Detonation mechanism of organic high explosives and production of nanocarbon

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Abstract. Results of our experiments with isotope tracers contained in HE and on the measurement of the conductivity in a detonation front allow us to make the reliable assertion. Carbon in diamond and non-diamond phases condenses at the initial stages of the detonation decomposition. At the late stages, the partial oxidation of carbon at the boundaries of structures formed occurs.

Introduction

Transformations of inert materials and HEs can start immediately in the front of the initiating shock wave. In HEs, exothermal chemical reactions proceed until the Chapman-Jouguet plane. Additional reactions with the release of heat can take place also in the subsequent rarefaction wave. Products of detonation and shock decomposition of carbon containing materials with the negative oxygen balance usually contain free carbon in the diamond and non-diamond phases, according to Greiner, Titov, Anisichkin and other authors.[1-4]

Reactions in the detonation front proceed in less than nanosecond, for the HEs investigated below. Present-day methods are so far unable to immediately identify the composition of intermediate products of such fast processes. Therefore, different indirect methods are used including computational ones.

In the works,[5,6] the detonation mechanism was investigated by introducing the carbon isotope ^{13}C into the methyl group (CH_3) of molecules of TNT, which is a carbon-reach component of HE mixtures. The second component of the mixture, HMX or RDX is relatively oxygen negative and it produces almost no free carbon in the reaction.

During the detonation decomposition, HE components become more and more mixed. Therefore, in the HE mixture under investigation, the content of ^{13}C atoms in the particles of free carbon should be higher if these particles are formed earlier, and if the particles of HE are larger. This was found in the experiments.

Another method for the investigation of the carbon-involving detonation mechanism is the measurement of the electrical conductivity.[7] It was shown in the work[8] that the time dependence of conductivity allows one to reveal the conducting form of carbon and to discover the evolution of carbon nanostructures.

In this paper, the results obtained by the isotope tracers method and the method of electrical conductivity are compared in order to reveal the dynamics and the mechanism of carbon-involving chemical reactions at the detonation of HEs.

Results of the experiments with isotope tracers in TNT molecules

Table 1 shows the measurement results of the content of carbon isotope tracers in the charge before the explosion and in the explosion products depending on the average size of HE particles d.

Table 1. Isotope ratios in the components of charge and in the explosion products, experimental data.[5,6]

Composition	$^{13}C/^{12}C$ $d = 50$ µm	$^{13}C/^{12}C$ $d = 120$ µm
HE charge	0.057±0.002	0.053±0.002
TNT	0.102±0.002	0.102±0.002
Methyl group (CH_3) of TNT	1.38±0.02	1.38±0.02
RDX (HMX)	0.012±0.001	0.012±0.001
TNT/RDX(HMX) compound	0.064±0.002	0.064±0.002
Free carbon	0.058±0.002	0.063±0.002
Diamond phase	0.073±0.002	0.087±0.002
Non diamond carbon	0.030±0.002	0.044±0.002
CO_2	0.059±0.006	0.039±0.004
CO	0.054±0.005	0.052±0.005

In the works,[9,10] similar investigations were performed for the mixture TNT/HMX 50/50. TNT contained the ^{14}C isotope in the benzene ring of the molecule. In one case, HMX with the grain size about 6.9 µm, in another case the size was about 175 µm.

Assuming that all carbon atoms of the TNT molecules equally participate in the formation of explosion products, the obtained results allow one to determine the origin of the free carbon phases and other carbon containing products and the sequence of their formation from the HE components.

In the works,[11-16] a quantitative analysis was performed of the contents of carbon isotope tracers in explosion products given in the works.[5,6,9,10] The composition of the explosion products for large particles of HE components was assumed to be the same both for independently reacting HEs at sufficiently high detonation pressure and for the components in the HE mixtures.[2]
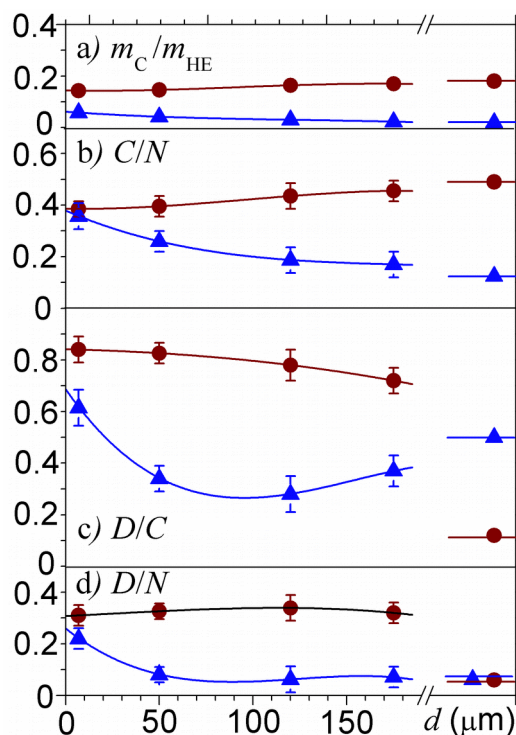
Calculation results are shown in Fig. 1.

Fig.1. Dependence of the quantity and the composition of condensed detonation products of TNT (●) and RDX (HMX) (▲) on the size of HE grains.

a) m_C/m_{HE} – ratio of the mass of free carbon to the mass of the HE component;

b) C/N – fraction of released carbon of the HE component;

c) D/C – content of the diamond phase in the free carbon of the HE component;

d) D/N – fraction of carbon of the HE component converted to the diamond phase.

Discussion of the results of experiment with carbon isotope tracers

It can be seen in Table 1 that the content of the isotope tracer is higher in the diamond phase of carbon than in the non-diamond phase and in the

carbon oxides. From this fact we can conclude that the diamond is formed at earlier stages than the non-diamond free carbon and the carbon oxides.

The content of tracer in gaseous carbon compounds is close to the overall tracer content in the charge. This allows us to conclude that the oxidation of a part of carbon occurs at later stages when the components of reacting HEs are essentially mixed.

It follows from Figs. 1a) and 1b), that carbon atoms are sufficiently mixed before the oxidation in a finely grained HE mixture (d = 6.9 µm). In coarsely grained HEs, the TNT carbon is preserved in a free state to a higher degree than the RDX (or HMX) carbon.

Figures 1c) and 1d) show that the fraction of carbon released in the diamond phase is essentially different for different HE components. Assuming that pressure and temperature in the detonation wave is the same for HE components, we can suppose that the degree of conversion of carbon into diamond and non-diamond phase depends on the chemical composition of the HE component.

It can be concluded form the results of experiments with isotope tracers that in the HEs investigated, the carbon of components is almost totally mixed before the oxidation. However, the content of diamond in the free carbon released from TNT is essentially higher than in the free carbon from RDX or HMX. Hence, the formation of the diamond phase occurs before the mixture of HE components and it depends essentially on the detonation parameters as well as on the chemical composition of the HE component.

The following mechanism of the release of the free carbon can explain the results obtained. Molecules of HE are partially destructed in the front of sufficiently strong initiating shock waves, but the hydrogen remains chemically bound with the carbon,[17,18] in this case, in the form of methane (CH_4) which is the most stable at high pressure and temperature. The similar statement about the stability of methane was made, e.g., in the work.[19]

Remaining free carbon forms the diamond phase according to the phase diagram of carbon.[19-21] The non-diamond phase forms at the later stage after the oxidation of the hydrogen of methane and the release of new portions of the free carbon. This carbon is released in the non-diamond form because the physical and chemical parameters of the medium are changed.
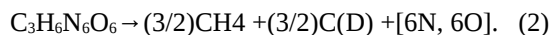
Such behavior of media is characteristic for the shock compression. Materials usually undergo transformations with the formation of phases or chemical compounds with higher density. This corresponds in the case of carbon-containing materials to the formation of the high density diamond phase in the front of the initiating shock wave.

The possibility of essential physical and chemical transformations of HE molecules immediately in the initiating shock front is pointed out, e.g., in the work.[18]

Thus, the initial state of transformation of the TNT carbon in a sufficiently strong initiating shock wave (e.g., in a mixture with RDX) can proceed in the following way:[11-16]

$$C_7H_5N_3O_6 \rightarrow (5/4)CH_4 + (23/4)C(D) + [3N, 6O]. \quad (1)$$
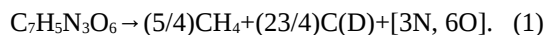
For RDX, the process is similar:

$$C_3H_6N_6O_6 \rightarrow (3/2)CH4 + (3/2)C(D) + [6N, 6O]. \quad (2)$$

Thus, all hydrogen is bound in methane, and remaining carbon is condensed into the diamond phase (C(D)). At the following stage, the hydrogen of methane is oxidized, and the non-diamond carbon is released as individual particles and precipitated at the surface of diamond particles. At the initial stages of the detonation decomposition, elongated conductive structures can be formed from carbon particles. Therefore, the maximum electrical conductivity in the detonation front should depend on the total carbon content in the HE.

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At later stages, a part of the released carbon (both diamond and non-diamond) is oxidized by the remaining oxygen. This process, however, does not change significantly the content of diamond in the free carbon of different components because carbon particles have time to mix essentially before the oxidation processes.

Then, according to equations (1) and (2), the fraction of carbon in the free carbon of TNT should be $(23/4)/(23/4+5/4)=0.82$ (82%). In the free carbon of RDX or HMX, the fraction of diamond should be $(3/2)/(3/2+3/2)=0.5$ (50%). The fraction of diamond in the TNT/RDX 40/60 mixture should be about 73% which practically coincides with the experimental results.[2,5,6] It can be seen however from the experiments with the isotope tracer that the fraction of the diamond phase in the carbon of the HE components is not constant, and it depends on the size of the HE grains. This result can be explained by the different degree of mixing of HE components during the process of detonation.
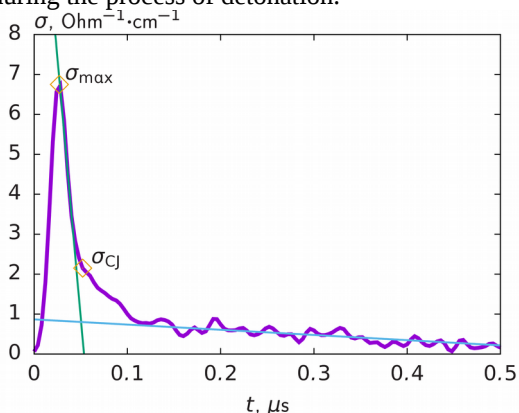

Fig. 2. Graph of electrical conductivity at the detonation of RDX with the density of 1.7 g/cm^3.

Thus, we show that at the detonation of HE, the free carbon is released immediately behind the front of the initiating shock wave before the main exothermal reactions. It can be therefore supposed that at the detonation of HE mixtures with inert organic component, the main carbon-involving reactions should proceed in a similar way. Namely, the formation of the diamond phase from the carbon of the inert component should occur according to the relations (1), (2). In the works,[3,4] mixtures of HMX with benzene (C_6H_6), acetone (C_6H_6O), and paraffin ($C_{14}H_{30}$) were investigated which produced in the sufficiently strong initiating shock wave the content of diamond phase in the total carbon of 85%, 80%, and 44%, correspondingly. These values are close to ones given by formulas analogous to (1), (2). Herewith, the influence of hydrogen should be noted. At the initial stages of the decomposition, hydrogen binds a part of carbon preventing its transformation into the diamond phase.

Measurements of the electrical conductivity in a detonation front

The time dependence of the electrical conductivity at the detonation of RDX, HMX, PETN, BTF, TNT with different initial density is measured using a high resolution scheme.[7,22-26] A typical conductivity profile measured at the detonation of RDX is shown in Fig. 2. Here, σ_{max} is the maximum value of conductivity, σ_{CJ} is the conductivity in the Chapman–Jouguet point (CJp). In the graph, the region with higher values is distinctly seen. We associate this region with the reaction zone. It was shown in works,[27,28] that the maximum conductivity σ_{max} is determined by the total carbon content, and the value in the inflexion point σ_{CJ} which is associated with the CJp is explained by the free carbon.[29] The link between the value of conductivity and the content of carbon was justified in the work.[30]

The evidence of the correctness of this assertion is the universal dependence of conductivity on the fraction of carbon which includes the values of σ_{max} and σ_{CJ} the HEs investigated taking into account the initial density.[29]

The conductivity data allow us to suppose that the order of chemical transformations in a detonation wave is following. First, the carbon condensation occurs at times of order of tens of nanoseconds, and conductive structures are formed which penetrate all the material. This moment corresponds to the maximum conductivity value σ_{max} in Fig. 2. The following decrease of the conductivity is connected with the second stage of chemical transformations, the oxidation of carbon. The value of σ_{CJ} is determined by the amount of free carbon. The subsequent evolution reflects the disruption of conductive structures when compact carbon particles are formed which are found in preserved explosion products.

Results and Conclusion

According to the common knowledge, the additional energy release behind the Chapman–Jouguet plane is explained by the formation of free carbon particles at the late stages of the detonation decomposition of HEs.[31,32] Our results do not support this mechanism of the detonation of HE.

We show that the primary condensation of carbon occurs at the initial stages of the detonation decomposition of carbon-containing HEs. The release of energy in the rarefaction wave can be explained by the oxidation of carbon as well as the transformation of the form of rest carbon.

We show that the primary condensation of carbon occurs in the reaction zone near the front at times of order of tens of nanoseconds. The so called free carbon in explosion products is the residue after the reactions of the oxidation of carbon nanostructures. The release of energy in the rarefaction wave can be explained by chemical reactions occurring due to the shift of the chemical equilibrium at the pressure decrease.

In further investigations, we expect to detail the mechanism of the detonation of carbon containing HEs of different chemical composition. It is expedient to investigate the detonation mechanism starting from the simple case of individual HEs where the interaction of components is absent.

References

1. Greiner, N. R., Phillis, D. S., Johnson, J. D., and Volk, F., "Diamonds in Detonation Soot", *Nature*, Vol. 333, pp. 440-442, 1988.

2. Titov, V. M., Anisichkin, V. F., and Mal'kov, I. Yu., "The Study of Synthesis Process of Ultradispersed Diamond in Detonation Waves", *Fiz. Goren. Vzryva*, [Combust. Explos., Shock Waves], Vol. 25, pp. 117-126, 1989.

3. Anisichkin, V. F., Mal'kov, I. Yu., and Titov, V. M., "Synthesis of Diamond with Dynamic Loading of Organic Substances", *Dokl. Akad. Nauk SSSR*, Vol. 303, pp. 625-627, 1988.

4. Titov, V. M., Anisichkin, V. F., and Mal'kov, I. Yu., "Diamond Synthesis from Dynamically Loaded Organic Matter", in *Shock Compression of Condensed Matter—1989*, Elsevier. Sc. Publ., pp. 659-662, 1990.

5. Anisichkin, V. F., Derendyaev, B. G., Koptyug, V. A., Mal'kov, I. Yu., Salakhutdinov, N. F., and Titov, V. M., "Investigation of the Decomposition Process in a Detonation Wave by the Isotope Method", *Fiz. Goren. Vzryva*, [Combust. Explos., Shock Waves], Vol. 24, pp. 121-122, 1988.

6. Anisichkin, V. F., Derendyaev, B. G., Mal'kov, I. Yu., Salakhutdinov, N. F., and Titov, V. M., "Study of the Detonation Process of Condensed Explosives by the Isotope Method", *Dokl. Akad. Nauk SSSR*, Vol. 314, pp. 879-881, 1990.

7. Ershov, A. P., Satonkina, N. P., and Ivanov, G. M., "Electroconductivity profiles in dense high explosives" *Russ. J. Phys. Chem. B*, Vol. 1, 588–599 (2007).

8. Satonkina N.P., and Medvedev D. A., "On the Mechanism of Carbon Nanostructures Formation at Reaction of Organic Compounds at High Pressure and Temperature" *AIP Advances*, Vol. 7, p. 085101, 2017; doi: 10.1063/1.4990710

9. Kozyrev, N. V., Brylyakov, P. M., Sen Chel Su, and Shtein, M. S., "Investigation of the Process of Ultradispersed Diamond Synthesis by the Tracer Atom Method", *Dokl. Akad. Nauk SSSR*, Vol. 314, pp. 889-891, 1990.

10. Kozyrev, N. V., Kalashnikova, G. S., Golubeva, E. S., et al., "*Proceedings of the 10th Symposium on Combustion and Explosion. Detonation*", Chernogolovka, p. 120, 1992.

11. Anisichkin V. F., "Mechanism of Carbon Release During Detonation Decomposition of Substances" *Combust. Explos., Shock Waves*, Vol. 30, pp. 667-673, 1994.

12. Anisichkin V. F., and Dolgushin D. S., "Mechanism of Diamond Synthesis from High Explosives", in *Advances in New Diamond Science and Technology. ICNDST-4*. pp. 569-572, 1994.

13. Anisichkin V. F., "Isotope studies of detonation mechanisms of TNT, RDX, and HMX" *Combust. Explos., Shock Waves*, Vol. 43, pp 580–586, 2007.

14. Anisichkin V. F., "Mechanism of the Detonation of TNT–RDX Mixtures as Studied by the Isotope Tracer Method" *Russ. J. Phys. Chem. B*, Vol. 5, pp. 304–307, 2011.

15. Anisichkin V. F., "Molecular Mechanism of Detonation of Organic High Explosives" *Goreniye i Plazmokhim.*, Vol. 10, pp. 21–35, 2012.

16. Anisichkin V. F., "On the Mechanism of the Detonation of Organic High Explosives" *Russ. J. Phys. Chem. B*, Vol. 10(3), pp. 451–455, 2016.

17. Anisichkin V. F., "Calculation of shock adiabatic curves for chemical compounds", *Fiz. Goren. Vzryva*, [Combust. Explos., Shock Waves], Vol. 16, pp. 151-153, 1980.

18. Voskoboynikov, I. M., and Voskoboynikova, O. I., "Transformation of some organic compounds under shock-wave compression", *Khimich. Fiz.* ,Vol. 20, pp. 70-74. 2001.

19. Badziag, W. S. Verwoerd, W. P. Ellis, and N. R. Greiner, "Nanometre-sized diamonds are more stable than graphite" *Nature*, Vol. 343, pp. 244-245, 1990.

20.Viktorov, B., Gubin, S. A., Maklashova, I. V., and Pepekin, V. I., "Predicting the detonation characteristics of hydrogen-free HEs" *Khimich. Fiz.*, Vol. 24, pp. 22-45, 2005.

21. Danilenko, V. V., "Phase Diagram of Nanocarbon", *Combust. Explos., Shock Waves*, Vol. 41, pp. 460-466, 2005.

22. Ershov, A. P., Satonkina, N. P., and Ivanov, G. M., "High-resolution conductivity profile measurements in detonating pressed explosive". *Techn. Phys. Lett.*, Vol. 30, pp. 1048–1050, 2004.

23. Ershov, A. P., and Satonkina, N. P., "Investigation of the reaction zone in heterogeneous explosives substances using an electrical conductivity method" *Combust. Explos., Shock Waves*, Vol. 45, pp. 205–210, 2009.

24. Ershov, A. P., and Satonkina, N. P., "Electrical conductivity distributions in detonating low-density explosives - grain size effect". *Combust. Flame*, Vol. 157, pp. 1022–1026 (2010).

25. Satonkina, N. P., and Rubtsov, I. A., "Electrical conductivity distribution during detonation of a

TATB-based explosive". *Techn. Phys.,* Vol. 61, pp. 142–145, 2016.

26. Satonkina, N. P., Ershov, A. P., Kashkarov, A. O., Mikhaylov, A. L., Pruuel, E. R., Rubtsov, I. A., Spirin, I. A. and Titova, V. B., "Electrical Conductivity Distribution in Detonating Benzotrifuroxane" *Scient. Rep.,* 2018. DOI:10.1038/s41598-018-28028-2

27. Satonkina, N. P., "The dynamics of carbon nanostructures at detonation of condensed high explosives" *J. Appl. Phys*. Vol. 118, p. 245901, 2015.

28. Satonkina, N. P., "Correlation of electrical conductivity in the detonation of condensed explosives with their carbon content" *Combust. Explos.*, *Shock Waves,* Vol. 52, pp. 488–492, 2016.

29. Tanaka, K., "Detonation Properties of Condensed Explosives Computed Using the Kihara-Hikita-Tanaka Equation of State" *National Chemical Laboratory for Industry, Tsukuba Research Center.* Tsukuba, Japan, 1983.

30. Satonkina, N. P., "Chemical composition of detonation products of condensed explosives and its relationship to electrical conductivity" *J. Phys: Conf. Ser.,* Vol. 946, p. 012059, 2018.

31. Tarver, C. M., Kury, J. W., and Breithaupt, R. D., "Detonation Waves in Triaminotrinitrobenzene" *J. Appl. Phys*., Vol. 82, pp. 3771-3782, 1997.

32. Tarver, C. M., Forbes, J.W., and Urtiew, P. A., "Nonequilibrium Zeldovich-Von Neumann-Doring Theory and Reactive Flow Modeling of Detonation" *Russ. J. Phys. Chem. B*, Vol. 1, pp.39-45, 2007.