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Shock Discontinuity Zone Effect: The Main Factor in the Explosive Decomposition Detonation Process

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Shock discontinuity zone effect: the main factor in the explosive decomposition detonation process

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A new qualitative conception of the detonation mechanism in condensed explosives has been developed on the basis of experimental and numerical modelling data. According to the conception the mechanism consists of two stages: non-equilibrium and equilibrium. The mechanism regularities are explosive characteristics and they do not depend on explosive charge structure (particle size, nature of filler in the pores, explosive state, liquid or solid, and so on). The tremendous rate of loading inside the detonation wave shock discontinuity zone (*ca.* 10^{-13} s) is responsible for the origin of the non-equilibrium stage. For this reason, the kinetic part of the shock compression energy is initially absorbed only by the translational degrees of freedom of the explosive molecules. It involves the appearance of extremely high translational temperatures for the polyatomic molecules. In the course of the translational–vibrational relaxation processes (that is, during the first non-equilibrium stage of *ca.* 10^{-10} s time duration) the most rapidly excited vibrational degrees of freedom can accumulate surplus energy, and the corresponding bonds decompose faster than behind the front at the equilibrium stage. In addition to this process, the explosive molecules become electronically excited and thermal ionization becomes possible inside the translational temperature overheat zone. The molecules thermal decomposition as well as their electronic excitation and thermal ionization result in some active particles (radicals, ions) being created. The active particles and excited molecules govern the explosive detonation decomposition process behind the shock front during the second equilibrium stage. The activation energy is usually low, so that during this stage the decomposition proceeds extremely rapidly. Therefore the experimentally observed dependence of the detonation decomposition time for condensed explosives is rather weak.

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1. Introduction

The condensed explosives detonation decomposition mechanism problem is still the least investigated in the theory of detonation. Lately the problem has again attracted the attention of many scientists (Eyring 1975; Eyring & Leu 1975; Karo *et al.* 1977; Owens & Sharma 1979; Coffey & Toton 1981; Delpuech *et al.* 1981; Zerilli & Toton 1983; Schmidt *et al.* 1983; Peyrard *et al.* 1984; Trott & Renlund 1985; Trevino & Tsai 1985; Dufort & Delpuech 1985; Schmidt *et al.* 1986*a*, *b*; Moore *et al.* 1986; Peyrard *et al.* 1986; Odiot *et al.* 1986; Eloy & Delpuech 1987; Walker 1988; Renlund & Trott 1988; Lambrakos *et al.* 1988; Tarver & Calef 1988; Dlott & Fayer 1989; Trott & Renlund 1989; Delpuech 1989; Moore & Schmidt 1989; Gilman 1989;

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Lambrakos *et al.* 1989; Walker 1990*a*, *b*; Kim & Dlott 1990; Odiot 1990). Nevertheless, so far no detailed molecular interpretation of the mechanism has been advanced. Most of the investigators have tried to elucidate how the high parameters (pressure and density) of the explosive shock-compressed state affect the chemistry of the explosive molecules. But how the state is formed, namely the process of explosive shock-compression has not been taken into account. However, a fundamentally new conception of the problem has been developed in the High Dynamic Pressure Department (HDPD). The most important aspect of the conception is the notion of the opportunity for the excitation of complex explosive molecules and their non-equilibrium destruction within the detonation wave shock front. This idea has come into being to interpret the weak dependence of the detonation reaction time of condensed explosives on pressure, as revealed experimentally in the HDPD (Shvedov & Koldunov 1972). Then to substantiate the idea some special experiments have been performed consisting of shocking many organic compounds (Dremin & Babare 1982) as well as shock front structure calculations by non-equilibrium molecular dynamics, developed in the HDPD (Klimenko & Dremin 1978; Dremin & Klimenko 1981). As a result of the investigations, the detonation decomposition mechanism for condensed explosives appears to be in two stages: the first intrafront stage is non-equilibrium, the second afterfront stage is equilibrium. In accordance with the above mechanism, some active particles originate during the first stage inside the detonation wave shock front, on the one hand, and the low value of the activation energy for the reaction of the active particles with explosive molecules during the second afterfront stage, on the other, are responsible for the weak dependence of the detonation decomposition time for condensed explosives on pressure. Our investigations of the detonation decomposition mechanism of condensed explosives were based in the beginning on the Zeldovitch–von Neuman–Doring (ZND) theory of detonation developed in the 1940s. It is known that the Chapman–Jouguet theory deals only with the energetic characteristics of detonation waves. This theory does not take into account chemical reaction kinetics. However, the followers of the theory implied that explosives at detonation should transform into detonation products practically instantaneously; it might be during the process of their compression within the detonation wave shock front (Sokolic 1960). On the contrary, according to the ZND theory, explosives do not undergo any chemical change within the detonation wave shock front; they are only compressed within the front, and their decomposition takes place behind the front in the shock-compressed state under the effect of the shock compression high temperatures. The explosive decomposition zone is characterized by high pressure and has been called a chemical spike. The spike width in time t_{cs} is the time of the explosive transformation into the detonation products.

Detailed investigations of the detonation wave structure of condensed explosives have been performed at the Institute since the mid-1950s (Dremin *et al.* 1970). One may emphasize two basic results of these investigations. First, detonation waves with unstable fronts have been discovered. It has been revealed that the reaction originates and progresses non-simultaneously over the unstable detonation front surface. As a result the front looks like a seething uneven surface and flow behind the front becomes turbulent. Naturally, unstable detonation differs considerably from the one-dimensional ZND detonation. The physical model of unstable detonation has been elaborated elsewhere (Ribanin 1966; Trofimov & Dremin 1966) and therefore is not discussed here. In this paper only detonation waves with stable fronts are considered.

However, it should be noted that the instability is basically a property of weak liquid explosives. As far as powerful explosives are concerned, their detonation fronts are stable (Dremin 1983). It has been shown experimentally that the stable, smooth detonation front surface in liquid explosives reflects a beam of light like a mirror (Dremin & Savrov 1966). It means that the width of the shock discontinuity zone of the detonation wave is considerably smaller than the wave length of the visible light used in the experiments.

The second result of our investigations of the structure of the detonation wave front of condensed explosives is directly related to the problem of the present paper. It has been found that the detonation reaction time, that is, the duration in time t_{cs} of the chemical spike does not in practice depend on the structural features of the explosive charge (on explosive particle size, on the nature of the filler in the pores, on the explosive state, liquid or solid, and so on; Shvedov & Koldunov 1972). The time turned out to be a characteristic of the explosive itself. It should be pointed out that the time depends only on the detonation wave pressure, the dependence being rather weak. For example, t_{cs} for the detonation of TNT changes from *ca.* 1.5 μs to *ca.* 0.2 μs while the detonation wave pressure changes from 5 GPa to *ca.* 20 GPa. It is obvious that the temperature of the explosive changes considerably in this same pressure interval. If the shock decomposition mechanism were the same as the mechanism under ambient conditions, the change in t_{cs} would be much greater. However, experiment has shown that the dependence of t_{cs} on pressure is really weak.

In searching for an explanation for the weak dependence of t_{cs} (p), we surmize on the possible break-up of explosive molecules during the process of explosive compression within the detonation wave shock front. It has been assumed after the ZND detonation theory founders that detonation reactions proceed in a similar way to thermal explosions. (The considerations proposed below are also valid for chain explosion regularities.) It is known that during the explosion induction period (activation-stage time), which is the main part of the entire reaction time, only a small portion of the explosive decomposes but, the reaction later becomes of an explosive nature. It follows also from the theory that the activation-stage time of the explosive is a strong function of the chemical state and, on the contrary, the time for the final stages depends only weakly on the initial chemical state (Frank-Kamenecky 1987). Logically the surmise – whether the reaction tail is only registered at detonation – is based on understanding various features of the explosion, which are that only a small part of the explosive decomposes during the explosion activation-stage, and that the final stage of the explosion only depends weakly on the initial state. If this is so, it means that the process activation stage does not take place during the explosive's compression within the shock front. In essence it means the following. Events which occur during the induction period of a thermal explosion take up most of the time of explosion. However, in a detonation the events proceed an order of magnitude faster within the extremely narrow shock front zone. The final stages of both processes proceed rapidly with times which depend only weakly on the initial state of the explosive.

It should be mentioned that it has since become clear that some experimental results testify in favour of the surmize. The point is that an induction period for detonation has not yet been observed in any of the explosives investigated. One has always registered a very sharp decrease of pressure (or particle velocity) within the chemical spike (Dremin *et al.* 1970; Seits *et al.* 1989; Green *et al.* 1989). It corresponds to the maximum reaction behind the detonation wave shock front. Therefore, one could infer that the progress of the reaction had been conditioned by some preparatory process inside the shock front which is still beyond the reach of observation by present techniques. However, the possibility of the destruction of complex polyatomic molecules inside the shock front has been substantiated by special experiments in which samples of aromatic compounds (benzene, naphthalene, antracene) have been recovered and investigated after shocks of 1.1–1.5 GPa (100–200 °C) intensity. It was found that the compounds partly decomposed (*ca.* 1%); the destruction corresponding to the rupture of bonds of the benzene ring (see Dremin & Babare 1982 and references therein). It should be noted that at the same static pressure and temperature the compounds investigated never decompose entirely (Block *et al.* 1970). At normal pressure and high temperature they decompose without breaking the benzene ring. Chemical ring condensation and hydrogen elimination happen during the process. Complete graphitization occurs when the temperature reaches *ca.* 2000 °C (Magaril 1970). Taking the above facts into account, one can assume that the data testify in favour of the specific action of the shock wave front, that is, the shock front effect is responsible for the unusual destruction products of the aromatic compounds observed in the experiments.

Many explosives are complex organic compounds. Therefore, the decomposition of the explosives molecules inside the shock wave front seem to be a highly probable process. The portion decomposed is not known at present. Obviously it is some function of the wave intensity and can be significant at the detonation of powerful explosives in which the chemical spike pressure amounts to ten or more giga Pascals.

2. Results and Discussion

Naturally the question arises: What is the mechanism of the intrafront destruction of complex explosive molecules? Some of our papers have been devoted to the problem (Dremin 1973; Dremin & Shvedov 1976; Klimenko & Dremin 1980; Dremin 1987; Dremin *et al.* 1989). The ‘accumulation mechanism’ has been introduced for polyatomic molecules (Klimenko & Dremin 1980). The gist of the accumulation mechanism is as follows. Because of a tremendous rate of material loading inside the shock discontinuity zone (*ca.* 10^{-13} s), an excessively high translational temperature (overheat) appears at the beginning, and it is followed by the other-excitation of certain bonds. The overheat effect means a higher temperature level than the equilibrium one behind the front. The over-equilibrium translational temperature arises due to the fact that the kinetic part of the shock compression energy, which behind the shock front, is equally distributed among all the translational, vibrational and rotational degrees of freedom of the polyatomic molecules, is absorbed only by the translational degrees of freedom within the shock discontinuity zone. The maximum translational temperature overheat value is $T_{0h} = 2(n-1)(T-T_0)$, where n is the number of atoms in a molecule, and T_0 and T are equilibrium temperatures in front of and behind the shock wave front. It is obvious that due to the translational–vibrational relaxation process the energy of the translational degrees of freedom is redistributed to the vibrational degrees of freedom. At first, the energy flow will be directed towards those vibrational degrees of freedom which are most easily excited. If the energy flow towards these degrees of freedom exceeds the loss owing to the vibrational–vibrational relaxation process, they will over-excite and decompose faster in the shock front than behind it, where the state is one of equilibrium.

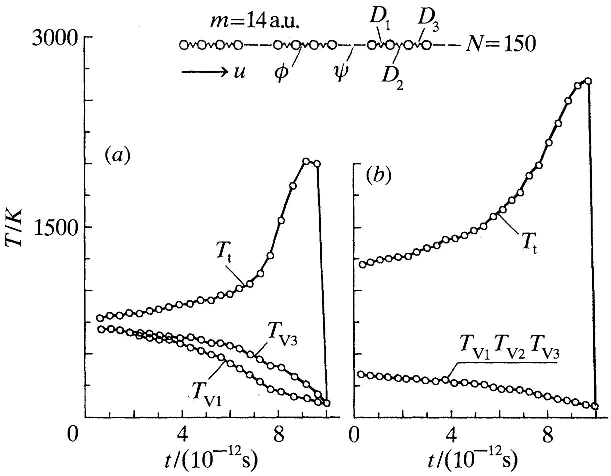

Figure 1. Translational temperature overheat for two sets of Morse potential parameter values, (*a*) and (*b*).

The considerations presented above are phenomenological. However, they have been verified by direct simulation of the process of excitation of polyatomic molecules inside the shock front (Dremin *et al.* 1989). The passage of the shock wave along a one-dimensional system consisting of tetratomic molecules has been calculated by the non-equilibrium molecule dynamic method developed in the HDPD (Klimenko & Dremin 1978; Dremin & Klimenko 1981). There were 150 molecules in the system (see figure 1). The exponential 6 potential

$$\psi(r) = \epsilon\left\{\frac{6}{\alpha-6}\exp\left[\alpha\left(-\frac{r}{\sigma}\right)\right]-\frac{\alpha}{\alpha-6}\left(\frac{\sigma}{r}\right)^{6}\right\},$$

with parameters $\epsilon = 50$ K, $\alpha = 13.0$ and $\sigma = 0.385$ nm, was used to describe the interaction of the various atoms in different molecules. The 'shock wave' was generated by the forced motion of the boundary molecule with a velocity of 1000 m s^{-1}. The motion, in essence, is the shock wave particle velocity U. The Morse potential

$$\phi(r) = D\{1-\exp[-\zeta((r/r_e)-1)]\}^2,$$

was used to describe the interaction of neighbouring atoms inside the molecules. The potential parameters were varied to change the characteristic frequencies of the corresponding bonds. The translational temperature T_t as well as the profiles of the vibrational temperatures T_{v_1}, T_{v_2} and T_{v_3} of the three bonds in the molecule have been calculated for two sets of Morse potential parameters values:

(*a*) $r_e = 0.11$ nm; $D_1 = 5.10^4$ K, $\zeta_1 = 2.5$; $D_2 = 7.10^4$ K, $\zeta_2 = 2.5$; $D_3 = 1.5\ 10^4$ K, $\zeta_3 = 1.5$; and

(*b*) $r_e = 0.11$ nm; $D_1 = D_2 = D_3 = 3.10^4$ K, $\zeta_1 = \zeta_2 = \zeta_3 = 2.5$.

One can see from the figure that the translational temperature overheat (which was predicted by Klimenko & Dremin (1980)) takes place in both cases. As to overheat of the first excited mode, it has not been observed in this numerical experiment. It is quite probable that the fact that the model is only one-dimensional is responsible for the negative result. However, this does not exclude the phenomenon for other complex molecules.

The origin of the translational temperature overheat is of great significance for understanding the mechanisms of the shock compression of complex molecules. The translational temperature overheat for molecules consisting of tens of atoms can be tens of thousands of degrees for shock wave intensities characteristic of the detonation of powerful explosives. At such temperatures the process of electronic excitation (activation energy 2–5 eV (Barltrop & Coyle 1975)) and even the thermal ionization process (activation energy 6–10 eV (Kondratiev 1974)) become possible inside the overheat zone.

Thus the non-equilibrium dissociation of polyatomic molecules inside the detonation wave shock front can proceed in three ways: through the accumulation mechanism, through electronic excitation as well as by thermal ionization. The accumulation mechanism has been developed before (Klimenko & Dremin 1980; Dremin *et al*. 1981; Dremin 1987). The decomposition mechanism through thermal ionization has not been investigated so far. As far as decomposition by electronic excitation is concerned, there are some experimental data supporting the mechanism. For example, hexogen (RDX, cyclotrimethylene trinitramine) samples recovered in special ampoules after the effect of shocks of 2.0–4.0 GPa have been investigated by X-ray photoelectron spectroscopy and paramagnetic resonance methods (Owens & Sharma 1979). It has been found that shock decomposition products of hexogen differ from those of its thermal decomposition, and are identical to those of the photochemical decomposition. The data testify in favour of decomposition by electronic excitation under the shock, because it is well known that the photochemical decomposition proceeds through the electronic excitation. It is interesting to note that the bonds in the hexogen molecule whose destruction is the origin of the recovered products, are identical to those excited bonds observed with high-speed Raman spectrometry in the shock-compressed state of hexogen (Delpuech *et al*. 1981; Dufort & Delpuech 1985; Delpuech 1989). The investigation has shown that approximately 100 ns behind the shock front of 10 GPa intensity the excited bonds are the bonds of the nitro-groups with the nitrogen of the ring.

Besides the aforesaid, the significant assumption of some preliminary electronic excitation of the molecules, introduced to explain the experimentally observed correlation between the electron structure of the molecules and their detonation ability should also be noted (Odiot *et al*. 1986). However, the assumption has been introduced without any reliable and convincing interpretation of the excitation. But from the results obtained by us it follows that it is just the high-energy molecular collisions inside the translational temperature overheat zone that are responsible for the excitation.

It is obvious that owing to the three aforementioned ways in which polyatomic molecules can be destroyed inside the detonation wave shock front, some active particle (radicals, ions and so on) will originate. The particles behave as if they had been injected into the compressed and heated explosive. Naturally, they influence the subsequent decomposition of the explosive. The explosive detonation decomposition proceeds behind the shock front (that is, during the second afterfront stage) in a state of chemical and thermodynamic equilibrium when the translational temperature overheat and overexcitation of certain bonds disappear. The interaction of the explosive molecules with the active particles originating inside the front (that is, during the first intrafront stage) is the main process behind the front. As a rule, the activation energy for this interaction is low (5–15 kcal mol^{-1}) (Kondratiev 1971). Because of the low value of the activation energy the decomposition proceeds extremely fast and is almost independent of the temperature change.

3. Conclusions

Thus, in accordance with our conception of the detonation decomposition mechanism of condensed explosives reaction is homogeneous rather than by the 'hot spot' mechanism. The mechanism regularities are the explosives characteristics. The decomposition process does not depend on the initial physical state (powder, pressed, cast or liquid) of the explosive charge. The process consists of two stages. The principal stage is the first intrafront stage. Its duration is equal to the time necessary for the most slowly excited bonds of complex polyatomic explosive molecules to be excited (*ca.* 10^{-10} s). The stage begins with the shock discontinuity zone of *ca.* 10^{-13} s time duration (Klimenko & Dremin 1978; Klimenko & Dremin 1980). The activation and non-equilibrium destruction of some explosive molecules takes place during the first stage and it leads to the fast transformation of the explosive into the final detonation products during the second stage. So, the first stage largely governs the detonation decomposition regularities of condensed explosives. Unfortunately this stage has not been investigated yet. Some Raman spectroscopy techniques have been developed by French (see Delpuech 1989 and references therein) and American scientists (see Schmidt *et al.* 1986*a*, *b* and references therein) for the investigation of shock processes. However, the spectral and time resolution of the techniques is for the present still insufficient. Indeed the spectral resolution of 10–20% and the time resolution of about 1 ns have been achieved. It is evidently too low a resolution for the study of the problem discussed since the entire time of the intrafront stage is even smaller. Therefore, one now needs elaboration of theoretical and experimental methods of at least picosecond resolving power. In that case one will have the possibility of studying the stage in detail. Obviously, until the problem is solved the chemical pathway controlling explosive energy release will be unknown.

In spite of the fact that the detonation decomposition mechanism of condensed explosives presented above is still mostly qualitative, it is possible even now to advance a certain hypothesis: the highest detonation ability corresponds to the explosive, the electronic structure of which changes at compression in such a way that it favours the explosive molecules electron excitation, as well as explosives in which molecule bonds excitation times differ considerably from each other. However, the problem needs some further investigation. Probably it will be solved when the chemical pathways of molecules inside the detonation wave shock front are studied from the very beginning of explosive loading.

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