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Thermochemical properties of 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane in dimethyl sulfoxide

Na Li[1] · Feng-Qi Zhao[1] · Chun-Lei Xuan[1] · Ting An[1] · Yan-Jing Yang[1] · Hong-Xu Gao[1] · Li-Bai Xiao[1] · Rong-Zu Hu[1]

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Abstract The dissolution properties of 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (Keto-RDX) in dimethyl sulfoxide (DMSO) were studied by using a RD496-2000 Calvet microcalorimeter at four different temperatures under atmospheric pressure. The heat effects, molar enthalpies ($\Delta_{diss}H$), and differential enthalpies ($\Delta_{dif}H$) of dissolution were determined. Furthermore, the corresponding kinetic equations describing the dissolution processes at the four experimental temperatures are $d\alpha/dt = 10^{-2.43}(1-\alpha)^{0.63}$ ($T = 298.15$ K), $d\alpha/dt = 10^{-2.41}(1-\alpha)^{0.67}$ ($T = 303.15$ K), $d\alpha/dt = 10^{-2.40}(1-\alpha)^{0.75}$ ($T = 308.15$ K), and $d\alpha/dt = 10^{-2.38}(1-\alpha)^{0.76}$ ($T = 313.15$ K). The determined values of the activation energy E and pre-exponential factor A for the dissolution process are 5.99 kJ mol^{-1} and $10^{-1.38}$ s^{-1}, respectively.

Keywords 2-Oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (Keto-RDX) · Dimethyl sulfoxide · Dissolution · Enthalpy of dissolution · Thermokinetics

Introduction

The propellant industry is constantly striving for compounds that have high energy and high density characteristics for use in munitions, including both explosives and propellants. Some current high-volume ingredients such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are very effective in providing energy for numerous munitions applications [1–3]. The industry, however, continues to seek new compounds having densities near 2.0 g mL^{-1}, detonation pressures greater than 400 kbar, detonation velocities greater than 9000 ms^{-1}, favorable oxygen balance, and good thermal and hydrolytic stability.

One candidate for this type of energetic compound is 2-oxo-1,3,5-trinitro-1,3,5-triazacyclohexane (Keto-RDX or K-6). Keto-RDX is one of the high energy density materials bearing a cyclic dinitro-urea molecule. This compound has a calculated density of near 2.0 g mL^{-1}, a favorable oxygen balance, a calculated detonation velocity of 9270 ms^{-1}, and a calculated detonation pressure of 402 kbar [4–6].

Keto-RDX is more energetic and more dense than both RDX and HMX. Keto-RDX has a lower heat of formation but a more favorable oxygen balance than either of the other two. In addition, differential scanning calorimetry measurements show that Keto-RDX has a sharp exothermal peak at 206 °C [7, 8].

Earlier work has mostly focused on synthesis, thermal stability, detonation properties, sensitivity and its use in propellants [9–12]. However, the thermochemical properties of its solution at different temperatures have never been reported until now.

In the present study, we investigated the dissolution behaviors for Keto-RDX in dimethyl sulfoxide (DMSO) using a RD496-2000 Calvet microcalorimeter. The molar enthalpies ($\Delta_{diss}H$) and the differential enthalpies ($\Delta_{dif}H$) for Keto-RDX in DMSO at different temperatures were obtained, and the kinetic equations of the dissolution processes were also obtained, which will be useful for purification of Keto-RDX in production and can provide valuable information for its applications in the future.

✉ Na Li
lina8167@163.com

[1] Science and Technology on Combustion and Explosion Laboratory, Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

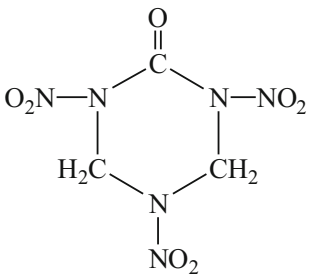
Experimental

Materials

Keto-RDX used in the experiment was prepared and purified by Xi'an Modern Chemistry Research Institute. Its structure was identified by ^{1}H NMR, IR, and elemental analysis, and its purity was more than 99.5%. IR (KBr, υ cm): 3010, 1441 (C–H), 1760 (C=O), 1610, 1282 (N–NO_2), 1240, 1153, 1062 (C–N); ^{1}H NMR (500 MHz, DMSO-d_6) δ: 6.36 (s, 4H, 2 × CH_2); Elemental anal. (%), calcd. for $C_3H_6N_6O_4$: C 15.25, N 35.39, H 1.70; found: C 15.23, N 35.21, H 1.69. The structure of Keto-RDX is shown in Scheme 1. The sample was stored under vacuum before the experimental measurements. DMSO ($\rho = 1.098 - 1.102$ g cm^{-3}) as solvent was of analysis reagent grade, and its purity was greater than 99.5%. Deionized water with an electrical conductivity of 0.8×10^{-4}–1.2×10^{-4} S m^{-1} used in the experiments was obtained by purification two times via a sub-boiling distillation device.

Equipment and conditions

All the measurement experiments were performed on a RD496-2000 Calvet microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., Ltd.), which had a sensitivity of 66.5 μV mW^{-1} at 298.15 K. The microcalorimeter was calibrated by the Joule effect, and the calibration was repeated after each experiment. The standard molar enthalpy of the dissolution of KCl (spectrum purity) in distilled water measured on a RD496-2000 Calvet microcalorimeter at 298.15 K was 17.234 ± 0.041 kJ mol^{-1}, and the relative error was less than 0.04% compared with the literature value 17.241 ± 0.018 kJ mol^{-1} [13]. This showed that the device for measuring the enthalpy used in this work was reliable. The heat effects were measured at 298.15, 303.15, 308.15, and 313.15 K.



Scheme 1 Structure of Keto-RDX

Results and discussion

Thermochemical behavior

The experimental and calculated values of the heat effects of Keto-RDX dissolved in DMSO at different temperatures are given in Table 1. The molar enthalpies ($\Delta_{diss}H$) for each process are obtained and also listed in Table 1, where a is the amount of the substance, b is the molality of the solution, and Q is the heat effect produced during dissolution. The dissolution is an endothermal process.

In Table 1, the molality of the solution (b) has little influence on the values of the molar enthalpies ($\Delta_{diss}H$) at different temperatures. 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 versus a relationships of Keto-RDX at different temperatures are shown in Fig. 1. The resulting linear equations for Keto-RDX dissolved in DMSO at different temperatures are shown in Table 2. In Table 2, r is the correlation coefficient. The differential enthalpy ($\Delta_{dif}H$) is the heat effect produced when a molar amount of solute is added to an infinite amount of solution having the same solute already in it [14–16].The differential enthalpies ($\Delta_{dif}H$) are obtained from the slope of the equations, and the results are shown in Table 2.

Kinetics of the dissolution processes

Equations (1) and (2) were chosen as the model functions describing the dissolution of Keto-RDX in DMSO [17–19].

$$d\alpha/dt = kf(\alpha) \quad (1)$$

$$f(\alpha) = (1-\alpha)^n \quad (2)$$

Combining Eqs. 1 and 2 yields

$$d\alpha/dt = k(1-\alpha)^n \quad (3)$$

Substituting $\alpha = H/H_\infty$ into the Eq. 3, we get

$$\ln\left[\frac{1}{H_\infty}\left(\frac{dH}{dt}\right)_i\right] = \ln k + n\ln\left[1-\left(\frac{H}{H_\infty}\right)_i\right] \quad (4)$$

In these equations, α is conversion degree, $f(\alpha)$ is the kinetic model function, H represents the enthalpy at time of t, i is any time during the process, H_∞ is the enthalpy of the whole process, k is the dissolution rate of Keto-RDX in DMSO, n is the reaction order, and L is the counting number.

Table 1 Enthalpies of dissolution of Keto-RDX in DMSO

T/K	10^5 a/mol	10^2 b/mol kg^{-1}	Q/J		$\Delta_{diss}H$/kJ mol^{-1}
			Experimental	Calculated	
298.15	3.6368	1.6531	0.1118	0.1144	3.0735
	4.7842	2.1746	0.1462	0.1496	3.0551
	5.6684	2.5766	0.1751	0.1768	3.0890
	6.7526	3.0694	0.2092	0.2102	3.0984
	7.7263	3.5120	0.2363	0.2401	3.0580
Mean					3.0748 ± 0.0169
303.15	3.9421	1.7919	0.1411	0.1455	3.5804
	4.9474	2.2488	0.1787	0.1816	3.6117
	5.9263	2.6938	0.2119	0.2168	3.5760
	6.6947	3.0431	0.2430	0.2444	3.6291
	7.3737	3.3517	0.2636	0.2689	3.5749
Mean					3.5944 ± 0.0219
308.15	3.6105	1.6411	0.1521	0.1574	4.2115
	4.6053	2.0933	0.1939	0.1993	4.2105
	5.5211	2.5096	0.2317	0.2379	4.1959
	6.5947	2.9976	0.2819	0.2832	4.2750
	7.3526	3.3421	0.3073	0.3151	4.1796
Mean					4.2145 ± 0.0324
313.15	3.1474	1.4306	0.1507	0.1554	4.7897
	4.3789	1.9904	0.2082	0.2141	4.7535
	5.2947	2.4067	0.2505	0.2578	4.7314
	6.2421	2.8373	0.3019	0.3029	4.8373
	7.0737	3.2153	0.3355	0.3426	4.7432
Mean					4.7710 ± 0.0384

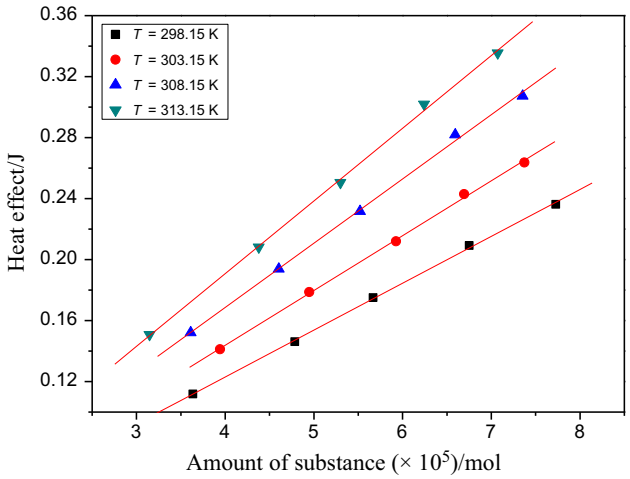


Fig. 1 Relationships of Q versus a of Keto-RDX at different temperatures

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

Substituting the original data in Table 3, $-(dH/dt)_i$, $(H/H_\infty)_i$, H_∞, $i = 1,2,\ldots,L$, into the kinetic Eq. 4 yields the values of n and ln$k$ that are listed in Table 4.

From Table 4, the values of n and ln$k$ show that the reaction order and the dissolution rate for Keto-RDX in DMSO vary with the experimental temperature, and the values of ln$k$ increase slightly with the experimental temperature increasing.

Substituting the values of n and k in Table 4 into Eq. 3, the kinetic equations describing the dissolution processes of Keto-RDX dissolved in DMSO can be described as

$$d\alpha/dt = 10^{-2.43}(1-\alpha)^{0.63}(T = 298.15K) \quad (5)$$

$$d\alpha/dt = 10^{-2.41}(1-\alpha)^{0.67}(T = 303.15K) \quad (6)$$

$$d\alpha/dt = 10^{-2.40}(1-\alpha)^{0.75}(T = 308.15K) \quad (7)$$

$$d\alpha/dt = 10^{-2.38}(1-\alpha)^{0.76}(T = 318.15K) \quad (8)$$

Table 2 Thermochemical equations and differential enthalpies ($\Delta_{dif}H$) of Keto-RDX in DMSO

T/K	Thermochemical equation	$\Delta_{dif}H$/kJ mol^{-1}	r
298.15	Q/J = 3074.68517 (a/mol) + 0.00254	3.075	0.9993
303.15	Q/J = 3594.01703 (a/mol) + 0.00389	3.594	0.9995
308.15	Q/J = 4214.08586 (a/mol) + 0.00533	4.214	0.9993
313.15	Q/J = 4769.17633 (a/mol) + 0.00530	4.739	0.9994

Table 3 Original data of the dissolution process of Keto-RDX in DMSO at different temperatures

T/K	m/g	t/s	$-(dH/dt)_i$/mJ s^{-1}	$(H/H_0)_i$	$-H_\infty$/kJ mol^{-1}
298.15	0.00691	500	0.350316	0.2618	3.07
		570	0.291885	0.4507	
		640	0.230307	0.6001	
		710	0.181656	0.7132	
		780	0.151326	0.7964	
		850	0.120162	0.8567	
		920	0.097325	0.9006	
		990	0.076032	0.9322	
		1060	0.060911	0.9547	
		1130	0.045981	0.9704	
303.15	0.00749	430	0.458321	0.2238	3.58
		500	0.400034	0.3959	
		570	0.324330	0.5386	
		640	0.270339	0.6521	
		710	0.219499	0.7404	
		780	0.175735	0.8083	
		850	0.140693	0.8598	
		920	0.117254	0.8984	
		990	0.095289	0.9276	
		1060	0.076478	0.9493	
308.15	0.01049	360	0.810180	0.2361	4.20
		430	0.688108	0.4130	
		500	0.534860	0.5601	
		570	0.424889	0.6759	
		640	0.334577	0.7641	
		710	0.262288	0.8300	
		780	0.207958	0.8786	
		860	0.158378	0.9142	
		930	0.118645	0.9400	
		1000	0.093780	0.9584	
313.15	0.00599	290	0.538520	0.1914	4.79
		360	0.456432	0.3521	
		430	0.383985	0.4949	
		500	0.309167	0.6131	
		570	0.260571	0.7067	
		640	0.202720	0.7797	
		710	0.161999	0.8358	
		780	0.129285	0.8784	
		850	0.101860	0.9110	
		920	0.077145	0.9356	

Table 4 Values of n, ln$k$, and the correlative coefficient r for the dissolution process at different temperatures

T/K	n	ln$k$	r
298.15	0.626	−5.599	0.9998
303.15	0.667	−5.559	0.9998
308.15	0.749	−5.518	0.9995
313.15	0.764	−5.484	0.9997

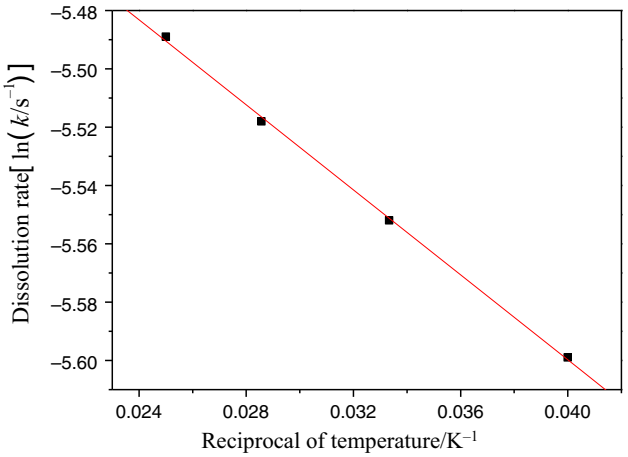


Fig. 2 Relationship of reaction rate constant (k) versus temperature (T) for the dissolution of Keto-RDX in DMSO

Equation (9) [20–22] is applied to calculate the values of the activation energy E and pre-exponential factor A by the slope and the intercept of the linear equation

$$\ln k = \ln A - \frac{E}{RT} \tag{9}$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the temperature.

The resulting values of E and A for the dissolution process are 5.99 kJ mol^{-1} and $10^{-1.38}$ s^{-1}, respectively, and the correlation coefficient is 0.9995. The value of E is very low, showing that the reaction proceeds easily over the temperature range of 298.15–313.15 K. The relationship of ln$k$ versus 1/T for the dissolution of Keto-RDX in DMSO is shown in Fig. 2.

Conclusions

1. The values of heat effects of Keto-RDX dissolved in DMSO were determined at different temperatures. The enthalpies can be regarded as the corresponding enthalpies at infinite dilution because of the very low molalities.
2. The differential enthalpies ($\Delta_{\mathrm{dif}}H$) are 3.075, 3.594, 4.214, and 4.739 kJ mol^{-1}, and the values of the molar enthalpies ($\Delta_{\mathrm{diss}}H$) are 3.075, 3.594, 4.215, and 4.771 kJ mol^{-1} at temperatures of 298.15, 303.15, 308.15, and 313.15 K.
3. In the dissolution processes of Keto-RDX in DMSO, the reaction order and the dissolution rate vary with temperature during the experimental measurements, and the kinetic parameters E and A thus obtained are 5.99 kJ mol^{-1} and $10^{-1.38}$ s^{-1}, respectively. The small values of E and A explain from kinetic viewpoint that DMSO is a very good solvent for Keto-RDX.

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