Dissolution Properties of 1,2,4-Triazole Nitrate in *N*-Methyl Pyrrolidone

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The enthalpies of dissolution of 1,2,4-triazole nitrate in *N*-methyl pyrrolidone (NMP) were measured using a RD496−2000 Calvet microcalorimeter at four different temperatures under atmospheric pressure. Differential enthalpies ($\Delta_{dif}H$) and molar enthalpies ($\Delta_{diss}H$) were determined for 1,2,4-triazole nitrate in NMP. The corresponding kinetic equations that describe the four dissolution processes are discussed.

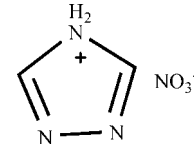
Introduction

Triazole is a five-membered heterocycle compound, which contains three nitrogen atoms. The three nitrogen atoms are on positions 1,2,4 or 1,2,3 of a five-membered heterocycle. The triazole derivative has proved to be a novel energetic compound with high nitrogen content. Its high energy comes from very high positive enthalpy of formation.[1−4] In comparison with TNT with negative enthalpy of formation (−62.73 kJ·mol^{-1}), this difference of enthalpy of formation gives energetic triazole ionic salts an advantages in the explosive performance. Changing cations, anions, and groups can make their performances, including sensitivity, energy, density and melting point be easy to adjust to achieve the purpose of decreasing sensitivity, enhancing energy and density, and controlling melting point, and synthesized energetic triazole ionic salts have the advantages of high thermal stability, low volatility and more high density.[4,5] Triazole ionic salts in the liquid state are nontoxic; these can reduce the cost and danger. Because the strong interaction exists between ions, triazole ionic salts as a continuous phase in B explosives can inhibit the migration effect, resolve the permeability problems of explosives, and improve the safety performance of explosives.[1−3] Rich nitrogen ionic salts have a strong solubility, high density, and good or fair compatibility with solid propellant components.[6−9] The polarity of ionic salts can be used for propellant combustion performance adjustment; therefore, energetic triazole ionic salts are energetic materials with good application prospect.[10−13]

However, most research has focused on the synthesis and application of energetic triazole ionic salts while these have been few studies on the fundamental thermochemical and thermodynamic properties.[1−13] As far as we know, the dissolution properties of energetic triazole ionic salts are important properties that reflect the structure but are rarely reported.

In the present study, a RD496-2000 Calvet microcalorimeter was used to measure the enthalpy of dissolution of 1,2,4-triazole nitrate in *N*-methyl pyrrolidone (NMP). The relationships for the measured heat effects and amounts of substance were studied, and the differential enthalpies ($\Delta_{dif}H$) and the molar enthalpies ($\Delta_{diss}H$) for 1,2,4-triazole nitrate in NMP at different temperatures were obtained. The kinetic behavior was investigated at the same time.

Scheme 1. Structure of 1,2,4-Triazole Nitrate



Experimental Section

Materials. 1,2,4-Triazole nitrate in this research was prepared by Beijing Institute of Technology and Xi'an Modern Chemistry Research Institute, The structure was characterized by means of organic elemental analysis, ^{15}N NMR, ^{13}C NMR, and LC-MS. The sample's mass fraction was more than 0.995. The structure for 1,2,4-triazole nitrate is shown in Scheme 1. The 1,2,4-triazole nitrate was further purified by evacuating the sample to a pressure of about 5×10^{-3} Pa at a temperature of about 70 °C for approximately 5 h. This procedure removed any volatile chemicals and water from the triazole ionic salt. *N*-Methyl pyrrolidone (NMP) (ρ/g·cm^3 = 1.029 to 1.035) used as solvent was AR grade, and its mass fraction purity was more than 0.999.

Equipment. All measurements were made using a RD496-2000 Calvet microcalorimeter (Mianyang CAEP Thermal Analysis Instrument Company, China). The enthalpy of dissolution of KCl (spectrum purity) in distilled water (0.0481 g in 2.000 g) measured by RD49-2000 Calvet microcalorimeter at 298.15 K was 17.234 ± 0.004 kJ·mol^{-1}(α = 0.05), and the literature value was 17.241 kJ·mol^{-1}.[14,15] This showed that the device for measuring the enthalpy was reliable.

The heat effects were measured at 298.15 K, 303.15 K, 308.15 K, and 313.15 K. Each process was repeated five times to ensure the precision of the data.

Results and Discussion

Thermochemical Behaviors. The experimental and calculated values of heat effect of 1,2,4-triazole nitrate dissolved in NMP at different temperatures are in Table 1. The molar enthalpies ($\Delta_{diss}H$) for each process is obtained and also listed in Table 1.

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Table 1. Enthalpies of Dissolution of 1,2,4-Triazole Nitrate in NMP

T	10^5a	10^8b	$-Q$ / J		$\Delta_{diss}H$
K	mol	mol·L^{-1}	experimental	calculated	kJ·mol^{-1}
298.15	4.85	2.42	0.4982	0.4830	10.28
	6.21	3.10	0.6375	0.6515	10.26
	8.79	4.40	0.9661	0.9713	10.99
	10.20	5.10	1.1405	1.1461	11.23
	12.00	6.00	1.3791	1.3692	11.52
mean					10.86 ± 0.57
303.15	5.08	2.54	0.4975	0.4907	9.80
	7.12	3.56	0.7553	0.7715	10.61
	9.09	4.54	1.0570	1.0427	11.63
	9.62	4.81	1.1118	1.1157	11.56
	11.70	5.85	1.4011	1.4020	11.93
mean					11.10 ± 0.88
308.15	6.21	3.10	0.6591	0.6544	10.61
	7.80	3.90	0.8463	0.8586	10.84
	9.24	4.62	1.0495	1.0436	11.36
	10.78	5.39	1.2480	1.2414	11.60
	12.04	6.02	1.3984	1.4032	11.61
mean					11.20 ± 0.46
313.15	5.30	2.65	0.6001	0.6089	11.32
	6.74	3.37	0.7624	0.7663	11.31
	8.71	4.36	0.9971	0.9815	11.45
	10.83	5.42	1.2305	1.2132	11.36
	12.42	6.21	1.3668	1.3869	11.00
mean					11.28 ± 0.17

In Table 1, a is the amount of the substance, b is the molality of the solution, and Q is the heat effect produced during the processes. The entire process was repeated three times and is shown as Figure 1. The dissolution is an endothermal process. The heat flow curves obtained under the same conditions overlap with each other, indicating that the reproducibility of the measurement is satisfactory.

In Table 1, the molality of the solution (b) has little influence on the values of the molar enthalpies ($\Delta_{diss}H$) at different temperature. So the average value of $\Delta_{diss}H$ can represent the molar enthalpies of the infinite diluted solution due to the very low molalities of the solution.

The Q *vs* a relationships of 1,2,4-triazole nitrate at different temperatures are shown in Figure 2.

The according linear equations for 1,2,4-triazole nitrate dissolved in NMP at different temperatures respectively are shown in Table 2. In Table 2, R is correlation coefficient, SD is standard deviation. The differential enthalpies ($\Delta_{dif}H$) are obtained from the slope of the equations, and the results are shown in Table 2.

Kinetics of Dissolution Processes. Equations 1 and 2[16−20] are chosen as the model function describing the dissolution process of 1,2,4-triazole nitrate in NMP

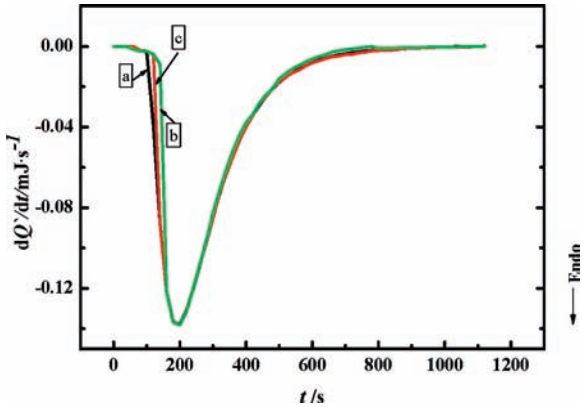

Figure 1. Curve describing the entire dissolution process of 1,2,4-triazole nitrate in NMP at 298.15K. (a) 10^5 a/mol = 4.85; (b) 10^5 a/mol = 4.86; (c) 10^5 a/mol = 4.85.

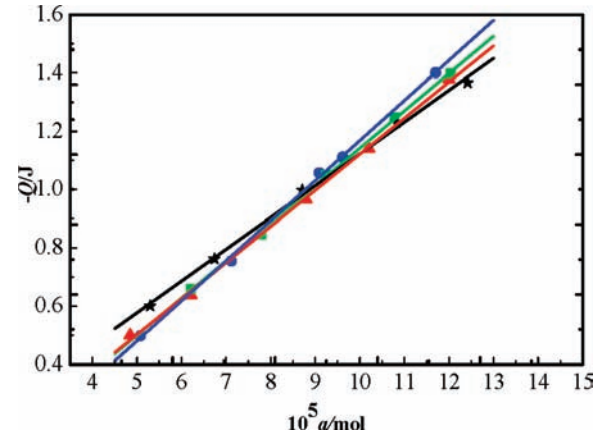

Figure 2. Relationships of Q vs n at different temperatures. ▲, T = 298.15 K; ●, T = 303.15 K; □, T = 308.15 K; ★, T = 313.15 K.

Table 2. Thermochemical Equation and Differential Enthalpies of Dissolution ($\Delta_{dif}H$) of Dissolution Process in NMP of 1,2,4-Triazole Nitrate

T		$\Delta_{dif}H$		
K	thermochemical equation	kJ·mol^{-1}	R	SD
298.15	Q/J = −12395(a/mol) + 0.1182	12.395	0.9994	0.0140
303.15	Q/J = −13767(a/mol) + 0.2087	13.767	0.9994	0.0133
308.15	Q/J = −12845(a/mol) + 0.1433	12.845	0.9996	0.0096
313.15	Q/J = −10926(a/mol) − 0.0299	10.926	0.9987	0.0186

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

$$f(\alpha) = (1 - \alpha)^n \tag{2}$$

Combining eqs 1 and 2, yields

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \tag{3}$$

Substituting $\alpha = Q'/Q_+$ into the eq 3, we get

$$\ln\left[\frac{1}{Q_+}\left(\frac{dQ'}{dt}\right)_i\right] = \ln k + n\ln\left[1 - \left(\frac{Q'}{Q_+}\right)_i\right] \qquad i = 1, 2, ..., L \tag{4}$$

In these equations, α is the conversion degree, $f(\alpha)$ is the kinetic model function, Q' is the heat at time of t, i is any time during the process, Q_+ is the heat of the whole process, k is the rate of 1,2,4-triazole nitrate dissolved in NMP, n is the reaction order, and L is counting number.

The data needed is summarized in Table 3, and four processes are selected at random at each temperature.

By substituting the data taken from Table 3 into the kinetic eq 4, the obtained values of n and ln k at different temperatures are listed in Table 4.

From Table 4, we can see that the values of n and ln k show that the reaction order and the dissolved rate of 1,2,4-triazole nitrate in NMP vary during the experiment temperatures, and the values of ln k increase slightly at higher temperature.

Substituting the values of n and k in Table 4 into eq 3, we can get

$$\frac{d\alpha}{dt}/s^{-1} = 10^{-3.67}(1 - \alpha)^{0.93} \quad (T = 298.15\ \text{K}) \tag{5}$$

$$\frac{d\alpha}{dt}/s^{-1} = 10^{-3.66}(1-\alpha)^{0.95} \quad (T = 303.15\ \text{K}) \quad (6)$$

$$\frac{d\alpha}{dt}/s^{-1} = 10^{-3.64}(1-\alpha)^{0.94} \quad (T = 308.15\ \text{K}) \quad (7)$$

$$\frac{d\alpha}{dt}/s^{-1} = 10^{-3.63}(1-\alpha)^{0.93} \quad (T = 313.15\ \text{K}) \quad (8)$$

Equations 5 to 8 are applied to calculate the values of activation energy E and pre-exponential factor A by the slope and the intercept of the linear in Figure 2. Equation 9[16−20] is chosen as the model function describing the process of 1,2,4-triazole nitrate in NMP. The values of E is 5.22×10^3 kJ·mol^{-1} and of A is 1.76×10^{-3} s^{-1}, the correlative coefficient of the line is 0.9997. The relationship of k vs $1/T$ for the dissolution of 1,2,4-triazole nitrate in NMP is shown in Figure 3.

$$\ln k = \ln A - \frac{E}{RT} \quad (9)$$

Conclusions

The values of heat effect of 1,2,4-triazole nitrate in NMP was determined at different temperatures. The enthalpies can be regarded as the enthalpies at infinite dilution because of its very low molalities.

The differential enthalpies ($\Delta_{dif}H$) are 12.78 kJ·mol^{-1}, 13.10 kJ·mol^{-1}, and 13.14 kJ·mol^{-1} and the values of the molar enthalpies ($\Delta_{diss}H$) are 10.86 kJ·mol^{-1}, 11.10 kJ·mol^{-1}, 11.20 kJ·mol^{-1}, and 11.28 kJ·mol^{-1} at 298.15 K, 303.15 K, 308.15 K, and 313.15 K, respectively.

The thermokinetic equations of dissolution processes of 1,2,4-triazole nitrate in NMP at different temperatures are $(d\alpha/dt)/s^{-1} = 10^{-3.67}(1-\alpha)^{0.93}$ ($T = 298.15$ K), $(d\alpha/dt)/s^{-1} = 10^{-3.66}(1-\alpha)^{0.95}$ ($T = 303.15$ K), $(d\alpha/dt)/s^{-1} = 10^{-3.64}(1-\alpha)^{0.94}$ ($T = 308.15$ K), and $(d\alpha/dt)/s^{-1} = 10^{-3.63}(1-\alpha)^{0.93}$ ($T = 313.15$ K), respectively. The values of activation energy E and pre-exponential factor A are obtained as 5.22×10^3 kJ·mol^{-1} and 1.76×10^{-3} s^{-1}.

Table 3. Original Data of the Dissolution Process of the Title Compound in NMP at Different Temperatures

T/K	m/g	t/s	$-(dQ'/dt)_i$/mJ·s^{-1}	$(Q'/Q_+)_i$	$-Q_+$/kJ·mol^{-1}
298.15	0.0116	120	0.1378	0.2894	11.00
		160	0.1310	0.3752	
		200	0.1206	0.4555	
		240	0.1085	0.5285	
		280	0.0962	0.5937	
		320	0.0843	0.6512	
303.15	0.0127	440	0.0458	0.8463	11.56
		480	0.0391	0.8698	
		520	0.0332	0.8897	
		560	0.0283	0.9067	
		600	0.0241	0.9212	
		640	0.0206	0.9336	
308.15	0.0159	200	0.1385	0.5770	11.60
		240	0.1215	0.6340	
		280	0.1065	0.6840	
		320	0.0931	0.7278	
		360	0.0809	0.7660	
		400	0.0701	0.7991	
313.15	0.0164	160	0.2008	0.3727	11.00
		200	0.1815	0.4585	
		240	0.1609	0.5352	
		280	0.1409	0.6029	
		320	0.1224	0.6618	
		360	0.1056	0.7129	

Table 4. Values of n, ln k, and the Correlative Coefficient r for the Dissolution Process at Different Temperatures

T/K	n	ln(k/s^{-1})	R	SD
298.15	0.9314	−8.4442	0.9998	0.0508
303.15	0.9518	−8.4164	0.9999	0.0613
308.15	0.9352	−8.3812	0.9998	0.0524
313.15	0.9316	−8.3509	0.9997	0.0196

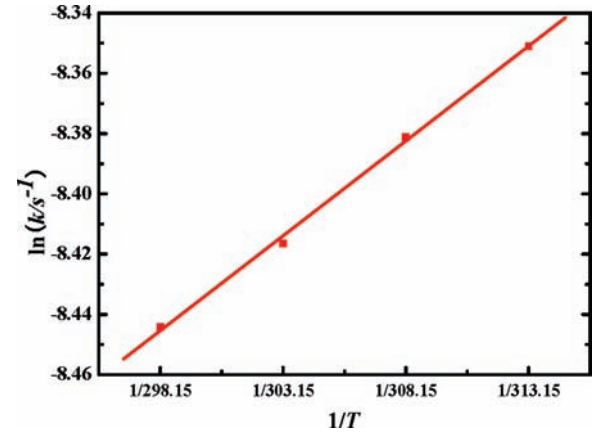

Figure 3. Relationship of reaction rate constant (k) vs temperature (T) for the dissolution of 1,2,4-triazole nitrate in NMP.

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