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THE RELATIONSHIP BETWEEN THE KINETIC DATA OF THE LOW-TEMPERATURE THERMOLYSIS AND THE HEATS OF EXPLOSION OF INORGANIC AZIDES

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ABSTRACT

The primary chemical processes of the thermal decomposition and detonation change of inorganic azides possessing explosive character is considered by means of the linear relationship between the activation energies, E, of the initial stage of low-temperature thermolysis, and the heats of explosion of these substances. Also, the possibility of applying E values in the estimation of the initiation capability of azides is considered.

INTRODUCTION

Until recently, correlations existing between the kinetic data of low-temperature thermolysis and the detonation characteristics of individual explosives were thought of as being unlikely. They have been shown to occur, however, in organic polynitro compounds [1–4], and polynitrosamines [3]. As indicated [2–4], these correlations are important for the study of the micromechanisms of initiation of detonation and the mechanisms of the primary chemical processes of the thermolysis of explosives. For this reason it is also necessary to verify the validity of this kind of relationship in other categories of compounds possessing explosive character.

From the point of view of the kinetics of low-temperature thermolysis, inorganic azides are fairly well described in the literature (see, e.g., refs. 5–9). The activation energies, E, are applied in this paper in order to verify their

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relationship to the corresponding published values of heats of explosion, Q, using the equation

$$E = C + aQ \tag{1}$$

which was derived and discussed by Zeman et al. [4]. At the same time, the other relationships involved are considered, since they are important for the practical application of inorganic azides as detonation initiators.

DATA SOURCES

A survey of the studied azides and their numeration is contained in Table 1. In the same table, values of heats of explosion, Q, are also presented, which were taken from an encyclopedia [7,10].

Activation energies of decomposition considered, correspond to the lowest temperature ranges of their thermolysis from the published ones [5–9]. These values are also included in Table 1.

Values of minimum azide amounts were also taken from the encyclopedia [7]; these are important for the detonation of high explosives, i.e., 2,4,6-trinitrotoluene (TNT), 1-methylnitramino-2,4,6-trinitrobenzene (TETRYL), and 2,4,6-trinitrophenol (PA). These values are also contained in Table 1.

RESULTS AND DISCUSSION

A mathematical treatment of azide data 2,5,6,9–11, in the sense of eqn. 1, using the method of least-squares resulted in the following coefficients: $C = 248.64$ kJ mol^{-1}; $a = -63.74$ g mol^{-1}; $r = 0.9826$; estimated standard error = 8.21; average relative deviation = $\pm 5.5\%$. This result shows that eqn. (1) also holds for inorganic azides. In the light of the information given by Zeman et al. [4], this means that in these compounds of ionic character, there is also a relationship between their primary chemical thermolytic processes and the primary chemical processes of their detonation change.

Evidence for the above, for ionic compounds, has been given by Owens [12] who, by way of example, proved the relationship between the primary products thermolysis of solid copper tetramine nitrate, and its primary products of decomposition, by means of a shock wave.

Using the above results for eqn. (1), the calculated E values for azides 1, 7 and 8 are given in Table 1. The Q values for azides 3 and 4, obtained in an analogous manner, are also given in Table 1.

To analyse the mutual relationship between Q values and the corresponding amounts, w, of azides, which are necessary to bring about the detonation of high explosives, the following equation was found to be the most suitable

$$\ln w = d + b \ln Q \tag{2}$$

TABLE 1

Data of the azides studied

No.	Azide	Heat of explosion		Thermolysis data			Minimum initiating azides charge w (g) required for high explosive [7]		
		Q ($kJ\ g^{-1}$)	Ref.	Temp. region (K)	E ($kJ\ mol^{-1}$)	Ref.	TNT	TETRYL	PA
1	NH_4^+	2.173	7	–	110.11 [a']	this paper	0.050 [b] 0.055 [c]	0.013 [b] 0.013 [c]	0.025 [b] 0.030 [c]
2	Ca^{2+}	2.615	7	333–403	75.31–79.50	5, 6	0.034 [b] 0.025 [c]	0.009 [b] 0.006 [c]	0.018 [b] 0.013 [c]
3	Sr^{2+}	2.574 [a]	this paper	373–408	84.51	5, 6	0.035 [b] 0.030 [c]	0.009 [b] 0.006 [c]	0.019 [b] 0.015 [c]
4	Ba^{2+}	2.358 [a]	this paper	373–423	98.32	5, 6	0.043 [b] 0.042 [c]	0.011 [b] 0.010 [c]	0.022 [b] 0.022 [c]
5	Cu^+	2.326	7	443–468	110.87	11	0.095	0.025	0.045
6	Ag^+	1.891	10	483–543	121.33	5, 6	0.070	0.020	0.035
7	Cd^{2+}	2.335 $\leqslant$ 2.615	7	–	90.29 [a]	this paper	0.040	0.010	0.020
8	Hg^+	1.113	7	–	177.69 [a]	this paper	0.145	0.045	0.075
9	Tl^+	0.970	7	below 501	179.91	7	0,335	0.070	0.115
10	α-Pb^{2+}	1.535	10	493–533	158.99	5, 6	0.090	0.025	0.025
11	β-Pb^{2+}	1.535	10	473–543	154.81	5, 6	0.090	0.025	0.025

[a] Calculated according to eqn. (1).
[b] Calculated according to eqn. (2).
[d] Calculated according to eqn. (3).

TABLE 2

Coefficients of eqn. (2)

High explosive	Structure of azide group [a]	Coefficient			Standard error of estimate	Average relative deviation (%)
		d	b	r		
TNT	6, 7, 8, 9, 10	−1.4441	−1.9870	0.9693	0.2241	±9.04
TETRYL	6, 7, 8, 9, 10	−2.7989	−1.9578	0.9898	0.1251	±2.60
PA	6, 7, 8, 9	−2.2979	−1.7597	0.9913	0.1193	±2.97
PA	5, 6, 10	−4.2811	1.4143	0.9967	0.0338	±0.54

[a] Azides numbered as in Table 1.

coefficients for solutions of this equation for each high explosive are given in Table 2.

For PA, eqn. (2) has two solutions possessing common data of azide 6. Data of azide 5 do not correlate with the solutions of eqn. (2) for TNT and TETRYL; this may be due to the specific influence exercised by the cation. By means of the solution of eqn. (2) for these high explosives, the "average" value of $Q = 2.484$ kJ g^{-1} was obtained for azide 7; this Q value was used for calculating the corresponding E value.

It follows from a mutual comparison of eqns. (1) and (2) that there must be a relationship between E and w; using a more detailed analysis of the problem, the following equation was derived whose coefficients are represented in Table 3

$$\ln w = m + s \ln E \qquad (3)$$

This relationship may be of some importance for technological practice.

CONCLUSION

The linear relationship existing between the activation energies of low-temperature thermolysis and heats of explosion [4] also exists in inorganic

TABLE 3

Coefficients of eqn. (3)

High explosive	Structure of azide group [a]	Coefficient			Standard error of estimate	Average relative deviation (%)
		m	s	r		
TNT	6, 7, 8, 9, 10, 11	−13.7099	2.3013	0.8532	0.4194	±16.70
TETRYL	6, 7, 8, 9, 10, 11	−15.0726	2.3094	0.9167	0.3000	±5.90
PA	6, 7, 8, 9	−14.2826	2.2931	0.9757	0.2092	±5.09

[a] Azides numbered as in Table 1.

azides. This relationship, along with the experimental knowledge gained by Owens from the decomposition of solid copper tetramine nitrate using a shock wave [12], bears evidence in favour of the relationship between the primary chemical processes of thermolysis and the detonation change of inorganic salts possessing an explosive nature. From the point of view of technological practice there is considerable scope for estimating the initiation capability of inorganic azides from values of their activation energies, released on their thermolysis within the lowest temperature ranges.

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