

The Research of Detonation Nanodiamond Structure by Optical Methods

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Introduction

The investigation of the detonation ultradispersed diamond formation or detonation nanodiamond is connected with considerable difficulties because of non-equilibrium, high chemical activity, and the short periods of time.

The ultradispersed diamond of detonation synthesis (UDD) [1,2] is formed in the non-equilibrium reaction zone of detonation wave. The main evidence of this fact is connected with the following results: the reiteration of the UDD distribution curves for the charges of different shapes and sizes [3].

The UDD structure consists of the diamond grains of 2-12nm (parameter of crystal lattice is 0.3562 ± 0.0004 nm, according to other sources the parameter is 0.3572-3nm). From the point of view of crystallography it is a diamond system with large quantity of stable impurities. From the standpoint of chemistry the principle feature of UDD is its structural non-homogeneity. Several scientific groups [4,5,6,7,8] were made this conclusion. Ref. [4] introduced the idea of "primary explosive cluster" 20 – 60nm, work [5] studied oxidation of the "composite UDD material", the structure of the "diamond-like carbon phase" was examined in [6] and in [7] the "supermolecular UDD system" was researched. Mention should be made of [8,19], where the authors tried to support this assumption. Evidently, all this UDD structural non-homogeneity is feature of the non-equilibrium processes in the reaction zone.

The functional groups and heteroatoms of the UDD produced this structural non-homogeneity [5,6,7,8]. By studying the properties and structures of these functional groups it is possible to try to understand the non-equilibrium physical and chemical processes of the detonation wave.

The kinetic aspects of the UDD formation

The UDD technological synthesis needs the application of two different high explosives (HE). One is an aromatic explosive and the other is an explosive based on the nitrogen heteroatoms. Usually a mixture of trinitrotoluene (TNT) and hexogen (RDX) is used (Table 1).

Table 1. The UDD and condensed carbon (CC) output for the TNT/RDX mixture [10].

| mass ratio of TNT/RDX | Charge mass, g | Density of charge, g/cm ³ | CC/HE mass % | UDD/ HE mass % |
|-----------------------|----------------|--------------------------------------|--------------|----------------|
| 80/20 | 300 | - | 20 | 2.12 |
| 70/30 | 300 | 1.562 | 18.3 | 3.53 |
| 60/40 | 300 | 1.580 | 16.6 | 4.40 |
| 50/50 | 300 | 1.587 | 16.0 | 2.28 |
| 40/60 | 300 | 1.605 | 15.0 | 5.99 |
| 30/70 | 300 | 1.601 | 15.6 | 3.56 |

The problem of the UDD preservation was solved in [1,11]. It allowed applying the method of isotope atoms for investigation of the UDD synthesis. The experiments with isotope atom ¹³C application (Fig.1) showed high content of the carbon atom of the TNT methyl group in the UDD [3,12,13,14] (Table 2).

Table 2. The result of some isotope atoms experiments [3, 12-14]. The isotope mark is the carbon of the TNT methyl group.

| Parameters | TNT/RDX 40/60 | TNT/HMX 40/60 |
|---|---------------|---------------|
| Original charge | | |
| Charge mass, g | 35 | 31.14 |
| The isotope ration of ¹³ C / ¹² C in the original charge, % | | |
| TNT | 9.3 | 9.23 ± 0.1 |
| HE | 6.0 | 5.03 ± 0,1 |
| The isotope ration in the detonation product % | | |
| UDD | 6.8 | 8.05 ± 0.13 |
| Condensed carbon (CC) | 5.9 | 5.94 ± 0.17 |
| CO | 4.2 | 4.94 |
| Non-diamond carbon | 4.1 | 4.2 ± 0.3 |
| CO ₂ | 4.6 | 3.78 |
| CH ₄ | 3.9 | - |
| C ₂ H ₄ | 6.8 | - |
| UDD mass/CC mass, % | - | 45 ± 2 |

To explain the results of the experiment the following samples (Table 3) were analyzed.

Table 3. Comparison of methyl group concentration for the UDD samples (20).

| Mixture of HE, mass ratio | Indication of samples | Output | | $(D_1 - D_0)/m$ 1/mg |
|---------------------------------|-----------------------|----------|-----------|-------------------------|
| | | CC/HE, % | UDD/HE, % | |
| 1. Trinitrobenzol - RDX 40/60 | TNB/RDX -40 | 7.77 | 4.66 | 0.0197 |
| 2. Trinitrobenzol - RDX - 50/50 | TNB/RDX -50 | 6.64 | 3.82 | 0.0164 |
| 3. Trinitrobenzol - RDX 60/40 | TNB/RDX -60 | 8.45 | 5.48 | 0.0200 |
| 4. Picric acid - RDX 60/40 | Pa/RDX-60 | 5.17 | 2.6 | 0.0215 |
| 5. Picric acid - RDX 40/60 | Pa/RDX-40 | 4.89 | 3.0 | 0.0199 |
| 6. Trinitroresorcin - RDX 70/30 | TNR/RDX -70 | 5.37 | 2.4 | 0.0194 |
| 7. Trinitroresorcin - RDX 20/80 | TNR/RDX -20 | 1.91 | 1.1 | 0.0175 |
| 8. Trinitrotoluene - RDX 40/60 | TNT/RDX -40 | 15.0 | 5.99 | 0.0251 |
| 9. Trinitrotoluene - RDX 60/40 | TNT/RDX -60 | 16.6 | 4.4 | 0.0343 |
| 10. Trinitrotoluene - RDX 60/40 | TNT/RDX -60 | 16.6 | 4.4 | 0.0259 |

The conditions for the samples synthesis were as follows: the chamber was 0.175cm^3 , the medium was molecular nitrogen under pressure of 0.7MPa ., the charge mass was 100g , initiation by ED-8 and 5g RDX. The refinement was made by boiling of chloric and sulphuric acid treatment. TNT/RDX-40 sample synthesis was performed in CO_2 atmosphere, and the refinement was performed by oxidation with boron anhydride presence. Sample 10 was refined by the air oxidation. CC is mass of the condensed carbon, UDD is mass of the UDD, HE is mass of high explosive. The UDD and CC output is according to [10]

The right most column of the table indicates value that is proportional to concentration of methyl groups in the sample. Optical density D_1 was determined in spectral area $2920\text{-}2975\text{cm}^{-1}$ (the maximum of the asymmetric C-H vibration of the methyl group). There were no absorption bands almost for all samples in spectral area $2400\text{--}2450\text{cm}^{-1}$ therefore optical density D_0 was determined in this part of the spectrum, m is the UDD mass in the pellet (Table 3). The estimation of the absolute value of the methyl groups concentration is not important in this case.

If the data of the TNT/RDX system were removed from the Table then the behavior characterizing the UDD output would be evident.

It is well known that any appearance of a methyl radicals source (paraffin, explosive mixtures with alkane participation [24], a preservation atmosphere with alkanes [23]) in the system increases the condensed carbon output. These results allow to discuss that an important condition for the UDD preservation in the chemical aggressive medium is the formation of methyl functional groups. Possibly, the chemically and physically inert methyl groups slow down the oxidation of the forming UDD-grain. This assumption is in accordance with the results [12,14] about UDD synthesis and with [4,5,6,7,15] about UDD structure.

The method of isotope atoms showed (Fig.2) [9,16,17] that RDX carbon took disproportionate part in the formation of the UDD. For TNT/RDX 40/60, the mass of RDX carbon was 39.7% of the mass of all carbon atoms in the explosive and only 14% of the UDD mass was formed from this carbon [9,16,17]. The attempts to change TNT/RDX system to one-component thermodynamic analogue were not successful (the UDD output decreased) [21,22]. It meant that the hexogen (RDX) was necessary for the UDD formation but their participation was not connected with carbon. It is necessary to discuss hexogen (RDX) influence to the UDD formation.

Fig.3 showed UV-spectra of UDD-samples synthesized from explosives with different content of hexogen (RDX). For samples with low content of hexogen (RDX) in the original explosive, there was no specific absorption connected with A-defect (and the UDD output dropped). The original explosive had rather much nitrogen, for example it was almost every third atom in hexogen (RDX).

The chemical processes in the reaction zone and the UDD-grain formation had to be connected with each other. Otherwise a part of the nitrogen atoms had to occur in the diamond lattice as a result of random processes and most likely, it had to be single nitrogen atoms or C-defects. The defects of this type were not found in the UDD [6,19]. Consequently, the A-defect formation contains some information about processes influencing on the UDD formation.

One of the main gaseous detonation products is molecular nitrogen, to a lesser extent the nitrogen oxides and ammonia are formed [18]. The formation of molecular nitrogen results in considerable heat absorption (945kJ/mol). Analyzing the data and the results of the experimental work [5,16,17], it is possible to assume that the formation of molecular nitrogen and A-defect should be connected with each other. It is quite possible that under the non-equilibrium conditions there appear some "cold" centers for the "adherence" of various radicals forming the UDD functional cover. The methyl groups and may be some other functional groups hinder oxidation and increase the probability UDD-system survival under these chemical aggressive conditions.

Conclusion

It is possible to add that the impurity system of the modern experimental science is as usual as autumn rains or tiredness after long way. Tell to truth, they are impurities only from the standpoint of the equilibrium thermodynamic approach. They are not comfortable for investigation but they are reality of the real physical processes. This work (as a part of publications [19,20]) is trying to support this idea and it examines the UDD like "a photo" of the non-equilibrium detonation processes.

Thus, a great amount of the experimental works on the UDD synthesis revealed that the structure of the original HE systematically influenced on the UDD and condensed carbon (CC) output. In this work the structural influence was divided into several parts. The first feature was the methyl group formation it was tendency of substance condensation. The oxidation weakened this tendency while the molecular nitrogen formation increased it. As a whole, this problem has a lot of peculiarities. The second feature was connected with the aromatic HE. From the standpoint of the UDD synthesis, aromatic HEs were the main source of the UDD carbon and consequently a main source of chemically active carbon in the reaction zone of the detonation wave.

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Reference

- [1] Lyamkin AI, Petrov EA, Ershov AP, Sakovich GV, Staver AM, Titov VM. Production of Diamonds from Explosive Substances. *Doklady Acad. Nauk SSSR* 1988;302(3):611-613.
- [2] Greiner RN, Phillips DS, Johnson JD, Volk F. Diamonds in Detonation Soot. *Nature* 1988;333:440-442.
- [3] Titov VM, Anisichkin VF, Mal'kov IYu. The study of synthesis process of ultradispersed diamond in detonation waves. *Combustion, Explosion and Shock Waves*. (Fizika Gorenia i Vzryva). Translation by Kluwer Academic/ Plenum Publishers. 1989;25(3):65-67.
- [4] Sakovich GV, Gubarevich VD, Badaev FZ, Brylyakov PM, Besedina OA. Aggregation of diamonds obtained from explosives. *Doklady Acad. Nauk SSSR* 1990;310(2):402-404.
- [5] Gubarevich TM, Kulagina LS, Larionova IS, in: Proc. 5-th All-Union Detonation Meeting, Krasnoyarsk, (1991), 130-134 (in Russian).
- [6] Vereschagin AL, Sakovich GV, Komarov VF, Petrov EA. Properties of ultrafine diamond clusters from detonation synthesis. *Diamond and Related Materials*. 1993;2(3):160-162.
- [7] Chiganova GA, Chiganov AS. *Inorg. Mat.* 1999;35(5):580-583 (in Russian).
- [8] Mironov E, Koretz A, Petrov E. Detonation synthesis ultradispersed diamond structural properties investigation by infrared absorption, in: Proc. 12-th Europ. Conf. "Diamond, Diamond-like materials, carbon nanotubes, nitrides&Silicon carbide". *Diamond and Related Materials*. 2002;11(3-6):872-876.
- [9] Sakovich GV, Petrov EA, Komarov VF, Kozyrev NV, in: Proc. of the NATO Advanced Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Moscow, May 1994, Kluwer Academic, 1997, Series 1, v.14, 55—72.
- [10] Petrov EA. Dissertation. Biysk, 1987, p.160 (in Russian).
- [11] Petrov EA, Sakovich GV, Brylyakov PM. Condition of diamond preservation in detonation synthesis. *Doklady Acad. Nauk SSSR* 1990;313(4):862-864.
- [12] Anisichkin VF, Gilev SD, Ershov AP, Medvedev DA, Satonkina NP, Trubachev AM. Reaction zones in detonations of dense explosives, in: Proc. 12-th Int. Detonation Symp., Wyndham San Diego, August 2002.
- [13] Anisichkin VF, Derendyaev BG, Mal'kov IYu, Salahutdinov NF, Titov VM. Study of the detonation process of the condensed explosives by the isotope method. *Doklady Acad. Nauk SSSR*. 1990;314(4):879-881.
- [14] Anisichkin VF. Mechanism of carbon release during detonation decomposition of substances. *Combustion, Explosives and Shock Waves (Fizika Gorenia i Vzryva)*. Translation by Kluwer Academic/ Plenum Publishers. 1994;30(5):667-673.
- [15] Vereschagin AL., Petrov EA. and et al, in: Proc. 5-th All-Union Detonation Meeting, Krasnoyarsk, 1991, 99-102 (in Russian).
- [16] Kozyrev NV, Brylyakov PM, Sen Chel Su, Shtein MA. Study of ultrafine diamonds synthesis by method of labelled atoms. *Doklady Acad. Nauk SSSR*. 1990;314(4):889-891.
- [17] Kozyrev NV, Sakovich GV, Sen Chel Su, Shtein MA, in: Proc. 5-th All-Union Detonation Meeting, Krasnoyarsk, 1991, 176-179 (in Russian).
- [18] Mader ChL., Numerical Modeling of Detonations. Berkly – Los Alamos – London. Calif. Press, 1979.
- [19] .Korets AYa, Mironov EV., Petrov EA. IR Spectroscopic Study of the Organic Component of Ultrafine Diamond Produced by Detonation Synthesis. *Combustion,*

Explosion and Shock Waves (Fizika Gorenia i Vzryva) Translation by Kluwer Academic/ Plenum Publishers, 2003;39(4):464-469.

- [20] Mironov E., Petrov E., Koretz A. Chemical Aspect of Ultradispersed Diamond Formation. *Diamond and Related Materials*. 2003;12(9):1472 – 1476. Mironov E., Petrov E., Koretz A. Technical principle "The Baykal Morning" Krasnoyarsk - Biysk 2001, unpublished results (in Russian).
- [21] Pershin SV, Tsaplin DN, in: Proc. 5-th All-Union Detonation Meeting, Krasnoyarsk, 1991, 237-249 (in Russian).
- [22] Petrov EA, in: Proc. 10-th All-Union Symp. on Combustion and Explosion, Chernogolovka, 1992, 114—115 (in Russian).
- [23] Petrov EA, in: Proc. Interregional Conference, Krasnoyarsk, 1996, p.13-14 (in Russian).
- [24] Anisichkin VF, Mal'kov IYu, Titov VM. Synthesis of diamond with dynamic loading of organic substances. *Doklady Acad. Nauk SSSR* 1988;303(4):65-67.

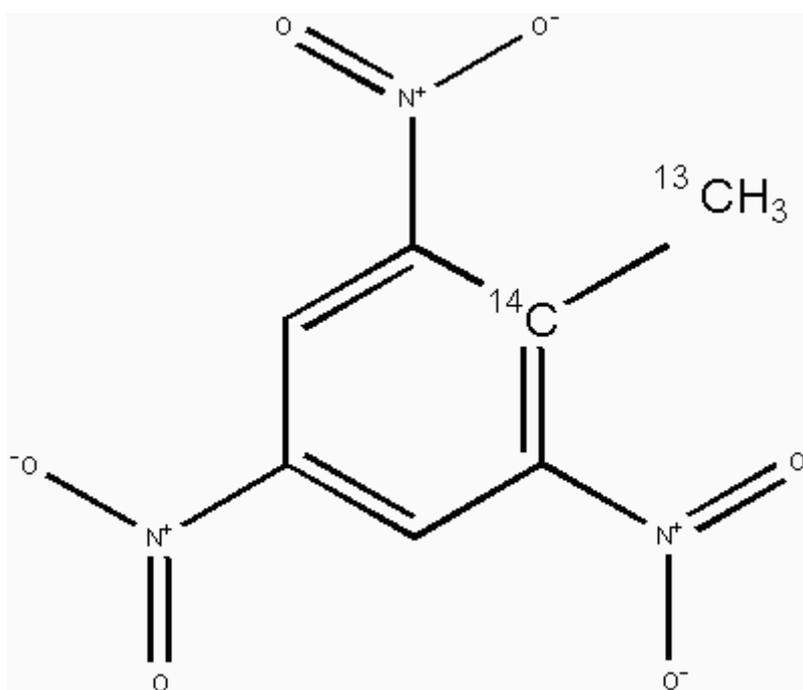


Fig.1. Trinitrotoluene with isotope atoms ^{14}C and ^{13}C in the methyl group. Experiments with ^{13}C isotope shown high content of this atom in the UDD [3,12,13,14]. Experiments with ^{14}C isotope were performed in [9,16,17].

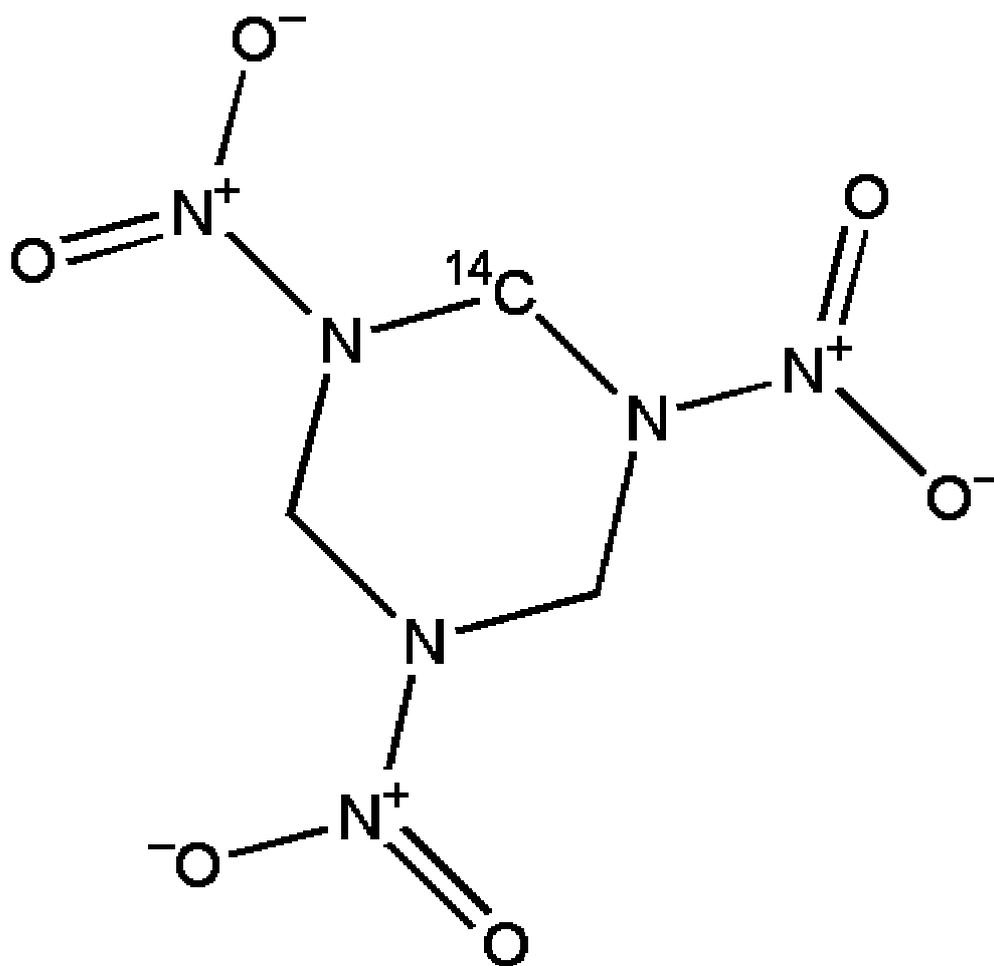


Fig.2. Hexogen (RDX – Research Department eXplosive) with isotope ^{14}C . Experiments with this isotope were performed in [9,16,17].

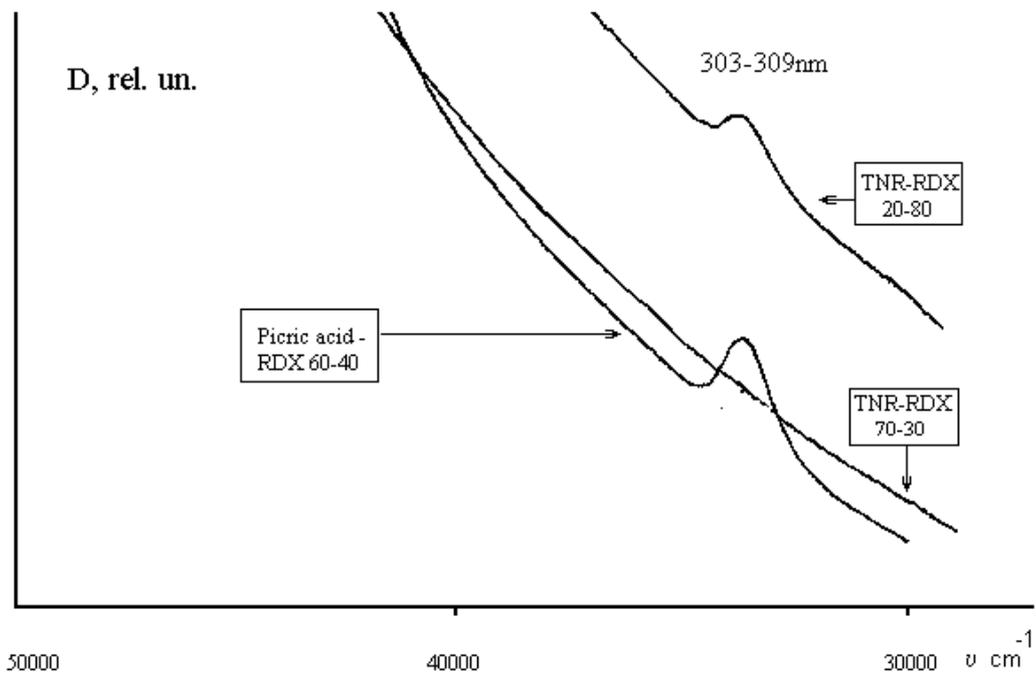
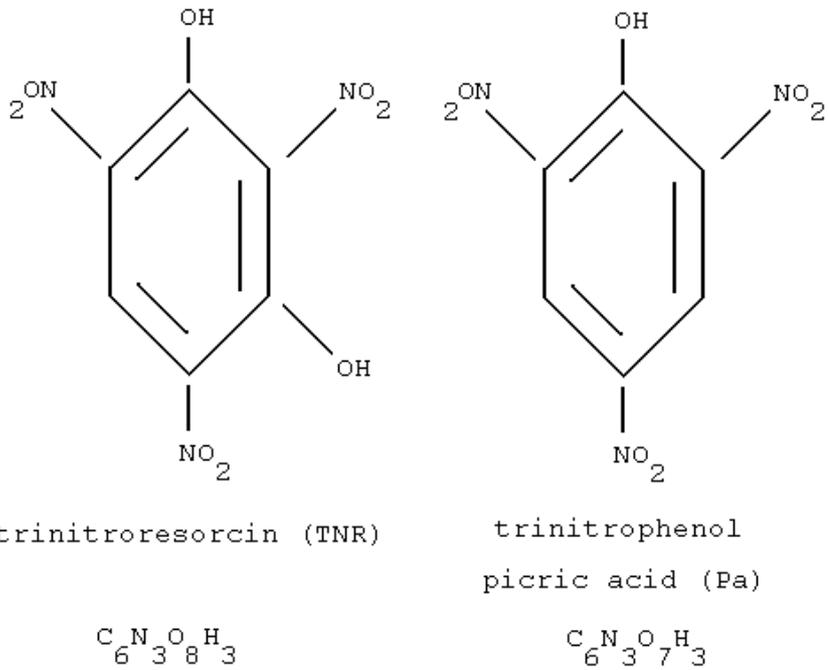


Fig.3. Trinitroresorcin (styphnic acid) and trinitrophenol (picric acid). There are some UV-spectra of the UDD obtained with participation of these explosives. 306nm – A-defect.