given medium can be expressed by the enthalpy of formation of dinitrogen trioxide from the corresponding source, i.e. from a nitrite and an acid stronger than nitrous acid. By means of this enthalpy, the thermostability of the resulting DNPT can also be interpreted and ideas concerning the mechanism of HMTA nitrosolysis can be formulated.

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