



The Molecular Modeling of Detonating and Explosive Processes Based on the Activated Complex Theory

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Author's contribution

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Research Article

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ABSTRACT

The present paper offers a molecular model of explosive and detonating processes based on the activated complex theory (a transition state theory). It is demonstrated that bond breaking within a molecule of an explosive occurs not simultaneously but successively with the formation of various intermediate complexes. Formal decay schemes of a classical 2, 4, 6-trinitrotoluol explosive are presented, detonation speeds at different temperatures at the detonation wave front are calculated. It is shown that the main factor which influences the speed of a detonating process is the temperature at the detonation wave front. The design 2, 4, 6-trinitrotoluol detonation speed falls within the range of 7 000 – 8 000 m/s that conforms to the experimental value. It is shown that at the temperatures of 4000 – 4500K qualitative and quantitative changes in the detonation mechanism take place. At the detonation wave front it is necessary to mark out limiting stages of the process, i.e. the time of particle (atoms) motion before the activated complex formation and the bond breaking time. The solution of the differential equations system of the kinetics process makes it possible to forecast a quantitative and qualitative composition of explosion products.

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1. INTRODUCTION

One of the important tasks for increasing explosion technology safety is the reduction in toxic and harmful substances that escape into the natural environment and the calculation of explosion parameters, i.e. speed, pressure at the detonation wave front. Thus, the regulation of the oxygen balance of explosives (EXP) allows reducing the negative impact of harmful substances on the biosphere, but the problem of explosive technologies safety is still urgent.

This paper considers the detonation model based on the activated complex theory (a transition state theory). Some theoretical aspects of detonation have been examined quite profoundly [1-5], but methodologically the modeling of explosive processes based on the transition state theory has not been not studied.

2. MAIN BODY

Modeling a substance decay process in the form of the detonation wave front propagation over a substance with a particular interface temperature, it is possible to calculate the speed constant of the process with the help of the transition state theory. [5,6]. The calculation is performed on the assumption that the entropy S^* and the enthalpy H^* of the transition complex formation are known:

$$= \kappa \frac{kT}{h} \cdot e^{\frac{\Delta S^*}{R}} \cdot e^{\frac{-\Delta H^*}{RT}} . \quad (1)$$

Here κ is the reaction constant, s^{-1} ; τ is the transmission coefficient equaling 0... 1; k is the Boltzmann constant equaling to $1, 38 \cdot 10^{-21}$ J/Deg; T is the temperature, ; h is the Planck constant equaling to $6,626 \cdot 10^{-34}$ J/s.

In the calculations assumed that the value of the transmission coefficient is unity. It should be noted that an explosion, a detonation can be also modeled for chemical reactions which develop in small local amounts that are called "hot points".

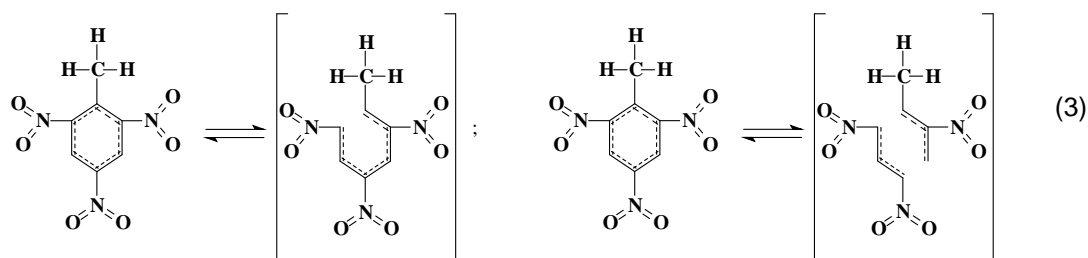
The main problem of the transition state theory is the definition of the structure of the transition complex which leads to the formation of reaction products while disintegrating. The problem specified is solved by calculating the molecule life span at the detonation wave front.

Marking out a fragment of the detonation wave or a "hot point" with the linear dimensions (cube edge), we get the speed of detonation wave propagation over the substance:

$$v = \frac{1}{10 \ddagger \sqrt[3]{d \frac{N_A}{M}}} \quad \ddagger = \frac{1}{N_0} \int_0^\infty t dN; \quad dN = N dt; \quad dN = N_0 e^{-t}; \quad \ddagger = \frac{1}{N_0} \int_0^\infty t N_0 e^{-t} dt = 1. \quad (2)$$

Here v is detonation wave speed, m/s; N_0 is general number of molecules; t is molecule life span, current time, s; d is density of matter, kg/m³; M is molar mass, g/mole; N_A is the Avogadro number, $6,022 \cdot 10^{23}$ mole⁻¹.

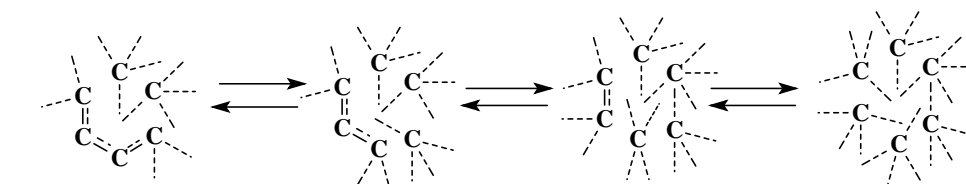
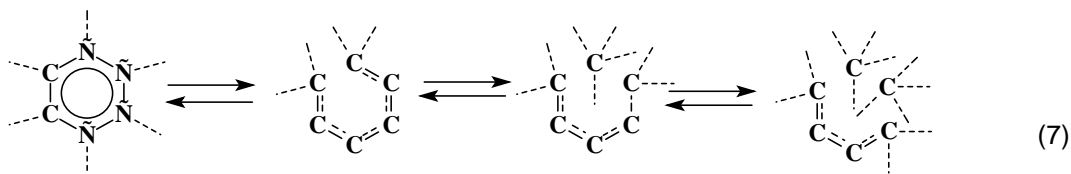
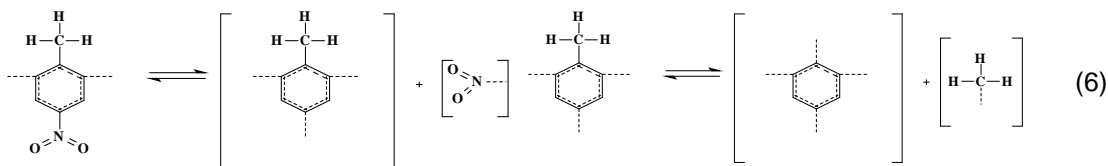
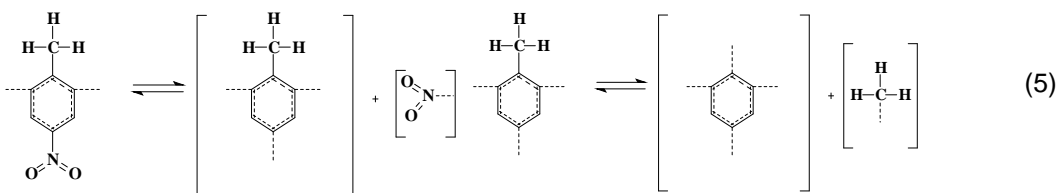
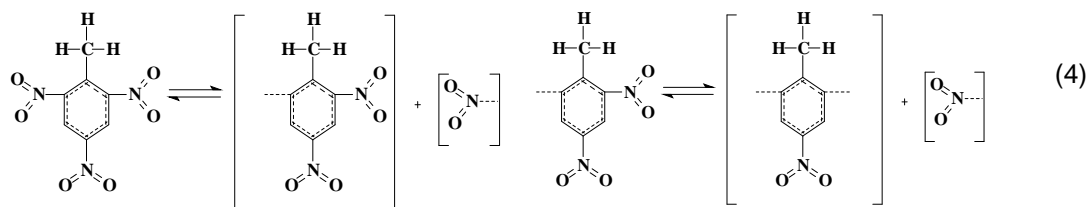
Examining the structures of the transition complexes, we can draw a conclusion that for a molecule of 2,4,6-trinitrotoluol (TNT) the formation of reaction products by detonation occurs by means of successive chemical bond opening, not simultaneously. We shall illustrate the point by calculating the speed constant of aromatic bond opening in benzene ring of TNT molecule using Chart 1. The data on entropies and opening energies have been taken from the literary sources [7]. We shall compose the formal opening schemes of one and two bonds:



Let us define (equation 1) that the speed constant of one aromatic TNT molecule bond opening is equal to $8,427 \cdot 10^{13}$ s⁻¹ (the process time is $1,187 \cdot 10^{-14}$ s). If we assume that the simultaneous opening of two aromatic bonds takes place, the calculated value of the speed constant equals to $1,70 \cdot 10^9$ s⁻¹ (the process time is $5,88 \cdot 10^{-10}$ s). Comparing the calculations, we can point out that simultaneous opening of two bonds is hardly probable – the two bonds opening speed constant is five times less than the one bond opening speed constant. Therefore the bond opening in molecules undergoes a number of successive stages followed by the formation of the transition complexes of various structures.

Thus, the TNT molecule decay can be presented as the reactions shown in the schemes (4-7). At the beginning the fastest processes take place: the detachment from the benzene ring of nitro groups, methyl group – speed constants are correspondingly equal to $5,697 \cdot 10^{16}$; $1,278 \cdot 10^{16}$ s⁻¹. It is followed by a successive detachment of two protons $5,697 \cdot 10^{16}$ (the speed constant is $9,626 \cdot 10^{15}$ s⁻¹) and the bond breaking of the benzene ring (the speed constant is $8,427 \cdot 10^{13}$ s⁻¹). Simultaneously methyl and nitro groups bonds break.

The formal schemes of the TNT decay are presented by the following equations:



Let us estimate the TNT molecule life span, considering the slowest processes:

$$\tau = 6.1,187 \cdot 10^{-14} + 2.2,062 \cdot 10^{-15} + 3.1,755 \cdot 10^{-17} + 7,825 \cdot 10^{-17} = 7,458 \cdot 10^{-14} \text{ ns}$$

Let us calculate the speed of the TNT detonation wave propagation (equation 2) at the temperature of 4000 (the density is 1604 kg/m³) – 8178 m/s.

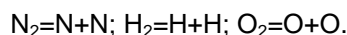
2, 4, 6-Trinitrotoluol Detonation Parameters

Parameter name	Energy and kinetics characteristics of TNT molecule decay				
	Bond breaking energy, kJ/mole	Bond breaking entropy, J/mole Deg	Estimated time of bond breaking, molecule (s) at the temperature , ; detonation speed, m/s		
			3500	4000	4500
Bond= = , benzene	487,4	44,9	$9,63 \cdot 10^{-14}$	$1,19 \cdot 10^{-14}$	$2,33 \cdot 10^{-15}$
Bond N=O	435,0	43,4	$1,91 \cdot 10^{-14}$	$2,94 \cdot 10^{-15}$	$6,85 \cdot 10^{-16}$
Bond Ar-H	421,6	43,0	$1,26 \cdot 10^{-14}$	$2,06 \cdot 10^{-15}$	$5,05 \cdot 10^{-16}$
Bond - , methyl	413,2	46,6	$6,13 \cdot 10^{-15}$	$1,04 \cdot 10^{-15}$	$2,61 \cdot 10^{-16}$
Bond Ar-CH ₃	332,0	47,8	$2,71 \cdot 10^{-14}$	$7,83 \cdot 10^{-17}$	$2,58 \cdot 10^{-17}$
Bond C-N	275,9	46,2	$5,75 \cdot 10^{-17}$	$1,76 \cdot 10^{-17}$	$6,99 \cdot 10^{-18}$
Molecule life span			$6,17 \cdot 10^{-13}$	$7,46 \cdot 10^{-14}$	$1,50 \cdot 10^{-14}$
Detonation speed			1000	8178	8374

At sufficiently high temperatures at the detonation wave front it is necessary to single out the limiting stages of the process – particle (atoms) motion time up to the formation of the activated complex, and bond breaking time. Without taking the molecule decay limiting stages into consideration the calculation gives over-estimates of the TNT detonation speed at the detonation wave front temperature of 4500 and higher (41 109 m/s). Considering the time of the particle motion up to the formation of the activated complex, we can estimate the TNT detonation wave speed at 4500 as 8374 m/s, Chart 1. Thus, at the temperatures of 4000 – 4500 some qualitative and quantitative changes of the detonation mechanism take place. In the area of lower temperatures (less than 4000) the limiting stage of the process is the explosive molecule bond breaking time. In the area of higher temperatures (4500 and higher) the slowest stage is the atom motion time up to the formation of the activated complex.

The model presented has some considerable advantages over other models. The modeling allows setting up a correspondence between the explosive molecular structure, the process performance conditions, the detonation wave propagation speed and the explosive products composition. Thus, according to the transition state theory the life span of oxygen, nitrogen and hydrogen bonds breaking and the formation at the detonation wave front at 4000 degrees makes up $10^{-20} \dots 10^{-26}$ s. The specified values of the lifetime of the chemical bonds do not have physical meaning, because it needs the accounting values of transmission coefficient ($\ll 1$).

The formal schemes of bond decay processes can be presented as follows:

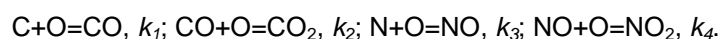


Analyzing the formal schemes of the bond formation and the activated complex structure it should be noted that, as opposed to explosives decay, the slowest – limiting – stage of carbon oxide, nitrogen formation is not the bond formation time, but the time of the atom length up to the mutual collision of atoms (the ratio of the atom length to the motion speed):

$$\ddagger = \frac{M^{5/6}}{10 \cdot N_A^{5/6} \cdot \sqrt[3]{d \cdot N_A} \cdot \sqrt{3 \cdot k \cdot T}}$$

At the average free length of $(3-5) \cdot 10^{-10}$ m, and the atom motion speed of approximately 9000 m/s, the detonation products formation constant can be estimated within the range from $1,8 \cdot 10^{13}$ to $3 \cdot 10^{13} \text{ s}^{-1}$.

The speed constant of the reaction with protons is much higher because protons have a greater mobility; therefore the formal schemes, the kinetics of reaction products accumulation and consumption can be presented as follows:



$$\left. \begin{aligned} \frac{dx}{dt} &= k_1(7-x)(3,5-x-y-z-f), \\ \frac{dy}{dt} &= k_2(x-y)(3,5-x-y-z-f), \\ \frac{dz}{dt} &= k_3(3,5-z)(3,5-x-y-z-f), \\ \frac{df}{dt} &= k_4(z-f)(3,5-x-y-z-f) \end{aligned} \right\}$$

Here x, y, z, f are correspondingly the quantity of moles $\text{CO}, \text{CO}_2, \text{NO}, \text{NO}_2$ which had been formed by the instant of time t ; 7 is the quantity of carbon atoms in the TNT molecule; 3, 5 is the quantity of oxygen atoms which remain in the system after all protons entered into interaction with water formation, k_1, k_2, k_3, k_4 are speed constants of corresponding reactions, s^{-1} .

Taking into consideration that the motion speed of NO is 1.3 times less than the motion speeds of atoms C, N, O, the following correlations have been received:

$$k_1 \approx k_3 \approx 2,67 \cdot 10^{13} \text{ s}^{-1}; \quad k_2 \approx k_4 \approx 2,05 \cdot 10^{13} \text{ s}^{-1}.$$

The differential equation system is solved rather simply by means of numerical methods, Fig. 1, 2. Carbon and nitrogen oxides are accumulated at the detonation wave front. The delay in the nitrogen oxides accumulation curve is presumably caused by the correlation between the nitrogen oxide consumption and the accumulation speed constants (II).

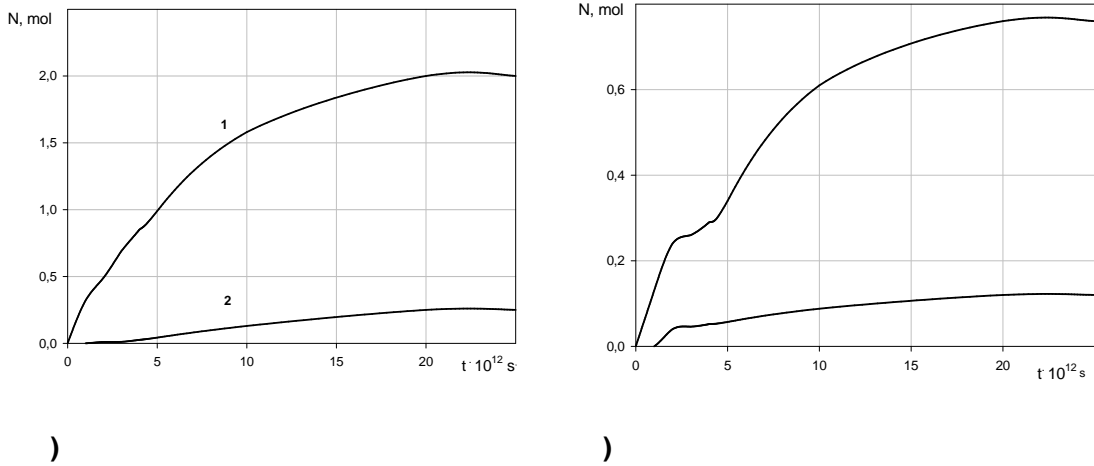


Fig. 1.): 1, 2 are the carbon oxide accumulation kinetics (II) (), carbon oxide (IV) () correspondingly under TNT decay;): 1, 2 are the nitrogen oxide accumulation kinetics (II) (NO), nitrogen oxide (IV) (NO₂) correspondingly under TNT decay

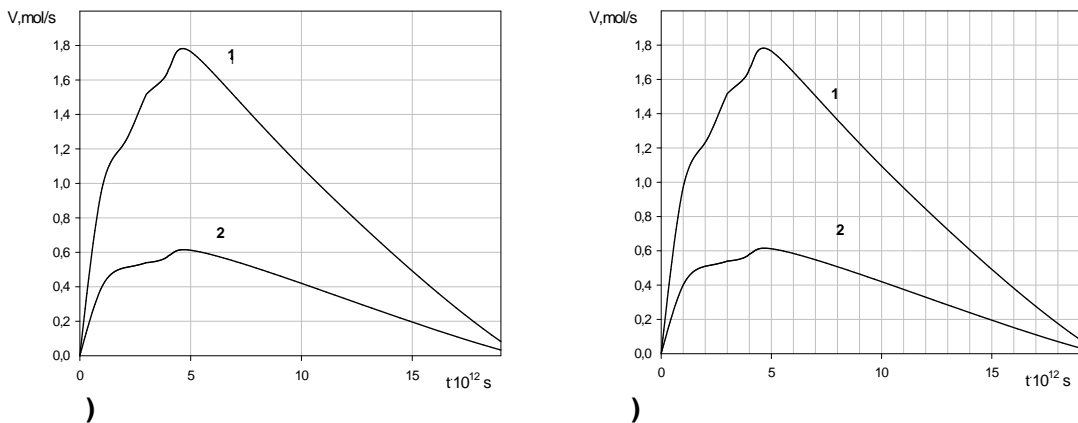
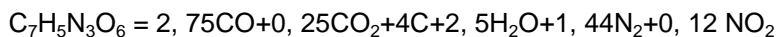


Fig. 2.): 1, 2 are the nitrogen oxide formation speed (II) (NO), nitrogen oxide (IV) (NO₂) correspondingly under TNT decay;): 1, 2 are the carbon oxide formation speed (II) (), carbon oxide (IV) (O₂) correspondingly under TNT decay

The formation speed of the nitrogen oxides intermediate products goes through the maximum; it is determined by the correlation of the nitrogen and oxygen atoms in the molecule. The TNT oxygen deficiency (-74%) contributes to the decay of nitrogen oxide NO (the heats of nitrogen oxides NO, NO₂ formation are equal to +89,924; +33,873 kJ/mole correspondingly) with the additional formation of 0, 75 mole carbon oxide (II).

In spite of the fact that, based on the TNT explosion conditions, several hundreds of substances come out, the main stages of the process can be presented by the following formal scheme:



The calculation of the specified process enthalpy, made according to the energies of the chemical bonds breaking, corresponds to the explosion energy equaling to 961,55 kJ/mole (4,285 MJ/kg); it closely matches the experimental values of 4,1-4,3 MJ/kg [5].

3. CONCLUSIONS

1. The modeling of detonation processes according to the activated complex theory (a transition state theory) defines some routes of the process: the bond breaking in the TNT molecule occurs not simultaneously but consequently with the formation of the intermediate complexes of different structures.
2. The main factor influencing the detonation process speed is the temperature at the detonation wave front. As a rule, the temperature at the detonation wave front does not exceed 3800 – 4000 K, that is why the estimated substance detonation speed lies within the range of 7 000 – 8 000 m/s, which corresponds to the experimental values.
3. At the temperatures of 4000 – 4500 K at the detonation wave front some qualitative and quantitative changes in the detonation mechanism take place. At the temperatures less than 4000 K the limiting stage of the process is the molecule bond breaking time of the explosive. Within the range of 4500 K and higher temperatures the slowest stage is the atom motion time of the explosive up to the activated complex formation.
4. The calculation of the speed constants of various routes is the ground for defining the qualitative and quantitative composition of explosion products. The speed of nitrogen oxide formation increases goes through the maximum and drops to zero. The speed of the carbon oxide formation decreases during the decay process.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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