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EFFECTS OF SUBSTRATE STRUCTURE IN NEUTRAL HYDROLYSIS OF CROWDED SULFOCHLORIDES OF ANILIDES OF SULFONIC ACIDS IN ORGANIC-WATER MEDIUM

Annotation

The neutral hydrolysis of sulfochlorides of anilides of sulfoacids with the screened sulphonilamid substituents was researched with the purpose of structural effects influence study in amide and sulphochloride fragments of molecule. A steric hindered sulphonic systems have actually reachable low isokinetic temperature data and the interpretation of structure factors of substituents as a mechanism criteria must consider a presence of entropy control in solvolysis reaction.

Last time «Positive» rejections are [1, p.1219] exposed in reactivity of steric hindered arensulfochlorides in the conditions of nucleophilic attack on the Sulphur atom of sulphonic group. The observed acceleration of solvolysis reaction is not related to with the change of process mechanism [1, p.1219; 2, p.43; 3, p.118; 4, p.39] and registered when methyl groups take place nearby Sulphur center. This effect was explained by electronic factors. The nature of steric factors was not clear in this case.

With purpose the studing of structural effects influence in amide and sulphochloride fragments of molecule the neutral hydrolysis of sulfochlorides of anilides of sulfoacids of with the screened sulphonilamid substituents was researched.

RESULTS AND DISCUSSION

Research compounds correspond the next general formula: 5-[N-(XArSO₂) - N-Me]-YArSO₂Cl (series I – III) and 3-[N-(XArSO₂) -N-Me]-4-MeO-C₆H₃SO₂Cl (series IV), where X =4-Me, H, 4-Cl, 4-F, 3-NO₂, 4-NO₂; Y=2,4-Me₂ (series I), 2,6-Me₂ (series II), 2,4,6-Me₃ (series III). Media: 70% (volume) water dioxane

(w.d.). The interval of temperatures is 303-323K (Table 1). Methods of research are: acid-basic titration, element analysis, PMR-spectroscopy.

The tendency of a reaction rate increasing with growth of electronic-acceptor character of X-substituent in substrate was registered. The low electronic density on the electronic centre - Sulphur atom of sulpho- group is favorable for substitution processes. Substituents X are far from reaction centre, and their electronic and the steric properties insignificantly reflect on the reaction rate. But a substituent influence X is difficulty in every series and depends on the temperature. The approaching of rate constants k_{eff} values is observed by temperature decreasing in series I, III. Simultaneously the influence of X-character changes in every series limits and depends on temperature (Table 1).

For example for X=3-NO₂ (series IV) the rate varies from the least at row at the highest at 323K. For X=4-Cl we have an opposite regularity: the relative reactivity increasing on the temperature growing.

The varying of X - substituent doesn't change an enthalpy factor ΔH^\ddagger but has a great influence on a values of entropy factor ΔS^\ddagger in the transitional state (TS). The increasing of reaction ability of substrates is not explained by enthalpy activation advantage, but it's minor growth is seen. The absolute value of activation enthalpy $|\Delta S^\ddagger|$ decreases with growing electron-acceptor character of X. Simultaneously ΔH^\ddagger values are various lightly in series limits (50 ÷68 kJ / mol), and $|\Delta S^\ddagger|$ values variety in grate boundaries from 28 to 186 kJ / mol·K, and are minimal for methoxysubstituted compounds.

A quantity and location change of methyl groups Y in arensulphochloride part of substrate causes the significant vibrations of X reactivity from maximal in methoxy substituted row. Meanwhile series of number (III) is characterized by ΔH^\ddagger values which are comparable with (IV) but $|\Delta S^\ddagger|$ values for (III) are more great then same for IV data.

Table 1 – Some effective constants of $k_{\text{eff}} \cdot 10^4$ (s^{-1}) and parameters of TS activating for the hydrolysis of sulfochlorides of anilides of sulfoacids in 70% w.d.

5-[N(XArSO ₂)-NMe]-2,4-Me ₂ C ₆ H ₂ SO ₂ Cl (series I)						
X	$k_{\text{eff}} \cdot 10^4 (\text{c}^{-1})$			ΔH^\ddagger , kJ / mol	$-\Delta S^\ddagger$, J / (mol · K)	ΔG_{313}^\ddagger , kJ / mol
	303	313	323			
H	0,603	1,16	2,17	49,5±3,1	186±9	108±6
4-Me	0,557	1,02	2,05	50,4±2,3	184±1	108±3
4-Cl	0,648	1,26	2,56	53,3±2,1	173±7	107±4
3-NO ₂	1,02	2,07	4,25	55,4±1,5	162±5	106±3
4-NO ₂	1,02	2,11	4,21	55,1±1,0	163±7	106±6
5-[N(XArSO ₂)-NMe]-2,6-Me ₂ -C ₆ H ₂ SO ₂ Cl (series II)						
H	0,69	1,49	3,79	66,8±2,3	128±1	107±3
4-Me	0,69	1,54	3,41	62,2±0,2	143±1	107±1
4-Cl	0,79	1,80	3,59	59,0±0,5	152±1	107±1
4-F	0,79	1,71	3,82	65,1±1,3	133±4	107±3
3-NO ₂	0,76	1,63	4,01	61,4±2,3	144±5	106±4
5-[N(XArSO ₂)-NMe]-2,4,6-Me ₃ -C ₆ H ₂ SO ₂ Cl (series III)						
H	2,5	4,68	9,59	52,0±2,5	172±10	106±6
4-Me	2,53	5,49	10,9	56,9±3,0	155±8	105±5
4-Cl	2,40	5,02	11,2	60,0±1,5	139±10	104±5
3-NO ₂	2,24	5,04	11,3	63,0±3,8	129±11	103±7
3-[N-(XArSO ₂)-N-Me]-4-CH ₃ O-C ₆ H ₃ SO ₂ Cl (series IV)						
H	0,392	0,711	1,78	59,0±8,7	58,6±27,7	77,3±15
4-Me	0,424	0,696	1,70	54,1±9,9	74,3±31,6	77,4±17
4-Cl	0,487	0,860	1,89	52,2±6,3	79,0±20,0	76,9±10
4-F	0,470	0,782	1,97	55,5±10,9	68,8±35,0	77,0±14
3-NO ₂	0,371	0,821	2,12	68,3±4,9	28,1±15,8	77,1±11

Note. An error in determination of k_{eff} in all of series does not exceed 3 %

There are causes for hypotheses about total S_N2 substitution mechanism for series (I-IV) similarly to model row of arensulphochlorides. The competence of such approach with responsible criteria of reaction's mechanism is indicated in [4, p.39]. It means that difficulties and ambiguities of kinetic data in all sets of

sulphonic acids anilides sulphochlorides can be associated with peculiarities of “packing” of TS of S_N2 – type that was shown by activation parameters data. The attempt of interaction estimate the substrate – reactivity by according to Hammet equation:

$$\lg k = \lg k_0 + \rho_x \sum \sigma \quad (1)$$

where ρ_x – the factor of sensitivity to electronic effects of substituents X in arensulphonicamide fragment of molecule indicates unimportant reaction sensitivity to substituent effects for row (I) (Table 2) and actual absent of dependence for series (II) and (III) with approximate value $\rho_x=0,03 \div 0,07$. That fact confirms an existence of isoperimetric region nearby studied temperature interval. We have similar situation for practical absence of selectivity for X influence in work temperature area for substrates (IV).

Table 2 – Some correlated parameters of equalization (1) for the hydrolysis of sulfochlorides of anilides of sulfoacids in 70% w.d.

T, K	5-[N(XArSO ₂)- NMe]-2,4-Me ₂ C ₆ H ₂ SO ₂ Cl [1, p.1219 ;2, p.43] (series I)		3-[N(XArSO ₂)- NMe]-4-MeO-C ₆ H ₃ SO ₂ Cl (series IV)	
	-lg k ₀	ρ_x	-lg k ₀	ρ_x
303	4,22±0,14	0,30±0,03	4,36±0,03	-0,06±0,05
313	3,94±0,13	0,33±0,03	4,12±0,02	0,08±0,05
323	4,36±0,14	0,36±0,03	3,75±0,01	0,109±0,002

Note. Statistical parameters (1): for 2,4-dimethyl derivatives S 0,023 0,025; R= 0,990; for methoxy derivatives at T=323 to T₀; S=0,0005 0,025; R=0,9995; for T= 303K and 313K estimating values were given, the dependence (1) is absent.

The calculation on equation (1) of substrate selectivity for substituents of Y, series (I-III) produces very high values (Table 3). The reaction inhibition by the acceptor substitutes abides by the values $\rho_Y < 0$. It means that action of alkyl groups Y is inversely to influence of X- substituents in arylsulphonilamid molecule fragment. The compensation effect is not achieved owing to remoteness X from

the reaction centre. The accumulation of methyl groups nearby sulphonic Sulphur and the reaction accelerating of such kind was marked earlier [1, p.1219; 5, p.1056] for arenesulphoclorides and was explained by formation of “friable” TS of S_N2 type.

The change ρ_Y by temperature is ambiguous. Always, there is an inflection on the dependence of ρ_Y from T^{-1} . Similar character of curve indicates that the activation enthalpy is not the dominating deposit in free activation energy.

Meanwhile the entropy activation deposit for hydrolysis of sulphoclorides [1, p.1219; 2, p.43; 3, p.118; 4, p.39] is quite significant. The change of $|\Delta S^\ddagger|$ for ones compensates of the occurrence of enthalpy factor subsides in the ΔG^\ddagger value and is the possible reason the reacting acceleration for methyl-substituted substrates.

Table 3 - Correlation Parameters acound to Gammet equation for 5-[N(XArSO₂)-NMe]-YArSO₂Cl in 70% w.d. at varying of Y (series I – IV)

T, K	X	$-\rho_Y$	$-\lg k_0$	R	S
303	H	3,77±1,33	5,05±0,39	0,943	0,161
	4-Me	3,99±1,18	5,12±0,34	0,959	0,143
	4-Cl	3,45±0,93	4,94±0,27	0,961	0,113
313	H	3,66±0,95	4,72±0,27	0,968	0,114
	4-Me	4,38±0,82	4,92±0,23	0,983	0,099
	4-Cl	3,595±0,62	4,65±0,18	0,952	0,075
323	H	3,81±0,16	4,44±0,05	0,999	0,019
	4-Me	4,32±0,52	4,58±0,15	0,993	0,063
	4-Cl	3,35±0,54	4,41±0,15	0,979	0,065

Note. n is an amount of experimental points

The data for the calculation of isokinetic temperature T_{iso} for series I-IV (Table 4) by Eksner method [6,p. 230] indicate that the work region of temperature is higher (I-III) or in the kinetic zone (II, IV). The example of the such estimation T_{iso} for IV is presented on fig. 1. Some magnitudes T_{iso} for series I and II are verified by experiment and results agree with theoretical values.

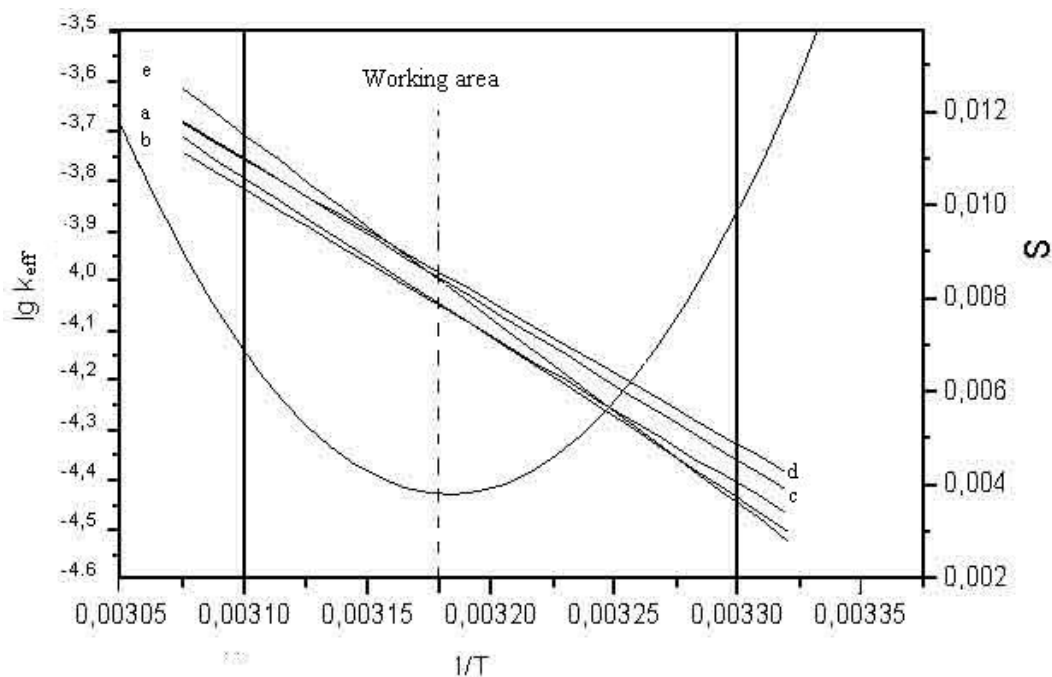


Fig. 1 - Example of calculation of T_{iso} for series IV

Thus, there is an exclusive phenomena - isokinetic temperature is found in actually obtainable region in hydrolysis conditions. This fact explains the ambiguity of kinetic data and values of activation parameters of TS (Table 4).

Table 4 -The theoretical value T_{iso} for the series of I-IV, by Eksner method [6, p. 230; 7, p. 69] for the hydrolysis of sulfochlorides of anilides of sulfoacids in 70% w.d.

Y	T_{iso}^{theor}, K	T_{iso}^{exper}, K
2,4 – Me ₂ (series I)	292	291 [4, p.39]
2,6 – Me ₂ (series II)	318	320
2,4,6 – Me ₃ (series III)	296	-
4-OMe (series IV)	314	-

The substituent variation in this cause does not change the reaction rate enough but considerably affects the ΔH^\ddagger and ΔS^\ddagger values. 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 miscellany at temperature above and below T_{iso} . At the

most low temperatures electronic interactions dominate in TS, at the highest ones – kinetic regularities are defined the steric effects on the transition state.

The ΔS^\ddagger values are measured by the degrees of free changing of an internal movement on transition from initial state to TS. The ΔS^\ddagger value becomes more negative and TS has more difficult configuration (series I-III) at the degrees of free losing. But the TS for III with lesser absolute values $|\Delta S^\ddagger|$ is not unscramble enough and difference between initial and transition states for IV is minimal in studied series in table 1. Probably, the accumulation of methyl groups in the sulphochloride part of molecule promotes insignificant relaxation of steric interactions “packing” of TS. It is explained by deviation of TS from trigonal-bipyramidal structure [8, p.261], and connected reduction of values of free activation energy $|\Delta G^\ddagger|$ for III (Table 1). Probably, for substrates (IV) a limiting of free rotation of methoxy group by N-methyl-N-arenesulfonilamid substituent promotes occurrence of the effect of through conjugation while reaction centre of the methoxy group is in benzene plane. This factor assists reduction $|\Delta G^\ddagger|$ and is favorable to reaction.

Conclusions

1) It is necessary to conduct the kinetic studying at several temperatures for estimating of location of work temperature region relatively T_{iso} and homogeneity of experimental data in studied series.

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

3) The substituent nature in crowded systems can not be explained by electronic factors but a complex of steric interactions in TS is really studied.

Список літератури

1. Визгерт Р.В., Максименко Н.Н., Рублева Л.И. // Укр. хим. журнал, 1993. т.59, №11 С. 1219 – 1230

2. Рублева Л.И., Максименко Н.Н., Визгерт Р.В. // Кинетика и катализ. 1992. Т.33, вып.1. С.43-48.
3. Рублева Л.И., Крутько И.Н. // Укр. хим. журн. 2002. Т.68, вып.4. С.118-120.
4. Мысык Д.Д., Рублева Л.И., Крутько И.Н., Левандовский В.Ю. // Вопросы химии и химической технологии. 2004. № 4. С.39-42.
5. Рублева Л.И., Визгерт Р.В. // Журн. орг. химии. 1998. Т.34, вып.7. С.1056 -1058.
6. Шмид Р., Сапунов В. Н. Неформальная кинетика. В поисках путей химических реакций. М.: Мир, 1985. С. 230 – 236 .
7. Л.И.Рублева, В.Ю.Левандовский, Д.Д.Мысык, Н.А.Языков // Наукові праці ДонНТУ. Серія: Хімія і хімічна технологія. 2007. Вип.119(9) - С.69-72.
8. Рублева Л.И., Ляшук С.Н., Максименко Н.Н., Визгерт Р.В. // Журн. орг. химии. 1994. Т.30, вып.2. С. 261-265.