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STUDIES ON THE SYNTHESIS AND THERMAL DECOMPOSITION MECHANISMS OF RARE-EARTH METAL (Pr, Nd, Sm) SALT HYDRATES OF 3-NITRO-1,2,4-TRIAZOL-5-ONE

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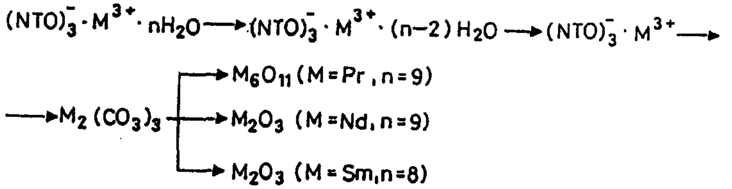
Three new rare-earth metal (Pr, Nd and Sm) salt hydrates of 3-nitro-1,2,4-triazol-5-one (NTO) were prepared and characterized. The thermal behaviour of the three salt hydrates, $M(NTO)_3{\cdot}nH_2O$ (M=Pr and Nd, n=9; M=Sm, n=8) were studied by means of TG and DSC under conditions of linear temperature increase. The thermal decomposition intermediates were determined by means of IR, MS and X-ray diffraction spectrometry. The thermal decomposition mechanisms of these hydrates were proposed as follows:



$$(NTO)_3^- \cdot M^{3+} \cdot nH_2O \longrightarrow (NTO)_3^- \cdot M^{3+} \cdot (n-2)H_2O \longrightarrow (NTO)_3^- \cdot M^{3+} \longrightarrow M_2(CO_3)_3 \longrightarrow \begin{cases} M_6O_{11}\ (M=Pr,\ n=9) \\ M_2O_3\ (M=Nd,\ n=9) \\ M_2O_3\ (M=Sm,\ n=8) \end{cases}$$

Keywords: decomposition mechanisms, metal salt hydrates of 3-nitro-1,2,4-triazol-5-one, rare-earth, synthesis

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Introduction

3-Nitro-1,2,4-triazol-5-one (NTO) is a new explosive with high energy and low sensitivity, whose salts are also energetic materials. The synthesis, chemical structure and properties of various salts have been reported [1–8], but not the preparation and thermal behaviour of the praseodymium, neodymium and samarium salts of NTO (PrNTO, NdNTO and SmNTO). In this paper, we report studies on the preparation of PrNTO, NdNTO and SmNTO, which were characterized by means of elemental analysis, IR spectrometry, nuclear magnetic resonance spectrometry and X-ray diffraction, while their thermal behaviour was investigated under conditions of linear temperature increase by means of TG and DSC.

Experimental

Materials

The purities of the starting Pr_6O_{11}, Nd_2O_3 and Sm_2O_3 were more than 95%. They were commercial products of the Shanghai Yuelong Chemical Engineering Factory. Nitric acid and aqueous ammonia were of chemical purity. NTO was prepared in our Institute and was purified by recrystallization from water; its purity was more than 99.5%.

Experimental

The structures of PrNTO, NdNTO and SmNTO were characterized by using a 60 SXR–FTIR spectrometer (Nicolet Co., USA), a D_{max}III–C X-ray instrument (Rigaku Co., Japan), an FX–90Q NMR apparatus (Nippon Elec. Co.), and a MOD1106 element analyzer (Carlo Erba Co.). The percentage of the rare-earth metal (Pr, Nd and Sm) in PrNTO, NdNTO and SmNTO was measured via EDTA titration.

The thermal decomposition processes were studied by using the TG technique on a Dalta Series TGA instrument (Perkin-Elmer Co., USA). The conditions of TG were as follows: sample mass, about 1 mg; heating rate, 10 deg/min; atmosphere, a flowing N_2/O_2 mixture. The kinetic parameters of thermal decomposition were determined with a differential scanning calorimeter (Shanghai Tianping Instrumental Factory, China) with an aluminium cell (diameter 5 mm x 3 mm) with a rolled-up side. The conditions of DSC were as follows: sample mass, about 1 mg; heating rates, 1, 2, 5, 10 and 20 deg·min^{-1}; calorimetric sensitivities, ±10.46, ±20.92, ±41.84 mJ/s; atmosphere, static air; reference sample, α–Al_2O_3; thermocouple plate, Ni/Cr–Ni/Si. The intermediates in the coacervate phase were analyzed by using a 60 SXR–FTIR spectrometer (Nicolet Co., USA) and a MAT-312/200 MS spectrometer (MAT Co., Germany).

Results and discussion

Preparation of PrNTO, NdNTO and SmNTO

Pr_6O_{11} (or Nd_2O_3 or Sm_2O_3) was ignited at 500°C for 2 h, then dissolved in HNO_3/H_2O (1:1, v/v) solution in a water bath at 60°–70°C until pH=1~2. A light-green solution of $Pr(NO_3)_3$ (or a purplish-red solution of $Nd(NO_3)_3$ or a yellow solution of $Sm(NO_3)_3$) was obtained. The solution was diluted with a 5-fold volume of water and aqueous ammonia solution was added dropwise until pH=8~9; a sediment of $Pr(OH)_3$ (or $Nd(OH)_3$ (purplish-white) or $Sm(OH)_3$ (milk-white)) was obtained. The sediment was separated by centrifugation and washed with distilled water until pH=7, equivalent NTO and a little distilled water were added under stirring and the mixture was allowed to react at 40°C for 1 h. It was next filtered and cooled to obtain a sediment of $M[NTO]_3 \cdot nH_2O$ (M=Pr, and Nd, n=9; M=Sm, n=8). This was recrystallized from distilled water, filtered and dried in a vacuum oven at 40°C for 4 h. A green powder of PrNTO (or a yellow-red powder of NdNTO, of a yellow powder or SmNTO) was obtained.

Structure identification of PrNTO, NdNTO and SmNTO

Analysis for $Pr[NTO]_3 \cdot 9H_2O$ — Calculated: C, 10.44%; H, 3.07%; N, 24.35%; Pr, 20.41%. Found: C, 10.19%; H, 2.73%; N, 24.29%; Pr, 20.03%.

IR ν: 1638 (>C=O), 1620 (>C=N), 1518, 1305 ($-C-NO_2$) cm^{-1} (Fig. 1). ^{13}C NMR δ (DMSO–d_6 as solvent, TMS as reference standard): 146.51 and 172.74 ppm (for >C=O or $-C-NO_2$) (Fig. 2).

Analysis for $Nd[NTO]_3 \cdot 9H_2O$ — Calculated: C, 10.39%; H, 3.05%; N, 24.23%; Nd, 20.80%. Found: C, 9.91%; H, 2.85%; N, 23.70%; Nd, 20.24%.

IRν: 1642 (>C=O), 1622 (–C=N), 1518, 1305 ($-C-NO_2$) cm^{-1} (Fig. 1). ^{13}C NMRδ (DMSO–d_6 as solvent, TMS as reference standard): 145.46 and 166.36 ppm (for >C=O or $-C-NO_2$) (Fig. 2).

Analysis for $Sm[NTO]_3 \cdot 8H_2O$ — Calculated: C, 10.57%; H, 2.81%; N, 24.66%; Sm, 22.06%. Found: C, 10.55%; H, 2.43%; N, 24.95%; Sm, 22.02%.

IR ν: 1623 (>C=O), 1546 (>C=N), 1518, 1305 ($-C-NO_2$) cm^{-1} (Fig. 1). ^{13}C NMRδ (DMSO–d_6 as solvent, TMS as reference standard): 150.73 and 156.00 ppm (for >C=O or $-C-NO_2$) (Fig. 2).

The X-ray diffraction spectra of PrNTO, NdNTO and SmNTO are shown in Fig. 3.

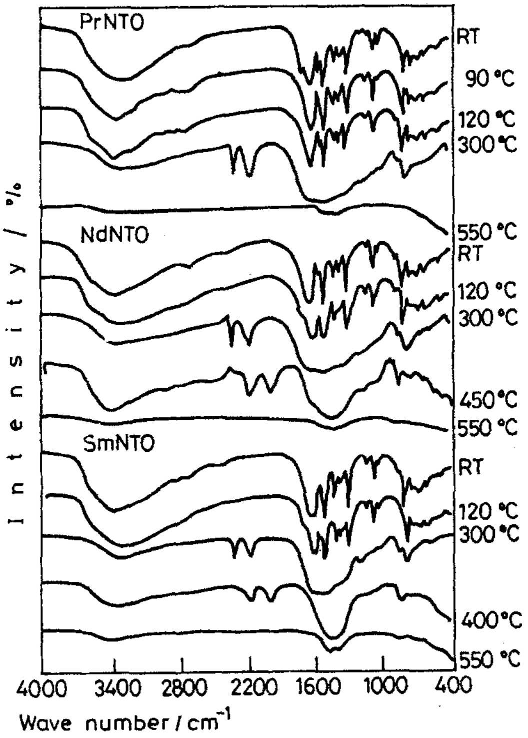


Fig. 1 IR spectra of PrNTO, NdNTO and SmNTO and their decomposition products

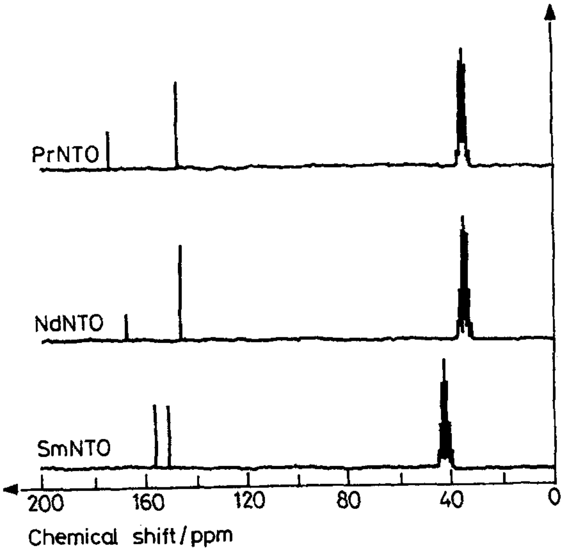


Fig. 2 ^{13}C NMR spectra of PrNTO, NdNTO and SmNTO

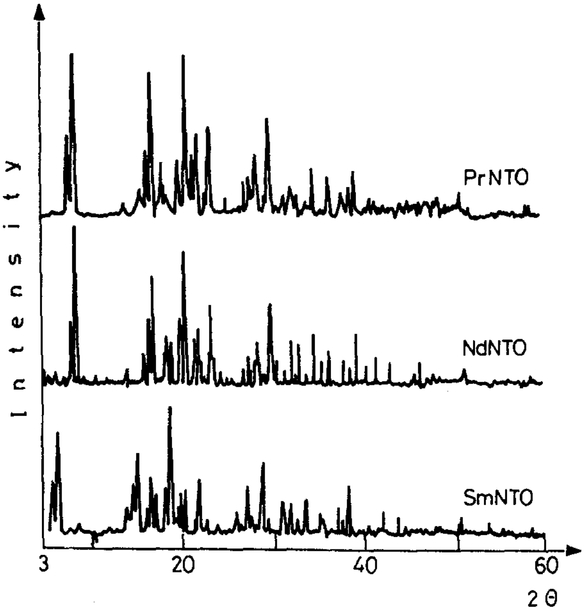


Fig. 3 X-ray diffraction spectra of PrNTO, NdNTO and SmNTO

Thermal behaviour of PrNTO, NdNTO and SmNTO

Typical TG and DSC curves of $M[NTO]_3 \cdot nH_2O$ (M=Pr and Nd, n=9; M=Sm, n=8) under the above conditions are shown in Fig. 4. Mass losses (%) with temperature under non-isothermal conditions are shown in Table 1. It can be seen from Fig. 4 that under the given conditions the thermal decompositions of these salts show three stages in the TG and DSC curves: dehydration, ring breaking and metal oxide formation. Their dehydration processes can be divided into two steps. The first step is connected with the loss of two molecules of water in the temperature ranges 34°–78°C for PrNTO, 33°–76°C for NdNTO and 33°–73°C for SmNTO. The mass losses of 4.9, 5.6 and 6.2% are in agreement with the calculated values of 5.2% for PrNTO, 5.2% for NdNTO and 5.3% for SmNTO. The second step of the dehydration processes is connected with the loss of seven molecules of water in the temperature ranges 78°–170°C for PrNTO and 76°–160°C for NdNTO, and with the loss of six molecules of water in the temperature range 73°–130°C for SmNTO. The mass losses of 18.5, 17.8 and 16.0% in this step are in good agreement with the respective calculated values of 18.3% for PrNTO, 18.2% for NdNTO and 16.0% for SmNTO. After dehydration, the characteristic absorption peaks of N–H and >C=O appear at 3300 and 1700 cm^{-1}, coinciding with the characteristic absorption peak of H_2O, and thus their IR spectra do not clearly change (Fig. 1).

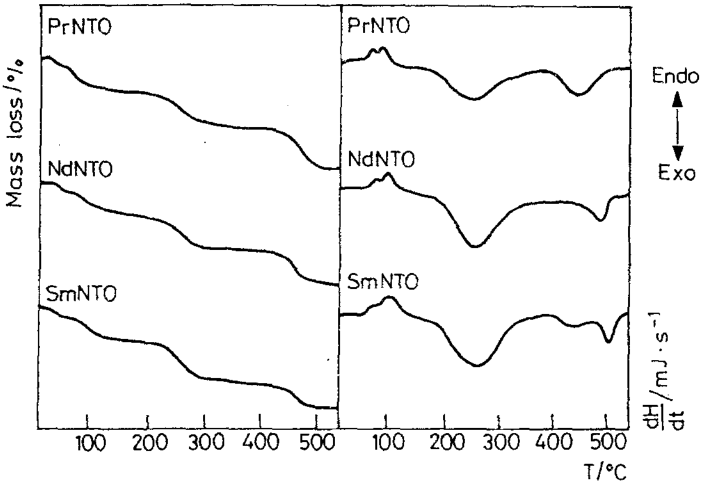


Fig. 4 Typical TG and DSC curves of PrNTO, NdNTO and SmNTO

The second stage is the thermal decomposition of the dehydrated PrNTO, NdNTO and SmNTO, in the temperature ranges 170°–400°C for PrNTO, 160°–404°C for NdNTO and 130°–410°C for SmNTO. The mass losses of 31.6, 32.4 and 35.1% are lower than the calculated values of 43.0% for PrNTO, 42.8% for NdNTO and 43.6% for SmNTO according to the reactions

$$M\,[NTO]_3(M=Pr, Nd \text{ and } Sm) \rightarrow M_2(CO_3)_3$$

By the end of the second stage, the mass spectra of the products (Fig. 5) exhibit a large peak for mass 44, which is CO_2. The characteristic absorption peaks of the $-C-NO_2$ group at 1518 and 1305 cm^{-1} have disappeared and new IR characteristic absorption peaks appear at about 1500 cm^{-1} and at 2335 and

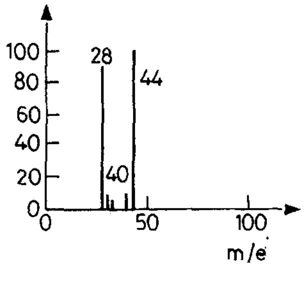


Fig. 5 Mass spectra of the products of the second-stage decomposition of the rare-earth metal salts of NTO

Table 1 Data on the thermal decompositions of PrNTO, NdNTO and SmNTO

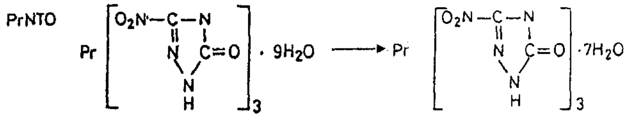
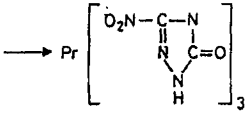
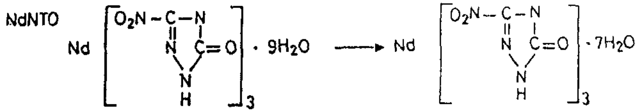
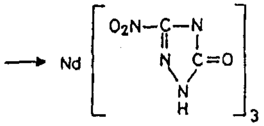
Compound	Decomposition stage	Temperature range / °C		Mass loss / %	
		TG	DTG	Obs.	Calc.
PrNTO		34–78	34–74–78	4.9	5.2
		78–170	78–110–170	18.5	18.3
	$\longrightarrow$ $Pr_2(CO_3)_3$ + coacervate products	170–400	170–267–400	31.6	43.0
	$\longrightarrow$ Pr_6O_{11}	400–530	400–510–530	$\frac{20.3}{75.3}$	$\frac{8.8}{75.3}$
NdNTO		33–76	33–62–76	5.6	5.2
		76–160	76–104–160	17.8	18.2

Table 1 Continued

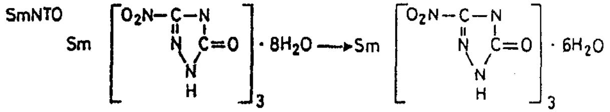
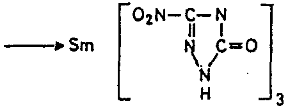
Compound	Decomposition stage	Temperature range / °C		Mass loss / %	
		TG	DTG	Obs.	Calc.
	→ $Nd_2(CO_3)_3$ + coacervate products	160–404	160–280–404	32.4	42.8
	→ Nd_2O_3 + coacervate products	404–500	404–484–500	11.9	9.5
	→ Nd_2O_3	500–590	500–523–590	$\frac{7.0}{74.7}$	$\frac{\quad}{75.7}$
SmNTO		33–73	33–59–73	6.2	5.3
		73–130	73–101–130	16.0	15.8
	→ $Sm_2(CO_3)_3$ + coacervate products	130–410	130–277–410	35.1	43.6
	→ Sm_2O_3 + coacervate products	410–490	410–468–490	13.6	9.7
	→ Sm_2O_3	490–524	490 – 524	$\frac{3.2}{74.1}$	$\frac{\quad}{74.4}$

Table 2 Kinetic parameters* for PrNTO, NdNTO and SmNTO

Sample	Heating rate /	Temperature /	E_K /	E_o /	log A /	r_K	r_o	k /
	deg·min^{-1}	°C	kJ·mol^{-1}		s^{-1}			s^{-1}
PrNTO	2.104	237.8	153.9	154.7	13.1	0.9927	0.9934	$4.50\cdot10^{-3}$
	5.137	248.8						
	10.61	262.5						
	22.74	270.0						
NdNTO	2.089	230.3	130.5	132.3	10.9	0.9991	0.9992	$4.90\cdot10^{-3}$
	5.409	246.3						
	10.10	255.0						
	22.74	269.0						
SmNTO	2.048	234.5	148.8	149.8	12.7	0.9952	0.9957	$5.53\cdot10^{-3}$
	5.379	246.3						
	10.10	258.5						
	21.35	267.3						

*E_K and E_o: apparent activation energies obtained by Kissinger's method and Ozawa's method, respectively;
r_K and r_o: linear correlation coefficients obtained by Kissinger's method and Ozawa's method, respectively.

2182 cm^{-1}. These facts show that there are carbonates and a N=C=N (or C=N) group in the molecule of the decomposed products.

In the third stage, the intermediates in the coacervate phase further decompose to Pr_6O_{11}, Nd_2O_3 and Sm_2O_3.

The total mass loss in the three stages for the three rare-earth metal (Pr, Nd and Sm) salt hydrates are 75.3, 74.7 and 74.1%, respectively, which are in good agreement with the calculated values of 75.3% for PrNTO, 75.7% for NdNTO and 74.4% for SmNTO.

The various analytical data conform with the decomposition mechanisms postulated in Table 1. The apparent activation energy, pre-exponential factor and linear correlation coefficient obtained by Kissinger's method and Ozawa's method and the reaction rate constant (*k*) at 250°C for the three dehydrated rare-earth metal salts are listed in Table 2. According to the values of *k*, their heat resistance decreases in the sequence PrNTO > NdNTO > SmNTO.

Conclusions

The Pr, Nd and Sm salt hydrates of 3-nitro-1,2,4-triazol-5-one (NTO) were prepared and characterized. Their thermal decomposition mechanisms under atmospheric conditions can be expressed by the schemes shown in Table 1.

* * *

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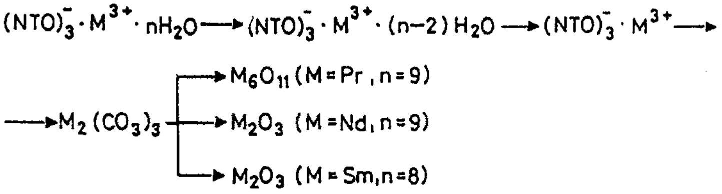
Zusammenfassung — Drei neue Seltenerdenmetallsalzhydrate (Pr, Nd und Sm) wurden erstmals hergestellt und charakterisiert. Bei linearer Temperaturerhöhung wurde mittels TG und DSC das thermische Verhalten der drei Salzhydrate mit der allgemeinen Formel $(NTO)_3\cdot nH_2O$ (M=Pr, Nd, n=9; M=Sm, n=8), gekennzeichnet als PrNTO, NdNTO und SmNTO, untersucht. Die Zwischenprodukte der thermischen Zersetzung wurden mittels IR-, MS- und Röntgendiffraktions-

spektrometrie bestimmt. Für den thermischen Zerfall der genannten Hydrate wird folgender Mechanismus vorgeschlagen:



$$(NTO)_3^- \cdot M^{3+} \cdot nH_2O \longrightarrow (NTO)_3^- \cdot M^{3+} \cdot (n-2)H_2O \longrightarrow (NTO)_3^- \cdot M^{3+} \longrightarrow$$

$$\longrightarrow M_2(CO_3)_3 \begin{cases} \longrightarrow M_6O_{11}\ (M = Pr,\ n = 9) \\ \longrightarrow M_2O_3\ (M = Nd,\ n = 9) \\ \longrightarrow M_2O_3\ (M = Sm,\ n = 8) \end{cases}$$