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POSSIBILITIES OF APPLYING THE KISSINGER METHOD IN THE DIFFERENTIAL THERMAL ANALYSIS OF POLYNITROARENES

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ABSTRACT

Kissinger activation energies, E_K, are determined for twenty polynitroarenes. These E_K values are compared with the kinetic data of the Soviet manometric method and with the characteristics of detonation of the studied substances. It is shown that the E_K values are not applicable to the study of the problems linked up with the initiation of explosion.

INTRODUCTION

From the point of view of the reaction kinetics, the interpretation of the DTA results, continues to be complicated[1,2]. Recently, however, relationships between the results obtained from the isothermal Soviet manometric method /SMM/ and the results of non-isothermal DTA of polynitroarenes have been specified[3-7]. The said DTA results are derived from the application of Piloyan method in the sense of papers[3,8,9]; quite recently, their relationship to the characteristics of the detonation of condensed individual explosives has been proved[10-13].

In the lighg of the above-mentioned new knowledge, verification of possibilities of analogous application of Kissinger method[14] results is presented in this paper; the said method was most popular in DTA of explosives /see for example refs. 15-17/.

EXPERIMENTAL

The origin ahd purity of substances measured are described in refs. 3-6, and 10. To be specific, the following substances were involved: 1-methyl-2,4,6-trinitrobenzene /TNT/[3], 1,3-dimethyl-

2,4,6-trinitrobenzene /TNX/[3], 1,3,5-trimethyl-2,4,6-trinitrobenzene /TNMs/[3], 1-chloro-2,4,6-trinitrobenzene /CTB/[3], 1,3-dichloro-2,4,6-trinitrobenzene /DCTB/[3], 1-amino-2,4,6-trinitrobenzene /PAM/, 1,3-diamino-2,4,6-trinitrobenzene /DATB/[4], 1,3,5-triamino-2,4,6-trinitrobenzene /TATB/[4], 1-hydroxy-2,4,6-trinitrobenzene /PA/[4], 1-hydroxy-3-methyl-2,4,6-trinitrobenzene /TNCr/[4], 2,2',4,4',6,6'-hexanitrobiphenyl /HNB/[6], 2,2',2'',4,4',4'',6,6',6''-nonanitro-m-terphenyl /NONA/[6], 2,4,6-tripicryl-1,3,5-triazine /TPT/[6], 2,2',4,4',6,6'-hexanitrostilbene /HNS/[5], 2,2',4,4',6,6'-hexanitrooxanilide /HNO/[5], 2,2',4,4',6,6'-hexanitrodiphenylsulfone /DIPSO/[5], 2,4,6-tris/2,4,6-trinitrophenylamino/-1,3,5-triazine /TPM/[5], and 1,3,7,9-tetranitrophenothiazine-5,5-dioxide /TNPTD/[10], and 1,4,5,8-tetranitronaphthalene /TENN/[6].

Measurements were carried out in the apparatus Derivatograph Q 1500 D /made by MOM, Budapest/ operating within the range 0.1 mV on the scale. Linear rates of temperature increase 1.25, 2.5, 5 and 10 °C per minute were used, the weight of the sample being 28--30 mg. Measurements were carried under atmospheric pressure in the contact of the sample with air atmosphere.

RESULTS AND DISCUSSION

The values of Kissinger activation energies, E_K, from the DTA measurements are summed up in Table 1, which also contains the values of detonation velocities, D /taken from ref. 10/, and of heat of explosion, Q /taken from ref. 13/.

Analysis of the mutual relationship of the E_K values and published values of Arrhenius parameters E and log A /see on Table 1/ did not result in finding a satisfactory linear or semilogarithmic dependence which, in the realm of the studied substances, would arrange these polynitro compounds also from the angle of the primary thermolysis mechanism /i. e. no analogues of logical substances groups have been found as in refs. 3-7/.

Using Polanyi-Semenov rule[18], linear relationship has recently been found existing between activation energies of low-temperature non-autocatalysed thermolysis, on the one hand, and heats of explosion of individual explosives, on the other /see refs. 13, 19, 20/; this relationship holds for Piloyan activation energies /obtained in the sense of refs. 3, 8, 9/ and for Arrhenius parameters resulting from application of SMM or also DSC Rogers methods /methods see e. g. refs. 15, 21, 22/. The shape of the above-

TABLE 1: Survey of results

Sub stance No.	Substance	Kissinger energies E_K /kJ.mol^{-1}/			Arrhenius parameters from SMM			Detonation	
		this paper	published[a]	Ref.	E /kJ.mol^{-1}/	log A /s^{-1}/	Ref.	velocity D /km.s^{-1}/	heat Q /kJ.g^{-1}/
1	TNT	104.36	145.60	16	144.44	9.3	24	7.02	4.277
2	TNX	66.52	-		146.95	9.1	24	6.76	4.074
3	TNMs	197.58	-		185.05	12.3	24	6.23	3.801
4	PAM	96.07	383.83	16	129.79	7.1	25	7.54	4.263
5	DATB	237.69	-		196.77	13.2	26	7.71	4.138
6	TATB	214.75	-		175.00	11.6	26	7.95	3.990
7	PA/1st peak/	143.09	123.43	16,17	161.18	11.7	25	7.37	4.372
8	TNCr	141.58	-		192.46	15.6	27	7.42	4.072
9	TNR/1st peak/	201.79	-		144.68	11.2	25	7.71	4.130
10	CTB	91.93	249.37	16	118.07	5.7	28	7.20	4.479
11	DCTB	53.69	-		177.09	10.5	28	6.74	4.039
12	HNB	219.41	-		207.24	16.1	25	7.50	4.698
13	HNS	258.33	-		126.77	9.2	21	7.27	4.480
14	HNO	89.45	-		215.62	16.0	26	7.31	4.189
15	DIPSO	228.07	-		106.76	5.6	29	6.70	3.773
16	TPT	89.48	-		269.45	18.2	30	7.08	4.259
17	TPM	187.61	-		257.06	19.0	26	7.42	4.064
18	NONA	226.36	-		214.11	14.1	6	7.61	4.748
19	TENN	154.60	-		223.05	15.0	6	7.30	4.422
20	TNPTD	382.09	-		200.96	11.7	26	6.50	3.765

a/ DTA measurements under pressure 4.9 MPa

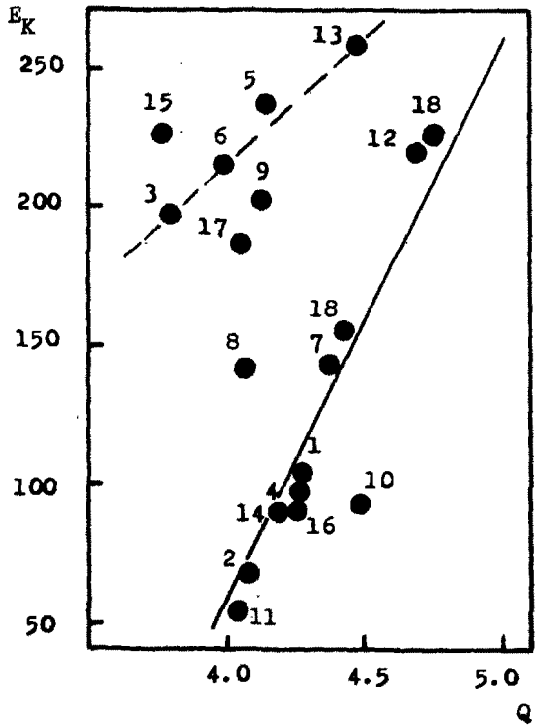

Fig. 1: Graphic representation of relationship between E_K and Q values.

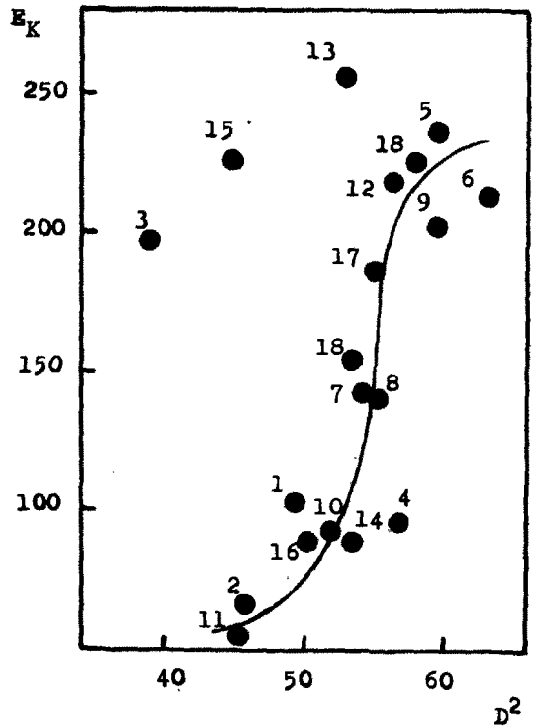

Fig. 2: Graphic representation of relationship between E_K and D^2 values.

mentioned relationship for E_K values is evident from Fig. 1: the group of polynitroarenes under investigation breaks up into two sub-groups essentially whose composition, however, does not correspond to Polanyi-Semenov rule /they are sets of substances with mutually different mechanisms of primary thermolysis/. By substituting Q value in this relationship with the square of detonation velocity, D^2, the relationship continues to be not only linear /in general/ but becomes closer /see e. g. ref. 23/; for the E_K values, however, non-linear dependence results from this substitution /see Fig. 2/.

From what has just been said as well as from the knowledge contained in papers[3-13] conclusion is arrived at that the results of Kissinger method do not correspond to the results obtained from the SMM application and are therefore inappliable to the study of problems linked up with the initiation of explosion of condensed systems.

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