Variation of physicochemical properties in the aggregates of structual isomers

V. A. Shlyapochnikov, A. V. Evtushenko, and B. B. Smirnov*

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

The regions of variation of density, enthalpy of formation, and detonation velocity of all of the formally possible structual isomers were determined for several molecular formulas of C,H,N,O-containing explosives. The histograms of the distribution of the structual isomers over these parameters were constructed.

Key words: structural isomers, variation of properties; enthalpy of formation; density; detonation velocity.

It is known that the number of structural isomers (SI) rapidly increases as the number of atoms in the molecule increases. This trend is quantitatively represented by the Polya equation,[1] which evaluates the upper bound of a number of nonisomorphic graphs with a settled number of nodes. For example, according to this equation, about 10^{45} nonisomorphic graphs exist for 20 nodes. Of course, for SI, this estimate is much overstated, since the order of nodes of a chemical graph is bounded above by their chemical nature, rather than by their number.

However, the distribution of the SI formally possible for a certain molecular formula (MF) over one or another physicochemical parameter seems to be more important than the precise number of SI. It has been implicitly assumed in some works that the limits in which the properties of SI vary are rather narrow. If this were true, the search for new compounds with desired properties would be appreciably reduced to the identification of suitable MF, and the field of activity of chemists dealing with synthesis would be narrowed down as far as possible. However, no anywhere-near rigorous investigations in this direction have been carried out. These studies require the use of computational methods that are sufficiently quick, on the one hand, and sufficiently accurate, on the other hand. The methods for approximation of density (ρ) and enthalpy of formation ($\Delta_f H^\circ$) by Fourier series[2,3] developed by us previously are fully suited for this purpose, since they combine a rather high rate with reasonable accuracy: ± 0.06 g cm^{-3} for ρ and ± 20 kcal mol^{-1} for $\Delta_f H^\circ$. The detonation velocity (D) was determined using the previously described method.[4–6] The computer construction of SI was carried out using the NGIOS structure generator developed by V. P. Suboch and A. P. Pavlova at the Institute of Physics of the Belarussian Academy of Sciences.

The following molecular formulas were used as the objects of the investigation: CH_5N_3, CH_5N_3O, CH_4N_4O, $CH_3N_3O_2$, $CH_4N_4O_2$, and $C_3H_6N_2O_2$. This selection is quite subjective; therefore, the results obtained should not be automatically extended to other MF. Nevertheless, we were able to gain an impression of the possible scattering of the physicochemical properties of SI. For all of the SI, the values of ρ, $\Delta_f H^\circ$, and D have been calculated. The results are presented in Table 1, in which the number of SI whose parameters fit in the given intervals is presented for each MF.

A series of histograms was constructed (Fig. 1) that show the distribution of SI over the ρ, $\Delta_f H^\circ$ coordinate plane. From Fig. 1, one can clearly see that the number of formally possible SI increases dramatically as the MF is extended by one or two atoms. As this takes place, the SI occupy a progressively increasing area in the ρ, $\Delta_f H^\circ$ coordinate plane. As can be seen from the histograms, most of the SI are arranged rather compactly. This probably gave some grounds for the attempts to calculate physicochemical properties of substances on the basis of their elemental composition. However, the number of SI with essentially different ρ and $\Delta_f H^\circ$ is rather great.

For some of the SI having the greatest calculated $\Delta_f H^\circ$ values, quantum-chemical calculations by the semiempirical MNDO method were also carried out. A comparison of the $\Delta_f H^\circ$ values obtained by quantum-chemical calculations with those determined by the previously described[3] method and, for some compounds, also with the experimental data available (Table 2) confirms the inference that the $\Delta_f H^\circ$ values are scattered. The results obtained for even this modest set of MF with rather small numbers of atoms, show how wide the scatter of the values of physicochemical parameters for a single MF can be.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 859—862, May, 1995.

1066-5285/95/4405-0832 $12.50

From the foregoing, one may conclude that the prediction of the target products of the synthesis is not so much a search for the molecular structure with a suitable set of physicochemical properties, but it is rather a correct comparative estimate of the possibility of the existence, routes for the synthesis, and opera-

Table 1. The numbers of SI corresponding to various MF (n_{MF}) that fit in the specified ranges of density, $\Delta\rho$, the enthalpy of formation, $\Delta(\Delta_f H^\circ)$, and the detonation velocity, ΔD ($n_{\Delta\rho}$, $n_{\Delta(\Delta_f H^\circ)}$, and $n_{\Delta D}$, respectively)

MF	n_{MF}	$\Delta\rho$ /g cm^{-3}	$n_{\Delta\rho}$	$\Delta(\Delta_f H^\circ)$ /kcal mol^{-1}	$n_{\Delta(\Delta_f H^\circ)}$	ΔD /km s^{-1}	$n_{\Delta D}$
$C_3H_6N_2O_2$	6394	0.8—0.9	14	−190 to −170	17	4.5—4.8	190
		0.9—1.0	189	−170 to −150	94	4.8—5.1	334
		1.0—1.1	177	−150 to −130	147	5.1—5.4	760
		1.1—1.2	1221	−130 to −110	722	5.4—5.7	1250
		1.2—1.3	1509	−110 to −90	594	5.7—6.0	1493
		1.3—1.4	1046	−90 to −70	1144	6.0—6.3	604
		1.4—1.5	2047	−70 to −50	1644	6.3—6.6	559
		1.5—1.6	102	−50 to −30	706	6.6—6.9	358
		1.6—1.7	13	−30 to −10	728		
		1.7—1.8	38	−10 to 10	270		
		1.8—1.9	31	10 to 30	245		
		2.0—2.1	7	30 to 50	80		
				50 to 70	3		
$CH_4N_4O_2$	2142	0.8—0.9	4	−100 to −80	71	5.6—5.9	290
		0.9—1.0	10	−80 to −60	4	5.9—6.2	216
		1.0—1.1	7	−60 to −40	624	6.2—6.5	78
		1.1—1.2	582	−40 to −20	605	6.5—6.8	129
		1.2—1.3	233	−20 to 0	32	6.8—7.1	243
		1.3—1.4	249	0 to 20	182	7.1—7.4	253
		1.4—1.5	323	20 to 40	127	7.4—7.7	243
		1.5—1.6	511	40 to 60	342	7.7—8.0	188
		1.6—1.7	7	60 to 80	151	8.0—8.3	109
		1.7—1.8	123	80 to 100	4	8.3—8.6	247
		1.8—1.9	93			8.6—8.9	1
						8.9—9.2	56
						9.2—9.5	12
						9.5—9.8	77
$CH_3N_3O_2$	411	1.0—1.1	21	−100 to −80	23	5.6—5.9	19
		1.1—1.2	17	−60 to −40	119	5.9—6.2	102
		1.2—1.3	91	−40 to −20	113	6.2—6.5	23
		1.3—1.4	79	−20 to 0	25	6.5—6.8	28
		1.4—1.5	27	0 to 20	45	6.8—7.1	20
		1.5—1.6	31	40 to 60	65	7.1—7.4	18
		1.6—1.7	98	60 to 80	21	7.4—7.7	128
		1.7—1.8	37			7.7—8.0	18
		1.8—1.9	10			8.0—8.3	8
						8.3—8.6	23
						8.6—8.9	15
						8.9—9.2	15
CH_4N_4O	374	0.9—1.0	73	−50 to −30	9	5.3—5.6	99
		1.0—1.1	26	−30 to −10	93	5.9—6.2	113
		1.1—1.2	77	−10 to 10	145	6.2—6.5	8
		1.2—1.3	72	10 to 30	3	6.5—6.8	14
		1.3—1.4	51	30 to 50	7	6.8—7.1	3
		1.4—1.5	30	50 to 70	54	7.1—7.4	14
		1.5—1.6	26	70 to 90	38	7.4—7.7	11
		1.6—1.7	3	90 to 110	25	7.7—8.0	33
		1.7—1.8	2			8.0—8.3	48
		1.8—1.9	17			8.6—8.9	11
						8.9—9.2	11
						9.2—9.5	4

Table 1. (*continued*)

MF	n_{MF}	Δρ /g cm^{-3}	$n_{\Delta\rho}$	$\Delta(\Delta_f H°)$ /kcal mol^{-1}	$n_{\Delta(\Delta_f H°)}$	ΔD /km s^{-1}	$n_{\Delta D}$
CH_5N_3O	59	0.9—1.0	19	−80 to −60	1	4.4—4.7	11
		1.0—1.1	19	−60 to −40	23	5.0—5.3	23
		1.1—1.2	12	−40 to −20	21	5.3—5.6	6
		1.3—1.4	6	0 to 20	2	5.9—6.2	2
		1.4—1.5	3	20 to 40	5	6.5—6.8	6
				40 to 60	4	6.8—7.1	1
				60 to 80	3	7.1—7.4	3
						8.0—8.3	4
CH_3N_5	8	0.8—0.9	2	−20 to 0	3	5.1—5.4	2
		0.9—1.0	2	0 to 20	3	5.4—5.7	1
		1.0—1.1	3	60 to 80	2	6.6—6.9	2
		1.2—1.3	1				

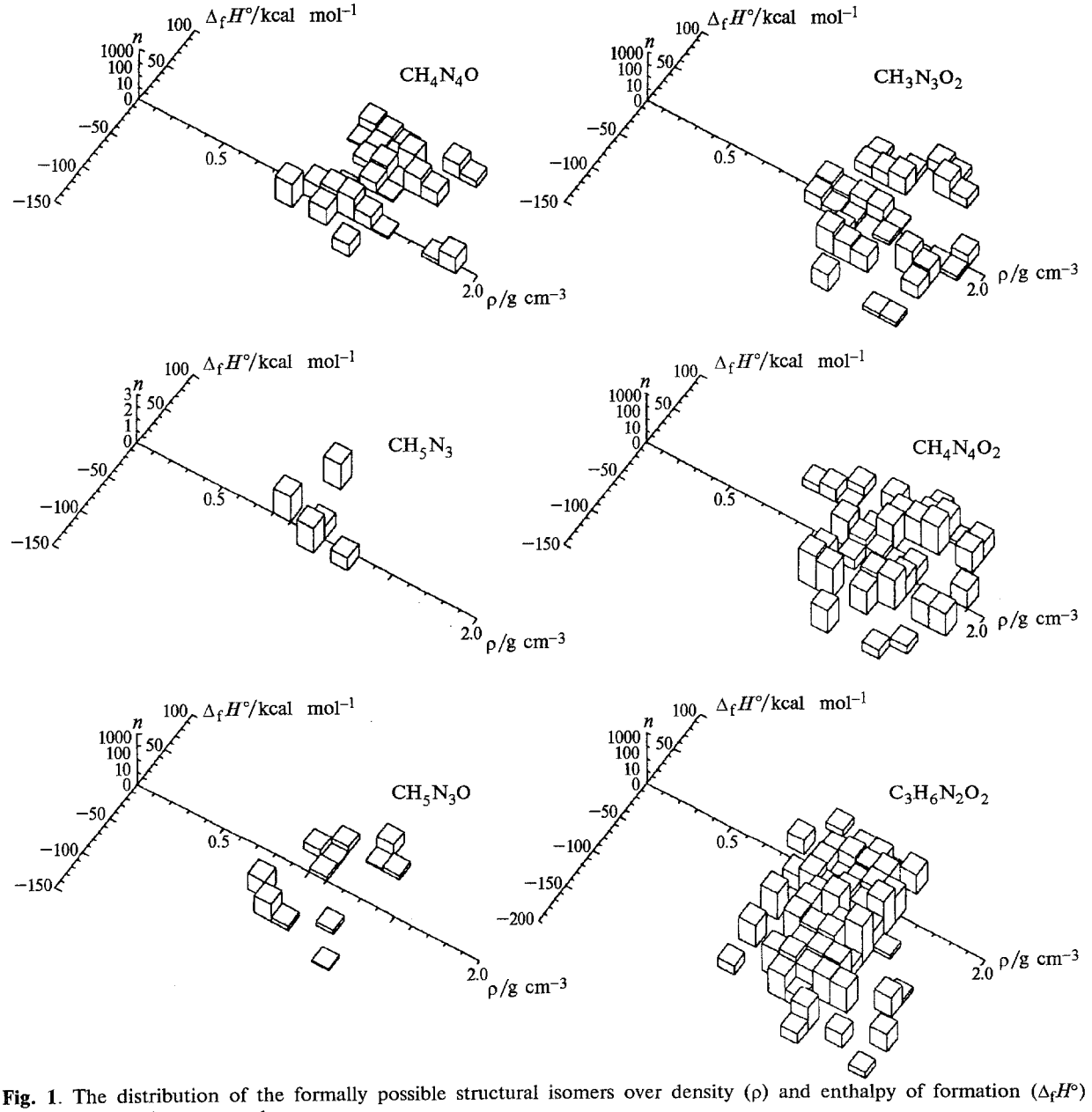

Fig. 1. The distribution of the formally possible structural isomers over density (ρ) and enthalpy of formation ($\Delta_f H°$) for the molecular formulas presented.

Table 2. The experimental ($\Delta_fH°$(exp.)), approximated by Fourier series[3] ($\Delta_fH°$(calc.[3])), and MNDO calculated ($\Delta_fH°$(*MNDO*)) enthalpies of formation (kcal mol^{-1})

Structure	$\Delta_fH°$ (exp.)	$\Delta_fH°$ (calc.[3])	$\Delta_fH°$ (MNDO)
HON=CHC(Me)=NOH	−29.6	−57.0	
$CH_2(CONH_2)_2$	−130.0	−142.4	
$NH_2C(O)NHC(O)Me$	−126.0	−107.0	
$(CH_2{=}N{\rightarrow}O)_2CH_2$		66.3	79.0
$CH_2N{=}N{\rightarrow}O{-}N{=}NH$		95.7	91.3
$(NH_2)_2C{=}NNO_2$	−29.9	4.1	
MeN=N→O		65.7	41.5
$NH{=}NCH_2N{=}NH$ (→O)	105.9	81.9	
MeN=N→O		106.9	78.3
$NH_2NHC(O)NH_2$	−39.9	−72.3	
$NH_2N{=}NMe$ (→O)		72.5	47.1
$(NH_2)_2C{=}NH$	−17.0	−13.4	
$MeN{=}NNH_2$		79.7	39.0
$NH_2CH_2N{=}NH$		65.5	30.8

tional characteristics of the structural isomers having similar sets of the target parameters.

The authors are grateful to Mrs. I. D. Solodukhina for the design of the graphical material.

The work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 94-03-09323).

References

1. V. N. Sachkov, *Vvedenie v kombinatornye metody diskretnoi matematiki* [*Introduction to Combinatorial Methods of Discrete Mathematics*], Nauka, Moscow, 1982 (in Russian).
2. A. V. Evtushenko and B. B. Smirnov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 22 [*Russ. Chem. Bull.*, 1994, **43**, 13 (Engl. Transl.)].
3. A. V. Evtushenko and B. B. Smirnov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1389 [*Russ. Chem. Bull.*, 1994, **43**, 1315 (Engl. Transl.)].
4. V. I. Pepekin, M. N. Makhov, and Yu. A. Lebedev, *Dokl. Akad. Nauk SSSR*, 1977, **232**, 852 [*Dokl. Chem.*, 1977, **232** (Engl. Transl.)].
5. V. I. Pepekin, M. N. Makhov, and Yu. A. Lebedev, *Dokl. Akad. Nauk SSSR*, 1977, **234**, 105 [*Dokl. Chem.*, 1977, **234** (Engl. Transl.)].
6. V. I. Pepekin and Yu. A. Lebedev, *Dokl. Akad. Nauk SSSR*, 1977, **234**, 1391 [*Dokl. Chem.*, 1977, **234** (Engl. Transl.)].
7. L. Medard and M. Thomas, *Met. Poudres*, 1949, **31**, 173.
8. D. R. Stull, E. F. Westram, and G. C. Zinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969.
9. M. Kh. Karapet'yants and M. L. Karapet'yants, *Osnovnye termodinamicheskie konstanty organicheskikh i neorganicheskikh veshchestv* [*The Main Thermodynamic Constants of Organic and Inorganic Compounds*], Khimiya, Moscow, 1968 (in Russian).

Received October 11, 1994;
in revised form November 22, 1994