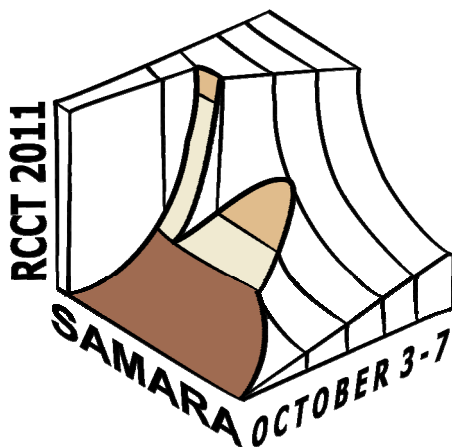# XVIII International Conference on Chemical Thermodynamics in Russia

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ABSTRACTS

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This volume presents papers of the participants of XVIII International Conference on Chemical Thermodynamics in Russia (RCCT-2011). The Conference is traditionally one of the most reputable and prestigious international chemical forums, the main participants of which are prominent scientists and leading experts in the field of chemical thermodynamics and related fields of science in Russia and countries near and far abroad. The object of the conference is sharing knowledge and new developments in physical chemistry, further development of cooperation in the field of chemical science, technology and education.

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THE APPLICATION OF THERMODYNAMIC PARAMETERS OF TRANSITION STATE FOR INTERPRETATION OF MECHANISM OF NUCLEOPHILIC SUBSTITUTION IN SULPHOCHLORIDES OF ANILIDES OF SULPHOACIDS

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Last time «positive» rejections are exposed in reactivity of steric hindered derivatives of aromatic sulphoacids in the conditions of nucleophilic attack on the Sulphur atom of sulphonic group. The effect of increased reaction ability of ortho-alkylsubstituted derivatives is confirmed. Therefore the dependence on Hammet equation carries nonlinear character and a reactivity of the ortho-methylderivatives becomes comparable and even exceeding the reaction rate for p-nitrosubstituted substrate. The observed acceleration of solvolysis reaction is not related to with the change of process mechanism. The attempt of interpretation of reactivity of crowded derivatives by electronic factors was ineffectual. The nature of steric factors was not clear in this case.

With purpose the studying of influence of structural effects in amide and sulphochloride fragments of molecule in the neutral hydrolysis of sulphochlorides of anilides of sulphoacids with the screened sulphonilamide substitutiens was researched.

The compounds correspond the next general formula: $5\text{-}[N\text{-}(XArSO_2)\text{-}N\text{-}Me]\text{-}YArSO_2Cl$ (series I – III) and $3\text{-}[N\text{-}(XArSO_2)\text{-}N\text{-}Me]\text{-}4\text{-}MeO\text{-}C_6H_3SO_2Cl$ (series IV), where X =4-Me, H, 4-Cl, 4-F, 3-NO$_2$, 4-NO$_2$; Y=2,4-Me$_2$ (series I), 2,6-Me$_2$ (series II), 2,4,6-Me$_3$ (series III) has been studied. Media: 70% (volume) water dioxane. The interval of temperatures is 303-323K. Methods of research are: acid-basic titration, spectrophotometry.

The approaching of rate constants k_{eff} values is observed by temperature decreasing in series I, III and temperature increasing in series II, IV. For example for X=3-NO$_2$ (series IV) the rate varies from the least (303K) to the highest (323K). For X=4-Cl we have an opposite regularity: the relative reactivity increasing on the temperature growing.

The activation parameters of the reaction don't allow us to ascertain the features of a mechanism of the process. The transition state of S_N2-type is characterized by nonsymmetrical structure defined by the properties of substituent in substrate and solvatation features of reagents and transitional states. The varying of X-substituent doesn't change an enthalpy factor $\Delta H^{\neq}$ but has a great influence on values of entropy factor $\Delta S^{\neq}$ in the transitional state (TS). The increasing of reaction ability of substrates is not explained by

enthalpy activation advantage, but its minor growth is seen. The absolute value of activation enthalpy $|\Delta S^{\neq}|$ decreases with growing electron-acceptor character of X. Simultaneously $\Delta H^{\neq}$ values are various lightly in series limits (50 ÷68 kJ/mol), and $|\Delta S^{\neq}|$ vary over a wide range from 28 to 186 kJ/mol·K, and are minimal for methoxysubstituted compounds. The data for the calculation of isokinetic temperature T_{iso} for series I-IV by Eksner method indicate that the work region of temperature is higher (I-III) or in the kinetic zone (II, IV).

The most interesting consequence from relation between the enthalpy and entropy factors is the change of a sequence of substrate reactivity via T_{iso}. Certainly the explanation of structure peculiarities of TS must be different at temperatures above and below T_{iso}. At the most low temperatures electronic interactions dominate in TS, at the highest ones – kinetic regalities are defined by the steric effects of the transition state.

Thus, steric hindered sulphonic systems have actually reachable low T_{iso} data and interpretation of structure factors of substituents as mechanism criteria must consider a presence of entropy control in solvolysis reaction.

APPLICATION OF GRAND THERMODYNAMIC POTENTIAL TO SOLIDS

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Grand thermodynamic potential Ω is one of the most fundamental quantities in thermodynamics and statistical mechanics. It is related to free energy F as (μ_i is the chemical potential and N_i the number of molecules of component i in a fluid system)

$$\Omega = F - \sum_i \mu_i N_i , \qquad (1)$$

and is governed by the fundamental equation (S is the entropy, T the temperature, p the pressure, and V the volume of the system)

$$d\Omega = -SdT - pdV - \sum_i N_i d\mu_i , \qquad (2)$$

where the chemical potentials play the role of independent variables. This is possible for an equilibrium fluid system with the uniformity of chemical potentials, which is secured by the free mobility of molecules. The situation in solids is principally different. An ideal solid includes at least a single sort of molecules or ions that form the crystalline lattice and are incapable of mobility, so that the uniformity of chemical potentials is never attained in solids. For this reason, grand thermodynamic potential was not applied earlier to solids.