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Physical Chemistry

Quantum-Chemical Study of the Solvent Effect on the Formation Ability of Complexes Formamide and N-Methylsubstituent Formamides with Metal

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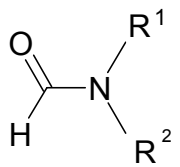
ABSTRACT. The solvent effect on the ability of formation of complexes with metal of formamide (1), N-methylformamide (2) and N,N-dimethylformamide (3) is studied by means of the quantum-chemical semiempirical method AM1. It is shown that the solvents cause increase of stability and dipole moments of the investigated formamides. The population of 2s-orbitals of atoms of oxygen and nitrogen, depending on the influence of the solvent does not change.

On the other hand, 2s-orbitals of atoms of oxygen are characterized by high population and its ability is accordingly great to form complexes with metals. Hexane as a solvent promotes a favorable spatial condition of C=O group for formation of complexes with metals.

Key words: *formamide, N-methylformamide, N,N-dimethylformamide, quantum-chemical method, solvent effect.*

It is known that solvents influence the ability of ligands to form complexes with metals.

With the purpose of studying the solvent influence on the ability of formamide (1), N-methylformamide (2) and N,N-dimethylformamide (3) of a complex with metal formation by means of the semiempirical quantum-chemical method AM1[1] the energetic, electronic and structural characteristics in gas phase and different solvents are calculated. The results of calculations are given in Tables 1-3.



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

From Table it is visible that the heat of formation (ΔH) of these formamides (1-3) in the solvents in comparison with gas phase considerably decreases. Hence, the solvent stabilizes formamides, especially in a water solution. The solvent also increases the dipole moment (η) of all formamides, which is explained by the appereance of an additional dipole moment, stimulated by the solvent.

The solvent causes an increase of the charge on atom of oxygen (q_o) and the maximal value is observed for water. On the other hand, the methyl group causes reduction of the value of q_o. In particular,

$q_o(1) = -0.643$ (Table 1), $q_o(2) = -0.615$ (Table 2) and

$q_o(3) = -0.588$ (Table 3).

Contrary to the atom of oxygen the charge on atom of nitrogen (q_N) decreases under the influence of the

Table 1.

The values of dielectrical permeability of solvents (ε), heat of formation (ΔH), dipole moment (η), charge on atoms (q), atomic orbitals (s,p) and bond orders (P_{ij}) of formamide (1).

№	Solvent, ε	ΔH, kJ mol^{-1}	η, D	q_C q_O, q_N	2s	$2p_x$	$2p_y$	$2p_z$	$P_{1,2}$	$P_{1,3}$	$P_{1,4}$	$P_{3,5}$	$P_{3,6}$
1	-	-187.4	3.70	q_C = +0.258 q_O, = -0.371 q_N =-0.448	1.240 1.916 1.457	0.894 1.108 1.103	0.863 1.879 1.101	0.745 1.467 1.788	1.772	1.129	0.899	0.913	0.907
2	H_2O, 78.5	-260.4	6.18	q_C = +0.306 q_O, = -0.643 q_N =-0.386	1.251 1.916 1.457	0.871 1.161 1.147	0.896 1.920 1.102	0.675 1.645 1.680	1.519	1.323	0.895	0.891	0.895
3	C_2H_6SO, 49.0	-259.1	6.14	q_C = +0.306 q_O, = -0.638 q_N =-0.388	1.251 1.916 1.457	0.872 1.161 1.147	0.895 1.919 1.102	0.675 1.642 1.682	1.524	1.319	0.895	0.891	0.896
4	CH_3OH, 32.6	-257.4	6.07	q_C = +0.305 q_O, = -0.632 q_N =-0.390	1.251 1.916 1.457	0.873 1.159 1.146	0.894 1.918 1.102	0.676 1.638 1.685	1.531	1.314	0.896	0.892	0.896
5	C_2H_5OH, 24.3	-255.7	6.01	q_C = +0.305 q_O, = -0.626 q_N =-0.392	1.250 1.916 1.457	0.873 1.158 1.145	0.894 1.917 1.102	0.678 1.634 1.688	1.537	1.309	0.896	0.892	0.896
6	$(CH_3)_2CO$, 20.7	-254.6	5.97	q_C = +0.304 q_O, = -0.621 q_N =-0.394	1.250 1.916 1.457	0.874 1.157 1.144	0.893 1.917 1.102	0.678 1.631 1.690	1.541	1.305	0.896	0.893	0.896
7	$CHCl_3$, 4.7	-233.3	5.21	q_C = +0.294 q_O, = -0.541 q_N =-0.419	1.247 1.916 1.457	0.881 1.142 1.131	0.883 1.906 1.103	0.694 1.578 1.727	1.620	1.241	0.898	0.900	0.899
8	C_6H_{12}, 1.9	-208.3	4.36	q_C = +0.276 q_O, = -0.447 q_N =-0.439	1.243 1.916 1.457	0.889 1.123 1.116	0.872 1.891 1.102	0.720 1.516 1.736	1.707	1.175	0.899	0.908	0.903

Table 2.

The values of dielectrical permeability of solvents (ε), heat of formation (ΔH), dipole moment (η), charge on atoms (q), atomic orbitals (s,p) and bond orders (P_{ij}) of N-methylformamide (2)

№	Solvent, ε	ΔH, kJ mol^{-1}	η, D	q_C q_O, q_N	2s	$2p_x$	$2p_y$	$2p_z$	$P_{1,2}$	$P_{1,3}$	$P_{1,5}$	$P_{3,4}$	$P_{3,6}$
1	-	-176.1	3.77	$q_{C\,1}$ = + 0.258 q_O, = - 0.368 q_N = - 0.401 q_{C4} = - 0.070	1.244 1.916 1.464 1.222	0.891 1.110 1.069 0.814	0.861 1.876 1.102 1.022	0.745 1.467 1.766 1.012	1.776	1.103	0.898	0.964	0.893
2	H_2O, 78.5	-238.3	6.18	q_{C1} = + 0.307 q_O, = - 0.615 q_N = - 0.352 q_{C4} = - 0.105	1.253 1.915 1.464 1.230	0.872 1.159 1.094 0.786	0.891 1.914 1.109 1.053	0.676 1.626 1.685 1.035	1.519	1.323	0.895	0.891	0.895
3	C_2H_6SO, 49.0	-237.2	6.14	$q_{C\,1}$ = + 0.307 q_O, = - 0.611 q_N = - 0.354 q_{C4} = - 0.104	1.253 1.915 1.465 1.230	0.873 1.158 1.094 0.787	0.890 1.913 1.109 1.052	0.676 1.624 1.687 1.034	1.555	1.263	0.895	0.946	0.880
4	CH_3OH, 32.6	-235.8	6.08	q_{C1} = + 0.306 q_O, = - 0.605 q_N = - 0.356 q_{C4} = -0.103	1.253 1.915 1.464 1.230	0.873 1.157 1.093 0.787	0.889 1.913 1.108 1.052	0.677 1.620 1.689 1.034	1.561	1.258	0.895	0.947	0.880
5	C_2H_5OH 24.3	-234.4	6.08	q_{C1} = +0.306 q_O, = -0.605 q_N = -0.356 q_{C4} = -0.103	1.253 1.916 1.465 1.230	0.873 1.157 1.093 0.787	0.889 1.913 1.108 1.052	0.677 1.620 1.689 1.034	1.561	1.258	0.895	0.947	0.880
6	$(CH_3)_2CO$, 20.7	-233.4	5.98	q_{C1} = +0.305 q_O, = -0.596 q_N = -0.359 q_{C4} = -0.102	1.253 1.915 1.465 1.230	0.874 1.155 1.092 0.789	0.888 1.912 1.108 1.051	0.679 1.614 1.693 1.033	1.570	1.251	0.895	0.948	0.881
7	$CHCl_3$, 4.7	-215.3	5.26	$q_{C\,1}$ = +0.295 q_O, = -0.525 q_N = -0.378 q_{C4} = -0.093	1.250 1.915 1.465 1.227	0.881 1.141 1.084 0.797	0.880 1.901 1.107 1.043	0.695 1.567 1.721 1.025	1.639	1.199	0.898	0.952	0.884
8	C_6H_{12}, 1.9	-194.6	4.43	$q_{C\,1}$ = +0.277 q_O = -0.440 q_N = -0.393 q_{C4} = -0.080	1.246 1.916 1.464 1.224	0.887 1.124 1.076 0.807	0.868 1.888 1.105 1.029	0.721 1.513 1.746 1.019	1.715	1.144	0.898	0.960	0.889

Table 3.

The values of dielectrical permeability of solvents (ε), heat of formation (ΔH), dipole moment (η), charge on atoms (q), atomic orbitals (s,p) and bond orders (P_{ij}) of N,N-dimethylformamide (2).

№	Solvent, ε	ΔH, kj mol^{-1}	η, D	q_C q_O, q_N	2s	$2p_x$	$2p_y$	$2p_z$	$P_{1,2}$	$P_{1,3}$	$P_{1,6}$	$P_{3,4}$	$P_{3,5}$
1	-	-154.6	3.55	$q_{C\,1}$= + 0.262	1.245	0.890	0.857	0.746	1.780	1.080	0.897	0.950	0.942
				$q_{O,}$= - 0.365	1.915	1.110	1.873	1.466					
				q_N = - 0.353	1.471	1.063	1.073	1.746					
				q_{C4} = - 0.071	1.225	0.811	1.020	1.015					
				q_{C5} = - 0.081	1.226	1.011	0.840	1.004					
2	H_2O, 78.5	-208.5	5.85	q_{C1} = + 0.310	1.253	0.872	0.891	0.676	1.581	1.217	0.892	0.932	0.934
				$q_{O,}$= - 0.588	1.915	1.159	1.914	1.626					
				q_N = - 0.312	1.464	1.094	1.109	1.685					
				q_{C4} = - 0.101	1.230	0.786	1.053	1.035					
				q_{C5} = - 0.106	1.231	1.002	0.839	1.033					
3	C_2H_6SO 49.0	-204.7	5.88	$q_{C\,1}$ = + 0.307	1.254	0.873	0.882	0.684	1.591	1.213	0.893	0.930	0.933
				$q_{O,}$= - 0.580	1.914	1.157	1.908	1.601					
				q_N = - 0.314	1.473	1.082	1.107	1.685					
				q_{C4}= - 0.102	1.232	0.780	1.053	1.036					
				q_{C5} = - 0.101	1.231	0.994	0.844	1.032					
4	CH_3OH, 32.6	-203.0	5.81	q_{C1} = + 0.305	1.255	0.874	0.881	0.685	1.597	1.208	0.893	0.931	0.934
				$q_{O,}$= - 0.575	1.914	1.156	1.908	1.597					
				q_N = - 0.315	1.473	1.082	1.073	1.686					
				q_{C4} = - 0.102	1.232	0.782	1.053	1.035					
				q_{C5} = - 0.100	1.231	0.992	0.846	1.032					
5	C_2H_5OH, 24.3	-205.0	5.69	q_{C1} = + 0.308	1.255	0.874	0.877	0.685	1.595	1.207	0.892	0.934	0.935
				$q_{O,}$= - 0.571	1.914	1.154	1.905	1.601					
				q_N = - 0.316	1.472	1.084	1.073	1.687					
				q_{C4} = - 0.099	1.232	0.784	1.048	1.036					
				q_{C5} = - 0.104	1.230	1.004	0.839	1.031					
6	$(CH_3)_2CO$ 20.7	-204.2	5.67	q_{C1} = +0.308	1.254	0.875	0.877	0.686	1.597	1.206	0.893	0.934	0.935
				$q_{O,}$= -0.571	1.915	1.153	1.905	1.599					
				q_N = -0.316	1.471	1.084	1.073	1.688					
				q_{C4} = -0.099	1.232	0.784	1.048	1.036					
				q_{C5} = - 0.104	1.230	1.004	0.838	1.031					
7	$CHCl_3$, 4.7	-188.9	4.96	$q_{C\,1}$= +0.297	1.251	0.880	0.870	0.701	1.657	1.162	0.895	0.939	0.937
				$q_{O,}$= -0.507	1.915	1.140	1.895	1.557					
				q_N = -0.331	1.471	1.077	1.073	1.710					
				q_{C4} = -0.091	1.229	0.793	1.039	1.029					
				q_{C5} = - 0.098	1.229	1.008	0.838	1.022					
8	C_6H_{12}, 1.9	-170.4	4.17	$q_{C\,1}$= +0.280	1.247	0.886	0.862	0.724	1.727	1.115	0.897	0.945	0.940
				q_O = -0.429	1.915	1.124	1.884	1.507					
				q_N = -0.345	1.471	1.070	1.073	1.732					
				q_{C4} = -0.080	1.227	0.803	1.029	1.022					
				q_{C5} = - 0.089	1.228	1.010	0.839	1.012					

solvent, and the maximal value q_N is observed in hexane. The methyl groups in this case cause reduction of charge q_N. In particular, $q_N(1)$ = -0.439 (Table 1), $q_N(2)$ = -0.393 (Table 2) and $q_N(3)$ = -0.345 (Table 3).

From the analysis of populations of atomic orbitals it is seen that in the investigated formamides the population of 2s-orbital of oxygen and nitrogen atoms depending on influence of the solvent does not change. 2s-(O) = 1.916, and 2s-[N(1)] = 1.457, 2s-[N(2)] = 1.464 and 2s-[N(3)] = 1.471. Hence, the methyl groups cause increase of the population of 2s-orbital of nitrogen atoms. 2s-orbital of oxygen atom is characterized by high population in comparison with nitrogen atom and its ability to form complexes with metals is accordingly great.

The solvent causes reduction of orders of carbonyl group (P_{CO}) and minimal value meaning is observed for water solution. In particular, $P_{CO}(1)$ = 1.519, $P_{CO}(2)$ = 1.519 and $P_{CO}(3)$ = 1.581. On the other hand, the length of carbonyl group (R_{CO}) increases at transition from gas phase to solvent and the maximal value is observed in water and dimethylsulfoxide. In particular, $R_{CO}(1)$ = 1.271, $R_{CO}(2)$ = 1.267 and $R_{CO}(3)$ = 1.264. Considering that reduction of orders and increase of the length of bonds cause an increase of its reactivity it may be assumed that the highest reactivity, of carbonyl group is characteristic of formamide (1). It means that methyl groups reduce the reactivity of the carbonyl group. Besides, in formamide (1) solvent causes increase of C-N bond orders (P_{CN}), which has

maximal value in water.- [$P_{CN}(1) = 1.323$]. We have the same value for N-methylformamide (2), and N,N-dimethylformamide (3) $P_{CN}(1) = 1.217$. On the other hand, in formamide (1) the lengths of C-N bond in water – $R_{CN}(1) = 1.361$Å, in N-methylformamide (2) $R_{CN}(1) = 1.368$Å and in N,N-dimethylformamide (3) $R_{CN}(3) = 1.375$Å. According to the above discussion of bond reactivity, based on these values, the C-N bond shows high reactivity in the water solution of N,N-dimethylformamide. It means that the methyl group in formamides promotes an increase of reactivity. The solvent causes also reduction of HCO and NCO valence angles and the maximum of these angles is reached in hexane. Hence, hexane promotes favorable spatial order of C=O group for the formation of complexes with metals.

Thus, analysis of changes of the energetic, electronic and structural characteristics of formamide (1), N-methylformamide (2) and N,N-dimethylformamide (3), as a result of influence of the solvent enables a quantitative description of their ability of formation of complexes with the metals studied.

ფიზიკური ქიმია

ფორმამიდის და N-მეთილჩანაცვლებული ფორმამიდების მეტალებთან კომპლექსწარმოქმნის უნარიანობაზე გამხსნელის გავლენის კვანტურ-ქიმიური გამოკვლევა

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ქვანტურ-ქიმიური ნაზვრადემპირიული AM1 მეთოდის გამოყენებით შესწავლილია გამხსნელის გავლენა ფორმამიდის და N-მეთილჩანაცვლებული ფორმამიდების მეტალებთან კომპლექსწარმოქმნის უნარიანობაზე. ნაჩვენებია, რომ გამხსნელი იწვევს საკვლევი ფორმამიდების მდგრადობისა და დიპოლური მომენტების ზრდას. ჟანგბადისა და აზოტის ატომური ორბიტალების დასახლების ცვლილება, გამხსნელისგან დამოკიდებულებით, არ შეიმჩნევა. სამივე ფორმამიდის ჟანგბადის ატომის 2ს-ორბიტალზე აღინიშნება მაღალი დასახლება, რაც მიუთითებს მეტალებთან მათი კომპლექსწარმოქმნის მაღალ უნარიანობაზე.

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