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Physical Chemistry

Quantum-Chemical Study of the Solvent Effect on the Formation Ability of Complexes Acetamide and N,N-Dimethylacetamide with Metals

Maia Tsintsadze[*], **Jumber Kereselidze**[**]

* *R. Agladze Institute of Organic and Electrochemistry*
** *I. Javakhishvili Tbilisi State University*

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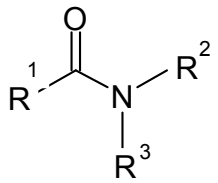
ABSTRACT. The structural, energy and electronic characteristics of acetamide and N,N-dimethylacetamide in the form of gas as well as in solvents has been calculated by means of the quantum-chemical semiempirical AM1 method. It is shown that to estimate the effect on the formation ability of complex with metals individual analysis of structural, energetic and electronic characteristics in the state of gas and in solvents is necessary. The results obtained are used in estimating the effect of polarity of solvent. *© 2011 Bull. Georg. Natl. Acad. Sci.*

Key words: *acetamide, dimethylacetamide, solvent effect, quantum-chemical calculation.*

Solvents have an effect on the formation ability of ligand complexes with metals [1]. For the purpose of quantitative description of the effect of solvent on the ability of formation of complexes acetamide with metals (1), dimethylacetamide (2) structural, energetic and electronic characteristics in the state of gas and in solvents have been calculated by means of the quantum-chemical semiempirical AM1 method [2]. The calculation results are given in Tables 1-3. During transition from gas condition to solvent for the two molecules reduction of heat formation (ΔH) at an increase of dielectric permeability (ε) of the solvent is observable. It means that the stability of amides increases together with the polarity of solvents.

From the analysis of Table 1 it is seen that solvents in acetamide (1), and in N,N-dimethyl acetamide (2) cause charge reduction on atom of nitrogen, but among them the highest values of a charge are observable for chloroform and hexane. In contrast to it, the value of a charge on the atom of oxygen of these two molecules grows considerably in polar solvents. Thus, less polar solvents (chloroform and hexane) for nitrogen atom and more polar solvents (water, dimethyl sulfoxide and methanol) for oxygen atom promote the ability of formation of a complex with metals.



(1) – $R^1 = CH_3$, $R^2 = R^3 = H$; (2) – $R^1 = R^2 = R^3 = CH_3$.

As to the population of 2s-orbital on atoms of nitrogen and oxygen, solvents practically cannot have an effect on them, but they have high values, especially on atoms of oxygen that shows a high ability of forming of a complex with metals. The population of $2p_z$-orbital also is characterised by high values, but they cannot participate in the formation of σ-bonds for their orientations. The dependence of the distance between atoms of amides (R_{ij}), bond orders (P_{ij}) and valency angles under study on solvents is also considered. The analysis shows that more polar solvents in all three molecules cause a decrease of the R_{CN} bond length and increase of P_{CN} bond orders point-

Table 1

Values of heat formation (ΔH), dipole moment (η), charge on atoms (q) and of atomic orbitals population (2S,2P) of acetamide (1)

N	Solvent, ε	ΔH, kJ mol^{-1}	η, D	q_N	q_O	2s (N)	2s (O)	$2p_x$(N)	$2p_y$(N)	$2p_z$(N)	$2p_x$(N)	$2p_y$(N)	$2p_z$(N)
1	-	-212.3	3.8	-0.442	-0.374	1.452	1.917	1.111	1.080	1.797	1.616	1.305	1.473
2	H_2O, 78.5	-279.5	6.2	-0.389	-0.615	1.454	1.917	1.141	1.093	1.700	1.725	1.336	1.639
3	DMSO,49.0	-279.3	6.1	-0.389	-0.615	1.454	1.917	1.141	1.093	1.700	1.725	1.336	1.637
4	CH_3OH,32.6	-276.8	6.1	-0.389	-0.615	1.454	1.917	1.141	1.093	1.700	1.725	1.336	1.637
5	C_2H_5OH,24.3	-275.3	6.0	-0.392	-0.605	1.453	1.916	1.139	1.093	1.706	1.725	1.332	1.629
6	$(CH_3)_2CO$,20.7	-274.2	6.0	-0.394	-0.600	1.454	1.916	1.139	1.093	1.708	1.723	1.333	1.627
7	$CHCl_3$, 4.7	-255.1	5.2	-0.416	-0.529	1.454	1.916	1.130	1.088	1.742	1.709	1.324	1.579
8	C_6H_{12}, 1.9	-232.0	4.3	-0.434	-0.445	1.454	1.917	1.121	1.084	1.776	1.691	1.314	1.522

Table 2

Values of heat formation (ΔH), dipole moment (η), charge on atoms (q) and of atomic orbitals population (2S,2P) of N,N-dimethylacetamide (2)

	Solvent, ε	ΔH, kJ mol^{-1}	η, D	q_N	q_O	2s (N)	2s (O)	$2p_x$(N)	$2p_y$(N)	$2p_z$(N)	$2p_x$(N)	$2p_y$(N)	$2p_z$(N)
1	-	-173.4	3.6	-0.343	-0.369	1.469	1.916	1.067	1.055	1.751	1.692	1.287	1.473
2	H_2O, 78.5	-222.7	6.0	-0.308	-0.571	1.468	1.915	1.078	1.063	1.697	1.730	1.321	1.606
3	DMSO,49.0	-221.8	5.9	-0.308	-0.571	1.468	1.915	1.078	1.063	1.697	1.730	1.321	1.604
4	CH_3OH,32.6	-220.6	5.9	-0.308	-0.571	1.468	1.915	1.078	1.063	1.697	1.730	1.321	1.604
5	C_2H_5OH,24.3	-219.4	5.8	-0.310	-0.562	1.468	1.915	1.077	1.063	1.697	1.728	1.329	1.598
6	$(CH_3)_2CO$,20.7	-218.7	5.8	-0.311	-0.558	1.468	1.915	1.077	1.063	1.702	1.726	1.320	1.594
7	$CHCl_3$, 4.7	-204.1	5.1	-0.326	-0.500	1.468	1.915	1.074	1.061	1.722	1.715	1.312	1.557
8	C_6H_{12}, 1.9	-186.1	4.3	-0.339	-0.428	1.468	1.916	1.070	1.057	1.743	1.699	1.303	1.503

Table 3

Values of interatomic distances (R_{ij}, Å), and bond orders (P_{ij}) of acetamide (1) and dimethylacetamide (2).

N	Solvent, ε	R_{CC} (1)	R_{CC} (2)	P_{CC} (1)	P_{CC} (2)	R_{CO} (1)	R_{CO} (2)	P_{CO} (1)	P_{CO} (2)	R_{CN} (1)	R_{CN} (2)	P_{CN} (1)	P_{CN} (2)
1	-	1.508	1.508	0.938	0.940	1.248	1.247	1.952	1.755	1.374	1.390	1.117	1.066
2	H_2O, 78.5	1.503	1.503	0.954	0.954	1.272	1.267	1.518	1.568	1.352	1.372	1.288	1.194
3	DMSO, 49.0	1.503	1.503	0.953	0.954	1.272	1.267	1.523	1.572	1.352	1.372	1.285	1.192
4	CH_3OH, 32.6	1.503	1.503	0.953	0.954	1.272	1.266	1.528	1.576	1.353	1.372	1.280	1.189
5	C_2H_5OH, 24.3	1.503	1.503	0.953	0.954	1.272	1.263	1.533	1.580	1.353	1.373	1.277	1.185
6	$(CH_3)_2CO$,20.7	1.503	1.503	0.953	0.953	1.270	1.265	1.537	1.581	1.354	1.374	1.277	1.185
7	$CHCl_3$, 4.7	1.505	1.504	0.948	0.949	1.262	1.259	1.607	1.639	1.361	1.379	1.217	1.144
8	C_6H_{12}, 1.9	1.506	1.505	0.943	0.945	1.254	1.252	1.686	1.704	1.369	1.385	1.159	1.101

ing to an increase in the stability of these bonds. And we have an opposite fact for C=O bond. Solvents in the same three molecules cause an increase of the length of this bond and decrease of the same bond orders. It means that through the effect of more polar solvents, the reactivity of C=O bond, in particular, the ability to form a complex with metals increases.

It should be underlined that the compounds: MX_nL_mqA, where M = Mg, Ca, Ba, Mn, Fe, Co, Ni, Cu, Zn, Hg; $X = Cl^-, Br^-, I^-, XCN^-$ (X=S,Se); L = acetamide and N,N-dimethylacetamide, n = 1 , 3; m = 2 ,4; q = 0 ,6 [3-7] with acetamide and N,N-dimethylacetamide coordination compounds of metals were synthesized and studied (by roentgenography, infrared spectroscopy, Raman spectroscopy, electron spin resonance, electron spectra and magnetochemistry). On the basis of these data the physical-chemical properties and the structure of complexes were established. It must be stressed that the molecules of acetamide and N,N-dimethylacetamide in these compounds are coordinated with metals by oxygen atoms of carbonyl groups. The data of quantum-chemical calculations and experimental data are in good agreement in connection with coordination of these molecules with metals. Thus, to estimate the effect on the ability of formation of complex with metals of acetamide (1), N,N-dimethyl acetamide (2) it is necessary to carry out individual analysis of structural, energy and electronic characteristics in the form of gas as well as in solvents. The results obtained are used to assess the impact of the solvent polarity.

ფიზიკური ქიმია

აცეტამიდის და N,N-დიმეთილაცეტამიდის მეტალებთან კომპლექსების წარმოქმნის უნარიანობაზე გამხსნელის გავლენის კვანტურ-ქიმიური შესწავლა

მ. ცინცაძე[*], ჯ. კერესელიძე[**]

[*] *რ. აგლაძის არაორგანული ქიმიის და ელექტროქიმიის ინსტიტუტი, თბილისი*
[**] *ი. ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტი*

(წარმოდგენილია აკადემიკოს კ. ჯაფარიძის მიერ)

ნახევრადემპირიული კვანტურ-ქიმიური AM1 მეთოდის გამოყენებით გამოთვლილია აცეტამიდის და N,N-დიმეთილაცეტამიდის ენერგეტიკული, ელექტრონული და სტრუქტურული მახასიათებლები როგორც აირად მდგომარეობაში, ასევე გამხსნელებში. ნაჩვენებია, რომ შესწავლილი ამიდების მეტალებთან კომპლექსების წარმოქმნის უნარიანობაზე გამხსნელის გავლენის შეფასებისათვის საჭიროა ენერგეტიკული, ელექტრონული და სტრუქტურული მახასიათებლების ინდივიდუალური ანალიზი. მიღებული შედეგები გამოიყენება გამხსნელის გავლენის შეფასებისათვის.

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