Thermochemistry of Heteroatomic Compounds: Interdependence between of Some Thermochemical Parameters of the Different Classes Organic Nitro Compounds and a Number of Valence Electrons in their Molecules

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Author's contribution

This work was carried out independently. Author read the final manuscript and agreed with all text.

Research Article

ABSTRACT

The linear equation $\Delta_c H^o = i + f (N - g)$, in which i and f are the factors of correlation, describing interdependence between then heat of combustion organic compounds and their number (N) valence electrons except for a number of lone electron pairs (g) heteroatoms in them, it has been applied besides to the most thermochemical parameter for mono-, di- and trinitroalkanes, arenes and alkylated nitramines. It has appeared, that the given equation also is good applicable to calculation of the heats of formation, vaporization and atomization of nitro compounds in condensed and gas phases. Twenty six similar equations for calculation of thermochemical characteristics of substances with NO_2 groups have been deduced on the basis of the analysis known in literary thermochemical parameters for 53 organic nitro compounds. The estimation of value coefficients f in these equations for calculation of the heats of combustion, formation in condensed and gaseous phases, vaporization, sublimation and atomization mononitro alkanes, various nitramines, dinitro alkanes and arenes, trinitroalkanes and arenes is made.

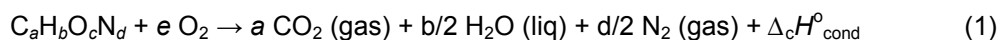*Corresponding author: Email: chem_vvo@mail.ru;*

1. INTRODUCTION

Organic nitro compounds during long time serve as object for chemical researches because they have the properties useful to the industry and agriculture [1, 2]. Application of various classes nitro compounds demands knowledge of their physical properties, such as the heats of combustion and formation in various phases, solubility, vaporization etc. Researchers have accumulated an essential experimental material in this area. However the need of deeper understanding of chemical activity of this class compounds does necessary the recurrence of calculations of some important experimental data.

The knowledge of these data is especially necessary for calculation various bond energies in mentioned above types of molecules. This circumstance also has induced us to carry out some theoretical calculation of the heats of combustion ($\Delta_c H^o$) and vaporization ($\Delta_{vap} H^o$) or sublimation ($\Delta_{sub} H^o$) of nitro compounds, with the use of which is possible to calculate the heats of formation ($\Delta_f H^o$) and atomization ($\Delta_a H$) in a gas phase.

2. RESULTS AND DISCUSSION

The heat of combustion organic nitro compound in the condensed phase ($\Delta_c H^o_{cond}$) can be calculated by the Equation (1)

$$C_a H_b O_c N_d + e\ O_2 \rightarrow a\ CO_2\ (gas) + b/2\ H_2O\ (liq) + d/2\ N_2\ (gas) + \Delta_c H^o_{cond} \qquad (1)$$

in which *a, b, c, d,* and *e* are stoichiometric coefficients. The required heats of formation values for CO_2 -395.5 and H_2O -285.8 kJ mol^{-1} for the $\Delta_f H^o$ calculation of the initial nitrogen containing substance could be taken from the known monograph of J.D. Cox and G. Pilcher [3].

We multiple showed that $\Delta_c H^o_{cond}$ values can be effectively calculated within the limits of one-factorial regression analysis [4-7]. This position is into accordance with electronic concept of M.S. Kharasch and B. Sher [8] for the calculation of the heats of combustion of organic compounds. Thus, there is a necessity for the construction of the various equations like (2) on the basis of the known experimental data on the heats of combustion of organic or heteroatomic compounds.

$$\Delta_c H^o = i + f\ (N - g) \qquad (2)$$

In correlation (2) factor *i* corresponds to the contribution of structure compound in heat of combustion and the factor *f* defines sensitivity of the heat of combustion to the general number electrons *N*, from which excluded a number (*g*) lone electron pairs of heteroatoms in various functional groups. So, for the fourth group of Periodic System of elements (C^{IV} and below) *g* is equally 0, for the fifth group (N^V and below) *g* is equally 0, for (N^{III} and below) *g* is equally 1, for the sixth group (O^{II} and below) *g* is equally 2 [4-7].

Taking it into account, we analyzed the known experimental data on the heats of combustion, vaporization and formation in the condensed and gaseous phases of

nitroalkanes, nitroarenes, alkynitramines, dinitro alkanes, dinitro arenes, dinitro alkylendiamines, trinitro alkanes, trinitro arenes and 1,3,5-trinitro-1,3,5-triazacyclohexane (Table 1) and compared it with the calculated dependences similarly to Eq. (2).

2.1 Nitroalkanes, Nitroarenes and N-Alkylnitramines

The equations (3) and (4) have been calculated with the use of the heat of combustion and formation values for condensed nitroalkanes (**1 – 7**, Table 1) and the number of their valence electrons.

$$\Delta_c H^o = (165.4 \pm 9.0) - (108.8 \pm 0.4)(N-g) \tag{3}$$
$$r \;\; 0.999, \; S_o \;\; 8.1, \; n \;\; 7,$$

$$\Delta_f H^o{}_{cond} = (-82.6 \pm 9.1) - (4.4 \pm 0.2)(N-g) \tag{4}$$
$$r \;\; 0.979, \; S_o \;\; 8.1, \; n \;\; 7.$$

Necessary to note, that the use of the number of valence electrons in offered $(N-g)$ form has been applied by us for the first time for the calculation of the heat of formation of nitroalkanes. Also necessary to add that all received equations are summed in Table 2 for the convenience of the perception of the discussed material.

To calculate the heats of formation nitroalkanes in a gas phase necessary to know the heats of their vaporization. Two experimental values are known only: for nitromethane (**1**) and nitroethane (**2**). We used the known in literature [9] the boiling temperature (T_b K) for 1-nitropentane (**7**) for the calculation of $\Delta_{vap}H^o$ on Wadsö-equation (5) [3] (Table1)

$$\Delta_{vap}H^o = 20.9 + 0.17(T_b - 273) \tag{5}$$

The heat of vaporization for 1-nitro pentane (**7**) received via this equation (Table 1) allows us to apply again the dependence of experimental thermochemical parameters from the number of the valence electrons (Eq. 6)

$$\Delta_{vap}H^o{}_{exp,\, liq} = (33.4 \pm 0.4) + (0.6 \pm 0.1)(N-g) \tag{6}$$
$$r \;\; 0.999, \; S_o \;\; 0.3, \; n \;\; 3 \text{ (compounds } \mathbf{1, 2, 7}\text{)}.$$

Such situation allows us to calculate the heats of formation of nitroalkanes (**1-7**) in a gas phase through the Eq. 7. The dependence (8) can be formed from the $\Delta_f H^o{}_{gas,}$ and $(N-g)$ factor.

$$\Delta_f H^o{}_{gas} = \Delta_f H^o{}_{cond} + \Delta_{vap}H^o \tag{7}$$

$$\Delta_f H^o{}_{gas} = (-47.9 \pm 9.1) - (3.8 \pm 0.4)(N-g) \tag{8}$$
$$r \;\; 0.972, \; S_o \;\; 8.2, \; n \;\; 7.$$

Table 1. The thermochemical parameters (kJ mol^{-1}) of the different classes of nitrocompounds. P 101kPa; T 298.15 K; all compounds are in condensed state

No.	Compound, formula	*N-g*	$-\Delta_c H^o$		$\Delta_{vap}H^o$ (±5%)	$-\Delta_f H^o$		$\Delta_a H$ (±5%)
			Lit.	Calc. (±0.5%)		cond	gas	
1	2	3	4	5	6	7	8	9
Nitroalkanes								
1	Nitromethane, $CH_3N^VO_2$	8	709.6 [10]		38.4 [3]	113.0 [10]	74.5 [3]	2429.9 ±12.1
2	Nitroethane, $C_2H_5N^VO_2$	14	1358.0 [10]		41.5 [3]	144.0 [10]	102.0 [3]	3593.2 ±18.0
3	1-Nitropropane, $C_3H_7N^VO_2$	20	2014.0 [10]		45.4 a	167.0 [10]	121.6 c	4764.0 ±23.8
4	2-Nitropropane, $C_3H_7N^VO_2$	20	2000.7 [11]		45.4 a	180.3 [10]	134.9 c	4777.0 ±23.9
5	1-Nitrobutane, $C_4H_9N^VO_2$	26	2667.8 [12]		49.0 a	192.6 [12]	143.6 c	5936.8 ±29.7
6	2-Nitrobutane, $C_4H_9N^VO_2$	26	2652.8 [12]		49.0 a	207.6 [10]	158.6 c	5951.8 ±29.8
7	1-Nitropentane, $C_5H_{11}N^VO_2$	32	3324.0 [10]		52.6 b	215.0 [10]	162.4 c	7106.6 ±35.5
Nitroarenes								
8	Nitrobenzene $C_6H_5N^VO_2$	30	3088.1 [13]	3098.6 d ±15.4	55.0 [17]	16.0 [18]	-39.0 c	6312.4 ±31.6
9	1-Methyl-2-nitrobenzene $C_7H_7N^VO_2$	36	3745.3 [14]	3751.4 d ±18.7	58.8 e			
10	1-Methyl-3-nitrobenzene $C_7H_7N^VO_2$	36	3723.5 [14]	3751.4 d ±18.7	60.5 f	46.0 [18]	-14.5 c	7487.9 ±37.4
11	1-Methyl-4-nitrobenzene $C_7H_7N^VO_2$	36	3706.9 [14]	3751.4 d ±18.7	61.4 g	48.2 [17]	-13.2 c	
12	1-Ethyl-4-nitrobenzene $C_8H_9N^VO_2$	42	4379.0 [15]	4404.2 d ±22.0		55.3 [15]		
13	1-Ethyl-2-nitrobenzene $C_8H_9N^VO_2$	42	4385.7 [15]	4404.2 d ±22.0				
14	1,3-Dimethyl-2-nitrobenzene $C_8H_9N^VO_2$	42	4383.5 [16]	4404.2 d ±22.0	59.4 [16]	50.8 [16]	-8.6 [16]	8644.8 ±43.2
N-Alkyl- and N,N-dialkyl-N-nitramines								
15	N-Ethylnitramine $C_2H_6N^{III}N^VO_2$	16	1559.0 [19]	1575.4 d ±7.9				

Table 1 (continued)

1	2	3	4	5	6	7	8	9
16	N-Propyl-nitramine $C_3H_8N^{III}N^VO_2$	22	2216.0 [19]	2228.2 d ±11.1				
17	N-Butylnitramine $C_4H_{10}N^{III}N^VO_2$	28	2887.0 [19]	2881.0 d ±14.4				
18	N, N-Dimethyl- nitroamine $C_2H_6N^{III}N^VO_2$	16	1574.0 [11]	1575.4 d ±7.9	52.7 h	71.1 [11]	18.4 c	4200.7 ±21.0
19	N,N-Diethyl-nitramine $C_4H_{10}N^{III}N^VO_2$	28	2897.0 [11]	2881.0 d ±14.4	53.1 [11]	106.0 [11]	18.7 c	6536.9 ±32.7
20	N,N-Dipropyl-nitramine $C_6H_{14}N^{III}N^VO_2$	40	4188.6 [19]	4186.6 d ±20.9				
Dinitroalkanes								
21	1,2-Dinitroethane $C_2H_4N^V_2O_4$	14	1180.0 [20]			179.0 [20]		
22	1,1-Dinitroethane $C_2H_4N^V_2O_4$	14	1210.0 [20]		52.4 i	148.0 [20]	95.6 c	4340.0 ±21.7
23	1,3-Dinitropropane $C_3H_6N^V_2O_4$	20	1831.0 [20]			207.0 [20]		
24	1,1-Dinitropropane $C_3H_6N^V_2O_4$	20	1875.0 [20]		62.5 [12]	163.0 [20]	100.5 c	5495.9 ±27.5
25	1,1- Dinitropentane $C_5H_{10}N^V_2O_4$	32	3180.0 [20]			217.0 [20]		
26	2,3-Dimethyl-2,3- Dinitrobutane $C_6H_{12}N^V_2O_4$	38	3765.0 [20]			311.0 [20]		
27	2,2-Dinitropropane $C_3H_6N^V_2O_4$	20	1846.0 [20]		52.5 j	192.0 [20]	139.5 c	5534.9 ±27.7
28	1,4- Dinitrobutane $C_4H_8N^V_2O_4$	26	2468.0 [20]			249.0 [20]		
29	2,2- Dimethyl -1,3- dinitropropane $C_5H_{10}N^V_2O_4$	32	3121.6 [21]					
Dinitroarenes								
30	1,3-Dinitrobenzene $C_6H_4N^V_2O_4$	30	2905.0 [22]	2918.9 k ±14.6	83.0 [23]	36.0 [18]	-47.0 c	7057.7 ±35.3
31	1,2-Dinitrobenzene $C_6H_4N^V_2O_4$	30	2931.0 [22]	2918.9 k ±14.6				

Table 1 (continued)

1	2	3	4	5	6	7	8	9
32	1,4-Dinitrobenzene $C_6H_4N_2O_4$	30	2894.0 [22]	2918.9 ^{k} ±14.6	89.0 [23]	38.0 [22]	-51.0 ^{c}	7053.6 ±35.3
33	2-Methyl-1,3-dinitrobenzene $C_7H_6N^V_2O_4$	36	3556.8 [24]	3563.5 ^{k} ±17.8	98.3 [25]	55.2 [24]	-43.1 ^{c}	8212.5 ±41.1
34	2-Methyl-1,4-dinitrobenzene $C_7H_6 N_2O_4$	36	3574.0 [26]	3563.5 ^{k} ±17.8				
35	1-Methyl-2,4-dinitrobenzene $C_7H_6 N^V_2O_4$	36	3560.0 [14]	3563.5 ^{k} ±17.8	100.0 [14]	66.4 [14]	-33.2 [14]	8222.4 ±41.1
36	1-Methyl-3,5-dinitrobenzene $C_7H_6 N^V_2O_4$	36	3569.0 [26]	3563.5 ^{k} ±17.8				
N,N′-Dinitroalkylenediamines								
37	N,N′-Dinitroethylene diamine $C_2H_6N_2^{III}N_2^VO_4$	18	1540.0 [27]	1628.9 ^{k} ±8.1		101.0 [27]		
38	N,N′-Dimethyl- N,N′-dinitro methylene diamine $C_3H_8N_2^{III}N_2^VO_4$	24		2273.9 ^{k} ±11.4		29.8 [28]		
Trinitroalkanes								
39	Trinitromethane $CHN^V_3O_6$	8	458.5 [12]		54.8 [29]	68.0 [29]	-13.2 ^{c}	3833.4 ±19.2
40	2-Methyl-2,3,3-trinitrobutane $C_5H_9N^V_3O_6$	32	2922.2 [21]			331.5 [3]		
41	2-Methyl-2,3,3-trinitropentane $C_6H_{11}N^V_3O_6$	38	3642.8 [21]			290.3 [3]		
42	2,2,2-Trinitro-1-phenyl-ethane $C_8H_7N^V_3O_6$	42	4130.0 [30]				-65.7 [30]	
Trinitroarenes								
43	1,3,5-Trinitrobenzene $C_6H_3 N^V_3O_6$	30	2785.0 [26]	2798.8 ^{l} ±14.0	99.6 [32]	37.0 [33]	-70.3 ^{c}	7787.5 ±38.9
44	1,2,4-Trinitrobenzene $C_6H_3 N^V_3O_6$	30	2828.0 [26]	2798.8 ^{l} ±14.0				
45	2,3,6-Trinitrotoluene $C_7H_5 N^V_3O_6$	36	3453.0 [26]	3341.8 ^{l} ±17.1				

Table 1 (continued)

1	2	3	4	5	6	7	8	9
46	2,3,4-Trinitrotoluene $C_7H_5N^V_3O_6$	36	3485.0 [26]	3341.8 [l] ±17.1				
47	2,3,5-Trinitrotoluene $C_7H_5N^V_3O_6$	36	3447.0 [26]	3341.8 [l] ±17.1				
48	3,4,5-Trinitrotoluene $C_7H_5N^V_3O_6$	36	3465.0 [26]	3341.8 [l] ±17.1				
49	2-Methyl-1,3,5-trinitrobenzene $C_7H_5N^V_3O_6$	36	3410.0 [m]	3341.8 [l] ±17.1	118.4 [34]	50.0 [35]	-68.4 [c]	8941.0 ±44.7
50	1-Methyl-2,4,5-trinitrobenzene $C_7H_5N^V_3O_6$	36	3554.0 [26]	3341.8 [l] ±17.1				
51	2-Ethyl-1,3,5-trinitrobenzene $C_8H_7N^V_3O_6$	42	4080.7 [31]	4064.8 [l] ±20.3	130.3 [n]	67.8 [31]		
52	2,2,2-Trinitro-m-xylene $C_8H_7N^V_3O_6$	42	4065.3 [35]	4064.8 [l] ±20.3	129.8 [32]	83.1 [35]		
1,3,5-Trinitro-1,3,5-triazocyclohexane								
53	1,3,5-Trinitro-hexahydro-1,3,5-triazine $C_3H_6N_3^{III}N^V_3O_6$	24	2100.0 [19]	2146.9 [l] ±10.8				

[a] *Calc. through Eq. (6);* [b] *Calc. through Eq. (5),* $T_b = 455.7$ *K [9];* [c] *Calc. through Eq. (7);* [d] *Calc. through Eq. (3);* [e] *Calc. through Eq. (5),* $T_b = 496$ *K [9];* [f] *Calc. through Eq. (5),* $T_b = 506$ *K [9];* [g] *Calc. through Eq. (5),* $T_b = 511$ *K [9];* [h] *Calc. through Eq. (5),* $T_b = 460.2$ *K [9];* [i] *Calc. through Eq. (5),* $T_b = 458.7$ *K [9];* [j] *Calc. through Eq. (5),* $T_b = 458.7$ *K [9];* [k] *Calc. through Eq. (15);* [l] *Calc. through Eq. (23);* [m] *Average of 8 values;* [n] *Calc. through Eq. (27).*

At last, these is a possibility to calculate the $\Delta_a H$ values in the gas phase for the presented nitroalkanes (Table 1), taking into account the heats of formation of the gaseous atoms ($\Delta_f H^o_{atom}$) in their ground state at 298.15 K given in the monograph [3] (213.8, 715.0, 472.8 and 249.2 kJ atom^{-1} for H, C, N and O correspondingly) and equation (9)

$$\Delta_a H = \Sigma \Delta_f H^o_{atom} - \Delta_f H^o_{gas} \qquad (9).$$

The similar comparative-correlative approach has been applied for the known and new calculated thermochemical characteristics of nitroarenes (**8 – 14**) and N-alkylated-nitramines (**15 – 20**, Table 1). The excellent dependences (10) and (11) have been founded in the case of both types substances (Table 2).

Table 2. The parameters of equations $\Delta_{c, f, vap, sub, a} H^{(o)}$ (kJ mol^{-1}) = i + f (N-g) for combustion, formation, vaporization, sublimation and atomization processes; P 101kPa; T 298 K, all compounds in condensed state

The heats of processes	No Eq. in text	i	f	r	S_o	Nos. of compounds in Table 1
1	2	3	4	5	6	7
Nitroalkanes						
$\Delta_c H^o$	3	165.4 ± 9.0	-108.8 ± 0.4	0.999	8.1	1-7
$\Delta_f H^o_{cond}$	4	-82.6 ± 9.1	-4.4 ± 0.4	0.979	8.1`	1-7
$\Delta_{vap} H^o_{cond}$	6	33.4 ± 0.4	0.6 ± 0.1	0.999	0.3	1,2,7
$\Delta_f H^o_{gas}$	8	-47.9 ± 9.1	-3.8 ± 0.4	0.972	8.2	1-7
$\Delta_a H$	28	853.9 ± 9.4	195.6 ± 0.4	0.999	8.4	1-7
Nitroarenes						
$\Delta_c H^o$	10	168.9 ± 46.3	-108.3 ± 1.0	0.999	13.5	8-14
$\Delta_f H^o_{cond}$	14	60.4 ± 29.9	-2.8 ± 0.7	0.895	8.0	8,10,11,12,14
$\Delta_a H$	29	484.5 ± 9.4	194.4 ± 0.4	0.999	6.8	8,10,14
N-alkyl-and N,N-dialkyl-N-nitramines						
$\Delta_c H^o$	11	184.1 ± 14.6	-109.5 ± 0.5	0.999	11.2	15-20
Dinitroalkanes						
$\Delta_c H^o$	15	306.1 ± 33.3	-107.5 ± 1.0	0.999	25.4	21-29
$\Delta_f H^o_{cond, vice}$	16	-99.5 ± 6.4	-5.6 ± 0.2	0.998	4.4	21,23,26,28
$\Delta_f H^o_{cond, gemi}$	17	-89.6 ± 11.4	-3.9 ± 0.5	0.992	6.4	22,24,25,27
$\Delta_a H$	30	1597 ± 102	195.9 ± 5.6	0.999	8.4	22,24,27
Dinitroarenes						
$\Delta_c H^o$	18	364.7 ± 57.7	-109.1 ± 1.7	0.999	17.8	30-36
$\Delta_{sub} H^o$	19	-20.2 ± 17.2	-2.2 ± 0.5	0.948	3.1	30,32,33,35
$\Delta_f H^o_{cond}$	20	109.0 ± 43.3	-4.7±1.3	0.931	7.8	30,32,34,35
$\Delta_f H^o_{gas}$	21	115.2 ± 27.3	-2.1 ± 0.8	0.878	4.9	30,32,33,35
$\Delta_a H$	31	1247 ± 30	193.6 ± 0.9	0.999	5.5	30,32,33,35
Trinitroalkanes						
$\Delta_c H^o$	22	421.1 ± 89.3	-107.0 ± 3.0	0.999	79.4	39-42
$\Delta_f H^o_{cond}$	25	-10.7 ± 88.5	-8.4 ± 2.8	0.944	66.1	39-41
Trinitroarenes						
$\Delta_c H^o$	23	336.9 ± 126.7	-105.5 ± 3.5	0.996	42.0	43-48, 50-52
$\Delta_f H^o_{cond}$	26	64.2 ± 32.4	-3.3 ± 0.8	0.938	8.5	43,49,51,52
$\Delta_{sub} H^o$	27	25.3 + 12.9	2.5 ± 0.3	0.990	3.0	43,49,52

$$\Delta_c H^o = (168.9\pm46.3) - (108.3\pm1.2)\ (N\text{-}g) \tag{10}$$
$$r\ 0.999,\ S_o\ 13.5,\ n\ 7\ (\text{compounds } \mathbf{8}\text{-}\mathbf{14})$$

$$\Delta_c H^o = (184.1\pm14.6) - (109.5\pm0.5)\ (N\text{-}g) \tag{11}$$
$$r\ 0.999,\ S_o\ 11.2,\ n\ 6\ (\text{compounds } \mathbf{15}\text{-}\mathbf{20})$$

Dependences (12) and (13) between the experimentally received and calculated on Eq. (3) values of the heats of combustion for the same types of compounds (**8 − 14**) and (**15 − 20**) are excellent also

$$\Delta_c H^o{}_{exp} = (4.2\pm44.3) + (1.0\pm0.01)\Delta_c H^o{}_{calc} \tag{12}$$
$$r\ 0.999,\ S_o\ 13.5,\ n\ 7\ (\text{compounds } \mathbf{8}\text{-}\mathbf{14})$$

$$\Delta_c H^o{}_{exp} = (17.6\pm13.2) + (1.0\pm0.1)\Delta_c H^o{}_{calc} \tag{13}$$
$$r\ 0.999,\ S_o\ 11.2,\ n\ 6\ (\text{compounds } \mathbf{15}\text{-}\mathbf{20}).$$

There are a five magnitudes of the experimental heats of formation for liquid nitro arenes (**8**, **10**, **11**, **12**, **14**), however they are worse correlate with the $(N - g)$ factor (Eq. 14).

$$\Delta_f H^o{}_{cond} = (60.4\pm29.9) - (2.8\pm1.0)\ (N\text{-}g\ ) \tag{14}$$
$$r\ 0.895,\ S_o\ 8.0,\ n\ 5.$$

2.2 Dinitroalkanes, Dinitroarenes and N,N′-Dinitroalkylenediamines

The interrelation between the heats of combustion of dinitroalkanes in condensed phase (**21-29**, Table 1) and a number of bond-forming electrons has been presented in dependence (15). It is similar to the previous equations (3, 10, 11) for mononitroalkanes, -arenes and -nitroamines.

$$\Delta_c H^o = (306.1\pm26.8) - (107.5\pm1.0)\ (N\text{-}g) \tag{15}$$
$$r\ 0.999,\ S_o\ 25.4,\ n\ 9.$$

However there is some feature for these compounds, which is expressed in two linear equations (16) and (17) depending on *vic*(1,2)- or *gemi*(1,1)-arrangements of nitro groups

$$\Delta_f H^o{}_{cond,\ vic} = (-99.5\pm6.4) - (5.6\pm0.2)\ (N\text{-}g) \tag{16}$$
$$r\ 0.998,\ S_o\ 4.4,\ n\ 4\ (\text{compound } \mathbf{21, 23, 26, 28})$$

$$\Delta_f H^o{}_{cond,\ gemi} = (-89.6\pm11.4) - (3.9\pm0.5)\ (N\text{-}g) \tag{17}$$
$$r\ 0.992,\ S_o\ 6.4,\ n\ 4\ (\text{ compounds } \mathbf{22, 24, 25, 27}).$$

In the comparative plan it is necessary to consider the sizes of the slope coefficients in the equations (3, 10, 11, 15), describing the heats of combustion processes, and the sizes of slope coefficients for the processes of formation (Eqs. 4, 8, 14, 16, 17) of mononitro- and dinitrocompounds. It is possible to see, that the absolute size of the slope of factor *f* (Eq. 2) 107.5 - 109.5 in the first series of the equations practically does not differ from size 109.0 offered Kharasch and Sher for the calculation of the heats of combustion of organic compounds [8]. The same factors in the equations (4, 8, 14, 16, 17) on the average at 20-30 times is less (2.8 - 5.6) and also characterize just as in the equations (3, 10, 11, 15) the energy of "moving" of one electron (kJ • mol-1 •electron^{-1}) at the formation of a molecule nitro compound from the specified above H, C, N, O atoms.

The fact of the existence of Eq. (18) between the experimental heats of combustion of dinitroarenes (**30-36**) and the number of valence electrons additively characterizes the correctness of the offered by us approach of calculation of the heats of combustion of various nitrogen containing organic compounds with the use of the correlation equations similar to the equation (2).

$$\Delta_c H^o = (364.7 \pm 57.7) - (109.1 \pm 1.7)\,(N\text{-}g) \qquad (18)$$
$$r\ 0.999,\ S_o\ 17.8,\ n\ 7\ (\text{compounds }\mathbf{30\text{-}36}).$$

It is necessary to note also the presence of quite good dependences (19) and (20), describing interrelations of sublimation and formation processes dinitroarenes (**30-35**) and (*N-g*) parameters of their molecules. However, in the Eq. (21) we do not find such obvious correspondence between the same parameters in a gas phase.

$$\Delta_{sub} H^o = (-20.2 \pm 17.2) - (2.2 \pm 0.5)\,(N\text{-}g) \qquad (19)$$
$$r\ 0.948,\ S_o\ 3.1,\ n\ 4\ (\text{compounds }\mathbf{30,\ 32,\ 33,\ 35})$$

$$\Delta_f H^o{}_{cond} = (109.0 \pm 43.3) - (4.7 \pm 1.3)\,(N\text{-}g) \qquad (20)$$
$$r\ 0.931,\ S_o\ 7.8,\ n\ 4\ (\text{compounds }\mathbf{30,\ 32,\ 34,\ 35})$$

$$\Delta_f H^o{}_{gas} = (115.2 \pm 27.3) - (2.1 \pm 0.8)\,(N\text{-}g) \qquad (21)$$
$$r\ 0.878,\ S_o\ 4.9,\ n\ 4\ (\text{compounds }\mathbf{30,\ 32,\ 33,\ 35}).$$

To the listed above we should add, that the atomization heats of dinitroalkanes (**22, 24, 27**) dinitroarenes (**30, 32, 33, 35**) are calculated by us with the use of equations (8 and 9) and are presented in Table 1. For dinitroalkylenediamines (**37** and **38**) the heats of formation for the condensed phase are known only.

2.3 Trinitroalkanes, Trinitroarenes and 1,3,5-Trinitro-1,3,5-Triazacyclohexane

The last classes of nitro compounds are trinitroalkanes,-arenes and N, N, N-trinitrocyclotriasine, for which it is necessary to consider the thermochemical parameters. It is necessary to inform, that the heats of combustion of trinitroalkanes (**39-42**) and -arenes (**43-48, 50-52**) also well form linear dependences (22 and 23) from the number valence electrons in their molecules. The compound (**49**) is not included in the correlation (24) because of it represents an average value from eight experiments.

Also as it is shown in section 2.2, the dependence (22) was used for theoretical calculation of values $\Delta_c H^o$ trinitroaromatic compounds and trinitrazine (**43-53**, Table 1; Eq. 24). Good correlations have been received for a small amount of the experimental heats of formation and sublimation of the specified three groups of compounds (**39-41**; Eq. 25), (**43, 49, 51, 52**; Eq. 26) and (**43, 49, 51**; Eq. 27).

$$\Delta_c H^o = (421.1 \pm 89.3) - (107.0 \pm 3.0)\,(N\text{-}g) \qquad (22)$$
$$r\ 0.999,\ S_o\ 79.4,\ n\ 4\ (\text{compounds }\mathbf{39\text{-}42})$$
$$\Delta_c H^o = (336.9 \pm 126.7) - (105.5 \pm 3.5)\,(N\text{-}g) \qquad (23)$$
$$r\ 0.996,\ S_o\ 42.0,\ n\ 9\ (\text{compounds }\mathbf{43\text{-}48,\ 50\text{-}52})$$

$$\Delta_c H^o = (-134.1 \pm 217.8) + (1.0 \pm 0.1)\Delta_c H^o{}_{calc} \qquad (24)$$
$$r\ 0.985,\ S_o\ 81.3,\ n\ 9\ (\text{compounds }\mathbf{43\text{-}48,\ 50\text{-}52})$$

$$\Delta_f H^o_{cond} = (-10.7 \pm 88.5) - (8.4 \pm 2.9)\ (N\text{-}g) \tag{25}$$
$$r\ 0.944,\ S_o\ 66.1,\ n\ 3\ (compounds\ \textbf{39-41})$$

$$\Delta_f H^o_{cond} = (64.2 \pm 32.4) - (3.3 \pm 0.8)\ (N\text{-}g) \tag{26}$$
$$r\ 0.938,\ S_o\ 8.5,\ n\ 4\ (compounds\ \textbf{43, 49, 51, 52}).$$

$$\Delta_{sub}H^o = (25.3 \pm 12.9) + (2.5 \pm 0.3)\ (N\text{-}g) \tag{27}$$
$$r\ 0.990,\ S_o\ 3.0,\ n\ 3\ (compounds\ \textbf{43, 49, 52}).$$

2.4 About the Interrelation of the Heats Atomization of Nitro, Dinitroalkanes, Nitro and Dinitroarenes with the Number of Valence Electrons in Their Molecules

It is necessary to note separately, that the values of the heats atomization of all the given above types of nitro compounds, depend from the number valence electrons in molecules. The consideration shows, that there is a true presence of linear dependences (28-31). Such phenomenon is noted by us for the first time. Also it is necessary to note an especially sizes (193-196 kJ electron^{-1}), which also characterize the moving of one electron from the initial compounds to the end products at the atomization process of nitro molecules in a gas phase.

$$\Delta_a H\ = (853.9 \pm 9.4) + (195.6 \pm 0.4)\ (N\text{-}g) \tag{28}$$
$$r\ 0.999,\ S_o\ 8.4,\ n\ 3\ (compounds\ \textbf{1-7}),$$

$$\Delta_a H = (484.5 \pm 9.4) + (194.4 \pm 0.4)\ (N\text{-}g) \tag{29}$$
$$r\ 0.999,\ S_o\ 6.8,\ n\ 3\ (compounds\ \textbf{8, 10, 14}),$$

$$\Delta_a H\ = (1597 \pm 102) + (195.9 \pm 5.6)\ (N\text{-}g) \tag{30}$$
$$r\ 0.999,\ S_o\ 8.4,\ n\ 3\ (compounds\ \textbf{22, 24, 27}),$$

$$\Delta_a H\ = (1247 \pm 30) + (193.6 \pm 0.9)\ (N\text{-}g) \tag{31}$$
$$r\ 0.999,\ S_o\ 5.5,\ n\ 4\ (compounds\ \textbf{30, 32, 33, 35}).$$

3. CONCLUSIONS

On the basis of the done work it is possible to make some conclusions. The ranges of values of the slope coefficients in nitro molecules change not especially widely: 1) from -2.2 up to +2.6 for processes of vaporization and sublimation, 2) from -2.1 up to - 8.4 for processes of formation in the condensed and gaseous phases, 3) from -107.5 up to-109.5 for processes of combustion, 4) from +193.6 up to +195.9 kJ electron^{-1} for atomization processes of a molecule on the separate atoms in a gas phase accordingly. Thus, the analysis of all known experimental data in the open literature on the heats of combustion, vaporization, sublimation, formation and atomization in a various phases and their subsequent treatment within the limits of one-factorial correlations leads to the conclusion, that the use of such parameter as a number of valence electrons of the investigated molecules, containing nitro groups, is very useful to a prediction of similar properties for the unknown nitrogen containing substances.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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