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Mathematic Expression of Kinetic Compensation Effect and Relationship between the Exothermic Decomposition Temperature and Critical Temperature of Thermal Explosion of Eighty-six Energetic Materials

HU Rong-zu[1], YANG De-suo[2], ZHANG Jiao-qiang[3]

(1. *Department of Chemistry, Northwest University*, *Xi'an* 710065, *China*;
2. *Department of Chemistry and Chemical Engineering*, *Baoji College of Arts and Science*, *Baoji* 721007, *China*;
3. *Department of Chemical Engineering*, *Northwestern Polytechnical University*, *Xi'an* 710072, *China*)

Abstract: Two relationships are established using the least-squares method, between the kinetic parameters (the apparent activation energy and pre-exponential constant), and the exothermic decomposition temperature and thermal explosion critical temperature for eighty-six energetic materials.

Key words: critical temperature of thermal explosion; decomposition temperature; DSC; energetic materials.

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In reference [1], the initial data (β_i, T_{pdi}, $i=1,2,\cdots,n$) used to analyze the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the thermal decomposition reaction of eighty-six energetic materials (EM) were reported. In order to obtain information about the kinetic compensation effect and the correlation of the exothermic decomposition peak temperature corresponding to $\beta \longrightarrow 0$ (T_{pd0}) and the critical temperature of thermal explosion (T_b) of above-mentioned materials under the non-isothermal DSC condition from the initial data (the values of heat rate (β) and exothermic decomposition peak temperature (T_{pd})) tabulated in reference [1], the values of the apparent activation energy (E_k) and pre-exponential constant (A_k) obtained by Kissinger's method[2] and the values of T_{pd0} and T_b obtained by Zhang-Hu-Xie-Li method [Eqs. (1) and (2)][3] (data see Table 1) are fitted to the equations (3) and (4).

$$T_{pdi} = T_{pd0} + b\beta_i + c\beta_i^2 + d\beta_i^3 \quad i = 1,2,\cdots,n \quad (1)$$

$$T_b = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{pd0}}}{2R} \quad (2)$$

$$\log A_k = 0.3457 + 0.0927E_k \quad r = 0.9793 \quad (3)$$

$$T_b = 11.41 + 0.9995T_{pd0} \quad r = 0.9793 \quad (4)$$

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where b, c and d are coefficients; E_0 is the apparent activation energy obtained by Ozawa's method[4]; R is the gas constant; r is the linear correlation coefficient.

Equations (3) and (4) show that two linear relationships between the parameters $\log A_k$ and E_k, T_{pd0} and T_b for the exothermic decomposition reaction of eighty-six energetic materials.

The temperature difference between T_b and T_{pd0}, $\Delta T = T_b - T_{pd0} = 11.3 \pm 0.9$, where the uncertainty interval, ± 0.9, denotes 99% confidence limits, calculated using Student's t-test at $f = 85$.

Table 1　Data for eighty-six energetic materials determined by DSC

No.	EM[1)]	E_k /kJ·mol^{-1}	$\log(A_k/s^{-1})$	E_0 /kJ·mol^{-1}	T_{pd0} /℃	T_b /℃
	Trinitromethyl compounds					
1	TNMA	122.8	12.1	123.9	157.0	170.2
2	BTNEDA	200.7	20.6	198.2	166.2	174.6
3	BTNNA	128.0	12.9	128.9	153.2	165.6
4	TTNOE	170.4	16.3	169.7	190.1	201.1
5	TNTNNA	145.3	13.9	145.6	174.6	186.7
6	BNTF	138.2	12.9	139.0	181.9	195.0
7	TNDACPO	122.2	12.5	123.1	140.0	152.2
8	DTNDAPO	176.9	17.7	175.6	175.1	185.0
9	DTNGU	175.1	16.8	174.1	190.6	201.4
10	BTNDNG	206.6	20.7	203.9	184.4	193.3
11	BTNTABCNO	159.1	15.4	158.8	176.2	187.3

Table 1 (continued)

No.	EM 1)	E_k /kJ·mol^{-1}	$\log(A_k/s^{-1})$	E_0 /kJ·mol^{-1}	T_{pd0} /℃	T_b /℃
12	DNBTNTABCNO	182.0	18.2	180.6	174.5	184.1
13	DMBTNGU	208.7	20.4	206.1	193.1	202.2
14	DMBTNDNGU	221.2	21.8	218.1	196.5	205.2
15	TNTNTABCNO	208.0	20.6	205.3	192.9	202.0
	Polynitroaromatic compounds					
16	DATB	196.4	15.1	196.2	290.4	304.5
17	TATB	214.7	15.1	214.4	342.5	357.9
18	DPDATB	390.9	37.0	380.0	241.1	247.0
19	TNOHTAN	161.0	12.8	162.0	256.0	271.2
20	ONTHTAN	145.1	10.7	147.2	274.1	292.2
21	HNTABP	212.9	18.8	211.0	244.6	255.6
22	BDNPATNB	180.3	13.7	180.9	307.7	324.1
	Nitramines					
23	RDX	140.0	12.5	141.8	200.6	214.5
24	RS	169.6	16.9	168.5	167.0	177.0
25	HMX	373.7	33.8	364.0	259.0	265.6
26	HNDACO	210.7	18.2	208.9	237.0	247.8
27	NQ	291.6	27.8	285.4	227.6	235.1
28	PNAH	111.9	10.1	114.1	184.4	200.8
29	BNQ	203.9	20.8	201.3	177.7	186.4
30	Keto-RDX	184.7	18.6	182.9	170.7	180.0
31	TNBAB	115.0	11.1	116.8	154.1	167.9
	Nitric ester					
32	PETN	112.3	10.4	114.2	158.2	172.7
	Nitrosustituted azetidines					
33	TNAZ	128.5	10.45	130.6	224.2	231.4
34	DNAZDNA	134.9	15.49	134.7	111.0	120.6
35	DNAZN	106.3	11.53	107.5	109.9	122.0
36	DNAZNFS	93.2	9.78	95.0	106.6	120.1
37	DNAZDNBA	122.3	13.01	122.9	123.6	134.9
38	DNAZPAC	93.6	9.41	95.6	118.4	132.7
39	DNAZNTO	121.4	12.37	122.4	138.0	150.2
40	BDNAZDNP	140.0	14.71	140.0	139.3	149.9
41	TNDNAZ	139.3	14.27	139.5	148.0	159.1
42	DNAZPC	104.5	11.32	105.8	174.2	191.1
43	DNAZDNP	100.8	8.78	103.3	165.0	181.6
44	DNAZTNBA	24.3	7.88	87.0	127.8	144.5
45	BDNAZK	166.9	13.96	167.2	236.1	249.7
46	DNBDNAZ	183.4	15.75	182.8	238.6	251.1
47	TNBDNAZ	150.0	12.31	151.2	233.7	248.7
48	BDNAZO	120.4	9.18	123.1	233.7	252.4
	Compounds containing furazan group					
49	TABFD	157.4	13.83	157.8	214.4	227.6
50	TNTABCNOF	235.9	23.77	231.9	192.7	200.8
51	TABCNOF	156.0	13.94	156.3	206.6	219.5
52	TNTADF	218.1	25.10	214.1	136.8	143.5
53	TNTAHF	282.4	32.03	275.4	152.5	158.1
	Composite explosives					
54	GO-97	404.4	36.4	393.4	272.6	279.0
55	JO-96	442.5	40.1	429.2	275.4	281.4
56	JO-94	615.3	56.3	593.9	276.2	280.5
57	GO-86	214.4	19.2	212.3	231.0	241.4
58	RTH-10	147.7	13.3	148.4	211.6	225.5
59	HT-17	237.0	22.6	233.4	220.4	229.4
60	JH-915	156.6	14.1	156.9	203.9	216.6
61	JH-97-1	203.7	18.9	201.7	221.1	231.6
62	JH-96	132.6	11.7	134.0	197.4	212.0
63	JH-94	129.1	11.3	130.7	200.4	215.6
64	JH-92-1	176.2	16.1	175.5	209.9	221.5
65	JH-92	161.9	14.7	161.9	208.6	221.2
66	JH-82	225.1	21.1	222.1	210.7	219.8
67	JH-86	193.6	18.2	192.0	212.6	223.3
68	DH-95	145.2	12.8	146.0	200.4	213.9
69	DH-80	259.2	24.5	254.5	220.3	228.5
70	DH-32	176.9	16.1	176.2	210.2	221.8
71	DH-24	242.1	24.3	237.9	203.4	211.6
72	DH-20	217.6	21.4	214.6	205.5	214.7
73	CH-84	160.6	14.7	160.6	204.6	217.0
74	GH-82	213.1	20.1	210.6	209.6	219.2
75	GH-37	123.2	11.2	124.8	179.9	194.5
	Propellants					
76	SB propellant 21	147.0	14.0	147.3	177.3	189.4
77	SB propellant CT	160.2	15.4	159.8	166.4	176.9
78	SB propellant CT-2	183.0	18.0	181.6	187.0	197.1
79	SB propellant CT-5	188.7	18.6	186.9	187.5	197.4
80	DB propellant DB-1	149.3	14.5	149.4	178.3	190.3
81	DB propellant DB-3	236.9	24.1	232.8	195.5	203.6
82	DB propellant 2-3	149.3	14.5	149.4	173.3	185.0
83	DB propellant D-4	149.0	14.4	149.1	172.3	184.0
84	DB propellant 12	232.5	23.8	228.5	184.6	192.5
85	TB propellant 32	175.8	17.5	174.6	168.5	178.2
86	TB propellant SD	206.4	20.9	203.7	181.4	190.2

Note: 1) The meanings of abbreviations of energetic materials (EM) see Ref. [1].

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