Chemical composition of detonation products of condensed explosives and its relationship to electrical conductivity

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Chemical composition of detonation products of condensed explosives and its relationship to electrical conductivity

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Abstract. A comparative analysis of the detonation products and thermodynamic parameters of four individual explosives is performed, and their effect on experimental electrical conductivity is considered. With a carbon fraction greater than 0.1, the electrical conductivity is determined by the carbon content.

1. Introduction

High electrical conductivity in detonations of condensed explosives has been studied for more than 60 years. In recent years, there has been a significant breakthrough in the development of measurement techniques.

This has made it possible to obtain reliable experimental data on the electrical conductivity of a number of explosives during detonation over a wide range of initial density [1–7]. In the present paper, four individual condensed explosives are considered: cyclotrimethylene-trinitramine (hexogen, RDX, $C_3H_6N_6O_6$), cyclotetramethylene-tetranitramine (octogen, HMX, $C_4H_8N_8O_8$), pentaerythritol tetranitrate (PETN, $C_5H_8N_4O_{12}$), and trinitrotoluene (TNT, $C_7H_5N_3O_6$). A comparative analysis of electrical conductivity with regard to the thermodynamic parameters and elemental composition of the detonation products (DP) of the explosives is performed based on the numerical data obtained in work [8].

## 2. Experimental data on electrical conductivity

A detonation wave consists of a shock front, an adjacent chemical reaction zone (chemical or von Neumann spike), and a Taylor rarefaction wave separated from the chemical spike by the Chapman–Jouguet (CJ) point. The Zeldovich–von Neumann–Doring theory assumes that at the CJ point, chemical reactions are completed.

Typical electrical conductivity profile in detonation is shown in figure 1. The conductivity first rapidly increases to a maximum value $\sigma_{\max}$, then decreases (the gradient depends on the material), and, after the inflection point in the Taylor wave, varies slightly around a small value σ. Here we use the notions of maximum conductivity $\sigma_{\max}$ and the conductivity at the CJ point σ_{CJ} introduced in work [9]. A procedure for determining the length of the region of high (compared with the value in the Taylor wave) conductivity at $0 < t < 0.05$ μs is presented.
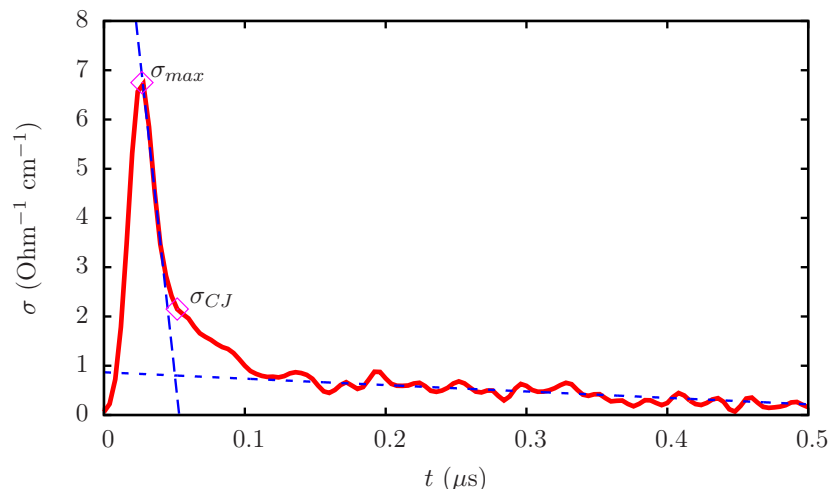
Figure 1. Conductivity profile for HMX detonation, $\rho = 1.8$ g/cm^3.
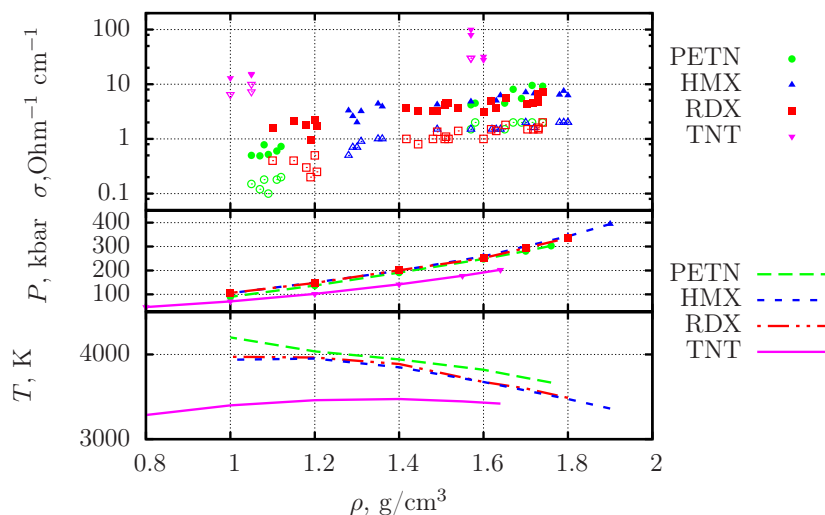
Figure 2. Electrical conductivity (top graph, data [1–7]), filled symbols correspond to the maximum value $\sigma_{\max}$, open symbols to the value at the Chapman–Jouguet point σ_{CJ}. Pressure (middle graph) and temperature (bottom graph) versus the density of the explosives, data [8].

As shown in work [2], the length of the region of high electrical conductivity is close to that of the reaction zone. Experimental data on the electrical conductivity of TNT, PETN, HMX, and RDX in the chemical reaction zone $\sigma_{\max}$ (filled symbols) and at the CJ point σ_{CJ} (open symbols) versus density are shown in the semi-log scale in figure 2. For each explosive at a fixed density ρ, σ_{CJ} is always lower than $\sigma_{\max}$. Both quantities show a general tendency to increase with increasing density. When the explosive density is lower than the crystal density, detonation is sensitive to the heterogeneous structure of the explosive charge, so that the values of $\sigma_{\max}$ and σ_{CJ} are subject to statistical fluctuations.

For $\rho < 1.3$ g/cm^3, we use the results of a study [5], in which the length of the region of high electrical conductivity decreased by a factor of 1.5 with increasing dispersion of explosive. The

effect of the grain size on $\sigma_{\max}$ and σ_{CJ} is due to an increase in the sensitivity of the explosive with increasing dispersion [10], which leads to a change in the rate of decomposition of the explosives at the chemical spike.

3. Relationship between thermodynamic parameters and electrical conductivity

Often, electrical conductivity in detonation is related to high thermodynamic parameters. Figure 2 shows the temperature and pressure at the CJ point versus the density of the explosives. For easiness of comparison, the density scale is the same for the three graphs. The pressure increases monotonically by a factor of 4 with increasing density. There is a certain correlation between pressure and electrical conductivity. However, there is no uniform relationship for the four explosives; maximum electrical conductivity values for TNT correspond to lower pressures.

Unlike to pressure, the temperature–density correlation is not uniform for the four explosives. For RDX, HMX, and PENT, the temperature decreases monotonically with increasing density. For TNT, the dependence is non-monotonic at a much lower temperature. There are densities that correspond to the same T, and this should be reflected in the conductivity graph. However, when comparing $\sigma(\rho)$ and $T(\rho)$, it is clear that a strong exponential dependence does not manifest itself. In our opinion, this proves that temperature does not play a key role in the conduction process.

Thus, neither pressure nor temperature nor density are key factors for conduction.

4. Relationship between the composition of CHNO detonation products of explosives with electrical conductivity

No correlations have been found between maximum electrical conductivity and the content of hydrogen, nitrogen, and oxygen in the molecule. The maximum value of $\sigma_{\max}$ for TNT is observed at a carbon fraction of 0.37 in the molecule. For the remaining explosives, a fraction of ≈ 0.18 corresponds to lower values of $\sigma_{\max}$.

According to article [8], for RDX, HMX, PETN, and TNT, the products NO, NH_3, O_2, OH, CH_4, H, and H_2 at any density have a total mass fraction of less than 2.5%. The main detonation products (DP) which account for at least 97.5% of the mass fractions are H_2O, CO, CO_2, N_2, and C.

HMX and RDX of the same density are similar in DP and thermodynamic parameters.

The mass fraction of nitrogen N_2 at the CJ point weakly depends on the density and is 0.37–0.38 for RDX and HMX, 0.18 for TNT, and 0.175 for PETN. Nitrogen does not manifest itself through electrical properties.

4.1. Water

It is generally agreed that the electrical conductivity of explosives with a small negative oxygen balance is due to water [13].

Figure 3(a) shows the mass fraction of water r_{H_2O} at the CJ point versus explosive density. For RDX, HMX, and PETN, the dependence of r_{H_2O} on the density is weak, and the value of r_{H_2O} for TNT is significantly lower than for the other explosives. No correlation with maximum electrical conductivity is observed.

Note that in the range of detonation pressures of 10–35 GPa, the electrical conductivity of pure water increases rapidly (from 0.06 to 28 $Ohm^{-1}cm^{-1}$ [11, 12]). This provides a satisfactory explanation for the "equilibrium" (in the Taylor wave) electrical conductivity for explosives of balanced composition.

Figure 3(b) shows experimental data on the electrical conductivity at the CJ point σ_{CJ} for RDX, HMX, and PETN and the electrical conductivity of water with a coefficient of 0.2 to account for the fraction of water in the DP. At pressures higher than 25 GPa, σ_{H_2O} is greater than
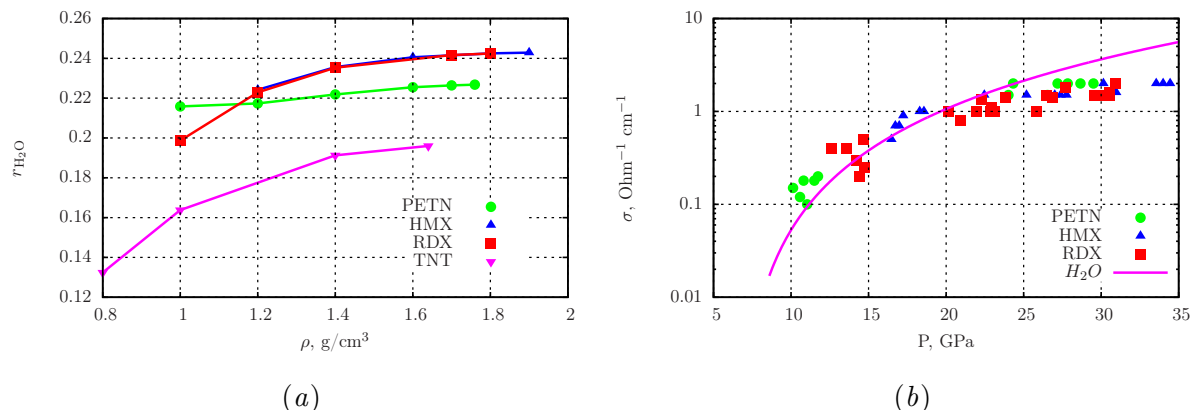
Figure 3. (a) Mass fraction of water at the CJ point versus the density of the explosives, data [8]. (b) Electrical conductivity at the CJ point for three explosives and for water at different pressures. The value of σ for water is obtained from the data [11, 12] and multiplied by a factor of 0.2.

Table 1. Data of experiments with loose explosives of bulk density with the addition of water, data [3, 5–7].

Explosive	ρ, g/cm^3	σ_{max}, Ohm^{-1}cm^{-1}	σ_{CJ}, Ohm^{-1}cm^{-1}	Δ, mm	P, GPa	σ_{H_2O}, Ohm^{-1}cm^{-1}
TNT	1.0	14.5 ± 2.0	7.93 ± 1.76	1.41 ± 0.41	5.8	0.0012
TNT+H$_2$O	1.4	23 ± 2.7	8.5 ± 1.8	3.63 ± 0.64	10.8	0.21
RDX	1.2	1.79 ± 0.308	0.35 ± 0.081	0.36 ± 0.061	12.2	0.54
RDX+H$_2$O	1.5	1.5 ± 0.23	0.58 ± 0.136	0.8 ± 0.104	19.4	3.63

$\sigma_{CJ\ HE}$ with increasing yield of water in the PD, see figure 3(a). This suggests that conduction may be caused by water ions. However, even at 30 GPa, a different explanation is required.

For percolation conduction, the percolation threshold is $\approx 26\%$ of the volume [14]. Thus, in spite of the similar electrical conductivities (figure 3(b)), conduction cannot be explained only by the presence of water as the percolation threshold is not overcome.

To elucidate the role of water, we discuss experimental data for the detonation of a mixture of explosive with H$_2$O. Experiments with water-filled RDX were described previously in work [15]. The composition of the products was calculated from data on the DP composition of the original RDX at a density of 1.1. An analytical equation of the state of the products was constructed, and the amount of condensed carbon was considered to be the same for dry RDX and water-filled RDX. Good agreement with the experimental data was obtained, showing that the interaction of the products with water can be neglected.

Table 1 gives values for loose explosives and with the addition of water at about the same partial density of the active substance (explosive). The grain size of RDX $d = 160$ μm, and that of TNT $d = 5$ μm. The data are averaged over two to three experiments with similar densities. The following notation is used: ρ is the density of explosive or mixture, σ_{max} and σ_{CJ} are the maximum electrical conductivity and the electrical conductivity at the CJ point, respectively, Δ is the width of the zone of high electrical conductivity (determined using the procedure shown in figure 1, where $\Delta = 0.05$ μs), σ_{H_2O} is the electrical conductivity of pure water versus pressure
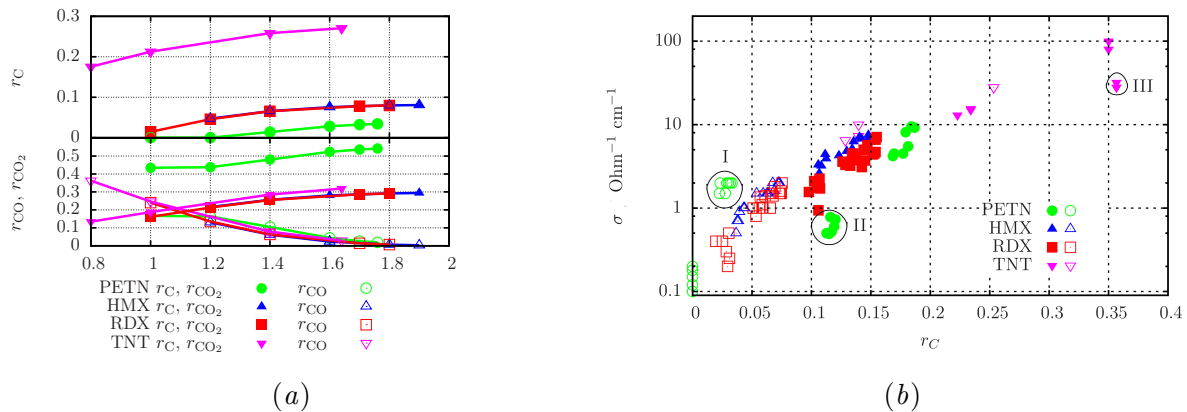
Figure 4. (*a*) Mass fraction of carbon (top graph), CO, and CO_2 (bottom graph) at the CJ point at different density of the explosives, data [8]. (*b*) Electric conductivity at mass fraction of carbon. Regions I and II correspond to PETN, region III for the maximum value in cast TNT indicates an incomplete chemical reaction.

(data [11, 12]), P is the pressure estimated for the CJ point by the formula $P = \rho D^2/4$. For the experiments with water, the upper-bound estimate of the pressure is used on the basis that the density of explosive in the above formula is equal to the density of the mixture with water in the table. The real pressure at the CJ point for mixtures is slightly lower than the obtained estimate [15], and in the chemical spike, it is higher [16]. The mass fraction of water in the detonation products of TNT in a mixture of THT+H_2O is 0.21, and for RDX+H_2O, it is 0.236. Under the assumption of no significant changes during chemical reactions, the total mass fraction of water in the products (including water added to the explosive) for both mixtures is about 0.4.

The addition of water to loose TNT led to an increase in the maximum value σ_{max} by a factor of one and one half. This cannot be explained by the electrical conductivity of water at the corresponding pressure (table 1, column 7) as the value of σ_{CJ} remained the same. For RDX, the difference between the values of σ_{max} for the pure explosive and for its mixture with water is within the error for the doubled σ_{CJ}. Also in both cases, with the addition of water, there is a broadening of the length of the region of high conductivity Δ. A similar broadening of the reaction zone in RDX+H_2O by a factor of 1.7 relative to dry RDX was described in work [15].

The results can be explained as follows. The addition of water shifts the chemical equilibrium toward increased carbon yield as the pressure increases. This leads to an increase in the maximum σ_{max} for TNT. However, for RDX, due to the lower carbon content, water serves as a layer with lower conductivity, which leads to a decrease in the value of σ_{max}. At the CJ point, the carbon fraction for RDX is less than 0.1, and the amount of water is sufficient to form a contiguous region and to ensure ionic conductivity, which leads to an increase in σ_{CJ}.

Thus, we conclude that in detonations of RDX, HMX, and PETN, the electrical conductivity at the CJ point may be caused by the presence of water.

4.2. Carbon and its compounds
The top graph in figure 4(*a*) shows the mass fraction of condensed carbon at the CJ point versus density. For all the explosives, it increases with the density. For PETN at a density of less than 1.2 g/cm^3, the mass fraction of carbon is zero, and for TNT, it is much higher. In our opinion, this indicates a relationship between condensed carbon and conduction.

The lower graph in figure 4(*a*) shows the mass fraction of CO (open symbols) and CO_2 (filled symbols) versus explosive density. With increasing ρ, the content of CO decreases and that of

CO_2 increases. There is no uniform correlation of the mass fraction in products and the initial density of the four explosives. The relationship with carbon can be considered through its density and volume and mass fractions. Each of the parameters has its advantages. Density most fully reflects the influence of conduction in carbon networks and provides an objective estimate of the amount of carbon. The volume fraction, as shown in work [7], admits analytical dependence under certain assumptions. However, the mass fraction, unlike the first two parameters, is always known.

Consideration of the effective reduction in carbon density is required. Formally, the effect of the initial density of explosives can be taken into account through an effective reduction in the mass fraction of the conductive material. We introduce the notion of the effective mass fraction of carbon at the maximum of $r_{\max} = \rho r_c/\rho_c$, where ρ is the explosive density in the experiment, r_c is the mass fraction of carbon in the molecule, and ρ_c is the maximum (crystal) density of the explosive.

Figure 4(b) gives the data of all the experiments present in figure 2. Maximum electrical conductivity $\sigma_{\max}$ is shown versus the effective total mass fraction of carbon, and σ_{CJ} versus the mass fraction of condensed carbon. That is, under the assumption that the electrical conductivity both at the maximum and at the CJ point is due to carbon, the dependence becomes universal. The semi-log scale made it possible to plot data for the zero fraction of carbon.

Regions I, II, and III on figure 4(b) do not fit the general pattern. Regions I and II correspond to PETN and are apparently related to the nonclassical detonation propagation mode via a jet mechanism. In this mode, there may be no CJ plane. Nonclassical modes are discussed in several papers. Kolesnikov and Utkin [17] report the absence of a chemical spike in a range of densities and explain this by under driven detonation and the reaction in the front. Apin [18] proposed a jet mechanism of detonation propagation with an irregular shape of the front and the presence of unreacted substance. Fedorov [16] detected traces of jets on the witness plate and obtained pressure profiles for low-density PETN that are not typical of the classical model. Ershov et al. [19] obtained a nonclassical mode for PETN.

Region III for the maximum value in cast TNT indicates an incomplete chemical reaction, resulting in a change in the course of the chemical reactions compared to the pressed explosive.

5. Conclusions
The results of experiments with condensed explosives were analyzed over a wide range of the fraction of carbon from 0 (at the CJ point for loose PETN) to 0.37 (fraction of carbon in the TNT molecule). The effect of various factors on the electrical conductivity, such as the composition of detonation products, the content of chemical elements in the molecule, density, temperature, and pressure, was examined.

A correlation between the electrical conductivity and the mass fraction of carbon was shown for a carbon fraction higher than 0.1. For PETN, RDX, and HMX, the maximum electrical conductivity is related to the total mass fraction of carbon; at the CJ point, the fraction of carbon is lower than the threshold value and the ionic conductivity mechanism becomes apparent. At small fractions of carbon, the electrical conductivity can be caused by water.

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