УДК 614.833

D. Tregubov, *PhD, Associate Professor, Doctoral Student (ORCID 0000-0003-1821-822X)*
N. Minska, *DSc, Associate Professor, Associate Professor of the Department (ORCID 0000-0001-8438-0618)*
E. Slepuzhnikov, *PhD, Head of the Department (ORCID 0000-0002-5449-3512)*
Yu. Hapon, *PhD, Associate Professor of the Department (ORCID 0000-0002-3304-5657)*
D. Sokolov, *PhD, Associate Professor, Lecturer of the Department (ORCID 0000-0002-7772-6577)*
National University of Civil Defence of Ukraine, Kharkiv, Ukraine

SUBSTANCES EXPLOSIVE PROPERTIES FORMATION

Formation mechanisms of substances explosive properties based on the supramolecular structure prediction were studied and the appropriate analytical index was developed. The explosiveness index K_p was introduced based on the "melting ease" parameter, taking into account the equivalent length n_{Ceq} of the smallest supramolecular structure in the cluster form. The model performance was tested for the simplest explosive – nitromethane and similar compounds. It is shown that for values of the index $K_p<1$, combustible substances are not capable of the detonation, and for $K_p>1$, this index is proportional to the explosives detonation velocity. According to the presence of the explosive properties oscillation, using the example of alkanes homologous series, a connection was established with supramolecular structure features of the substance in the solid state. It is explained that such oscillation is the phenomenon consequence of molecules "evenity-oddity" in a homologous series and indicates the transition in the flame front of a substance to a solid state. It is proposed to consider the spread of the deflagration and detonation combustion as different mechanisms of clustering in the flame front. A model is considered that for combustible substances due to the pressures in the flame front, the condensation or peroxide clustering can occur in a similar way to their clustering during the phase transition to the solid state at the melting temperature, which involves the formation of supramolecular polymer-like structures that are easier to condense under increased pressure in flame front. It has been proven that the difference between the detonation process of combustible mixtures and the detonation of explosive compounds is the need for a phase transition to a condensed state in the substance clusters form or its peroxides.

Keywords: self-ignition, melting ease, explosion hazard index, cluster, equivalent length, detonation velocity

1. Introduction

Explosive processes are used with benefit in many industry fields and technology, but they can also be undesirable consequences of the careless handling of corresponding substances. Therefore, forecasting and prevention of such processes is an important and urgent matter. An explosive transformation of explosives (EXS) can be considered as an auto-ignition, which does not require a mixture with air and occurs at the expense of its own oxidizer by a chain mechanism. The auto-ignition basis is the "explosive" self-acceleration of oxidation reactions. According to the auto-ignition model as a thermal explosion, each part of the combustible air mixture is heated to a critical temperature, at which a slow oxidation reaction is initiated with the negligible heat release. But at the same time, simultaneous release of the heat occurs at all neighboring points, so heat loss does not occur, heat accumulates. This causes a sharp increase in the oxidation reaction rate with the combustion appearance at mixture each point without the combustion spread (or with extremely fast combustion spread). Such a process is similar to "cooperative": an instantaneous and jump-like formation or destruction of the substance supramolecular structure.

So, during an explosion, it is possible to predict the formation of an intermediate supramolecular unstable compound at the first stage, which decomposes into small components, followed by the oxidation reactions completion. The explosion pressure formation can be conditionally divided into two stages: the first is the many moles for-

mation of cold combustion products, that at the first moment occupy the volume that was previously occupied by 1 mole of the explosive substance; the second is the combustion heat transfer to combustion products and a proportional increase in the system temperature, and as a result, the pressure in it. This creates two coefficients of the pressure increase in the combustible substance primary volume of 1 mole.

Knowing the reasons for the formation of substance explosive properties, on the one hand, opens up new ways to develop explosive substances, on the other hand, it creates grounds for forecasting and preventing explosions. Therefore, it is urgent to carry out scientific research on the new methods development for taking into account the peculiarities of the substances structure in formation mechanisms of their explosive hazard, which will allow solving the specified issues more effectively.

2. Analysis of literature data and problem statement

A parameter of the auto-ignition possibility is the auto-ignition temperature (t_{ai}). t_{ai} at high pressure decreases sharply and for some substances can reach ambient temperatures. If the EX explosion is also considered as an auto-ignition, then this process must have the ability to initiate at normal ambient temperatures. At the same time, the initiation by impact or friction acts as a local increase in the pressure sufficient to initiate a certain cooperative process in the material entire volume. In this case, the determining parameter, as for t_{ai}, is the molecule equivalent length [1]. That is, a substance auto-ignition (thermal explosion), as well as the EXS explosion, should be characterized at the occurrence moment by a global clustering cooperative process with the intermediate state formation of a new form combustible substance. Such a cluster is not stable, therefore it can decompose with the combustion products formation simultaneously in the entire system, even without the flame front spread. This initiation effect of the substances cooperative self-organization can be caused by increased temperature of the system, pressure, sharp shock, etc. Thus, the problematic question regarding the EXS explosion mechanism by the auto-ignition has a solution in the plane of elucidating the structure and equivalent length of the corresponding cluster, for example, a dimer. Then this length takes into account all carbon atoms in the two molecules continuous chain, but without taking into account the dimer side part, if the clustering did not take place at the terminal carbon.

A similar technique has been implemented for calculating t_{ai} of benzene hydrocarbons with functional groups in the ortho-position (adjacent) [1, 2]: the molecule length is calculated taking into account only those benzene ring carbon atoms that are included in the shortest chain between these functional groups. That is, most of the benzene ring does not affect t_{ai}. The t_{ai} value for such a substance turns out to be much smaller than for a similar compound, but with functional groups in the meta- and para-positions (o-xylene – 460 ℃, m- and p-xylene – 530 ℃) [3]. But for other indicators calculations of the substance, such a principle was not used before.

For the solid and liquid states, we noted the substance formation not in the molecules form, but in the clusters form. This affects the value of the melting point t_{mp} and is taken into account by the "equivalent length" parameter of the cluster [4]. Therefore, an opportunity arises of creating calculations based on t_{mp}, as a parameter correlated with the substance supramolecular structure. The t_{mp} connection with explosive properties can be seen in the fact that the simplest hydro- and alkyl peroxides do not have a t_{mp} (freezing), because at the moment of the crystallization initiation they explode [5].

In studies of the detonation development of such explosive substances as methane

and nitromethane, their state in the compression wave is considered as a liquid or a solid [6]. Thus, it was established that in the presence of vacancies, nanopores or defects in the three-dimensional crystal of the nitromethane, the explosion initiation is facilitated. It is assumed that sufficient compression occurs in the shock wave front to achieve the molecules dissociation into atoms within pairwise intermolecular interactions with the further reactions initiation leading to the combustion products formation. At the same time, attention is drawn to the fact that temperature effects alone are not enough to the initiate detonation. The authors developed criteria for the homogeneous and heterogeneous detonation. For liquid EX, the homogeneous detonation model is acceptable [7]. The possibility of the molecular clustering in this model is indirectly accepted by taking into account the micropores presence in the explosive liquid, which creates centers of the heterogeneous detonation, which makes its occurrence 4 times easier. Under the dissociation condition, a plasma-chemical "hot spot" is formed in the nanopore. The authors [6] consider the such nanopores presence to be the basis of the increased susceptibility of some condensed systems to the detonation. An alkane cluster with nitro groups can be imagined as a macromolecule with an isomeric structure (for similar alkanes, the cluster structure is related to t_{mp} [4, 8]). But authors of [6] do not indicate the nature of the nanopores appearance in the liquid, calculations are performed for the molecular, not the cluster, substance state. Taking micropores into account in this model indirectly assumes the cyclic cluster presence. The liquid formation by direct gas condensation at the flame front is doubtful for substances such as methane. Also, the authors did not consider the oxygen role in considered processes.

Separate studies record EX supramolecular structures using X-ray structural analysis and spectroscopy [9]. For methyl nitrate, the presence of intermolecular bonds between O and N atoms of different molecules has been established. The authors predict the trimer existence with a length of 9 links, the middle of which is the N atom of the middle molecule. But this study does not offer taking methods into account the substance supramolecular structure to predict its explosive hazard.

Thus, the explosive processes occurrence in substances or combustible air mixtures can be explained by the supramolecular structures formation, they rearrangements, as well as condensation processes under high pressures. The scientific problem of taking into account the supramolecular structure of a substance in methods of predicting its explosive hazard needs to be solved. One of the ways to solve this problem is to conduct research to establish the relationship between characteristic parameters of substance's properties, a certain model of the supramolecular structure, and the substance's ability to undergo explosive transformations. Therefore, there is a need to establish the relationship between the substance t_{mp} and the fire and explosion hazard parameters for the solid and gaseous states.

3. The purpose and tasks of the research

This work purpose is a theoretical study of formation mechanisms of substances explosive properties and the search for a suitable general indicator.

To achieve the purpose, the following tasks are to be solved:

– establish the relationship between melting point and the explosive transformation of explosives cluster structure in the form of an explosiveness indicator;

– establish the difference in the origin of explosive transformation of explosives and alkanes explosive properties.

4. Research materials and methods

The supramolecular formations emergence in the state of "clusters" is considered, which determines and modulates parameters of the explosive and fire hazard of the substance in the solid state. In contrast to the monomeric state of the molecules, the "cluster" has a larger molecular weight M and a proportional increase in the t_{mp} [8]. It was also previously established that clustering due to the valence angle phenomenon in the carbon chain of a hydrocarbon molecule provides different principles of the complementation of "even" and "odd" molecules. This causes oscillation of the values in the homologous series for hydrocarbons most properties [4]. Corresponding regularities should also be manifested in the fire and explosion hazard parameters of substances and materials. Thus, this work is based on the search for ways to take into account the hydrocarbons supramolecular structure in the methods of forecasting certain parameters for substances in different aggregate states.

The changes indicator in the substance properties is t_{mp}, and the factor affecting this parameter is the equivalent length of the atoms chain in the cluster, similar to the determination of the molecule length in the calculating t_{ai} method [1]. The connection between the substance properties in the solid state and its fire-explosive properties in the gaseous state is assumed based on the fact that significant pressures are created at the flame front [6], which may be sufficient for the phase transition to the condensed state. We also mean that under conditions of increased pressure and in the case of the supramolecular structures formation, their condensation will be facilitated. For alkanes and their closest derivatives, the smallest supramolecular structures in the range from the dimer to the heptamer were previously found [4].

The research will be conducted by identifying the correlation presence between substance explosive fire properties and its t_{mp}, the equivalent length of the cluster (n_{Ceq}) and its M. At the same time, it is planned to use the previously developed "melting ease" index [4, 8] in the study.

5. Study of the relationship between the melting point and the explosives cluster structure

The decisive reason for the errors presence in the case of calculating the substances auto-ignition conditions is the methods inaccuracy of the determining the molecule equivalent length (ℓ_{eq}) as the substance smallest structural unit.

The substance cluster structure is most pronounced for the solid state. The size and structure of the corresponding cluster are determining factors in the substance properties formation, the most important of which is the t_{mp}. We assume that the mobility of a cluster of a given size and molecular weight is lost in a liquid at a given temperature. Previously, we established a relative indicator for solids "melting ease" n_M as a function of the cluster length and its equivalent molecular weight M [4, 8] $n_M = n_{Ceq} M^{0,2}$ (ℓ_{eq} – equivalent length of a complex molecule, n_{Ceq} – equivalent cluster length). With this indicator use, a generalized dependence was developed for the primary estimation of hydrocarbons t_{mp}: $t_{mp} = 101{,}85 \ln(n_M) - 452{,}37$.

The simplest hydrocarbon EXS is nitromethane. For a close compound, methyl nitrate, the intermolecular bonds existence between O and N atoms of different molecules has been proven [9], authors proposed a trimer model with an O-N-O intermolecular chain. In nitromethane, the frame-forming atoms are located in the same plane, so its molecules packing in the substance is considered as a layering of counter-directed disks [10]. Based on the analysis of nitromethane physicochemical characteristics [11]

© D. Tregubov, N. Minska, E. Slepuzhnikov, Yu. Hapon, D. Sokolov

and similar substances in composition or structure, it is possible to analyze the substances explosiveness origins in general, since t_{mp} is an indicator of the supramolecular formations presence.

For such an analysis, the chemical substance explosiveness indicator has been introduced; we are considering options: 1) $K_p = n_M/\mu$; 2) $K_{p\ eq} = n_M/\mu_{eq}$ (μ and μeq are the molecular weight of the monomer state and the cluster monomer basis without taking into account the side chains relative to the cluster linear structure, g/mol). That is, this parameter calculation is carried out either taking into account the molecule entire atomic mass, or the molecule base, in which we do not take into account the side functional groups atomic mass, for example, NO_2. At this stage of the analysis, it is assumed that if $K_p > 1$ – the substance has certain explosive properties, and if $K_p < 1$ – it does not. Calculated values of K_p and reference data on explosive substances indicators [12] are given in tab. 1. We take the cluster basis based on the analogy of a carbon chain, as in the case of alkanes clusters and their closest derivatives [4, 13].

The analysis of calculation results for methyl nitrate shows that cluster basis should be a molecule part with a length of "2". For example, a nitro group will not be taken into account in the clustering chain. Then it can be assumed that, as for alkanes, clustering occurs through a carbons chain or a C-O base, and nitro groups are lateral. On the other hand, N-O intermolecular bonds were found in the liquid methyl nitrate [9]. The model we used did not allow us to obtain calculations convergence for such the methyl nitrate structure in the trimer form (in order to reach the reference t_{mp} with this structure, we had to increase the cluster to a hexamer). In addition, this study is devoted to the substance liquid state, while the current study focuses on the parameter t_{mp}. And in the solid state, other supramolecular structures and intermolecular bonds presence is likely. Nevertheless, given the present study, there remains the possibility of an N-O molecular basis for the cluster formation. We assume in the calculation for clusters a linear regular structure, similar to polymers.

If we consider polymers as stable clusters, then a monomer is the same basic characteristic as a molecule. On this fact basis, it is possible to conduct a comparative analysis of nitrocellulose explosive properties based on the structure of the monomer. Depending on the accepted molecular weight of the entire polymer and the known t_{mp} nitrocellulose range, the calculations gave the K_p value significantly greater than "1", which indicates the power of this explosive.

A comparison of the substances K_p indicator under study with the detonation velocity (according to data [12]) allows us to conclude that there is a certain correlation: a higher K_p corresponds to a higher detonation velocity, substances with $K_p < 1$ are not capable of the detonation under the condition of the initiation by impact, friction or other initiating influence (correlation between K_p and IS or FS has not yet been found). For example, such substances as methane and propane are not capable of detonation initiation this type, but they are capable of detonation in long pipes, where several stages of the flame acceleration are successively implemented and ultra-high pressure conditions occur, which changes certain properties of these substances in the compression zone.

6. Study of the difference in the explosive properties origin of explosives and alkanes

The data in tab. 1 show that propane knock limits are narrowed by 18 % relative to its CLFP, while for methane such narrowing reaches 50 %. That is, propane is more prone to detonation.

Tab. 1. Properties of the investigated EXS [12] and the explosiveness index

EXS, state	Chem. formula, basis	μ	t_{mp}, °C	n_M	K_p	n_{Ceq}	K	Characteristics* of EXS
Nitromethane, NM, liquid	CH_3NO_2	61	-28,6	64,1	1,05			insensitive, indicators close to TNT, DV 6500 m/s, CPV 1059 l/kg, OB "-39,3%"
	1) CNO	45			**1,43**	18	**6**	
	2) CN	29			**2,21**	18	**9**	
	3) C	15			4,27	16	16	
Methylnitrite, gas	CH_3NO_2	61	-16	73,6	1,19			thermosensitive
	1) CONO	61			1,19	24	6	
	2) CON	45			**1,61**	21	**7**	
	3) CO	31			**2,34**	20	**10**	
	4) C	15			4,84	18	18	
Methylnitrat, liquid	CH_3NO_3	77	-82,5	37,8	0,49			powerful, very sensitive IS 0,2 Н·м, FS 353 H, explosiveness like nitroglycerin, DV 6300 m/s, CPV 873 l/kg, OB "-10,4%"
	1) CONO	61			0,62	12	3	
	2) CON	45			0,84	12	4	
	3) CO	31			**1,22**	12	**6**	
	4) C	15			2,52	10	10	
	5) CONONONOC	45			0,84	11	6	
Trinitrome-thane, low-melting solid	$CH(NO_2)_3$	151	26,4	110,0	0,73			sensitive to impact, quick heating, OB +37,1%
	1) ONCNO	72			**1,53**	30	**6**	
	2) NCN	40			**2,75**	27	**9**	
	3) C	13			8,46	22	22	
TNM, liquid	$C(NO_2)_4$	196	14,2	97,3	0,5			weak, insensitive, DV 6360 m/s, CPV 685 l/kg, OB +49%
	1) ONCNO	72			**1,36**	25	**5**	
	2) NCN	60			**1,63**	24	**8**	
	3) C	12			8,13	19	19	
Pentaerythritol tetranitrate, PETN, solid	$C(CH_2)_4(ONO_2)_4$	316	141,3	340	1,08			powerful (130 % of TNT), IS 3 Н·м, FS 45 H, DV 8500 m/s, CPV 780 l/kg, OB "-10,1%"
	1)ONOCCCONO	132			**2,58**	72	**8**	
	2) NOCCCON	100			3,4	70	10	
	3) OCCCO	72			4,72	65	13	
	4) CCC	40			8,5	60	20	
Erythritol tetranitrate, solid	$H_2(CHNO_2)_4$	302	61,3	155	0,51			powerful, sensitive 2 Н·м, DV 8100 m/s, CPV 704 l/kg, OB "-5,3 %"
	1)ONOCCONO	120			1,29	40	4	
	2) NOCCON	88			1,76	40	5	
	3) OCCO	62			**2,5**	36	**6**	
	4) CCCC	54			2,87	32	8	
Piroksilin, (Nitrocellulose) solid	$C_6H_7O_2(ONO_2)_3$	297	160-200	408-596	1,37-**2,01**	104	**26**	powerful, CPV 871 l/kg, IS 3 Н·м, FS 353 H, OB "-28,7%"
Methane (gas), state «liquid», «solid»	CH_4	16	-183	14,2	**0,88**			CLFP: 5–15 %; KL: 10–15 % (33 % of CLFP)
		32			0,44	2	**2**	
		96			0,15	6	**6**	
Propane (gas), state «liquid», «solid»	C_3H_8		-188	13,5	**0,31**	6	**2**	CLFP: 2,2–9,5 %; KL: 2,5–8,5% (82 % of CLFP)
		44						
		88			0,15			
Dimethyl peroxide, gas	$C_2H_6O_2$	62	-100	31,8	1,03	10	5	very sensitive
	1) CO		-50**	52,0	**1,68**	16	8	

* – for pure EXS without impurities; EXS – explosives; OB – oxygen balance; CPV – combustion products volume; TNT – trinitrotoluene, CLFP – concentration limits of the flame propagation, KL – knock limits, DV – detonation velocity, IS, FS – impact and friction sensitivity;

** – for dimethyl peroxide, the t_{mp} is not given in handbooks (it explodes during crystallization), so we set the conditional (expected) t_{mp}.

Indeed, during the study of the gas-air mixtures explosion under standard conditions, the pre-detonation distance for propane is shorter than that for methane. But the

© D. Tregubov, N. Minska, E. Slepuzhnikov, Yu. Hapon, D. Sokolov

K_p methane indicator is much closer to the critical explosiveness condition (under conditions of the high pressure, resistance to detonation is higher in propane [14, 15]). This may indicate the supramolecular structure transition of alkanes air mixtures under pressure to the state of an oxygen-containing unstable cluster, for example, of the peroxide type (alkyl peroxides are more stable if they have longer hydrocarbon radicals [1, 16]). That is, there are different mechanisms during the transition from flaming to detonation combustion.

The following difference was also found between methane and propane: starting with propane, the structure of all alkanes in solid and liquid states is dimeric, and for methane, t_{mp} correlates with the hexameric structure, and the boiling point t_{bp} – with the dimeric structure [13]. A broader analysis of differences in the fire hazard of substances of the alkanes homologous series is given in tab. 2.

Tab. 2. The explosion and fire hazard parameters of alkanes in the gaseous state

Alkan (M)	t_{ai}, °C	u_n, m/s	CLFP (range CLFP), %			KL, %	P_{max}, kPa	$V_{\Delta P}$, MPa/s	E_{min}, mJ
			air	oxygen	growth				
Methane (16)	537	0,338	5–15 (10)	5,1–61 (55,9)	5,6	10–15	706	18,0	0,28
Ethan (30)	515	0,476	2,9–15 (12,1)	3–66 (63)	5,2	-	675	17,2	0,24
Propane (44)	470	0,39	2,2–9,5 (7,3)	2,3–55 (52,7)	7,2	2,5–8,5	843	24,8	0,25
Butane (58)	405	0,45	1,8–9,1 (7,3)	1,8–49 (47,2)	6,5	-	843	-	0,25
Pentane (72)	286	0,39	1,47–7,7 (6,23)	-	-	-	850	-	0,22

Analysis of the alkanes explosiveness according to tab. 2 shows that the main factor affecting it from the above is t_{ai}. Also, many parameters show oscillation according to the "evenness-oddness" principle of the molecules chain, which is the solid state characteristic. In addition, it is clear that heavier alkanes have a higher the combustion molar heat Q_L. A decrease in t_{ai} and an increase in Q_L in the homologous series from methane to pentane act in antiphase on the fire hazard: with a larger t_{ai} and a smaller Q_L, the next layer heating, which is in contact with the flame front, and its ignition become more difficult. This is manifested in the form of a decrease in the flame propagation normal velocity u_n and an increase in the minimum ignition energy E_{min}, which is observed for methane among the closest homologues. An increase in the alkanes molar mass works to complicate combustion, since it requires oxygen greater consumption for complete oxidation. Therefore, for the stoichiometric methane-air mixture, in contrast to other alkanes, the smallest diffusion complications are observed due to the close to optimal ratio between the combustible substance and air oxygen and, accordingly, the fastest combustion. As a result of these factors combination, the explosion pressure and the rate of the explosion pressure increase for methane are greater than for ethane, but less than for propane. It is also noticeable for propane that the KL are only slightly narrower relative to the CLFP (coefficient of 0,82, against 0,5 for methane), the largest expansion of the explosive concentrations area was noted for the oxygen environment relative to air (the coefficient of 7,2, versus 5,6 for methane). Therefore, under normal conditions, the methane ability to accelerate the flame front to detonation is less than that of propane.

The data in tab. 2 also allow us to assume that even with u_n at least in the monomolecular layer on which the flame front acts, pressures are formed sufficient to transfer the substance (or the its clustering products in the high-molecular peroxides form) into a solid state, as evidenced by the u_n oscillation and other indicators. It was previously shown [4] that the properties oscillation in homologous series is characteristic of

the substance solid state as a result of a change in the clustering principle for "even" and "odd" molecules.

If we do not take into account the t_{mp} oscillation, then the dependence between $\Delta t=(t_{bp}–t_{mp})$ and the carbon atoms number n_C of the alkane in the homologous series has a clear linear character [4], which is not obeyed only for methane and ethane (for methane $\Delta t=21$ ºC, for propane $\Delta t=145,6$ ºC). This is explained by the fact that if the all alkanes t_{mp} correlates with the presence of dimeric structures, then the hexameric model acts for methane, and the trimer model for ethane [13]. The linearity of the dependence $\Delta t(n_C)$ indicates the storage of the alkanes cluster structure in the liquid state, but with the same principle of the substance supramolecular organization. The deviation from this dependence for methane and ethane indicates the supramolecular structure change under the condition of a phase transition to the dimer principle. Then a small difference between t_{bp} and t_{mp} indicates the multimolecularity of certain substance clusters in the solid state and its disappearance during the phase transition (the sublimation process may correspond to some substances in which $t_{mp}=t_{bp}$).

Under explosion conditions, methane in the shock wave compression zone is considered as a nanoporous liquid [6], which indirectly takes into account the proposed cluster structure in the hexamer form. In this work, a model is proposed in which methane molecules are emitted from nanopores walls with velocities and energies that are sufficient for the molecules dissociation into atoms. This place becomes a "hot spot" and initiates the further development of the explosive process. At the same time, the thermodynamic parameters of the dissociation initiation of liquid methane molecules are close to the homogeneous detonation parameters in liquid NM [6]. At a high detonation velocity (up to 3500 m/s in gases, 9000 m/s in liquids and solids [15]), pressure develops, which in liquids and solids reaches tens of GPa. In nitromethane, upon detonation initiation, an "ultra-fast" detonation wave with a pressure of up to 2,5 GPa is formed. The chemical reaction zone in the front of the such wave is very thin and cannot be fixed by experimental methods [6].

Most of considered substances are liquids or gases. If a quasi-liquid or quasi-solid substance is formed from a gas in a compression wave, then the supramolecular cluster structure should also be appropriate. Then a phase transition occurs in the shock wave front for such substances. The entire cluster unit of the substance takes part in the phase transition, even if it ceases to exist under new conditions. Such proportionality is characteristic of azeotropic mixtures. According to Dalton's law, it turns out that in the temperatures entire range, a cluster of a complete structure evaporates from the such solution, and then it condenses in this form.

The inflated t_{mp} presence for a given M determines the multimolecular cluster structure presence, which is observed for methane in the solid state (hexamer). Such a cluster can form in a knock shock wave and is an unstable substance, so it can emit one of its molecules with energy sufficient to destroy another molecule. Methane in a deflagration shock wave can pass into a quasi-liquid or even a quasi-solid state. In the liquid state, its t_{bp} correlates with the dimer structure, which does not form porous structures and the detonation does not occur. But at elevated initial pressures in the shock wave, conditions are created for reaching a quasi-solid state according to the hexamer principle, for which a porous structure can already be modeled.

If we summarize the above, following phase transformations or supramolecular rearrangements can be considered in the flame front depending on the pressure (defla-

© D. Tregubov, N. Minska, E. Slepuzhnikov, Yu. Hapon, D. Sokolov

gration or detonation mechanism): volumetric peroxide cluster, condensation of a combustible substance in the form of droplets (the formation of diamond-like nanostructures is observed in the flame detonation front [6]), combustible substance or peroxide cluster condensation in the film form. For methane, it is possible to form the smallest clusters in the form of a dimeric or hexameric structure.

Thus, for the gaseous state of a combustible substance, the fundamental difference in the explosiveness formation, in contrast to explosives, is the need for a phase transition to a condensed state in the clusters form of the substance or its peroxic intermediate formations, as well as the appropriate conditions presence.

7. Discussion of the results of formation peculiarities of substance explosive properties

The developed model based only on t_{mp} and M allows to predict the cluster equivalent length, and with it the clustering degree. In explosives, various functional groups of molecules participate in the formation of the clusters instability [17]. Thus, for methyl nitrate, the molecule part with a length of "2" is taken as the cluster basis. It can be suggested that clustering, as in the alkanes case [8], occurs through a carbon chain or "C-O" basis, then nitro groups become lateral. The developed index of the explosiveness can be calculated in two ways: 1) for M of the molecule; 2) for M of the cluster basis as the molecule length-forming part. A small value of the indicator "1" for a large value of the indicator "2" partially indicates the explosive sensitivity; indicator "2" indicates the substance explosive power (detonation velocity). For this study, the ratio "2" turned out to be more interesting, but it does not reflect the ability of air-combustible mixtures to detonate (for alkanes, it may be related to the tendency to detonation in a compressed quasi-solid state). Calculation principle "1" does not separate combustible and explosive substances.

The overestimated methane t_{mp} (relative to ethane and propane) can be explained by taking into account the length and molecular weight of the cluster in the hexamer form. The basis of the molecule performs the function of the substance length property (at this stage it is not important what atoms it consists of), as well as in the calculation of K_p, which takes into account the equivalent molecular weight of the basis, which already requires accurate knowledge of its elemental composition. Note that for different variants of the explosive substances cluster structure, close values of its equivalent length were obtained. In the developing process of the t_{mp} dependence on the substance structure, it was established that side chains in the cluster linear structure have little influence on this parameter [13], therefore, when determining K_p, calculations were made both for the substance molecular weight and the equivalent molecular weight without taking into account side chains. The developed model on the basis of only t_{mp} and M allows to predict the cluster equivalent length, and with it the clustering degree K (which for the more probable bases of the most substances turned out to be in the range of 6–9, which is highlighted in bold in tab. 1). Also note that K_p was calculated for linear structure clusters. At the same time, during the explosive clusters cyclization, sometimes the end groups of linear clusters can become lateral, which will increase K_p.

Thus, the combustible substances explosion and fire-hazardous properties in all aggregation states are in some way related to their properties in the solid state. For gases and liquids, this is explained by the fact that the peroxide clustering of their molecules in the flame occurs in a similar way to their clustering at t_{mp}. This involves the supramolecular polymer-like structures formation, which are easier to condense under in-

creased pressure in the flame front. Such a model explains the various parameters oscillation of the explosion and fire hazard, which are considered on the example of the alkanes homologous series. To analyze this danger, it is proposed to use the parameters "cluster equivalent length" (analogous to the t_{ai} calculation [1]) and "melting ease". The given model also makes it possible to explain anomalies in the methane propensity to detonate at different pressures, as well as the velocity oscillation of the detonation wave front (as a layer-by-layer formation of clusters).

The n_M indicator needs to be improved, as it does not allow for an accurate determination of the coordination number. The research was carried out on the analysis basis of hydrocarbons homologous series with n_C up to 15 and the "melting ease" index up to 180, therefore, calculations using the specified methods for substances based on molecules with more carbon atoms are an extrapolation, since the developed logarithmic dependence for t_{mp} [8] begins to give inflated values. In addition, the scheme for the cluster bases selection with the determination of the corresponding K_p indicator and the clustering coefficient is currently of a conditional nature. Also, the method of taking into account the properties of isomeric structure substances for calculating the K_p indicator has not yet been developed.

8. Conclusions

1. It was established that the explosive properties of combustible substances in all aggregation states are related to their properties in the solid state. Therefore, based on the "melting ease" parameter, a methodology for calculating the explosiveness index Kr has been developed. The "melting ease" parameter calculation, in turn, is based on the value of the expected equivalent length of the smallest supramolecular structure in the cluster form and its molecular weight. Based on the explosiveness index calculation for the simplest hydrocarbon explosive – nitromethane and compounds similar to it, including methane, with reference to the value of the cluster basis molecular weight, it was established that explosive compounds have $K_p>1$, and simply combustible compounds have $K_p<1$. At the same time, the K_p indicator is proportional to the value of the explosives detonation velocity.

2. It was established that the fundamental difference between the explosiveness formation for the alkanes gaseous state and explosives is the need for a phase transition to a condensed state in the clusters form of the substance or its peroxide intermediates under the increased flame front pressure. These conclusions were obtained on the analysis basis of changes in fire hazard indicators in the alkanes homologous series: the indicators oscillation, which is characteristic of solid substances due to the molecules "evenity-oddity" phenomenon during the clusters formation, different changes in the width of explosive concentrations areas in air and oxygen, as well as detonation conditions. Thus, the explosiveness range of methane in oxygen relative to air expands by 5,6 times compared to 7,2 for propane, the narrowing coefficient of knock limits relative to the concentration limits of flame propagation for methane is 0,5, and for propane – 0,82. That is, at standard atmospheric pressure, propane has a greater tendency to the detonation, which is explained by the more difficult conditions for the methane transition into a liquid condensed state, i.e., the supramolecular structures remain dimeric. At higher atmospheric pressure, propane is already less prone to the detonation, which is explained by the possibility of the transition to a solid condensed state, where methane has a hexamer structure.

References

1. Glassman, I., Yetter, R. A. (2014). Combustion. London: Elsevier. doi:10.1016/C2011-0-05402-9

2. Goldsborough, S., Hochgreb, S., Vanhove, G., Wooldridge, M., Curran, H., Sung, C.-J. (2017). Advances in rapid compression machine studies of low-and intermediate-temperature autoignition phenomena. Progress in Energy and Combustion Science, 63, 1–78. doi: 10.1016/j.pecs.2017.05.002

3. Sharma, R. K. (2020). A violent, episodic vapour cloud explosion assessment: Deflagration-to-detonation transition. Journal of Loss Prevention in the Process Industries, 65, 104086. doi: 10.1016/j.jlp.2020.104086

4. Tregubov, D., Tarakhno, O., Deineka, V., Trehubova, F. (2022). Oscillation and Stepwise of Hydrocarbon Melting Temperatures as a Marker of their Cluster Structure. Solid State Phenomena, 334, 124–130. doi: 10.4028/p-3751s3

5. Olson, A. S., Jameson, A. J., Kyasa, S. K., Evans, B. W., Dussault, P. H. (2018). Reductive Cleavage of Organic Peroxides by Iron Salts and Thiols. ACS omega, 3(10), 14054–14063. doi: 10.1021/acsomega.8b01977

6. Kaim, S. D. (2016). Korelyatsiyna teoriya nanokrapel′ i nanopor. Odesa: VMV. Retrieved from:http://irbis-nbuv.gov.ua/publ/REF-0000644666

7. Partom, Y. (2013). Revisiting shock initiation modeling of homogeneous explosives. Journal of Energetic Materials, 31(2), 127–142. doi: 10.1080/07370652.2012.674626

8. Trehubov, D., Sharshanov, A., Sokolov, D., Trehubova, F. (2022). Forecasting the smallest super molecular formations for alkanes of normal and isomeric structure. Problems of Emergency Situations, 35, 63–75. doi: 10.52363/2524-0226-2022-35-5

9. Reichel, M., Krumm, B., Vishnevskiy, Yu., Blomeyer, S., Schwabedissen, J., Stammler, H.-G., Karaghiosoff, K. (2019). Solid-State and Gas-Phase Structures and Energetic Properties of the Dangerous Methyl and Fluoromethyl Nitrates. Angewandte Chemie International Edition, 58(51), 18557–18561. doi: 10.1002/anie.201911300

10. Gubbins, K. (2016). Perturbation theories of the thermodynamics of polar and associating liquids: A historical perspective. Fluid Phase Equilibria, 416, 3–17. doi: 10.1016/j.fluid.2015.12.043

11. Shrestha, K., Vin, N., Herbinet, O., Seidel, L., Battin-Leclerc, F., Zeuch, T., Mauss, F. (2020). Insights into nitromethane combustion from detailed kinetic modeling – Pyrolysis experiments in jet-stirred and flow reactors. Fuel, 261, 116349. doi: 10.1016/j.fuel.2019.116349

12. Meyer, R., Köhler, J., Homberg, A. (2016). Explosives. Weinheim: Wiley-VCH. ISBN: 9783527689613

13. Hapon Yu., Tregubov D., Slepuzhnikov E., Lypovyi V. (2022). Cluster Structure Control of Coatings by Electrochemical Coprecipitation of Metals to Obtain Target Technological Properties. Solid State Phenomena, 334, 70–76. doi: 10.4028/p-4ws8gz

14. Oran, E. S., Chamberlain, G., Pekalski, A. (2020). Mechanisms and occurrence of detonations in vapor cloud explosions. Progress in Energy and Combustion Science, 77, 100804. doi: 10.1016/j.pecs.2019.100804

15. Hou, Sh., Liu, Y., Wang, Zh., Jing, M., Zhang, Y., Zhang, B. (2022). The potential for deflagration to detonation transition (DDT)-Lessons from LPG tanker transportation accident. Journal of Loss Prevention in the Process Industries, 80, 104902. doi: 10.1016/j.jlp.2022.104902

16. Boot, M., Tian, M., Hensen, E., Mani Sarathy, S. (2017). Impact of fuel molecular structure on auto-ignition behavior: design rules for future high performance gasolines. Progress in Energy and Combustion Science, 60, 1–25. doi: 10.1016/j.pecs.2016.12.001

17. Paraskos, A. J. (2017). Energetic Polymers: Synthesis and Applications. Challenges and Advances in Computational Chemistry and Physics, 25, 91–134. doi: 10.1007/978-3-319-59208-4

Д. Г. Трегубов, *к.т.н., доцент, докторант*
Н. В. Мінська, *д.т.н., доцент, доц. каф.*
Є. Д. Слепужніков, *к.т.н., нач. каф.*
Ю. К. Гапон, *к.т.н., доц. каф.*
Д. Л. Соколов, *к.т.н., доцент, викл. каф.*
Національний університет цивільного захисту України, Харків, Україна

ФОРМУВАННЯ ВИБУХОНЕБЕЗПЕЧНИХ ВЛАСТИВОСТЕЙ РЕЧОВИН

Досліджено механізми формування вибухових властивостей речовин на підставі прогнозування надмолекулярної будови та розроблено відповідний аналітичний показник. Впроваджено показник вибуховості $K_р$ на підставі параметру «легкість плавлення» за еквівалентною довжиною $n_{Секв}$ найменшої надмолекулярної будови у вигляді кластеру. Проведено перевірку роботи моделі для найпростішої вибухової речовини – нітрометану та схожих на нього сполук. Показано, що за значень $K_р<1$ – горючі речовини не здатні до детонації, а за $K_р>1$ даний показник є пропорційним до швидкості детонації вибухових речовин. Встановлено, що вибухонебезпечні властивості горючих речовин певним чином пов'язані з особливостями їх надмолекулярної будови у твердому стані. Продемонстровано осциляційність різних параметрів вибухонебезпеки, які розглянуто на прикладі гомологічного ряду алканів. Пояснено, що це є наслідком явища «парності-непарності» молекул у гомологічному ряду та свідчить про перехід у фронті полум'я горючого або первинних продуктів його окиснення у твердий стан за рахунок утворення більш масивних кластерів та наявності збільшених тисків. Запропоновано розглядати поширення дефлаграційного та детонаційного горіння як різні механізми кластеризації у фронті полум'я. Розглядається модель, що для горючих речовин за рахунок тисків у фронті полум'я може відбуватись конденсація або перекисна кластеризація схожим шляхом до їх фазового переходу у твердий стан за температури плавлення, що передбачає утворення надмолекулярних полімероподібних структур, яким легше сконденсуватися за збільшеного тиску у фронті полум'я. Доведено, що відмінність процесу детонації горючих сумішей від детонації вибухових сполук полягає у необхідності фазового переходу у конденсований стан у вигляді кластерів речовини або її перекисів.

Ключові слова: самоспалахування, легкість плавлення, показник вибухонебезпеки, кластер, еквівалентна довжина, швидкість детонації

Література
1. Glassman I., Yetter R. A. Combustion. London: Elsevier, 2014. 757 p. doi: 10.1016/C2011-0-05402-9

2. Goldsborough S., Hochgreb S., Vanhove G., Wooldridge M., Curran H., Sung C.-J. Advances in rapid compression machine studies of low-and intermediate-temperature autoignition phenomena. Progress in Energy and Combustion Science. 2017. Vol. 63. C. 1–78. doi: 10.1016/j.pecs.2017.05.002

3. Sharma R. K. A violent, episodic vapour cloud explosion assessment: Deflagration-to-detonation transition. Journal of Loss Prevention in the Process Industries. 2020. Vol. 65. P. 104086. doi: 10.1016/j.jlp.2020.104086

4. Tregubov D., Tarakhno O., Deineka V., Trehubova F. Oscillation and Stepwise of Hydrocarbon Melting Temperatures as a Marker of their Cluster Structure. Solid

State Phenomena. 2022. Vol. 334. P. 124–130. doi: 10.4028/p-3751s3

5. Olson A. S., Jameson A. J., Kyasa S. K., Evans B. W., Dussault P. H. Reductive Cleavage of Organic Peroxides by Iron Salts and Thiols. ACS omega. 2018. Vol. 3(10). P. 14054–14063. doi: 10.1021/acsomega.8b01977

6. Каім С. Д. Кореляційна теорія нанокрапель і нанопор. Одеса: ВМВ, 2016. 95 с. URL: http://irbis-nbuv.gov.ua/publ/REF-0000644666

7. Partom Y. Revisiting shock initiation modeling of homogeneous explosives. Journal of Energetic Materials. 2013. Vol. 31(2). P. 127–142. doi: 10.1080/07370652.2012.674626

8. Трегубов Д. Г., Шаршанов А. Я., Соколов Д. Л., Трегубова Ф. Д. Прогнозування найменших надмолекулярних структур алканів нормальної та ізомерної будови. Проблеми надзвичайних ситуацій. 2022. № 35. С. 63–75. doi: 10.52363/2524-0226-2022-35-5

9. Reichel M., Krumm B., Vishnevskiy Yu., Blomeyer S., Schwabedissen J., Stammler H.-G., Karaghiosoff K. Solid-State and Gas-Phase Structures and Energetic Properties of the Dangerous Methyl and Fluoromethyl Nitrates. Angewandte Chemie International Edition. 2019. № 58(51). P. 18557–18561. doi:10.1002/anie.201911300

10. Gubbins K. Perturbation theories of the thermodynamics of polar and associating liquids: A historical perspective. Fluid Phase Equilibria. 2016. Vol. 416. P. 3–17. doi: 10.1016/j.fluid.2015.12.043

11. Shrestha K., Vin N., Herbinet O., Seidel L., Battin-Leclerc F., Zeuch T., Mauss F. Insights into nitromethane combustion from detailed kinetic modeling – Pyrolysis experiments in jet-stirred and flow reactors. Fuel. 2020. Vol. 261. P. 116349. doi:10.1016/j.fuel.2019.116349

12. Meyer R., Köhler J., Homberg A. Explosives. Weinheim: Wiley-VCH, 2016. 442 p. ISBN: 9783527689613

13. Hapon Yu., Tregubov D., Slepuzhnikov E., Lypovyi V. Cluster Structure Control of Coatings by Electrochemical Coprecipitation of Metals to Obtain Target Technological Properties. Solid State Phenomena. 2022. Vol. 334. P. 70–76. doi: 10.4028/p-4ws8gz

14. Oran E., Chamberlain G., Pekalski A. Mechanisms and occurrence of detonations in vapor cloud explosions. Progress in Energy and Combustion Science. 2020. Vol. 77. P. 100804. doi: 10.1016/j.pecs.2019.100804

15. Hou Sh., Liu Y., Wang Zh., Jing M., Zhang Y., Zhang B. The potential for deflagration to detonation transition (DDT)-Lessons from LPG tanker transportation accident. Journal of Loss Prevention in the Process Industries. 2022. Vol. 80. P. 104902. doi: 10.1016/j.jlp.2022.104902

16. Boot M., Tian M., Hensen E., Mani Sarathy S. Impact of fuel molecular structure on auto-ignition behavior: design rules for future high performance gasolines. Progress in Energy and Combustion Science. 2017. Vol. 60. P. 1–25. doi: 10.1016/j.pecs.2016.12.001

17. Paraskos A. J. Energetic Polymers: Synthesis and Applications. Challenges and Advances in Computational Chemistry and Physics. 2017. Vol. 25. P. 91–134. doi: 10.1007/978-3-319-59208-4