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Relationship between the Arrhenius parameters of the low-temperature thermolysis and the ^{13}C and ^{15}N chemical shifts of nitramines

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Abstract

A linear relationship is shown to exist between the Arrhenius parameters E and log A of the initial stage of the non-autocatalysed, low-temperature thermolysis and the ^{13}C and ^{15}N chemical shifts of six nitramines. The existence of this relationship is interpreted from the point of view of the primary fragmentation in the thermolysis of the nitramines, i.e. homolysis of the $N-NO_2$ bond. A linear relationship is also found between the heat of explosion (represented as the square of the detonation velocity and the ^{15}N chemical shift of the nitro groups of four of the nitramines and as well as the ^{13}C chemical shift in the derivatives with the methylene–nitramine grouping within their molecules.

INTRODUCTION

The study of the relationships between NMR chemical shifts of organic polynitro compounds and certain characteristics of their reactivity or their thermochemical parameters is important for the interpretation of the reactivities of these compounds and their explosive behaviour. One of the earliest papers [1] dealing with this phenomenon specified correlations between the ^{1}H and ^{13}C shifts of eight polynitrobenzenes, on the one hand, and their heats of combustion and formation, on the other hand. Patent protection has been obtained for the application of the ^{13}C NMR spectroscopy of polynitroarenes, and also of a number of cyclic nitramines to the determination of their detonation velocities [2] and heat of explosion [3]. The relationships between the shifts of *para*-^{1}H in trinitroaromatic molecules and the impact sensitivities and the detonation velocities of the corresponding nitro compounds have been found by Owens [4].

An already established and proved fact is the existence of straightforward relationships between the characteristics of detonation of organic

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nitro compounds [5–10], or their characteristics of impact sensitivity [11–13], on the one hand, and the characteristics of the low-temperature non-autocatalysed thermolysis of the same compounds, on the other hand. Considering the papers [1–4] already mentioned, a direct relationship should exist between the chemical NMR shifts and the Arrhenius parameters for the previously mentioned thermolysis reactions. This hypothesis is verified in the following paragraphs for nitramines, whose mechanism of thermolysis has been the subject of numerous special reports in the literature [8,11,14–17]. Some attention is also paid to the relationship between the chemical shifts and the characteristics of detonation of these nitro compounds.

SOURCES OF DATA

A survey of the nitramines studied and of the Arrhenius parameters E and log A of their low-temperature non-autocatalysed thermolysis is presented in Table 1. These parameters have been obtained by applying the Soviet manometric method (SMM) [19,20,25–28,31,32], (DSC) [22,24,29], (TGA) [23], mass spectroscopy (MS) see the results of B.B. Goshgarian cited in ref. 30 and IR spectroscopy [20] to the problem under discussion. Table 1 presents values of ^{13}C and ^{15}N chemical shifts taken from ref. 18. Table 1 also includes values of detonation velocities, D, calculated by the method of Kamlet and Jacobs [33] for maximum densities of crystals.

RESULTS

By comparing values of E and chemical shifts, δ, for ^{13}C and ^{15}N, a linear relationship of the form

$$E = a\delta + b \qquad (1)$$

resulted, according to which the nitramines being examined can be divided into a number of groups, according to the state of thermolysis and the molecular structure. The composition of these groups and the coefficients of the corresponding individual forms of eqn. (1) are shown in Table 2.

In an analogous manner, a linear correlation was found between the value of log A and the chemical shift δ, the relation having the general form

$$\log A = a_1\delta + b_1 \qquad (2)$$

The breaking up of the group of nitramines into subgroups is identical with the breaking up according to eqn. (1), and the subgroups together with the coefficients of the corresponding individual forms of eqn. (2) are presented in Table 3.

Comparing the values of the detonation velocity D and the values of chemical shifts, δ, resulted in an equation of the form

$$D^2 = a_2\delta + b_2 \qquad (3)$$

which has, for the set of nitramines considered only a limited validity, as documented in Table 4.

DISCUSSION

To interpret the relationships found, it is necessary to start from the primary fragmentation of nitramine molecules in their thermolysis. In this investigation, owing to selection of unsuitable physical conditions for the thermolysis experiments [17] and/or owing to the incorrect interpretation of the corresponding results (criticism in the case of the kinetic deuterium isotope effect as in ref. 11), invalid discussion is often found in the literature.

It has been proved unambiguously that the primary step of the thermal decomposition of secondary nitramines in both gaseous and condensed states is homolysis of the $N-NO_2$ bond [15,17]. This homolysis is, at the same time, also a limiting stage in the thermolysis of primary nitramines in the gaseous state, whereas their thermolysis in the condensed state is a bimolecular autoprotolytic reaction [19].

In view of the limiting thermal fragmentation of secondary nitramines, the existence of the given individual forms of eqns. (1) and (2) for ^{15}N chemical shifts of nitrogroups (individual forms 1 and 2 in Tables 2 and 3) and amine nitrogen atoms carrying these nitrogroups (individual forms 5 and 6 in Tables 2 and 3) can be understood. The data for dimethylnitramine are not correlated with individual forms 5 and 6 of eqns. (1) and (2) owing to lower shielding of its amine nitrogen atom caused by the inductive and conjugational effect of the nitro group (in contrast to cyclic nitramines or **5**, a negative-induction counter-effect of nitramino groups or of picryl is absent in dimethylnitramine).

The data for the primary nitramine **1** do not correlate in the above-mentioned sense, owing to its primary fragmentation by a bimolecular mechanism (see ref. 19). If, however, individual forms 1 and 2 of eqns. (1) and (2) are applied to calculate the Arrhenius parameters of its hypothetical monomolecular fragmentation in the condensed state, $E = 188.2$ kJ mol^{-1} and log $A = 14.1$ for the solid state decomposition and $E = 153.2$ kJ mol^{-1} and log $A = 14.1$ for the liquid state decomposition result. The published values for nitramine **1** thermolysis in the gaseous state are [19] $E = 175.9$ kJ mol^{-1} and log $A = 14.01$ (within the range 493–553 K).

The individual forms 3 and 4 of eqns. (1) and (2) (^{13}C chemical shifts; see Tables 2 and 3) are concerned with the correlation of the data for dimethylnitramine and cyclic derivatives derived theoretically from it (with

TABLE 1

Survey of the nitramines studied, their ^{13}C and ^{15}N chemical shifts, their Arrhenius parameters of thermolysis and their calculated detonation velocities

Substance (Data) no.	Nitramine	Chemical shift δ [18] (ppm)			Arrhenius parameters of thermolysis						Detonation velocity [33] (km s^{-1})
		^{13}C	^{15}N (nitro groups)	^{15}N (amino nitrogen atoms)	Method of following thermolysis	State of thermal decomposition	Temperature range (K)	E (kJ mol^{-1})	log A (s^{-1})	Reference	
1	N-Monomethylnitramine	32.4	−22.2	−220.2	SMM	Liquid	358–413	128.1	13.0	19	6.699
2	N,N-Dimethylnitramine	40.0	−23.6	−215.6							6.290
(2.1)					IR	Solid		192.5		20	
(2.2)					SMM	Solution		162.4 [a]		20	
(2.3)					Calculated [b]	Liquid		159.8	14.7	This paper	
(2.4)					Calculated [c]	Solid			14.2	This paper	
3	1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX)	62.0	−32.9	−198.1							8.89
(3.1)					Manometric	Liquid	486–572	198.9	18.5	21	
(3.2)					DSC	Liquid	495–525	197.1	18.3	22	
(3.3)					TGA	Liquid	478–493	200.4	18.7	23	
(3.4)					DSC	Liquid	487–513	211.8	19.6	24	
(3.5)					SMM	Solid	423–470	213.5	18.6	25	
(3.6)					SMM	Solid	423–470	217.6	19.1	26	
(3.7)					SMM	Solid	413–463	167.0	11.2	27, 28	

4	1,3,5,7-Tetra-nitro-1,3,5,7-tetraazacyclo-octane (HMX)	64.0	−34.7	−199.1							9.13
(4.1)					Manometric	Liquid	544–587	220.5	19.5	21	
(4.2)					DSC	Liquid	544–558	214.6	18.8	29	
(4.3)					MS	Solid	534–549	209.0	17.8	30	
(4.4)					SMM	Solid	449–503	158.7	11.2	26	
(4.5)	α-HMS				SMM	Solid	403–453	159.0	10.8	28, 31	
(4.6)	β-HMX				SMM	Solid	403–413	159.0	9.2	28, 31	
(4.7)	δ-HMX				SMM	Solid	413–503	159.0	11.3	28, 31	
5	1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclo-octane	69.6	−25.3	−203.7							7.13
(5.1)					Extrapolated	Solid		192.3	16.6	8	
(5.2)					Calculated [d]	Solid		195.1	15.4	This paper	
(5.3)					Calculated [b]	Liquid		167.8	15.4	This paper	
6	1-(Methylnitra-mino)-2,4,6-tri-nitrobenzene	40.8 [f]	−23.1	−208.8							7.77
(6.1)					– [e]	Liquid	403–438	156.9	14.5	32	
(6.2)					Calculated [d]	Solid		190.4	14.6	This paper	

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[a] The averaged value from the thermolysis in solution.

[b] Calculated from individual form 2 of the eqns. (1) and (2).

[c] Calculated from individual form 2 of eqn. (2).

[d] Calculated from individual form 1 of eqns. (1) and (2).

[e] The averaged value from ref. 32.

[f] ^{13}C chemical shift of the carbon atom in the methyl group.

TABLE 2

Coefficients of the individual forms of eqn. (1)

Individual form no.	Structure of group [a]	State of thermal decomposition	Chemical shift group	Coefficient		
				a	*b*	Correlation coefficient
1	2.1, 3.5, 3.6, 4.3, 5.1	Solid	^{15}N nitro groups	-2.15 ± 0.54	140.56 ± 16.49	-0.9159
2	2.2, 3.1, 3.2, 3.3, 4.1, 4.2, 6.1	Liquid	^{15}N nitro groups	-4.68 ± 0.45	49.36 ± 14.13	-0.9772
3	2.1, 3.5, 3.6, 4.3	Solid	^{13}C	0.89 ± 0.26	157.32 ± 15.40	0.9212
4	2.2, 3.1, 3.2, 3.3, 4.1, 4.2	Liquid	^{13}C	1.87 ± 0.37	86.31 ± 21.87	0.9457
5	3.5, 3.6, 4.3, 5.1, 6.1	Solid	^{15}N amino	2.48 ± 0.57	704.51 ± 115.31	0.9286
6	3.1, 3.2, 3.3, 4.1, 4.2, 5.3, 6.1	Liquid	^{15}N amino	4.92 ± 1.30	1181.04 ± 260.81	0.8610
7	1, 2.2, 6.1	Liquid	^{15}N nitro groups	-10.03 ± 0.14	-74.62 ± 3.23	-0.9999
8	1, 2.2, 6.1	Liquid	^{13}C	3.86 ± 0.93	3.36 ± 0.35	0.9722
9	1, 2.2, 6.1	Liquid	^{15}N amino	2.27 ± 2.27	637.62 ± 487.64	0.7078

[a] Data numbered as in Table 1.

TABLE 3

Coefficients of the individual forms of eqn. (2)

Individual form no.	Structure of group [a]	State of thermal decomposition	Chemical shift group	Coefficient		
				a_1	b_1	Correlation coefficient
1	2.1, 3.5, 3.6, 4.3, 5.1	Solid	^{15}N nitro groups	−0.37 ± 0.12	5.93 ± 3.82	−0.8633
2	3.1, 3.2, 3.3, 4.1, 4.2, 6.1	Liquid	^{15}N nitro groups	−0.40 ± 0.03	5.20 ± 0.94	−0.9838
3	2.1, 3.5, 3.6, 4.3	Solid	^{13}C	0.21 ± 0.04	5.24 ± 2.61	0.9572
4	2.2, 3.1, 3.2, 3.3, 4.1, 4.2	Liquid	^{13}C	0.20 ± 0.01	6.11 ± 0.90	0.9889
5	3.5, 3.6, 4.3, 5.1, 6.2	Solid	^{15}N amino	0.38 ± 0.04	93.82 ± 8.16	0.9833
6	3.1, 4.2, 3.3, 4.1, 4.2, 5.3, 6.1	Liquid	^{15}N amino	0.43 ± 0.07	105.39 ± 15.23	0.9322
7	1, 2.3, 6.1	Liquid	^{15}N nitro groups	−0.50 ± 0.01	2.78 ± 0.23	−0.9996
8	1, 2.3, 6.1	Liquid	^{13}C	0.19 ± 0.04	6.64 ± 1.46	0.9812
9	1, 2.3, 6.1	Liquid	^{15}N amino	0.20 ± 0.11	39.71 ± 23.54	0.7367

[a] Data numbered as in Table 1.

TABLE 4

Coefficients of the individual forms of eqn. (3)

Individual form no.	Structure of group [a]	Chemical shift group	Coefficient		
			a_2	b_2	Correlation coefficient
1	2, 3, 4, 5	^{15}N nitro groups	-49.46 ± 8.36	-3.86 ± 0.28	-0.9947
2	2, 3, 4	^{13}C	-33.15 ± 1.87	1.86 ± 0.03	0.9998
3	2, 3, 4, 5	^{15}N amino	Data do not correlate		

[a] Data numbered as in Table 1.

methylene–nitramine building units within the molecule). This is why data for substances **5** and **6** do not correlate here.

The individual forms 7–9 of eqns. (1) and (2) (see Tables 2 and 3) correspond to the data for monomethylnitramine derivatives. The good correlation of these data according to individual form 7 (^{15}N nitro group shifts) and the simultaneous lack of correlation according to individual form 9 (^{15}N shifts of amino nitrogen atoms carrying nitro groups) are connected to the heterogeneity of the mechanism of primary fragmentation in the thermolysis of substances **1**, **2** and **6** in the condensed state.

From what has been said so far it follows that the data which do not correlate with individual forms 1–6 of eqns. (1) and (2) (i.e. data 3.7, 4.4, 4.5, 4.6 and 4.7) do not correspond to the primary thermal fragmentation of the corresponding nitramines.

Using individual forms 1–4 of eqns. (1) and (2), and by means of the relationships found in ref. 8, it is possible to specify the range of the Arrhenius parameters for the non-autocatalysed thermolysis of the technically attractive substances hexogen (**3**) and octogen (**4**). The results are shown in Table 5.

Values of E and $\log A$ for octogen in Table 5 indicate the lack of influence of the solid–liquid phase transition for this nitramine in the

TABLE 5

Values of the Arrhenius parameters for hexogen and octogen thermolysis, obtained from individual forms 1–4 of eqns. (1) and (2) and from ref. 8

Nitramine	State of thermal decomposition	Temperature range (K)	E (kJ mol^{-1})	$\log A$
Hexogen	Liquid	480–530	198–203	18.4–18.5
	Solid	420–470	211–215	18.3–19.4
Octogen	Liquid	540–590	206–215	18.8–19.2
	Solid	530–550	214–216	18.7–19.5

initial stage of its thermolysis. This is in agreement with the conclusions of Brill and Karpowicz [30], on the influence exercised by intermolecular forces on the decomposition of nitramine **4** in the condensed phase.

Equation (3) represent the relationship between the heat of explosion (expressed by means of the square of the detonation velocity) and chemical shifts. It can be understood from this point of view why the individual form 1 of this equation (^{15}N shifts of nitro groups; see Table 4) does not correspond to compounds **1** and **6**. Differences in the molecular structures of these two nitramines from the remaining members of the group of substances considered also cause the differences in the thermochemical description of their detonation. Form 2 of eqn. (3) represents only the group of nitramines with the methylene nitramine arrangement within the molecule. Relationship 3 is not valid for ^{15}N chemical shifts of amino nitrogen atoms carrying nitro groups.

CONCLUSION

It is a well-known fact that induction and conjugation effects are, through their effects on the electron density of atoms within a molecule, primarily reflected in values of the ^{13}C and ^{15}N chemical shifts, and also in the thermal reactivity of polynitro compounds. This is shown by the existence of linear relationships between these shifts and the Arrhenius parameters E and log A of low-temperature non-autocatalysed thermolysis of nitramines. Homolysis of the $N-NO_2$ bond as the primary fragmentation in the thermolysis of secondary nitramines in the condensed state is characterized by the existence of these relationships for the ^{15}N shift of each participating nitrogen atom in the given bond, considered separately.

The above-mentioned relationships, together with the information in refs. 8, 15, 17 and 19 enable us to determine which of the published values of the Arrhenius parameters in the thermolysis of secondary nitramines in the condensed state correspond to the homolytic fission of the $N-NO_2$ bond. Application of these relationships, in combination with the information in refs. 8 and 30, confirms that the solid–liquid phase transition has no influence on the initial stage of the thermolysis of octogen.

The relationship found between the ^{13}C and ^{15}N chemical shifts and the heats of explosion (represented by the square of the detonation velocity) of nitramines is consistent with the literature about the analogous relationships in general between NMR chemical shifts and thermochemical parameters of polynitro compounds.

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