

THERMAL ANALYSIS OF NITRAMINOCARBOXYLIC ACIDS AND THEIR SODIUM AND BARIUM SALTS

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The thermal stabilities of nitraminomonocarboxylic acids, nitraminodicarboxylic acids, and their monosodium, disodium and barium salts were studied. The effects of the position of the nitramino group and the aliphatic chain length on the decomposition temperature peak and the pK and ($pK_2 - pK_1$) values were followed. The experimental results revealed that the thermal stabilities of the acids and their pK values are influenced by the relative position of the nitramino group in the molecule. The thermal stabilities of acids and salts increase with increasing chain length. A lower value of pK was found to correspond to a lower thermal stability of the acids. Barium salts of nitraminodicarboxylic acids were subjected to drop-hammer sensitivity and nearly all of them were found to grow more active.

Nitraminomono- and dicarboxylic acids form a most interesting group of compounds and much attention has been paid to their syntheses in recent years. These compounds are starting materials for nitroisocyanate and diisocyanate, nitropolyester, and nitropolyurethane preparations. There are however, no data in the literature as regards the thermal stabilities of the nitraminocarboxylic acids or their salts.

In this paper, the results of thermal stability measurements on 38 nitraminocarboxylic acids and their monosodium, disodium and barium salts are presented. Though only a limited number of compounds were suitable from a structural aspect, useful conclusions, were arrived at showing the influence of the chemical structure on the pK value for the acids and the position of the decomposition temperature peak.

Experimental

Nitraminomono- and dicarboxylic acids were prepared either by the given method or by methods already reported (see references in Tables 1 and 2). The purities of the acids were checked by determination of the neutralization equivalent, by paper-chromatography and by comparing their melting points with the published data.

Disodium salts were prepared by neutralization of the acid with the stoichiometric amount of 0.1 *N* NaOH. Monosodium salts were prepared by mixing

aqueous solutions of the disodium salt with the stoichiometric amount of free acid. The sodium contents of the monosodium salts were determined by flame-photometry. Barium salts were prepared by neutralization of the corresponding acid with 0.1 *N* Ba(OH)₂. The salt solutions thus obtained were concentrated by evaporating in vacuum at room temperature and the salts were then crystallized. The prepared salts were kept in a desiccator over NaOH. The water content was determined according to Wernimont and Hopkinson [1]. The DTA and TG measurements were carried out with a Derivatograph. The compounds were tested in air with a heating rate of 6°/min up to 300°. The sample weight was 100 mg. Glass powder was used as reference material.

The *pK* and (*pK*₂ - *pK*₁) values were taken from paper [2]. The impact sensitivities of the barium salts were determined with a Kast drop-hammer (with the "up and down" method) for salts of acids 5, 8 and 9. Due to the low sensitivities of the remaining compounds, it was impossible to determine their sensitivities by the same method; these were therefore determined from the drop-height of 100 cm, the result being expressed in % activation cases from 20 attempts (excepting compound 14). A 5 kg hammer was used for this purpose. The samples, which were stored in a desiccator over NaOH were weight into tin foil, 0.02 g on each occasion. Decomposition of the compound served as an indication of the activation. The decomposition was not accompanied by a sound effect.

Results and discussion

Thermal properties of nitraminomonocarboxylic acids

Results on the thermal stabilities of nitraminomonocarboxylic acids of the type CH₃N(NO₂)(CH₂)_nCOOH for *n* = 1 - 2 and CH₃N(NO₂)(CH₂)_nN(NO₂)(CH₂)_mCOOH for *n* = 2 and *m* = 1 - 2 are given in Table 1. It follows that with increasing chain length of the acid the exo peak is shifted towards higher temperatures (compounds 1 and 2, 3 and 4). As pointed out in connection with the study of the *pK* values of nitraminocarboxylic acids [2], substitution of the methylene group in the chain of aliphatic acid by a nitramino group cause the expected increase in

Table 1
Thermal properties of nitraminomonocarboxylic acids

Compound	Acid	Ref- erence	DTA peak tempera- ture °		<i>pK</i> H ₂ O	Weight loss, %
			Endother- mic	Exother- mic		
1	3-Nitro-3-azabutanoic	5	103	182	3.19	92
2	4-Nitro-4-azapentanoic	6	66, 262	243	4.16	92
3	3,6-Dinitro-3,6-diazaheptanoic	2	126	183	3.23	84
4	4,7-Dinitro-4,7-diazaoctanoic	2	129	238	4.21	85

its acidity but, at the same time a decrease in its thermal stability. The comparison of the pK of butanoic acid (4.85) with that of 3-nitro-3-azabutanoic acid (3.19) and that of heptanoic acid (4.89) with that of 3,6-dinitro-3,6 diazaheptanoic acid (3.23), reveals that the pK difference in the case of the two pairs is the same, the value being 1.66, implying that insertion of another nitramino group into the chain has no influence upon its acidity. A similar phenomenon is manifested in the values of the decomposition temperatures of the substances under consideration; these are practically the same (compounds 1 and 3 : 182° and 183°) or very near (compounds 2 and 4 : 243° and 238°).

4-nitro-4-azapentanoic acid (compound 2) undergoes distillation when heated, with decomposition. A part of the acid always remains in the crucible in the form of carbonaceous decomposition residue.

Thermal properties of nitraminodicarboxylic acids

The acids studied involved a range of compounds having 1, 2 or 3 nitramino groups in the molecule, the total number of atoms in the chain being 5–18. The acids can be divided into the following groups with regard to their general formulae.

A) Acids of the type $\text{HOOCCH}_2\text{N}(\text{NO}_2)(\text{CH}_2)_n\text{N}(\text{NO}_2)\text{CH}_2\text{COOH}$ for $n = 1-3$ (Table 2, compds. 8–10).

These acids exhibit some different features from the regularities valid for most acids. The increasing chain length causes a decrease of ($pK_2 - pK_1$) but no increase in thermal stability is involved. This can be accounted for by the behaviour of these acids (compounds 8–10) when heated. Acids 8 and 9 do not melt, and the DTA and TG curves obtained reveal that their decompositions commence in the solid state. Acid 10, unlike acids 8 and 9 does melt under the experimental conditions; as decomposition proceeds more quickly in the liquid state, the lower value of the exopeak can be accounted for. It is typical for the acids which have their nitramino group isolated from the carboxyl by one methylene, either that they decompose in the solid state or that the melting endotherm changes smoothly into an exotherm.

B) Acids of the type $\text{HOOCCH}_2\text{CH}_2\text{N}(\text{NO}_2)(\text{CH}_2)_n\text{N}(\text{NO}_2)\text{CH}_2\text{CH}_2\text{COOH}$ for $n = 1-3, 6$ and 10 (Table 2, compounds 11–15) and $\text{HOOC}(\text{CH}_2)_n\text{N}(\text{NO}_2) - (\text{CH}_2)_m\text{COOH}$ for $n = m = 1, n = 1$ and $m = 2, n = m = 2$ (Table 2, compds. 5–7). In the investigation of the influence of the chemical structure of the acid upon the position of the decomposition temperature peak, the same conclusions were drawn as in the case of the nitraminomonocarboxylic acids. Thermal stability increases proportionally to the chain length (Table 2, compounds 5–7, 12–15) and inversely proportionally to the ($pK_2 - pK_1$) decrease. The nitramino group can therefore be said to have strong electron acceptor properties in its aliphatic chain, which make themselves felt in the form of an inductive effect through the electron molecules skeleton in the acidity increase of the carboxyls [3], though a free electron pair is present on the amine nitrogen. As the inductive effect de-

Table 2
Thermal properties of nitraminodicarboxylic acids

Compound	Acid	Ref- erence	DTA peak tempera- ture °		$(pK_2 - pK_1)_{H_2O}$	Weight loss, %
			Endother- mic	Exother- mic		
5	3-Nitro-3-azapentanedioic	7	154	167	1.91	87
6	3-Nitro-3-azahexanedioic	8	160	184	1.48	87
7	4-Nitro-4-azaheptanedioic	9	170, 265	250, 277	1.30	89
8	3,5-Dinitro-3,5-diaza- heptanedioic	10	—	198	1.24	94
9	3,6-Dinitro-3,6-diaza- octanedioic	11	—	197	1.11	90
10	3,7-Dinitro-3,7-diaza- nonanedioic	2	150	180	1.02	94
11	4,6-Dinitro-4,6-diaza- nonanedioic	13	203	228, 236	0.96	84
12	4,7-Dinitro-4,7-diazadeca- nedioic	12	148	248	0.95	82
13	4,8-Dinitro-4,8-diazaun- decanedioic	14	152, 254	248, 262	0.91	86
14	4,11-Dinitro-4,11-diaza- tetradecanedioic	2	138, 258	251, 268	0.73	81
15	4,15-Dinitro-4,15-diaza- octadecanedioic	2	136, 256	250, 270	—	81
16	3,5,7-Trinitro-3,5,7- triazanonanedioic	10	205	239	—	84

creases with lengthening aliphatic chain, the acidity decrease of the carboxyl can also be explained by an increasing number of methylene groups between the carboxyls and the nitramino groups. It should be noted however that the positive influence upon the thermal stabilities of acids having two nitramino groups in the molecule which are separated by a growing number of methylene groups (compounds 12–15) is not so pronounced (about $12^\circ/\text{CH}_2$), and is in agreement with the small ($pK_2 - pK_1$) difference, which in these compounds varies within the range 0.94–0.73.

A weakened inductive effect by the nitro group upon the carboxyl, due to its isolation from the carboxyl by two (not one) methylene groups, brings about an acidity decrease and at the same time an essential thermal stability increase, as seen from Table 2 in the acid pairs 8 and 11, 9 and 12 and 10 and 13. This stability increase amounts on the average to $26^\circ/\text{CH}_2$. The melting point endopeak of these acids is separated from the exopeak by a relatively long stability period.

C) Acids of the type $\text{HOCH}_2[\text{N}(\text{NO}_2)\text{CH}_2]_n\text{COOH}$ for $n = 1-3$ (Table 2, compds. 5, 8 and 16).

In homologous dicarboxylic acids, differing from each other by a varying number of homologous increments $-\text{CH}_2\text{N}(\text{NO}_2)-$ (1–3, compounds 5, 8 and 16) the

thermal stability increases in parallel with the increase of the number of these increments in the molecule.

Unlike the non-substituted paraffinic dicarboxylic acids (C_3-C_{10}) (distilling during DTA) (except for C_9 and C_{10}) [4], all nitramino analogues undergo decomposition, an unburnt carbonaceous residue remaining in the crucible.

Thermal properties of monosodium salts of nitraminodicarboxylic acids

Monosodium salts of nitraminodicarboxylic acids were prepared in the anhydrous state; their thermal characteristics are given in Table 3.

Table 3
Thermal properties of monosodium salts of nitraminodicarboxylic acids

Compound	Monosodium salt of acid	Na content, %		DTA peak temperature, °		Weight loss, %
		Calc.	Found	Endothermic	Exothermic	
17	3-Nitro-3-azahexanedioic	10.74	10.62	—	192	68
18	4-Nitro-4-azaheptanedioic	10.08	9.88	150, 232	250, 292	54
19	3,5-Dinitro-3,5-diazaheptanedioic	8.36	8.36	—	179	89
20	3,6-Dinitro-3,6-diazaoctanedioic	7.98	7.68	—	190	89
21	4,6-Dinitro-4,6-diazanonanedioic	7.61	7.55	185	225	72
22	4,7-Dinitro-4,7-diazadecanedioic	7.28	7.27	129, 208	242	74
23	4,8-Dinitro-4,8-diazaundecanedioic	6.97	6.76	167	242	71

Two structurally different categories of compounds were measured: One group involved salts of acids with nitramino groups isolated from the carboxyls by one methylene group. These salts (compounds 17, 19 and 20) did not melt in the course of their heating, their exothermic decomposition proceeding quickly, and practically explosively. The second group involved salts of acids having two methylene groups between the nitramino and carboxyl groups. These salts (compounds 18, 21–23) were much more thermally stable, melting in the course of heating; their exothermic decomposition was not so intensive. Comparison of the two groups of compounds reveals a positive influence of chain prolongation between the nitramino and carboxyl groups upon the exopeak.

Thermal properties of disodium and barium salts of nitraminocarboxylic acids

Results of thermal stability measurements on disodium and barium salts of dicarboxylic acids are summarized in Tables 4 and 5.

Most disodium salts contained crystal water (excepting salt 25, 27 and 28) as did the barium salts (excepting 35, 37 and 38 substances). The experimental

results reveal that the salts are thermally stable up to relatively higher temperatures on losing crystal water. The DTA curves for compounds 26, 30, 31 and 37 clearly show the melting endotherm, which changes suddenly into the exotherm of the decomposition process. Similarly as in the starting dicarboxylic acids, in the

Table 4
Thermal properties of disodium salts of nitraminodicarboxylic acids

Compound	Disodium salt of acid	DTA peak temperature, °		Weight loss, %
		Endothermic	Exothermic	
24	3-Nitro-3-azapentanedioic	98	232	46
25	3-Nitro-3-azahexanedioic	—	255	48
26	4-Nitro-4-azaheptanedioic	92, 241	253, 298	36
27	3,5-Dinitro-3,5-diazaheptanedioic	—	235	89
28	3,6-Dinitro-3,6-diazaoctanedioic	—	253	90
29	3,7-Dinitro-3,7-diazanonanedioic	128	242	88
30	4,7-Dinitro-4,7-diazadecanedioic	82, 98, 236	244	75
31	4,8-Dinitro-4,8-diazaundecanedioic	108, 118, 232	247	65
32	4,11-Dinitro-4,11-diazatetradecanedioic	77, 120	250	48

Table 5
Thermal properties of barium salts of nitraminodicarboxylic acids

Compound	Barium salt of acid	DTA peak temperature, °		Weight loss, %
		Endothermic	Exothermic	
33	4-Nitro-4-azaheptanedioic	115	275	35
34	3,5-Dinitro-3,5-diazaheptanedioic	120	226	39
35	3,6-Dinitro-3,6-diazaoctanedioic	—	239	40
36	4,7-Dinitro-4,7-diazadecanedioic	160	252	42
37	4,8-Dinitro-4,8-diazaundecanedioic	250	260	43
38	4,11-Dinitro-4,11-diazatetradecanedioic	—	268	49

neutral salts of these acids the thermal stability is positively influenced by the increasing chain lengths between the carboxyls and between the carboxyls and nitramino groups.

Some barium salts were not measured because of their possible explosion under the given conditions.

Sensitivity of barium salts of nitraminodicarboxylic acids to impact

Table 6 contain data obtained on measuring the sensitivities of the barium salts to impact with the Kast drop-hammer. All the barium salts, except the

Table 6

Sensitivity of barium salts of nitraminodicarboxylic acids to impact on Kast's drop-hammer

Barium salt of acid	Fall height 100 cm, total number of attempts	Fall height \bar{x} , cm	Standard deviation $S_{\bar{x}}$	Activation, %
3-Nitro-3-azapentanedioic	—	77	1.0	50
3-Nitro-3-azahexanedioic	20	—	—	20
4-Nitro-4-azaheptanedioic	20	—	—	0
3,5-Dinitro-3,5-diazaheptanedioic	—	41	1.5	50
3,6-Dinitro-3,6-diazaoctanedioic	—	76	1.0	50
4,7-Dinitro-4,7-diazadecanedioic	20	—	—	25
4,8-Dinitro-4,8-diazaundecanedioic	20	—	—	25
4,11-Dinitro-4,11-diazatetradecanedioic	7	—	—	28.6
4,15-Dinitro-4,15-diazaoctadecanedioic	20	—	—	20

\bar{x} — Fall-height for 50% probability of activation

4-nitro-4-azaheptanedioic acid salt, were activated, their decomposition taking place without any sound effect. It is obvious from Table 6 that salts of the acids which contain a nitramino group isolated from the carboxyl by one methylene are more sensitive to impact than analogous salts of acids containing two methylenes.

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References

1. G. WERNIMONT and F. J. HOPKINSON, *Ind. Eng. Chem. Anal. Ed.*, 15 (1943) 273.
2. V. KADĚŘÁBEK and K. KALFUS, *Collection Czech. Chem. Commun.*, 41 (1976) 433.
3. H. BECKER, *Einführung in die Elektronentheorie organisch-chemischer Reactionen*, VEB Deutsche Verlag der Wissenschaft, Berlin, 1964.
4. S. GÁL, J. SZAMMER, T. MEISEL, L. ERDEY and L. ÖTVÖS, *Proceedings of the Analytical Conference, Budapest, 1966*.
5. M. B. FRANKEL, *J. Org. Chem.*, 23 (1958) 1812.
6. M. B. FRANKEL and K. KLAGER, *J. Am. Chem. Soc.*, 78 (1956) 5428.
7. A. P. N. FRANCHMONT and J. V. DUBSKY, *Rec. Trav. Chim.*, 36 (1916) 86.

8. V. KADEŘÁBEK, Ph. D. Theses, University of Chemical Technology, Pardubice, 1963.
9. W. J. CHUTE, G. E. DUNN, J. C. MACKENZIE, G. S. MYERS, G. U. R. SMART, J. W. SUGGITT and G. F. WRIGHT, *Can. J. Research B*, 26 (1948) 127.
10. J. DENKSTEIN and V. KADEŘÁBEK, *Collection Czech. Chem. Commun.*, 31 (1966) 2928.
11. V. KADEŘÁBEK and J. DENKSTEIN, *Collection Czech. Chem. Commun.*, 31 (1966) 2915.
12. L. W. KISSINGER and M. SCHWARTZ, *J. Org. Chem.*, 23 (1958) 1342.
13. V. KADEŘÁBEK and J. DENKSTEIN, *Collection Czech. Chem. Commun.*, in press.
14. J. S. IVANOVA, G. F. BOGDANOVA, T. A. ALEXEJEVA and S. S. NOVIKOV, *Izv. Akad. Nauk SSSR, Otd. Chim. Nauk.*, 12 (1962) 2236.

RÉSUMÉ — La stabilité thermique d'une série d'acides nitraminomonocarboxyliques, nitraminodicarboxyliques et de leurs sels monosodiques, bisodiques et barytiques a été étudiée. On a suivi l'influence du groupe nitramino et de la longueur de la chaîne aliphatique sur la position du maximum de la température de décomposition et de la valeur du pK , respectivement ($pK_2 - pK_1$) des acides. Les résultats des mesures ont montré que la stabilité thermique des acides et les valeurs du pK sont influencées par la position relative du groupe nitramino dans la molécule. La stabilité thermique des acides et des sels augmente avec la longueur de chaîne. Il est généralement vérifié qu'une valeur faible du pK correspond à une stabilité thermique plus faible des acides. Les sels de baryum des acides nitraminodicarboxyliques ont été soumis à un essai de sensibilité au marteau tombant. On a établi que presque tous y subissent une activation.

ZUSAMMENFASSUNG — Die thermische Stabilität einer Reihe von Nitraminomonokarbonsäuren, Nitraminodikarbonsäuren und ihrer Mononatrium-, Dinatrium- und Bariumsalze wurde geprüft. Es wurde der Einfluß der Nitraminogruppe und der Länge der aliphatischen Kette auf die Lage des Spitzenwertes der Zersetzungstemperaturen und pK -Werte, beziehungsweise ($pK_2 - pK_1$) der Säuren, untersucht. Die Messergebnisse zeigten, daß die thermische Stabilität der Säuren ebenso wie ihre pK -Werte durch die relative Lage der Nitraminogruppe in Molekül beeinflußt wird. Die thermische Stabilität von Säuren und Salzen nimmt mit zunehmender Kettenlänge zu. Als allgemein erwiesen gilt, daß der niedrigere pK -Wert einer niedrigeren thermischen Stabilität der Säuren entspricht. Die Bariumsalze der Nitraminodikarbonsäuren wurden der Empfindlichkeitsprobe mit dem Fallhammer-Apparat unterworfen. Es wurde ermittelt, daß es fast bei allen zur Aktivierung kommt.

Резюме — Изучена теплостойкость ряда нитраминомоно- и дикарбоновых кислот, а также их монанатриевых, динатриевых и бариевых солей. Исследовалось влияние нитраминовой группы и длины алифатической цепи на положение пика температуры разложения и pK или ($pK_2 - pK_1$) кислот. Установлено, что относительное положение нитраминовой группы в молекуле оказывает влияние на теплостойкость кислот и их pK значения. Теплостойкость кислот и солей увеличивается с удлинением алифатической цепи. Показано, что более низкое значение pK отвечает более низкой теплостойкости кислот. Бариевые соли нитраминодикарбоновых кислот были подвергнуты испытанию чувствительности на падающем молоте. Определено, что почти для всех это приводит к их активации.