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ABSTRACT

Among 28 polynitroarenes and their derivatives relationships are demonstrated between their impact, E_{dr}, and electric spark, E_{ES}, sensitivities, on the one hand, and the volume heats of their explosion, ρQ_{max}, and their enthalpies of formation, ΔH_{form}, on the other. While the impact sensitivity increases with increasing values of the ρQ_{max} variable (with certain exceptions), a change in the electric spark sensitivity in the aforesaid sense leads mostly to a decrease in this sensitivity. Taking the energy content of molecules, represented by the ΔH_{form} values, instead of the heat of explosion, gives ambiguous linear relationships for impact sensitivity. The semi-logarithmic relationship between the E_{ES} and ΔH_{form} values divides into sub-relationships. Both the impact and electric spark sensitivities increase with an increase in the ΔH_{form} values, with several exceptions in both these cases. From the results obtained is possible to see that it is necessary to distinguish between the influence of performance and the influence of energetic content of the energetic materials on their initiating reactivity.

Introduction

Since 2000, a considerable amount of attention has been paid to the relationship between sensitivity (initiation reactivity) and performance of energetic materials (Keshavarz and Klapötke 2017; Licht 2000; Politzer and Murray 2003; Zeman 2007; Zeman and Jungova 2016; Zeman et al. 2018b). The overriding interest in this area has been the study of impact sensitivity (Licht 200, Keshavarz and Klapötke 2017; Politzer and Murray 2003, 2016; Zeman 2007; Zeman and Jungova 2016; Zeman et al. 2018a), but recently attention has turned to a study of sensitivity to electric spark (Zeman, Friedl, and Kočí 2007b; Zeman et al. 2006b; Zeman and Jungova 2016) and, to a lesser degree, to sensitivity to friction (Zeman and Jungova 2016; Zeman et al. 2018b). In theoretical treatment of sensitivity in general, the quantum-chemical approaches have been the most used (Politzer and Murray 2003, 2016; Zeman 2007; Zeman and Jungova 2016). Prediction models have also been built based on statistical processing of sensitivity data (Keshavarz and Klapötke 2017). A summary of the situation in this area up to2016 is provided by Zeman and Jungova (2016).

Based on an analysis of a considerable amount of experimental data Licht (Licht 2000) has stated that a high level of performance is usually accompanied by an enhanced sensitivity and that insensitive explosives do not exhibit top performance. It has subsequently been shown that this can be considered as a general rule, but the author has stated that this result has not yet been documented by theory (Licht 2000). It has already been shown that this is true with nitramines and PBXs containing them, with the exception of pure 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5-trinitro-1,3,5-triazepane (TTAZ), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) and ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazawurtzitane (ε-HNIW, with impact sensitivity above 9 J) (Elbeih et al. 2012; Zeman and Jungova 2016). Even for pure nitramines, unambiguous

relationships have not been obtained. They have been differentiated into a group for linear and a group for cyclic nitramines (Zeman and Jungova 2016), which is understandable from the point of view of the intermolecular forces acting in the molecular crystals of the individual groups (Zeman and Krupka 2003). It is also understandable that it is impossible to describe this relationship for chemically different energetic materials by using a single function, as Politzer and Murray (2016) have explained.

For a study of initiation reactivity, we have used a set of linear, cyclic, and crowded nitramines, because such compound shave been extensively studied and they have relatively simple molecular structures (Zeman 2006, 2007; Zeman and Jungova 2016). The present paper intends to show how the problem of the "performance-sensitivity" relationship manifests itself with structurally more complicated compounds, such as the polynitroarenes. For a better illustration, a similar analysis has been applied not only to impact sensitivity but also to the sensitivity of polynitroarenes to an electric spark. Last but not least, this work intends to show what influence exists of the energy content in molecules of the polynitroarenes used in the study on both these sensitivities.

Data Sources

The Polynitroarenes in This Study

Chemical names, code designations, theoretical maximal densities (TMD), enthalpies of formation, calculated maximal heats of detonation, Q_{max}, and detonation velocities, D, impact sensitivity (expressed as a drop energy, E_{dr}), and sensitivity to electric spark (expressed as spark energy, E_{ES}) of the polynitroarenesin this study are summarized in Table 1. For a better illustration, their structural formulae are presented in Scheme 1.

Performance and sensitivity characteristics

Detonation parameters D and Q_{ma} were calculated by the well-known method described here (Kamlet and Jacob 1968), the results from which perfectly correspond to the experimental values and also to the calculation results from the CHEETAH and Explo5 software (Elbeih et al. 2010). Enthalpies of formation, as representative of energetic content of the energetic materials (EMs), studied (Zeman et al. 2019) were taken from the literature (see in Table 1).

Values of the impact sensitivity, expressed as drop energy, E_{dr}, for a 50% probability of initiation, were taken from the literature (Flippen-Anderson et al. 1992; Mayer, Köhler, and Homburg 2002; Storm, Stine, and Kramer 1990); if they were originally published using the *cm* unit, they were recalculated to J units for unification when hammers with different weights were used.

Electric spark sensitivity, expressed as the energy of electric spark, E_{ES}, for a 50% probability of initiation, has been determined by the method described in two papers (Zeman, Kočí, and Majzlík 2007a; Zeman, Friedl, and Kočí 2007b) in which the sample measured is in direct contact with the electrodes (Zeman, Kočí, and Majzlík 2007a).

The sensitivities of polynitrocompounds are expected to increase with decreasing absolute values of the net charges on the nitrogroups; from the viewpoint of electronic structure, the lowest absolute value of Q_{NO2} corresponds to the most reactive nitro group Q_{NO2} (Zhang et al. 2005). The Q_{NO2} values for the polynitroarenes investigated here were obtained from the work described in the paper (Zeman, Friedl, and Kočí 2007b) by means of a Mulliken population analysis of electron densities obtained at *ab initio* level by the DFT B3LYP/6-31G(d,p) method without frequency analysis. The selected relevant data for this paper are summarized in Table 2; the selection was performed not only on the basis of their own values of Q_{NO2} but also on their correlations with electric spark sensitivity in the paper mentioned (Zeman, Friedl, and Kočí 2007b) and partially also with activation energies of thermal decomposition in another paper by the same authors (Zeman, Friedl, and Roháč 2006a).

Table 1. A survey of the studied polynitroarenes, their maximal theoretical crystal densities, enthalpies of formation, calculated detonation parameters by the Kamlet & Jacob method (Kamlet and Jacob 1968), impact sensitivities and sensitivities to electric spark (Zeman, Friedl, and Kočí 2007b).

Data No.	Chemical name	Code designation	Crystal density maximal ρ (g.cm^{-3})	Enthalpy of formation ΔH_{form} (kJ mol^{-1})	Ref	Calculated parameters of detonation for TMD D (km s^{-1})	Q_{max} (MJ kg^{-1})	Impact sensitivity E_{dr} (J)	Ref	Electric spark sensitivity[n] E_{ES} (mJ)
1	1,3-Dinitrobenzene	1,3-DNB	1.567	−26.0	a	6.52	5069	39.0	h	256.7
2	1,3,5-Trinitrobenzene	TNB	1.688	37.6	a	7.42	6038	24.6	i	109.7
3	2,2',4,6,6'-Hexanitrobiphenyl	HNBP	1.74	61.1	b	7.49	5927	20.9	i	288.9
4	2,4,6,4',6'',4''',6'''-Octanitro[1,1',3',1'']-terphenyl	ONT	1.80	82.4	b	7.46	5735	15.7	i	128.9
5	2,2'',4,4'',6,6'-Nonanitro[1,1',3',1'']-terphenyl	NONA	1.78	109.6	b	7.60	5955	9.1	i	86.5
6	2,2'',2''',4,4',4'',4'''-Dodecanitro-[1,3',1,1'']quaterphenyl	DODECA	1.81	211.7	b	7.70	5993	9.8	i	157.8
7	2,4,6-tris(2,4,6-Trinitrophenyl)-[1,3,5]triazine	TPT	1.67	306.3	b	7.08	5580	22.8	i	150.0
8	1,4,5-Tetranitronaphthalene	TENN	1.80	54.0	b	7.31	5580	24.5	i	95.0
9	N,N-bis(2,4-Dinitrophenyl)-2,4,6-trinitroaniline	NTFA	1.77	−201.0	c	7.01	4883	8.9	j	50.2
10	1,3,7,9-Tetranitro[1,2,3]benzotriazolo[2,1-d]-[1,2,3]benzotriazole-5,11-diium-6,12-diide	TACOT-Z	1.85	462.3	b	7.43	5482	69.0	i	
11	1-(2,4,6-Trinitrophenyl)-5,7-dinitrobenzotriazole	BTX	1.74	296.6	b	7.34	5606	6.62	k	135.0
12	2,2',4,4',6,6'-Hexanitroazobenzene	HNAB	1.775	284.1	b	7.73	6053	7.85	l	112.0
13	1-Methyl-2,4,6-trinitrobenzene	TNT	1.654	−50.2	b	7.04	5478	39.2	l	111.8
14	1,3-Dimethyl-2,4,6-trinitrobenzene	TNX	1.60	−100.4	a	6.67	5139	10.5	i	
15	1,3,5-Trimethyl-2,4,6-trinitrobenzene	TNMs	1.48	−127.6	a	6.17	4928	20.4	l	292.7
16	3,3'-Dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl	BITNT	1.75	−14.5	d	7.31	5592	33.1	i	206.7
17	2,2',4,4',6,6'-Hexanitrobibenzyl	DPE	1.789	−43.5	e	7.47	5838	28.1	i	167.0
18	1,1'-Methylenebis(2,4,6-trinitrobenzene)	DPM	1.75	14.22	d	7.41	5733	28.6	i	136.4
19	2,2',4,4',6,6'-Hexanitrostilbene	HNS	1.74	78.2	b	7.28	6045	11.5	i	
20	1-Amino-2,4,6-trinitrobenzene	PAM	1.762	−74.5	a	7.51	4432	43.4	i	156.7
21	1,3-Diamino-2,4,6-trinitrobenzene	DATB	1.837	−114.2	b	7.68	4138	78.5	i	175.0
22	2,4,6-Triamino-1,3,5-trinitrobenzene	TATB	1.938	−139.75	f	7.95	4560	114.3	i	293.3
23	2,2',4,4',6,6'-Hexanitrodiphenylamine	DPA	1.77	41.42	a	7.59	4810	11.8	i	103.0
24	2,6-bis(Picrylamino)-3,5-dinitropyridine	PYX	1.77	87.4	b	7.48	5780	15.4	i	
25	1-Hydroxy-2,4,6-trinitrobenzene	PA	1.767	−214.16	a	7.57	5376	21.3	i	115.5
26	1,3-Dihydroxy-2,4,6-trinitrobenzene	TNR	1.83	−523.0	g	7.56	4568	10.5	i	
27	1-Methyl-3-hydroxy-2,4,6-trinitrobenzene	TNCr	1.688	−252.3	a	7.14	5095	46.8	i	
28	1-Methoxy-2,4,6-trinitrobenzene	TNA	1.61	−151.9	a	7.05	5509	47.1	i	

Notes – data taken from:

a Stull et al. 1969; b) Prince 1976; c) Zhukov 2000; d) Keshavarz 2009; e) Bathlet et al. 2004; f) Dobratz 1994; g) Fukuyama et al. 1986; h) Meyer et al. 2002; i) Storm et al. 1990; j) Zeman et al. 2006; k) Flippen at al. 1992; l) Kamlet and Adolph 1979; m) Bliss et al. 1991; n) Zeman et al. 2007b.
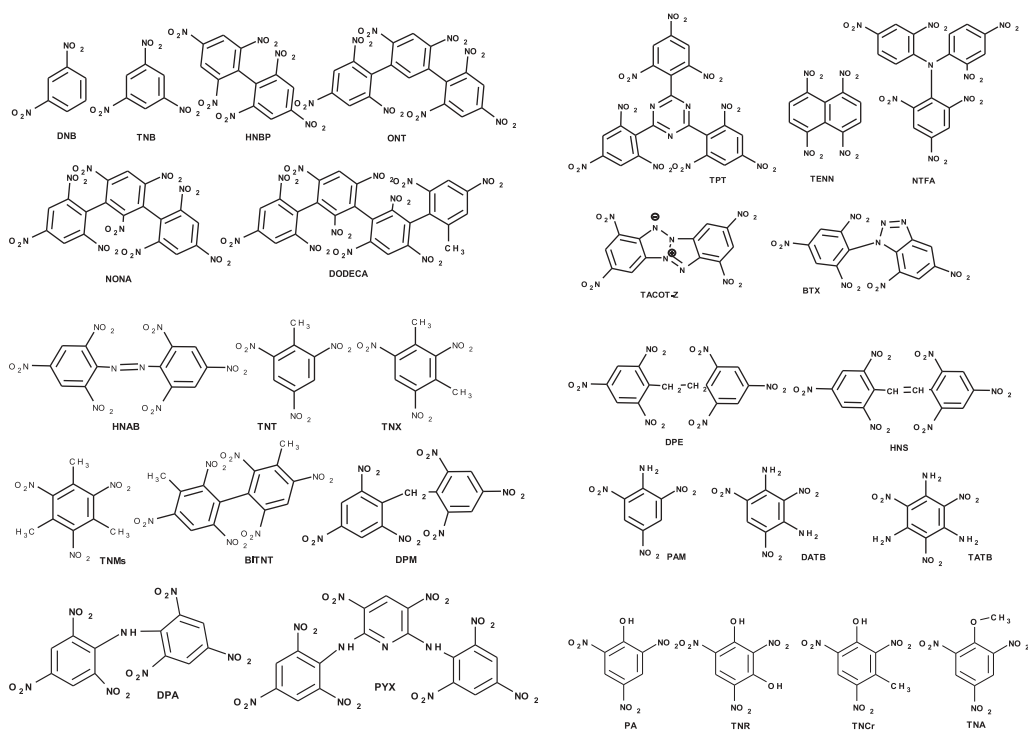
Scheme 1. Formulas of the studied polynitroarenes.

Table 2. A survey of the net charges on nitro groups, Q_{NO2}, of the studied polynitroarenes – selected data from paper (Zeman, Friedl, and Kočí 2007b) and for TACOT-Z (Zeman, Friedl, and Roháč 2006a).

Polynitro arene	Net charge on nitro group		Polynitro arene	Net charge on nitro group	
	position in molecule	Q_{NO2}/e		position in molecule	Q_{NO2}/e
1,3-DNB	1,3-	−0.3603	TNT	2-	−0.3529
TNB	1,3,5-	−0.3335		4-	−0.3516
HNBP	4-	−0.3384	TNMs	1,3,5-	−0.3738
NONA	2′-	−0.3407	PAM	2-	−0.3852
ONT	2-	−0.3313		4-	−0.3764
DODECA	2′-	−0.3232	DATB	3-	−0.4205
NTFA	2-	−0.2977	TATB	1,3,5-	−0.5042
	4-	−0.3400	PA	2-	−0.3388
TENN	1,4,5,8-	−0.3218	DPA	6-	−0.3404
BTX	2- (in picryl)	−0.3242	DPM	2-	−0.3218
TPT	2-	−0.3073	DPE	6-	−0.3404
TENN	1,4,5,8-	−0.3218	BITNT	2-	−0.3506
TACOT-Z	1-	−0.3346		6-	−0.3404
	3-	−0.3599	HNAB	2-	−0.3007
				4-	−0.3386

Results and Discussion

Background

In the past, the study of the relationship between the initiatory reactivity and performance of individual energetic materials (EMs) has started from the modified Evans-Polanyi-Semenov equation (Elbeih et al. 2013; Zeman 2002, 2005, 2006, 2007, 2018; Zeman and Jungova 2016; Zeman, Q-L, and Vlček 2014), i.e. from the relationship between the heat of explosion or the square of the detonation velocity (D^2) or a product of loading density and D^2, on the one hand, and appropriate sensitivity characteristics, on the

other. In this case, the heat of explosion, Q_{max}, was given in units of kJ.kg^{-1}, which is common practice in calculations involving the physics of explosion. Mainly the values of detonation velocity, D, and pressure, P, are influenced by the chemical entity and the amount of primary fragments entering into the reaction zone of the detonation wave; it is best documented for nitromethane in which the NO$_2$-radical, produced from a pure sample of the substance, corresponds to a detonation pressure of 13 GPa, while the entering OH-radical from the nitromethane alkalized by diethylenetriamine can lead to a detonation pressure of 20 GPa (Zeman et al. 2009 and references therein) – the latter radical should create a narrower reaction zone in the detonation wave. It is clear that structurally similar energetic materials will produce the most reactive fragments (in nitromethane NO$_2$ or OH radicals) and that in the molecular crystals of the compounds related molecular structures, a similar intermolecular interaction should exist. In contrast to statements in by Politzer and Murray (2016) such factors are a reason why mutually related energetic compounds form, in the sense of the modified Evans-Polanyi-Semenov equations, a narrow set of substance structures with good correlation coefficients (see mainly in Zeman 2005, 2007, 2018; Zeman and Jungova 2016).

The Modern Approach

The first partial fission of EM molecules in detonation begins with compression, i.e. before the front of the detonation wave (Dremin 1999; Zeman 2006, 2007). It is well known that further decomposition of the explosive in detonation does not continue in a coherent layer of compressed molecules but rather in "hot spots" (Dremin, Savrov, and Trofimov 1970). Moreover, it is also well known that the rate of a stable detonation does not depend upon the concentration of the given EM in a just detonating charge. This means that detonation can be taken as a zero order reaction from the point of view of classical reaction kinetics, and the corresponding heat of explosion is thus expressed in Joules per unit volume. Inserting this volumetric heat instead of the gravimetric Q_{max} values into relationships for initiatory reactivity produced relationships in which the molecular-structural influence on this reactivity is more clearly perceptible (Elbeih et al. 2013; Zeman and Jungova 2016), and this approach began to be used by other authors also (Politzer and Murray 2015). The said is similar to the case of the modified Evans-Polanyi-Semenov equation for EMs (Elbeih et al. 2013; Zeman 2006, 2007; Zeman and Jungova 2016). However, the originally linear relationship between Q_{max} and impact sensitivity is thus changed into a logical and entirely satisfactory semi-logarithmic relationship between the ρQ_{max} values and drop energies, E_{dr} (Elbeih et al. 2013; Zeman and Jungova 2016).
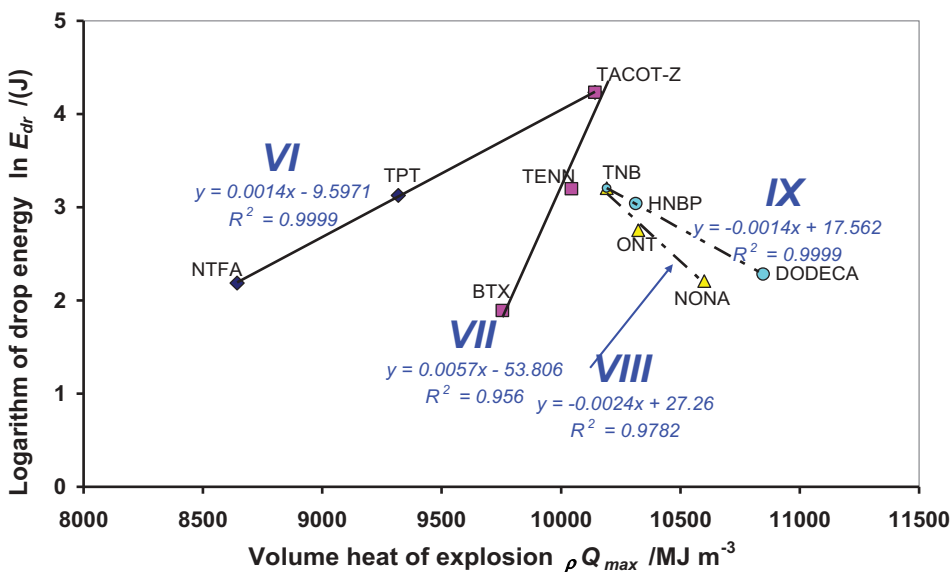
A Relationship between Impact Sensitivity and performance for Polynitroarenes

The study of this relationship in polynitroarenes was a topic of interest around the turn of the last century using a modified Evans-Polanyi-Semenov equation (Zeman 2002, 2006). But later, attention has been turning mainly to nitramines as has already been mentioned. A comparison of impact sensitivity (as drop energy, E_{dr}) and volume heat of explosion, $\rho.Q_{max}$, using this new approach, produces semi-logarithmic relationships which are represented by Figures 1 and 2.

Figure 1 summarizes relationships for derivatives of polynitroarenes whose constituent parts introduce a hydrogen atom, bound in the gamma-position of the nitro group (with the exception of DNB and HNAB). These kinds of compound primarily decompose by the so-called "trinitrotoluene" mechanism (Manelis et al. 2003; Varga and Zeman 2006; Zeman 2007, and references therein), i.e. through a six-membered transition state (in the case of TNA a seven-membered one) with subsequent loss of the OH radical. In the case of DNB, the first fission occurs in the C-NO$_2$ bond (its correlation here might be accidental). Primary fission of the HNAB molecule should start at the bond between the carbon atom and the azo-bridge (Zeman 2007 and references herein – a similarity with fission of the C-S bond in 1,3,5-trinitro-2-[(2,4,6-trinitrophenyl)thio]benzene) whereby the interaction of the oxygen atom from nitro group in the ortho-position with the azo-bridge may participate (through a five-membered transition state). It is evident that the division of the compounds into groups in Figure 1 is given both by the thermochemical aspect of detonation and by the nature and intensity of the intermolecular interaction in their molecular crystals (more simply said – by the molecular structure). This figure
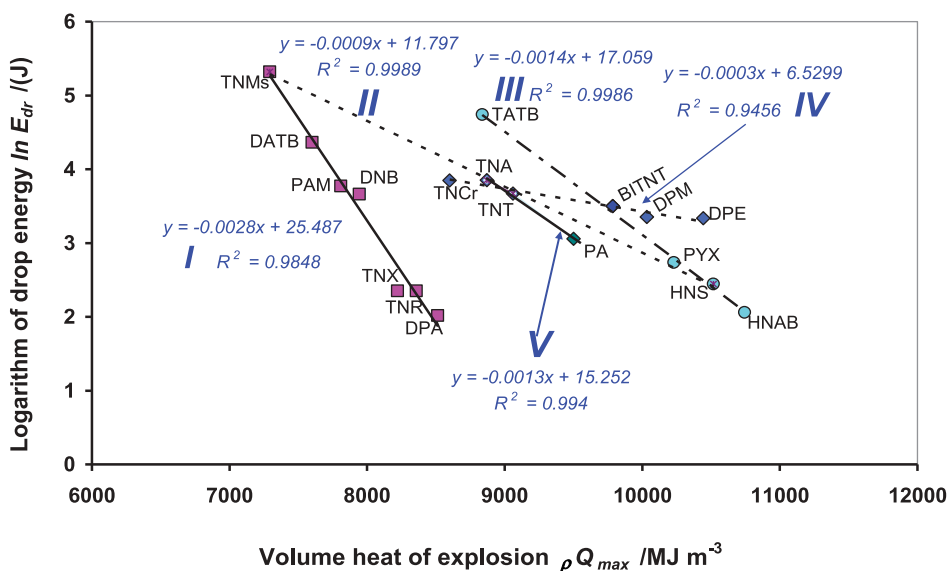
Figure 1. Semilogarithmic relationship between the impact sensitivity, expressed as drop energy, E_{dr}, and volume heat of explosion, ρQ_{max}, for the studied derivatives of polynitroarenes.

Figure 2. Semilogarithmic relationship between the impact sensitivity, expressed as drop energy, E_{dr}, and volume heat of explosion, ρQ_{max}, mostly for the studied "genuine" polynitroarenes and polynitro-polyazaarenes.

expressly documents the increase in initiatory reactivity (here the impact sensitivity) with an increase in the performance of the polynitroarene derivatives under study, which is in line with expectations.

Figure 2 shows the same relationships for "genuine" polynitroarenes and also polynitroazaarenes the primary fission step of which is expected to be homolysis of the C-NO$_2$ bond. Here the slope of straight lines VI and VII are contrary to expectations; in the nitramine series a similar situation (i.e. stabilization effect) for this relationship was found for 1,3,5-trinitro-1,3,5-triazepane, 1,3,5-trinitro-1,3,5-triazinane, β-1,3,5,7-tetranitro-1,3,5,7-tetrazocane and the α-, β- and ε-polymorphs of 2,4,6,8,10,12-hexanitro

-2,4,6,8,10,12-hexaazaisowurtzitane (Zeman and Jungova 2016). However, unlike nitramines, the poly-nitro-aromatic compounds around the lines VI and VII are, at first sight, most likely stabilized by their molecular structure. It might be a strong stabilization effect of the crystal lattice which is possible to show on the centro-symmetrical molecule of TPT – onset of the DTA-thermal decomposition of pure TPT is at 592.8 K (319.7°C) while for its solution in TNB decomposition starts at 449.3 K (176.2°C)(Zeman 1979); the stabilization effect is here very clear. Another member of this group, TACOT-Z, is a semi-ionic compound with very high thermal stability (Mayer, Köhler, and Homburg 2002; Zeman 2006). The centro-symmetric molecule of TENN does not melt, but at 271°C, a polymorphic transition appears in the differential thermal analysis (with the onset of decomposition at 305.5°C – see in Zeman 1973). While straight line IX represents multiples of TNB-units, the line VIII represents the relationship of polynitro m-terphenyls to TNB. Both these straight lines represent a good demonstration of the molecular–structural relationship. With the exception of HNBP, all other polynitroarenes in Figure 2 have onsets in their thermal analysis above 302°C in their solid state, and TNB has distilled without decomposition (Zeman 2006).

A Relationship between Impact Sensitivity and the Energy Content of Polynitroarenes

In a recent paper (Zeman et al. 2019), we have shown that initiatory reactivity of nitramines and of their PBXs unambiguously increases with an increase in their energy content, which was represented there by the corresponding enthalpies of formation, ΔH_{form}. The same approach to impact sensitivity of poly-nitroarenes in the current paper produces Figure 3. In comparison with Figures 1 and 2, it is evident that the relationship is linear and is divided into sub-dependencies on the basis of molecular structure, namely according to the mechanism of primary fission and, at the same time, the influence of the intermolecular interactions is perceptible (a thermochemical factor is taken for granted here). The first named factor should be characterized by the "trinitrotoluene" mechanism of fission of the mono-nuclear compounds, DPE, DPA and partially also DPM, and both these factors should influence DPE and BITNT (they form a group along with "genuine" polynitroarenes). The bi- and multi-nuclear compounds (mostly with primary fission of the C-NO$_2$ bonds), form three sub-dependencies, where the data for
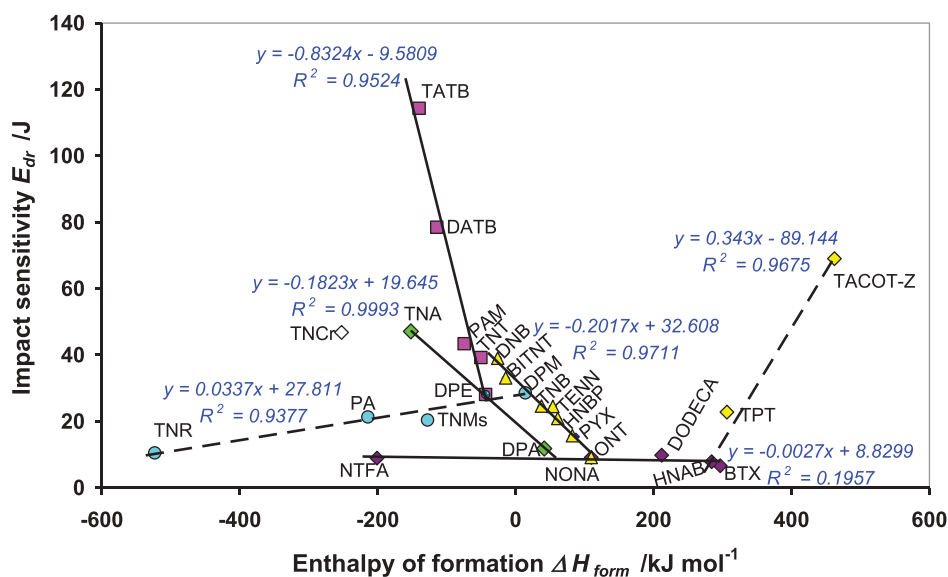

Figure 3. Relationship between the impact sensitivity, expressed as drop energy, E_{dr}, and enthalpies of formation, $\Delta H_{form.}$, for the studied polynitroarenes.

HNAB correlates with one of them; the first fission reaction of HNAB has already been mentioned. It is also possible to see here the opposing character of the two relationships against all expectations: one in compounds with the hydrogen atom in the gamma-position relative to the nitro group (TNR – DPM), and the second one in highly thermostable polynitroazaarenes (BTX, TPT, and TACOT-Z).

A Relationship between Electric Spark Sensitivity and Performance

The primary step of polynitroarene fission by electric spark should be different from those during mechanical and thermal initiation. In measurements with samples in direct contact with electrodes (Zeman, Kočí, and Majzlík 2007a), the first step is an electron entrance on the nitrogen atom of the nitro group which has the lowest absolute value of the net charge at the nitro group, Q_{NO2} among all nitro groups in the given molecule (Zeman, Friedl, and Kočí 2007b); thus, for example, electro-reduction of TNT begins on the nitro group in position 4 (Kang, Lee, and Silvester 2016) which has the lowest absolute Q_{NO2} value (see Table 2). In this way, the attacked nitro group might be the source of the given polynitro compound's own reactivity. However, Zeman, Friedl, and Kočí (2007b) showed that the requirement of the lowest absolute Q_{NO2} value may not always be the case for this initiation. From Figure 4 it is noticeable that the separation of derivatives with the hydrogen atom in the gamma-position relative to the nitro group from the group of other polynitroarenes is not as sharp as demonstrated by Figures 1 and 2 – it is practically limited to the straight lines G and A. Data around the straight line B are mixed and around the lines C and D they correspond to "genuine" polynitroarenes. This is similar to the relationship between the half-wave potentials from polarography of polynitroarenes and the squares of their detonation velocities (a version of the modified Evans-Polanyi-Semenov equation) where the sub-relationships for amino- and hydroxy-derivatives of dinitro- and trinitro-benzenes were separated (Zeman and Zemanová 2004). Figure 4 also shows that in the bi- and multi-nucleated compounds an increase in performance corresponds to an increase in their resistance to initiation by electric spark.
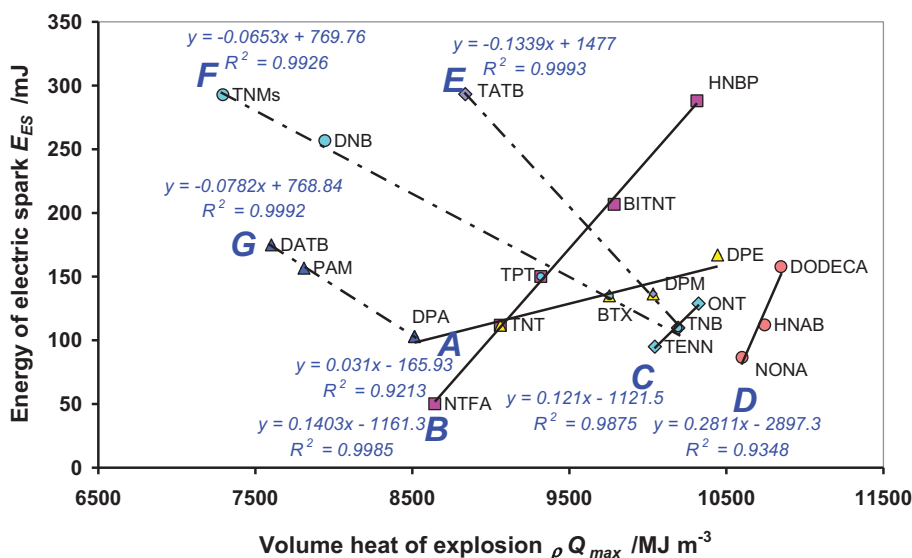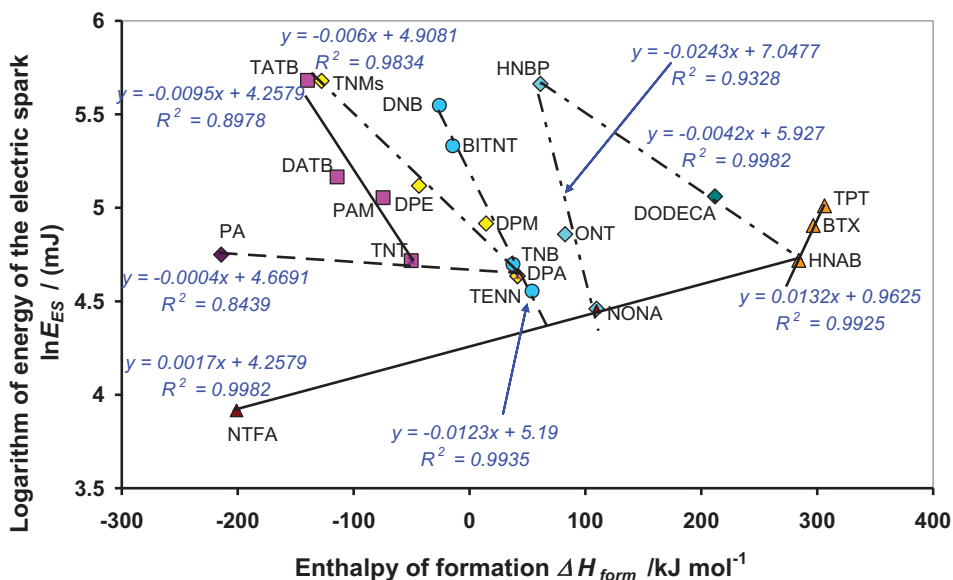

Figure 4. Relationship between the electric spark sensitivity, expressed as energy of electric spark, E_{ES}, for 50% probability of initiation, and volume heat of explosion, ρQ_{max}, for the studied polynitroarenes.

Figure 5. Semilogarithmic relationship between the electric spark sensitivity, expressed as energy of the electric spark, E_{ES}, and enthalpies of formation, $\Delta H_{form.}$, for the studied polynitroarenes.

A Relationship between Electric Spark Sensitivity and the Energy Content of Polynitroarenes

Comparison of the E_{ES} values and enthalpy of formation for most of the polynitroarenes under study led to Figure 5. With increasing energy content this sensitivity also generally increases. However, especially for thermostable substances, i.e. NTFA, NONA, HNAB, BTX and TPT, this relationship is the reverse of what is expected; the group of polynitroarenes mentioned has a specific position also in Figure 3, i.e. in the analogous relationship for impact sensitivity. Similarly, as in Figure 3, with the exception of PA and amino-derivatives of TNB, the compounds with the hydrogen atom in the gamma-position toward the nitrogroup are not sharply separated from other polynitroarenes (here BITNT, DPA, and DPM). The reason for this is the same as that in the case of Figure 3, i.e. the ΔH_{form} values correspond to the "quiescent condition" of the compounds studied.

Net Charge on Nitro Groups and Performance

The relationships between the net charge on the nitro group, Q_{NO2}, and impact sensitivity (Zeman 2007; Zeman, Friedl, and Roháč 2006a) or electric spark sensitivity (Zeman, Friedl, and Kočí 2007b) have already been published. An interesting case is found in the comparison of the volume heat of explosion and the Q_{NO2} values of the polynitroarenes under study, as Figure 6 shows.

In Figure 6, mono-nucleated derivatives with the hydrogen atom in the gamma-position versus the nitro group again form separate groups (TATB, PAM, PA, DATB, TNMs) with the exception of TNT. The latter, although the nitro group is in position 4, is, however, in the group with DPA (an acidic compound) and the thermostable NTFA, which at the same time correlates through the nitro group in position 2 with data for the multi-nucleated polynitroarenes. That a big polynitroaromatic molecule can have several reaction centers has been confirmed for HNBP, ONT, TPT and DODECA by using X-ray, Q_{NO2} values and ^{15}N NMR chemical shifts (Zeman et. al. 2010b, Zeman et al. 2010a) using modified versions of the Evans-Polanyi-Semenov equations (concerning the last of these, see in Zeman 2007). Data for BITNT, and perhaps also for DNB, do not correlate, most probably due to the method for calculating the Q_{NO2} values (for isolated molecules). In each case, however, Figure 6 clearly shows that an increase in
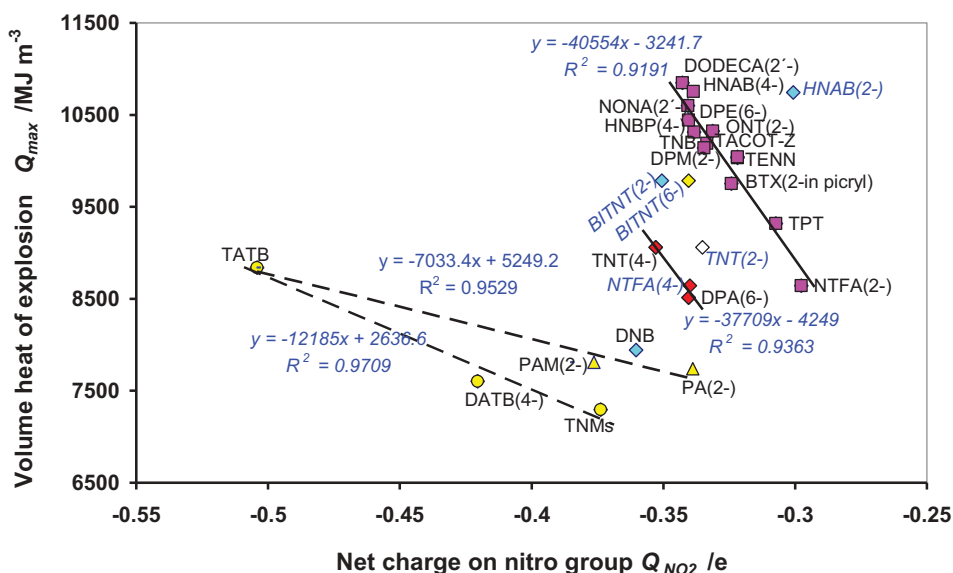
Figure 6. Relationship between the volume heat of explosion, ρQ_{max}, and the net charges, Q_{NO2}, on the nitro groups for the studied polynitroarenes (numbers in parentheses mean position of the nitro group in the molecule).

negativity of the net charge on the most reactive nitro group corresponds to an increase in the performance of the polynitroarenes studied.

Comments

The modified Evans-Polanyi-Semenov equation (Zeman 2007, 2018) has been used with several versions, in which the activation energies of thermal decomposition are replaced by other sensitivity characteristics (including NMR chemical shifts, charges at nitrogen atom, etc. – see in Zeman 2007). In addition, all such relationships are limited by the similarity of the chemical mechanism of the primary fission process and by molecular structure (Zeman 2007, 2018) as has already been mentioned (the important thermochemical factor is taken for granted here). New relationships, based on the concept of detonation as a zero order reaction (here Figures 1 and 2) are limited by the same factors, which is very well documented by both these Figs. Differentiation of the polynitroarenes under study into sub-groups in Figures 1 and 2 is undoubtedly due to the character and intensity of the intermolecular interactions in their crystals, which is also one of the decisive factors in impact sensitivity (Zeman and Krupka 2003).

Relationships of impact sensitivity with enthalpies of formation, ΔH_{form} (i.e. with the energy content of the EMs' molecules), shown in Figure 3, have different mathematical forms compared with Figures 1 and 2, and a different affiliation of the data for individual compounds with the sub-relationships in Figure 3, again compared with Figures 1 and 2. For mono-nuclear derivatives with the hydrogen atom in the gamma-position relative to the nitro group such association is visible in separate sub-relationships, together with DPE and perhaps also DPA; on the other hand, in multi-nuclear polynitroarenes, including also BITNT, DPM, and PYX, the size and shape of their molecules dominate in this association. The differences between relationships in Figure 3, on the one hand, and in the Figures 1 and 2, on the other, are related to the logical absence of the reaction zone of detonation for the dependencies in the first mentioned Fig. This means that the relationships in Figures 1 and 2 might be understood to be the "kinetics" ones (they are going from the zero order reaction) while in Figure 3 they might be considered as the "thermodynamic" ones.

Concerning electric spark sensitivity, it should be noted that such sensitivity displayed by polynitroarenes and their derivatives decreases with an increased negativity of the Q_{NO2} values at the most reactive nitro groups (Zeman, Friedl, and Koči 2007b). At first sight, this roughly corresponds to the comparison of the relationships in Figures 4 and 6, mainly in the case of the straight lines B-D (an increase in negativity of the Q_{NO2} values should correspond to an increase in performance of the polynitroarenes). From what has been said so far, it is logical that the increasing negativity of the Q_{NO2} values must correspond to the impeded electron transfer to the nitro group nitrogen. It should be added that, in contrast with polynitroarenes, the relationships between the E_{ES} and Q_{NO2} values in nitramines are not so clear (Zeman, Friedl, and Koči 2007b). The dependence of electric spark sensitivity on the volume heat of explosion should be more complicated in comparison with the dependencies of other sensitivity characteristics. This is because the first reaction of the nitro group only occurs after the entrance of electron on its nitrogen atom, so that the nitro fragment enters the reaction zone only after this entity has been changed. In addition, as has already been mentioned, the quality and quantity of the fragments entering into the reaction zone are co-determining factors for the detonation characteristics. However, especially in crowded molecules, the nitro groups, which are primarily splitting off under the influence of the electric spark (in the example with direct electrode contact), should be the same as those that are reacting under influence of mechanical or heat impulses. As for the relationship (here a semi-logarithmic one) of electric spark sensitivity with enthalpies of formation (Figure 5), it is possible to say roughly the same as for the case of impact sensitivity.

It is appropriate to mention that, for the primary chemical initiation processes, frequently referred to in this work, many of the big polynitroarenes molecules and their derivatives may have several reaction centers (Zeman 2003), which may not be detected simply by correlations based on the net charge on the nitro groups (this paper and Zeman 2007) but more by correlation of the results of other structural analyses (Zeman 2018, Zeman et al. 2010a) with the results from of other sensitivity measurements.

Conclusions

The linear correlations of sensitivity characteristics of energetic materials with their explosion heats (in kJ.kg^{-1}) and/or the square of their detonation velocities have recently been described and explained (Zeman 2005, 2007; Zeman and Jungova 2016), including their division into sub-relationships conditioned by the first fission processes and intermolecular interactions. Considering detonation as a zero order reaction, the volume heat of explosion, ρQ_{max} (in MJ m^{-3}) becomes useful for this study, by inserting values of the impact sensitivity (as drop energy, E_{dr}) giving the logical semi-logarithmic relationships. In this case, it is shown that impact sensitivity of the derivatives of polynitroarenes decreases with an increase in the ρQ_{max} values (this is in line with expectations). However, in "genuine" polynitroarenes some exceptions exist, namely in compounds with a strong stabilizing effect from their crystal lattice (TPT, TACOT-Z) where the impact sensitivity relationship runs counter to this general rule. Besides these structural effects, the mechanism of the primary fission differentiates the mentioned relationship into sub-relationships. Substitution of the ρQ_{max} values by the energy content of the polynitroarene molecules, represented by enthalpy of formation, ΔH_{form}, provides a corresponding linear dependence. Its division into sub-relationships is based mainly on the size and shape of the corresponding molecules, with the primary fission mechanism dominating in the case of mono-nucleated derivatives (i.e. the "trinitrotoluene" mechanism of fission).Impact sensitivity generally increases with an increase in the ΔH_{form} values, but for several compounds, an opposite trend is observed (the thermostable polynitroarenes are between these compounds).

In the linear relationship between the electric spark sensitivity (expressed as energy of the electric spark, E_{ES}) and volume heat of explosion, a clear separation into sub-relationships according to the primary scission mechanism is noticeable. The first process in this initiation is the electron entrance on

a nitrogen atom of the nitro group, usually with the lowest absolute value of net charge on this group (Zeman, Friedl, and Kočí 2007b) and, in this way, the changed nitro group then undergoes its own chemical reaction which is not necessarily the same chemical mechanism as with thermal decomposition. However, the reacting nitro groups, specifically in the sterically crowded polynitroarenes, might be the same as under mechanical and thermal impulses. Given that increasing the ρQ_{max} values corresponds to the growth of negativity in the net charge on nitro group, particularly in the multi-nuclear polynitroarenes, its relationship with impact sensitivity is the opposite to what is expected. Substitution of the ρQ_{max} values by the enthalpy of formation changes the relationship for electric spark sensitivity into a linear one according to which this sensitivity is mostly increased when the enthalpy values increase. There are also several other compounds for which this dependency shows an opposite trend (the more thermostable compounds NTFA, NONA, HNAB, BTX, and TPT).

From the above-mentioned results, it is possible to see clearly that it is necessary to distinguish between the influence of performance and the influence of energetic content of energetic materials on their initiating reactivity.

Acknowledgments

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