March 2016 Synthesis, Structure, and Energetic Properties of 1,5-Diaminotetrazolium Sulfate Salts

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1,5-diaminotetrazolium chloride (DATC) and 1,5-diaminotetrazolium sulfate (DATS) were synthesized in this work. The structures of DATS and DATC were characterized. The single crystal of DATS was first cultured, and its structure was analyzed. The thermal behavior of DATS was investigated. The activation energy and pro-exponential factor were calculated, $E_k = 120.86 \text{ KJ/mol}$, $A_k = 10^{12.96} \text{ s}^{-1}$. The density, heat of formation, detonation pressure, and detonation velocity of DATS were first calculated. The detonation pressure and detonation velocity of DATS are P = 11.877 GPa, $D = 5.617 \text{ km s}^{-1}$, which are smaller than those of 1,5-diaminotetrazolium nitrate (DATN) (P = 33.3 GPa, $D = 8.77 \text{ km s}^{-1}$).

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INTRODUCTION

Nitrogen-rich compounds, which have good potential applications in the military chemistry field, are a new type of energetic material [1–4]. The thermal decomposition products of these energetic ionic salts are mostly nitrogen, with low vapor pressure [5–7] and high density, so they are friendly to the environment.

The introduction of amino group to energetic ionic salt is conducive to form strong hydrogen bonding, improve the stability, and reduce the sensitivity [8]. Now, some energetic ionic salts with amino group were reported, such as: 5-aminotetrazolium nitrate [9], 5-aminotetrazolium chloride [10], 1-amino-5-methyltetrazolium iodide [11], 2-amino -5-methyltetrazolium perchlorate [12], and so forth. About 1,5-diaminotetrazole (DAT) inorganic acid salts, there are DATN and DATC were reported, but there is no introduction about the other structure and performance characterization of DATS.

In this study, DATC was synthesized with DAT and hydrochloric acid. DATS was first synthesized with DATC and silver sulfate. The structure was characterized by elemental analysis, IR, ¹HNMR, and MS. The single crystal of DATS was cultivated, and the single crystal structure was analyzed. The density, heat of formation, detonation pressure, and detonation velocity were first calculated. The kinetic parameters including activation energy and proexponential factor were calculated by the Kissinger equation.

MEASUREMENTS

German vario EL elemental analyzer, U.S. companies Nicolet FT-IR4700 infrared spectroscopy, Switzerland ARX400 Bruker NMR spectrometer, AZB-HS mass spectrograph, Rigaku 742+ single crystals diffractometer.

RESULTS AND DISCUSSION

Structure Characterization. 1,5-diaminotetrazolium Chloride. Elemental analysis (CH₅N₆Cl,136.5 g \cdot mol⁻¹): calculated value, C 17.71,H 3.69,N 61.99; measured value, C 17.73,H 3.58,N 61.86.

IR (cm⁻¹,KBr):3313, 3163 and 1578 cm^{-1} (5-NH₂), 3277 cm⁻¹ (4-N–H), 3251, 3068 and 1620 cm⁻¹ (1-NH₂), 1724 cm⁻¹ (C1–N5), 1117–1039 cm⁻¹ (tetrazole ring).

¹H NMR (DMSO-*d*₆,δ): 7.84

MS (EI,70 eV): m/z 100 (DAT molecular peak), m/z 36 (HCl⁺ ion peak).

DATS. Elemental analysis $(C_2H_{10}N_{12}SO_{4,2}98 \text{ g} \cdot M^{-1})$: calculated value, C 8.05,H 3.36,N 56.38; measured value, C 8.12,H 3.23,N 56.39.

IR (cm⁻¹,KBr):3338 and 3194 cm^{-1} (5-NH₂), 3294 cm^{-1} (4-N–H), 3085 and 1619 cm⁻¹ (1-NH₂), 1720 cm⁻¹ (C1–N5), 1107–1039 cm⁻¹ (tetrazole ring).

¹H NMR (DMSO- d_6, δ): 6.98

MS (EI,70 eV): m/z 100 (DAT molecular peak), m/z 64 (SO2 ion peak), m/z 48 (SO ion peak).

Crystal Structure of 1,5-diaminotetrazolium Sulfate. Crystal structure of DATS is shown in Figure 1. The view of the 3D structure of DATS is shown in Figure 2. The crystal data, the bond and angle date, and hydrogen bonding data of DATS are listed in Supplementary Information.

Seen from Figure 1, the hydrogen atom connected to N4 atom, tetrazole ring and the two nitrogen atoms of amino are in the same plane, N11 atom deviated from tetrazole ring for the furthest distance of 0.014 Å. The two nitrogen atoms outside the ring connected to the N and C atoms are sp3 and sp2 hybridization, respectively. Bond lengths of N–N in tetrazole ring are longer than N=N double bond (Bond length of N = N in HN = NH is 1.252 Å [14]), and shorter than N-N single bond (Bond length of N-N in H2N–NH2 is 1.449 Å [14]). Bond lengths of C–N in tetrazole ring are longer than C = N double bond (Bond length of C=N in H₂C=NH is 1.273 Å [14]), and shorter than C-N single bond (Bond length of C-N in H₃C-NH₂ is 1.471 Å [14]). Bond length of C-N bond of the amino connected with C atom outside the ring is also between C = Nand C-N, and it is in the same plane with tetrazole ring.



Figure 1. Crystal structure of DATS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Bond lengths become average, so there are aromaticity and big π conjugated system in the DAT⁺.

Space group of DATS crystal has 2-m point group of monoclinic system, each crystal contains four molecules DATS. The anion and cation form stable structure by electrostatic forces in the compound. Seen from Figure 2, the dihedral angle of ring 1 (N1,N2,N3,N4,C1) and ring 2 (N7,N8,N9,N10,C2) is 74.99°. The distance from center of the ring 2 to ring 1 plane is 3.638 Å. There is side to face $\pi-\pi$ interaction between ring 1 and 2 and there are two kinds of hydrogen bond N-H...O and N-H...N in the molecule. Hydrogen bond N5-H5A ··· N2iii (symmetric code: (iii) - x, -y, -z) connected the tetrazole cationic rings together in the same plane. R4, 4 (18) is a 18 atomic ring composed of four donors and receptors. It connects the tetrazole cationic rings in the different plane together. The hydrogen bonds make crystal structure form threedimensional network structure (Figure 3).

Thermal Analysis. TG–DSC. Thermogravimetry technology is measuring the relationship between the



Figure 2. The view of the 3D structure for DATS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 3. The coordination environment (hydrogenbonds) for DTAS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

change of material quantity and the change of temperature under the process temperature. The TG-DSC curves of DATS with the heating rate $20 \,\mathrm{C}\,\mathrm{min}^{-1}$ are shown in Figure 4 and 5. There are two exothermic peaks during the entire thermal decomposition process in the DSC curve, the first temperature peak is 214.70C, and the thermal decomposition enthalpy is $720.79 \,\mathrm{J g^{-1}}$, there is mass loss in the process. The decomposition process contains two processes, corresponding to two mass loss platforms. The mass loss rate of the first platform in the TG curve is 43.59%, corresponding to that the one peak temperature is 214.70 C. The mass loss rate of the second platform in the TG curve is 25.58%, corresponding to that the second peak temperature is 296.73 C, and the thermal decomposition enthalpy is 5.88 Jg^{-1} . The total mass loss rate is 70.17% in the entire thermal decomposition process.

The Calculation of Activation Energy. Differential scanning calorimetry curves of DATS with the heating rate 2, 5, 10, 15 and $20 \,\mathrm{C\,min^{-1}}$ are shown in Figure 6.About DATS (Figure 6), it has two endothermic peaks. The thermal decomposition kinetics data of DATS treated by Kissinger method [15] are shown in Table 1. The Kissinger equation is listed as follows:

$$\ln \frac{\beta_i}{T_i^2} = \ln \frac{A_K R}{E_K} - \frac{E_K}{R T_i}$$

where β is heating rate (K min⁻¹), T_p is peak temperature (K), A_k is pre-exponential factor (s⁻¹), E_k is activation energy (kJ mol⁻¹), R is gas constant (J min⁻¹ K⁻¹).



Figure 4. DSC curve of DATS with heating rate 20 C min⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 5. TG curve of DATS with heating rate 20 C min⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

According to Kissinger equation, the pre-exponential factor and activation energy of these two compounds were calculated by the slope and intercept of the straight line, respectively. We can get Figure 7 (detailed calculations are showed in support materials), in the stage, the activation energy is 120.86 KJ mol⁻¹, the pre-exponential factor is $10^{12.96}$ s⁻¹, and linear equation is y=20.25-14.54x, R=0.995.

Meanwhile, authors have performed some works about DATN and DATC and obtained some dates that are show

in Table 1. The activation energy of DATN is biggest, the date of DATC between DATN and DATS, in this view, DATS is more stable.

THEORETICAL CALCULATION

Density. In 2007, the density prediction method of energetic ionic salts and compounds at room temperature was reported by Shreeve [16,17]. The molecular volume



Figure 6. DSC curves of DATS with the heating rate 2, 5, 10, 15, 20 C min⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 7. The activation energy of linear fitting equation of DATS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can be estimated through this method, and then the density of compounds can be rapidly estimated. The molecular volumes of tetrazolium, H bonded to C, H bonded to N, NH₂ are 66, 5, 7, and 20, respectively [14,15]. Isodesmic reactions were designed to obtain the density of DAT⁺ as follows in Figure 8.

V (DAT⁺)=V (tetrazolium)-V (H bonded to C)-V (H bonded to N)+2V (NH₂)=66-5-7+2*20=94 (Å³). The molecular volume of NO₃⁻, Cl⁻and SO₄²⁻are64, 47 and 91 Å³ respectively from Jenkins' research [18]. It is assumed that the molecular volume of ionic salts: V=V (+) +V (). The density of DATN, DATC, and DATS can be calculated according to the molecular molar mass as follows: ρ =M/0.6022 V. The calculated density of DATS is listed in Table 2. It is close to the crystalline density (the X-ray density value is 1.796).

Heat of Formation. The heat of formation is one of the important characteristics for the energetic salts [19]. All *ab initio* calculations were carried out by using the program package Gaussian 98 [20]. The single-point energies were calculated at the MP2 (full)/6-311++G** level. Heats of formation of the simple cations or anions were determined using atomization energies at G2 level. Isodesmic reactions were designed to obtain the heats of formation of cations and anions [21]. The enthalpy of



Figure 8. Isodesmic reactions of DAT⁺

 Table 1

 Activation energy and pre-exponential factor of DATN, DATC and DATS

| Material | E _K (KJ/mol) | $A_{K} (s^{-1})$ |
|----------------------|----------------------------|--|
| DATN DATC DATS | 194.78 149.64 120.86 | $10^{20.26} \\ 10^{14.79} \\ 10^{12.96}$ |

isodesmic reaction (ΔH°_{r298}) was obtained by combining the MP2/6-311++G^{**} energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31+G^{**}), and other thermal factors.

The heat of formation for DATS was calculated by Born-Haber energy cycles through the formula

$$\Delta H f^{0} \text{ (ionic salt, 298K)} = \Delta H f^{0} \text{ (cation, 298K)} + \Delta H f^{0} \text{ (anion, 298K)} \cdot \Delta H_{L}.$$
(1)

The lattice energy of ionic salt $\Delta H_{\rm L}$ could be predicted by Jenkins' method [formula (2)] [22] where $U_{\rm POT}$ is the lattice potential energy, $n_{\rm M}$ and $n_{\rm X}$ depend on the nature of the ions $M_{\rm p}^+$ and $X_{\rm q}^-$, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

$$\Delta H_L = U_{\rm POT} + [p(_{n\rm M}/2 - 2) + q(nx/2 - 2)] \rm RT \quad (2)$$

The lattice potential energy, U_{POT} , can be calculated using equation:

$$U_{\text{POT}}\left(\text{KJ mol}^{-1}\right) = \gamma(\rho m/Mm)^{1/3} + \delta, \qquad (3)$$

in which ρ is the density (g cm⁻³), *M* is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol⁻¹ cm) and δ (kJ mol⁻¹) were assigned literature values [20]. The calculated thermochemical values of DATS were presented in Table 2.

Detonation Pressure and Detonation Velocity. In order to assess the expected detonation properties of DATS, the expected detonation pressure and detonation velocity were calculated using the semi-empirical equations [23] (eq. 4, 5, and 6).

$$P = K\rho^2 \varphi \tag{4}$$

$$d = A\varphi^{1/2}(1 + B\rho) \tag{5}$$

$$\varphi = N\sqrt{M(-\Delta_E H)} \tag{6}$$

With: P = detonation pressure GPa; D = detonation velocity km/s; ρ = density (g/cm³);

| The calculated density and thermochemical values of DATS. | | | | | |
|---|-------------------------------|--|---|--|---------------------------------|
| Materials | $\rho_{cryl}~(g/cm^3)$ | ${}^{\vartriangle}_{\rm f} H_{\rm cation}$ | ${}^{\vartriangle}_{\rm f} H_{\rm anion}$ | ${}^{\vartriangle}{}_{\mathrm{f}}H_{\mathrm{L}}$ | △ _f <i>H</i> (298 K) |
| DATS | 1.808 | +1042.56 | -585.0 | 1355.76 | +144.36 |
| Note: detailed calcula | tions are showed in support n | naterials. | | | |
| | | Tabl | le 3 | | |
| | The | detonation pressure and d | letonation velocity of DA | ATS. | |

| | | Table 2 | | |
|---------------|-------------|----------------|-----------|------|
| he calculated | density and | thermochemical | values of | DATS |

| The detonation pressure and detonation velocity of DATS. | | | | | | | |
|--|------------------------|------------------------|-------|-------|------|---------|----------|
| Compound | $\rho_{cryl} (g/cm^3)$ | $\Delta_E H^0$ (cal/g) | Ν | М | φ | P (GPa) | D (km/s) |
| DATS | 1.808 | -115.73 | 0.047 | 21.29 | 2.33 | 11.877 | 5.167 |

N =moles of gas per g of explosive;

M = average molar mass of formed gases (g/mol);

 $\Delta_E H$ = estimated or guessed heat of detonation (kal/g);

A = 1.01;

B = 1.30.

According to the Le-Chatelier and Brinkley-Wilson method, the explosion and reaction equation isDATS:

$$C_2SN_{12}O_4H_{10}(S) \rightarrow 5H_2(g) + 2CO(g) + 6N_2(g).$$

The calculated detonation pressure and detonation velocity of DATS are shown in Table 3, the detonation pressure and detonation velocity of DATS are P = 11.877 GPa, D = 5.617 km s⁻¹, which are smaller than those of DATN (P = 33.3 GPa, D = 8.77 km s⁻¹) [13].

CONCLUSION

1,5-diaminotetrazolium chloride was synthesized with DAT and relevant acid. DATS was first synthesized with DATC as raw material. The structure was characterized by elemental analysis, IR, ¹H NMR, and MS. The single crystal of DATS was first cultivated. The density, heat of formation, detonation pressure, and detonation velocity of DATS were first calculated. Both the detonation pressure and detonation velocity of DATS are smaller than that of DATN. The activation energy and pre-exponential factor of DATN are higher than those of DATC and DATS. Therefore, DATN can be used as gas-generating agent, and DATS can be used as low energy propellant.

EXPERIMENTAL

Synthesis of 1,5-diaminotetrazolium Chloride According to Ref [12]. 1,5-diaminotetrazole (DAT) was synthesized according Ref [13]. A solution of diaminoguanidinium chloride (25.1 g, 0.2 *M*) in 333 mL of water and 8.3 mL (0.1 *M*) concentrated HCl (37%) was cooled to 0 C (some solid reprecipitated). With the temperature kept at 0-2 C, a solution of sodium nitrite (13.8 mg, 0.2 *M*) in 83 mL of water was added slowly. The solution obtained was allowed to stand in ice-water for 30 min. It was then brought to pH8 with solid sodium carbonate, stirred for 20 min at 40°C, and steamed out part of the water, then cooled in the refrigerator overnight, pure 1,5diaminotetrazole, which was recrystallized from solution.

1,5-diaminotetrazole (2.0043 g, 20.04 mM) suspended in 40 mL of methanol, was reacted with 10 mL concentrated HCl. The reaction mixture was refluxed for 2 h, and then the solvent was evaporated until precipitation occurred. The concentrated solution was then placed in the refrigerator, and the white 1,5-diaminotetrazolium hydrochloride was obtained. The precipitate was filtered off and washed with water. The max yield is 81.15%.

Synthesis of 1,5-diaminotetrazolium Sulfate. 1,5diaminotetrazolium chloride (2.0183 g, 20.0 mM) and deionized water (100 mL) were added into a threenecked flask equipped with a stirrer and a reflux apparatus. After stirring gently at 80C to fully dissolve, silver sulfate (3.1295 g, 10 mM) was added into the solution to react for 20 min under exclusion of light, because silver sulfate is light sensitive. The filtrate was evaporated after filtration. The white DATS was obtained. Crystals suitable for Xray structure determination were obtained by slow evaporation of a solution in methanol at ambient room temperature. The yield is 96.59%. Acknowledgments. Financial support of this work by the basic research fund of Beijing Institute of Technology (20130242017), the project fund of State Key Laboratory of Explosion Science and Technology (Beijing Institute of Technology) (YBKT16-09), and fund the project of State Key Laboratory of Explosion Science and Technology (Beijing Institute of Technology) (KFJJ12-13 M).

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