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DETERMINATION OF HEATS OF DECOMPOSITION OF SOME 1,3,5,7-TETRAAZACYCLOOCTANE AND 1,3,5-TRIAZACYCLOHEXANE DERIVATIVES USING DIFFERENTIAL SCANNING CALORIMETRY

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Differential scanning calorimetry was used to determine the heats of decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane *(HMX)*, 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane *(DADN)*, 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane *(DPT)*, 1,3,5-trinitro-1,3,5-triazacyclohexane *(RDX)*, 1,3,5-trinitroso-1,3,5-triazacyclohexane (*R*-salt), and 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane *(DNPT)*. The value of the decomposition heat of unit mass of sample was found to increase in *HMX*, *DADN* and *RDX* with decreasing degree of filling of the reaction volume. In the R-salt and in *DNPT*, however, the trend of this dependence was found to be the reverse and more pronounced. No analogous dependence was found to exist for *DPT* under the given experimental conditions.

1,3,5,7-tetraazacyclooctane and 1,3,5-triazacyclohexane derivatives are most important intermediates or products of some special branches of organic chemistry and technology. Quite a number of them are unstable or metastable compounds, which evokes considerable interest in their behaviour during thermal treatment.

A comparatively large number of data on the thermal decompositions of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane *(HMX)* and 1,3,5-trinitro-1,3,5-triazacyclo hexane *(RDX)* have been obtained by DSC [1–8]. The activation energy of the thermal decomposition of 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane *(DPT)* and the decomposition heats of *HMX*, *RDX* and *DPT* were determined by Hall [9] using a DSC-1 apparatus. So far, however, the decomposition heats of 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane *(DNPT)*, a blowing agent used in the rubber industry, and a by-product of its preparation 1,3,5-trinitroso-1,3,5-triazacyclohexane (*R*-salt), have not been published. The case is the same for 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane *(DADN)*. In order to fill the gap in the literature, we have endeavoured in the present work to determine the decomposition heats of *DNPT*, *R*-salt and *DADN*, and to carry out comparative measurements on *HMX*, *RDX* and *DPT*.

Experimental

Materials

1,3,5-Trinitro-1,3,5-triazacyclohexane *(RDX)* was obtained by nitration of *R*-salt with a $H_2SO_4+HNO_3$ – mixture [10], the product being crystallized several times from acetone. For measurements, from 0.015 to 0.040 mg RDX was weighed.

1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane *(HMX)* was used in the quality [8] resulting from a technical sample obtained by alkalization [11] with subsequent crystallization from acetone, dimethylformamide and finally acetone again. For measurements, from 0.007 to 0.046 mg *HMX* was weighed.

1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane *(DADN)* was synthesized from hexamethylenetetramine by means of known methods [12, 13], the crude product being crystallized from dimethylformamide. From 0.033 to 0.196 mg *DADN* was weighed for measurements.

1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane *(DPT)* was prepared from hexamethylenetetramine by nitrolysis in an acetic anhydride–HNO_3 mixture [14], the crude product being crystallized from dimethylformamide. From 0.015 to 0.151 mg *DPT* was weighed.

1,5-Endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane *(DNPT)* was obtained by nitrosation splitting of hexamethylenetetramine [15]; from the crude product, on extraction of *R*-salt with hot acetone, a pure substance was obtained by crystallization from a dimethylformamide–acetone mixture. From 0.022 to 0.189 mg DNPT was weighed.

1,3,5-Trinitroso-1,3,5-triazacyclohexane (*R*-salt) was prepared by nitrosation of hexamethylenetetramine [16] with subsequent repeated crystallization of the crude product from acetone. From 0.031 to 0.136 mg *R*-salt was weighed for measurement.

The purities of the substances were checked, using thin-layer chromatography with Silufol UV 254 as anchored phase and acetone-cyclohexane as mobile phase (in 3 : 1 and 2 : 1 volume ratios) with stain identification, using UV-light.

Methods

The DSC curves of samples were obtained using a DSC-1B apparatus (Perkin-Elmer), calibrated for indium (melting point 429.4 K and $\Delta H_m = 28.05$ $J.g^{-1}$) and for $AgNO_3$ (melting point 485.0 K and $\Delta H_m = 69.91$ $J.g^{-1}$). During measurement, nitrogen was introduced into the furnace of the apparatus. The heating rate was 8°/minute, the sensitivity was 4 $\mu cal \cdot s^{-1}$, and the shift rate of the paper in the recorder was 20 mm $\cdot$ min^{-1}. A4–20 microbalances were used to weigh samples in aluminium pans fitted with lids (Perkin-Elmer, Part No. 219–0062).

Results and discussion

A detailed analysis of the results obtained in this way revealed that the decomposition heats of unit mass of *RDX*, *HMX*, *DADN*, *DNPT* and *R*-salt are dependent upon the quantity of the weighed substance, i.e. upon the degree of filling of the reaction volume with the corresponding substance.

For *RDX*, *HMX* and *DADN* this dependence is best expressed by the general relationship

$$\log q = b \cdot x + a \tag{1}$$

Table 1

Relationship coefficients from Eq. 1

Substance	b	a	r
RDX	-4.17409	3.62261	-0.9358
HMX	-3.92501	3.52901	-0.7917
DADN	-1.94175	3.09927	-0.9213

where q is the absolute value of the enthalpy change due to the decomposition, in $J \cdot g^{-1}$, x being the weight of the sample in mg. Table 1 gives values of the relationship (1) coefficients together with the selection coefficient of the correlation, r, resulting from mathematical treatment of the experimental results by the least squares method.

The increase of the heat effect from the decomposition of unit mass of *RDX* and *HMX* with the decrease in the degree of filling of the reaction volume is not in agreement with the data published by Hall [9]. The tendency found for *RDX*, however, corresponds well with that obtained by Cosgrove and Owen [17, 18], who studied the thermal decomposition of this substance in a static system at 468 K. In order to reduce the filling of the reaction volume (here 0.090 mM in 150 ml), using the results obtained from analysis of the products [17] and tabulated standard enthalpies of formation [19], an approximate estimation of the decomposition heat was carried out under the same conditions as used by Cosgrove and Owen [17], i.e. -824.2 kJ $\cdot$ mole^{-1}; for maximum applied filling (0.885 mM in 150 ml) the value -717.2 kJ $\cdot$ mole^{-1} was estimated.

The tendency in the decomposition heat of *RDX* is manifested at the expense of secondary reactions of decomposition products. It follows from the survey in [8] that the increasing filling of the reaction volume inhibits the thermal decomposition not only of *RDX*, but also of *HMX*. This finding of Cosgrove and Owen [20] has been confirmed by Maksimov [21].

Rauch and Fanelli [22] found that change in the degree of filling of the reaction volume is accompanied by a change in the NO_2 content of the products of *RDX* pyrolysis. The NO_2 content is directly proportional to the increase in the degree of filling of the reaction volume. Though the NO_2 content of the products of thermal decomposition of *RDX* rapidly decreases to zero as the pyrolysis proceeds [22], the NO_2 content is most probably the factor influencing the degree of filling of the reaction volume and is manifested in the heat effect of unit mass in the *RDX* thermolysis.

Batten [23] confirmed that both NO_2 and oxygen inhibit the thermal decomposition of *RDX* because they remove catalysts of its thermal decomposition, the catalysts being hydroxymethylformamide [17, 18] (one of the *RDX* thermolysis products) and formaldehyde [23, 24]; the resulting variability of the partial reaction mechanisms of *RDX* pyrolysis makes itself felt in the overall enthalpy change of the reaction.

In the case of *HMX*, which is a higher *RDX* homologue, interpretation of the dependence found is possible if the structural analogy of the two substances is taken into consideration.

Analogously, the trend found in the heat of decomposition of *DADN*, which is also a structural *HMX* analogue, can be understood. The less pronounced dependence as compared to those for *RDX* and *HMX* is due to the lower number of nitramino groups in its molecule.

Under the conditions of the experiment, the dependence of the decomposition heat of unit mass of sample upon the degree of filling was not observed for *DPT*, in this case a certain degree of agreement being found with Hall's data [9]. It is true that *DPT* is a nitramine, but at the same time, it is also an N-Mannich base, and it is therefore most probable that NO_2 will not be produced in its decomposition.

A trend in the heats of decomposition in contrast to that exhibited by *RDX*, *HMX* and *DADN*, was found for *DNPT* and *R*-salt. For *DNPT* there is a pronounced dependence of the decomposition heat of unit mass of sample upon the degree of filling of the reaction volume; in our case it is best described by the relationship:

$$q = 1945 \cdot 67 \cdot \log x + 4021 \cdot 95 \tag{2}$$

with the selection correlation coefficient $r = 0.9561$. Graphical presentation of this dependence as a plot of q vs. x revealed that the corresponding function converges to the value $q = -2637.6$ $J.g^{-1}$, i.e. -491.05 kJ $\cdot$ $mole^{-1}$. The increase of the heat of decomposition in the sense of relation (2) was interpreted in [25], which summarizes the results as follows: on pyrolysis, *DNPT*, as an N-Mannich base, gives primarily reactive intermediates, whose conversion to stable decomposition products (above all, polymethyleneiminic systems) is hastened by the increasing pressure, the autocatalytic course of these secondary reactions being quite possible.

For the *R*-salt a reasonably large number of measurements ($n = 14$) revealed the very strong dependence of the decomposition heat of unit mass of sample

Table 2

Survey of results

Substance	Weights of samples, mg	Initial decomposition, K	
		published [9]	measured
RDX	0.015–0.040	483–534	484–490
β-HMX	0.007–0.046	ca. 540	553–558
DADN	0.033–0.196	–	550–552
DPT	0.015–0.151	ca. 471	470–476
DNPT	0.022–0.189	–	466–487
R-salt	0.031–0.136	–	415–450

upon the degree of filling of the reaction volume; this dependence is best described by the following linear relationship:

$$q = 10398.62\,x + 751.04 \tag{3}$$

with the selection correlation coefficient $r = 0.8236$. The extrapolated value of the *R*-salt decomposition heat for zero weighed substance is -130.83 kJ · mole^{-1}. The upper limit of the value yielded by this heat cannot be assessed within the given weight ranges of the substances; however, it can be estimated as not exceeding -800 kJ · mole^{-1}. Hall [9], using a DSC-1 apparatus, determined the heat of polymorphic transition of the *R*-salt (17.75 ± 0.53 kJ · mole^{-1}) and its heat of melting (3.77 ± 0.12 kJ · mole^{-1}), but he did not study its heat of decomposition.

The results of our research are given in Table 2. For comparison, averaged and extrapolated values of heats of decomposition of nitramines, as well as published data from this field [9], are also given.

Conclusion

Under the experimental conditions used it was found that, in contrast to the conclusion arrived at by Hall [9], the value of the reaction heat given off by unit mass of *HMX* and *RDX* depends upon the degree of filling of the reaction volume. However, this is in good agreement with the conclusions of Cosgrove and Owen [17, 18] and can be interpreted via the negative influence of NO_2 (a decomposition product) upon the thermolyses of these nitramines [8, 20–23]. An analogous, though less pronounced dependence, was found in the case of *DADN*, a structural analogue of *HMX*. From what has been said so far, the hypothesis may be suggested that the mechanisms of the primary and the subsequent fission processes in *HMX*, *RDX* and *DADN* thermolyses are very similar. This hypothesis, however, cannot hold for the thermal decomposition of *DTP*, during which the decomposition heat of unit mass of sample, under the given experimental conditions, is independent of the degree of filling of the reaction volume and is near the value published by Hall [9].

Heats of decomposition, kJ.mole^{-1}		
published [9]	average measured	maximum extrapolated
−569.39± 8.36	−669.72± 25.56	−932.96
−695.00±37.70	−796.05±120.32	−1002.82
—	−259.26± 36.71	−335.11
−146.50±25.10	−117.20± 15.50	—
—	—	ca. −491.05
—	—	under −800.0

The dependence found for the *DNPT* decomposition heat proves that the mechanism of its thermolysis is entirely different from those for the above nitramines, as well as the *R*-salt. In contrast to the examined nitramines, the decomposition heat of unit mass of sample for these two nitrosamines was found to increase with the degree of filling of the reaction volume. Only for *DNPT* could the limiting value of the heat of decomposition be successfully assessed. Within the weight range applied, however, a similar assessment was impossible for the *R*-salt, which, of all the 1,3,5,7-tetraazacyclooctane and 1,3,5-triazacyclohexane derivatives studied, exhibits the most pronounced dependence of the thermolysis heat effect upon the degree of filling. A higher degree of filling of the reaction volume in the *R*-salt and in other compounds could not be employed, due to sample pans cracking during thermolysis.

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References

1. R. N. Rogers and L. C. Smith, Thermochim. Acta, 1 (1970) 1.
2. R. N. Rogers, Anal. Chem., 44 (1972) 1336.
3. R. N. Rogers, Thermochim. Acta, 3 (1972) 437.
4. R. N. Rogers and G. W. Daub, Anal. Chem., 45 (1973) 596.
5. R. N. Rogers, Thermochim. Acta, 9 (1974) 444.
6. R. N. Rogers, Jahrestag., Inst. Chem. Treib-Explosivstoffe Fraunhofer-Ges., p. 41, 1971, publ. 1972.
7. R. N. Rogers, Thermochim. Acta, 11 (1975) 131.
8. S. Zeman, Thermostable Polynitroaromatic Compounds. Part I. Ph. D. Theses, Univ. Chem. Technol., Pardubice, June, 1973.
9. P. G. Hall, Trans. Faraday Soc., 67 (1971) 556.
10. J. Šimeček, Chem. Listy, 51 1325.
11. Engineering Design Handbook. Explosives Series. U. S. Govt. Report AD-764 340 (1974) 173.
12. V. I. Siele, M. Warmen and E. E. Gilbert, J. Heterocycl. Chem., 11 (1974) 237.
13. V. I. Siele and N. J. Succasunna, U. S. pat. 3.850.923 (1974)
14. W. E. Bachman, W. J. Horton, E. Jenner, N. W. McNaughton and L. B. Scott, J. Am. Chem. Soc., 73 (1951) 2769.
15. F. Meyer, Ber. Dtsch. Chem. Ges., 21 (1888) 2883.
16. W. E. Bachman and N. C. Deno, J. Am. Chem. Soc., 73 (1951) 2777.
17. J. D. Cosgrove and A. J. Owen, Combust. Flame, 22 (1974) 13.
18. J. D. Cosgrove and A. J. Owen, Combust. Flame, 22 (1974) 19.
19. D. R. Stull, E. F. Westrum and G. G. Sinke, The Chemical Thermodynamics of Organic Compounds. John Wiley and Sons, Inc., 1969.
20. J. D. Cosgrove and A. J. Owen, Chem. Commun., (1968) 286.
21. Yu. Ya. Maksimov, Teoryia vzryvch. vesch. Trudy MCHTI, vypusk 53 (1967) 73.
22. F. C. Rauch and A. J. Fanelli, J. Phys. Chem., 73 (1969) 1604.
23. J. J. Batten, Austral. J. Chem., 24 (1971) 945.
24. J. J. Batten, Austral. J. Chem., 24 (1971) 2025.
25. S. Zeman, Some problems of production of dinitrosopentamethylenetetramine. Unpublished work. Chemko Strážke, March, 1974, p. 77.

RÉSUMÉ — On a déterminé par analyse calorimétrique différentielle les chaleurs de décomposition des composés suivants: 1,3,5,7-tétranitro-1,3,5,7-tétraazacyclooctane *(HMX)*, 1,5-diacétyle-3,7-dinitro-1,3,5,7-tétraazacyclooctane *(DADN)*, 1,5-endométhylène-3,7-dinitro-1,3,5,7-tétraazacyclooctane *(DPT)*, 1,3,5-trinitro-1,3,5-triazacyclohexane *(RDX)*, 1,3,5-trinitroso-1,3,5-triazacyclohexane (sel*R*) et 1,5-endométhylène-3,7-dinitroso-1,3,5,7-tétraazacyclooctane *(DNPT)*. La valeur de la chaleur de décomposition par masse unité d'échantillon augmente dans le cas de *HMX*, *DADN* et *RDX*, quand le degré de remplissement du volume réactionnel diminue. On a trouvé, cependant, avec le sel *R* et le *DNPT*, une dépendance inverse et plus prononcée. Aucune dépendance similaire n'a été trouvée, dans les conditions expérimentales appliquées dans le cas du *DPT*.

ZUSAMMENFASSUNG — Die Bestimmung der Zersetzungswärmen von 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooktan *(HMX)*, 1,5-Diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooktan *(DADN)*, 1,5-Endomethylen-3,7-dinitro-1,3,5,7-tetraazacyclooktan *(DPT)*, 1,3,5-Trinitro-1,3,5-triazacyclohexan *(RDX)*, 1,3,5-Trinitroso-1,3,5-triazacyclohexan (*R*-salz) und 1,5-Endomethylen-3,7-dinitroso-1,3,5,7-tetraazacyclooktan *(DNPT)* wurde mittels Differential-Abtastkalorimetrie durchgeführt. Es wurde festgestellt, daß der Wert der Zersetzungswärme der Masseneinheit der Probe bei *HMX*, *DADN* und *RDX* mit abnehmendem Füllungsgrad des Reaktionsvolumens zunimmt. Bei *R*-salz und *DNPT* war hingegen die Richtung der Abhängigkeit umgekehrt und stärker. Keine analoge Abhängigkeit wurde für *DPT* unter den Bedingungen des obigen Versuchs gefunden.

Резюме — Используя дифференциальную сканирующую калориметрию, было выполнено определение теплот раложения для 1,3,5,7-тетранитро-1,3,5,7-тетраазоциклооктана (*HMX*), 1,5-диацетил-3,7-динитро-1,3,5,7-тетраазоциклооктана (*DADN*), 1,5-эндометилен-3,7- динитро-1,3,5,7-тетраазоциклооктана (DPT), 1,3,5-тринитро-1,3,5-триазоциклогексана (Р-соль) и 1,5-эндометилен-3,7-динитрозо-1,3,5,7-тетраазоциклооктана (*DNPT*). Было найдено, что значение теплоты разложения единичной массы образца увеличивается в ряду *HMX*, *DADN* и *RDX* с уменьшением степени наполнения реакционного объема. Однако, для *R*-соли и *DNPT*, было найдено, что эта тенденция обратна и более выражена. Не было найдено при данных экспериментальных условиях аналогичной зависимости для *DPT*.