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Quantitative Structure–Property Relationship: XVIII.[1] Enthalpy of Formation of Aliphatic Polynitro Compounds

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Abstract — The quantitative structure–property relationship was applied to calculate the enthalpy of formation of aliphatic polynitro compounds, which was estimated from data for alkane molecules using appropriate corrections. Two alternatives of the suggested approach were considered, in which the molecule of a nitro compound is constructed by replacement of an H atom or CH_3 group with the NO_2 group in a definite position of a saturated hydrocarbon.

The previously suggested quantitative structure–property relationship [2] describes with a good accuracy many properties of saturated hydrocarbons and compounds R–X containing a single functional group X [1, 3]. The problem becomes considerably more complicated with molecules containing several functional groups X, since the X···C and especially X···X interactions are considerably stronger than the C···C interactions, are influenced in a more complicated manner by the mutual arrangement of the fragments, etc. In general, specifically these problems are of most interest, but papers concerning them are few, because, as a rule, the required experimental data are lacking. In [4] we applied the suggested approach to estimating the properties of some polyhydric alcohols, polyphenols, and isoelectronic chlorinated derivatives of saturated hydrocarbons and benzene, in which the functional groups are arranged in a certain regular fashion. In this paper, using aliphatic nitro compounds as examples, we consider application of the quantitative structure–property relationship to estimating properties of aliphatic hydrocarbons containing several functional groups arranged irregularly, including geminal arrangement. Estimation of the properties of aliphatic polynitro compounds is of not only methodical but also practical interest, since these highly reactive compounds are used in production of explosives, pesticides, drugs, solvents for purification of lubricating oils, etc. [5, 6].

Among physicochemical properties of aliphatic polynitro compounds, the most experimentally studied aree thermochemical properties, in particular, the enthalpies of formation ΔH_f^0 [7]. The enthalpies of formation of various organic compounds, including aliphatic polynitro compounds [8], are estimated in numerous papers. We believe that the most important, from the conceptual viewpoint, are papers [9–13] in which it was shown that, to estimate the enthalpies of formation, as well as many other properties determined by the whole set of molecular orbitals, it is possible to pass from the basis of canonical molecular orbitals to the basis of localized molecular orbitals and to represent ΔH_f^0 as the sum of contributions corresponding to formation of bonds and interaction between them. In our designations, this corresponds to consideration of one- and two-particle contributions only (α, β, γ).

Since, using the approach developed in [2], we succeeded in estimating various properties of saturated hydrocarbons of diverse structures with a very good accuracy [1], we will then assume that molecules of aliphatic polynitro compounds are constructed by introducing NO_2 groups into definite positions of saturated hydrocarbon molecules and that the properties of aliphatic polynitro compounds can be estimated from the data on saturated hydrocarbon molecules, using appropriate corrections.

Two alternatives of this approach are possible. In the first case, to calculate a property of aliphatic polynitro compounds, we will assume that a nitro compound molecule is constructed by replacement of an H atom in a definite position of a saturated hydrocarbon by an NO_2 group, which can be described by introducing corrections for one- and two-particle interactions ($\Delta_{1,2}$). Then, according to [2], we obtain

[1] For communication XVII, see [1].

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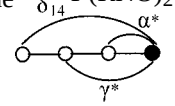
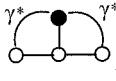
$$P(RNO_2) = P(RH) + \Delta_{1,2}, \quad (1)$$

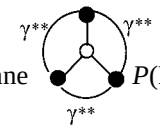
$$\Delta_{1,2} = k_1 + n(\alpha_N + \beta_{CN}) + n_{13}\gamma^* + n_{14}\delta_{14}^* + n_{15}\delta_{15}^* + \ldots + n'_{13}\gamma^{**} + n'_{14}\delta_{14}^{**} + n'_{15}\delta_{15}^{**} + \ldots \quad (2)$$

Here $P(RNO_2)$ is a property of a nitro compound; $P(RH)$, property of the saturated hydrocarbon from which this nitro compound is constructed; k_1, absolute term; $(\alpha_N + \beta_{CN})$, contribution of the NO_2 group and CN bond (since the number of contributions β_{CN} corresponding to formation of the CN bond will be equal to the number of contributions α_N, we will denote this contribution as α^*); γ^*, contribution corresponding to 1···3 interactions of N^1CC^3 fragments; δ_{14}^*, contribution corresponding to 1···4 interactions of N^1CCC^4 fragments; γ^{**}, contribution corresponding to 1···3 interactions of N^1CN^3 fragments; δ_{14}^{**}, contribution corresponding to 1···4 interaction of N^1CCN^4 fragments, etc.; n_{ij} and n'_{ij}, numbers of the corresponding contributions.

For example, the properties of certain nitro compounds can be written in the following form.

1-Nitropropane  $P(RNO)_2 = P(RH) + \alpha^* + \gamma^* + \delta_{14}^*$

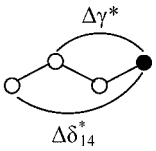
2-Nitropropane  $P(RNO)_2 = P(RH) + \alpha^* + 2\gamma^*$

Trinitromethane  $P(RNO)_2 = P(RH) + 3\alpha^* + 3\gamma^{**}$

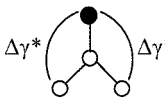
To understand what contributions are significant, it is useful to make certain approximate estimates. The expressions for corrections $\Delta_{1,2}$ and their experimental values are given as examples in Table 1. These data allow estimation of the parameters. The experimental enthalpies of formation of saturated hydrocarbons were taken from [14].

The parameters corresponding to 1···n interactions (δ_{1n}^*, Δ_{1n}^{**}) should decrease in the absolute value with increasing n, and, as there are no grounds to believe that these quantities change sign, the quantities Δ_{15}^* and Δ_{16}^{**} should be close to zero, so that it will suffice to take into account the contributions α^*, γ^*, δ_{14}^*, γ^{**}, δ_{14}^{**}, and δ_{15}^{**}. Despite the fact that the parameters α^* and γ^* obtained from data for linear molecules give large errors in the case of 2-nitropropane (Table 1) and the parameter γ^{**} determined from data for dinitromethane gives approximately the same error in the case of trinitromethane, averaging of these parameters, apparently, will give fairly accurate results. The rms deviation of the previously calculated enthalpies of formation of aliphatic polynitro compounds is 10.9 kJ mol^{-1} [8].

In the second procedure for calculating properties of aliphatic polynitro compounds, we will assume that the nitro compound molecule is constructed from the corresponding saturated hydrocarbon by replacement of a CH_3 group by an NO_2 group. For example, the 1-nitropropane molecule is constructed from butane, and 2-nitropropane molecule, from 2-methylpropane. Then, in accordance with the perturbation theory, it is necessary to introduce corrections for the perturbation reflecting the difference between the properties of the NO_2 and CH_3 groups and between the contributions corresponding to their interactions. The expression for a property in this case will be similar to Eq. (1). For example, for the 1-nitropropane molecule,

 $P(RNO_2) = P(RCH_3) + \Delta\alpha^* + \Delta\gamma^* + \Delta\delta_{14}^*$;

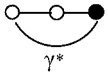
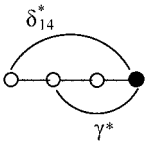
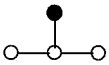
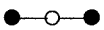
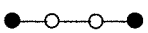
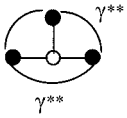
for the 2-nitropropane molecule,

 $P(RNO_2) = P(RCH_3) + \Delta\alpha^* + 2\Delta\gamma^*$,

which, on the whole, coincides with the above expressions, but with different physicochemical sense of the contributions involved. In this case, we obtain

$$P(RNO_2) = P(RCH_3) + \Delta_{1,2}. \quad (3)$$

Table 1. Parameters describing introduction of nitro groups into saturated hydrocarbon molecule

Molecule	$\Delta_{1,2}$		Parameter
	expression	experimental value, kJ mol^{-1}[a]	
Nitromethane 	α^*	–5.8	α^* –5.8
Nitroethane 	$\alpha^* + \gamma^*$	–15.9	γ^* –10.0
1-Nitropropane 	$\alpha^* + \gamma^* + \delta_{14}^*$	–21.3	δ_{14}^* –5.4
1-Nitrobutane	$\alpha^* + \gamma^* + \delta_{14}^* + \delta_{15}^*$	–17.6	δ_{15}^* 3.8
2-Nitropropane 	$\alpha^* + 2\gamma^*$	–35.9	$\alpha^* + 2\gamma^* = -25.9$
Dinitromethane 	$2\alpha^* + \gamma^*$	15.0	γ^{**} 26.8
1,2-Dinitroethane 	$2\alpha^* + 2\gamma^* + \delta_{14}^{**}$	–11.3	δ_{14}^{**} 20.5
1,3-Dinitropropane	$2\alpha^* + 2\gamma^* + 2\delta_{14}^{**} + 2\delta_{15}^{**}$	–24.2	δ_{15}^{**} 18.4
1,4-Dinitrobutane	$2\alpha^* + 2\gamma^* + 2\delta_{14}^{**} + 2\delta_{15}^{**} + 2\delta_{16}^{**}$	–35.5	δ_{16}^{**} –0.4
Trinitomethane 	$3\alpha^* + 3\gamma^{**}$	74.0	$3\alpha^* + 3\gamma^{**} = 62.7$

[a] The experimental value of $\Delta_{1,2}$ is equal to the difference between the enthalpies of formation of a nitro compound [7] and the saturated hydrocarbon from which the nitro compound is constructed [14].

Here, $P(RCH_3)$ is a property of the saturated hydrocarbon from which a nitro compound is constructed; $\Delta_{1,2}$ is determined by Eq. (2). The reasonings concerning the significance of various contributions in (3) are similar to those for the previous case and will not be repeated here.

The results of calculating the enthalpies of formation of aliphatic polynitro compounds using expressions (1) and (3) are listed in Table 2, and the parameters used in the calculations, in Table 3. In the first case, the contributions α^* and δ_{14}^*, and in the second case, δ_{14}^*, appeared to be insignificant. The calculated values are well consistent with the experimental data.

As expected, the contributions from the N···C interactions are smaller in the absolute value than those of the N···N interactions, and the 1···*n* contributions decrease with increasing *n*. The estimates of the properties obtained using the second approach are better consistent with the experiment. This is due to more accurate consideration of the contributions δ_{14}^* and δ_{14}^{**}. In particular, at more accurate determination of $\delta_{14}^* = a_{trans}\delta_{14}^{*trans} + a_{gauche}\delta_{14}^{*gauche}$ (δ_{14}^{*i} is the contribution to a property, corresponding to 1···4 interaction for *i*th conformer; a_i is the weight of the conformer in the equilibrium mixture) the parameters δ_{14}^{*i} and a_i usually unknown, but they are, to certain extent, effectively taken into account in contributions to $P(RCH_3)$. This makes such an approach the most promising.

Table 2. Enthalpies of formation (kJ mol^{-1}) of aliphatic polynitro compounds

Molecule	Experiment [7]	Caculation[a]	
		(1)	(3)
Nitromethane	–80.67	–89.37	–79.84
Dinitromethane	–59.77	–63.08	–53.38
Trinitromethane	–0.84	–10.35	–6.10
Tetranitromethane	77.33	68.51	73.40
Nitroethane	–100.32	–108.68	–104.96
1,2-Dinitroethane	–95.72	–100.28	–102.83
1,1-Dinitroethane	–101.99	–92.08	–96.06
1,1,1-Trinitroethane	–52.67	–49.16	–55.05
Hexanitroethane	153.64	163.44	161.60
1-Nitropropane	–124.98	–127.91	–127.53
2-Nitropropane	–139.61	–135.80	–141.74
1,3-Dinitropropane	–132.09	–130.50	–132.59
1,1-Dinitropropane	–119.55	–111.31	–115.70
2,2-Dinitropropane	–129.58	–130.71	–139.15
1,1,1-Trinitropropane	–76.91	–68.38	–74.70
1,1,1,2,2-Pentanitropropane	33.86	27.63	25.16
1-Nitrobutane	–143.69	–150.48	–147.60
2-Nitrobutane	–166.36	–160.18	–161.39
3-Nitro-2-methylpropane	–177.65	–169.88	–178.94
1,1-Dinitrobutane	–142.54	–133.88	–135.77
1,4-Dinitrobutane	–161.77	–160.18	–161.26
1,1,1,4-Tetranitrobutane	–104.08	–100.65	–106.30
1,1,1,3-Tetranitro-2-methylpropane	–83.60	–87.70	–84.35
1,1,3,3-Tetranitrobutane	–119.97	–117.96	–119.26
2,2,3,3-Tetranitrobutane	–84.44	–93.42	–93.84
1,1-Dinitropentane	–159.68	–153.95	–156.25
1,1,1-Trinitropentane	–121.22	–111.02	–113.57
1,1,1,3,5,5,5-Heptanitropentane	–38.46	–38.00	–
2,3-Dinitro-2,3-dimethylbutane	–222.38	–232.32	–225.80
2,3,3-Trinitro-2-methylpentane	–196.88	–194.29	–179.82
1,1,1,4,4-Pentanitro-2,2-dimethylpentane	–175.14	–183.29	–
r		0.9964	0.9972
s		1.7443	1.5804

[a] Calculations by relationships (1) and (3). ΔH_f^0 of 1,1,1,3,5,5,5-heptanitropentane and 1,1,1,4,4-pentanitro-2,2-dimethylpentane was not calculated because of the lack of the experimental data for the corresponding hydrocarbons.

Table 3. Parameters used for calculating the enthalpy of formation of aliphatic polynitro compounds (kJ mol^{-1})[a]

Parameter	Calculation	
	(1)	(3)
k_1	–14.5616 ± 2.4677	–8.5262 ± 5.0873
α^*	–	13.1160 ± 4.1124
γ^*	–9.7111 ± 0.7477	–5.8718 ± 1.0230
γ^{**}	26.3362 ± 0.8477	32.6046 ± 2.3420
δ_{14}^{**}	18.1021 ± 0.9142	17.4582 ± 1.0661
δ_{15}^{**}	7.1074 ± 1.2690	7.7425 ± 1.8447

[a] Calculation by relationships (1) and (3).

REFERENCES

1. Golovanov, I.B. and Zhenodarova, S.M., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 6, p. 900.
2. Golovanov, I.B. and Zhenodarova, S.M., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 1, p. 90.
3. Golovanov, I.B. and Zhenodarova, S.M., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 4, p. 553.
4. Golovanov, I.B. and Zhenodarova, S.M., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 7, p. 1164.
5. Tartakovskii, V.A., Ioffe, I.L., Dil'man, A.D., and Tishkov, A.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, no. 1, p. 1850.
6. Novikov, S.S., Shvekhgeimer, G.A., Savost'yanova, V.V., and Shlyapochnikov, V.A., *Khimiya alifaticheskikh i alitsiklicheskikh nitrosoedinenii* (Chemistry of Aliphatic and Alicyclic Nitro Compounds), Moscow: Khimiya, 1974.
7. Lebedev, Yu.A., Miroshnichenko, E.A., and Knobel', Yu.K., *Termokhimiya nitrosoedinenii* (Thermochemistry of Nitro Compounds), Moscow: Nauka, 1970.
8. Baskin, I.I., Palyulin, V.A., and Zefirov, N.S., *Vestn. Mosk. Gos. Univ., Ser. 2: Khim.*, 2001, vol. 42, no. 6, p. 387.
9. Brown, R.D., *J. Chem. Soc.*, 1953, no. 9, p. 2615.
10. Dewar, M.J.S. and Pettit, R., *J. Chem. Soc.*, 1954, no. 5, p. 1625.
11. Klopman, G., *Tetrahedron*, 1963, vol. 19, suppl. 2, p. 111.
12. Pople, J.A. and Santry, D.P., *Mol. Phys.*, 1964, vol. 7, no. 3, p. 269.
13. Dewar, M.J.S. and Dougherty, R.C., *The PMO Theory of Organic Compounds*, New York: Plenum, 1975.
14. Stull, D.R., Westrum, E.F., and Sinke, G.C., *The Chemical Thermodynamics of Organic Compounds*, New York: Wiley, 1969.