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Article

Thermal Decomposition Behavior and Non-isothermal Decomposition Reaction of Copper(II) Salt of 4-Hydroxy-3,5-dinitropyridine Oxide and Its Application in Solid Rocket Propellant†

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The thermal decomposition behavior and kinetic parameters of the exothermic decomposition reactions of the title compound in a temperature-programmed mode have been investigated by means of DSC, TG-DTG and lower rate thermolysis/FTIR. The possible reaction mechanism was proposed. The critical temperature of thermal explosion was calculated. The influence of the title compound on the combustion characteristic of composite modified double base propellant containing RDX has been explored with the strand burner. The results show that the kinetic model function in differential form, apparent activation energy E_a and pre-exponential factor A of the major exothermic decomposition reaction are $1-\alpha$, 207.98 kJ•mol^{-1} and $10^{15.64}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 312.87 ℃. The kinetic equation of the major exothermic decomposition process of the title compound at 0.1 MPa could be expressed as: $\frac{d\alpha}{dT}=10^{16.42}(1-\alpha)e^{-2.502\times10^4/T}$. As an auxiliary catalyst, the title compound can help the main catalyst lead salt of 4-hydroxy-3,5-dinitropyridine oxide to enhance the burning rate and reduce the pressure exponent of RDX-CMDB propellant.

Keywords decomposition, copper(II) salt of 4-hydroxy-3,5-dinitropyridine oxide, kinetics, mechanism, application, propellant

Introduction

Copper(II) salt of 4-hydroxy-3,5-dinitropyridine oxide (4HDNPOCu) is an energetic material containing energetic groups of NO_2, which can be used as an energetic auxiliary catalyst substituting the inertia copper salt to improve the catalysis of the main catalyst (lead salt) in Composite Modified Double Base propellant containing RDX (RDX-CMDB propellant).[1] Thermal behavior is one of the most important aspects affecting its catalytic efficiency for propellant. However, its kinetic parameters of thermal decomposition and its application in RDX-CMDB propellant have not yet been reported. In this work, the kinetic parameters and the mechanism of the major exothermic decomposition reaction of 4HDNPOCu were studied by DSC, TG-DTG and lower heat rate/FTIR, and the burning rate of RDX-CMDB propellant containing 4HDNPOCu was measured by the strand burner.[2] This is quite useful in the evaluation of its thermal stability under non-isothermal condition, in the study of its thermal changes at high temperature, and in the exploration of its practical application possibilities in RDX-CMDB propellant.

Experimental

4HDNPOCu used in this work was prepared in Shanghai Institute of Organic Chemistry according to Ref. 3. Its purity was more than 99.5%. The sample was kept in a vacuum desiccator before use. Anal. calcd for $C_{10}H_{12}N_6O_{16}Cu$ (4HDNPOCu): C 22.35, N 15.90, Cu 11.95; found C 22.40, N 15.69, Cu 12.07; *m/z*: 528.5; IR (KBr) ν: 3577, 3428, 3143, 3120, 1665, 1575, 1495, 1460, 1567, 1345, 1260 cm^{-1}. The structural formula is shown in Figure 1.

The DSC data were obtained by a model DSC190S differential scanning calorimeter made in American TA Company. The conditions of DSC were as follows:

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† Dedicated to Professor Chengye Yuan on the occasion of his 80th birthday.

sample mass, less than 2.00 mg; heating rate, 2, 5, 10 and 20 ℃•min^{-1}; atmosphere, flowing N_2 gas, 40 mL•min^{-1}; reference sample, aluminum oxide. The TG-DTG curve was obtained using a model TGA2950 thermobalance. The conditions of TG were as follows: sample mass, less than 1.00 mg; heating rate, 10 ℃•min^{-1}; atmosphere, flowing N_2 gas, 60 mL•min^{-1}. The lower rate thermolysis/FTIR spectra of the condensed phase products for 4HDNPOCu were determined using KBr disc (4000—400 cm^{-1}) on a solid reaction cell of a Nicolet 60SXR FTIR spectrometer. The heating rate is 10 ℃•s^{-1}, 16 scans•file^{-1} and 8.8 files•s^{-1} were recorded at a resolution of 4 cm^{-1}. The remains were measured by a JDX-7S2 model X-diffractometer. The burning rate was measured in strand burner[2] filled with nitrogen. The sample prepared was the cylinder strand with Φ5×100 mm, coated by polyvinyl formal.

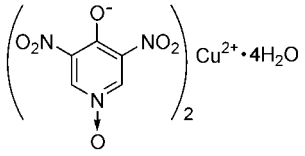

Figure 1 Structure of 4HDNPOCu.

Results and discussion

Thermal behavior and decomposition mechanism

Typical TG-DTG and DSC curves for 4HDNPOCu are shown in Figures 2 and 3. DSC curve shows an endothermic peak (132.30 ℃) and three exothermic peaks (252.20, 328.14 and 444.19℃), and correspondingly there are four peaks (118.74, 255.34, 321.88 and 459.60 ℃) on DTG curve indicating that the decomposition process of 4HDNPOCu can be divided into four stages. The first stage completes at 146.29 ℃ accompanying with 13.02% mass loss. It is in agreement with the theoretical value of the mass loss of 13.45%, corresponding to the loss of $4H_2O$. The second stage ceases at 267.94 ℃ accompanied with 8.49% mass loss, which approaches to the theoretical value of the mass loss of 8.59% of one nitryl. The third stage ends at 347.13 ℃ accompanied with 40.16% mass loss. The fourth stage is over at 533.06 ℃ with mass loss 15.14%. After the fourth stage the mass of the residue is 23.19% according with the mass summation (23.16%) of Cu＋5C. The result of X-diffraction experiment proves that the major ingredients in the residue are copper and carbon.

In order to further understand the decomposition process of 4HDNPOCu, the lower rate thermolysis/FTIR spectra of the condensed phase products for 4HDNPOCu were conducted with FTIR spectrograph. By the end of the first-stage at about 140 ℃, the characteristic absorption peaks for —OH group disappear at 3577 and 3428 cm^{-1}. But characteristic absorption peaks of other groups still exist. With temperature increasing, for the characteristic absorption peak of NO_2 at 1567 cm^{-1}, its intensity decreases and it shifts to

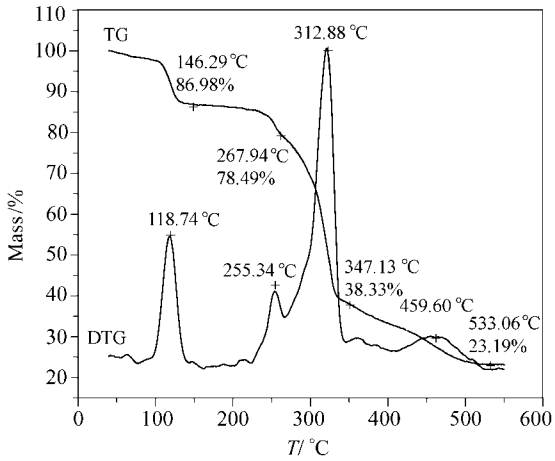

Figure 2 TG-DTG curve for 4HDNPOCu at a heating rate of 10 ℃•min^{-1}.

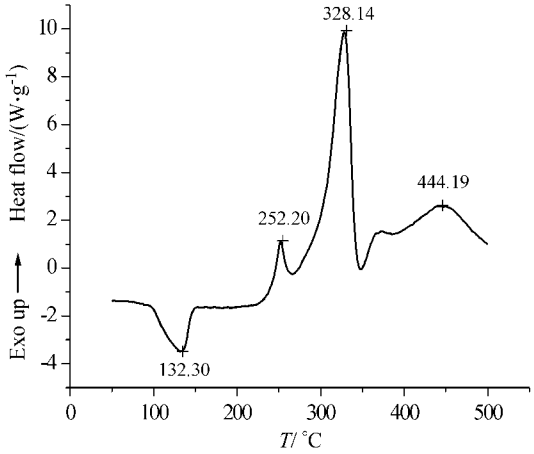

Figure 3 DSC curve for 4HDNPOCu at a heating rate of 10 ℃•min^{-1}.

1592 cm^{-1} gradually until at about 260 ℃. The result indicates that one NO_2 has been broken off from the pyridine ring matrix, which results in the chemical situation of other NO_2 changing in the molecule, as a result, the absorption peak of the band of NO_2 moves in IR spectrum. With temperature increasing further, the band of NO_2 (1592, 1345 cm^{-1}) completely disappears at 310 ℃. In 300—350 ℃, the characteristic absorption peak for the pyridine ring at 1655 cm^{-1} diminishes slowly until disappearance, and a new band at 1610 cm^{-1} appears by degrees, then dies down slowly and disappears at about 500 ℃. These results show that these processes occur in sequence: the pyridine ring breaking, new structure forming and then completely decomposing.

On the basis of the above-mentioned experiments and the calculated results, the pyrolysis mechanism for 4HDNPOCu could be shown as follows:

$$\text{4HDNPOCu} \xrightarrow[50-146.29\ ℃]{4H_2O} \xrightarrow[200-267.94\ ℃]{NO_2}$$

$$\xrightarrow[270-347.13\ ℃]{3\ NO_2+\text{other fragment}} \xrightarrow[350-533.064\ ℃]{\text{hydrocracking}} \text{Cu+5C}$$

Analysis of kinetic data

In order to obtain the kinetic parameters (apparent activation energy E_a and pre-exponential factor A) of the first and second exothermic decomposition reactions for 4HDNPOCu, a multiple heating method[4] (Kissinger's method) was employed. From the original data in Table 1, for the first exothermic process, that is, one nitryl being broken off from the pyridine ring, E_k is determined to be 180.74 kJ•mol^{-1} and A $10^{16.06}$ s^{-1}. The linear correlation coefficient r_k is 0.9985. The values of E_o and r_o obtained by Ozawa's method[5] are 188.00 kJ•mol^{-1} and 0.9938, respectively. The value of E_o approaches the dissociation energy of the C—NO_2 bond (188.3 kJ•mol^{-1}),[6] further indicating that the breakage of the C—NO_2 bond happens in the second-stage indeed.

For the second exothermic process, E_k is determined to be 205.10 kJ•mol^{-1} and A $10^{15.89}$ s^{-1}. The linear correlation coefficient r_k is 0.9996. The values of E_o and r_o obtained by Ozawa's method[5] are 212.60 kJ•mol^{-1} and 0.9921, respectively.

For the second exothermic process, that is the major exothermal decomposition process of 4HDNPOCu, the differential Eq. (1) and integral Eq. (2) are cited to obtain the values of E_a, A and the most probable kinetic model function $f(\alpha)$ from a single non-isothermal DSC curve.[7]

$$\ln\frac{d\alpha/dT}{f(\alpha)\left[E_a(T-T_0)/RT^2+1\right]}=\ln\frac{A}{\beta}-\frac{E_a}{RT} \quad (1)$$

$$\ln\frac{G(\alpha)}{T-T_0}=\ln\frac{A}{\beta}-\frac{E_a}{RT} \quad (2)$$

where $f(\alpha)$ and $G(\alpha)$ are the differential and integral model functions, respectively, T_0 the initial point at which DSC curve deviates from the baseline, R the gas constant, β the heating rate, α the conversion degree ($\alpha=H_t/H_o$), dH_t/dt the exothermic heat flow at time t, H_o the total heat effect (corresponding to the global area under the DSC curve), H_t the reaction heat at a certain time (corresponding to the partial area under the DSC curve), T the temperature (K) at time t, $\frac{d\alpha}{dt}=\frac{1}{H_0\beta}\frac{dH}{dt}$.

Forty-one types of kinetic model functions[8] and the data in Tables 2—5 are put into Eqs. (1) and (2) for calculation, respectively. The values of E_a, A, linear correlation coefficient r, standard mean square deviation Q and believable factor d (where $d=(1-\alpha)Q$) are obtained by the linear least-squares and iterative methods. The probable kinetic model function of two methods selected by the better values of r, Q and d and satisfying ordinary range of the thermal decomposition kinetic parameters for energetic materials (E=80—250 kJ•mol^{-1} and log A=7—30, A is in unit of s^{-1}) is $G(\alpha)=-\ln(1-\alpha)$ and $f(\alpha)=1-\alpha$, which indicates that the reaction mechanism of the major exothermic decomposition process of 4HDNPOCu is classified as nucleation and growth, and the mechanism function is the Mample equation with n=1. The values of E_a and A obtaind by Eqs. (1) and (2) are in good agreement with the calculated values by Kissinger and Ozawa's methods. Substituting $f(\alpha)$ with $1-\alpha$, E with 207.98 kJ•mol^{-1}, β with 0.1667 K•s^{-1} and A with $10^{15.64}$ s^{-1} in Eq. (3),

$$d\alpha/dT=\frac{A}{\beta}f(\alpha)e^{-E/RT} \quad (3)$$

we can now establish the kinetic equation of the major exothermic decomposition process of 4HDNPOCu as follows: $\frac{d\alpha}{dT}=10^{16.42}(1-\alpha)e^{-2.502\times10^4/T}$

Table 1 Kinetic parameters of the first and second exothermic decomposition reactions of 4HDNPOCu obtained by the multiple heating method

	β/(℃•min^{-1})	T_e/℃	E_o/(kJ•mol^{-1})	r_o	T_p/℃	E_k/(kJ•mol^{-1})	log A_k (A_k in s^{-1})	r_k	E_o/(kJ•mol^{-1})	r_o
First exothermic process	2.0	227.17	195.90	0.9889	234.05	180.74	16.06	0.9985	180.10	0.9987
	5.0	235.07			245.33					
	10.0	240.76			252.20					
	20.0	251.70			261.84					
Mean: E_0=(195.90+180.10)/2=188.00 kJ•mol^{-1}										
Second exothermic process	2.0	282.51	220.70	0.9845	306.33	205.10	15.89	0.9996	204.50	0.9996
	5.0	288.67			317.79					
	10.0	300.81			328.14					
	20.0	307.07			337.58					
Mean: E_0=(220.7+204.5)/2=212.60 kJ•mol^{-1}										

β, Heating rate; T_e, onset temperature in the DSC curve; T_p, maximum peak temperature; E, apparent activation energy; A, pre-exponential constant; r, linear correlation coefficient; subscript k, data obtained by Kissinger' s method; subscript o, data obtained by Ozawa' s method.

Table 2 Data of 4HDNPOCu determined by DSC[a]

T_i/℃	α_i	$(dH/dt)_i$/(mJ•s^{-1})	$(d\alpha/dT)_i\times10^3$/K^{-1}
261	0.0004	0.0104	0.10
262	0.0012	0.0359	0.34
263	0.0023	0.0466	0.44
264	0.0036	0.0757	0.71
265	0.0054	0.0979	0.92
266	0.0078	0.1110	1.04
267	0.0102	0.1713	1.60
268	0.0134	0.1657	1.55
269	0.0168	0.1903	1.78
270	0.0204	0.2289	2.14
271	0.0247	0.2622	2.45
272	0.0298	0.3096	2.90
273	0.0348	0.3447	3.22
274	0.0408	0.3684	3.45
275	0.0479	0.4242	3.97
276	0.0544	0.4473	4.18
277	0.0620	0.4850	4.54
278	0.0700	0.5419	5.07
279	0.0787	0.5876	5.50
280	0.0882	0.6450	6.03
281	0.0975	0.7051	6.60
282	0.1081	0.7718	7.22
283	0.1197	0.8339	7.80
284	0.1319	0.9026	8.44
285	0.1454	0.9713	9.09
286	0.1585	1.0471	9.79
287	0.1730	1.1293	10.56
288	0.1885	1.2183	11.40
289	0.2052	1.3046	12.20
290	0.2215	1.4091	13.18
291	0.2396	1.5230	14.25
292	0.2610	1.6351	15.30
293	0.2806	1.7585	16.45
294	0.3031	1.8923	17.70
295	0.3260	2.0288	18.98
296	0.3512	2.1983	20.56
297	0.3785	2.3314	21.81
298	0.4055	2.4681	23.09
299	0.4336	2.6677	24.96
300	0.4644	2.8316	26.49
301	0.4988	2.9848	27.92
302	0.5333	3.1423	29.40
303	0.5686	3.2727	30.62
304	0.6056	3.3699	31.52
305	0.6420	3.4244	32.03
306	0.6800	3.4201	31.99
307	0.7191	3.3249	31.10
308	0.7561	3.1654	29.61
309	0.7909	2.9468	27.57
310	0.8265	2.5897	24.23
311	0.8582	2.1816	20.41
312	0.8866	1.7269	16.15
313	0.9102	1.2761	11.94
314	0.9305	0.8147	7.62
315	0.9477	0.3494	3.27

[a] T_o=532.15 K; H_o=3206.94 mJ; β=0.0333 K•s^{-1}.

Table 3 Data of 4HDNPOCu determined by DSC[a]

T_i/℃	α_i	$(dH/dt)_i$/(mJ•s^{-1})	$(d\alpha/dT)_i\times10^3$/K^{-1}
266	0.0003	0.0235	0.27
267	0.0007	0.0348	0.41
268	0.0014	0.0556	0.65
269	0.0023	0.0704	0.82
270	0.0035	0.1065	1.25
271	0.0049	0.1233	1.45
272	0.0067	0.1474	1.73
273	0.0086	0.1809	2.12
274	0.0109	0.1990	2.33
275	0.0135	0.2265	2.65
276	0.0164	0.2600	3.05
277	0.0197	0.2841	3.33
278	0.0234	0.3062	3.59
279	0.0275	0.3464	4.06
280	0.0318	0.3678	4.31
281	0.0365	0.3926	4.60
282	0.0412	0.4335	5.08
283	0.0465	0.4616	5.41
284	0.0520	0.4945	5.80
285	0.0580	0.5320	6.24
286	0.0644	0.5688	6.67
287	0.0715	0.6204	7.27
288	0.0800	0.6518	7.64
289	0.0875	0.7060	8.28
290	0.0960	0.7399	8.67
291	0.1053	0.7803	9.15
292	0.1146	0.8402	9.85

Continued

T_i/℃	α_i	$(dH/dt)_i$/(mJ•s^{-1})	$(d\alpha/dT)_i\times10^3$/K^{-1}
293	0.1245	0.9023	10.58
294	0.1353	0.9590	11.24
295	0.1470	1.0205	11.96
296	0.1597	1.0781	12.64
297	0.1727	1.1465	13.44
298	0.1862	1.2043	14.12
299	0.2012	1.2756	14.95
300	0.2165	1.3537	15.87
301	0.2327	1.4252	16.70
302	0.2504	1.5005	17.59
303	0.2690	1.5874	18.61
304	0.2883	1.6764	19.65
305	0.3089	1.7675	20.72
306	0.3301	1.8680	21.90
307	0.3527	1.9642	23.02
308	0.3762	2.0770	24.35
309	0.4010	2.1815	25.57
310	0.4281	2.2626	26.52
311	0.4563	2.3819	27.92
312	0.4862	2.4911	29.20
313	0.5174	2.5755	30.19
314	0.5449	2.6887	31.52
315	0.5753	2.7731	32.51
316	0.6089	2.8442	33.34
317	0.6439	2.8837	33.80
318	0.6778	2.9185	34.21
319	0.7120	2.9252	34.29
320	0.7447	2.8864	33.83
321	0.7778	2.7959	32.77
322	0.8107	2.6458	31.01
323	0.8410	2.4576	28.81
324	0.8690	2.2298	26.14
325	0.8944	1.9698	23.09
326	0.9162	1.6920	19.83
327	0.9348	1.4206	16.65
328	0.9504	1.1546	13.53
329	0.9629	0.9285	10.88
330	0.9734	0.7014	8.22
331	0.9812	0.5521	6.47
332	0.9872	0.4060	4.76
333	0.9912	0.3283	3.85
334	0.9945	0.2318	2.72
335	0.9970	0.1776	2.08
336	0.9988	0.1159	1.36

[a] T_o=537.15 K; H_o=1023.76 mJ; β=0.0833 K•s^{-1}.

Table 4 Data of 4HDNPOCu determined by DSC[a]

T_i/℃	α_i	$(dH/dt)_i$/(mJ•s^{-1})	$(d\alpha/dT)_i\times10^3$/K^{-1}
269	0.0001	0.0367	0.10
270	0.0003	0.0763	0.20
271	0.0007	0.1276	0.34
272	0.0011	0.1796	0.48
273	0.0017	0.2316	0.62
274	0.0024	0.2923	0.78
275	0.0032	0.3664	0.98
276	0.0044	0.4661	1.25
277	0.0057	0.5664	1.52
278	0.0074	0.6609	1.77
279	0.0092	0.7498	2.01
280	0.0113	0.8316	2.23
281	0.0136	0.9222	2.47
282	0.0161	1.0148	2.72
283	0.0188	1.1081	2.97
284	0.0219	1.2021	3.22
285	0.0251	1.2873	3.45
286	0.0285	1.3756	3.68
287	0.0322	1.4734	3.95
288	0.0361	1.5833	4.24
289	0.0404	1.6991	4.55
290	0.0449	1.8034	4.83
291	0.0497	1.9077	5.11
292	0.0548	2.0238	5.42
293	0.0602	2.1453	5.75
294	0.0659	2.2759	6.10
295	0.0719	2.4106	6.46
296	0.0783	2.5505	6.83
297	0.0851	2.6970	7.22
298	0.0922	2.8488	7.63
299	0.0997	3.0099	8.06
300	0.1075	3.1788	8.51
301	0.1159	3.3715	9.03
302	0.1250	3.6012	9.65
303	0.1348	3.8467	10.30
304	0.1454	4.0804	10.93
305	0.1563	4.2995	11.52
306	0.1675	4.5094	12.08
307	0.1790	4.7364	12.69
308	0.1913	5.0453	13.51
309	0.2047	5.3977	14.46
310	0.2192	5.7805	15.48
311	0.2346	6.1607	16.50

Continued

T_i/℃	α_i	$(dH/dt)_i$/(mJ•s^{-1})	$(d\alpha/dT)_i\times10^3$/K^{-1}
312	0.2510	6.5593	17.57
313	0.2684	6.9870	18.71
314	0.2866	7.4358	19.92
315	0.3060	7.9255	21.23
316	0.3267	8.4575	22.65
317	0.3489	9.0079	24.13
318	0.3724	9.5623	25.61
319	0.3975	10.1260	27.12
320	0.4240	10.6566	28.54
321	0.4518	11.1543	29.88
322	0.4806	11.6017	31.08
323	0.5104	12.0136	32.18
324	0.5414	12.3977	33.21
325	0.5735	12.7369	34.12
326	0.6068	13.0194	34.87
327	0.6408	13.2174	35.40
328	0.6755	13.3006	35.63
329	0.7108	13.2438	35.47
330	0.7460	13.0115	34.85
331	0.7806	12.5825	33.70
332	0.8147	11.9225	31.93
333	0.8470	11.0487	29.59
334	0.8771	9.9570	26.67
335	0.9039	8.7136	23.34
336	0.9270	7.4094	19.85
337	0.9462	6.1171	16.38
338	0.9615	4.9027	13.13
339	0.9735	3.8164	10.22
340	0.9825	2.8845	7.73
341	0.9889	2.1109	5.65
342	0.9934	1.5179	4.07
343	0.9964	1.0769	2.88
344	0.9983	0.7504	2.01
345	0.9994	0.5095	1.36
346	0.9998	0.3431	0.92

[a] T_o=539.15 K; H_o=2240.04 mJ; β=0.1667 K•s^{-1}.

The corresponding kinetic parameters are summarized in Table 6.

The value T_{po} of the peak temperature T_p corresponding to $\beta\rightarrow0$ obtained by Eq. (4) taken from Ref. 9 is 299.38 ℃.

$$T_{pi}=T_{po}+b\beta_i+c\beta_i^2,\ i=1-4 \quad (4)$$

where b and c are coefficients.

Table 5 Data of 4HDNPOCu determined by DSC[a]

T_i/℃	α_i	$(dH/dt)_i$/(mJ•s^{-1})	$(d\alpha/dT)_i\times10^3$/K^{-1}
283	0.0001	0.0143	0.04
284	0.0004	0.0343	0.10
285	0.0008	0.0642	0.19
286	0.0014	0.1010	0.29
287	0.0022	0.1372	0.40
288	0.0032	0.1810	0.53
289	0.0045	0.2294	0.67
290	0.0060	0.2794	0.81
291	0.0077	0.3364	0.98
292	0.0097	0.3986	1.16
293	0.0119	0.4670	1.36
294	0.0145	0.5321	1.55
295	0.0174	0.6033	1.76
296	0.0205	0.6800	1.98
297	0.0240	0.7649	2.23
298	0.0278	0.8513	2.48
299	0.0320	0.9495	2.76
300	0.0365	1.0479	3.05
301	0.0414	1.1384	3.31
302	0.0467	1.2426	3.62
303	0.0524	1.3542	3.94
304	0.0586	1.4637	4.26
305	0.0652	1.5885	4.63
306	0.0722	1.7165	5.00
307	0.0797	1.8617	5.42
308	0.0876	2.0016	5.83
309	0.0961	2.1482	6.26
310	0.1051	2.3079	6.72
311	0.1147	2.4861	7.24
312	0.1250	2.6696	7.77
313	0.1356	2.8577	8.32
314	0.1471	3.0695	8.94
315	0.1594	3.2820	9.56
316	0.1722	3.5117	10.23
317	0.1860	3.7546	10.93
318	0.2003	4.0140	11.69
319	0.2156	4.2958	12.51
320	0.2317	4.5895	13.36
321	0.2487	4.8977	14.26
322	0.2669	5.2224	15.21
323	0.2861	5.5584	16.19

Continued

T_i/℃	α_i	$(dH/dt)_i$/(mJ•s^{-1})	$(d\alpha/dT)_i\times10^3$/K^{-1}
324	0.3065	5.9082	17.20
325	0.3279	6.2679	18.25
326	0.3507	6.6309	19.31
327	0.3745	6.9873	20.35
328	0.3992	7.3371	21.36
329	0.4248	7.6605	22.31
330	0.4518	7.9641	23.19
331	0.4794	8.2347	23.98
332	0.5080	8.4723	24.67
333	0.5372	8.6571	25.21
334	0.5676	8.7891	25.59
335	0.5982	8.8749	25.84
336	0.6294	8.8947	25.90
337	0.6605	8.8617	25.80
338	0.6913	8.7693	25.54
339	0.7221	8.5845	25.00
340	0.7521	8.3007	24.17
341	0.7821	7.9047	23.02
342	0.8105	7.4031	21.56
343	0.8377	6.7998	19.80
344	0.8633	6.1009	17.77
345	0.8867	5.3208	15.49
346	0.9080	4.4898	13.07
347	0.9266	3.6483	10.62
348	0.9428	2.8187	8.21
349	0.9565	2.0241	5.89
350	0.9680	1.2888	3.75
351	0.9776	0.6121	1.78
352	0.9853	0.0146	0.04

[a] T_o=554.87 K; H_o=1030.26 mJ; β=0.3333 K•s^{-1}.

The critical temperature of thermal explosion T_b obtained from Eq. (5) taken from Ref. 9 is 312.87 ℃.

$$T_b=\frac{E_o-\sqrt{E_o^2-4E_oRT_{po}}}{2R} \quad (5)$$

where R is the gas constant (8.314 J•mol^{-1}•K^{-1}), E_o is the value of E obtained by Ozawa's method.

Burning catalysis in RDX-CMDB propellant

For the sake of the possible application of 4HDNPOCu in propellant as the adjuvant of the burning catalyst (the lead salt), the burning rates u of three systems: minimum smoke propellant of RDX-CMDB (binder/RDX/No. 2 centralite/auxiliary = 66/26/2.0/6 (mass percent)) system (I), I/4HDNPOPb (lead salt of 4-hydroxy-3,5-dinitropyridine oxide)=100/2.5 system (II) and I/4HDNPOPb/4HDNPOCu=100/2.0/0.5 system (III) were measured at different pressure p. The results in Table 7 show that in the help of 4HDNPOCu the catalysis of 4HDNPOPb for the burning rate of propellant is improved. In order to study the effect of 4HDNPOCu on the combustion characteristic of RDX-CMDB propellant, the pressure exponent n of burning rate was calculated, and the mean catalysis efficiency $\bar{Z}$ was compared before and after 4HDNPOCu was added into RDX-CMDB propellant. The experiment data in Table 7, p_i and u_i (i=1—10) were put into Eqs. (6) and (7) respectively

$$u_i=ap_i^n \qquad i=1-10 \quad (6)$$

$$\bar{Z}=\sum_{i=1}^{k}(u_{\mathrm{II\ (or\ III)}i}/u_{\mathrm{I}i})/k \quad (7)$$

where a is the factor.

The values of u, n and $\bar{Z}$ were obtained: for I, in 2—20 MPa, $u=1.69p^{0.843}$, n=0.843, r=0.996, $\bar{Z}_{2\text{-}6}$=1, $\bar{Z}_{8\text{-}12}$=1, $\bar{Z}_{14\text{-}18}$=1; for II, in 10—14 MPa, n=0.563, r=0.9995, $\bar{Z}_{2\text{-}6}$=1.46, $\bar{Z}_{8\text{-}12}$=1.15, $\bar{Z}_{14\text{-}18}$=1.07; for III, in 8—16 MPa, n=0.557, r=0.9998, $\bar{Z}_{2\text{-}6}$=1.53, $\bar{Z}_{8\text{-}12}$=1.29, $\bar{Z}_{14\text{-}18}$=1.15, which indicate that ,as an auxiliary catalyst, 4HDNPOCu can help the main catalyst 4HDNPOPb to enhance the burning rate and reduce the pressure exponent of RDX-CMDB propellant.

Table 6 Calculated values of kinetic parameters of the major exothermal decomposition reaction for 4HDNPOCu

β/℃	$G(\alpha)$	$f(\alpha)$	Eq. (1)		Eq. (3)	
			E_a/(kJ•moL^{-1})	log A (A in s^{-1})	E_a/(kJ•moL^{-1})	log A (A in s^{-1})
2	$-\ln(1-\alpha)$	$1-\alpha$	219.10 [a]	16.54 [a]	208.02 [b]	15.71 [b]
5	$-\ln(1-\alpha)$	$1-\alpha$	198.95 [c]	14.89 [c]	198.70 [d]	14.86 [d]
10	$-\ln(1-\alpha)$	$1-\alpha$	215.81 [e]	16.39 [e]	209.82 [f]	15.80 [f]
20	$-\ln(1-\alpha)$	$1-\alpha$	202.39 [g]	14.98 [g]	211.02 [h]	15.93 [h]
Mean E_a=207.98 kJ•mol^{-1}, log A=15.64						

[a] r=0.9746, Q=5.1433, d=0.1306; [b] r=0.9825, Q=3.1505, d=0.0550; [c] r=0.9867, Q=4.2732, d=0.0566; [d] r=0.9864, Q=4.3726, d=0.0594; [e] r=0.9679, Q=15.9240, d=0.5117; [f] r=0.9816, Q=8.4564, d=0.1559; [g] r=0.9163, Q=26.7304, d=2.2384; [h] r=0.9821, Q=5.5809, d=0.0970.

Table 7 The burning rates (mm•s^{-1}) of systems I—III at different pressure

System	Pressure/MPa									
	2	4	6	8	10	12	14	16	18	20
I	3.09	5.34	7.42	9.85	11.88	14.04	15.75	17.54	19.23	20.92
II	5.01	7.95	10.11	11.95	13.79	15.20	16.67	18.87	20.79	22.22
III	4.89	8.25	11.06	13.57	15.50	17.09	18.59	20.00	21.74	23.26

Conclusions

The kinetic parameters of the first and second exothermic decomposition reactions for 4HDNPOCu have been investigated. The possible mechanism of the decomposition reaction is proposed. The kinetic model function in differential form, apparent activation energy E_a and pre-exponential factor A of the major exothermic reaction are $1-\alpha$, 207.98 kJ•mol^{-1} and $10^{15.64}$ s^{-1}, respectively. The critical temperature of thermal explosion of the compound is 312.87 ℃. As an auxiliary catalyst, 4HDNPOCu can help the main catalyst 4HDNPOPb to enhance the burning rate and reduce the pressure exponent of RDX-CMDB propellant.

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