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Sulfuric Acid Influence on the Nitrocompounds Detonation Reactions

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Abstract: The detonation failure diameter d_f and detonation velocity D of mixtures of nitromethane, trinitrotoluene, dinitrotoluene, and trinitrobenzene with sulfuric acid and oleum have been measured in the wide range of concentrations. It was shown that the detonation ability 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 pure melted TNT, and practically equal to d_f of nitroglycerine. In some cases, the temperature dependencies of failure diameter have been determined. Dremin theory of detonation failure diameter was used to treat quantitatively the results of experiments with the NM and TNT solutions in the frameworks of the Arrhenius chemical kinetics.

1. INTRODUCTION

The strong sensibilizing effect of small quantity of the inorganic acids on the nitrocompounds detonation was observed earlier [1]. Nitromethane was used as a model. There was shown that the nitromethane detonation is greatly influenced by small concentration of additives. Of course it would be interesting to find out how it is affected by the large ones.

In this paper the sulfuric acid influence on the detonation ability of mixtures of sulfuric acid or oleum with nitromethane (NM), trinitrotoluene(TNT), dinitrotoluene(DNT), and trinitrobenzene(TNB) was studied in a wide range of the components concentrations¹ (from 93 to 108% H_2SO_4 in the concentrated sulfuric acid and oleum, and up to 64% of the acid in the mixture with nitrocompound). Dremin theory of detonation failure diameter [2-4] was used to treat quantitatively the results of experiments with NM and TNT solutions.

The work was mainly implemented during 1986-1990 as a constituent part of investigations were to reveal and to remove causes of accidents being arisen under the TNT production on the third stage of DNT to TNT nitration.

¹ Concentration of oleum and acid is expressed by percentage of sulfuric acid S . Content of suitable sulfuric ingredient in mixture with explosive is denoted by C_s .

2. EXPERIMENTAL

The experiments were carried out using the commercial grade TNT (solidification temperature, S.T.=80.2°C) and 2,4-DNT (S.T.=68.9-69.2°C). TNB was produced in the laboratory and purified by recrystallization from nitric acid (S.T. of TNB recrystallized was 122.8°C). The commercial-grade NM was distilled at atmospheric pressure over P₂O₅. The main fraction 100.7-101.3°C was taken for the experiments. The detonation failure diameter of this fraction of NM measured repeatedly every 1-2 months during about two years was 13±0.5 mm. The commercial-grade sulfuric acid (94% concentration) and oleum containing 60% "free" sulfuric anhydride were used to prepare the solutions containing up to 108.2% H₂SO₄. The H₂SO₄ concentration was determined by titration.

The detonation failure diameter d_f was measured in glass tubes (the wall thickness is ~1.5 mm) by the method go-no-go. Dark, open, and half-dark points (Fig.1,3,5) correspondingly designate detonation, failure of detonation immediately after initiation, and detonation extinguishment after more or less prolonged (up to several d in length) path of the detonation process. The tubes had the smooth widening in the upper part for initiator or booster setting, and for the continuous transition to the steady-state detonation. A pellet of pressed phlegmatized RDX (d=12 mm, m=2 g, $\rho=1.66$ g/cm³) used as the booster was protected by the thin film of fluoropolymer to avoid the strong acid action on the booster. The result of the experiment was determined by means of the metal witness-plate attached directly to the tube wall.

The experiments at high temperature were carried out in the glass tubes inserted in tubes of higher diameter and isolated by the layer of cotton wool placed between the tubes walls. The assembly was heated to temperature 5°C higher the proposed experiment temperature. After that the liquid investigated heated to the same temperature was quickly poured into the central glass tube, all the setting 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 mm, $\delta=13$ mm, $l=180$ -250 mm). The detonation process luminosity was registred by the Russian streak camera SFR-2 through the radial holes (d=1.5-2.0 mm), drilled in the wall of the tube at distance of 15 mm one from another. The holes as well as the bottom of the tube were closed by the glass plates, adhered by the acid persistent glue.

The measurements were made mainly under the initial temperature $T_0=18.5^\circ\text{C}$ for NM solutions, 85-86°C for TNT and DNT solutions, and 110°C for TNB solutions (except the cases where the effect of initial temperature was estimated).

3. RESULTS

NM: The results of experiments with the solutions of NM in H₂SO₄ concentration of 93% and 100.5% are represented in Figs.1 and 2. The sulfuric acid addition leads to the failure diameter quick decrease, after that the flat minimum (about 1.5 mm) is reached, and progressive grow of the d_f value follows. The detonation velocity at $C_S \leq 20\%$ ($S=100.5\%$) is practically constant, and equal to that of the neat NM (6.34 mm/ μs at $T=18.5^\circ\text{C}$). For $S=93\%$ the $D(C_S)$ dependence was not measured.

TNT: Oleum of concentration 100.6, 101.7, 103.8 and 108.2% H₂SO₄ was used to obtain TNT solutions. The results of the measurements of failure diameter of the solutions are represented in the Figures 3 and 4. 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. Minimum critical diameter $d_f^{\min}$ (mm) depends on S :

$$\log_{10} d_f^{\min} = 1.2 \cdot 10^7 \cdot \exp(-0.1619 \cdot S)$$

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.

The influence of oleum content on detonation velocity of TNT is shown in Fig.2. The velocity of detonation is almost 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.

Influence of nitric acid on detonation of TNT solutions in oleum is of 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. Introducing of extra quantity of nitric acid results in emulsion formation, and experiments in this concentration region were not carried out.

DNT: The detonation failure diameter of pure melted DNT up to now is not estimated. Using some approximation, we can appraise it at 80-90°C as about 0.5 m. In the steel tubes ($d=10$ mm, $\delta=13$ mm) the detonation extinguished even at 190°C. However, the steady-state detonation of the DNT solutions in oleum at $S=103.8\%$, $C_s=50\%$ and 60% ($T_0=85^\circ\text{C}$) was observed. The mean detonation velocity of the solutions was equal to 5.5 mm/ μs (Fig.2). At $C_s=40\%$ the detonation of the solution after considerable (110-130 mm) propagation failed, at $C_s=70\%$ the detonation was not observed. It is quite obviously that oleum reacts with DNT sensitizing its detonation.

Fig.1. Influence of sulfuric acid on detonation failure diameter of NM. Dark, open, and half-dark points correspondingly designate detonation, failure of detonation, and detonation extinguishment. The points and the solid line (which separates the detonation region from the region of detonation failure) represent the results for $S=100.5\%$. The dashed line corresponds to $S=93\%$.

Fig.2. The results of detonation velocity measurements of the mixtures of nitrocompounds and oleum:

- Δ - TNB/oleum ($S=103.5\%$, $T_0=110^\circ\text{C}$),
- $\bullet$ - TNT/oleum ($S=103.8\%$, $T_0=85-86^\circ\text{C}$),
- $\circ$ - TNT/oleum ($S=101.6\%$, $T_0=85-86^\circ\text{C}$),
- $\diamond$ - DNT/oleum ($S=103.8\%$, $T_0=85^\circ\text{C}$),
- $\blacktriangle$ - NM/oleum ($S=100.5\%$, $T_0=18.5^\circ\text{C}$).

Fig.3. The results of detonation failure diameter measurements in the TNT/oleum mixtures, $T_0=85-86^\circ\text{C}$. Dark, open, and half-dark points correspondingly designate detonation, failure of detonation, and detonation extinguishment. The curve separates the detonation region from the region of detonation failure.

Fig.4. The detonation failure diameter of the mixtures of TNT (a-d) and NM (dashed line) with oleum versus its content in the solution. Oleum concentration S, %: a - 100.6%, b - 101.7%, c - 103.8%, d - 108.2%, and 100.5% for the mixtures of NM. The points are the mean experimental values; the solid lines are calculated for TNT mixtures using the kinetic scheme suggested.

Fig.5. The detonation failure diameter versus inverse equivalent ratio α_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. The curve is common for two mixtures, and separates the detonation region from the region of detonation failure.

TNB: The experiments with TNB solutions were carried out at the oleum concentration $S=103.5\%$. At 110°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 estimations are shown in Figs.2 and 5. Comparing these data with the results observed for TNT in oleum solutions ($S=103.8\%$, Fig.3), one can conclude, that the curves are not only similar to each other, but even the values of $d_f^{\min}$ for TNT and TNB 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 $1/\alpha_0$ the data for TNT and TNB coincide with each other (Fig.5). Here α_0 is the equivalent ratio of the mixture

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

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

Effect of initial temperature: The $d_f(T_0)$ dependencies were determined for 50/50 mixtures of H_2SO_4 with NM (at $S=93.0\%$), TNT (at $S=103.0\%$), and TNB ($S=103.5\%$). As for number of other explosives, the straight lines $\log_{10} d_f = A + B/T_0$ were obtained. Constants A and B together with the data [5] for neat TNT and NM are represented in the Table 1.

Table 1. The constants A and B of the straight lines $\log_{10} d_f = A+B/T_0$.

Explosive	T_0 , K	A	B	d_f (353 K), mm (calculation)
TNT/oleum 50/50 (S=103.0%)	336-370	-2.176	1041	5.9
TNB/oleum 50/50 (S=103.5%)	358-383	-0.898	675	10.3
NM/H ₂ SO ₄ 50/50 (S=93.0%)	253-338	-1.194	585	2.9
TNT	357-513	-1.667	1231	66.1
NM	273-358	-0.866	581	6.0

4. DISCUSSION

The quantitative treatment of results in this paper is represented only for mixtures on base of NM and TNT, because the information on d_f dependencies for DNT and TNB mixtures is not sufficient for calculation. Dremine theory of detonation failure diameter [2-4] was used to treat the results. According to this theory based on conception of pulsating reaction zone we can calculate the adiabatic induction period τ_3 in this zone near the limit of detonation propagation at temperature of shock-compressed substance T_3 . The calculation procedure in all details is given in [6]. The same velocity of the reaction failure wave $v = 3.8$ mm/ μ s for all the mixtures of NM as well as for neat NM [7] was accepted. Similarly, the value $v = 2.76$ mm/ μ s, reported in [3] for liquid TNT, was used for all TNT mixtures. The generalized Hugoniot of liquids $D = C_0 + 0.29 + 1.63u$ [8] was used for oleum. The sound velocity C_0 was determined in paper [9]. The Hugoniot adiabat of the mixture was defined supposing the components specific volume additivity.

4.1. NM solutions.

The polytropic exponent of detonation products γ for the NM solutions is assumed to be the same function of initial density ρ_0 as for pure nitromethane [7]: $\gamma = (0.656/\rho_0) + 0.703 + 1.105\rho_0$ (ρ_0 in g/cm³). The shock temperature of the solutions was calculated by the method [8]. These data were used to calculate the temperature T_3 , and the corresponding ignition delays τ_3 along the solid curve on Fig.1.

The decomposition rate constant of pure nitromethane [5] is

$$k_1 = k_0 \exp(-E_1/RT), \quad (1)$$

where $k_0 = 8 \cdot 10^{14} \text{ s}^{-1}$, $E_1 = 210 \text{ kJ/mol}$. The activation energy is close to the values reported in [4], and obtained for thermal decomposition of NM at pressure of order of 10^4 - 10^5 Pa (see compilation [10]).

The decomposition rate on addition of sulfuric acid increases, obviously due to CH_3NO_2 - H_2SO_4 interaction. It is known [11], that this interaction gives $\text{CH}_3\text{NO}_2\text{H}^+$ ion, which is allowed to be named the nitromethonium ion by analogy with $\text{H}_2\text{O}-\text{H}^+$ hydroxonium ion. The possible complexes of this ion with sulfuric acid are the nitromethonium bisulfate $\text{CH}_3\text{NO}_2\text{H}^+ \cdot \text{HSO}_4^-$, and the nitromethonium sulfate $[\text{CH}_3\text{NO}_2\text{H}^+]_2 \cdot \text{SO}_4^{2-}$. Our analysis shows that the sulfate ion formation is more essential source of the detonation reaction acceleration. When sulfuric acid content in the mixture is large enough (more than 30-35%), one can suppose that this complex is formed quantitatively, and nitromethane in the shock wave reacts quickly with sulfuric acid according to reaction

The complex formed is decomposed. The decomposition rate constant supposedly is

$$k_2 = k_{02} \exp(-E_2/RT), \quad (3)$$

and $k_2(T_3) \gg k_1(T_3)$. Our estimation shows that $E_2 \cong E_1/2$. In this case to compute the constants ratio, one can use the expression

$$\tau_3 N / (\tau_3^0 N_0) = 2Y[1 - Y \ln(1 + 1/Y)], \quad Y = (k_1 N / k_2 a C_2) \quad (4)$$

being integral of the differential equation of adiabatic self-heating for two parallel reactions of the first order at the fixed (time-independent) reagents concentrations. In Eq.(4) N_0 and N are the initial and the current molar concentration of nitromethane, C is the molar concentration of the complex. For bisulfate $a = 1$, for sulfate $a = 2$. τ_3^0 is the hypothetical period of induction in the system, where the complex is not formed, nitromethane concentration remains equal to N_0 , and the heat release rate is not influenced by sulfuric acid:

$$\tau_3^0 = C_V \rho R T_3^2 / (N_0 Q_V E_1 k_{01}) \cdot \exp(E_1/RT_3) \quad (5)$$

Here Q_V is the heat of NM decomposition, C_V and ρ are the heat capacity and density of mixture. As the sulfuric acid is added to the system τ_3^0 increases rapidly. For example, $\tau_3^0/\tau_3 = 570$ when $C_S = 60\%$.

If the proposed model is true, the straight line must be obtained in $1/T_3 - \log_{10}(k_1/k_2)$ coordinates. The slope and intercept of this line give the difference of the activation energies $E_1 - E_2$, and the ratio of the pre-exponential factors k_{01}/k_{02} .

By assuming that nitromethonium sulfate is formed, the experimental results allow to obtain the constants k_{02} and E_2 directly: when $C_S > 44.5\%$ there is no free nitromethane in the system, and the self-heating equation reduces to the usual relation of the type (5) for $k(T) = k_2(T)$.

Fig.6. The k_1/k_2 ratio calculated by the formula (4) versus $1/T_3$ for mixtures NM/ H_2SO_4 : ● - on the basis of $d_f(C_S)$ for $S=100.5\%$, ○ - using $d_f(T_0)$ for $S=93\%$.

Fig.7. The ratio of the effective rate constant k_2^{eff} given by Eq.(4), to the decomposition rate constant of the nitromethonium sulfate k_2 as a function of the molar ratio of sulfuric acid to nitromethane.

The dependence of the $\log_{10}(k_1/k_2)$ versus $1/T_3$ calculated by the formula (4) (Fig.6) gives the line $\log_{10}(k_1/k_2) = 4.89 - 6970/T_3$ obtained in the range of $30\% \leq C_S \leq 64\%$, from which $E_2 - E_1 = 133$ kJ/mol, and $k_{01}/k_{02} = 7.7 \cdot 10^4$. This corresponds to $E_2 = 77$ kJ/mol for $E_1 = 210$ kJ/mol. In the range of $44\% \leq C_S \leq 64\%$, where under the assumption $K_C \rightarrow \infty$ all nitromethane is turned to the nitromethonium sulfate, the dependence $\log_{10} k_2(1/T_3)$ results in $E_2 = 79$ kJ/mol, and $k_{02} = 1.7 \cdot 10^{10} \text{ s}^{-1}$.

When sulfuric acid content is less than 30% the points (Fig.6) tend to fall down, tracing out a loop with a minimum at $C_S = 6-8\%$, then tend to line again. The initial part of the dependence is demonstrated in Fig.7, where the relation of the effective rate constant k_2^{eff} to the value of k_2 , which is approximately constant in the concentration range considered, is plotted as a function of the molar ratio of sulfuric acid to nitromethane. Obviously, it does mean that the third group of reactions at low H_2SO_4 content takes place, probably connected with the aci-ion [12] formation under the acid influence. As sulfuric acid content increases, the conversion velocity of NM to aci-ion rises, but in the strong acid medium at high concentration of H_2SO_4 , aci-form does not exist. So, for the large enough concentration of the acid the reaction reduces to the formation and decomposition of the nitromethonium sulfate, the overall decomposition rate decreases, k_2^{eff}/k_2 ratio tends to 1.

Dependence $d_f(T_0)$ measured for the mixture 50/50 of nitromethane and sulfuric acid ($S=93\%$) was also processed in framework of Drenin theory. To do this it is required to know the experimental values of detonation velocity if only at any one value of initial temperature. The effect of T_0 on D was found using the coefficient of heat expansion. T_0 on T_3 influence was determined by the method proposed in [8].

The results of the calculations (for $D_{298} = 5.75$ mm/ μs) are shown in Fig.6 (open circles). The dependence $d_f(T_0)$ gives practically the same values of k_2 , as the dependence $d_f(C_S)$. The variation of the initial temperature is no effect on the main result: the interaction of nitromethane with sulfuric acid leads, with the qualitative yield, to the formation of nitromethonium sulfate, the decomposition rate of which under the conditions considered is two orders of magnitude greater than that of nitromethane.

4.2. TNT solutions

The values of τ_3 and T_3 calculated for mixture (50/50) TNT/ H_2SO_4 ($S=103.0\%$) at different initial temperature are placed on the line:

$$\log_{10}(\tau_3/T_3^2) = -a + b/T_3 \quad (6)$$

The values of a and b depend on equations of state of original components and explosion products, mainly, on polytropic exponent of detonation products γ . For mixtures of TNT and sulfuric acid this value is not determined as yet. Changing γ in the range of 2.8-3.2, one can get the a and b constants to be equal to 18 ± 1 and $(15.7 \pm 0.5) \cdot 10^3$, respectively. The activation energy of the reaction is changed correspondingly in the range of 100-120 kJ/mol. The activation energy of TNT detonation reaction calculated in [4], is equal to 109 kJ/mol, i.e. it corresponds to the middle of the interval obtained here. To simplify further calculations, the suggestion is proposed that the activation energies of the reactions determining d_f of the H_2SO_4 solutions, are equal to each other and close to the value of 109 kJ/mol.

The sequence of kinetic equations of the main reactions taken place at detonation of TNT/ $\text{H}_2\text{SO}_4/\text{SO}_3$ mixtures is

$$W_1 = k_1[\text{TNT}], \quad (7)$$

TNT decomposition, where $[\text{TNT}]$ is TNT molar concentration.

$$W_2 = k_2[\text{TNT} \cdot n\text{H}_2\text{SO}_4], \quad (8)$$

decomposition of TNT and sulfuric acid complex. The possibility of the formation of such complex follows from the data on solubility of TNT in sulfuric acid [13]. It is quite possible, that, as well as in the case of NM, this complex included the ionized TNT molecule. The relative number of H_2SO_4 molecules in the complex n has to be determined from the best correlation of the calculation results with the experimental data.

The considerable influence of "free" SO_3 shows, that a reaction with sulfuric anhydride is also essential. One can suppose, that this reaction proceeds between the complex and SO_3

One can suggest also, that the intermediate stage of transition of the reagents, entering into reaction (9), to its products is the formation of a complex with pyrosulfuric acid ($\text{H}_2\text{S}_2\text{O}_7$):

where $k_4 \gg k_3[\text{SO}_3]$.

Taking into account the reactions (7-9), the value of k_0 in the equation for the quasi first order reaction rate ($W = k_0[\text{TNT}]_0 \cdot \exp(-E_a/RT)$) can be represented in the form of

$$k_0 = \frac{k_{01}[\text{TNT}] + k_{02}[\text{TNT} \cdot n\text{H}_2\text{SO}_4] + k_{03}[\text{TNT} \cdot n\text{H}_2\text{SO}_4] \cdot [\text{SO}_3]}{[\text{TNT}]_0} \quad (10)$$

The values of the pre-exponential factors k_{01} , k_{02} , and k_{03} for the reactions (7), (8), and (9), as well as the coefficient n have to be defined from the experimental data.

The calculations were carried out at $E_a = 109 \text{ kJ/mol}$, $\gamma = 2.027 + 0.7429\rho_0$ (taken from [5]). Using the obtained ignition delay τ_3 , the value of k_0 was calculated as

$$k_0 = C_V \rho R T_3^2 / (Q_V M_{\text{TNT}} [\text{TNT}]_0 E_a \tau_3) \cdot \exp(E_a/RT_3) \quad (11)$$

where C_V is the heat capacity of the mixture, Q_V is the heat of TNT decomposition. The concentrations (mol/m^3) are defined by the relations:

$$\begin{aligned} [\text{TNT}]_0 &= (1 - C_S/100) \cdot \rho / M_{\text{TNT}}; \\ [\text{SO}_3] &= S_{\text{SO}_3} / 100 \cdot C_S / 100 \cdot \rho / M_{\text{SO}_3}; \\ [\text{H}_2\text{SO}_4] &= (1 - S_{\text{SO}_3}/100) \cdot C_S / 100 \cdot \rho / M_S; \\ S_{\text{SO}_3} &= M_{\text{SO}_3} / M_{\text{H}_2\text{O}} \cdot (S - 100), \end{aligned}$$

where M_{SO_3} , $M_{\text{H}_2\text{O}}$, M_{TNT} , and M_S are molecular weights of SO_3 , water, TNT, and sulfuric acid, correspondingly; ρ is the mixture density; S_{SO_3} is the mass concentration of "free" SO_3 in oleum. The pre-exponential factor k_{01} corresponds to the decomposition of TNT, remained after interaction with sulfuric acid:

$$[\text{TNT}] = [\text{TNT}]_0 - [\text{TNT} \cdot n\text{H}_2\text{SO}_4]$$

The value of k_{02} is responsible for $\text{TNT} \cdot n\text{H}_2\text{SO}_4$ complex decomposition rate, where n molecules of sulfuric acid are needed for one TNT molecule. At TNT surplus the concentration is defined by equality $[\text{TNT} \cdot n\text{H}_2\text{SO}_4] = [\text{TNT}]_0/n$, at sulfuric acid surplus it is found as $[\text{TNT} \cdot n\text{H}_2\text{SO}_4] = [\text{TNT}]_0$ (we suppose that the equilibrium is entirely moved to the complex formation). The value of k_{03} is connected with formation and decomposition under the action of sulfuric anhydride of still more reactive TNT form. The point

$[\text{TNT}]_0 = [\text{H}_2\text{SO}_4]/n$ corresponds to the transition from quadratic to linear plot. It allows us to determine the n value. It proved to be equal 2. The values of k_{01} , k_{02} and k_{03} obtained by optimization, are equal to $1.42 \cdot 10^{10} \text{ s}^{-1}$, $2.2 \cdot 10^{11} \text{ s}^{-1}$, and $1.2 \cdot 10^{11} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, respectively. The values of k_0 calculated using these constants are represented by curves in Fig. 8.

Fig.8. Influence of sulfuric acid ($X = [\text{H}_2\text{SO}_4] - [\text{SO}_3]$, mol/l) on decomposition rate of mixtures of TNT and oleum. The points represent the values of k_0 calculated on the basis of Dremin theory and the measurements of d_f ; the curves are obtained using the kinetic scheme suggested at $E_a = 109 \text{ kJ/mol}$, $k_{01} = 1.42 \cdot 10^{10} \text{ s}^{-1}$, $k_{02} = 2.20 \cdot 10^{11} \text{ s}^{-1}$, $k_{03} = 1.20 \cdot 10^{11} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$. Oleum concentration (S , %): a - 100.6, b - 101.7, c - 103.8, d - 108.2.

In Fig. 4 the points are experimental data, the curves a-d are the results of the calculations carried out using the Eqs. (7-11). Having in mind the model used, they are extended to the region of low acid content. The dashed curve represents the results for mixtures of NM and sulfuric acid ($S = 100.5\%$). It is the same curve as the solid line on Fig. 1. One can see, that the detonation failure diameter of TNT-based mixtures decreases less abruptly, than for the NM solutions, when acid is added to the system. It can be explained by the ability of nitromethane to form the aci-ion, which being quickly decomposed makes a supplementary contribution to the heat release rate.

5. CONCLUSIONS

The results obtained on detonation failure diameter prove a formation in the $\text{NM}/\text{H}_2\text{SO}_4$ and TNT/oleum mixtures of the complexes of the nitrocompounds with sulfuric acid having the composition of $[(\text{CH}_3\text{NO}_2)_2 \cdot \text{H}_2\text{SO}_4]$ and $[\text{TNT} \cdot 2\text{H}_2\text{SO}_4]$. The decomposition rate of the nitromethonium sulfate is two orders of magnitude greater than that of nitromethane under the conditions considered ($P \sim 10 \text{ GPa}$, $T \sim 1000 \text{ K}$). The TNT complex decomposes 15 times faster than the pure TNT. It is said about considerable change of TNT molecule in this complex, may be associated with ionization. This complex reacts with SO_3 in oleum. The reaction rate at the maximum concentration of SO_3 ($C_s = 64\%$, $S = 108.2\%$) is 4 times higher, than the decomposition rate of the complex, and, hence, 60 times higher, than the decomposition rate of TNT itself.

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