

Study on Crystal Structure and Thermal Behavior of Sodium Tetrazolate and Sodium 5-Chlorotetrazolate

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Abstract. Sodium tetrazolate and sodium 5-chlorotetrazolate crystals obtained by recrystallization centred on sodium ion, and the sodium ion was coordinated by tetrazolate rings and crystal water; the packing arrangements of sodium tetrazolate and sodium 5-chlorotetrazolate were rhombus structure which lead to highest thermostability and intersecting channel structure viewed along *b* axis, respectively; there was a gap between molecules and larger space viewed along *a* axis of sodium 5-chlorotetrazolate crystal drawing which can coordinate with nitrogen-rich groups and metal ion. The results of thermodynamics calculation indicated that the activation energy of sodium tetrazolate was about 200 kJ·mol⁻¹, sodium 5-chlorotetrazolate was 260-270 kJ·mol⁻¹ which was higher than sodium tetrazolate, however, the decomposition temperature of sodium 5-chlorotetrazolate (241 °C) was lower than sodium tetrazolate (320 °C) which can be explained that the pre-exponential factor (lgA) of sodium 5-chlorotetrazolate (27.8) was greater than that of sodium tetrazolate (18.2), in other words, sodium 5-chlorotetrazolate had more active sites.

Introduction

Tetrazole derivative is a kind of nitrogen-rich heterocyclic compound containing unsaturated five membered ring. It has flat structure, high nitrogen content and many N-N, C-N, N=N, C=N bonds, possessing aromaticity, high formation enthalpy, high density, low sensitivity, good thermal stability and other characteristics; the final product after combustion or explosion is nitrogen gas with low smoke that has no pollution and be environmentally friendly. Thus, tetrazole derivative is an ideal high energy density materials (HEDMs) ^[1, 2]. Besides, its chemical property is very active, a great varieties of derivatives can be obtained by deprotonation, protonation, substitution, coordination reactions ^[3-11] which are widely used in biomedicine, agriculture, energetic materials, gas generating agent and microelectronics fields.

At present, coordination complexes or metal salts of tetrazole derivatives have excellent explosion properties and are widely used as initiating explosive of blasting equipment and energetic catalyst. It becomes an important research of energetic materials and be a hot spot of the scientists all over the world ^[12-17].

This article analyzed the crystal structure of sodium tetrazole and sodium 5-chlorotetrazolate, studied the thermal decomposition behavior of the two crystals and calculated thermal dynamic parameters (activation energy and pre-exponential factor) using Kissinger and Flynn-Wall-Ozawa equations for the first time, discussed the effect of crystal structure and thermal dynamic parameters on the thermal stability, which has important academic values.

Experimental

Synthesis of sodium tetrazolate. 0.01 mol (0.7 g) 1H-tetrazole and 15 mL distilled water were added to a 50 mL round-bottom flask (the pH of the solution was about 3), then to the solution, 0.01 mol (0.4 g) sodium hydroxide solution was dropwise added with stirring at ambient temperature for 1 h (this moment the pH of the solution was about 7). The reaction solvent was removed using a rotary evaporator; A white solid matter was dried by distillation of azeotrope with three 20 mL portions of

ethyl alcohol and recrystallized from hot ethyl alcohol. The colorless crystalline solid of sodium tetrazolate was obtained; yield: 1.04 g (94.5 %); m.p. 275.97 °C; ^1H NMR (d_6 -DMSO, 400MHz) δ : 8.10 (s, 1H); ^{13}C NMR (d_6 -DMSO, 400MHz) δ : 148.41(s, C); IR (KBr) ν : 3158.51, 3057.05, 1658.26, 1524.31, 1401.98, 1256.77, 1145.02, 937.83 cm^{-1} ; ESI-MS m/z (%): 69.2 $[\text{M}]^-$, 41.0 $[\text{M}-\text{N}_2]^-$; Anal. Calcd for $\text{CH}_3\text{N}_4\text{NaO}$: C 10.91, H 2.75, N 50.92; found C 10.20, H 3.46; N 51.43.

Synthesis of sodium 5-chlorotetrazolate. 0.01 mol (0.7 g) 1H-tetrazole and 0.12 mol acetic acid solution (the concentration was 50 %) were added to a 100 mL round-bottom flask, then to the solution, 0.12 mol sodium hypochlorite solution was dropwise added with stirring at 55 °C for 6 h. All of the reaction solvents were removed using a rotary evaporator; the solid matter was dried by distillation of azeotrope with three 20-mL portions of ethyl alcohol and extracted with acetone; after filtering the NaCl, the filtrate was dried over MgSO_4 . Following the removal of acetone by purging with warm air, sodium 5-chlorotetrazolate dihydrate was obtained as a colorless crystal with a 92.76 % yield (1.3496 g); ^{13}C NMR (d_6 -DMSO, 400MHz) δ : 150.34(s, C); IR (KBr) ν : 3512.89, 1628.05, 1376.12, 1354.65, 1195.19, 724.49 cm^{-1} ; ESI-MS m/z (%): 102.8 $[\text{M}]^-$ (^{35}Cl), 104.8 $[\text{M}]^-$ (^{37}Cl), 75 $[\text{M}-\text{N}_2]^-$ (^{35}Cl), 76.8 $[\text{M}-\text{N}_2]^-$ (^{37}Cl), 42 $[\text{M}-\text{N}_2-\text{Cl}+2\text{H}]^-$; Anal. Calcd for $\text{CH}_4\text{ClN}_4\text{NaO}_2$: C 7.39, H 2.48, N 34.48; found C 7.30, H 2.44; N 34.32.

Results and discussion

Crystal structure. The crystal structure parameter and diffraction data of sodium tetrazolate and sodium 5-chlorotetrazolate were collected by Bruker SMART 1000 CCD and were shown in Table 1. The molecular structures and the crystal packing structures viewed along coordinate axis were shown in Fig 1-3, respectively.

Table 1 Crystallographic data of sodium tetrazolate and sodium 5-chlorotetrazolate^[18]

Compounds	Sodium tetrazolate	Sodium 5-chlorotetrazolate
Formula	$\text{CH}_3\text{N}_4\text{NaO}$	$\text{C}_{0.5}\text{H}_2\text{Cl}_{0.5}\text{N}_2\text{Na}_{0.5}\text{O}$
Crystal system	Orthorhombic	Orthorhombic
Space group	Pmc2 (1)	Pnma
Temperature (K)	153(2) K	293(2) K
Wavelength(\AA)	0.71073	0.71073
a (\AA)	5.847 (4)	6.8611(19)
b (\AA)	5.605 (3)	6.9243(19)
c (\AA)	6.387 (4)	12.281(4)
Volume (\AA^3)	209.3(2)	583.5(3)
Z	2	8
D_c ($\text{Mg}\cdot\text{m}^{-3}$)	1.746	1.850
Crystal size (mm)	$0.67 \times 0.20 \times 0.08$	$0.48 \times 0.35 \times 0.28$
θ range	3.48° to 31.52°	3.32° to 31.52°
Dataset	-8:8, -8:7, -9:9	-9:10, -10:10, -17:18
R indices (all data)	$R_1 = 0.0328$, $wR_2 = 0.0666$	$R_1 = 0.0283$, $wR_2 = 0.0780$
CCDC	1028253	1028254

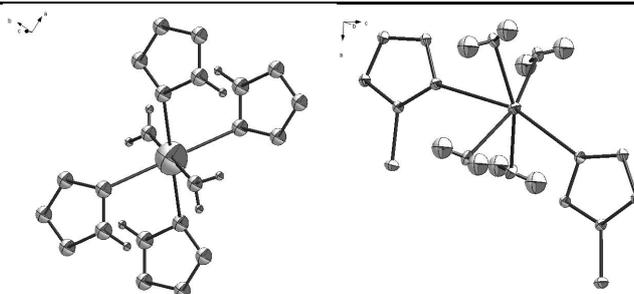


Fig. 1 Molecular structures of sodium tetrazolate (left) and sodium 5-chlorotetrazolate (right)

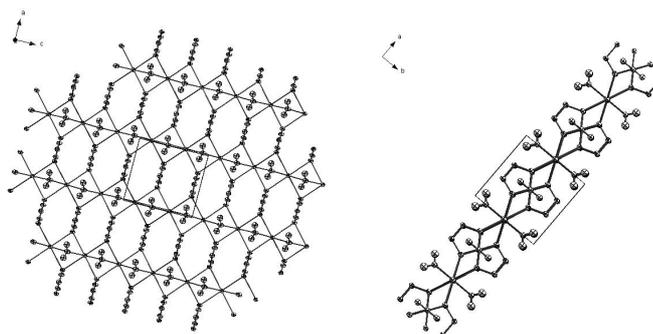


Fig. 2 Viewed along *b* (left) and *c* (right) axis in the crystal packing structure of sodium tetrazolate

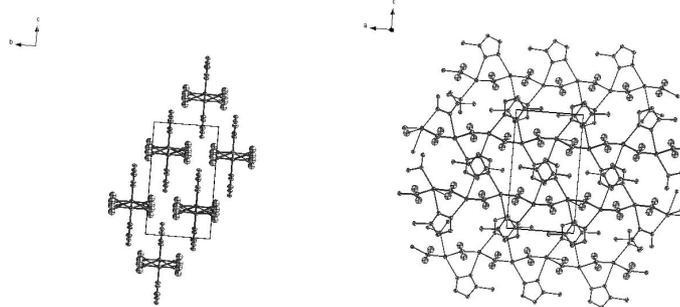


Fig. 3 Viewed along *a* (left) and *b* (right) axis in the crystal packing structure of sodium 5-chlorotetrazolate

From the Table 1, sodium tetrazolate crystallizes in the orthorhombic space group $Pmc2(1)$ with a cell volume of $209.3(2) \text{ \AA}^3$, density of $1.746 \text{ Mg}\cdot\text{m}^{-3}$; sodium 5-chlorotetrazolate crystallizes in the orthorhombic space group $Pnma$ with a cell volume of $583.5(3) \text{ \AA}^3$, density of $1.850 \text{ Mg}\cdot\text{m}^{-3}$. Fig. 1 showed that the two crystals were composed of Na^+ central metal ion, tetrazole ring ligand and crystal water, and the Na^+ of sodium tetrazolate linked four tetrazole rings and two water molecules, while the Na^+ of sodium 5-chlorotetrazolate linked two tetrazole rings and four water molecules. Viewed along *b* axis, the crystal packing structure of sodium tetrazolate was rhombus and it was long-chain viewed along *c* axis (Fig. 2); the crystal packing structure of sodium 5-chlorotetrazolate was intersecting channel viewed along *b* axis, and it existed gap between intermolecular that offered space for coordination of metal salt and other groups viewed along *a* axis (Fig. 3). Compared with the intersecting channel structure of sodium 5-chlorotetrazolate, the rhombus structure of sodium tetrazolate was more stable.

Thermal behavior and stability. The thermal behaviors of sodium 5-chlorotetrazolate dihydrate and sodium tetrazolate monohydrate were investigated by TG/DSC at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in the temperature range from $35\text{--}450 \text{ }^\circ\text{C}$ with an amount of 1.6088 mg and 3.4073 mg , respectively. Fig. 4 showed the TG/DSC curves of sodium tetrazolate and sodium 5-chlorotetrazolate.

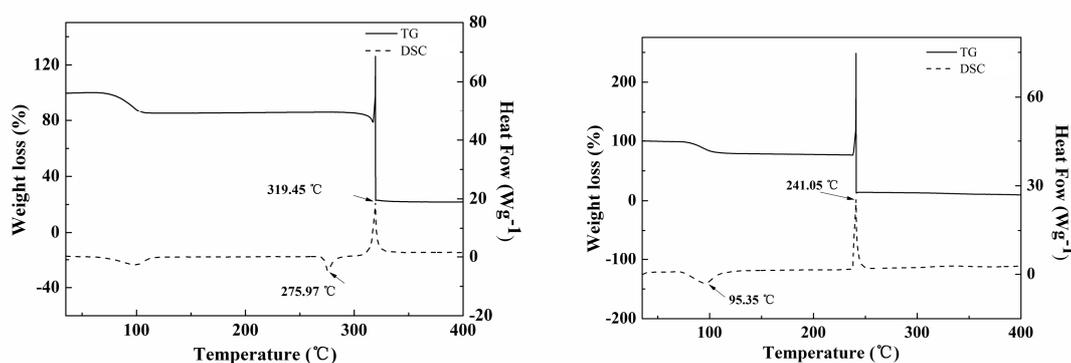


Fig. 4 TG/DSC of sodium tetrazolate (left) and sodium 5-chlorotetrazolate (right) at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$

The results of Fig. 4 indicated that the TG curves of the two compounds all had two phase of weightlessness, the first weight loss stage was caused by the evaporation of crystal water at about 100 °C; from the DSC curves, sodium tetrazolate and sodium 5-chlorotetrazolate showed endothermic peak and the decomposition temperatures were 320 °C and 241 °C, respectively; the TG curves appeared overweight which was caused by the rapid decomposition and the release of nitrogen gas. In addition, there was a melting phenomenon at the temperature of 276 °C in the thermal analysis of sodium tetrazolate, and sodium 5-chlorotetrazolate didn't.

Thermodynamics. Testing the thermogravimetry and differential thermal gravity (TG/DTG) curves of the two compounds at a heating rate of 2.5, 5, 10, 20 °C·min⁻¹ in the temperature range from 35-400 °C under a nitrogen flow of 20 mL·min⁻¹; using the obtained heating rate β and corresponding thermal decomposition peak T_p , the thermodynamic parameter (i.e. activation energy and pre-exponential factor) was calculated by Kissinger and Flynn-Wall-Ozawa (FWO) methods, respectively.

The Kissinger and FWO equations were:

$$\ln\left(\frac{b}{T_p^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E_K}{RT_p} \quad (1)$$

$$\lg b = \lg\left(\frac{AE}{RG(\alpha)}\right) - 2.305 - 0.4567 \frac{E_O}{RT} \quad (2)$$

Where β = heating rate [K·min⁻¹], A = pre-exponential factor [min⁻¹], R = gas constant (= 8.314 J·K⁻¹·mol⁻¹), E = activation energy [kJ·mol⁻¹] (E_K and E_O are calculated by Kissinger and FWO, respectively), T = absolute temperature [K], $G(\alpha)$ = integral function describing decomposition reaction.

Table 2 showed the kinetic data of the two compounds in different heating rate. The activation energy and pre-exponential factor (Table 3) was calculated by the linear fitting curves (Fig. 5).

Table 2 The kinetics data of sodium tetrazolate and sodium 5-chlorotetrazolate under different heating rate

Compounds	β (K·min ⁻¹)	T_p (K)	$1/T_p$ ($1 \times 10^{-3} \text{K}^{-1}$)	Kissinger $\ln(\beta/T_p^2)/(\text{K}^{-1} \cdot \text{min}^{-1})$	FWO $\lg\beta/(\text{K}^{-1} \cdot \text{min}^{-1})$
Sodium tetrazolate	2.5	576.07	1.73590	-11.7961676	0.397940
	5	585.23	1.70873	-11.1345720	0.698970
	10	595.82	1.67836	-10.4772921	1.000000
	20	602.82	1.65887	-9.8075050	1.301030
Sodium 5-chlorotetrazolate	2.5	515.32	1.94054	-9.2665779	0.397940
	5	506.40	1.97472	-10.8452158	0.698970
	10	512.15	1.95255	-10.1746500	1.000000
	20	517.15	1.93367	-9.5009337	1.301030

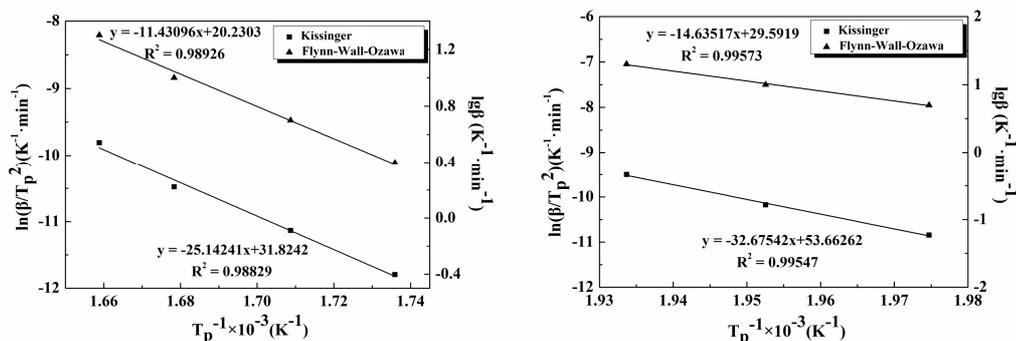


Fig. 5 The linear fitting curves of Kinssinger and FWO for sodium tetrazolate and sodium 5-chlorotetrazolate(the TG/DTG data was unsatisfied at the heating rate of 2.5 °C·min⁻¹)

Table 3 Kinetic parameter of the two compounds

Compounds	Activation energy $E_K(\text{kJ}\cdot\text{mol}^{-1})$	Linear correlation coefficient R_K^2	$\lg A_K$	Activation energy $E_O(\text{kJ}\cdot\text{mol}^{-1})$	Linear correlation coefficient R_O^2
Sodium tetrazolate	209.03	0.98829	18.2	208.10	0.98926
Sodium 5-chlorotetrazolate	271.66	0.99547	27.8	266.43	0.99573

The results showed that the values of kinetic parameter were reliable and valuable because the linear correlation coefficient R^2 was close to one and the data relevancy was higher; the values of E_K and E_O were similar that indicated the thermal decomposition kinetic method was reasonable; the larger the activation energy is, the greater the energy of decomposition need, and that is to say the higher the decomposition temperature is, the E_K of sodium 5-chlorotetrazolate (271.66) was higher than sodium tetrazolate (209.03), however, the pre-exponential factor $\lg A$ of sodium 5-chlorotetrazolate (27.8) was greater than that of sodium tetrazolate (18.2), in other words, having more active sites. So, the decomposition temperature of sodium 5-chlorotetrazolate was lower than sodium tetrazolate.

Conclusions

This article in-depth studied the crystal structures, thermal decomposition behavior and thermal dynamic of sodium tetrazolate and sodium 5-chlorotetrazolate. From the crystal packing axial direction figures, we got the results: the rhombus structure of sodium tetrazolate was more stable than the intersecting channel structure of sodium 5-chlorotetrazolate, and it existed gap between the crystal molecules of sodium 5-chlorotetrazolate, providing enough space for the coordination with rich nitrogen groups and metal ion. The TG/DSC curves of the two crystals proved the decomposition temperature of sodium tetrazolate was significantly higher than sodium 5-chlorotetrazolate, and sodium 5-chlorotetrazolate had no melting point which indicated that its structure was easy to fracture; the activation energy and pre-exponential factor were calculated by using non-isothermal kinetic equation (Kissinger and FWO method) that demonstrated the activation energy values got by using Kissinger and FWO methods were similar and had reference value, in addition, the pre-exponential factor of sodium 5-chlorotetrazolate being higher than that of sodium tetrazolate indicated that sodium 5-chlorotetrazolate had more reactive sites, so the decomposition temperature of sodium 5-chlorotetrazolate was lower than that of sodium tetrazolate despite having higher activation energy.

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