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"Microscopic" and "Macroscopic" Level of the Errors for Detonation Characteristics Calculations: Pedigree of the Errors

T.S. Pivina, E.A. Arnautova, M.S. Molchanova and V.V. Shcherbukhin

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913, Russia

Abstract

The detonation velocity is one of the principal characteristics of energetic materials. Therefore, computer search for structures of materials with high detonation velocity is a very urgent problem.

We formulated the following task: to elaborate a concept of computer design and subsequent screening of target structures with high detonation velocities.

The present state of this concept and the operation of the program package are illustrated by computer generation of novel energetic compounds, including caged skeletons. Using some optimum gross formulas, we use methods of mathematical chemistry for computer generation of isomeric structural formulas, which may correspond to potentially interesting substances with high detonation velocity. Then, using different methods (mostly original) for estimating the properties of these compounds, we calculate their physicochemical characteristics and recommend some of them for synthesis.

We also analyzed the possible sources of errors during calculation of some detonation characteristics and determined the possible error ranges for the calculated properties at the micro level (enthalpies of formation and molecular crystal densities). As a result, the total (macro level) errors in calculations of detonation parameters were determined.

Introduction

Methods of computer chemistry are presently widely used for predicting structures of substances with the given characteristics. This fact is easy to understand: computer has fantastic potentialities for enumerating structural isomers

generated from the given molecular formula. For example, 217 isomers correspond to the composition C_6H_6 . Thus, theoretical computer design and subsequent computer screening turn out to be more efficient (from the economic standpoint) than direct synthetic search.

In addition, the "computer brain" has no accepted stereotypes (which often determine the direction of search for specialists in synthetic chemistry), and we should expect that computer chemistry will provide us with nontrivial structures possessing extremum characteristics.

The objective of this study was computer search for structures of compounds with high detonation velocities.

However, solving the problem of computer screening for compounds with high detonation velocity, we encountered the problem of different errors in velocity calculations. These errors depend on the inaccuracy of estimating the physicochemical characteristics that are used for calculating the velocity: energy content and molecular crystal density of the structures in question. Therefore, we had to study how the errors emerging at the micro level of computer search for compounds with high detonation velocity (i.e., during calculations of formation enthalpies and molecular crystal densities) affect to accuracy of calculations with respect to macro level characteristics (the macro level is the level of computer screening by detonation velocities and subsequent selection of the target structures).

This study does not touch upon the mechanism of such a complex phenomenon as detonation. It only considers, so to say, the purely "pragmatic" aspects of the relationships between the molecular and macroscopic levels of this phenomenon: the relationship between the calculated characteristics of the micro level (enthalpy of formation and molecular crystal density) with the calculated characteristics of the macroscopic level.

So, we analyzed the possible sources of errors in such calculations by several particular examples, trying to trace the "pedigree" of the errors from the micro level to some detonation characteristics of the macro level.

Methodology

The present state of our concept and the program package for computer search of promising structure [1] are illustrated by Fig. 1. Using some optimum gross

Fig. 1. The flow-chart of computer search for structures of target compounds.

formula, we use mathematical chemistry to perform computer generation of isomeric structural formulas corresponding to potentially interesting substances with possibly high detonation velocity. Then, using different methods for estimating the properties of these compounds, we calculate their physical and chemical characteristics.

This study illustrates the whole concept of search for structures of high-energy compounds with high detonation velocities by the example of caged-type compounds from the adamantane and wurtzitane series.

The problem was formulated as follows: starting from the gross formulas of adamantane $C_{10}H_{16}$ and wurtzitane $C_{12}H_{18}$, find their potentially interesting nitroamino derivatives [2]. The principal parameter characterizing the compounds was their detonation velocity, which is known to be directly related to energy content and crystal density.

From the structural viewpoint, the energy content is determined [3] by the optimum number of quaternary and/or tertiary carbon atoms, tertiary nitrogen atoms, condensed rings, and also by the presence of explosophoric groups. The crystal density depends on the molecule's own symmetry and is usually higher for symmetrical molecules [4].

The first step consisted in the generation of constitutional isomers, represented by molecular graphs. Among all the molecular graphs that could be found for the given gross formulae of the adamantane and wurtzitane series, we considered only those which obeyed the restrictions specified in [2].

Using the GEM program [2] and the conditions for selecting the appropriate structures, we finally sorted out 11 isomers for the adamantane series and 49 isomers for the wurtzitane series. Afterwards, we estimated the energy content of these molecules by computational methods of quantum chemistry and selected 3 isomers from the adamantane series and 5 isomers from the wurtzitane series as the most promising. Then, we considered their hexaazahexanitro derivatives: namely, only those which preserved maximum molecular symmetry after the insertion of six nitroamino groups into the skeleton (Table 1).

At the second step, the MOLGEO [2] program converted the isomers from two-dimensional molecular graphs into possible 3-dimensional molecular models. MOLGEO rapidly generates acceptable 3-dimensional Cartesian coordinates of

Table 1. The calculational parameters of target compounds (● - NNO_2 groups).

No. of Skeleton	Carcasses	Molecular crystal density, g/cm^3	Enthalpy of formation in solid state, kcal/mol	Detonation parameters		Combustion parameters; $\Delta=0.1 \text{ g/cm}^3$			
				CJ-pressure, kbar	Velocity, m/s	T, K	P, bar	Es, J/g	Qex, J/g
1		2.000	69.1	378.22 (471.11)	8614 (9948)	4102	1297	1165	1437
2		2.054	124.25	410.925 (520.96)	8862 (10444)	4249	1363	1224	1542
3		2.067	133.84	422.257 (532.17)	8945 (10550)	4282	1378	1237	1565

Continuation of Table 1.

No. of Skeleton	Carcasses	Molecular crystal density, g/cm ³	Enthalpy of formation in solid state, kcal/mol	Detonation parameters		Combustion parameters; $\Delta=0.1$ g/cm ³			
				CJ-pressure, kbar	Velocity, m/s	T, K	P, bar	Es, J/g	Qex, J/g
4		1.915	77.13	376.342 (396.70)	8678 (9170)	4322	1469	1314	1493
5		2.023	73.58	421.818 (450.342)	9008 (9609)	4346	1480	1324	1511
6		1.984	95.94	410.471 (436.55)	8932 (9529)	4431	1521	1360	1572
7		2.000	153.61	430.754 (461.45)	9080 (9819)	4576	1591	1422	1676
8		1.89	135.84	376.218 (399.41)	8690 (9271)	4490	1549	1385	1614

atoms according to the molecular connectivity table and the table of standard bond lengths and valence angles.

At the third step, the molecular geometry of the generated structures was refined, and the enthalpy of formation was estimated by subsequent application of the molecular mechanics method - the MM2 program [5] and the PM3 [6] quantum chemical method for the compounds in gas phase.

Then, we calculated molecular crystal densities of the resultant structures and their sublimation enthalpies, using the method of Atom-Atom Potential Functions (AAPF) [7,8]. Calculations of sublimation enthalpy for the crystals of the resultant compounds enabled us to estimate the energy content of these substances in the solid state and, afterwards, to calculate their detonation characteristics and combustion parameters.

However, the accuracy of estimating the detonation characteristics is very much dependent on the accuracy of calculating the energy content and molecular crystal density of the structures in question. Therefore, to reach our principal goal (the search for structures with high detonation velocities), we had to evaluate, so to say, the pedigree of the errors from the micro to the macro level. For this purpose, we first estimated this pedigree of errors by high-energy compounds, where a good experimental basis is available for such estimates and for "tracing" the resultant errors from the micro to the macro level. We selected hexogen (RDX) and octogen (HMX) as such "expert" compounds.

Results and discussion

Table 1 shows some characteristics of our compounds, as well as their principal calculated parameters of detonation and combustion.

On the whole, all the potential skeletons that obtained during directed computer generation have high detonation velocities. Among the compounds from the adamantane series, the hexaazahexanitro substituted frameworks N 3 ($D = 8945$ m/s) and N 1 ($D=8614$ m/s) have the highest and lowest detonation velocities, respectively (Table 1). In the wurtzitane series, compounds N 7 ($D=9080$ m/s) and N 4 ($D=8678$ m/s) have the highest and lowest detonation velocities, respectively.

Analyzing the results, we may note that hexanitrohexaazaisowurtzitane (CL-20) has the high detonation velocity (9.01 km/s) as calculated by the TIGER program package [9], or 9.61 km/s as obtained by the scheme developed in [10, 11, 12].

However, let us return to the combined effect of the errors in energy content and molecular crystal density calculations on the accuracy of detonation calculations. To consider this problem, let us analyze the calculated results for hexogen and octogen (Tables 2, 3). As follows from the results of our calculations, if the error in the enthalpy of hexogen formation is 1 kcal/mol (the experimental value - 17.0 kcal/mol [13]), the error in the calculated detonation velocity is 4 m/s (the experimental values are 8180 m/s [14] and 8700 m/s [15]). As the same time, if the error in molecular crystal density calculations is 0.02 g/cm^3 , the corresponding error in D calculations is up to 68 m/s.

Similar results are also typical for the calculated detonation properties of octogen (the results are obtained for the α -form of this compound): if the error in the calculated enthalpy of formation is 2 kcal/mol (the experimental value is 21.0 kcal/mol [13]) the inaccuracy of D calculations is 6 m/s; if the error in molecular crystal density calculations is 0.04 g/cm^3 (the experimental value is 1.84 g/cm^3 [14]), the inaccuracy of detonation velocity calculations is from 134 to 140 m/s.

Unfortunately, the data on physicochemical properties, combustion and detonation parameters of hexaazahexanitroisowurtzitane (CL-20) are not available from literature; therefore, we cannot estimate the pedigree of errors (at the macro and micro level) for CL-20. The calculated results for this compound are given in Table 4. If we take the calculated density (2.1 g/cm^3 [3]) and the enthalpy of formation (99.3 kcal/mol [16]), then the average inaccuracy of detonation velocity is 4 m/s for the error in formation enthalpy of 2 kcal/mol and 127 m/s for the density error of 0.04 g/cm^3 .

Thus, results of our calculations and their analysis let us conclude that errors in the calculated detonation velocity mostly depend on errors in molecular crystal density calculations rather than on errors in energy content calculations.

Conclusion

It may be noted that errors in energy content calculations only moderately affect the resultant errors in calculations of detonation characteristics, whereas the effect of errors in molecular crystal density calculations is very notable. A logical conclusion

Table 2

The results of the TIGER-calculations compared to results of calculations according to scheme [10,11,12] (in brackets) for the hexagen (RDX)

d = 1.75 g/cm³				
ΔH_f° , kcal/mol	15.0	16.0	17.0	18.0
P, kbar	334.3 (332.2)	334.7 (332.6)	335.2 (333.1)	335.6 (333.5)
D, m/s	8570 (8650)	8574 (8660)	8578 (8670)	8582 (8670)
T, K	2568	2576	2585	2593
I	(119.1)	(119.2)	(119.3)	(119.4)

$\Delta H_f^\circ = 15$ kcal/mol				
d, g/cm ³	1.76	1.78	1.80	1.84
P, kbar	338.5 (336.6)	347.0 (345.5)	355.7 (354.5)	364.6 (363.7)
D, m/s	8604 (8690)	8672 (8780)	8740 (8860)	8808 (8940)
T, K	2553	2521	2490	2457
I	(119.8)	(121.3)	(122.8)	(124.3)

$\Delta H_f^\circ = 16$ kcal/mol				
P, kbar	339.0 (337.0)	347.5 (345.9)	356.1 (355.0)	364.9 (364.1)
D, m/s	8608 (8700)	8676 (8780)	8743 (8870)	8812 (8950)
T, K	2561	2530	2498	2466
I	(119.2)	(121.4)	(123.0)	(124.5)

$\Delta H_f^\circ = 17$ kcal/mol				
P, kbar	339.4 (337.5)	347.9 (346.4)	356.6 (355.4)	365.4 (364.6)
D, m/s	8612 (8710)	8679 (8790)	8747 (8870)	8815 (8960)
T, K	2569	2538	2506	2474
I	(120.1)	(121.6)	(123.1)	(124.6)

$\Delta H_f^\circ = 18$ kcal/mol				
P, kbar	339.8 (337.9)	348.3 (346.8)	357.0 (355.9)	365.8 (364.1)
D, m/s	8616 (8710)	8683 (8800)	8751 (8800)	8819 (8960)
T, K	2578	2547	2515	2483
I	(120.2)	(121.7)	(123.2)	(124.7)

Table 3

The results of the TIGER-calculations compared to results of calculations according to scheme [10,11,12] (in brackets) for the octogen (HMX).

$\Delta H^{\circ}_f = 20.79 \text{ kcal/mol}$					
d, g/cm ³	1.76	1.80	1.84	1.88	1.92
P, kbar	338.8 (336.8)	355.9 (354.8)	373.7 (373.3)	392.0 (392.5)	410.9 (412.3)
D, m/s	8606 (8700)	8742 (8860)	8878 (9030)	9016 (9200)	9154 (9370)
T, K	2558 (119.9)	2495 (122.9)	2430 (126.0)	2363 (129.0)	2294 (132.2)
I					

$d = 1.76 \text{ g/cm}^3$					
ΔH°_f , kcal/mol	18	20	22	24	
P, kbar	337.9 (335.9)	338.5 (336.6)	339.2 (337.2)	339.8 (337.9)	
D, m/s	8598 (8680)	8604 (8690)	8610 (8700)	8616 (8710)	
T, K	2540 (119.6)	2553 (119.8)	2565 (120.0)	2578 (120.2)	
I					

$d = 1.80 \text{ g/cm}^3$					
ΔH°_f , kcal/mol	18	20	22	24	
P, kbar	355.0 (353.8)	355.7 (354.5)	356.3 (355.2)	357.0 (355.9)	
D, m/s	8734 (8850)	8740 (8860)	8745 (8870)	8751 (8880)	
T, K	2477 (122.6)	2490 (122.8)	2502 (123.0)	2515 (123.2)	
I					

$d = 1.84 \text{ g/cm}^3$					
ΔH°_f , kcal/mol	18	20	22	24	
P, kbar	372.7 (372.3)	373.4 (373.0)	374.1 (373.8)	374.8 (374.5)	
D, m/s	8870 (9020)	8876 (9030)	8882 (9040)	8888 (9050)	
T, K	2412 (125.7)	2425 (125.9)	2437 (126.1)	2450 (126.3)	
I					

$d = 1.88 \text{ g/cm}^3$					
ΔH°_f , kcal/mol	18	20	22	24	
P, kbar	391.0 (391.4)	391.7 (392.2)	392.4 (393.0)	393.1 (394.0)	
D, m/s	9008 (9180)	9014 (9200)	9019 (9210)	9025 (9220)	
T, K	2345 (128.8)	2358 (129.0)	2370 (129.2)	2383 (129.4)	
I					

$d = 1.92 \text{ g/cm}^3$					
ΔH°_f , kcal/mol	18	20	22	24	
P, kbar	409.8 (411.2)	410.6 (412.0)	411.3 (412.9)	412.0 (413.7)	
D, m/s	9147 (9360)	9152 (9370)	9158 (9380)	9163 (9390)	
T, K	2276 (131.9)	2289 (132.1)	2301 (132.3)	2314 (132.5)	
I					

Table 4

The results of the TIGER-calculations compared to results of calculations according to scheme [10,11,12] (in brackets) for the hexaazahexanitroizowurtzitane (CL-20).

d, g/cm ³	1.94	1.98	2.02	2.06	2.10
$\Delta H_f^\circ = 94$ kcal/mol					
P, kbar	385.8 (413.5)	403.1 (433.9)	421.0 (454.9)	439.4 (476.6)	458.4 (499.0)
D, m/s	8749 (9330)	8874 (9510)	9002 (9680)	9130 (9850)	9261 (10030)
T, K	2830	2763	2694	2623	2550
I	(131.5)	(134.6)	(137.8)	(140.9)	(144.2)
$\Delta H_f^\circ = 100$ kcal/mol					
P, kbar	387.2 (414.2)	404.6 (435.6)	422.5 (456.7)	440.9 (478.5)	460.0 (500.9)
D, m/s	8761 (9360)	8886 (9530)	9013 (9700)	9141 (9880)	9271 (10050)
T, K	2858	2791	2722	2651	2578
I	(131.9)	(135.0)	(138.2)	(141.4)	(144.6)
$\Delta H_f^\circ = 106$ kcal/mol					
P, kbar	388.7 (416.8)	406.1 (437.3)	424.0 (458.5)	442.5 (480.4)	461.5 (502.9)
D, m/s	8772 (9380)	8897 (9550)	9024 (9730)	9152 (9990)	9282 (10080)
T, K	2886	2819	2750	2679	2606
I	(132.3)	(135.4)	(138.6)	(141.8)	(145.1)
$\Delta H_f^\circ = 110$ kcal/mol					
P, kbar	390.0 (417.8)	407.0 (438.4)	416.0 (459.7)	443.5 (481.6)	462.6 (504.2)
D, m/s	8780 (9390)	8905 (9570)	8968 (9740)	9159 (9920)	9289 (10100)
T, K	2904	2838	2804	2698	2625
I	(132.6)	(135.7)	(138.9)	(142.1)	(145.4)

follows: high-precision calculations of detonation characteristics at the macro level require accurate calculations of the molecular crystal density. To a smaller degree, the errors depend on the inaccuracies in determining the energy content of compounds.

On the whole, we should note that our concept of computer search for structures of compounds with high detonation velocities may be efficiently used both for computer generation (with subsequent screening) by other molecular formulas and for computer search aimed at structures with other desired properties (for example, high impulse of launching ability, definite heat stability, or given sensitivity parameters).

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