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SIMPLE CALCULATION OF RELATIVE ENERGY OF C-H-N-O HIGH EXPLOSIVES

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Based on a simple decomposition equation and Kamlet's relations, a new F parameter in the form $F = \varphi\rho$ (where ρ is the density) has been suggested for representation of relative energy of C-H-N-O high explosives. Linear relation of the F parameter to detonation enthalpy and accelerating ability of high explosives enabling a simple and quick evaluation of newly suggested structures of energetic materials is shown on a series of 25 individual high explosives.

Introduction

Detonation velocity D and detonation pressure P are commonly used to express the performance of high explosives. These parameters that depend on density ρ are determined experimentally or by calculation based on equations derived from the theory of detonation [1,2]. On detonation of condensed high explosives a very rapid conversion occurs of the high explosive to predominantly gaseous products. This

process is, in principle, described by equations of conservation of mass, momentum, energy, and by equations of state (EOS) of the products. Several [3] equations of state have been suggested and their accuracy has been confirmed by experimental measurements of detonation parameters. Among others, one reason to keep searching for the optimum equation of state going on is the fact that so far it has not been possible to determine the composition of detonation products in the Chapman–Jouguet (CJ) plane with sufficient accuracy. Completing of chemical reactions is supposed to occur here and this is the place where the values of velocity, pressure, energy, temperature etc. remain constant during the detonation, whereby the stability of detonation is ensured.

When searching for new structures of highly energetic compounds and synthesizing them (which is usually a very demanding process) the chemists need to know the parameters the compound will have in advance. This is enabled by means of semi-empirical Kamlet's equations for calculation of detonation velocity and pressure in case we know the composition of the high explosive, its heat of formation and density. On the basis of these equations it is, however, possible to calculate other important parameters as e.g. energy, working ability and mass acceleration.

Theory

The Kamlet's equations [4] (Eqs (1) – (3), (5)) for high explosives of C-H-N-O composition are based on a simple decomposition equation

$$C_aH_bN_cO_d \rightarrow 0.5cN_2 + 0.5bH_2O + (0.5d - 0.25b)CO_2 + (a - 0.5d + 0.25b)C$$

The φ parameter in the following form

$$\varphi = NM^{1/2}Q_K^{1/2} \qquad (1)$$

where N – number of moles of gaseous products from 1 g high explosive, M – average molecular mass of gases, and Q_K – heat of detonation (cal) from 1 g high explosive has been constructed from known atomic composition and heats of formation of the original high explosive and the products.

If φ parameter and density are known, it is possible to calculate detonation velocity D (in $m\,s^{-1}$) and detonation pressure P (in Gpa) from equations

$$D = 1010\varphi^{1/2}(1 + 1.3\rho) \tag{2}$$

$$P = 1.558\varphi\rho^2 \tag{3}$$

The above-given equations were constructed on the basis of calculations utilizing BKW equation of state and experimental values of detonation velocities and pressures for a large series of high explosives [4,5].

On detonation, along with the conversion of the compound into products, the so-called heat of detonation Q_d is released that can be calculated from equation

$$Q_d = \frac{\sum n_i H_{f,i} - H_{f,ex}}{Mw} \tag{4}$$

where n_i – number of moles of i component, $H_{f,i}$ – heat of formation of i component, $H_{f,ex}$ – heat of formation of high explosive, and Mw – molecular weight of high explosive.

The form of equation (4) in Kamlet's equations is as follows

$$Q_K = 1000\frac{28.9b + 47(d - 0.5b) + H_{f,ex}}{Mw} \tag{5}$$

where heat of formation is introduced in kcal mol^{-1} and the resulting heat is expressed in kcal g^{-1}. It is necessary to say that these units are still in use so as to keep the φ parameter values (Eq. (1)) commensurable.

The value of energy in the CJ plane can be derived from the equation of state for detonation products. These products release compression energy E_c at consecutive expansion. Detonation energy E_d can be expressed as

$$E_d = E_{CJ} - E_c \tag{6}$$

Since the final effects as working or accelerating ability are in the focus of primal interest, Lee and Block-Bolten [6] have suggested, on the basis of known data about detonation velocity D_{CJ} and pressure P_{CJ}, an evaluation of explosives by means of detonation enthalpy H that expresses working ability.

From the thermodynamic identity

$$H \equiv E + Pv$$

and using the equations of conservation of mass, momentum and energy and polytropic equation of state for detonation products in the form

$$E = \frac{Pv}{\gamma - 1} - Q \tag{7}$$

where adiabatic coefficient γ is defined as

$$\gamma \equiv \left(\frac{\partial \ln P}{\partial \ln \rho} \right)_S \qquad \gamma = \frac{\rho D_{CJ}^2}{P_{CJ}} - 1$$

and heat of detonation Q and volume v_{CJ} is calculated from the equations

$$Q = \frac{C_{CJ}^2}{2\left(\gamma_{CJ}^2 - 1\right)} \qquad v_{CJ} = v_0 \frac{\gamma}{\gamma + 1} \tag{8}$$

they obtained the expression for specific detonation enthalpy

$$H = P_{CJ} v_{CJ} \frac{\gamma}{\gamma - 1} - Q \tag{9}$$

In Eqs (7) – (9) E – specific internal energy, P_{CJ} – detonation pressure, v_{CJ} – volume, D_{CJ} – velocity, and ρ – density of high explosive. Subscripts S and CJ refer to constant entropy and the state in the CJ plane, respectively.

Equation (9) expresses the amount of energy in the detonation plane that could be, theoretically, utilized. Among others, one way how to use it is acceleration of mass bodies at which the kinetic parameters can be measured, and thus it can be determined what part of the total amount of energy can be utilized.

Using φ parameter and density ρ, equations for the Gurney's velocity [7] were derived in the form [8]

$$\sqrt{2E} = 0.887 \varphi^{0.5} \rho^{0.4} \tag{10}$$

and the so-called cylinder velocity [9] V

$$V = 0.368\varphi^{0.54}\rho^{0.84} \tag{11}$$

where the resulting values of both equations have dimension of velocity (in km s^{-1}).

Both equations express accelerating ability of the high explosive for a standard casing. In case of the Gurney's velocity it is a matter of cylinder geometry and the so-called ballistic ratio (casing weight to high explosive weight ratio). Equation (11) is based on experimentally measured velocities of the standard copper tube wall expanding on detonation of its explosive filling (cylinder test).

The results of this test were also utilized for calculation of the energy needed for two-fold and seven-fold increase in tube volume due to the presence of the detonation products. This occurs when the original radius (12.7 mm) is enlarged by 6 or 19 mm respectively and therefore these energies are subscripted/marked E (6 mm) and E (19 mm). By means of φ and ρ they are calculated from equations [10]

$$E_{cy}(6\text{ mm}) = 0.0659\varphi\rho^{1.8} \tag{12}$$

$$E_{cy}(19\text{ mm}) = 0.0927\varphi\rho^{1.6} \tag{13}$$

where energy is expressed in MJ kg^{-1}

The F parameter in the form [11]

$$F = \varphi\rho \tag{14}$$

where ρ – theoretical maximum density (TMD) has been suggested for a relative evaluation of high explosives. This equation respects the dependence of performance parameters of detonation on three entering data: composition of high explosive, heats of formation and density. Linear relation between the F parameter and detonation enthalpy H has also been found.

Results and Discussion

Using Eqs (1) – (3) and (5), the φ parameter, heat of detonation Q_K, detonation velocity D_{CJ} and pressure P_{CJ} for the densities ρ_{TMD} have been calculated for a

series of 25 high explosives. Specific detonation enthalpy had been calculated from Eq. (9) and then the F parameter on the basis of which the compounds were tabulated (Table I).

The relation between enthalpy H and F parameter is linear and can be expressed in the following form

$$H = 1.377F - 0.12 \tag{15}$$

with regression coefficient $R = 0.9997$.

The calculated values of detonation velocity and pressure tend to have a similar trend with greater deviations, however. On the contrary, the Q_K values do not show any significant linear relation.

The values for E (6), E (19), $\sqrt{2E}$ and V (Table II) have been calculated from Eqs (10) – (13). By comparing the F parameter with expansion energy values we find that they comply relatively well with linear relation

$$E(6) = 0.121F - 0.16 \qquad \text{with} \quad R = 0.9712 \tag{16}$$

$$E(19) = 0.146F - 0.15 \qquad \text{with} \quad R = 0.9712 \tag{17}$$

There is a similar relation between the values for $\sqrt{2E}$ and V velocities and F parameter

$$\sqrt{2E} = 0.124F + 1.40 \qquad \text{with} \quad R = 0.9962 \tag{18}$$

$$V = 0.0878F + 0.64 \qquad \text{with} \quad R = 0.9861 \tag{19}$$

In Eqs (16) and (17) the energy is expressed in MJ kg^{-1}, in Eqs (18) and (19) in km s^{-1} (for a unit weight).

It can be seen from the above given relations (Eqs (15) – (19)) and Tables I and II that the F parameter represents with, a sufficient accuracy, the relative energy ratio between the individual C-H-N-O high explosives and, at the same time, it also enables a quick calculation of the individual energy parameters. It follows from the comparison of the calculated values H, E (6), E (19), $\sqrt{2E}$ and V by means of Eqs (9) – (13) that the maximum deviations do not exceed 7% and are within the

Table I Basic parameters of selected high explosives

No.	Name	ρ g cm^{-3}	ΔH_f kcal mol^{-1}	Q cal g^{-1}	φ	P GPa	D m s^{-1}	F	H kJ g^{-1}
1	CL–20	2.03	99.20	1588.1	6.8511	43.99	9620.2	13.91	19.11
2	HMX	1.90	17.40	1475.0	6.7669	38.06	9116.9	12.86	17.60
3	BTNEN	1.96	-175.90	1298.2	6.5295	39.08	9156.8	12.80	17.54
4	BTNEU	1.86	-71.70	1481.1	6.7856	36.57	8992.6	12.62	17.26
5	TNAZ	1.84	3.00	1596.9	6.8398	36.08	8959.8	12.59	17.21
6	RDX	1.80	14.40	1481.1	6.7808	34.23	8784.3	12.21	16.66
7	PETN	1.77	-129.00	1513.3	6.7875	33.13	8686.1	12.01	16.37
8	TNETB	1.78	-118.50	1481.6	6.5920	32.54	8593.8	11.73	16.02
9	EDNA	1.75	-25.80	1297.3	6.4700	30.87	8413.6	11.32	15.40
10	DINA	1.67	-74.00	1438.3	6.5689	28.54	8208.5	10.97	14.91
11	Ng	1.59	-118.70	1459.5	6.8723	27.07	8120.6	10.93	14.91
12	BDNPN	1.73	-65.30	1407.1	6.2834	29.30	8225.6	10.87	14.81
13	TEX	1.99	-129.20	1065.6	5.0611	31.23	8150.4	10.07	13.84
14	NQ	1.77	-22.00	900.0	5.5337	27.01	7842.8	9.79	13.48
15	NTO	1.92	-31.00	929.2	5.0944	29.26	7969.6	9.78	13.29
16	TE	1.73	8.00	1432.1	5.6390	26.29	7792.4	9.76	13.34
17	TATB	1.94	-33.30	1089.5	5.0043	29.34	7957.6	9.71	13.33
18	DATB	1.84	-23.60	1174.5	5.0772	26.78	7719.5	9.34	12.77
19	DIPAM	1.79	-3.50	1305.9	5.1500	25.71	7625.7	9.22	12.58
20	TNA	1.77	-18.00	1252.6	5.1014	24.90	7530.3	9.03	12.32
21	PA	1.76	-57.30	1257.2	5.1177	24.70	7512.6	9.01	12.26
22	HNS	1.74	16.10	1361.1	4.8697	22.97	7270.3	8.47	11.55
23	TNB	1.68	-24.60	1284.5	4.9972	21.97	7188.8	8.40	11.42
24	TACOT	1.77	110.00	1308.2	4.6797	22.84	7212.3	8.28	11.30
25	TNT	1.65	-18.00	1281.9	4.8435	20.54	6990.8	7.99	10.86

range of experimental errors.

On the contrary, the heat Q_K and φ parameter cannot be a direct criterion to express the relative energy. Probable explanation consists in the principle of detonation process where not only an exothermic reaction occurs but also very compressed and hot gaseous products are created. Physical dimension of the F parameter contains the amount of heat and gas in the volume unit and therefore it

Table II Calculated parameters of energy of selected high explosives

No.	Name	F	$\sqrt{2E}$ km s^{-1}	V km s^{-1}	$E(6)$ MJ kg^{-1}	$E(19)$ MJ kg^{-1}
1	CL–20	13.91	3.082	1.886	1.6149	1.9717
2	HMX	12.86	2.983	1.772	1.4159	1.7518
3	BTNEN	12.80	2.967	1.784	1.4449	1.7765
4	BTNEU	12.62	2.962	1.743	1.3665	1.6978
5	TNAZ	12.59	2.961	1.735	1.3508	1.6820
6	RDX	12.21	2.922	1.695	1.2872	1.6099
7	PETN	12.01	2.904	1.672	1.2501	1.5687
8	TNETB	11.73	2.868	1.654	1.2265	1.5373
9	EDNA	11.32	2.822	1.614	1.1675	1.4684
10	DINA	10.97	2.791	1.564	1.0896	1.3833
11	Ng	10.93	2.799	1.538	1.0435	1.3379
12	BDNPN	10.87	2.768	1.573	1.1106	1.4001
13	TEX	10.07	2.628	1.575	1.1510	1.4109
14	NQ	9.79	2.622	1.498	1.0192	1.2789
15	NTO	9.78	2.599	1.533	1.0862	1.3411
16	TE	9.76	2.623	1.484	0.9967	1.2565
17	TATB	9.71	2.587	1.532	1.0871	1.3394
18	DATB	9.34	2.551	1.477	1.0027	1.2486
19	DIPAM	9.22	2.541	1.454	0.9679	1.2119
20	TNA	9.03	2.517	1.433	0.9396	1.1790
21	PA	9.01	2.516	1.429	0.9330	1.1721
22	HNS	8.47	2.443	1.378	0.8697	1.0951
23	TNB	8.40	2.440	1.356	0.8378	1.0624
24	TACOT	8.28	2.411	1.368	0.8619	1.0816
25	TNT	7.99	2.385	1.314	0.7862	1.0005

Abbreviations used in Tables I and II:
HNIW – 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.$0^{5,9}$.$0^{3,11}$]dodecane
HMX – 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane; BTNEN - di(2,2,2-trinitroethyl)

nitramine; BTNEU – di(2,2,2-trinitroethyl) urea; TNAZ – 1,3,3–trinitroazetidine; RDX – 1,3,5-trinitro-1,3,5-triazacyclohexane; PETN – pentaerythritol tetranitrate; TNETB – 2,2,2-trinitroethyl-4,4,4-trinitrobutyrate; EDNA – ethylene dinitramine; Ng – glycerol trinitrate; DINA – di(nitratoethyl) nitramine; BDNPN – di(2,2-dinitropropyl) nitramine; TEX – 4,10-dinitro-4,10-diaza-2,6,8,12-tetraoxatetracyclo [5.5.0.$0^{5,9}$.$0^{3,11}$] dodecane; NQ – nitrogua-nidine; NTO – 3-nitro-1,2,4-triazol-5-one; TE – *N*-methyl-2,4,6,*N*-tetranitroaniline, TATB – 1,3,5-triamino-2,4,6-trinitrobenzene; DATB – 1,3-diamino-2,4,6-trinitrobenzene, TNA – 1-amino-2,4,6-trinitrobenzene; PA – 1-hydroxy-2,4,6-trinitrobenzene; DIPAM – 3,3-diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl; HNS – 2,2′,4,4′,6,6′-hexanitrostilbene; TNB – 1,3,5-trinitrobenzene; TACOT - tetranitro-2,3,5,6-dibenzo-1,3a,4,6a-tetraazapentalene; TNT - 2,4,6-trinitrotoluene

can express the relative amount of energy that can be, in an ideal case, obtained from detonation of the explosive.

From the structural formula of high explosive the atomic composition can be defined and heat of formation [12] and density [13] can be calculated. From these data the φ parameter is calculated and consequently also the F parameter. From the above given relations, both working ability and utilizable energy of the suggested compound can then be easily calculated.

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