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THERMAL DECOMPOSITION OF SOME NITROSAMINES

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ABSTRACT

Arrhenius parameters of four nitrosamines and two nitrosamides thermolysis are determined by means of DSC method according to R. N. Rogers. These results are compared with the published data which were derived from the application of the Soviet manometric method /SMM/ to the study of thermal reactivity of explosives. Relationships are derived between the above-mentioned parameters and the characteristics of detonation of the substances possessing $-CH_2-N/NO/-CH_2-$ grouping within the molecule.

INTRODUCTION

Unlike organic polynitro compounds and esters of nitrous acid, the study of the kinetics of N-nitroso compounds thermolysis has still been in statu nascendi: only a few papers have been published on thermal reactivity of nitrosamines in condensed state/1-5/, two of which dealing with the application of the Soviet manometric method /SMM/ to the problem in question/1,3//there has recently been another proof/6,7/ of the SMM being an important source of reliable kinetic data from the realm of thermolysis of unstable and metastable compounds/. Arrhenius parameters, as far as values is concerned, practically identical, resulting from the application of SMM, can be obtained from DSC measurements in the sense of Rogers methods /see, for example, refs. 8-11/. These circumstances made us select the application of DSC method/9-11/in order specify kinetic parameters of four nitrosamines and two nitrosamides thermolysis.

EXPERIMENTAL

Kinetic thermolysis data of bis/2,2,2-trinitroethyl/-N-nitrosoamine /BTN/ were taken from paper/1/. 1,4-Dinitroso-1,4-diazacyclohexane /DNSP/, 1,3,5-trinitroso-1,3,5-triazacyclohexane /NITROSOGEN/, 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane /DNPT/ and mixture of 1,6- and 1,4-dinitrosotetrahydroimidazo[4,5-d]imidazol-2,5(1H,3H)diones /DNSGU/ were taken for measurements in the same quality as i paper/4/. 1,4,5,8-Tetranitroso-1,4,5,8-tetraazadecaline /TNSAD/ was synthesized and purified in the described manner/12/.

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N-Methyl-N-nitrosourea /MNU/ was recrystalized before measurement from acetone and subsequently from methanol.

Measurements were carried out in Perkin-Elmer Model DSC-1B differential scanning calorimeter in the described manner/9-11/ with the weighed amounts 0.5 up to 1.1 mg sample.

RESULTS AND DISCUSSION

The results obtained are shown in Table 1; the data for nitrosamine 3 given here were, however, obtained by another method /see later/ as the measurement of it, due to its volatility under the given circumstances of the experiment, was not successful.

The obtained Arrhenius parameters E and log A for nitrosamines 2 up to 5 are in good agreement with those resulting /for compounds 1 and 5/ from the application of SMM. The increasing steric as well as the negative induction effect in the reaction centre of the molecule seems to correspond the increase in E and log A values.

There is a kinetic compensating effect between the E and log A values of compounds 1, 2, 4 and 5; it is expressed by the relationship

$$\log A = -34.93 + 0.34 \cdot E \qquad (1)$$

with correlation coefficient $r = 0.9144$, standard error of estimate $S_{x,y} = 0.39$ and the average relative deviation ard = ±1.58 %. There is, however, not a good correlation to this relationship of the parameters of N-nitrosoamide 6; and there is no correlation at all of the parameters of the mixed N-nitrosamide 7.

Summed up in Table 1 are also the thermodynamic data $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$ and $\ln K^{\neq}$ which were obtained from the Arrhenius parameters by current calculations /see the procedure, for example, in ref. 6/. Like in paper/6/, for compounds 1, 2, 4 and 5 the relation is confirmed between the equilibrium constants, $K^{\neq}$, and the corresponding values of detonation velocities, D, in shape

$$\ln D = 0.258 + 0.041 \cdot \ln K^{\neq} \qquad (2)$$

with the $r = 0.8757$, $S_{x,y} = 0.106$ and ard = ±3.70 %. Using eqn. (2), the corresponding value $\ln K^{\neq} = 34.84$ was calculated from D values of nitrosamine 3.

For nitrosamines with the arrangement $-CH_2-N/NO/-CH_2-$ within the molecule /compdn. 1, 4 and 5/, there is a relationship /in the sense of Polanyi-Semenov rule - see ref. 7/ between E values and heats of explosion, Q, in shape

$$E = 140.69 + 1.07 \cdot Q \qquad (3)$$

with $r = 0.8793$, $S_{x,y} = 1.35$ and ard = ±0.48 %; the values Q, given

TABLE 1: Survey of results

Substance	Arrhenius parameters				Thermodynamic parameters				Characteristics of detonation	
	Temp. region /K/	E[a]	log A[b]	Ref.	$\Delta H^{\neq}$[a]	$\Delta S^{\neq}$[c]	$\Delta G^{\neq}$[a]	ln $K^{\neq}$	D[d]	Q[e]
1 BTN[j]	388-433	148.11	15.3	/1/	-144.69	37.02	-159.88	46.84	8.69[g] 8.87[h]	7.171
2 TNSAD[i]	460-480	149.15	15.5	/f/	-145.24	39.71	-163.91	41.94	7.09[h]	4.60[o]
3 DNSP[j]	490-510[k]	143.94	14.0	/f/	-139.78	10.08	-144.83	34.84[m]	6.48[g] 4.57[h]	3.946
4 DNPT[i]	470-485	144.20	13.9	/f/	-140.23	8.96	-144.51	36.40	6.68[g] 4.90[h]	3.999
5 NITROSOGEN[j]	383-433	144.35	13.1	/3/	-140.96	-4.09	-139.29	41.06	7.46[g]	4.829
	455-470	146.94	15.5	/f/	-143.09	39.85	-161.52	42.00	7.88[h]	
6 MNU[j]	380-390	148.86	18.7	/f/	-145.66	102.51	-185.13	57.83	5.42[h]	3.95[o]
7 DNSGU[i]	475-490	177.72[p]	17.3[p]	/f/	-	-	-	-	6.48[n]	4.44[n]

[a] in kJ.mol^{-1};

[b] in s^{-1};

[c] in J.mol^{-1}.K^{-1};

[d] detonation velocity, in km.s^{-1};

[e] heat of explosion, calculated according to ref. 15 /in kJ.g^{-1}/;

[f] this paper;

[g] calculated according to ref. 13;

[h] calculated according to ref. 14;

[i] thermolysis in the solid state;

[j] thermolysis in the liquid state;

[k] estimated from the molecular-structural analogy /see on results in refs.4,5/;

[m] calculated by means of eqn. (2);

[n] taken from ref. 4;

[o] calculated by means of the relationship between D^2 and Q values for nitrosamines;

[p] unreal, high value;

in Table 1, were obtained using semiempirical equations of Pepekin et al.[15]. Using relation (3) and value Q of the compound 3, the corresponding value E = 144.93 kJ.mol^{-1} was calculated. By substituting Q values in eqn. 3 with squares of detonation velocities D^2, the relationship is obtained

$$E = 141.765 + 0.082 \cdot D^2 \qquad (4)$$

with the r = 0.9315, $S_{x,y}$ = 0.7299 and ard = ±0.30 %. With the above-given substitution a closer correlation is thus achieved. Using eqn. (4) and values D of nitrosamine 3, value E = 142.21 kJ.mol^{-1} is obtained. The remaining presented data of the said nitrosamine were obtained by calculations from values E and ln $K^{\neq}$ using definition relationships for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ together with eqn. (1).

The existence of eqns. (1),(2),(3), and (4) confirms homolysis N-NO bond as the primary fragmentation of N-nitroso compounds thermolysis, as well as the identity of primary chemical processes of thermolysis with the primary fragmentation of the detonation change of molecules in above mentioned compounds.

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