

Thermal Behavior, Non-Isothermal Decomposition Reaction Kinetics and Thermal-Safety Evaluation on 3-Amino-4-chloroximidofurazan

^{1,2}BIAO YAN, ^{1,2}HONGYA LI, ²HAIXIA MA*, ^{2,3}JIRONG SONG AND ⁴FENGQI ZHAO

¹*School of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Low Metamorphic Coal clean Utilization, Yulin University, Yulin 719000, P. R. China.*

²*School of Chemical Engineering, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Northwest University, Xi'an 710069, P. R. China.*

³*Conservation Technology Department, the Palace Museum, 4 Jingshan Qianjie Beijing 100009, P. R. China*

⁴*Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, P. R. China.*

donghuhai@qq.com*

(Received on 23rd June 2012, accepted in revised from 1st October 2012)

Summary: 3-Amino-4-chloroximidofurazan (ACOF) is an important precursor of synthesizing new furazanone (furoxano) energetic compounds. Its thermal behavior was studied by the differential scanning calorimetry (DSC) method. The results of this study show that there are three exothermic decomposition processes. Its kinetic parameters of the intense exothermic decomposition process were obtained from the analysis of the DSC curves. The apparent activation energy, pre-exponential factor and the mechanism function are 153.54 kJmol⁻¹, 10^{14.34} s⁻¹ and $f(\alpha) = 2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$, respectively. The specific heat capacity of ACOF was determined with a continuous C_p mode of micro-calorimeter. Using the relationship between C_p and T with the thermal decomposition parameters, the time of the thermal decomposition from initialization to thermal explosion (adiabatic time-to-explosion, t_{TIAD}), the self-accelerating decomposition temperature (T_{SADT}), thermal ignition temperature (T_{TIT}), critical temperatures of thermal explosion (T_b) and period of validity ($t_{0.9}$) were obtained to evaluate its thermal safety.

Key words: 3-Amino-4-chloroximidofurazan (ACOF), thermal behavior, Non-isothermal kinetics, Thermal safety.

Introduction

Many studies show that furazan ring is a perfect structure unit for constructing new high energy density material [1–10]. Most of the energetic compounds containing furazan ring (such as 3,4-bis (nitrofurazano) furoxan (BNFF) [3, 4], 3,4-bis (4'-azidofurazano-3'-yl) furoxan (DAZTF) [6], and, 4-amino-3-(5-tetrazole) furazan(HAFT) [7], etc.) have common characteristics such as high standard enthalpy of formation (ΔH_f^\ominus), high nitrogen content, high energy density, good thermal stability, and low melting point. Theoretical calculations show that when a nitro group is displaced by a furazan group in energetic compounds, the density and detonation velocity can increase by about 0.06 – 0.08 gcm⁻³ and 300 ms⁻¹, respectively [2]. Thus furazan compounds have received much attention worldwide. 3-Amino-4-chloroximidofurazan (ACOF) (Fig. 1) is an important precursor of synthesizing new furazano (furoxano) energetic compounds, such as 3,4-bis (nitrofurazano) furoxan (BNFF) [3, 4], 3,4-bis (aminofurazano) furoxan (BAFF) [3, 5], 3,4-bis (4'-azidofurazano -3'-yl) furoxan (DAZTF) [6], 4-amino-3-(5-tetrazole)furazan(HAFT) and its energetic salts [7], 3,3'-Dicyanodifurazanyl Ether(FOF-2) [8], Oxidative cyclocondensation of 4,4'-diamino-3,3'-bi-1,2,5-

oxadiazole and isomeric 3(4)-amino-4(3)-(4-amino-1,2,5-oxadiazol-3-yl)-1,2,5-oxadiazole 2-oxides [9] and 3,6-bis(3'-aminofurazan-4-yl)-1,4-dioxo-2,5-diazacyclohexa-2,5-diyne (BADDD) [10]. So, it is significant to study the chemophysical properties of ACOF. However, there're no reports on its thermal behavior. The purpose of the article is to describe its thermal decomposition processes, non-isothermal decomposition kinetics and thermal safety.

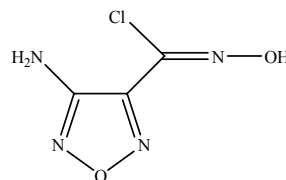


Fig. 1: Structures of ACOF.

Result and Discussion

Thermal Behavior

The DSC heat flow curve for ACOF at the heating rate of 10 Kmin⁻¹ is shown in Fig. 2. The

*To whom all correspondence should be addressed.

DSC curve indicates that the thermal decomposition of ACOF can be divided into three stages. The first stage is an intense exothermic decomposition process, the extrapolated onset temperature (T_e) and peak temperature (T_p) obtained at a heating rate of 10 Kmin^{-1} are 470.26 K and 485.89 K, respectively. The second stage is a mild exothermic decomposition process with T_e and T_p are 509.35 K and 541.32 K, respectively. The third stage is also a mild exothermic decomposition process with T_e and T_p are 589.40 K and 616.83 K, respectively. The basic data for the intense exothermic decomposition process are listed in (Table-1).

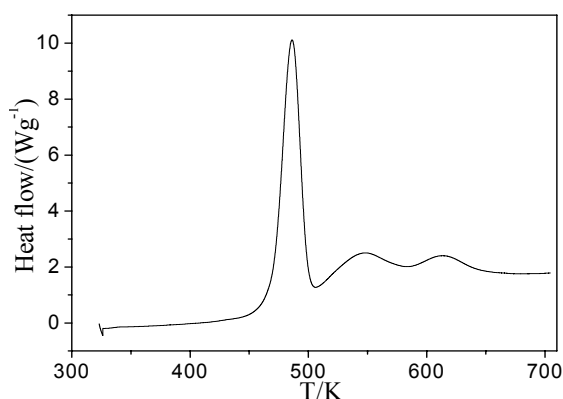


Fig 2: The DSC heat flow curve of ACOF at 10 Kmin^{-1} by DSC.

Table-1: Basic data for the intense exothermic decomposition process of ACOF.

$\beta/(\text{Kmin}^{-1})$	T_e/K	T_p/K	$\Delta H/(\text{Jg}^{-1})$
2.5	454.58	469.19	746.1
5	464.77	477.46	722.3
10	470.26	485.89	760.3
15	472.90	491.38	790.4

Note: T_e is the onset temperature for the intense exothermal decomposition reaction in DSC curve and T_p is the peak temperature; ΔH is the decomposition heat.

Non-Isothermal Decomposition Reaction Kinetics

To explore the reaction mechanism of the intense exothermic decomposition process of ACOF and obtain the corresponding kinetic parameters [apparent activation energy (E_a/kJmol^{-1}), pre-exponential constant (A/s^{-1})] and the most probable kinetic model function, the DSC curves at the heating rates of 2.5, 5.0, 10.0 and 15.0 Kmin^{-1} were dealt with the mathematic means, and the temperature data corresponding to the conversion degrees (α) were found. Six integral methods (MacCallum-Tanner, Šatava-Šesták, Agrawal, General integral, Universal integral, Flynn-Wall-Ozawa) and one differential

method (Kissinger) were employed [11–15]. The values of E_a were obtained by Ozawa's method from the isoconversional DSC curves at the heating rates of 2.5, 5.0, 10.0 and 15.0 Kmin^{-1} , and the E_a - α relation is shown in Fig. 3. One can see that the activation energy slightly changes in the section of 0.15–0.70 (α), and the ranges were selected to calculate the non-isothermal reaction kinetics in Fig. 3.

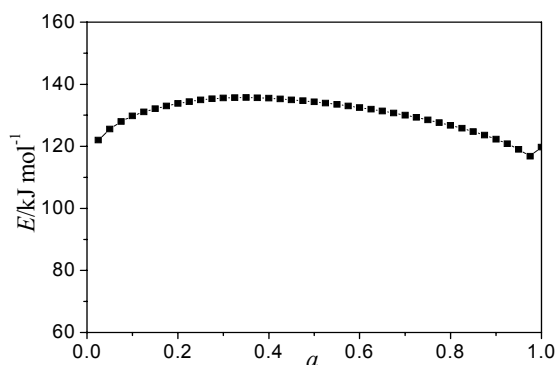


Fig. 3: E_a vs α curve of ACOF by Flynn-Wall-Ozawa's method.

Forty-one types of kinetic model functions and the basic data were put into the integral and differential equations for calculation. The kinetic parameters and the probable kinetic model function were selected by the logical choice method and satisfying the ordinary range of the thermal decomposition kinetic parameters for energetic materials ($E = 80$ – 250 kJmol^{-1} , $\lg A = 7$ – 30 s^{-1}). These data together with their appropriate values of linear correlation coefficient (r), standard mean square deviation (Q) and believable factor (d , where $d = (1-r)Q$), are presented in (Table-2). The values of E_a and $\log A$ obtained from a single non-isothermal DSC curves are in good agreement with the calculated values obtained by Kissinger's method and Ozawa's method. Therefore, we conclude that the reaction mechanism of the intense exothermic decomposition process of ACOF is classified as Avrami-Erofeev equation $G(\alpha) = [-\ln(1-\alpha)]^{1/2}$, $f(\alpha) = 2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$. Substituting $f(\alpha)$ with $2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$, E with $153.54 \text{ kJmol}^{-1}$ and A with $10^{14.34} \text{ s}^{-1}$ Eq. (1),

$$d\alpha/dT = \frac{A}{\beta} f(\alpha) e^{-E/RT} \quad (1)$$

Table-2: Kinetic parameters for the intense exothermic decomposition process of ACOF.

Method	β/Kmin^{-1}	E_a/kJmol^{-1}	$\log(A/\text{s}^{-1})$	r	Q	d
MacCallum-Tanner	2.5	148.66	14.05	0.9999	7.36×10^{-5}	7.52×10^{-9}
	5	168.47	16.25	0.9998	1.39×10^{-4}	2.67×10^{-8}
	10	157.43	14.95	0.9993	5.36×10^{-4}	3.99×10^{-7}
	15	142.06	13.23	0.9986	1.00×10^{-3}	1.39×10^{-6}
Šatava-Šesták	2.5	148.54	14.07	0.9999	7.36×10^{-5}	7.52×10^{-9}
	5	167.24	16.15	0.9998	1.39×10^{-4}	2.67×10^{-8}
	10	156.82	14.92	0.9993	5.36×10^{-4}	3.99×10^{-7}
	15	142.31	13.31	0.9986	1.00×10^{-3}	1.39×10^{-6}
Agrawal	2.5	148.48	14.08	0.9999	3.82×10^{-4}	4.22×10^{-8}
	5	167.99	16.24	0.9998	7.26×10^{-4}	1.51×10^{-7}
	10	156.88	14.94	0.9992	2.87×10^{-3}	2.38×10^{-6}
	15	141.52	13.23	0.9984	5.35×10^{-3}	8.39×10^{-6}
General integral	2.5	148.48	14.08	0.9999	3.82×10^{-4}	4.22×10^{-8}
	5	167.99	16.24	0.9998	7.26×10^{-4}	1.51×10^{-7}
	10	156.88	14.95	0.9992	2.87×10^{-3}	2.38×10^{-6}
	15	141.52	13.23	0.9984	5.35×10^{-3}	8.39×10^{-6}
Universal integral	2.5	146.83	12.67	0.9999	3.95×10^{-4}	4.62×10^{-8}
	5	166.57	14.81	0.9998	7.40×10^{-4}	1.60×10^{-7}
	10	155.67	13.56	0.9992	2.83×10^{-3}	2.36×10^{-6}
	15	140.44	11.91	0.9984	5.30×10^{-3}	8.35×10^{-6}
Mean		153.54	14.34			
Flynn-Wall-Ozawa		$162.05(E_{e0})$		0.9813	1.31×10^{-2}	
		$147.78(E_{p0})$		0.9999	5.88×10^{-5}	
Kissinger		$147.43(E_K)$	13.94	0.9999	3.23×10^{-4}	
Mean(E_{e0}, E_{p0}, E_K)		152.42				

Note: E with the subscript of eO and pO is the apparent activation energy obtained from the onset temperature (T_e) and the peak temperature (T_p) by Ozawa's method, E with the subscript of K is the apparent activation energy obtained from the peak temperature (T_p) by Kissinger's method.

The kinetic equation of the intense exothermic decomposition reaction may be described as:

$$d\alpha/dT = \frac{10^{14.34}}{\beta} 2(1-\alpha)[- \ln(1-\alpha)]^{1/2} \exp(-1.85 \times 10^4 / T)$$

Thermal Safety Studies

The values (T_{e0} and T_{p0}) of the onset temperature (T_e) and peak temperature (T_p) corresponding to $\beta \rightarrow 0$ are obtained by Eq. (2), and the self-accelerating decomposition temperature (T_{SADT}) is obtained by Eq. (3) [11–14]. The values (T_{SADT} and T_{p0}) are 436.03 K and 456.64 K, respectively.

$$T_{e(\text{or } p)} = T_{e0(\text{or } p0)} + a\beta_i + b\beta_i^2 + c\beta_i^3 \quad i=1\sim 4 \quad (2)$$

where a , b and c are coefficients.

$$T_{SADT} = T_{e0} \quad (3)$$

The thermal ignition temperature (T_{be0} or T_{TIT}) are obtained by substituting E_{e0} and T_{e0} into Zhang et al. equation [Eq. (4)] [16], and the critical temperatures of thermal explosion (T_{bp0} or T_b) are obtained by substituting E_{p0} and T_{p0} into equation. The values (T_{TIT} and T_b) are 446.25 K and 469.02 K, respectively.

$$T_{be0(\text{or } bp0)} = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{e0(\text{or } p0)}}}{2R} \quad (4)$$

The entropy of activation (ΔS^\ddagger), enthalpy of activation (ΔH^\ddagger) and free energy of activation (ΔG^\ddagger) of the main exothermic decomposition reaction of ACOF corresponding to $T = T_{p0}$, $E_a = E_K$ and $A = A_K$ are obtained by Eqs. (5) – (7) [11–14], are 26.07 $\text{Jmol}^{-1}\text{K}^{-1}$, 147.43 kJmol^{-1} and 135.53 kJmol^{-1} , respectively. The positive values of ΔG^\ddagger , indicate that the exothermic decomposition reaction of ACOF must proceed under the heating condition.

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} \quad (5)$$

$$A \exp(-E_a / RT) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (6)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (7)$$

where k_B is the Boltzman constant and h the Plank constant.

After the kinetic parameters (E_a and A) were obtained, the rate constant (k) for decomposition reaction could be calculated by the following equation:

$$\ln k = \ln A - E_a / RT \quad (8)$$

The period of validity of the ACOF could be determined by the following equation:

$$t_{0.9} = G(\alpha)/k \quad (9)$$

where k was the rate constant and could be obtained by Eq.(8), α is 0.1, $G(\alpha)$ is $[-\ln(1-\alpha)]^{1/2}$, E_a is 153.54 kJmol⁻¹, A is $10^{14.34}$ s⁻¹, T is 298.15 K. The period of validity for ACOF is 37.29 thousand years, indicate that ACOF is very stable under 298.15 K.

The adiabatic time-to-explosion (t_{TIAD}) of energetic materials is the time of decomposition transiting to explosion under the adiabatic conditions. It is an important parameter for assessing the thermal stability and the safety of energetic materials.

$$t_{TIAD} = \frac{1}{Q_d A} \int_{T_{co}}^{T_{bp0}} \frac{C_p \exp(E/RT)}{f(\alpha)} dT \quad (10)$$

$$\alpha = \int_{T_{co}}^{T_{bp0}} \frac{C_p}{Q_d} dT \quad (11)$$

where Q_d decomposition heat, 754.78 Jg⁻¹. A , pre-exponential constant, $A = 10^{14.34}$ s⁻¹; C_p is the specific heat capacity measured by microcalorimeter in Jg⁻¹K⁻¹, E , activation energy, 153.54 kJmol⁻¹; R , the gas constant, 8.314 Jmol⁻¹K⁻¹; $f(\alpha)$, differential mechanism function $f(\alpha) = 2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$.

Substituting the corresponding data into Smith equation Eqs. (10) and (11) [17, 18], The values of t_{TIAD} is 497.96 s. In the calculation process of adiabatic time-to-explosion, a little change in the activation energy located in the integral equation with exponential form can make a great difference in the result, and a small increase of the activation energy can induce t_{TIAD} to rise greatly.

Experimental

Materials and Analytic Instrument

ACOF was prepared and purified by a reported method [3]. The thermal behavior of ACOF was studied using a Q2000DSC (TA, USA) by the DSC method under atmospheric pressure. The sample mass is about 1.580 mg at the heating rates 2.5, 5.0, 10.0 and 15.0 Kmin⁻¹ with nitrogen as the purge and

the flow rate is 50 mlmin⁻¹. The temperature and heat were calibrated using pure indium and tin particles.

The specific heat capacity of ACOF was determined with a continuous C_p mode on a Micro-DSCIII apparatus (Setaram, France) under atmospheric pressure, heating rate, 0.15 Kmin⁻¹, sample mass, 285.40 mg; atmosphere, N₂; and the specific heat capacity determined for ACOF is $C_p(\text{Jg}^{-1}\text{K}^{-1}) = 1.6041 \times 10^{-7} T^3 - 1.6121 \times 10^{-4} T^2 + 5.6467 \times 10^{-2} T - 5.6373$ (283K < T < 354K).

Conclusions

The thermal behavior of ACOF under the nonisothermal condition by DSC methods was studied. The apparent activation energy and pre-exponential factor of the intense exothermic decomposition reaction are 153.54 kJmol⁻¹ and $10^{14.34}$ s⁻¹, respectively. The reaction mechanism of the intense exothermic decomposition process of ACOF is classified as Avrami-Erofeev equation $G(\alpha) = [-\ln(1-\alpha)]^{1/2}$, $f(\alpha) = 2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$. The specific heat capacity was determined with Micro-DSC method. The specific heat capacity equation is $C_p(\text{Jg}^{-1}\text{K}^{-1}) = 1.6041 \times 10^{-7} T^3 - 1.6121 \times 10^{-4} T^2 + 5.6467 \times 10^{-2} T - 5.6373$. The self-accelerating decomposition temperature, the thermal ignition temperature and the critical temperatures of thermal explosion are 436.03 K, 446.25 K and 469.02 K, respectively. The values of ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger of this reaction are 26.07 Jmol⁻¹K⁻¹, 147.43 kJmol⁻¹ and 135.53 kJmol⁻¹, respectively. The period of validity is 37.29 thousand years. The adiabatic time-to-explosion was calculated to be 497.96 s.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (No. 21073141), the education Committee Foundation of Shaanxi Province (No 11JK0564 and 11JK0582) and the Project-sponsored by SRF for AT, YLU (Grant No.09GK019).

References

1. A. B. Sheremetev, E. A. Ivanova, S. F. Melnikova, I. V. Tselinsky, K. Y. Suponitsky and M. Y. Antipin, *Journal of Heterocyclic Chemistry*, **42**, 1237 (2005).
2. C. Zhang, *Journal of Molecular Structure-Theochem*, **765**, 77 (2006).
3. C. H. Lim, T. K. Kim, K. H. Kim, K. H. Chung

- and J. S. Kim, *Bulletin of the Korean Chemical Society*, **31**, 1400 (2010).
4. J. Wang, H. S. Dong, Y. G. Huang, J. S. Li and X. Q. Zhou, *Chinese Journal of Energetic Materials*, **14**, 374 (2006).
 5. J. Wang, J. S. Li, Q. Q. Liang, Y. G. Huang and H. S. Dong, *Propellants Explosives Pyrotechnics*, **33**, 347 (2008).
 6. Y. S. Zhou, B. Z. Wang, C. Zhou, J. K. Li, Z. Q. Chen, P. Lian and Z. Z. Zhang, *Chinese Journal of Organic Chemistry*, **30**, 1044 (2010).
 7. R. H. Wang, Y. Guo, Z. Zeng, B. Twamley and J. M. Shreeve, *Chemistry-A European Journal*, **15**, 2625 (2009).
 8. Y. J. Fan, B. Z. Wang, W. P. Lai, P. Lian, J. Jiang, X. J. Wang and Y. Q. Xue, *Chinese Journal of Organic Chemistry*, **29**, 614 (2009).
 9. M. A. Epishina, A. S. Kulikov and N. N. Makhova, *Russian Chemical Bulletin International Edition*, **57**, 644 (2008).
 10. J. Wang, H. S. Dong, Y. G. Huang, X. Q. Zhou and J. S. Li, *Chinese Journal of Synthetic Chemistry*, **14**, 131 (2006).
 11. H. X. Ma, B. Yan, Y. H. Ren, Y. L. Guan, F. Q. Zhao, J. R. Song and R. Z. Hu, *Journal of Thermal Analysis and Calorimetry*, **103**, 569 (2011).
 12. H. X. Ma, B. Yan, J. F. Li, Y. H. Ren, Y. S. Chen, F. Q. Zhao, J. R. Song and R. Z. Hu, *Journal of Molecular Structure*, **981**, 103 (2010).
 13. H. X. Ma, B. Yan, Z. N. Li, J. R. Song and R. Z. Hu, *Journal of Thermal Analysis and Calorimetry*, **95**, 437 (2009).
 14. H. X. Ma, B. Yan, Z. N. Li, Y. L. Guan, J. R. Song, K. Z. Xu and R. Z. Hu, *Journal of Hazardous Materials*, **169**, 1068 (2009).
 15. H. X. Ma, J. R. Song, F. Q. Zhao, R. Z. Hu and H. M. Xiao, *Journal of Physical Chemistry A*, **111**, 8642 (2007).
 16. T. L. Zhang, R. Z. Hu, Y. Xie and F. P. Li, *Thermochimica Acta*, **244**, 171 (1994).
 17. L. C. Smith, *Thermochimica Acta*, **13**, 1 (1975).
 18. R. Z. Hu, H. Zhang, Z. M. Xia, P. J. Guo, S. L. Gao, Q. Z. Shi, G. E. Lu and J. Y. Jiang, *Chinese Journal of Energetic Materials*, **11**, 130 (2003).