



## Hazard of Runaway of Nitration Processes in Nitrocompounds Production

Georgii D. KOZAK and Vlada M. RAIKOVA

*Mendeleev University of Chemical Technology,*

*9 Miusskaya Square, Moscow 125190, Russia*

*E-mail: KozakGD@rambler.ru*

**Abstract:** Hazard of runaway of nitration processes in nitrocompounds production was investigated. Temperature rise in DNT nitration mixes under near adiabatic conditions was measured, and derivative  $dT/dt$  was computed. Heat evolution rate caused by nitration (primary reaction) and oxidation (secondary reaction) were examined by means of elaborated mathematical model. Limiting values of  $T$  and  $dT/dt$  for safe process were determined. The second part of investigation concerns detonability of solutions of nitrocompound in sulfuric acid. The detonation failure diameter  $d_f$  and detonation velocity  $D$  of solutions of trinitrotoluene, dinitrotoluene, and trinitrobenzene in sulfuric acid and oleum have been measured in the wide range of concentrations at  $T = 90$  °C. It was shown that the detonability of the nitrocompounds depends significantly on the sulfuric acid content. The minimum value of  $d_f$  for the mixture TNT/oleum is about 2 mm, i.e., 30 times less, than that for melted TNT, and practically equals to  $d_f$  of nitroglycerine.

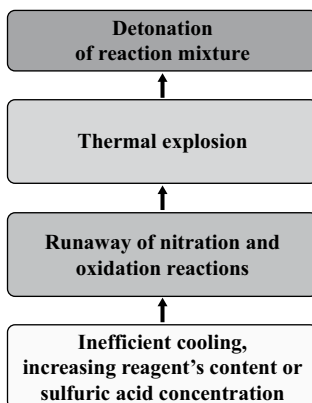
**Keywords:** runaway, nitration, oxidation, detonation, failure diameter, sulfuric acid

### Introduction

Runaway of nitration synthesis caused frequent accidents. Often not primary reaction (nitration) proceeds, but secondary reactions (oxidation) starting at higher than usual temperature and having a higher energy of activation than intended reaction proceed too. Careful investigation of nitration of DNT to TNT [1-4] has shown that the explosions were connected with the violent exothermal reactions and detonation of reaction mixtures. Hazard of runaway of nitration

processes in nitrocompounds production and investigation concerns detonability of solutions of nitrocompound in sulfuric acid are described in this work.

Inefficient cooling, increasing of reagent's content in the mixture and sulfuric acid concentration (oleum addition) may initiate runaway of reaction (Figure 1).

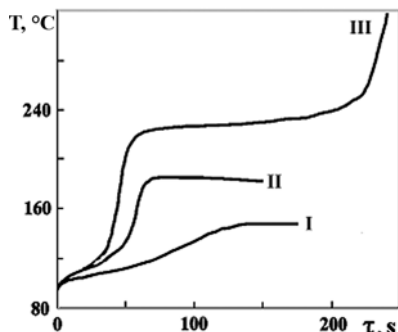


**Figure 1.** Logic diagram of development of accident at nitration of DNT.

## Experimental and Results

Thermokinetic reactor was used for hazard investigation of nitration processes [4-6]. Experiments were conducted in the glass spherical reactor with jacket and stirrer. Reactor volume was 250 cm<sup>3</sup>, diameter was 85 mm, and jacket diameter was 102 mm. The mass of reaction mix was 110-120 g. Reaction mixtures contained DNT, TNT, nitric acid (conc. 99%), and sulfuric acid (conc. 98-103%). Total concentration of DNT and TNT was 30% in mixture. A solution of TNT and DNT in sulfuric acid was poured into reactor and heated to  $T = 95-97$  °C. Then water was removed from the jacket, and nitric acid was introduced into the mix. Temperature of the mix during reaction was measured by differential thermocouple, protected by means of quartz capillary, and recorded by potentiometer. Thermograms  $T(\tau)$  were treated, and derivatives  $dT/d\tau$  were computed.

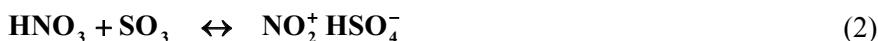
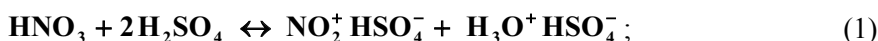
Typical dependencies  $T(\tau)$  for reaction mixtures contained DNT, TNT, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> are represented in Figure 2.



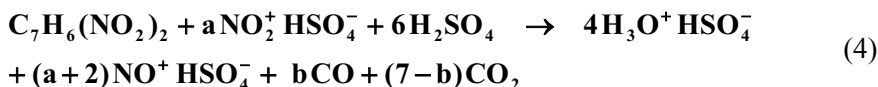
**Figure 2.** Experimental dependencies of temperature vs. time for reaction mixtures of DNT nitration. Curve I corresponds to safety process, curve II corresponds to runaway of reactions, curve III corresponds to thermal explosion.

Lower curve (I) corresponds to slow temperature rise, and reduction of  $dT/d\tau$ . Middle curve (II) corresponds to fast temperature rise, and increase of  $dT/d\tau$ . Upper curve (III) corresponds to further rise of temperature from 200 °C to 340-360 °C that leads to heat explosion.

Three consecutive steps of exothermal process were observed. First step is dissolving (ionization) of  $\text{HNO}_3$  in sulfuric acid or oleum (reactions 1 and 2):



Second step includes reactions of nitration and destructive oxidation of DNT (reactions 3 and 4):



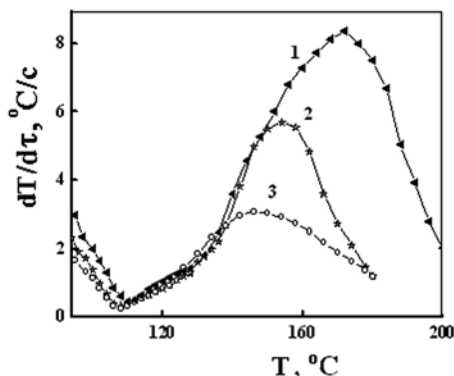
where  $a$  and  $b$  are stoichiometric factors.

In adiabatic conditions temperature increases because of two exothermal reactions, and growth of temperature is described by equation (5):

$$\rho \cdot C_p \frac{dT}{d\tau} = W_n \cdot Q_n + W_{ox} \cdot Q_{ox}, \quad (5)$$

where  $\rho$  is the density of solution,  $C_p$  is the specific heat of solution,  $W_n$  is the rate of nitration,  $W_{ox}$  is the rate of oxidation,  $Q_n$  and  $Q_{ox}$  are reactions heats of nitration and oxidation, correspondingly.

The dependence of  $dT/d\tau$  vs. temperature during nitration of DNT is shown in Figure 3. The value  $dT/d\tau$  is not tend to zero and increases with temperature rise. If temperature is higher than 120 °C, runaway of nitration DNT is greatly probable.



**Figure 3.** The dependence of  $dT/d\tau$  vs. temperature during nitration of DNT. DNT content in mixture is 22% (1, 2), 18% (3),  $HNO_3$  content is 7% (1) and 5.5% (2, 3).

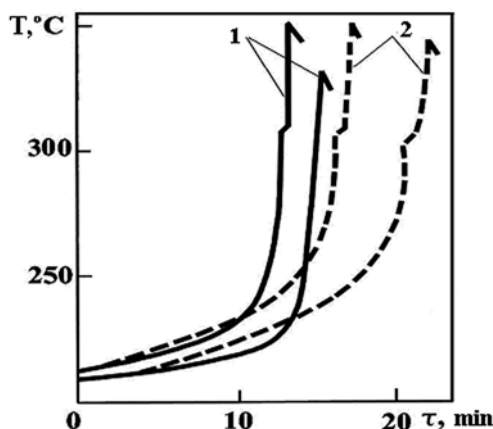
In third step at temperature above 200 °C interaction between DNT (TNT) and sulfuric, and nitrosylsulfuric ( $NOHSO_4$ ) acids occurs. These reactions run in the form forthcoming to autocatalytic thermal explosion (Figure 4). Final reaction products are  $CO_2$ ,  $CO$ ,  $SO_2$ ,  $N_2$ ,  $H_2O$  and condensed resinous substances.

The effective kinetic parameters of bimolecular reactions of nitrocompounds with  $H_2SO_4$  and  $NOHSO_4$  were estimated by means of equation for adiabatic heat explosion induction time (6):

$$\tau_{ad} = \frac{C_p RT_o^2}{Q_r E_a B[S]} \exp(E_a / RT_o), \quad (6)$$

where  $E_a$  is activation energy,  $B$  is pre-exponent factor,  $Q_r$  is heat of reaction,

[S] is concentration of  $H_2SO_4$  in the mixture. For mixtures contained nitrosylsulfuric acid [S] was replaced by concentration of  $NOHSO_4$ .



**Figure 4.** Experimental dependencies of temperature vs. time for solutions of DNT (1) and TNT (2) in sulfuric acid (conc. 98%).

Effective values of kinetic constants at 200 °C,  $E_a$  and B obtained by means of treatment of experimental curves  $T(\tau)$  are collected in Table 1.

**Table 1.** Effective kinetic parameters of reactions of DNT and TNT with sulfuric, and nitrosylsulfuric acids

	$K_{200\text{ °C}} \times 10^6$ , $l/(mol \times s)$	$E_a$ , kJ/mol	B, $l/(mol \times s)$
DNT - $H_2SO_4$	2.23	$118 \pm 6.0$	$2.4 \times 10^7$
TNT- $H_2SO_4$	1.43	$110 \pm 7.4$	$2.0 \times 10^6$
DNT- $NOHSO_4$ - $H_2SO_4$ *)	30.6	$136 \pm 4.5$	$3.2 \times 10^{10}$
TNT- $NOHSO_4$ - $H_2SO_4$ *)	12.3	$125.5 \pm 7.4$	$8.9 \times 10^8$

\*) Concentration of  $NOHSO_4$  in sulfuric acid is 17%.

It should be noted, that the calculated constants,  $K_{200\text{ °C}}$  for various mixtures presented in Table 1 differ one from another. The rates of decomposition of solutions of DNT are greater ones, than those for solutions of TNT. Oxidative activity of nitrosylsulfuric acid is far stronger, than that for sulfuric acid.

As a result of decomposition and self-heating of reaction mixtures gas-liquid system is formed, and detonation of solutions of nitrocompounds in concentrated sulfuric acid may be initiated easily [7]. It must be noted that in

stage III (Figure 2) nitric acid is absent in mixture because reaction of nitration and oxidation are completed, and reaction mixture consists from nitrotoluenes and concentrated sulfuric acid or oleum. On the contrary to normal reaction mixtures (nitrotoluenes, concentrated sulfuric or oleum and nitric acid) mixtures nitrotoluenes and concentrated sulfuric or oleum are not emulsions but they are solutions at  $t > 85\text{ }^{\circ}\text{C}$  [8].

The strong sensibilizing effect of small quantity of the inorganic acids on the nitrocompound detonation was observed earlier [9]. Nitromethane was used as a model. There was shown, that nitromethane detonability is greatly higher in presence acid. It would be interesting to find out how it is affecting the aromatic nitrocompounds.

The detonability of mixtures of sulfuric acid or oleum with trinitrotoluene (TNT), dinitrotoluene (DNT), and trinitrobenzene (TNB) was studied in a wide range of the components concentrations (from 93 to 108%  $\text{H}_2\text{SO}_4$  in the concentrated sulfuric acid and oleum, and up to 64% of the sulfuric acid in the mixture with nitrocompound).

The detonation failure diameter  $d_f$  was measured in glass tubes (the wall thickness is  $d \sim 1.5\text{ mm}$ ) by means of the method "go-no-go". Dark, open, and half-dark points (Figures 5 and 8) are, correspondingly, designate detonation, failure of detonation immediately after initiation, and detonation extinguishment after more or less prolonged. The tubes had the smooth widening in the upper part for booster setting, and for the continuous transition to the steady-state detonation. A pellet of pressed phlegmatized RDX ( $d = 12\text{ mm}$ ,  $m = 2\text{ g}$ ,  $r = 1.66\text{ g/cm}^3$ ) used as the booster was protected by means of the thin film of fluorocarbon polymer to avoid the strong acid action on the booster. The result of the experiment was determined by means of the steel witness-plate attached directly to the tube wall.

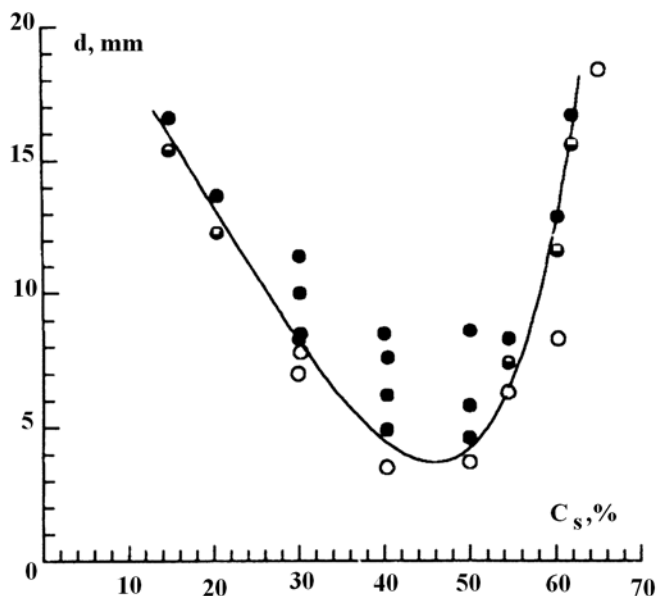
The experiments at high temperature were conducted in the glass tubes inserted in tubes of higher diameter and isolated by means of the layer of cotton wool placed between the tubes walls. The assembly was heated to temperature  $5\text{ }^{\circ}\text{C}$  higher the proposed experiment temperature, then it was placed into the explosion chamber, and after some delay monitored by means of the preliminary estimated cooling curve the detonation was initiated.

The detonation velocity  $D$  was measured in the steel tubes ( $d = 10\text{ mm}$ ,  $d = 13\text{ mm}$ ,  $L = 180\text{-}250\text{ mm}$ ). The detonation process luminosity was registered with Russian streak camera SFR-2 through the radial holes ( $d = 1.5\text{-}2.0\text{ mm}$ ), drilled in the wall of the tube at distance of  $15\text{ mm}$  one from another. The holes as well as the bottom of the tube were closed with the glass plates, adhered by means of the acid persistent glue.

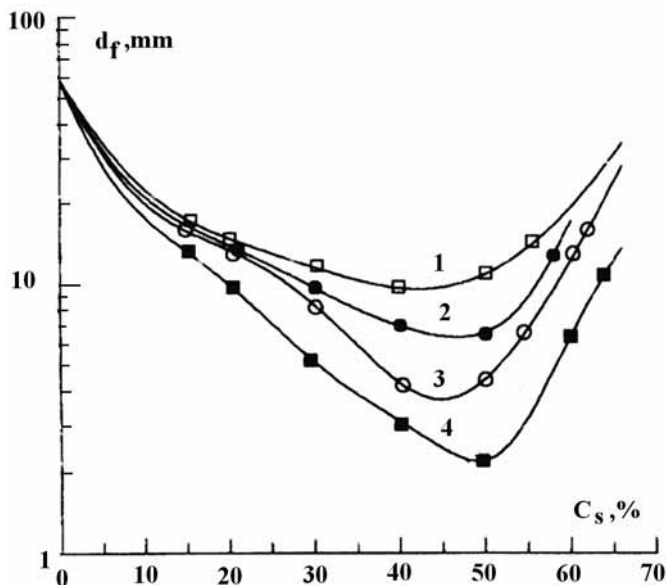
The measurements were made mainly at the initial temperature  $T_0 = 85\text{-}86\text{ }^{\circ}\text{C}$

for TNT and DNT solutions, and at  $T_0=110$  °C for TNB.

Oleum of concentration 100.6, 101.7, 103.8 and 108.2%  $H_2SO_4$  was used to obtain TNT solutions. The results of the measurements of failure diameter of the solutions are represented in Figures 5 and 6.



**Figure 5.** The results of detonation failure diameter measurements in the TNT/oleum mixtures (concentration of oleum  $S = 103.8\%$   $H_2SO_4$ ),  $T_0 = 85-86$  °C. Dark, open, and half-dark points are correspondingly designate detonation, failure of detonation, and detonation extinguishment. The curve separates the detonation region from the region of detonation failure.



**Figure 6.** The detonation failure diameter of the mixtures of TNT with oleum versus content oleum ( $C_s$ ) in solution. Oleum concentration  $S$ : 1 –  $S = 100.6\%$ , 2 –  $S = 101.7\%$ , 3 –  $S = 103.8\%$ , 4 –  $S = 108.2\%$ . The points are the mean experimental values from the experimental curves (Figure 5).

Curves received at different oleum concentrations are similar to each other: as the oleum content ( $C_s$ ) in mixture increases, detonation failure diameter reduces down to the minimum value and then rises. Dependence between the minimum critical diameter ( $d_f^{\min}$ ) and oleum concentration ( $S$ ) may be described by equation (7) as follows:

$$\log d_f^{\min} = 1.2 \cdot 10^7 \exp(-0.162 S), \quad (7)$$

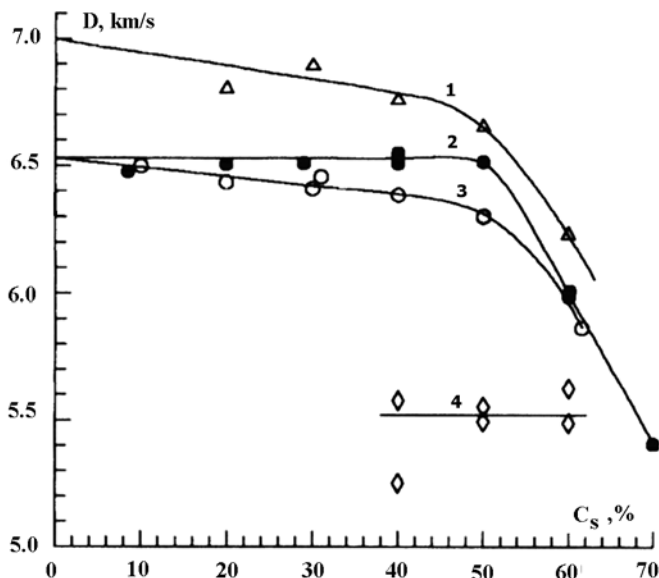
( $d^{\min}$ , mm  $S$ , % mass)

The content of oleum in the mixture corresponding to the minimum of the curve is about 40-50% and tends to rise in these limits, when  $S$  grows. The minimum value of  $d_f$  for TNT diluted by oleum,  $S = 108.2\%$ , is about 2 mm, i.e. 30 times less, than that for pure melted TNT. It is practically equal to the detonation failure diameter of nitroglycerine [10].

The influence of oleum content on detonation velocity of TNT is shown in Figure 7. The velocity of detonation is practically constant up to  $C_s = 50\%$ .



Further growth of oleum content results in the considerable decrease of the D value leading to extinguishment of detonation.

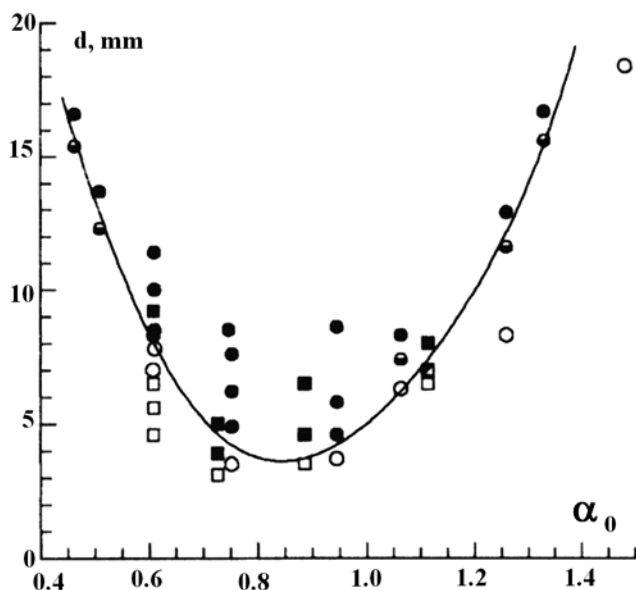


**Figure 7.** The results of detonation velocity measurements of the mixtures of nitrocompounds and oleum:  
 1 – TNB/oleum ( $S = 103.5\%$ ,  $T_0 = 110\text{ }^\circ\text{C}$ ), 2 – TNT/oleum ( $S = 103.8\%$ ,  $T_0 = 85\text{-}86\text{ }^\circ\text{C}$ ), 3 – TNT/oleum ( $S = 101.6\%$ ,  $T_0 = 85\text{-}86\text{ }^\circ\text{C}$ ), 4 – DNT/oleum ( $S = 103.8\%$ ,  $T_0 = 85\text{ }^\circ\text{C}$ ).

The detonation failure diameter of pure melted DNT up to now is not estimated. Using some approximation, we can evaluate it at  $80\text{-}90\text{ }^\circ\text{C}$  as about  $0.5\text{ m}$ . In the steel tubes ( $d = 10\text{ mm}$ ,  $d = 13\text{ mm}$ ) the detonation extinguished even at  $190\text{ }^\circ\text{C}$ . However, the steady-state detonation of the DNT solutions in oleum at  $S = 103.8\%$ ,  $C_s = 60\%$  ( $T = 85\text{ }^\circ\text{C}$ ) was observed. The mean detonation velocity of the solutions was equal  $D = 5.5\text{ km/s}$  (Figure 2). At  $C_s = 40\%$  the detonation of the solution after considerable ( $110\text{-}130\text{ mm}$ ) propagation failed, at  $C_s = 70\%$  the detonation was not observed. It is quite obviously that oleum reacts with DNT sensitizing it detonation.

The experiments with TNB solutions were carried out at the oleum concentration  $S = 103.5\%$ . At  $T_0 = 110\text{ }^\circ\text{C}$  one can get the solutions, containing up to  $80\%$  of TNB. The results of the detonation velocity measurements and the detonation failure diameter of the TNB solutions in oleum measurements are

shown in Figures 7 and 8.



**Figure 8.** The detonation failure diameter versus equivalent ratio  $\alpha_0$  for TNT/oleum ( $S = 103.8\%$ ,  $T_0 = 85^\circ\text{C}$ , circles) and TNB/oleum ( $S = 103.5\%$ ,  $T_0 = 110^\circ\text{C}$ , quadrangles) mixtures. Dark, open, and half-dark points correspondingly designate detonation, failure of detonation, and detonation extinguishment.

Comparing these data with the results observed for TNT in oleum solutions ( $S = 103.8\%$ , Figure 8), one can conclude, that the curves are not only similar to each other, but even the values of  $d_f$  for TNT and TNB solutions are almost exactly the same. However, to reach the same  $d_f$  values in case of TNB the higher temperature is required. In coordinates of  $d_f$  versus  $\alpha_0$  the data for TNT and TNB coincide with each other (Figure 8). Here  $\alpha_0$  is the equivalent ratio of the mixture:

$$\alpha_0 = (O)/[2(C)+(H)/2-(S)], \quad (8)$$

where (O), (C), (H) and (S) are the molecular fractions of the elements in the mixture.

The chemical mechanism of influence of sulfuric acid on  $d_f$  of nitrocompounds detonation was elaborated under scientific direction of Professor B.N. Kondrikov [1].

Influence of nitric acid on detonation of TNT solutions in oleum is important to the obvious practical interest. Solubility of nitrocompounds in the sulfuric-nitric acids mixture is far less, than in oleum or sulfuric acid alone. One can introduce without loss of solubility to the mixture containing 40/60 TNT/oleum ( $S = 103.8\%$ ) no more than 4% of nitric acid. Experiments carried out with such solution at concentration of nitric acid 2.5 and 4%, show that, regardless of wide-spread opinion,  $d_f$  of TNT solution in oleum does not grow. It remains constant and equal to 11-12 mm. Addition of extra quantity of nitric acid results in emulsion formation, and experiments in this concentration region were not carried out.

## Conclusion

Thus, runaway of nitration processes in nitrocompounds production leads to a rise of temperature, to acceleration of nitration and oxidation processes and to heat explosion. It is important, that detonability of acid reaction medium (emulsion) at evaluation of emergency conditions increases because of transformation of emulsion into solution of nitrocompounds in sulfuric acid. The failure diameter of detonation of such systems can be in dozens of times less than  $d_f$  of liquid TNT.

## Acknowledgement

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