Synthesis and thermal analysis of 2,4,6-trinitroresorcinol

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ABSTRACT

In this work, the preparation of 2,4,6-trinitroresorcinol by the sulfonation-nitration method of resorcinol through three stages was investigated. The results showed that the 2,4,6-trinitroresorcinol synthesis efficiency reached the highest value (82-83%) when the molar ratio of HNO_3/resorcinol was 3.45/1, the temperature of the nitrate stage was 30-70 ºC, and the concentration of HNO_3 solution was 72%. Besides, the results of 2,4,6-trinitroresorcinol thermal analysis by TGA/DTA methods demonstrated that there are one melting point and two thermal decomposition points in the temperature range from 50 to 400 ºC.

Keywords: 2,4,6-trinitroresorcinol; Styphnic acid; Thermal decomposition.

1. INTRODUCTION

2,4,6-trinitroresorcinol (also known as TNR) is a nitro explosive named styphnic acid. TNR has a structure and impact sensitivity similar to 2,4,6-trinitrophenol (named picric acid), but it is more powerful than picric acid. In the past, TNR was only interesting because it is an important material for the production of lead styphnate, which is used in the bullet primer composition. However, in recent years, salts of TNR with other explosives have been studied, and it was reported as potential explosives [1, 2].

TNR was first discovered in 1808, and until 1871, it was determined that TNR is a product of the nitration of resorcinol. TNR is usually synthesized by sulphonation of resorcinol and then by nitration of acid disulfonic using H_2SO_4 and HNO_3, respectively [3]. There are many methods of synthesizing TNR with different yields and product quality. Tetsuji Kametani's [4] and D.A. Salter's methods [5] uses HNO_3 and $NaNO_2$ for a high yield of TNR (90.5%) but a low melting point (168 ^oC), the purity of TNR is low. In addition, the method of synthesizing TNR by Tadeusz Urbanski [6] using H_2SO_4 to sulfonate resorcinol and then HNO_3 90% to nitrate disulfonic acid, HNO_3 was added in two parts. The yield of TNR was achieved from 80%-83%, melting point was 176 ^oC. The yield was good, but the reaction produced a lot of foam making it difficult to filter. If in the nitration stage, acid HNO_3 is introduced in three parts, the reaction will be smoother because of reducing foam of reaction and the yield and the quality of TNR will be improved.

Because for a long time, TNR was only considered as an intermediate product of lead styphnate, there have not been specific systematic studies on the factors affecting the yield of TNR as well as the thermal properties of TNR. Besides, recently there has been some research on the thermal decomposition of TNR [7, 8]. However, for TNR from different sources, the thermal properties are also different.

This work focused on investigating the effect of several factors (e.g., the mole ratio of HNO_3/resorcinol, the temperature of nitration process and the concentration of HNO_3 solution) on the yield of TNR, thereby finding the optimal conditions to improve the yield of TNR. Besides, thermal analyzes of TNR was also investigated to evaluate its thermal stability. The TNR was first prepared in the laboratory. Then, the melting point and infrared spectra of TNR

were determined to establish its purity. Finally, thermal analysis experiments were conducted by TGA/DTA methods. Based on the TGA/DTA curves, the activation energies of the thermal decomposition of TNR were calculated using Kissinger and Ozawa methods.

2. MATERIALS AND METHODS

2.1. Materials

All starting chemicals (AR grade) were purchased from commercial suppliers and used without further purification. Resorcinol (1,3-benzenediol) with purity greater than 99.5% was obtained from Xilong Scientific Co., Ltd.

2.2. Methods

2.2.1. Synthesis of TNR

The TNR was prepared by the sulfonation-nitration method of resorcinol.

Sulfonation: 11 grams (0.1 mol) of resorcinol was added in portions to a 56 ml of H_2SO_4 98% solution at 20 °C under continuous stirring for about 60 min. After that, the mixture was stirred for 60 min. at 80 °C. The final solution was cooled to 40 ^oC, and ready to be nitrated.

Nitration: 21.3 ml (0.345 mol) of HNO_3 72% solution was added to the sulfonation mixture in such a way that the first part of 6.2 ml (0.1 mol) of HNO_3 was introduced for 30 min at 30-40 °C. After the complete addition, the reaction was quenched by stirring the mixture for 10 min at a temperature of 40 ^oC. Next, the second part (6.2 ml, 0.1 mol) of HNO_3 was introduced to the above mixture for 30 min at 40-50 °C and then the mixture was kept for 10 min at 50 °C. Styphnic acid began to crystallize. Finally, the last part (8.9 ml, 0.145 mol) of HNO_3 was added to the mixture for 1 hour at 50-60 °C and the mixture was maintained at 70 °C for 20 min.

The suspension was cooled to room temperature and added to 500 ml cold water. The received crystals were filtered, washed with cold water until acid H_2SO_4 disappear (using $BaCl_2$ solution) in the washing water. The product was dried at 100 ^oC for 4 hours.

Samples were prepared and filtered in a special fuming hood equipped with a glass shelter and a powerful air suction system for ventilation. The preparation setup consisted of a round-bottom 0.5 L flask equipped with a mechanical stirrer, a dropping funnel, and a thermometer. Safety regulations have been strictly applied such as leather gloves and face shields.

The nitration stage is an important stage and the reaction conditions at this stage have a strong influence on the yield of TNR. In this study, several factors that strongly influence the yield and the quality of TNR were investigated as follows:

- The molar ratio of HNO_3 and resorcinol: in the range from 3.0 to 3.6;
- The temperature of nitration stage: in the range of 20 to 90 ^oC;
- The HNO_3 acid concentration: in the range of 66 to 90%.

Each experiment was run at least three times and the averaged values were obtained with a relative standard deviation of less than 1.2%.

2.2.2. Experimental techniques

- Melting points of TNR were determined by SPM-10 apparatus with a glass capillary and by Pyris Diamond DSC (PerkinElmer).
- The IR spectra of TNR were recorded with an FTIR-400 (PerkinElmer).
- Non-isothermal TG/DTA analyses of the explosive samples were carried out using the DTG-60H apparatus (Shimazu). The TG/DTA analysis experiments were conducted in argon air (flow rate of 20 $mL.min^{-1}$) at various heating rates of 2, 5, 10, 15, and 20 $K.min^{-1}$. The explosive sample of approximately 4.0-9.0 mg was heated from 50 to 400 ^oC in an aluminum oxide crucible.
- The ignition temperature was measured by DT-400 (Germany): SP1~100 °C, SP2~ 300 °C; heating of 150 mg sample at a heating rate of 5 $°C.min^{-1}$ until the point of ignition was reached.

3. RESULTS AND DISCUSSION

3.1. Effect of several factors on the yield and the quality of TNR

3.1.1. The molar ratio of HNO_3 and resorcinol

It was found that the molar ratio of HNO_3/resorcinol has a large influence on the yield of TNR. To reduce the amount of HNO_3 consumed in the reaction, the molar ratio from 3.0 to 3.6 was investigated using HNO_3 with a concentration of 66%. In all reactions, the amount of resorcinol will be fixed at 0.1 mol. The reaction temperature was maintained in the range of 40-80 ^oC in such a way that the first part of 0.1 mol of HNO_3 was introduced at 40-50 °C, the second part of 0.1 mol of HNO_3 was added at 50-60 ^oC, the last part of (0.1; 0.115; 0.13; 0.145; 0.16) mole of HNO_3 was added at 60-70 ^oC and the final suspension was maintained at 80 ^oC. The results were summarized in table 1.

Table 1. *The yield of TNR at different molar ratios HNO_3/resorcinol.*

Entry	Ratio of HNO_3/resorcinol	HNO_3, mol			Yield of TNR (%)	Melting point, ^oC	The ignition temperature, ^oC
		1st part	2nd part	3rd part			
1	3.00	0.1	0.1	0.1	50.4	175	270.1
2	3.15	0.1	0.1	0.115	63.9	175	271.3
3	3.30	0.1	0.1	0.13	67.9	178	269.7
4	3.45	0.1	0.1	0.145	74.4	178	270.5
5	3.60	0.1	0.1	0.16	76.1	176	271.1

As the molar ratio of HNO_3 and resorcinol increases from 3.00 to 3.60, the yield of TNR increases. However, when the HNO_3/resorcinol ratio increases from 3.45/1 to 3.60/1 (i.e., the yield of TNR increases from 74% to 76%), the foaming occurs, making it difficult to obtain the product and reducing the product quality. This is again demonstrated by the melting point values of the TNR samples corresponding to different HNO_3/resorcinol ratios at different ranges of temperature are shown in table 1. It can be seen that the melting points of TNR are in the range of 175-178 ^oC. The average ignition temperature of the samples was 270.5 ^oC. Thus, the optimal molar ratio of HNO_3/resorcinol can be determined at 3.45/1. This molar ratio is kept constant for the next experiments.

3.1.2. The temperature of the nitration process

In the procedure of the nitration of disulfonic acid, the effect of temperature on the yield of TNR was studied. The molar ratio of HNO_3/resorcinol was fixed at 3.45/1 and 66% HNO_3 was still used.

The TNR molecule has 3 positions with the $-NO_2$ group. Therefore, in the nitration process, it is necessary to use HNO_3 in 3 different stages to increase the quantity of 2,4,6-trinitroresorcinol. In the later stages, it is more difficult to attach the $-NO_2$ group than in the first stage, so it is necessary to increase the temperature of the reaction in each stage. Because of adding HNO_3 in 3 stages, the temperature of nitration is also kept in a wide range of temperatures such as 20-60 ^oC, 30-70 ^oC, 40-80 ^oC and 50-90 ^oC. In each range of temperature, acid HNO_3 was added in such a way that the first part of HNO_3 was introduced at (20-30; 30-40; 40-50; 50-60 ^oC), the second part of HNO_3 was added at 30-40; 40-50; 50-60; 60-70 ^oC, the last part of HNO_3 was added at 40-50; 50-60; 60-70; 70-80 ^oC and the final suspension was maintained at 60; 70; 80; 90^oC, respectively. The obtained yields of TNR at different ranges of temperature are shown in table 2.

Table 2. *The yield of TNR at different ranges of temperature.*

Entry	Range of temperature, ^oC				Yield of TNR (%)	Melting point, ^oC	The ignition temperature, ^oC
	1st part	2nd part	3rd part	end			
1	20-30	30-40	40-50	60	76.9	175	270.4
2	30-40	40-50	50-60	70	78.7	178	270.6
3	40-50	50-60	60-70	80	74.4	175	270.4
4	50-60	60-70	70-80	90	77.1	178	271.1

In Table 2, yields of TNR at different ranges of temperature are similar (76.9, 78.7, 74.4 and 77.1%), the difference between the yields is not significant. This means that the temperature of the nitration stage does not affect the yield too much. A selected range of temperature (30-70) ^oC was the optimal range of temperature to carry out process nitration because the starting temperature is close to the ambient temperature.

From Table 2 the melting points of TNR can be observed in the range of 175-178 ^oC. The average ignition temperature of the samples was 270.8 ^oC. Thus, it is possible to determine the optimal range of temperature was 30-70 ^oC. And that range is kept constant for the next experiment.

3.1.3. The HNO_3 acid concentration

According to Tadeusz Urbanski [6], the process of nitration can use acid HNO_3 50-90%, but a high concentration of HNO_3 can be the cause of high foaming in the nitration stage, reducing the yield and quality of TNR. Because HNO_3 is added in 3 parts, it is still possible to investigate at a high concentration of HNO_3. In this work, the HNO_3 solutions with different concentrations (e.g., 66%; 72%; 80% and 90%) were investigated. The molar ratio of HNO_3/resorcinol and the temperature of the nitration process were fixed at 3.45/1 and 30-70 ^oC, respectively. The yield of TNR is shown in Table 3.

Table 3. *The yield of TNR at different concentrations of HNO_3.*

Entry	Concentration of HNO_3, %	Yield of TNR (%)	Melting point, ^oC	The ignition temperature, ^oC
1	66	74.4	175	270.7
2	72	82.1	177	271.6
3	80	83.1	175	273.1
4	90	80.2	177	271.5

In Table 3, it can be seen that the increase of HNO_3 concentration leads to an increase in the yield of TNR. At a concentration of 90%, the decrease in the yield of TNR due to the reaction creates a lot of foam. Besides, when the concentration of HNO_3 is in the range of 72 to 80%, the yield and the quality of TNR are not significant. On the other hand, when the concentration of HNO_3 increased to 80%, the foam of reaction increased.

The melting points of TNR at different concentrations are shown in Table 3. The melting points of TNR are in the range of 175-177 ^oC. Moreover, the average ignition temperature of TNR was 271.7 ^oC.

It can be seen that at selected parameters (e.g., the molar ratio of HNO_3/resorcinol was 3.45/1, the temperature of the nitrate stage was 30-70 ^oC and the concentration of HNO_3 solution was 72%), the yield of TNR reached the high value (82.1%) and the melting point was 177 ^oC. Therefore, these parameters can be used as the optimal conditions of the reaction.

Table 4. *The DSC parameters of TNR samples.*

Sample	T_{ot}, °C	$T_{endo.p}$, °C
1	175.7	180.2
2	175.4	179.7
3	176.3	180.2
4	174.9	179.5
5	176.8	180.2

T_{ot} - Onset temperature of endotherm peak and $T_{endo.p}$ - The endothermic peak temperature of the DSC curve

Furthermore, the DSC thermograms of the TNR samples are shown in Table 4. These five curves of five samples in different conditions show a similar endothermic peak at about 180 °C, the onset temperature was 176-177 °C, which is consistent with the melting point of TNR.

The IR spectra of the product samples are the same and give characteristic peaks (cm^{-1}): 3583 (O-H stretch), 3195 (C-H, sp^2); 1646 (C=C stretch), 1593, 1542, 1310 (N-O stretch).

3.2. Thermal decomposition of TNR

The curves (TG, DTG) of TNR at different heating rates (i.e., 2, 5, 10, 15, and 20 $K \cdot min^{-1}$) were recorded and shown in Fig. 1. For comparison, the characteristic parameters of TG/DTG curves of TNR are summarized in Table 5.

Table 5. *Kinetic parameters from TG/DTG data of TNR.*

β ($K.min^{-1}$)	TG/DTG curve				DTA curve		
	T_{p1} (°C)	T_{p2} (°C)	Mass loss (%)	Residue (%)	T_{min} (°C)	T_{max1} (°C)	T_{max2} (°C)
2	193.6	222.1	98.1	1.9	174.3	193.8	228.4
5	204.9	244.1	97.3	2.7	175.3	206.1	249.4
10	201.9	264.9	93.9	6.1	177.5	206.9	266.3
15	215.6	268.2	93.5	6.5	179.3	218.2	270.8
20	-	278.2	91.3	8.7	181	219.6	279.2

T_{p1}, T_{p2} - The peak 1 and peak 2 temperature of the DTG curve, T_{min} - The endo temperature of the DTA curve and T_{max1}, T_{max2} - The peak 1 and peak 2 temperature of the DTA curve.

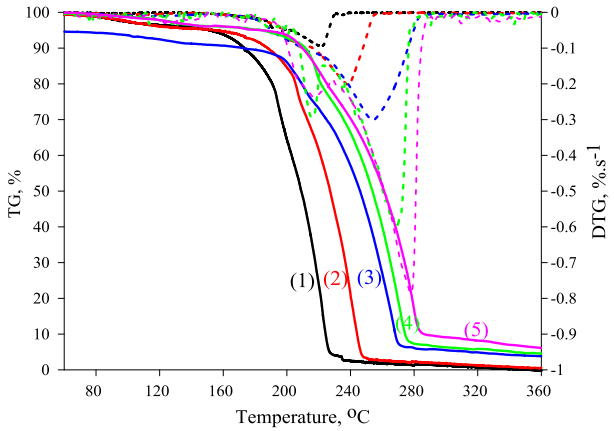

Figure 1. *TG/DTG curves of TNR at several heating rates (1–2 $K.min^{-1}$; 2–5 $K.min^{-1}$; 3– 10 $K.min^{-1}$; 4–10 $K.min^{-1}$; 5–20 $K.min^{-1}$).*

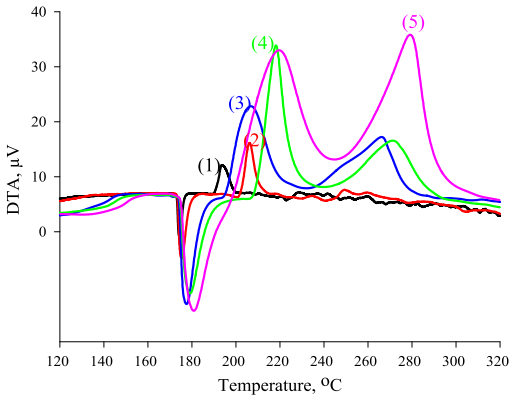

Figure 2. *DTA curves of TNR at several heating rates (1–2 K.min^{-1}; 2–5 K.min^{-1}; 3–10 K.min^{-1}; 4–10 K.min^{-1}; 5–20 K.min^{-1}).*

The TG curves of TNR indicate a mass loss in two step that is related to the thermal decomposition of TNR. TNR loses 91-98% weight in the temperature range corresponding to the thermal decomposition. According to DTG curves, at the main decomposition stage, there are two peaks of temperature (Fig. 1). The peaks in DTG curves for the thermal decomposition of TNR were observed in a range of 193.6-215.6 and 222.1-278.2 °C, respectively. The residue mass of TNR is the product of decomposition. It can be seen that at a high heating rate, the residue mass is quite large.

The DTA curves of TNR (Fig. 2) show an endothermic peak and two exothermic peaks. The endothermic peaks were observed in the temperature range of 174.3-181 °C due to the melting point of TNR [8]. The first exothermic peaks were observed at the temperatures range of 193.8-219.6 ^{o}C, while the second exothermic peaks appear in the range of 228.4-279.2 ^{o}C at different heating rates (2, 5, 10, 15 and 20 K.min^{-1}).

As seen, the decomposition rate of TNR is not too fast (the fastest rate is 0.8 %.s^{-1}). The temperature range of the thermal decomposition was from 193.8 to 279.2 ^{o}C. From the DTA data, it is apparent that the first exothermic peak relates to the decomposition of TNR and the second exothermic peak corresponds to the decomposition of products of the first process. The values of the T_{max} were shifted towards the higher temperature with increasing heating rates. Moreover, it can be seen that at low heating rates, the first exothermic peak is strong and the second exothermic peak is weak (Fig. 2), thus the main decomposition takes place at the first exotherm peak.

4. CONCLUSION

The preparation of 2,4,6-trinitroresorcinol through the action of sulfonating resorcinol and then nitrating disulfonic acid in 3 stages was studied. The results indicated that the optimal synthesis parameters were as follows: the molar ratio of HNO_3/resorcinol was 3.45/1, the temperature range of the nitration process was 30-70 ^{o}C and the concentration of HNO_3 was 72%. With such parameters, the maximum yield of TNR could reach 82-83%, the melting point of TNR was 176-178 ^{o}C.

The decomposition properties of TNR were studied by TG/DTG and DTA techniques at different heating rates. The thermal decomposition curves show that the decomposition of TNR takes place in two consecutive stages. The first exothermic peak is the decomposition of TNR and the second exothermic peak corresponds to the decomposition of products of TNR.

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TÓM TẮT

Nghiên cứu quy trình tổng hợp và tính chất phân hủy nhiệt của 2,4,6-trinitroresorcinol

Phương pháp tổng hợp 2,4,6 - trinitroresorcinol thông qua quá trình sulfo hóa và nitro hóa 3 bước ở 3 điều kiện nhiệt độ khác nhau đã được nghiên cứu. Kết quả cho thấy, hiệu suất tạo thành 2,4,6-trinitroresorcinol đạt được giá trị cao nhất (82-83)%, khi tỷ lệ mol HNO_3/resorcinol 3.45/1, nhiệt độ phản ứng từ 30-70 ^oC, nồng độ HNO_3 72%. Bên cạnh đó, kết quả phân tích nhiệt của 2,4,6-trinitroresorcinol bằng phương pháp TGA/DTA đã chứng minh rằng có một điểm nóng chảy và hai điểm phân hủy trong khoảng nhiệt độ từ 50-400 ^oC.

Từ khóa: 2,4,6-trinitroresorcinol; Styphnic acid; Phân hủy nhiệt.