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Physical Chemistry

Quantum-Chemical Study of the Solvent Effect on the Formation Ability of Benzoylhydrazine Complexes with Metals

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ABSTRACT. By means of the quantum-chemical semiempirical method AM1 the solvent effect on the formation ability of benzoylhydrazine complexes with metals is studied. It is shown that the atoms of oxygen and nitrogen of primary amine are characterized by heightened ability to form complexes with metals. On the basis of distribution of population of atomic orbitals to increase the ability to form complexes with metals the chloroform or hexane is recommended as the solvent. *© 2010 Bull. Georg. Natl. Acad. Sci.*

Key words: *benzoylhydrazine, quantum-chemical method, solvent effect.*

With a view to studying the solvent effect on the ability of benzoylhydrazine to form a complex with metals, the energetic, electronic and structural characteristics in gas phase and in solutions were calculated by the semiempirical quantum-chemical method AM1 [1]. The solvents were chosen by the values of their dielectric permeability (ε). The results of calculations are given in Tables 1 and 2.

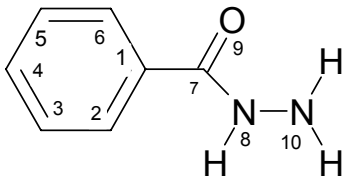

Table 1 shows that the heat of benzoylhydrazine formation in gas phase has positive, and in the solvents, except for hexane, negative value. This means that the solvents substantially increase the stability of benzoylhydrazine. The weak influence of hexane should be caused by its low polarity. The solvents at various values cause an increase of the dipole moment of benzoylhydrazine, which is explained by their additional induced polarity. As a result of the solvent effect, values of charges on atoms N_8 and O_9 increase, and on atom N_{10} decrease. Such distribution of a charge on these atoms is caused by the peculiarities of the effect of the solvents.

The population of atomic orbitals of oxygen and nitrogen atoms is of especial interest. At transition from gas phase to solutions the population of oxygen atom s-orbital decreases, though high population is observed for chloroform and hexane, in comparison with other solvents. Hence, to form a coordination bond of oxygen with metals it is better to choose hexane or chloroform as the solvent. The population of p-orbitals varies in the row: $p_y > p_z > p_x$ and their value in all solvents, except for DMSO, higher, than for gas phase. In all cases the population of s-orbitals of N_{10} and O_9 atoms is much higher than that of their p-orbital, whereas the population of s-orbital of N_8 atom in gas phase, DMSO and hexane

Table 1.

Values of dielectric permeability of the solvents (ε), of heat of formation of benzoylhydrazine (ΔH), of the dipole moment (η), of charge on atoms of nitrogen (q_N) and oxygen (q_O) and of atomic orbitals

№	ε Solvent	ΔH, kJ/mol	η,D	q_{NO}	2S	$2P_x$	$2P_y$	$2P_z$
1	Gas phase	+43.1	2.75	$q_{N8=}$ -0.172 $q_{N10=}$ -0.349 $q_{=0=}$ -0.369	1.468 1.633 1.917	1.293 1.241 1.202	1.086 1.028 1.827	1.501 1.269 1421
2	78.5 Water H_2O	-25.2	4.51	$q_{N8=}$ - 0.305 $q_{N10=}$ - 0.251 $q_{=0=}$ -0.538	1.474 1.629 1.915	1.372 1.294 1.336	1.094 1.047 1.839	1.365 1.282 1.447
3	49.0 Dimethylsulfoxide (DMSO) C_2H_6SO	-4.8	7.19	$q_{N8=}$ -0.309 $q_{N10=}$ -0.257 $q_{=0=}$ -0.547	1.464 1.632 1.915	1.113 1.199 1.135	1.017 0.952 1.893	1.715 1.473 1.603
4	32.6 Methanol CH_3OH	-22.6	4.42	$q_{N8=}$ -0.308 $q_{N10=}$ -0.250 $q_{=0=}$ -0.529	1.478 1.628 1.915	1.326 1.311 1.292	1.082 1.066 1.850	1.421 1.246 1.472
5	24.3 Ethanol C_2H_5OH	-21.4	4.43	$q_{N8=}$ -0.307 $q_{N10=}$ -0.249 $q_{=0=}$ -0.528	1.474 1.628 1.915	1.378 1.295 1.341	1.103 1.054 1.832	1.352 1.272 1.439
6	20.7 Acetone $(CH_3)_2$ CO	-20.4	4.35	$q_{N8=}$ -0.310 $q_{N10=}$ -0.247 $q_{=0=}$ -0.525	1.475 1.628 1.915	1.336 1.302 1.298	1.089 1.057 1.845	1.410 1.259 1.466
7	4.7 Chloroform $CHCl_3$	-2.6	3.78	$q_{N8=}$ -0.328 $q_{N10=}$ -0.227 $q_{=0=}$ -0.479	1.467 1.629 1.916	1.325 1.269 1.272	1.090 1.028 1.839	1.445 1.306 1.451
8	1.9 Hexane C_6H_{14}	+20.9	3.19	$q_{N8=}$ -0.341 $q_{N10=}$ -0.201 $q_{=0=}$ -0.419	1.468 1.631 1.916	1.302 1.254 1.229	1.085 1.031 1.835	1.486 1.284 1.439

is less than the population of s- and p-orbitals of N_{10} atom, which reduces the ability of formation of complexes in these conditions. Low population of s-orbital of N_8 atom is caused by delocalization of the non-divisible pair electrons on this orbital towards benzoyl fragment.

As a result of the analysis carried out it is possible to conclude that the carbonyl oxygen atom has a pronounced capacity to form complexes with metals. Among nitrogen atoms the nitrogen primary amine (N_8) has the same property. In comparison with the gas phase, solvents insignificantly reduce the ability of these atoms to form complexes with metals.

The applied quantum-chemical method includes a subprogram of molecular mechanics, enabling to study

Table 2.

Dielectric permeability of the solvents (ε), interatomic distances (R_{ij}), valence angles (α_{ijk}), and bond orders (P_{ij}) of benzoylhydrazine

№	ε, Solvent	$R_{1,7}$, Å	$P_{1,7}$	$R_{7,8}$, Å	$P_{7,8}$	$R_{7,9}$, Å	$P_{7,9}$	$R_{8,10}$, Å	$P_{8,10}$	$\alpha_{1,7,8}$	$\alpha_{1,7,9}$	$\alpha_{7,8,10}$
1	Gas phase	1.487	0.932	1.394	1.071	1.248	1.744	1.356	0.988	117.2	122.5	126.0
2	78.5 Water (H_2O)	1.486	0.940	1.379	1.177	1.263	1.598	1.359	0.987	117.8	121.5	126.0
3	49.0 DMSO (C_2H_6SO)	1.489	0.950	1.375	1.197	1.265	1.577	1.368	0.971	119.2	119.9	123.3
4	32.6 Methanol(CH_3OH)	1.485	0.942	1.382	1.161	1.262	1.608	1.358	0.988	118.1	121.4	125.8
5	24.3 Ethanol (C_2H_5OH)	1.485	0.938	1.381	1.168	1.262	1.608	1.359	0.987	117.7	121.6	125.9
6	20.7 Acetone($CH_3)_2CO$	1.485	0.941	1.382	1.162	1.261	1.611	1.358	0.987	117.9	121.5	125.9
7	4.7 Chloroform ($CHCl_3$)	1.486	0.938	1.383	1.136	1.257	1.650	1.358	0.986	117.6	121.9	126.1
8	1.9 Hexane (C_6H_{14})	1.486	0.935	1.389	1.099	1.252	1.702	1.357	0.987	117.4	122.3	126.0

the solvent effect on geometrical structures of benzoylhydrazine. This effect basically concerns interatomic distances(R_{ij}), valence angles (α_{ijk}), as well as bond orders (P_{ij}) of the reactionary centre from carbonyl and amine groups, whose values are given in Table 2. From this table it is seen that DMSO, as a solvent, has an extreme impact on the values of interatomic distances, valence angles and bond orders. In particular in this solvent the parameters: $R_{4,7}$, $P_{4,7}$, $P_{7,8}$, $R_{7,9}$, $R_{8,10}$ and $\alpha_{4,7,8}$ assume maximal, and parameters: $R_{7,8}$, $P_{7,9}$, $P_{8,10}$, $\alpha_{4,7,9}$ and $\alpha_{7,8,10}$ minimal values in comparison with other solvents. This result may be taken into consideration at choosing the solvent with respect to geometrical parameters and bond orders.

ფიზიკური ქიმია

ბენზოილჰიდრაზინის მეტალებთან კომპლექსების წარმოქმნის უნარიანობაზე გამხსნელის გავლენის კვანტურ-ქიმიური შესწავლა

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(წარმოდგენილია აკადემიკოს კ. ჯაფარიძის მიერ)

ნახევრადემპირიული კვანტურ-ქიმიური AM1 მეთოდის გამოყენებით შესწავლილია გამხსნელის გავლენა ბენზოილჰიდრაზინის მეტალებთან კომპლექსების წარმოქმნის უნარიანობაზე. ნაჩვენებია, რომ ჟანგბადის და პირველადი ამინის აზოტის ატომებისთვის დამახასიათებელია მეტალებთან კომპლექსების წარმოქმნის მაღალი უნარი. ატომური ორბიტალების დასახლების საფუძველზე მეტალებთან კომპლექსების წარმოქმნის უნარის გაზრდისათვის გამხსნელებად რეკომენდებულია ქლოროფორმი ან ჰექსანი.

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