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A study of kinetic behaviours of the effective centralite/stabilizer consumption reaction of propellants using a multi-temperature artificial accelerated ageing test

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Abstract

Using a multi-temperature artificial ageing testing apparatus and a standard method of determining the effective centralite/stabilizer content, the effective centralite/stabilizer content for varying time period in propellants heated at 95 °C, 90 °C, 85 °C, 75 °C and 65 °C was measured. Bethelot's equation and Semenov's equation in the temperature range of 65–95 °C for 81 propellants were established. The safe storage life at 30 °C, kinetic parameters [the apparent activation energy (E) and the pre-exponential constant (A)] and isolife temperatures obtained from the established equations and the activation energy ($E_{\alpha=0.5}$) obtained by integral isoconversional non-linear method for 81 propellants: single-base gun propellants (DF-01–DF-16), double-base gun propellants (SF-01–SF-13), tri-base gun propellants (SG-01–SG-02), nitramine gun propellants (GSF-01–GSF-18), double-base propellants (ST-01–ST-13), and composite modified double-base propellants (GST-01–GST-19), were given. Information was obtained on the effective centralite/stabilizer consumption reaction and the kinetic compensation effect.

Keywords: Physical chemistry; Thermal accelerated ageing test; Centralite/stabilizer consumption reaction; Bethelot's equation; Semenov's equation; Safe storage life; Kinetic parameters; Kinetic compensation effect

1. Introduction

The kinetic behaviours at thermal accelerated ageing temperature is one of the most important aspects of propellants. There are a few reports on study of the kinetic behaviours of propellants [1–7]. However, the check of the activation energy of the effective centralite/stabilizer consumption reaction of propellants and their kinetic compensation effects, and the isolife temperatures of Bethelot's equation and Semenov's equation have not yet been reported. The aim of this work is to study the kinetic behaviours of effective centralite/stabilizer consumption reaction of propellants with a multi-temperature artificial accelerated ageing testing apparatus and a standard method of determining the effective centralite/stabilizer content, to check the constancy and validity of activation energy by Semenov's equation, to discuss the kinetic compensation effect and to report the safe storage life at 30 and the isolife temperatures of Bethelot's equation and Semenov's equation for 81 propellants.

2. Theoretical and method

The classical isothermal differential kinetic equation describing the change of the degree conversion with time is

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

Separation of the variables leads to

$$\frac{d\alpha}{f(\alpha)} = k\,dt \quad (2)$$

and integration gives

$$\int_0^{\alpha} \frac{1}{f(\alpha)} d\alpha = G(\alpha) = \int_0^{\tau} k\,dt = k\tau \quad (3)$$

where α is the fraction of effective centralite/stabilizer reacted, k the reaction rate constant, $f(\alpha)$ and $G(\alpha)$ are differential and

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integral mechanism functions, respectively. The relationship between $f(\alpha)$ and $G(\alpha)$ is given by

$$f(\alpha) = \frac{1}{G'(\alpha)} \tag{4}$$

The relationship between the kinetic constant (k) and the absolute temperature (T) of reaction is expressed by the well-know Arrhenius equation

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{5}$$

where E and A are the activation energy and pre-exponential constant, respectively. R is the gas constant.

From Eq. (3), one can obtain, for a given conversion of a set of experiments performed at various temperatures (i = 1, 2, . . ., N):

$$G(\alpha) = k_{T+\mathrm{md}}\tau_{T+\mathrm{md}} = k_T\tau_T \tag{6}$$

$$\frac{k_{T+\mathrm{md}}}{k_T} = r_{\mathrm{d}}^{\mathrm{m}} = \frac{\tau_T}{\tau_{T+\mathrm{md}}} \tag{7}$$

$$G(\alpha) = \tau_1 A \exp\left(-\frac{E_\alpha}{RT_{\alpha,1}}\right) = \tau_2 A \exp\left(-\frac{E_\alpha}{RT_{\alpha,2}}\right) = \cdots = \tau_{\mathrm{N}} A \exp\left(-\frac{E_\alpha}{RT_{\alpha,\mathrm{N}}}\right) \tag{8}$$

$$\left|\sum_{i}^{N}\sum_{j\neq i}^{N}\frac{\tau_i \exp(-E_\alpha/RT_i)}{\tau_j \exp(-E_\alpha/RT_j)} - (N-1)N\right| = \min \tag{9}$$

where T is the test temperature, $(m+1)$ the number of test temperature, d the arithmetic progression common difference of test temperature, r temperature coefficient of reaction rate, $k_{T+\mathrm{md}}$ and k_T are the reaction rate constant at the temperatures (T + md) and T, respectively.

Eq. (9) is model-free isoconversional equation and allows the activation energy (E_α) to be independently obtained, the E_α value calculated using Eq. (9) is used to check the validity of activation energy by the other method.

From Eq. (7), we have

$$\tau_T = \tau_{T+\mathrm{md}} r_{\mathrm{d}}^{\mathrm{m}} = \tau_{T+\mathrm{md}} r_{\mathrm{d}}^{T_{\mathrm{m}}-T/d} \tag{10}$$

where $T_{\mathrm{m}} = T + md$.

Taking logarithm on both sides of the Eq. (10), Berthelot's equation [8,9] (11) used to estimate the safe storage life is obtained

$$\log \tau_{T_i} = a + bT_i, \quad i = 1, 2, \ldots, N \tag{11}$$

where $a = \log \tau_{T+\mathrm{md}} + (T_{\mathrm{m}}/d)\log r_{\mathrm{d}}$ and $b = (-1/d)\log r_{\mathrm{d}}$

Combining Eqs. (5) and (6), we have

$$\tau_T = \frac{G(\alpha)}{A} e^{E/RT} \tag{12}$$

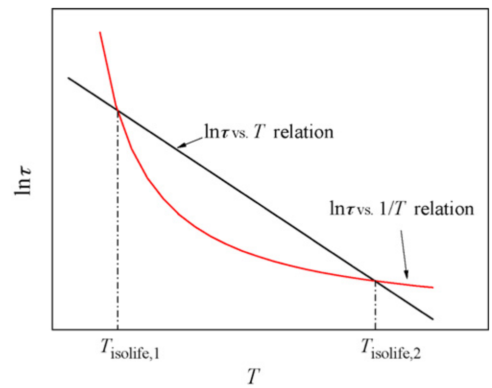

Fig. 1. Schematic diagram of determining the isolife temperatures.

Taking logarithm on both sides of the Eq. (12), Eq. (13) is obtained

$$\ln \tau_T = a' + \frac{b'}{T} \tag{13}$$

where $a' = \ln G(\alpha) - \ln A$ and $b' = E/R$

Because the value of A is much greater than that of $G(\alpha)$, Eq. (13) may be simplified to the form

$$\ln \tau_{T_i} = \frac{E}{RT} - \ln A = \frac{b'}{T_i} - a'', \quad i = 1, 2, 3, \ldots, N \tag{14}$$

where $a'' = \ln A$.

Eq. (14) is known as Arrhenius's formula or Semenov's formula [10] to estimate the safe storage life.

Combining Eqs. (11) and (14) yields

$$\left(\frac{b}{0.434294}\right) T_{\mathrm{isolife}}^2 + \left(\frac{a}{0.434294} - a'\right) T_{\mathrm{isolife}} - b' = 0 \tag{15}$$

where T_{isolife} is the isolife temperature, as shown in Fig. 1.

Once the values of T_i, τ_i, i = 1,2, . . ., N for a given conversion have calculated from an analysis of multi-temperature artificial aging test for varying time periods, the corresponding values of τ at 30 °C, E and A of the effective centralite consumption reaction, and isolife temperature obtained by combining Eqs. (11) and (14) can then be obtained from Eqs. (11), (14), (9) and (15).

3. Experimental

The 81 kinds of laboratory propellant samples: single-base gun propellants (DF-01–DF-16), double-base gun propellants (SF-01–SF-13), tri-base gun propellants (SG-01–SG-02), nitramine gun propellants (GSF-01–GSF-18), double-base propellants (ST-01–ST-13), modified double-base propellants (GST-01–GST-19), used in this work were prepared at the Xi'an Modern Chemistry Research Institute. The centralite/stabilizer used in the propellant samples were diphenylamine (DPA) for single-base gun propellants (DF-01–DF-16), 1,3-dimethyl-1,3-diphenlurca(C_2) for double-base gun propellants (SF-01–SF-13), tri-base gun propellants (SG-01–SG-02), nitramine

Table 1
Calculated values of the safe storage life and thermal decomposition kinetic parameters of various propellants obtained by thermal accelerated aging test

Propellant ID	Time (days) required to consume 50% centralite/stabilizer at temperature (°C)					Berthelot's Eq. $\log \tau = a + bT$			Semenov's eq.	$\ln \tau = a' + (b'/T) = -\ln A + (E/RT)$				Eq. (15)		Eq. (9)	
	95	90	85	75	65	$a/-b$	$-r$	$\tau_{30\,°C}$/ years	$-a'/-b'$	r	$\tau_{30\,°C}$/ years	E (kJ mol^{-1})	$\log A$ (s^{-1})	T_1 (K)	T_2 (K)	E (kJ mol^{-1})	min
Single-base gun propellants																	
DF-01	9.1	–	30.4	93	297	19.4728/0.050268	0.9999	46.98	36.8520/14399.1	0.9994	115.2	119.7	11.06	341.74	364.02	119.7	0.03419
DF-02	8.0	–	28.5	90	–	20.2609/0.052558	0.9996	58.31	39.9904/15499.9	0.9990	188.5	128.9	12.43	349.88	366.06	128.9	0.01771
DF-03	6	–	21	64	257	20.5761/0.053793	0.9991	50.87	40.0782/15422.2	0.9994	133.6	128.2	12.46	341.86	364.22	128.2	0.03337
DF-04	6	–	18	64	257	20.7958/0.054462	0.9986	52.87	40.6905/15624.6	0.9996	141.2	129.9	12.73	341.92	364.40	129.9	0.02293
DF-05	17.8	30.6	55	146.8	–	18.1538/0.045890	0.9992	47.87	33.7708/13505.9	0.9986	131.8	112.3	9.73	349.95	365.24	112.3	0.02812
DF-06	18.2	27.5	57.6	144	–	18.1812/0.045984	0.9953	47.74	33.8654/13534.6	0.9947	131.8	112.5	9.76	349.97	365.26	112.5	0.10576
DF-07	5.8	10.3	20.5	75	–	21.3770/0.056027	0.9996	67.61	43.0810/16503.0	0.9998	234.6	137.2	13.77	350.09	365.40	137.2	0.00655
DF-08	5.9	11.2	20.5	71	–	20.6112/0.053883	0.9999	51.81	41.2958/15865.9	0.9998	170.9	131.9	13.00	350.16	365.20	131.9	0.00640
DF-09	5.7	11.7	21.5	84.3	300	21.8550/0.057280	0.9998	84.76	42.7244/16394.6	0.9993	234.3	136.3	13.66	341.66	363.82	136.3	0.07002
DF-10	4.8	9.1	19.2	76	270	22.3401/0.058828	0.9997	87.89	44.1150/16835.2	0.9990	249.4	140.0	14.22	341.64	363.79	140.0	0.10386
DF-11	7.9	13.4	25.2	82.5	251	19.5016/0.050551	0.9998	41.19	37.2149/14469.7	0.9993	101.1	120.3	11.22	341.75	363.75	120.3	0.05124
DF-12	5.2	9.2	18	70	225	21.0936/0.055377	0.9995	55.43	41.3852/15849.7	0.9990	148.1	131.8	13.03	341.71	363.76	131.8	0.09576
DF-13	3.4	6.4	12.8	60	240	23.5055/0.062466	0.9996	101.5	47.3713/17887.2	0.9995	309.0	148.7	15.63	341.78	363.86	148.7	0.05569
DF-14	5.2	9.6	25.8	97	240	21.6838/0.056845	0.9926	77.45	42.3081/16233.4	0.9899	208.8	135.0	13.43	341.24	363.45	135.0	1.03001
DF-15	5.2	9.3	24.3	96	245	21.8660/0.057378	0.9940	81.22	42.7699/16391.5	0.9916	221.6	136.3	13.63	341.32	363.49	136.3	0.87155
DF-16	4.1	–	14.1	59.3	167	20.6989/0.054536	0.9982	40.18	40.9344/15610.8	0.9970	105.7	129.8	12.84	341.56	363.96	129.8	0.19192
Double-base gun propellants																	
SF-01	5.8	–	22.8	102.3	–	23.6978/0.062322	0.9996	174.79	48.2199/18396.0	0.9999	708.5	152.9	16.00	349.92	366.35	152.9	0.00136
SF-02	4.8	–	18.2	69.5	–	22.0471/0.058037	0.9999	77.78	44.9341/17124.2	0.9999	285.3	142.4	14.57	349.86	366.26	142.4	0.00228
SF-03	5.7	–	18.5	65.5	–	20.2683/0.053018	0.9998	43.00	40.7677/15648.2	0.9999	141.3	130.1	12.77	349.90	366.34	130.1	0.00018
SF-04	2.35	–	10.35	41.6	–	23.3507/0.062401	0.9998	74.38	49.1120/18406.0	0.9994	300.0	153.0	16.39	349.83	366.18	153.0	0.01474
SF-05	8	11.5	28.5	135	–	24.2330/0.063566	0.9922	251.5	48.9911/18747.4	0.9936	1044	155.9	16.34	350.38	365.56	155.9	0.24332
SF-06	7	10	22.8	125	–	24.5616/0.064654	0.9900	250.9	50.0591/19079.6	0.9920	1074	158.6	16.80	350.58	365.57	158.6	0.31575
SF-07	4.3	7.8	17.7	73	337	24.0261/0.063616	0.9995	150.9	48.0520/18220.4	0.9997	469.6	151.5	15.93	341.84	363.88	151.5	0.03861
SF-08	3.2	5.5	8.2	35	161	21.4459/0.057057	0.9952	38.61	43.4133/16369.6	0.9970	108.3	136.1	13.91	342.18	364.14	136.1	0.29957
SF-09	4.3	7.7	15.5	64	247	22.4588/0.059347	0.9997	80.46	44.7156/16994.9	0.9997	231.7	141.3	14.48	341.84	363.82	141.3	0.03283
SF-10	4.9	9.4	19.2	73.5	273	22.1901/0.058399	0.9999	84.00	43.7727/16715.9	0.9995	237.0	139.0	14.07	341.75	363.74	139.0	0.05483
SF-11	2.2	–	11.8	70	208	25.0559/0.067001	0.9950	152.1	51.0828/19154.5	0.9926	493.8	159.2	17.24	341.33	363.75	159.3	0.72564
SF-12	3.6	–	16.0	76.1	211.1	22.6164/0.059818	0.9961	83.21	45.0496/17105.0	0.9938	238.6	142.2	14.62	341.38	363.78	142.2	0.47397
SF-13	7.0	–	22.8	120.3	300	21.5315/0.056184	0.9944	86.50	41.6808/16077.8	0.9929	233.9	133.7	13.16	341.54	363.88	133.7	0.48374
Tri-base gun propellants																	
SG-01	4.6	9.6	18.1	63.4	254	21.7816/0.057327	0.9997	69.29	42.9824/16412.7	0.9995	192.1	136.4	13.73	341.77	363.81	136.5	0.05420
SG-02	4.4	7.8	15	65	210	21.6608/0.057135	0.9991	59.99	42.9383/16354.0	0.9986	165.5	136.0	13.71	341.70	363.80	136.0	0.13659
Nitramine gun propellants																	
GSF-01	2	–	7	25.2	98	21.0061/0.056269	0.9998	24.31	43.1052/16129.1	0.9999	66.68	134.1	13.78	341.82	364.19	134.1	0.00208
GSF-02	2.9	–	9.4	33.2	145.5	21.2308/0.056494	0.9986	34.86	42.9931/16207.5	0.9996	96.60	134.7	13.73	341.96	364.35	134.8	0.02685
GSF-03	5.3	9.8	19.4	68	267	21.5793/0.056671	0.9998	68.72	42.3942/16228.9	0.9999	188.7	134.9	13.47	341.77	363.90	134.9	0.01432
GSF-04	2.25	4.9	10.6	47	208	24.4408/0.065407	0.9999	112.3	49.9732/18721.3	0.9995	358.8	155.6	16.76	341.73	363.76	155.6	0.06942
GSF-05	3.5	6.5	13.1	48	205	22.1986/0.058863	0.9997	61.95	44.5392/16860.1	0.9999	177.2	140.2	14.40	341.87	363.87	140.2	0.00956
GSF-06	2.8	5.3	10.7	41	179	22.5790/0.060160	0.9997	60.16	45.7700/17231.3	0.9999	176.1	143.3	14.94	341.87	363.85	143.3	0.00538
GSF-07	5.0	8.2	14.4	52	153	19.2630/0.050482	0.9993	24.95	37.6637/14454.0	0.9990	61.30	120.2	11.42	341.80	363.80	120.2	0.07103
GSF-08	1.4	2.7	4.7	15.5	56	19.6267/0.052904	0.9998	10.62	40.7689/15149.9	0.9997	27.28	126.0	12.77	342.48	393.42	126.0	0.02212
GSF-09	1.16	–	5.83	18.5	–	22.2367/0.060136	0.9954	27.81	47.8800/17715.6	0.9938	105.4	147.3	15.85	349.68	365.88	147.3	0.14511
GSF-10	3.3	6.2	10.3	39	159	21.0889/0.055936	0.9989	37.12	42.3597/16029.4	0.9996	101.2	133.3	13.46	341.95	363.95	133.3	0.03630
GSF-11	5.7	11.1	21.6	70.2	–	20.8059/0.054425	0.9994	55.54	41.7190/16017.7	0.9987	184.7	133.2	13.18	349.98	365.22	133.2	0.03535
GSF-12	7.0	13.8	25.8	85	–	20.7208/0.053949	0.9996	63.66	41.1341/15878.6	0.9989	209.6	132.0	12.92	349.94	365.27	132.0	0.02880

Table 1 (*Continued*)

Propellant ID	Time (days) required to consume 50% centralite/stabilizer at temperature (°C)					Berthelot's Eq. $\log \tau = a + bT$			Semenov's eq.	$\ln \tau = a' + (b'/T) = -\ln A + (E/RT)$				Eq. (15)		Eq. (9)	
	95	90	85	75	65	$a/-b$	$-r$	$\tau_{30\,°C}$/ years	$-a'/-b'$	r	$\tau_{30\,°C}$/ years	E (kJ mol^{-1})	$\log A$ (s^{-1})	T_1 (K)	T_2 (K)	E (kJ mol^{-1})	min
GSF-13	3.0	6.0	12.0	46.0	143	21.2014/0.056232	0.9991	39.11	42.4948/16083.3	0.9979	105.6	133.7	13.52	341.53	363.70	133.7	0.20669
GSF-14	4.3	7.2	13	50	137	19.5241/0.051347	0.9986	24.88	38.4480/14694.5	0.9980	61.85	122.2	11.76	341.66	363.78	122.2	0.16574
GSF-15	2.3	6.0	10.6	43	109	20.8027/0.055288	0.9938	30.19	41.0143/15790.1	0.9912	79.25	131.3	13.18	−1	−1	131.3	0.84715
GSF-16	2.1	5.6	10.4	42	114	21.4244/0.057077	0.9944	36.24	43.2892/16302.3	0.9918	98.21	135.5	13.86	341.28	363.46	135.6	0.83375
GSF-17	3.7	7.7	15.7	70	250	23.1864/0.061404	0.9995	102.2	43.3399/17568.7	0.9986	303.1	146.1	15.18	−1	−1	146.1	0.15790
GSF-18	1.9	–	6.3	24.5	93.5	21.1190/0.056660	0.9996	24.00	43.4874/16243.5	0.9999	66.36	135.0	13.95	341.85	364.20	135.0	0.00686
Double-base propellants																	
ST-01	6.5	–	23	77	–	20.5788/0.053679	0.9999	55.43	41.1181/15834.6	0.9996	184.1	131.6	12.92	349.88	366.15	131.6	0.00774
ST-02	3	5.6	14	55	240	23.9666/0.063827	0.9993	113.5	48.5018/18270.2	0.9989	352.9	151.9	16.12	341.73	363.78	151.9	0.13889
ST-03	5.5	10.2	17.9	64	244	20.8969/0.054788	0.9996	53.18	40.9184/15694.4	0.9999	141.5	130.5	12.83	341.93	363.84	130.5	0.00461
ST-04	4	7.5	13.7	49	180	20.8657/0.055058	0.9999	40.98	41.4147/15766.5	0.9999	109.3	131.1	13.05	341.80	363.85	131.1	0.00828
ST-05	8.03	17.7	35.5	158.5	605.2	23.9624/0.062580	0.9997	268.4	46.4676/17906.7	0.9989	813.4	148.9	15.24	341.61	363.77	148.9	0.13549
ST-06	2.6	–	9.5	44	239	24.5062/0.065560	0.9983	117.3	50.2045/18811.5	0.9994	383.4	156.4	16.86	341.97	364.40	156.4	0.05230
ST-07	2.4	–	10.1	49	217	24.5004/0.065546	0.9999	116.9	50.1259/18783.1	0.9997	377.7	156.2	16.83	341.76	364.16	156.2	0.02599
ST-08	2.5	–	8.8	41	186	23.4947/0.062830	0.9990	76.81	48.06791/18019.2	0.9996	238.0	149.8	15.94	341.88	364.31	149.8	0.02779
ST-09	2.9	–	11.7	47	206	23.1272/0.061583	0.9999	78.71	46.8537/17650.1	0.9999	237.2	146.7	15.41	341.79	364.18	146.7	0.00749
ST-10	2.6	–	8.5	47	160	22.8830/0.061101	0.9974	62.79	46.6223/17508.4	0.9972	187.3	145.6	15.31	341.76	364.13	145.6	0.22237
ST-11	4.1	–	16.2	66	280	23.1108/0.061132	0.9999	103.9	46.1549/17519.8	0.9999	310.4	145.7	15.10	341.83	364.11	145.7	0.00781
ST-12	3.48	–	14.4	75.5	248.8	23.6797/0.062824	0.9982	118.1	47.5348/17983.3	0.9970	360.2	149.5	15.70	341.60	363.92	149.5	0.25521
ST-13	2.4	–	10.0	64.0	190.1	24.3299/0.065025	0.9956	113.6	49.5919/18605.8	0.9939	358.9	154.7	16.60	341.53	363.85	154.7	0.55609
Composite modified double-base propellants																	
GST-01	3	6	12	46	146	21.2014/0.056232	0.9991	39.11	42.4948/16083.3	0.9979	105.6	133.7	13.52	341.53	363.70	133.7	0.20669
GST-02	0.8	–	3.2	12.2	39.2	20.7313/0.056518	0.9992	10.85	44.0776/16177.5	0.9980	29.58	134.5	14.20	341.58	363.93	134.5	0.13799
GST-03	0.97	1.6	3.7	15.7	69.3	23.1080/0.062928	0.9989	29.45	49.0550/18025.9	0.9992	90.65	149.9	16.36	341.89	363.88	149.9	0.09381
GST-04	2.4	4.0	10.4	42.3	185	23.9057/0.063993	0.9987	87.88	48.9268/18323.0	0.9986	274.7	152.3	16.31	341.76	363.85	152.3	0.18254
GST-05	6.7	12.7	24.6	84	319	21.3232/0.055676	0.9999	76.32	41.3602/15941.6	0.9998	205.7	132.5	13.02	341.77	363.84	132.5	0.02310
GST-06	6.8	12.6	24.7	84	324	21.3582/0.055768	0.9998	77.58	41.4341/15969.7	0.9998	209.6	132.8	13.05	341.79	363.86	132.8	0.01810
GST-07	1.3	3.7	5.3	14.8	31.8	16.4506/0.044023	0.9846	3.49	33.6498/12602.0	0.9821	7.54	104.8	9.67	340.09	365.55	104.5	1.17193
GST-08	1.25	2.1	5.6	14.9	55	20.2370/0.054683	0.9962	12.51	42.2152/15645.6	0.9953	32.95	130.1	13.39	341.59	363.76	130.1	0.43494
GST-09	4.6	9	15.8	63	188	20.6112/0.054156	0.9992	42.82	40.4977/15495.0	0.9983	111.7	128.8	12.65	341.65	363.70	128.8	0.15466
GST-10	0.48	0.9	2.2	7.2	26	20.9866/0.057825	0.9984	7.85	45.5829/16541.4	0.9974	21.80	137.5	14.86	341.60	363.69	137.5	0.27269
GST-11	1.7	3.1	4.8	18	67	19.7931/0.053206	0.9985	12.63	40.9098/15248.3	0.9992	32.78	126.8	12.83	341.93	364.01	126.8	0.06515
GST-12	1.9	3.2	8.3	35	102	22.1963/0.059539	0.9962	38.45	45.5552/17022.6	0.9946	109.7	141.5	14.84	341.50	363.60	141.5	0.59904
GST-13	0.9	1.8	3.3	13.8	59.0	22.2087/0.060484	0.9996	20.45	47.1513/17324.8	0.9999	60.22	144.0	15.54	341.86	363.88	144.0	0.01092
GST-14	0.9	1.5	3.3	11.5	58.0	22.1467/0.060403	0.9980	18.76	47.1953/17313.3	0.9989	55.48	143.9	15.56	342.01	363.97	143.9	0.11657
GST-15	1.2	2.2	4.0	–	63	21.3142/0.057743	0.9995	17.67	44.5565/16465.0	0.9999	47.30	136.9	14.41	339.79	364.45	136.9	0.00482
GST-16	2.3	–	6.1	21.5	81.5	19.4452/0.051954	0.9976	13.59	39.7361/14910.4	0.9990	34.78	124.0	12.32	342.04	364.40	124.0	0.05862
GST-17	1.3	–	3.8	20	80	22.4766/0.060887	0.9969	28.61	47.2645/17466.3	0.9978	85.77	145.2	15.59	341.98	364.30	145.2	0.17587
GST-18	1.6	–	4.4	16	64	19.9175/0.053668	0.9976	12.18	41.4387/15403.0	0.9990	32.16	128.0	13.06	342.033	364.42	128.1	0.06235
GST-19	5.0	–	17.7	76	254	21.8658/0.057504	0.9994	74.31	43.1000/16471.3	0.9988	207.2	136.9	13.78	341.69	364.07	136.9	0.08373

gun propellants (GSF-01–GSF-18), double-base propellants (ST-01–ST-13) and modified double-base propellants (GST-01, GST-04–GST-19, GST-11, GST-12, GST-16, GST-17 and GST-19), the C_2/resorcinol mixture for modified double-base propellants (GST-02, GST-03, GST-10, GST-13–GST-15 and GST-18) and the 2-nitrodiphenylamine(2NDPA)/C_2 mixture for modified double-base propellant GST-10. The samples were kept in a desiccator before use.

For the determination of safe storage life, the chopped propellants were put into the sealed glass vessels and heated at 95 °C, 90 °C, 85 °C, 75 °C, and 65 °C under static air conditions in a multi-temperature artificial ageing testing apparatus, according to specifications of standardization method GJB 770-97-506.1 of estimating the safe storage life of propellants by using a thermal accelerating aging test [8]. The effective centralite/stabilizer content for varying time period was determined by standard bromine methods: GJB 770A-97-201.1 and GJB 770-97-210.1, which are equivalent to MIL-STD-286C-210.1.4 and 202.2.3, respectively [11,12]. The fraction of effective centralite/stabilizer reacted and the half-life periods of centralite/stabilizer depletion were calculated and extrapolated to 30 °C according to a Chinese standard method GJB 770A-97-506.1.

4. Results and discussion

The data of the time ($\tau_{\alpha=0.5}$) need for consuming the effective centralite/stabilizer of 50% at various temperature, T_i, $\tau_{\alpha=0.5,i}$, $i = 1, 2, \ldots, N$, are summarized in Table 1, which are used to calculate the values of a and b in Bethelot's equation and a' and b' in Semenov's equation, together with their appropriate linear correlation coefficients, r_B and r_S by the linear least-squares method. With the help of the obtained equations and Eqs. (9) and (15), the safe storage life at 30 °C, values of E and A, isolife temperatures, T_1 and T_2 and $E_{\alpha=0.5}$ for 81 propellants are obtained. The results are also tabulated in Table 1.

From Table 1 the following observations can be made.

[1] The values of E and $E_{\alpha=0.5}$ of each propellant obtained by the two method (Eqs. (14) and (9)) are almost the same, indicating that (1) the values of E and A in Table 1 obtained by Eq. (14) is acceptable; (2) in the derivation process of Eq. (14), the assumption of adopting $f(\alpha) = (1-\alpha)^n$, $n = 1$ and $A \gg G(\alpha)$ is rational.

[2] Rather low values of E means that the effective centralite/stabilizer consumption reaction easily took place.

[3] The $\ln A$ versus E relationship can be described by the mathematic expression for the kinetic compensation effect, $\ln A = a_1 E + b_1$,

for 16 single-base gun propellants
$\ln A = 0.0004E - 18.8$, $r_{kce} = 0.9985$
for 13 double-base gun propellants
$\ln A = 0.0003E - 14.031$, $r_{kce} = 0.9943$
for 2 tri-base gun propellants
$\ln A = 0.0001E + 15.911$, $r_{kce} = 1$
for 18 nitramine gun propellants

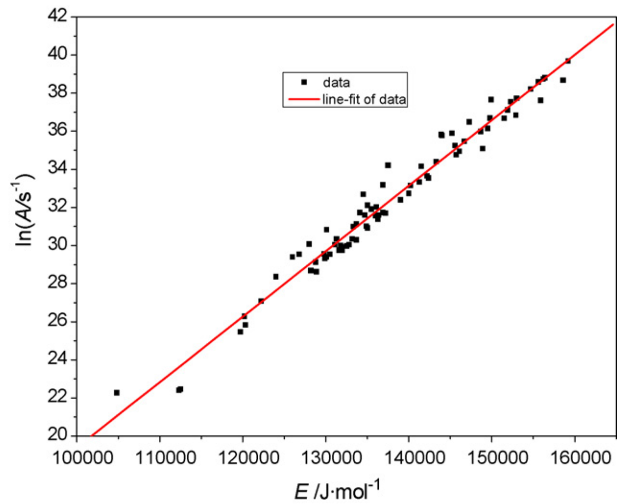

Fig. 2. The $\ln A$ vs. E relationship of 81 propellants.

$\ln A = 0.0003E - 14.805$, $r_{kce} = 0.9888$
for 13 double-base propellants
$\ln A = 0.0004E - 16.591$, $r_{kce} = 0.9946$
for 19 composite modified double-base propellants
$\ln A = 0.0003E - 14.344$, $r_{kce} = 0.9808$
for 81 propellants
$\ln A = 0.0003E - 14.995$, $r_{kce} = 0.9857$, as shown in Fig. 2.

where r_{kce} is the linear correlation fit coefficient for the kinetic compensation effect.

The above-mentioned kinetic compensation equations are used to obtain the value of A or E of same type propellant with known the E or A value.

[4] For all propellants in Table 1, the average value of $\tau_{30\,°C}$ obtained by Bethelot's equation is about 34% that obtained by Semenov's equation, showing that the safe storage life level of extrapolated to 30 °C by Bethelot's equation approaching that of extrapolated to 40 °C by Semenov's equation. Therefore, Bethelot's equation is better than Semenov's equation from the point of view of safety and reliability of estimating the safe storage life of propellants.

[5] The contents of nitroglycerine (NG) and centralite/stabilizer in propellants are two principal factors affecting the safe storage life. Lower the content of NG and higher the content of centralite/stabilizer in propellants is, longer the safe storage life of propellants.

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