QSPR approach to the calculation of rate constants of homolysis of nitro compounds in different states of aggregation

2.* The liquid phase

D. V. Sukhachev,[a] T. S. Pivina,[a] N. I. Zhokhova,[b] N. S. Zefirov,[b] and S. Zeman[c]*

[a]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328*

[b]*Department of Chemistry, M. V. Lomonosov Moscow State University, Vorob'evy Gory, 119899 Moscow, Russian Federation. Fax: +7 (095) 939 0126*

[c]*University of Pardubice, CZ-532 10 Pardubice, Czech Republic. Fax: (042) 40 514 530*

A method for theoretical estimation and prediction of rate constants of homolysis of C—N and N—N bonds is used for nitro compounds in the liquid phase. The method is based on the QSPR approach.

Key words: QSPR approach; homolysis, nitro compounds, rate constants; liquid phase.

Known theoretical methods (quantum-chemical and molecular-mechanics methods) for the calculation of parameters of the thermal stability of nitro compounds can not be applied to compounds in the liquid phase. To overcome the restrictions of theoretical computation methods and to estimate parameters of the thermal stability (the activation energies and the rate constants of homolysis)[1,2] of compounds in the liquid phase we developed a method based on the QSPR approach. In the present paper this method was used for estimation of the rate constants of homolysis of C—N and N—N bonds of nitro compounds in the liquid phase.

It is known that thermal stability of nitro compounds depends on different factors: the structure, the state of aggregation, an autocatalytic decomposition of compounds, *etc.* We examined the relationship between one of the factors, namely the chemical structure and the rate constant of homolysis of nitro compounds. The mechanism of their decomposition was ignored. It should be only noted that according to experimental thermochemical data the primary step of thermolysis of these compounds is a radical cleavage of C—N and N—N bonds.

Previously[2—5] the QSPR approach was applied to the calculations of some parameters (the thermal stability of nitro compounds and their sensitivity to the impact). This approach is based on the construction of a set of lineary "structure—property" correlation models by using the EMMA (Efficient Modeling of Molecular Activity)[2] program package.

The values of log k were recomputed using the Arrhenius equation and the average temperature of homolysis for the compounds studied (420 K).[1]

The experimental data base[6—43] consisted of 67 compounds in the training set (Table 1) and of 7 compounds in the test set (Table 2). When constructing models about 3000 descriptors of molecular structure were calculated for each compound. Then the descriptors that related to the correlation between the structure and the value of a parameter with the highest accuracy were selected by optimization of base sets of descriptors.

The results of seaching for the "structure—log k" correlations for one of the most stable regression model are shown in Fig. 1. The model is constructed on 6 descriptors and is represented by the equation

$$\log k = -22.31 + 18.86\,HB_{Acc}/N_{at} - 1.00\,\min S_i + 1.55\,TIC_1/N_{at} + 0.25\max_{fr_1} S - 0.21\max_{fr_2} S + 0.45\,n(fr_3), \quad (1)$$

$n = 67$, $R = 0.91$, $s = 1.08$, $F = 51.3$, $\Delta = 0.82$,

where n is the number of structures in the training set; R is the correlation coefficient; s is the standard deviation; F is the Fischer criterion; Δ is the average square error; N_{at} is the number of nonhydrogen atoms in the molecule; $HB_{Acc} = N_O + N_N$ is the sum of the O and N atoms in the molecule (index is proposed by D. E. Petelin and reflects the number of potential acceptors of hydrogen bonds in the molecule); $\min S_i$ is the lowest

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Table 1. Experimantal and calculated log k for homolysis of nitro compounds in the liquid state (from the training set)

Compound	Empirical formula	−log$k$		References
		calculated	experimental	
1,4-Dinitriso-1,4-diazacyclohexane	$C_4H_8N_4O_2$	5.4	3.9	6
1,3,5-Trinitriso-1,3,5-triazacyclohexane	$C_3H_6N_6O_3$	2.8	4.8	7
Bis(2,2,2-trinitroethyl)-*N*-nitrosamine	$C_4H_4N_8O_{13}$	3.6	3.1	8
Bis(2,2-dinitro-2-fluoroethyl)-*N*-nitrosamine	$C_4F_2H_4N_6O_9$	4.6	5.4	8
N-Monomethylnitramine	$CH_4N_2O_2$	3.5	2.9	9
Ethylenedinitramine	$C_2H_4N_4O_2$	4.6	3.5	9
Potassium monomethylnitraminate	$KCH_3N_2O_2$	8.0	6.1	9
Potassium ethylenedinitraminate	$K_2C_2H_2N_4O_4$	9.3	9.6	9
N,N-Dimethylnitramine	$C_2H_6N_2O_2$	6.2	5.2	10
1,3-Dinitro-1,3-diazacyclopentane	$C_3H_6N_4O_4$	5.6	5.1	11
1,4-Dinitro-1,4-diazacyclohexane	$C_4H_8N_4O_4$	6.7	7.4	12
1,3,5-Trinitro-1,3,5-triazacyclohexane	$C_3H_6N_6O_6$	5.1	6.2	12
1,5-Endomethylene-3,7-dinitro-1,3,5,7-tetra-azacyclooctane	$C_5H_{10}N_6O_4$	5.8	5.6	10
4-Nitrazavaleric acid	$C_5H_{10}N_2O_4$	7.9	7.2	13,14
1-(Methylnitramino)-2,4,6-trinitrobenzene	$C_7H_5N_5O_8$	7.5	5.0	13
Methyl nitrate	CH_3NO_3	4.7	6.2	15
Ethylene glycol dinitrate	$C_4H_4N_2O_6$	5.2	5.8	16
Diethylene glycol dinitrate	$C_4H_8N_2O_7$	5.4	5.4	17
1,3-Propylene glycol dinitrate	$C_3H_6N_2O_6$	5.4	5.5	18
1,4-Butylene glycol dinitrate	$C_4H_8N_2O_6$	5.7	5.2	18
2,3-Butylene glycol dinitrate	$C_4H_8N_2O_6$	5.2	4.9	18
2-Hydroxy-1,3-propylene glycol dinitrate	$C_3H_6N_2O_7$	4.0	5.3	18
Glycerol dinitrate	$C_3H_5N_3O_9$	5.0	4.9	19
Erythritol tetranitrate	$C_4H_6N_4O_{12}$	4.4	3.6	20
Xylitol pentanitrate	$C_5H_7N_5O_{15}$	3.7	3.1	20
Pentaerythritol tetranitrate	$C_5H_6N_4O_{12}$	5.1	4.8	16
Mannitol hexanitrate	$C_6H_8N_6O_{18}$	3.1	3.0	16
Dipentaerythritol hexanitrate	$C_{10}H_{16}N_6O_{19}$	5.1	5.5	21
N,N-Diethanolnitramine dinitrate	$C_4H_8N_4O_8$	4.7	5.1	22
Trimethylolnitromethane trinitrate	$C_4H_6N_4O_{11}$	4.6	3.6	23,24
Ethyl nitrate	$C_2H_5NO_3$	5.2	6.1	20
1,1,1-Triethylolpropane trinitrate	$C_9H_{17}N_3O_9$	5.1	5.7	25
Nitromethane	CH_3NO_2	7.3	8.8	26
Dinitromethane	$CH_2N_2O_4$	6.6	5.9	37
Trinitromethane	CHN_3O_6	5.2	4.7	37
Tetranitromethane	CN_4O_8	4.1	3.5	28
1,1,1-Trinitroethane	$C_2H_3N_3O_6$	5.4	6.0	29
1-Nitropropane	$C_3H_7NO_2$	10.6	11.7	20
2-Nitropropane	$C_3H_7NO_2$	8.0	7.8	20
1,1-Dinitropropane	$C_3H_6N_2O_4$	8.9	9.2	20
1,1,1-Trinitropropane	$C_3H_5N_3O_6$	5.7	4.9	20
1,1,1,3-Tetranitropropane	$C_3H_4N_4O_8$	5.4	7.9	30,20
2-Methyl-1,1,1,3-tetranitropropane	$C_4H_6N_4O_8$	4.4	4.2	30
1,1,1,2,2-Pentanitropropane	$C_3H_3N_5O_{10}$	0.1	1.5	30
Hexanitropropane	$C_2N_6O_{12}$	2.14	1.3	28,31
1-Fluoropentanitroethane	$C_2FN_5O_{10}$	2.1	1.7	28
2,4-Dinitrotoluene	$C_7H_6N_2O_4$	9.5	8.4	32
2,6-Dinitrotoluene	$C_7H_6N_2O_4$	9.7	10.4	32
3,5-Dinitrotoluene	$C_7H_6N_2O_4$	9.5	10.7	32
2,4,6-Trinitrotoluene	$C_7H_5N_3O_6$	8.8	8.7	33
1,3-Dimethyl-2,4,6-trinitrobenzene	$C_8H_7N_3O_6$	8.9	9.2	33
3,3′-Dimethyl-2,2′,4,4′,6,6′-hexanitro-diphenyl	$C_{14}H_8N_6O_{12}$	8.8	8.1	34
α,β-Bis(2,4,6-trinitrophenyl)ethane	$C_{15}H_{10}N_6O_{12}$	8.6	9.1	35
2,2′,4,4′,6,6′-Hexanitrosostilbene	$C_{14}H_6N_6O_{12}$	6.3	6.6	36
1-Chloro-2,4,6-trinitrobenzene	$C_6ClH_2N_3O_6$	10.3	11.5	32

Table 1. (*Continued*)

Compound	Empirical formula	−log*k*		References
		calculated	experimental	
1,3,5-Trichloro-2,4,6-trinitrobenzene	$C_6Cl_3N_3O_6$	11.3	11.7	32
1-Hydroxy-2,4,6-trinitrobenzene	$C_6H_3N_3O_7$	7.8	8.3	37,38
1,3,5-Trihydroxy-2,4,6-trinitrobenzene	$C_6H_3N_3O_9$	6.6	4.1	39
1-Methoxy-2,4,6-trinitrobenzene	$C_7H_5N_3O_7$	5.4	7.3	38
1-Amino-2,4,6-trinitrobenzene	$C_6H_4N_4O_6$	7.9	9.0	37
2,2′,4,4′,6,6′-Hexanitroazobenzene	$C_{12}H_4N_8O_{12}$	8.5	8.3	40
2,2′,4,4′,6,6-Hexanitrobenzophenone	$C_{13}H_4N_6O_{13}$	8.9	9.9	40
2,2′,4,4′,6,6-Hexanitrobiphenylsulfide	$C_{12}H_4N_6O_{12}S$	9.3	9.0	42
1,3,5-Trinitrobenzene	$C_6H_3N_3O_6$	9.6	11.5	33
2,2′,4,4′,6,6-Hexanitrodiphenyl	$C_{12}H_4N_6O_{12}$	9.7	9.7	37
Benzotrifuroxane	$C_6N_6O_6$	6.2	7.4	43

Table 2. Experimental and calculated log *k* for homolysis of nitro compounds in the liquid state (from the test set)

Compound	Empirical formula	−log*k*		References
		calculated	experimental	
Bis(2,2-dinitropropyl)-*N*-nitrosamine	$C_7H_{11}N_6O_9$	4.0	5.9	8
Methylenedinitramine	$CH_4N_4O_4$	3.5	3.3	9
1,2-Propylene glycol dinitrate	$C_3H_6N_2O_4$	5.2	4.9	18
2,2-Dinitropropane	$C_3H_6N_2O_4$	5.5	6.7	20
1,3,5-Trimethyl-2,4,6-trinitrobenzene	$C_9H_9N_3O_6$	10.7	9.2	33
1,3-Dichloro-2,4,6-trinitrobenzene	$C_6C_{12}HN_3O_6$	11.5	10.3	32
1,3-Dihydroxy-2,4,6-trinitrobenzene	$C_6H_3N_3O_8$	6.8	6.8	37

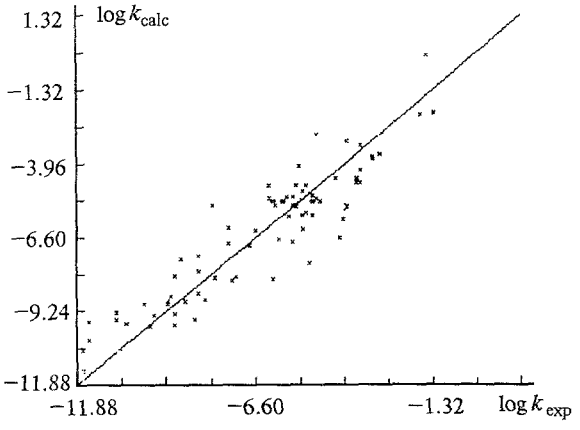
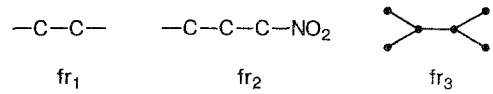


Fig. 1. Scattering diagram of experimental and calculated log *k* for the training set consisting of 67 compounds from different chemical classes.

value of electrotopological states of atoms in the molecule; $TIC_1 = n_i \log_2(n/n_i)$, where n is the total number of atoms, n_i is the number of atoms of different types taking into account neighboring atoms and adjacent hydrogen; S_i is the sum of electrotopological states of atoms in fragment fr_i; maxS is the highest value of index S for all fragments fr_i in the molecule; n(fr) is the number of fragments (fr) in the molecule.

Fragments used in the model (1) are given below:



In the training set (see Table 1) the biggest errors in log *k* (2.5) should be noted for 1,1,1-trinitropropane and 1,3,5-trihydroxy-2,4,6-trinitrobenzene. For potassium monomethylnitraminate an error is 2.0, and for 1,3,5-trinitrozo-1,3,5-triazacyclohexane, 1-methoxy-2,4,6-trinitrobenzene, and 1,3,5-trinitrobenzene they are 1.9.

As follows from the data obtained Eq. (1) describes the "structure—rate constant of homolysis" correlation for nitro compounds in the liquid phase less correctly than the equation for compounds in the gas phase[1]: the model has a lower correlation coefficient (R) and a higher average absolute error. Probably, this fact depends on the effects of the medium, particularly the intermolecular interaction. Thus, for nitro compounds in the gas phase the degree of adequacy of the molecular

structure for the parameter studied (log k) is higher then that revealed for nitro compounds in the liquid phase.

Comparing descriptors used in models of "structure—rate constant of homolysis" obtained for nitro compounds in gas and liquid phases one may noted that in both cases the most informative are indices of electrotopological states of atoms in fragments which reflect the electron density distribution at atoms. It also should be noted the presence of the topological index TIC_1 in the model for nitro compounds in the liquid phase, which is not informative for the "structure—log k" correlation for nitro compounds in the gas phase.

Data on the estimation of the prediction capability of the model for test compounds are presented in the Table 2. Relatively high errors should be noted for bis(2,2-dinitropropyl)-*N*-nitrosamine ($\Delta\log k = 1.9$) и 1,3,5-trimethyl-2,4,6-trinitrobenzene ($\Delta\log k = 1.5$).

In conclusion, the present investigation confirms that the QSPR approach allows one to estimate the rate constants of the thermal decomposition of nitro compounds in the liquid phase with sufficient accuracy.

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