TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

English Edition

of

Реакционная способность органических соединений

Vol. XXI
ISSUE 3(75)
November 1984

TARTU

TARTU STATE UNIVERSITY

ORGANIC REACTIVITY

English Edition

of

Реакционная способность органических соединений

Vol. XXI
ISSUE 3(75)
November 1984

TARTU

Title of original:

РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.
Том. XXI. Вып. 3(75). Ноябрь 1984.
Тартуский государственный университет.

Organic Reactivity
Vol.21. 3(75) 1984

REACTIVITY OF AROMATIC AND HETEROCYCLIC HYDRAZINE DERIVATIVES
II. REACTION KINETICS OF ACYLATION 2-CHLORINE-5--SULFAMOYLBENSOIC ACID HYDRAZIDE DERIVATIVES WITH BENZOYL CHLORIDE IN CHLOROFORM

E.N. Svechnikova, A.N. Gaidukevich, E.V. Dynnik , and S.G. Leonova

Kharkov State Pharmaceutical Institute, Kharkov, the Ukrainian SSR

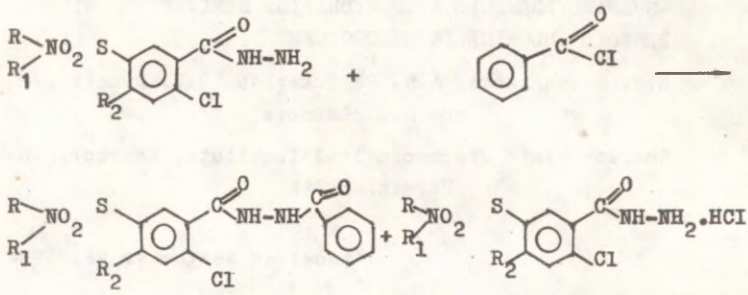
Received September 26, 1984

The reaction kinetics of acylation of 2-chlorine- - 5 - sulfamoylbensoic acid hydrazides with benzoyl chloride in chloroform has been studied in the temperature range 288-328 K. It was shown that the process obeys the second order kinetic equation for irreversible reactions. Rate constants, activation energies, enthalpies, entropies as well as free activation energies were calculated. The influence of the nature and position of substituents in the hydrazide molecule on the kinetic parameters of acylation reaction was studied.

In our previous contribution[1] of this series the reaction kinetics of acylation of chlorosubstituted aromatic carboxylic acid hydrazides with benzoyl chloride in chloroform was studied and the rate constants and activation parameters of the reaction were calculated.

In the present paper the reactivity of 2 - chloro - 5 - - sulfamoylbenzoic acid hydrazine derivatives, having a great future with respect to biology, has been studied in order to establish the probable relationship between its pharmacologic-

al effect and reactivity. Another goal of the work is to find optimum synthesis conditions for the derivatives of 2- - chlorine - 5- sulfamoylbensole acid hydrazide. To solve these problems, we have chosen the reaction of acylation of hydrazides with benzoyl chloride in chloroform which obeys the following equation:



Rate constants of hydrazides benzoylation reaction were determined by nitritometric potentiometric titration[2]. Interaction of arylhydrazides and benzoylchloride is quantitative and irreversible.

The reaction is described by the second order kinetic equation which is confirmed by the stability of rate constant values (Table 1) calculated according to the equation:

$$k = \frac{I}{2\beta t} \cdot \left(\frac{I}{a-x} - \frac{I}{a} \right) \qquad (I)$$

$$k = \frac{\ln \frac{2x + \Delta}{2x} - \ln \frac{2a + \Delta}{2a}}{\Delta\, \beta t} \qquad (II)$$

where k is the rate constant ($l \cdot mol^{-1} \cdot sec^{-1}$);

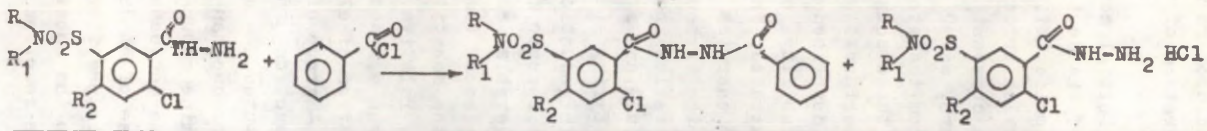
a - the initial concentration of benzoyl chloride (M);

x - the concentration of benzoyl chloride (M) at the moment of time t (sec);

β - the correction which takes into account the change in the concentration of reagents with

Table 1

Kinetic Parameters of Reactions



No	R	R_I	R_2	k l . mol^{-1} sec^{-1}				
				288 K	298 K	308 K	318 K	328 K
1.	H	H	H	-	0.330±0.015	0.500±0.014	0.727±0.031	1.037±0.049
2.	H	CH_3	Cl	0.142±0.006	0.218±0.010	0.338±0.012	0.506±0.021	0.734±0.029
3.	H	H	Cl	0.143±0.008	0.224±0.022	0.340±0.016	0.510±0.019	0.740±0.031
4.	CH_3	CH_3	H	0.224±0.009	0.346±0.012	0.517±0.022	0.744±0.036	1.045±0.037
5.	CH_3	CH_3	Cl	0.143±0.010	0.225±0.019	0.340±0.030	0.510±0.009	0.740±0.037
6.	C_2H_5	C_2H_5	Cl	0.140±0.014	0.214±0.017	0.331±0.028	0.484±0.024	0.682±0.041

the thermal extention of chloroform while going from 293 K up to the temperature of the experiment.

Δ - the difference between the initial concentration of arylhydrazide and that of the doubled initial concentration of benzoylchloride (M).

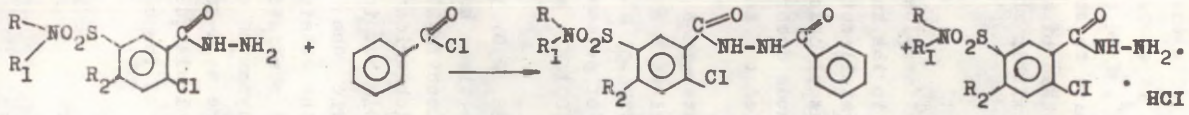
While the concentration a of benzoylchloride was two times lower than that of hydrazide, rate constant k was calculated according to eq. 1. In its turn, eq. 2 was used if the ratio of the reagents deviated from the stoichiometric one. Values k calculated according to these equations, coincide within the error range of the experiment.

The polyterms of rate constants are described by the Arrhenius equation which confirms the stability of reaction mechanism within the temperature range studied. This enabled us to calculate the values of activation energies (kcal/mol), pre-exponential factor A (according to the Arrhenius equation), as well as the thermodynamic activation parameters (enthalpy $\Delta H^{\neq}$ (kcal/mol), entropy $\Delta S^{\neq}$ (e.u.), and free activation energy $\Delta G^{\neq}$ (kcal/mol) according to Eyring[3] (Table 2).

The data of Table 1 shows that the introduction of electron - withdrawing substituents into the benzene ring of an arylhydrazide molecule leads to a considerable decrease in the reaction rate. Still, with the increase of temperature, the hydrazide molecules sensitivity to the substituent effect in benzene ring drops slightly (the relative variation of the rate constants of compounds 1,3 and 4,5 decreases with the growth of temperature). The introduction of electron - releasing substituents in the sulfamoyl - group of the nucleophile molecule slightly increases the reaction rate (compounds 1,4) of molecules with nonsubstituted H - atom in position 4. The insignificance of this increase can probably be explained by the remoteness of sulfamide group from the reaction center of the molecule. With the decrease of arylhydrazide nucleophile reactivity (because of conducting the electron - withdrawing chlorine atom into position 4) the sensitivity of arylhydrazide molecule to the substituent effect of sulfamide group on the acylation reaction rate drops

Table 2

Thermodynamic Activation Parameters of the Reaction



No	R	R_1	R_2	$\Delta H^{\neq}$ kcal/mol	$-\Delta S^{\neq}$ e. u.	$\Delta G^{\neq}$ kcal/mol (298 K)	E_A kcal/mol	ln A
1.	H	H	H	7.20±0.16	36.6±0.3	18.1	7.38±0.17	11.36±0.27
2.	H	CH_3	Cl	7.08±0.21	37.8±0.8	18.3	7.74±0.21	11.57±0.19
3.	H	H	Cl	7.46±0.07	36.5±2.4	18.3	7.74±0.14	11.56±0.23
4.	CH_3	CH_3	H	6.68±0.11	38.3±0.4	18.1	7.06±0.20	10.86±0.20
5.	CH_3	CH_3	Cl	7.52±0.09	36.4±0.3	18.4	7.71±0.18	11.52±0.29
6.	C_2H_5	C_2H_5	Cl	7.17±0.12	37.5±1.4	18.4	7.47±0.41	11.08±0.66

to zero. This agrees with other reports[4].

The analogical changes can be observed with the activation parameters of the reaction (Table 2). It should be pointed out that the variation of enthalpy $\Delta H^{\neq}$, free energy $\Delta G^{\neq}$ and activation energy E_A are more sensitive to the substituent effect in an arylhydrazide molecule than of activation enthropy $\Delta S^{\neq}$, which retain close values within the whole series of the compounds studied.

Experimental

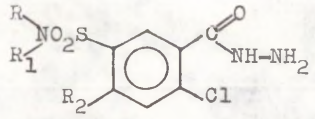
The derivatives of 2 - chloro - 5 - sulfamoylbenzoic acid hydrazide were synthesized according to the known methods[5,6] and were purified by multiple recrystallization up to the permanent melting point (Table 3). Benzoyl chloride and chloroform were purified according to methods described earlier[1]. The kinetic measurements were carried out analogously[2].

The concentration of hydrazides was determined by potentiometric titration using a pH-meter pH-121 with a 0.01 M solution of sodium nitrate with platinum ETPL-01 M and chlorosilver EVL-/M/ electrodes in the presence of potassium bromide as the catalyst and the mediator : 0.001 M solutions $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$.

The reaction rates were measured at 288, 298, 308, 318, 328 K. The experiments were repeated three times and th included 6-8 measurements. The initial concentration of the hydrazides (the variation range of benzoylchloride is 0.004--0.0002 M) was in some series stoichiametric but in other series its deviation from the stoichiometric one was $\Delta \approx -0.0001 - 0.0001$ M. The precision of the obtained values was assessed by the method of mathematical statistics (the confidence level being 0.95)[7]. The thermodynamic activation parameters were calculated according to the well-known least - squares method[4]. The precision of the calculated kinetic parameters was characterized by the value of the mean-squares deviation.

Table 3

Hydrazides of 2 - Chlorine - 5 - Sulfamoylbensoic Acid Derivatives



No	R	R_1	R_2	Melting point C	Found %		Brutto-formula	Calculated %	
					N	S		N	S
1.	H	H	H	181-183	17.00	12.87	$C_7H_8ClN_3O_3S$	16.83	12.84
2.	H	CH_3	Cl	207-209	14.22	10.89	$C_8H_9Cl_2N_3O_3S$	14.09	10.75
3.	H	H	Cl	198-200	14.51	11.26	$C_7H_7Cl_2N_3O_3S$	14.79	11.29
4.	CH_3	CH_3	H	175-177	15.18	11.48	$C_9H_{12}ClN_3O_3S$	15.13	11.55
5.	CH_3	CH_3	Cl	181-183	13.60	10.33	$C_9H_{11}Cl_2N_3O_3S$	13.46	10.27
6.	C_2H_5	C_2H_5	Cl	161-162	12.51	9.53	$C_{11}H_{15}Cl_2N_3O_3S$	12.35	9.42

References

1. E.N. Svechnikova, A.N. Gaidukevich, E.Ya. Levitin, A.A. Kravchenko, S.G. Leonova, and E.V. Dynnik, Organic Reactivity, 21, 76(1984).
2. A.M. Grekov and M.S. Soloveva, Ukr. khim. zh., 27, 251(1961).
3. S. Glasstone, K. Laidler, and H. Eyring, The Theory of Rate Processes (Russ.transl.,) "Inostrannaya Literatura", Moscow, 1948.
4. A.M. Grekov and V.A. Veselov, Physical Chemistry of Hydrazine (in Russ.) "Naukova dumka", Kiev, 1979.
5. H. Zimmer, J. Org. Chem., 24, 1140(1959).
6. A.M. Gulkov and V.Ya. Veselov, Zh. org. kh. (in Russ.), 13, 107(1977).
7. K. Doeffel, Statistics in Analytical Chemistry (in Russ.) "Mir", Moscow, 1969.

Organic Reactivity
Vol.21. 3(75) 1984

PROGRAM PACKAGE FOR COMPUTER STORAGE AND AUTOMATIC SEARCH OF CORRELATION EQUATIONS AND FOR CALCULATION OF RATE AND EQUILIBRIUM CONSTANTS. 1. DIGITAL CODING SYSTEM OF EQUATIONS OF CHEMICAL REACTIONS

T.J. Jüriado and V.A. Palm
Tartu State University, Department of Chemistry ,
202400 Tartu, Estonian S.S.R.

Received October 15, 1984

A program package for compact computer storage and search of the parameters of correlation equations and for calculation of rate and equilibrium constants of heterolytic organic reactions on the ground of these parameters has been compiled. The package was realised on an EC 10-60 computer. The parameters of approximately 2000 correlation equations have been inserted into the data arrays of the program. A numerical system is proposed for coding of chemical equations, where the latter are presented as certain sequences of model electrophiles and nucleophiles with variable substituents.

Introduction

The storage of large data arrays and automatic search of the data from these arrays is an important branch of computer usage. For exact sciences, it means the compilation of (experimental) data banks for computer storage and creation of programs connected with these sets for search and information output of randomly selected pieces of this information.

For the purposes of organic chemistry, the storage of standard reference data on some parameters (constants) of

organic compounds has certain practical importance. The rate and equilibrium constants of reactions with covalently bonded compounds have an especially important place among such parameters. Indeed, the values of all needed rate and equilibrium constants of the given processes contain sufficient information about their chemical nature.

Naturally, theoretical calculations as well as the experimental study may be the sources of information on the value of rate and equilibrium constants. Certainly, the computed estimation is to be preferred if one has sufficiently general, adequate and efficient (in the sense of the capacity of calculations) theoretical models, which is especially important for organic chemistry. It is easy to show that the number of different types of the compounds belonging to a certain class of organic substances tends to infinity. As there is more than one compound participating in any reaction and the reaction conditions (temperature, solvent, catalyst etc.) are also variables, the total number of rate and equilibrium constants for different processes is by no doubt infinity, too. Thus, it is practically impossible to get comprehensive experimental information about the rate and equilibrium constants of all possible reactions.

On the other hand, up to now we lack a sufficiently exact theoretical model enabling computational estimation of all these constants.

Nevertheless, the calculation of the values of constants for a number of reactions can be performed in the framework of formal approach which is realized in the form of correlation equations (see Ref. 1 for review and Ref. 2 for short summary).

The correlation equations give a possibility to use the known values of rate and equilibrium constants of some basic reactions for the computational estimation of a much larger number of analogical (concerning certain sets of attributes) reactions having no experimental values of these constants. Thus, the parameters of correlation equations for estimation of the rate and equilibrium constants of corresponding

reactions can be considered as the arrays of experimental data to be used like any other standard reference data. It enables dense storage of the experimental data already available. On the other hand, the number of reactions for which the values of constants can be estimated would be larger by several orders of magnitude. In most cases, the precision of the constant estimation by means of the formal approach is satisfactory for calculation of the sufficiently adequate data. Thus, it would be reasonable to add the set of the parameters of correlation equations and corresponding calculation scheme to the bank of experimental data. Such a possibility has been realized in Tables[2]. Obviously, the form of tables for storage and non-computational calculations heavily restricts both the possibilities of the operative addition of new data to information stored and the facilities for the check of correctness of the calculations in the framework of correlation equations. The guaranteed correctness is an additional argument in favor of automatic computation using the stored values of correlation parameters.

The computer storage of the parameters of correlation equations and the use of them for calculation of rate and equilibrium constants requires one or another solution of the problem of coding of chemical reactions and structures. For the input, storage and search of the set of the experimental data of rate and equilibrium constants, the universal language of linear coding of topologically given structures (LINKS) was created[3,4]. The transformation of input LINKS - code into a corresponding marked graph is the foundation of the information storage on the bases of this language.

However, the use of the LINKS - language for coding of reactions needs some special skill. Furthermore, those reaction codes do not always obviously and immediately reflect the logic of the estimation of reaction series with variable structure as adopted by the formal approach. Thus, it turned out to be expedient to apply another method of numerical coding of reactions and structures which was less general but easier for practical use and directly connected with the logic of correlation equations. The version described below

uses numerical coding as input language to prepare the orders for constant calculation. Later on it is possible to complement the system with corresponding code tables for translation of either LINKS - codes or any other language based on structure formulars into numerical codes used in our system.

The lists of the reaction series included, the types of correlation equations and their parameters correspond to the data presented in Tables[2].

Such a system can be supplemented with further reaction sets and with more sophisticated and general correlation equations. The program package was compiled in the FORTRAN - language and realized on an EC 10-60 computer in the computing center of Tartu State University. The main principle of its work is based on initialized arrays with the parameters of nearly 2000 correlation equations from Tables [2] for the following reaction types*: 1/(dissociation of hydrogen acids), 2/(proton transfer), 3/(nucleophile substitution at non-aromatic center), 4/ (bimolecular nucleophilic substitution at saturated center), 6/ (addition to multiple bonds), 8/(hydrolysis of carboxylic esters), 9/(reactions of carbonyl compounds), 10/(electrophilic substitution in aromatic ring), 11/(nucleophilic substitution at aromatic carbon atom), the tables of substituent and solvent constants as well as programs enabling the search of more general reaction types as well as the actual reactions making use of a special numerical code, search of solvents on the bases of coding system used in Tables[5], search of temperature, determination of the indexes of correlation equations by means of the results of the above mentioned search, the computation of rate and equilibrium constants on the virtue of equation index as well as the output (print) of constants calculated and the additional comments, if necessary.

The functioning of the program package is organized in the overlay-mode, the program occupies 210 kilobytes of computer's memory.

* The indexation of Tables[2,5] was used

The information arrays of the package can be supplemented with new data without any difficulties. It is possible to add new types of correlation equations without changes in the system of the search of reactions.

Digital Coding System of Equations of Chemical Reactions

1. General Notes

The program system described below must be feasible for any chemist. Thus, it turned out to be suitable to compile not entirely universal but sufficiently unambiguous and simple method for coding of chemical structures and reaction equations, proceeding actually from the logic of correlation analysis. To our mind, the somewhat limited degree of generality is not an essential shortcoming as the majority of cases with real practical meaning are involved. Moreover, the system can be extended adding some simple rules which do not bring along any changes in the existing segments of the program. It should be mentioned that the structures with highly branched substituents do not have special meaning in the framework of correlation equations on which the described program system is based.

2. General Principles

The method accepted arises from the following general principles:

2.1. The most appropriate code for the users because of the simplicity of the programs is a numerical code.

2.2. Any reaction equation of the types mentioned above could be represented as follows:

$$E_1Y_1 + E_2Y_2 + E_3Y_3 \longrightarrow \text{products},$$

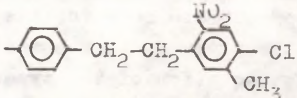
where E_i is electropositive leaving group (or electrophile $E_i^{\Delta+}$ if the corresponding Y_i is absent) and Y_i denotes electronegative leaving group (or nucleophile $Y_i:^{\Delta-}$ if the corresponding E_i is absent); any E_i or Y_i can be absent in certain cases. Our system excludes only the simultaneous absence of both E_1 and Y_1 (or if there are two reagents participating also the simultaneous absence of both E_2 and Y_2).

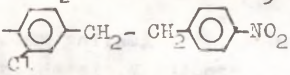
The demand for presenting of reaction equation in these terms is one of the major reasons why our system cannot be used for coding of some special reaction types (e.g. the elimination reactions with increasing unsaturation) and needs some supplementary rules.

2.3. All given chemical reactions of the named types could be represented in these terms using a restricted number of model E_i and Y_i which, as a rule, include one or more variable substituents, e.g. model E_i $XC(=O)-$, $X_2C:^{-} \equiv CX_1-$, $CX_1X_2X_3-$, $NX_3X_4CX_1X_2-$ etc., and model Y_i $XC\equiv C-$, $X_2N=\overset{+}{N}X_1-$, $\overset{+}{N}X_1X_2X_3-$, $C^{-}X_3X_4CX_1X_2-$ etc., where X_i is a variable substituent. Some model E_i and Y_i include a bivalent variable substituent, e.g. E_i $X\frown C_{arom.}-$ and Y_1 $X_1\frown\overset{+}{C}-\overset{X_2}{\overset{|}{\ }}{}_{arom.}$ $X\frown\overset{+}{N}-_{arom.}$ etc. A two-digit numerical code corresponds to any such structural unit. Our system includes 47 model E_i and 62 model Y_i. Their list could be complemented with additional units. The model E_i and Y_i (E_i^{A+} and $Y_i:^{A-}$) as well as their numerical codes are given in Tables 1 and 2.

2.4. Variable substituents connected with model E_i and Y_i could be represented as compiled from model bridges (fragments) and secondary substituents. Another limitation is included in order to further simplify the coding system, which, however, cannot be essential by the correlation approach, where, mainly, the simple substituents are included: the secondary substitution is allowed at the terminal bridge, only.

Examples:

- substituent  is formed from bridges phenyl - methylene- methylene- phenyl and of secondary substituents 2-NO_2, 4-Cl and 5-CH_3;

substituent  can be coded in case bridge  is described.

Trivalent model bridges (the fragments, as a rule) correspond to the bivalent variable substituents connected with model E_i and Y_i (see 2.3.).

A three-digit numerical code is associated with every typical bridge or secondary substituent. Model bridges and sec-

ondary substituents as well as their digital codes are given in Tables 3 and 4.

2.5. Practically all reactions of the mentioned types (except the reactions with extremely complicated substituents) could be coded by means of the codes of model nucleophiles and electrophiles and the included variable substituents strictly.

3. General Form of Reaction Code (GFRC)

The GFRC consist of one eight-figure and one four-digit constant. The former includes the codes of E_1, Y_1, E_2 and Y_2 and the latter the codes of E_3 and Y_3. 00 must be written instead of a missing structure unit.

Examples:

- reaction $\underbrace{CX_1X_2X_3H}_{Y_1\ E_1} + OH^- \longrightarrow CX_1X_2X_3^- + H_2O$ $\quad Y_2$

Codes: E_1(H-)=1, Y_1($CX_1X_2X_3$-)=2 and Y_2($XO:^-$) = 25

GFRC 1020025 0

GFRC can also be written using the inverse sequence of reagents, i.e. 250102 0;

- reaction $\underbrace{X_1COOX_2}_{E_1\ Y_1} + H_2O + H^+ \longrightarrow X_1COOH + \underbrace{X_2OH}_{E_1Y_2} + H^+$ $\quad E_3$

Codes: E_1(X CO-)=8, Y_1($XO:^-$)=Y_2=25, E_2(H-) = E_3 = 1

GFRC 8250125 100

or 1250825 100

Note:

In the framework of the reaction types under discussion, the third reagent is always a catalyst whose code is to be written the last. If in a catalytic reaction only one compound is participating besides the catalyst, the code of the catalyst can be written either at the first or at the second position. Nevertheless, it is recommended, in all cases, to follow the system of Tables [2,5], i.e. the first version of our examples, to make the functioning of the program more effective.

- reaction $\underbrace{ArOX_1}_{E_1\ Y_1} + \underbrace{X_2COOK}_{Y_2\ E_2} \rightarrow ArOOCX_2 + X_1OK$

17 25 26 29

GFRC 17253926 0 or 39261725 0

- reaction $\underbrace{X_1X_2C{=}CX_3X_4}_{Y_1} + \underbrace{Br_2}_{E_2\ Y_2} \rightarrow X_1X_2CBrCBrX_3X_4$

Br-Br

3 21 42

GFRC 32142 0 or 21420003 0

4. Codes of Variable Substituents Belonging to Model Nucleophiles and Electrophiles (CVS)

The CVS have been put into the identification arrays strictly in order of the increase of the indexes of electrophiles and nucleophiles, i.e. the substituents of the electrophile E_1 are listed first, then those of nucleophile Y_1, etc. Within the range of one structure unit (i.e. electrophile or nucleophile), the arrangement of the CVS is determined by the system of indexation of variable substituents in electrophiles and nucleophiles (if substituents are not in equivalent positions). In case the substituents are in equivalent positions, the program guarantees the reliability of operation by any arrangement of CVS. However, in the described version, a certain arrangement is used for the latter codes, too.

There are no codes for reactions with certain substituents in the identification arrays but the codes of reaction series which correspond to correlation equations, i.e. as a rule, in a single (as well as in two or three) substituent, there is a variable secondary substituent (VSS). In the identification arrays for substituents in equivalent positions, the substituents with VSS are always at the final place, the other CVS are entered in the order of growth of the substituents complexity.

Every CVS contains from 3 to ten integers. The substituents which could be coded using more than ten numbers, are

excluded from our system. The code includes the indexes of bridges (IB) (Table 3), the closing symbol of IB (-1), the total number of secondary substituents (NS) and the indexes of secondary substituents (IS) (Table 4) or the indexes of secondary substituents with the indication of the position of substituents (if the last bridge has more than one acceptable position of substitution), including the VSS code without indication of the position of secondary substitution (always takes the final position of IS). The VSS is coded as follows:

-1 - VSS in the phenyl (aromatic) ring,

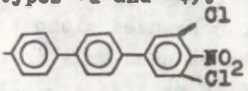
-2 - saturated alkyl,

-3 - functional groups as well as vinyl and other unsaturated groups, phenyl etc.,

-4 - VSS of the $CX_{i(i=1,n)}H_{3-n}$ type (methyl derivatives), where X is a functional group etc.,

-5 - VSS of "mixed" type (combined data processing for the substituent types -2 and -4).

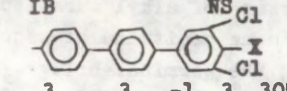
Examples:



Codes - C_6H_4 - bridge- 3, Cl - 54, NO_2 - 105

CVS: 3 3 3 -1 3 3054 4105 5054,

IB NS IS



CVS: 3 3 3 -1 3 3054 5054 -1,

IB NS IS

5. Representation of the CVS in User's Order for Program

This representation has an essential meaning for a program user. The data is used for the reaction identification as well as for the search of the corresponding correlation equation and the computing on the basis of this equation of needed rate and equilibrium constants.

The GFRC representation is identical to the code of identification arrays given in clause 3.

The representation of CVS has some differences if compared

with the system given in subdivision 4 because there are the codes of reaction series in the identification arrays while the codes of the actual reactions with definite substituents are represented in user's orders.

The CVS of the user's order contains the indexes of bridges (IB) and the closing symbol (-1) of IB followed by the indexes of secondary substituents with/without the indication of the substitution positions and the closing symbol of the codes of secondary substitution (-1).

5.1. The Regulations for Using of Bridge Indexes.

The bridges could be devided into the following groups (the indexes of Table 3 are indicated in brackets):

a) methylene and ethylene bridges (1-2).
b) the cycles with more than one acceptable position of secondary substitution /CMPS/ (3-40),
c) the cycles with one single position of secondary substitution, only /COPS/ (41-100),
d) other bridges /OB/ (101-150).

The methylene bridge can be used without any restrictions.

The ethylene bridge can be used only in case the final fragment of a substituent is written as $-CX_1X_2CX_3X_4$ but the $-CX_1X_2-$ bridge is missing in the bridge codes list. The application of the ethylene bridge is unacceptable in any case when connected with odering of alkyl substituents.

The CMPS could have some positions of secondary substitution but only as being the terminal bridge. Acceptable positions are indicated in Table 3. If the CMPS code is used for the bridges in another position, one should see the second column of Table 3, which indicates the whole set of fragments really represented in identification arrays. The corresponding CMPS cannot be used as an intermediate bridge in case the necessary fragment is missing in the column.

The positions accepted for COPS are presented in Table 3. Some COPS cannot be used as the terminal bridge (see bridges 57-60, 81, 85).

There are also OB that cannot function as terminal or penultimate bridge. The same applies to those belonging to secondary substituents. The latter should be used as the

terminal bridge only if the corresponding compilated secondary substituent is missing in Table 4. If there are some doubts, the order must be given for both variants to guarantee the positive output.

5.2. The Regulations for Using the Order of Secondary Substituents.

As mentioned above, the secondary substitution is allowed by the terminal bridge, exclusively. When ordering the alkyl substituents presented in Table 4 one should not be taken as consisting of bridges and secondary substituents. E.g. neopenyl must be ordered as substituent 14 but not as bridge 1 + substituent 13. The same, although less strictly, is valid for components containing bridges (e.g. 76 - 86, 96-103 etc.).

For the secondary substituents in CMPS, the position of substitution must always be indicated as

$$i_{total} = 1000 \times i_{position} + i_{substituent},$$

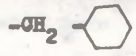
where i_{total}, $i_{position}$ and $i_{substituent}$ are the total index, the position index and the index of the substituent, respectively.

In the COPS, the secondary substituents can be ordered with/without indicating the positions. In the first case, the acceptable position is automatically regarded to be ordered, in another variant the correctness of the position is checked up. In case of divergence from the acceptable position a corresponding message should be printed.

5.3. The Examples of Writing the Codes of Substituents (comma has been put between separate digital codes).

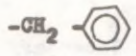
The codes of some substituents should be written as follows:

	IB	IS
-H	-1,	1, -1
$-CH_3$	-1,	2, -1
$-C(CH_2CH_3)_3$	-1,	18, -1
$-C(CH_2CH_3)(CH_2CH_2CH_3)_2$	1, -1,	3,4,4,-1



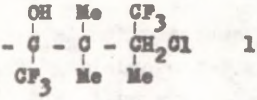
1, -1, 40, -1

or 1, 46, -1, 1, -1

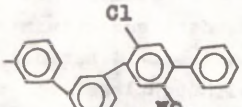


1, -1, 145, -1

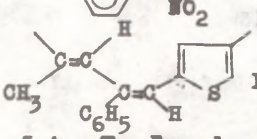
or 1, 3, -1, 1, -1



104,103,2,-1, 1002,1175,2054, -1

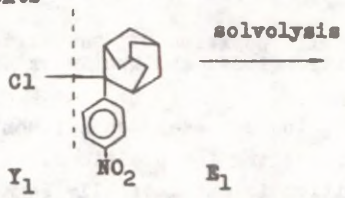


58,58,3, -1, 2054,5105,4145, -1



113,117,17,-1 4105, -1

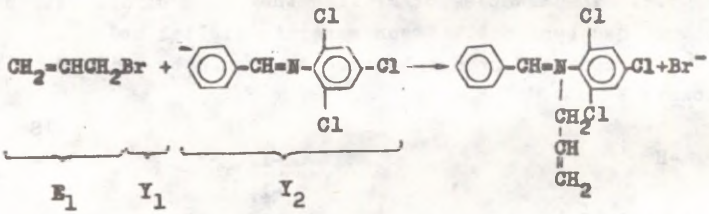
5.4. The Examples of Writing Reaction Codes Including Substituents



Reaction code 46410000 0

Substituent codes (in E_1): X_1 3, -1, 4105, -1

X_2 22,-1, 1, -1



Reaction code 4420012 0

Substituent codes (in E_1): X_1 -1, 1, -1

X_2 -1, 1, -1

X_3 -1, 51, -1

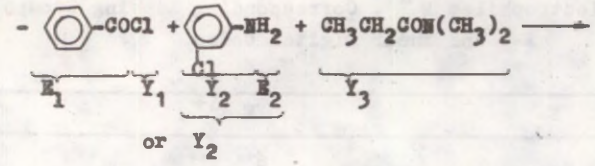
(in Y_2): X_1 3, -1, 2054,4054,6054,-1

X_2 -1, 1, -1

X_3 -1, 145, -1

(or 3, -1, 1, -1)

Or reaction code 120442 0, further $/Y_1/ = /Y_2/$ and $/E_2/ = /E_1/$.



Reaction code 8410116 0037 /or 1160841 0037/

or 8410011 0037 /or 110841 0037/

Substituent codes (in E_1): X_1 -1, 145, -1 (or 3,-1,1,-1)

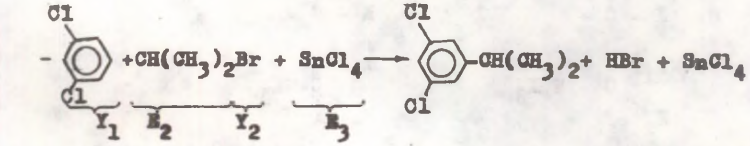
(in Y_2): X_1 -1, 1, -1

X_2 3, -1, 3054, -1

(in Y_3): X_1 -1, 3, -1

X_2 -1, 2, -1

X_3 -1, 2, -1



(E_1 = -H)

Reaction code 1090442 3500 (or 4420109 3500)

Substituent codes (in Y_1): X_1 6, -1, 3054, 5054, -1

(in E_2): X_1 -1, 1, -1

X_2 -1, 2, -1

X_3 -1, 2, -1

(in E_3): X_1 -1, 54, -1

X_2 -1, 54, -1

X_3 -1, 54, -1

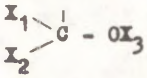
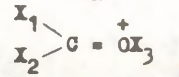
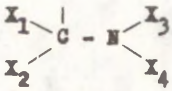
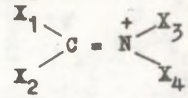
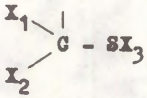
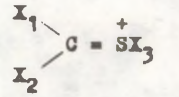
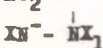
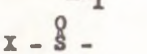
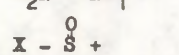
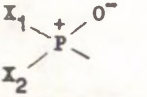
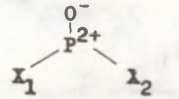
X_4 -1, 54, -1

Table 1

Model Electrophiles $E^{\Delta+}$, Corresponding Leaving Groups E- and Their Digital Codes

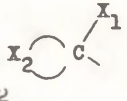
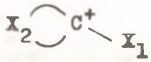
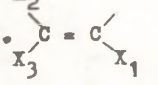
Code	E-	$E^{\Delta+}$
1.	H -	H^+
2.	D -	D^+
3.	T -	T^+
4.	$CX_1X_2X_3$-	$C^+X_1X_2X_3$
5.	$C^-:X_3X_4CX_1X_2$-	$CX_3X_4{=}CX_1X_2$
6.	$C^-X_2{=}CX_1$-	$CX_2{=}CX_1$
7.	$X_1X_2C(-O^-)$	$X_1-C(=O)-X_2$
8.	X - C(=O) -	X - $C^+(=O)$
9.	$X_1X_2C-N^-X_3$	$X_1X_2C{=}NX_3$
10.	$X_1X_2C-S^-$	$X_1-C(=S)-X_2$

Table 1 continued

Code	E-	$E^{\Delta+}$
11.		
12.		
13.		
14.		
15.		
16.		
17.	 m) See also electrophile 46	 m)
18.		
19.		
20.		
21.		
22.		
23.		
24.		
25.		
26.		
27.		

m - fragment of an aromatic ring

Table 1 continued

Code	E-	$E^{\Delta+}$
28.		$X_1 - B^+ - X_2$
29.	$B^-X_1X_2X_3$	$BX_1X_2X_3$
30.	$AlCl_3^-$ -	$AlCl_3$
31.	$X_1X_2X_3Al^-$ -	$AlX_1X_2X_3$
32.		ZnX_1X_2
33.		$FeX_1X_2X_3$
34.		$GaX_1X_2X_3$
35.		$SnX_1X_2X_3X_4$
36.		$TiX_1X_2X_3X_4$
37.		Li^+
38.		Na^+
39.		K^+
40.		$X - Mg^+$
41.		$X - Zn^+$
42.		$X - Hg^+$
43.	X - S -	
44.	N = O -	NO^+ -
45.		Cu^+
46.		 ***)
47.		***)

*** X_2-cycle fragment

**** - X_1 and X_2 at the trans - position

Table 2

Typical Nucleophiles $Y:^{\Delta-}$ and Corresponding Leaving Groups Y- and Their Digital Codes

Code	Y-	$Y:^{\Delta-}$	
1.	H -	H^-	
2.	$CX_1X_2X_3$ -	$X_1X_2X_3C:^-$	
3.	$C^+X_3X_4CX_1X_2$	$CX_3X_4 = CX_1X_2$	
4.	$C^+X_2 \equiv CX_1$ -	$CX_2 \equiv CX_1$	
5.	CX ≡ C -	$CX \equiv C:^-$	
6.	$N^+X \equiv C$ -	$N^+X \equiv C:^-$	
7.	N ≡ C -	$N \equiv C:^-$	
8.	X_1⌒$C^+_{arom.}$ X_2	X_1⌒C^+- X_2 (arom)	x)
9.	X⌒C^-_{arom}	X⌒$C:^-_{arom}$	x)
10.	X - C(=O) -	X - C(=O):$^-$	
11.	$N^+X_1X_2X_3$ - see also nucleophile 57	$N: X_1X_2X_3$	
12.	$CX_2X_3 = N^+X_1$ -	$CX_2X_3 = N:X_1$	
13.	$NX_2 = N^+X_1$-		
14.	$CX \equiv N^+$-		
15.	$N \equiv N^+$-		
16.	NX_1X_2-		
17.	$CX_1X_2 = N$-	$CX_1X_2 = N:^-$	

x) X - Fragment of aromatic ring

Table 2 continued

Code	Y -	Y: $^{\Delta-}$
18.	$C^- \equiv N^+$-	
19.	O = N-	O = N:$^-$
20.	O_2N -	$O_2N:^-$
21.	N_3-	N_3^-
22.		 m)
23.		 m)
24.	$O^+X_1X_2$-	X_1X_2O:
25.	OX -	XO:$^-$

see also nucleophiles 26-36 and 56

26.		
27.		
28.	NX_1X_2O -	
29.	O_2NO -	
30.		
31.		
32.		
33.		
34.		
35.		
36.	$BX(OH)O^{--}$	
37.	NX_2X_3-$C(X_1) = O^+$ -	
38.		
39.	$X_1X_2S = O^+$ -	

Table 2 continued

Code	Y -	Y: $^{\Delta -}$
40.	F -	
41.	Cl -	
42.	Br -	
43.	I -	
44.	F^+X -	
45.	Cl^+X -	
46.	Br^+X -	
47.	I^+X -	
48.	$P^+X_1X_2X_3$ -	
49.	 -	
50.	-	
51.	$S^+X_1X_2$ -	
52.	$CX_1X_2 = S^+$ -	
53.		BF_4^-
54.	-	
55.	-	
56.		
57.	$(X_4^-)N^+X_1X_2X_3^-$	
58.	O_4Cl -	
59.	-	
60.	-	

X_2 - cycle fragment

Table 3

Codes of Bridge Fragments

Code	Bridge	Notes
I	$-CH_2-$	
2	$-CH_2CH_2-$	

C M P S

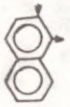
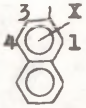
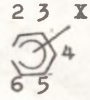
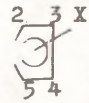
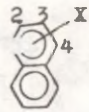
	As the intermediate bridge	As the terminal bridge		
		Formula	Accepted positions of substitution	
1	2	3	4	5
3			2,3,4,5,6	see also 57-60
4			2,3,4	
5			1,3,4	
6			2,3,4,5,6	other bridges - fragments of cycles see 19-33
7			2,3,4,5	
8			2,3,4	

Table 3 continued

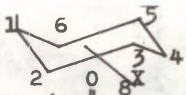
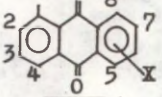
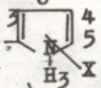
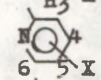
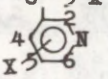
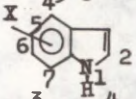
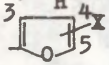
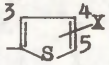
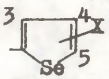
1	2	3	4	5
9			2,3,4,5,6	see also 45
10	-		2,3,4,5,8	
11	-		4,5	
12	-		4,5	
13			5,6	
14	-		2,6	
15	-		5,6	
16	-		4,5	
17	-		4,5	
18	-		4,5	
19	-		2,3,4	
20			2,3,4,5	

Table 3 continued

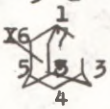
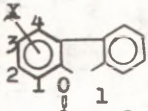
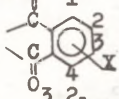
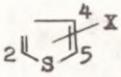
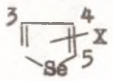
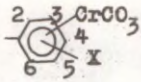
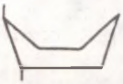
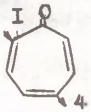
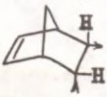
1	2	3	4	5
21	–		2,3,4,5,6	
22	–		1,3,5	
23			1,2,3,4	
24	–		1,2,3,4	
25	–		1,2,3,4,5,6	
26	–		2,4,5	
27	–		3,4,5,6	
28			2,4,6	
29	–		4,6	
30	–		2,3,5,6	
31	–		3,4,5	
32	–		2,4,5	

Table 3 continued

1	2	3	4	5
33	—		3,4,5	
37	—		2,3,4,5,6	

C O P S

(1)	Fragment (6)	5
41	cis- 	
42	trans 	
43		
44		
45		see also 9
46		" "
47		
48		
49		
50		

5

Table 3 continued

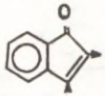
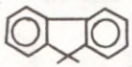
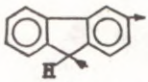
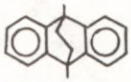
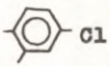
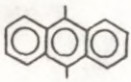
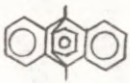
1	6	5
51		
52		
53		
54		
55		
56		
57		Not accepted as the terminal bridge (bridge 3 must be used)
58		
59		
60		
66		
67		

Table 3 continued

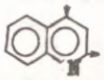
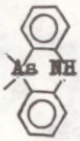
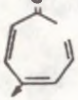
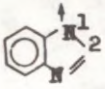
1	6	5
68		
74		
81		Not accepted as the terminal bridge (bridge 6 must be used)
82		
83		
84		
85		Not accepted as the terminal bridge (bridge 29 must be used)
86		
87		
88		
89		

Table 3 continued

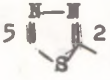
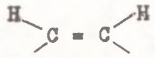
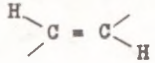
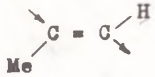
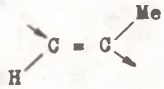
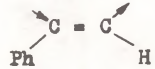
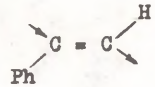
1	6	5
92		
		OB
101	-CHMe	Not accepted as the terminal or penultimate bridge before the methylene fragment (respectively, the methylene and ethylene should be used)
102	$-CH(CF_3)-$	
103	$-CMe_2-$	
104	$-C(OH)(CF_3)-$	
111		
112		
113		
114		
117		
118		
119	-C ≡ C -	
120	$-\overset{|}{C} = NSO_2Ph$	

Table 3 continued

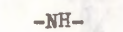
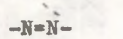
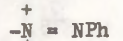
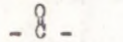
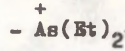
1		6	5
121			Accepted as the terminal bridge only if the corresponding complementary substituent is missing in Table 4
122			
124			
125			
126			
127			
128			
135			Accepted as the terminal bridge only if the corresponding complementary substituent is missing in Table 4
136	- O -		
137	- S -		
138	- S(O)-		
139	- SO_2 -		
140	- Se -		
141	- SeO_2-		
144			

Table 4

Codes of Secondary Substituents

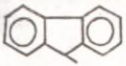
Code	X	Code	X	Code	X
1.	-H	50.		67.	- $O\overset{O}{\overset{\|}{\underset{O}{\|}}}SOH$
2.	$-CH_3$	51.	$-CH=CH_2$ see also 165	68.	- $O\overset{O}{\overset{\|}{\underset{O}{\|}}}SO^-$
3.	$-CH_2CH_3$	52.	$-C\equiv CH$	69.	- $O\overset{O}{\overset{\|}{\underset{O}{\|}}}SOCH_3$
4.	$-CH_2CH_2CH_3$	53.	-F	70.	$-OCF_3$
5.	$-(CH_2)_3CH_3$	54.	-Cl	71.	$-OC_6H_5$
6.	$-(CH_2)_4CH_3$	55.	-Br	72.	$-OCH_2C_6H_5$
7.	$-(CH_2)_5CH_3$	56.	-I	73.	- $O\overset{O}{\overset{\|}{P}}(CH_3)_2$
8.	$-(CH_2)_6CH_3$	57.	-OH	74.	- $O\overset{O}{\overset{\|}{P}}(OH)O^-$
9.	$-(CH_2)_7CH_3$	58.	$-O^-$	75.	- $O\overset{O}{\overset{\|}{P}}(O^-)_2$
10.	$-CH(CH_3)_2$	59.	$-OCH_3$	76.	- $\overset{O}{\overset{\|}{C}}H$
11.	$-CH_2CH(CH_3)_2$	60.	$-OR^{m)}$	77.	- $\overset{O}{\overset{\|}{C}}CH_3$
12.	$-CH(CH_3)CH_2CH_3$	61.	$-O\overset{O}{\overset{\|}{C}}CH_3$	78.	- $\overset{O}{\overset{\|}{C}}R^{m)}$
13.	$-C(CH_3)_3$	62.	$-O\overset{O}{\overset{\|}{C}}R^{m)}$	79.	- $\overset{O}{\overset{\|}{C}}OH$
14.	$-CH_2C(CH_3)_3$	63.	$-O\overset{O}{\overset{\|}{C}}C_6H_5$	80.	- $\overset{O}{\overset{\|}{C}}O^-$
15.	$-(CH_2)_2C(CH_3)_3$	64.	$-ONO_2$	81.	- $\overset{O}{\overset{\|}{C}}OCH_3$
16.	$-CH(CH_2CH_3)_2$	65.	$-O\overset{O}{\overset{\|}{S}}-H$	82.	- $\overset{O}{\overset{\|}{C}}OR^{m)}$
17.	$-CH(CH_2CH_2CH_3)_2$	66.	$-O\overset{O}{\overset{\|}{\underset{O}{\|}}}S^-$	83.	- $\overset{O}{\overset{\|}{C}}OC_6H_5$
18.	$-C(CH_2CH_3)_3$				
19-39	-				
40.					
41.					
42.					
43.					
44-49	-				

Table 4 continued

Code	X	Code	X	Code	X
84.	$-\overset{O}{\overset{\|}{C}}NH_2$	104.	$-NO$	123.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}OH$
85.	$-\overset{O}{\overset{\|}{C}}N(CH_3)_2$	105.	$-NO_2$	124.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}O^-$
86.	$-\overset{O}{\overset{\|}{C}}NHC_6H_5$	106.	$-N_3$	125.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}OCH_3$
87.	$-NH_2$	107.	$-CN$	126.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}C_6H_5$
89.	$-NHCH_3$	108.	$-SH$	127.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}NH_2$
90.	$-\overset{+}{N}H_2CH_3$	109.	$-S^-$	128.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}CF_3$
91.	$-\overset{+}{N}H(CH_3)_2$	110.	$-SR$ [m]	129.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}OC_6H_5$
92.	$-N(CH_3)_2$	111.	$-\overset{O}{\overset{\|}{S}}CH_3$	130-131.	- -
93.	$-\overset{+}{N}(CH_3)_3$	112.	$-\overset{O}{\overset{\|}{S}}C_6H_5$	132.	$-S^+(CH_3)_2$
94.	$-NHC_6H_5$	113.	$-\overset{O}{\overset{\|}{S}}CF_3$	133.	$-S^+(C_6H_5)_2$
95.	$-\overset{+}{N}H_2C_6H_5$	114.	$-\overset{O}{\overset{\|}{S}}CCH_3$	134.	$-SeC_6H_5$
96.	$-NH\overset{O}{\overset{\|}{C}}H$	115.	$-\overset{O}{\overset{\|}{S}}CC_6H_5$	135.	$-\overset{+}{P}R_3$ [m]
97.	$-NH\overset{O}{\overset{\|}{C}}CH_3$	116.	$-\overset{O}{\overset{\|}{S}}CNH_2$	136.	$-\overset{+}{P}(C_6H_5)_3$
98.	$-NH\overset{O}{\overset{\|}{C}}OCH_2CH_3$	117.	$-SCN$	137.	$-\overset{O}{\overset{\|}{P}}(OH)_2$
99.	$-NH\overset{O}{\overset{\|}{C}}C_6H_5$	118.	$-SCF_3$	138.	$-\overset{O}{\overset{\|}{P}}(OH)O^-$
100.	$-NH\overset{O}{\overset{\|}{C}}NH_2$	119.	$-SC_6H_5$	139.	$-\overset{O}{\overset{\|}{P}}(O^-)_2$
101.	$-NH\overset{O}{\overset{\|}{S}}Me$	120.	$-\overset{O}{\overset{\|}{S}}H$		
102.	$-NH\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}C_6H_5$	121.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}^-$		
103.	$-NH\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}O^-$	122.	$-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}Me$		

Table 4 continued

Code	X	Code	X	Code	X
140.	$-P(CH_3)_2$ (O)	149-159	-	175.	$-CF_3$
141.	$-P(C_6H_5)_2$ (O)	160.	$-CrCO_3$	176.	$-CCl_3$
142.	$-P(OCH_3)_2$ (O)	161-164	-	177.	$-CBr_3$
143.	$-Si(CH_3)_3$	165.	$-C(CH_3)=CH_2$	178.	$-C(CF_3)_3$
144.	$-Si(C_6H_5)_3$	166-170	-	179.	$-C(C_6H_5)_3$
145.	$-C_6H_5$	171.	$-CHF_2$		
146.		172.	$-CHCl_2$		
		173.	$-CHBr_2$		
147.		174.	$-CH(C_6H_5)_2$		
148.					

m) R - hydrocarbon radical

References

1. V.A. Palm, Foundations of Quantitative Theory of Organic Reactions. "Khimia", Leningrad, 1977 (in Russ.).
2. Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions. Vol.5(II), VINITI, Moscow, 1979.
3. J.K. Kiho, Reakts.sposobn.organ.soedin., 7, 94(1970).
4. J.K. Kiho, ibid., 7, 547(1970)
5. Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions. Vol.1-5(I), VINITI, Moscow,1975-1978

Organic Reactivity
Vol.21. 3(75) 1984

REACTIVITY OF AROMATIC AND HETEROLYTIC HYDRAZINE DERIVATIVES
III. REACTION KINETICS OF ACYLATION OF 9-HYDRAZINOAKRIDINE DERIVATIVES WITH BENZOYL CHLORIDE IN CHLOROFORM

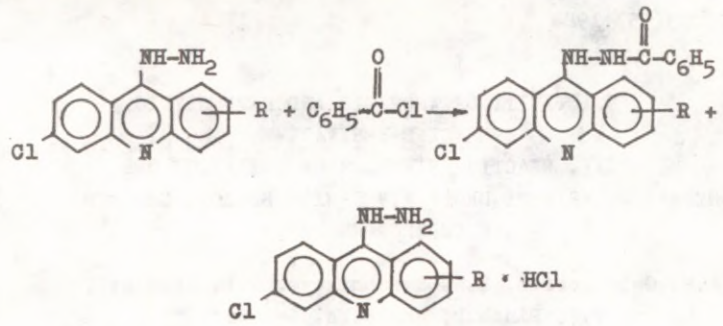
A.N. Gaidukevich, E.N. Svechnikova, G.P. Kazakov, V.V. Pinchuk, and E.Ya. Levitin

Kharkov State Pharmaceutical Institute, Kharkov, the Ukrainian S.S.R.

Received October 19,1984

The reaction kinetics of acylation of 9-hydrazinoakridine derivatives with benzoyl chloride in chloroform has been studied in the temperature range 25-55°C. The activation parameters were calculated. Correlation of the rate constants logarithms, activation energies and enthalpies with substituent constants has been carried out. It has been established that the reaction series under discussion belongs to the enthalpy-control type isokinetic reactions.

In the course of our research with the aim of establishing relationship between the structure, reactivity and biological activity of hydrazine derivatives, was studied the acylation reaction kinetics of 9-hydrazinoakridine derivatives (Table 1) with benzoylchloride in chloroform in the temperature range 25°- 55°. The reaction proceeded according to the following equation:



Changes in the concentration of bensoylchloride in time were determined by argentometric potentiometric titration.[2] The choicè of benzoyl chloride as the acylating reagent was caused by its high reactivity as well as by the absence of the autocatalytic effect in the reactions with aryl- and aroylhydrazines.[8]

The reaction of acylating 9-hydrazinoakridines with benzoyl chloride is irreversible and is described by the second order kinetic equation which is confirmed by the stability of rate constants (Table 2) calculated according to equation :

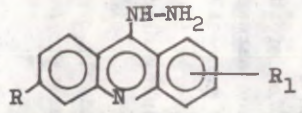
$$k = \frac{1}{2\beta t}\left(\frac{1}{a-x} - \frac{1}{a}\right)$$

where k - the rate constant ($l \cdot mol^{-1} \cdot sec^{-1}$);
a - the initial concentration of benzoyl chloride (M);
x - the concentration of benzoyl chloride (M) at the moment of time t (sec);
β - the correction which takes into account the change in the concentration of reagents when chloroform extends thermally from 293K up to the temperature of the experiment.

The reaction obeys the Arrhenius equation, thus, for 2-methyl-6-chlorine-9-hydrazinoakridine can be observed the following relationship:

Table 1

9 - Hydrazinoakridinee



Compound No	R	R_1	Melting t C°	Found % N	Brutto-formula	Calculated % N
I	H	H	171 - 172	19.81	$C_{13}H_{11}N_3$	20.08
II	6-Cl	H	172 - 173	17.46	$C_{13}H_{10}ClN_3$	17.24
III	6-Cl	2-CH_3	209 - 210	16,11	$C_{14}H_{12}ClN_3$	16.30
IV	6-Cl	4-CH_3	170 - 171	16.57	$C_{14}H_{12}ClN_3$	16.30
V	6-Cl	2-OCH_3	155 - 156	15.62	$C_{14}H_{12}ClN_3O$	15.35
VI	6-Cl	4-OCH_3	181 - 182	15.29	$C_{14}H_{12}ClN_3O$	15.35
VII	6-Cl	4-Cl	142 - 143	14.73	$C_{13}H_9Cl_2N_3$	15.10

$$\log k = (3.47 \pm 0.07) - (33.1 \pm 0.9)\, 10^2 \frac{1}{T}$$

$(r = 0.991 \qquad s = 0.021)$

It is possible to calculate the activation energy E (kcal/mol) and the pre-exponential factor A according to the Arrhenius equation and the thermodynamic parameters of activation enthalpy $\Delta H^{\neq}$ (kcal/mol), enthropy $\Delta S^{\neq}$ (e.u.), and free activation energy $\Delta G^{\neq}$ kcal/mol) according to Eyring[10] (Table 3).

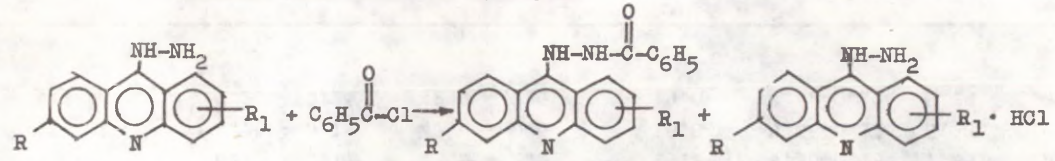
The values for acylation rate constants depend on the nature and position of substituents in the molecule of arylhydrazide. The introduction of electron-withdrawing substituents to the latter leads to a decrease in the reactivity of hydrazide group as well as in the reaction sensitivity on the nature of substituent effect, which has been observed earlier with carboxilic acid hydrazides.[1,3] Electron-donor substituent causes a contrary effect. The introduction of substituents leads to certain changes in the reaction parameters of energy: electron - withdrawing substituents increase energy (E_A), enthalpy ($\Delta H^{\neq}$) and free activation energy ($\Delta G^{\neq}$), but decrease the activation entropy ($\Delta S^{\neq}$) values. Electron -releasing substituents have an opposite effect. Great negative values of activation enthropy indicate a highly organized structure of the transition state, as compared to arylhydrazides[1].

Quantitative estimation of substituent effect on the reactivity of arylhydrazides was given according to the Hammett equation. The logarithms of the reaction rate constants, energy (E_A) and activation enthalpy ($\Delta H^{\neq}$) correlate with the quinoline substituent constants σ[5]. Reaction constant values in eqs. 1-4 (Table 4) refer to the low susceptibility of the reaction series studied to the changes in the structure of 9-hydrazinoakridine molecule. It is noteworthy that the higher the temperature, the lower the ρ values, i.e., the reaction becomes less sensitive to the substituent effect.

The existence of the isokinetic relationship in the reaction series under discussion is confirmed by the following

Table 2

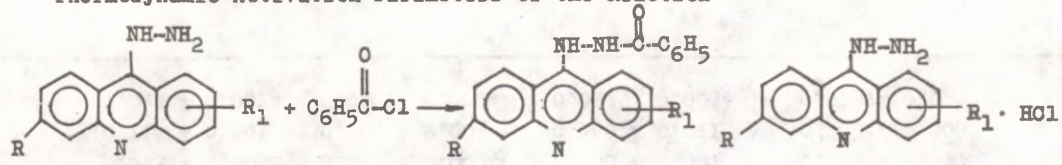
Kinetic Parameters of Reactions



Compound No	k l · mol^{-1} · sec^{-1}			
	298 K	308 K	318 K	328 K
I	0.287 ± 0.009	0.359 ± 0.012	0.457 ± 0.021	0.552 ± 0.017
II	0.0389± 0.0016	0.564 ± 0.0024	0.0818± 0.0020	0.112 ± 0.006
III	0.0457± 0.0032	0.655 ± 0.0017	0.0944± 0.0040	0.125 ± 0.013
IV	0.0447± 0.0028	0.0617± 0.0036	0.0902± 0.0065	0.120 ± 0.009
V	0.0537± 0.0038	0.0706± 0.0024	0.108 ± 0.007	0.140 ± 0.017
VI	0.118 ± 0.007	0.148 ± 0.009	0.188 ± 0.011	0.260 ± 0.008
VII	0.0240± 0.0024	0.0361± 0.0024	0.0529± 0.0034	0.0757± 0.027

Table 3

Thermodynamic Activation Parameters of the Reaction



Compound No	$\Delta H^{\neq}$ kcal/mol	$-\Delta S^{\neq}$ e. u.	$\Delta G^{\neq}$ kcal/mol (298K)	E_A kcal/mol	ln A
I	3.90 ± 0.08	48.0 ± 2.7	17.8	4.27±0.16	5.96 ± 0.19
II	6.76 ± 0.11	42.4 ± 3.6	19.4	6.86±0.31	8.34 ± 0.51
III	6.36 ± 0.09	43.4 ± 1.9	19.3	6.57±0.18	8.00 ± 0.17
IV	6.26 ± 0.12	43.8 ± 2.1	19.3	6.48±0.07	7.82 ± 0.11
V	6.17 ± 0.17	43.8 ± 2.2	19.2	6.38±0.15	7.85 ± 0.24
VI	4.75 ± 0.14	47.0 ± 0.5	18.8	5.06±0.12	6.38 ± 0.20
VII	7.28 ± 0.24	42.0 ± 2.5	19.8	7.42±0.17	8.79 ± 0.09

Table 4

Correlation Parameters of Reactions of Acylation 9 - Hydrazinoakridine with Benzoyl Chloride

Correlation equations	r	S	equation number
$\log k^{298} = (-1.411 \pm 0.008) + (-1.278 \pm 0.017)\,\sigma$	0.994	0.071	1
$\log k^{308} = (-1.258 \pm 0.013) + (-1.123 \pm 0.077)\,\sigma$	0.963	0.028	2
$\log k^{318} = (-1.094 \pm 0.020) + (-1.009 \pm 0.024)\,\sigma$	0.990	0.016	3
$\log k^{328} = (-0.960 \pm 0.013) + (-0.987 \pm 0.019)\,\sigma$	0.995	0.010	4
$E_A = (6.78 \pm 0.09) + (4.40 \pm 0.03)\,\sigma$	0.990	0.015	5
$\Delta H^{\neq} = (6.61 \pm 0.06) + (4.75 \pm 0.04)\,\sigma$	0.991	0.013	6

data:

1. Extrapolated Arrhenius graphs intersect at $T = 480 \pm 5^{\circ}K$.
2. According to the equation of temperature - dependence of reaction constants ρ [6,7]:

$$\rho = (2.01 \pm 0.08) + (-973 \pm 26)\frac{1}{T}$$

$$r = 0.992 \qquad s = 0.04$$

ρ values equal zero at $484^{\circ}K$.

3. Enthalpy ($\Delta H^{\neq}$) and enthropy ($\Delta S^{\neq}$) of the studied reaction series are linearly interrelated [6,7] with slope $480^{\circ}K$:

$$\Delta H^{\neq} = (27.0 \pm 0.4)\ 10^3 + (480 \pm 9)\Delta S^{\neq}$$

$$r = 0.986 \qquad s = 0.012$$

4. $\Delta H^{\neq}$ values are linear functions of rate constant logarithms[8]:

$$\Delta H^{\neq} = (5.89 \pm 0.9) - (0.285 \pm 0.011) \log k^{298}$$

$$r = 0.980 \qquad s = 0.060$$

5. The logarithms of reaction constants 9 at different temperatures correlate well:

$$\log k^{298} = (-14.6 \pm 0.4) + (-15.0 \pm 0.7) \log k^{328}$$

$$r = 0.990 \qquad s = 0.02$$

The above-mentioned criteria evidence about the existence of isokinetic relationship between the studied series and $T_{isokin.} = 480^{\circ}K$, which exceeds the temperature range of the experiment. Thus, the reactions of acylating arylhydrazines are characterized by the enthalpic control of rate constant changes at the variation of substituents.

Experimental

Reagents. The purification and drying of chloroform and benzoyl chloride were described earlier.[1]

9-hydrazinoakridines were obtained according to known methods[10,11] and were purified by multiple recrystallization.

Their purification level was checked chromatographically, by element analysis determining melting points (Table 1). Kinetic studies were carried out according to methods[2]. The concentration of benzoyl chloride was determined by potentiometric titration with a 0.02 M solution of sodium nitrate with platinum ETPL-0.1 M and chlorosilver EVL-1MI electrodes. The kinetics of acylation reactions was measured at 298, 308, 318, 328 K. Each experiment was repeated three times and it included 6-8 measurements. The precision of the obtained values was assessed by the method of mathematical statistics (the confidence level being 0.95)[12]. The thermodynamic activation parameters were calculated according to the well-known least-squares method[4].

References

1. E.N. Svechnikova, A.N. Gaidukevich, E.Ya. Levitin, A.A. Kpavchenko, S.G. Leonova, and E.V. Dynnik, Organic Reactivity, 21, 76 (1984).
2. A.P. Grekov and V.Ya. Veselov, Zh. organ. khimii, 8, 297(1972).
3. A.P. Grekov, and V.Ya. Veselov, Physical Chemistry of Hydrazine (in Russ.), Naumkova dumka, Kiev, 1979.
4. S. Glasstone, K. Laidner, and H. Eyring, The Theory of Rate Processes (Russ.transl.), "Inostrannaya Literatura", Moscow, 1948.
5. Handbook of Chemistry (in Russ.), vol.3, "Khimiya", Moscow, 1964.
6. J.E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, New York-London, 1963.
7. V.A. Palm, Foundations of Quantitative Theory of Organic Reactions.(in Russ.), "Khimiya", Leningrad, 1977.
8. C.D. Ritchie and W.J. Sayer in book "Contemporary Problems of Physical Organic Chemistry" (in Russ.), "Mir", Moscow, 1967.

9. O. Exner, Collection Czechoslovak Chem.Commun. 29, 1094 (1964).

10. A.B. Albert, The Akridines, E. Arnold, London, 1966.

11. A.A. Martynovsky, A.A. Shtojko, I.A. Mazur, V.V. Dunaev, V.R. Stets, and O.N. Lushchinskaya, Farm. zh., 4,40 (1984).

12. K. Doerfel, Statistics in Analytical Chemistry (in Russ.), "Mir", Moscow, 1969.

Organic Reactivity
Vol.21. 3(75) 1984

KINETICS OF NUCLEOPHILIC ADDITION OF PIPERIDINE AND GLYCINE TO N-SUBSTITUTED AND N,N-DISUBSTITUTED ACRYLAMIDES

G. Gavenas, G. Dienys, and O. Adomeniene

Vilnius State University, Chemistry Department
Enterprise for Science and Production "Fermentas", Vilnius, Lithuanian S.S.R.

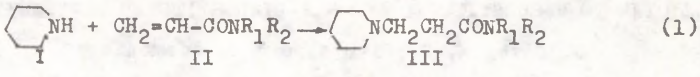
Received October 25, 1984

The rate constants of nucleophilic addition of piperidine and glycine (in the form of glycinate anion) to 24 N-substituted and N,N-disubstituted acrylamides in water at 25° were determined. It was demonstrated, that modified Taft equation including inductive (σ^{*}) and steric (E_s) constants describes satisfactorily separate reaction series of n-substituted and N,N-disubstituted acrylamides. Equation including inductive (σ^{*}), steric (E_s^{o}) and hyperconjugative (n_{HC}) parameters describes satisfactorily rate constants of both N-substituted and N,N-disubstituted acrylamides.

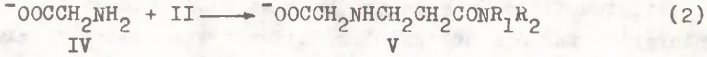
Kinetics of the nucleophilic addition of aliphatic amines to activated ethylenic bond is studied well enough. Many papers deal with addition of amines[1-4] and amino acids[5-9] to acrylonitrile. The reaction series of addition of amines to acrylonitrile[4], acrylamide[10], p-methoxyphenylvinylketone[4] p-tolylvinylsulphone[11] were studied. It was demonstrated that the reactivity of aliphatic amines in these series can be correlated by the two parameter equation including inductive and steric parameters.

The influence of activating group on the reactivity of conjugated ethylenic bond is considerably less studied[7,12]. It seems that the correlation analysis of such rate constants have not been undertaken yet. Introduction of substituents at nitrogen atom of acrylamide opens wide possibilities for variation of activating group.

We have synthesized 24 such compounds (Table 1) and studied the kinetics of their interaction with piperidine and glycinate:



(1)



(2)

Experimental

Materials. N-Substituted and N,N-disubstituted acrylamides were synthesized from acryloyl chloride and corresponding amines according to[13]. Structures of compounds obtained were confirmed by NMR spectra. Sec-butyl amine was synthesized from sec-butyl bromide[14]. Azetidine was synthesized by reduction of cyclic p-tolylsulphamide, obtained from 1,3-dibrompropane, with sodium in isoamyl alcohol[15]. N-methylpiperazine was obtained by cyclization of diethanolamine and methylamine hydrochloride[16].

Kinetic measurements. Kinetics of reactions (1,2) was studied in water at $25\pm0.1^{\circ}$ in thermostated cell of SF-16 spectrophotometer, at 255 nm for N-substituted- and 260 nm for N,N-disubstituted acrylamides. Kinetics of reactions (2) was studied in alcaline solutions at several pH and rate constants were calculated for anion $^{-}OOCCH_2NH_2$ according to method[5].All reactions were run with 15 to 15000-fold excess of nucleophile and rate constants were calculated by the equation of pseudo-first order kinetics[4].6 to 12 kinetic experiments with different concentrations of reagents were run for each reaction.Rate constant was found as a mean of values obtained in all these experiments.Rate constants were calculated at a TI-58 programmed calculator,correlation calculations were performed,using an ES 1033 computer with standard program of multiple linear regression.

Results and discussion

Rate constants of reactions (1,2) are given in Table 1.

Table 1

Rate Constants ($l.mol^{-1} .sec^{-1}$) of the Addition of Piperidine and Glycinate to N-substituted and N,N-disubstituted Acrylamides $CH_2=CH-CONR_1R_2$ in Water at 25°

No	$-NR_1R_2$	Piperidine $k \cdot 10^3$	Glycinate $k_A \cdot 10^5$	$\Sigma\sigma^*$	$-E_N$ [19]	$-E_N^o$ [19]	n_{HC} [23]
1	2	3	4	5	6	7	8
1	$-NH_2$	34.00 ± 3[a]	38.30 ± 2.2	0.98	0.00	0.00	0.0
2	$-NHCH_3$	3.40 ± 0.01	4.26 ± 0.27	0.49	0.07	0.27	3.0
3	$-NHC_2H_5$	3.72 ± 0.19	7.81 ± 0.02	0.39	0.36	0.56	2.4
4	$-NHC_3H_7$	2.44 ± 0.12	6.91 ± 0.45	0.375	0.39	0.59	2.4
5	$-NHCH(CH_3)_2$	3.10 ± 0.15	6.05 ± 0.16	0.30	0.93	1.13	1.8
6	$-NHC_4H_9$	3.15 ± 0.23	5.89 ± 0.29	0.36	0.40	0.60	2.4
7	$-NHCH(CH_3)C_2H_5$	2.51 ± 0.21	6.76 ± 0.35	0.28	1.10[b]	1.30	1.8
8	$-NHC(CH_3)_3$	1.14 ± 0.05	1.91 ± 0.08	0.19	1.74	1.94	1.2
9	$-NH-C_6H_5$	2.95 ± 0.12	5.39 ± 0.27	0.34	0.98	1.18	1.8
10	$-NHCH_2-C_6H_5$	7.84 ± 0.88	17.90 ± 1.3	0.705	0.38	0.58	2.4
11	$-NHCH_2CH=CH_2$	6.40 ± 0.43	14.40 ± 1.3	0.65[c]	0.20[c]	0.40	2.4
12	$-NHCH_2CH_2CN$	15.60 ± 0.01	43.70 ± 3.8	1.29	0.99[d]	1.19	2.4
13	$-N(CH_3)_2$	13.60 ± 0.5	13.20 ± 0.4	0.00	0.47	0.85	6.0
14	$-N(C_2H_5)_2$	7.46 ± 0.70	12.10 ± 0.55	-0.20	1.98	2.38	4.8
15	$-N(C_3H_7)_2$	6.36 ± 0.27	12.01 ± 0.10	-0.23	2.11	2.51	3.6
16	$-N[CH(CH_3)_2]_2$	1.86 ± 0.07	4.41 ± 0.22	-0.38	3.90[e]	4.30	4.8

Table 1 (continued)

1	2	3	4	5	6	7	8
17	$-N(C_4H_9)_2$	4.77 ± 0.40	12.60 ± 0.53	-0.26	2.04[c]	2.44	4.8
18	$-N[CH_2CH(CH_3)_2]_2$	6.84 ± 0.20	11.06 ± 0.56	-0.25	2.47[d]	2.87	4.8
19		19.20 ± 0.9	76.20 ± 0.7	-0.24	0.06	0.46	4.8
20		12.66 ± 0.85	26.11 ± 1.38	-0.26	0.51	0.91	4.8
21		7.35 ± 0.37	14.40 ± 0.37	-0.18	0.79	1.19	4.8
22		9.68 ± 0.60	20.25 ± 1.87	-0.20[b]	1.10	1.50	4.8
23		44.80 ± 3.0	41.10 ± 2.4	0.67	0.79[f]	1.19	4.8
24	$-N(CH_2CH_2CN)_2$	131.0 ±10.0	512.0 ± 37.0	1.60	2.11[g]	2.51	4.8
25		24.40 ± 0.6	85.20 ± 8.4	-	-	-	-

a) - standard deviations of 6 - 12 parallel experiments are given

b) - from[4]

c) - from[20]

d) - from[21]

e) - from[22]

f) - assumed that E_N of morpholine is equal to E_N of piperidine

g) - assumed that E_N of N,N-dicyanethylacrylamide is equal to E_N of N,N-dipropylacrylamide

By means of addition of piperidine and glycine to N-methylacrylamide and N,N-dimethylacrylamide it was possible to show that reactions (1,2) are practically irreversible and follow first order kinetics for every reactant.

In the case of addition of glycinate the next stage proceeds according to the following reaction (2):

$$\underset{V}{^{-}OOCCH_2NHCH_2CH_2CONR_1R_2} + II \longrightarrow \underset{VI}{^{-}OOCH_2N(CH_2CH_2CONR_1R_2)_2} \quad (3)$$

We did not take into consideration the contribution of the process (3) when calculating rate constants of reactions (2) like in [4,10], since we used manyfold excess of nucleophile reagent. It may be expected that rate constants of reactions (3) are somewhat greater than those of reactions (2)[4], but there are also opposite results[5].

Somewhat unexpected conclusion follows from the rate constant values, presented in Table 1: the introduction of one alkyl substituent into amino group of acrylamide decreases the rate of addition approximately tenfolds, but introduction of two alkyl substituents results in only 2 to 5-fold decrease.

Contradictory information is given in literature on the sequence of reactivity of substituted and unsubstituted acrylamides: for addition of alcoholates: CH_2=CH-CONHR < CH_2=CH-$CONH_2$ < CH_2=CH-$CONR_2$ [17], for addition of ethanolamine: CH_2=CH-$CON(CH_3)_2$ < CH_2=CH-$CONHCH(CH_3)_2$ < CH_2=CH-$CONH_2$ [18].

In order to evaluate quantitatively the simultaneous influence of inductive and steric effects of substituents in substituted acrylamides II we performed correlation of rate constants presented in Table 1 according to the modified Taft equation, with isosteric constants E_N or E_N^o [4,10]:

$$\log k = \log k_o + \rho^* \Sigma\sigma^* + \delta E_N \quad (4)$$

Correlation was poor when all available rate constants were used (table 2, series 1,9). When separate reaction series of N-substituted and N,N-disubstituted acrylamides were considered satisfactory correlations were obtained after exclu-

Table 2

Results of Correlation of Reactivity of N-substituted and N,N-disubstituted Acrylamides by Equation (4)

No of series	Nucleophile	n	Rate constants	-log k_o	ρ	δ	R	s
1	Piperidine	24	1-24[x]	2.202	0.414	0.021	0.496	0.149
2	"	12	1-12	2.604	0.859	0.206	0.866	0.033
3	"	11	1-12 No 7 excluded	2.639	0.924	0.264	0.922	0.022
4	"	10	2-12 No 7 excluded	2.538	0.814	0.337	0.951	0.015
5	"	9	2-12 No 4 and 7 excluded	2.561	0.778	0.270	0.952	0.009
6	"	13	1-and 13-24	1.756	0.634	0.148	0.948	0.021
7	"	12	13-24	1.672	0.723	0.185	0.979	0.009
8	"	11	13-24 No 21 excluded	1.635	0.711	0.197	0.987	0.006
9	Glycinate	24	1-24	3.983	0.463	-0.016	0.479	0.185
10	"	12	1-12	4.503	0.996	0.074	0.854	0.039
11	"	11	1-12 No 7 excluded	4.549	1.083	0.151	0.945	0.016
12	"	10	1-12 No 2 and 7 excluded	4.419	1.018	0.255	0.989	0.003
13	"	13	1 and 13-24	3.353	0.641	0.117	0.829	0.080
14	"	12	1 and 13-24 No 19 excluded	3.701	0.722	0.042	0.895	0.050
15	"	11	13-24 No 19 excluded	3.568	0.827	0.101	0.944	0.030
16	"	10	13-24 No 19 and 23 excluded	3.487	0.895	0.129	0.963	0.020

[x] Numeration of compounds is the same as in table 1

Table 3

Results of Correlation of Reactivity of N-substituted and N,N-disubstituted Acrylamides by Equation (5)

No of series	Nucleophile	n	Rate constants	-log k_o	a_1	a_2	a_3	R	s
1.	Piperidine	24	1-24[x]	2.934	0.669	0.077	0.219	0.818	0.065
2	"	23	2-24	3.192	0.638	0.053	0.274	0.918	0.029
3	"	22	3-24	3.142	0.644	0.075	0.274	0.939	0.023
4	"	21	3-24 No 7 excluded	3.223	0.658	0.077	0.292	0.955	0.017
5	"	20	3-24 No 7 and 13 excluded	3.275	0.658	0.103	0.323	0.972	0.011
6	"	19	3-24 No 7, 13 and 19 excl.	3.286	0.684	0.077	0.309	0.979	0.008
7	Glycine	24	1-24	4.761	0.735	0.043	0.230	0.786	0.092
8	"	23	1-24 No 19 excluded	4.821	0.817	-0.023	0.203	0.841	0.066
9	"	22	2-24 No 19 excluded	5.012	0.792	-0.039	0.245	0.891	0.047
10	"	21	3-24 No 19 excluded	4.947	0.794	-0.007	0.247	0.917	0.036
11	"	20	3-24 No 7 and 19 excluded	5.054	0.812	-0.005	0.270	0.942	0.026
12	"	19	3-24 No 7,13 and 19 excl.	5.118	0.799	0.044	0.319	0.974	0.013

[x] Numeration of compounds is the same as in table 1.

sion of 1-2 most deviating points (table 2, series 4,7,12 and 16). No further improvement was obtained by the exclusion of other relatively more deviating constants. Unsubstituted acrylamide did not fit any of reaction series. Correlation equations obtained using isosteric constants E_N^o, without any hyperconjugation component, are similar to those of Table 2.

In order to cover unsubstituted, N-substituted and N,N-disubstituted acrylamides by one correlation equation we used equation (5) including hyperconjugation parameter, like in [23,24]:

$$\log k = \log k_o + a_1 \Sigma \sigma^* + a_2 E_N^o + a_3 n_{HC}, \qquad (5)$$

where $n_{HC} = n_H + 0.4 n_C$, n_H and n_C are numbers of C-H and C-C bonds, which take place in hyperconjugation.

Correlation was unsatisfactory when all available rate constants were used (table 3, series 1,7). But satisfactory correlation was obtained after exclusion of 4-5 most deviating rate constants (acrylamide, N-methyl-, N-sec-butyl-, N,N-dimethylacrylamides, acryloylazetidine, table 3, series 6, 12). Thus, we succeed to correlate the rate constants of N-substituted and N,N-disubstituted acrylamides using equation (5).

References

1. Y.Ocata, M.Okano et al., J.Am.Chem.Soc., 78, 5426 (1956).
2. M.Wronski, J.Bogdanski, Zeczyty Nauk.Univ.Lodz., 14, 153 (1963).
3. G.Dienys and L.Archipova et al., Reakts.sposobn.organ. soedin., 9, 345 (1972).
4. G.Dienys, L.J.J.Kunskaite, A.Vaitkevicius, and A.Klimavicius, Organic Reactivity, 12, 275 (1975).
5. M.Friedman and J.S.Wall, J.Am.Chem.Soc., 86, 3735 (1969).
6. M.Friedman, J.P.Cavins, and J.S.Wall, J.Am.Chem.Soc., 87, 3672 (1965).
7. M.Friedman and J.S.Wall, J.Org.Chem., 31, 2888 (1966).
8. M.Friedman, J. Am.Chem.Soc., 89, 4709 (1967).

9. M.Friedman and J.A.Romersberger, J.Org.Chem.,33, 154 (1968).
10. M.Danileviciute, G.Dienys, and O. Adomeniene, Organic Reactivity, 16, 434 (1979).
11. S.T.McDowell and C.J.M.Stirling, J.Chem.Soc.(B), 1967, 343.
12. H.Shenhav, Z.Rappoport, and S.Patai, J.Chem.Soc.(B), 1970. 469.
13. M.M.Koton, T.A.Sokolova et al., Zh.Obshch.Khim., 21, 2239 (1977).
14. J.Houben, Methoden der organischen Chemie, Bd. II, T.1, Aufl., Stuttgart, Georg Thieme Verlag, 1940, S.478.
15. J.M.Yanbikov, Zh.Obshch.Khim., 8, 1545 (1938).
16. K.Mayako, Japan J.Pharm.Chem.,30, 46 (1958). USA Pat. No 3270004, (1966), Ref.Zh.Khim., 21 H 36217 (1968).
17. R.N.Ring, G.G.Tesoro, and D.R.Moore, J.Org.Chem., 32, 1091 (1972).
18. D.Rozenthal, G.Brandrup et al., J.Org.Chem., 30, 3689 (1965).
19. Handbook of chemistry (in Russian), vol.3, 1964,p.954.
20. L.M.Litvinenko, A.F.Popov, and Z.P.Gelbina, Dokl.Akad. Nauk SSSR, 203, 343 (1972).
21. C.Hansch and A.Leo, Substituent Constants for Correlation Analysis in Chemistry and Biology. "John Wiley & Sons, Inc." 1979.
22. L.M.Litvinenko, A.F. Popov,and Z.P.Gelbina, Dokl.Akad. Nauk SSSR, 189, 546 (1969).
23. A. Uri, Organic Reactivity, 20, 444 (1983).
24. J.Shorter, Correlation Analysis of Organic Reactivity. "Research Studies Press", 1982, p. 73.

Organic Reactivity
Vol.21. 3(75) 1984

KINETIC STUDY OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL TOSYLATES.
XIII. RESULTS OF KINETIC MEASUREMENTS IN 80% AQUEOUS DIMETHYLSULFOXIDE

V. Nummert and M. Rek
Laboratory of Chemical Kinetics and Catalysis, Tartu State University, 202400 Tartu U.S.S.R.

Received October 25,1984

The rate constants of the alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in 80% (v/v) (50.3 M%) aqueous dimethylsulfoxide (DMSC) at 25, 50 and 75°C, whereas X= H, 3-Cl, 3-NO_2, 4-NO_2 and at 75°C when X= 4-CH_3 and X= 4-F were measured. The rate constants for 4-fluorophenyl tosylate in water and phenyl tosylate in 50% (v/v) (34.1 M%) DMSO-water mixture at 75°C were determined also.

The investigation of the kinetics of the alkaline hydrolysis of substituted phenyl tosylates in 80% DMSO-water mixture is of interest since one has some reason to assume that in the case of this reaction series it is possible to study the solvent dependent substituent effects in a wide temperature range.

The rate of the alkaline hydrolysis of substituted phenyl benzoates in water is considerably higher than that in the case of substituted phenyl tosylates. The log k values in water at 50°C for phenyl benzoate and phenyl tosylate equal 0.238[1] and -2.940,[2] respectively. The rate of the alkaline hydrolysis of phenyl benzoates considerably increases while passing from water to 80% aqueous DMSO mixture (at 25°C for phenyl benzoate log k = 0.498[3] comparing with log k =

= -0.367[3] in water at the same temperature). The study of the kinetics of this reaction with varied substituent at higher temperatures requires the use of the experimental methods adopted for the monitoring fast reactions, (e.g. the method of stopped flow).

In the present work the kinetics of the alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in 80% (v/v) (50.3 M%) DMSO-water mixture at 25, 50 and 75°C whereas X = H, 3-Cl, 3-NO_2, 4-NO_2 and at 75°C when X = 4-CH_3 and 4-F was investigated. The kinetics of 4- fluorophenyl tosylate in water and phenyl benzoate in 50% (v/v) (34.1 M%) aqueous DMSO were studied at 75°C as well.

As the reagent tetra-n-butylammonium hydroxide (n-Bu_4NOH) was used. 4-Fluorophenyl tosylate was synthesized according to Ref. 4 and was several times recrystallized from EtOH; m.p. 58.7-59.1°C.

The preparation of other phenyl tosylates, the purification of hydroxide and dimethylsulfoxide and the technique of kinetic measurements are described in Refs. 1-3 of this series.

For the kinetic measurements the spectrophotometric method was applied. The wave lengths used are given in Table 1.

The kinetic measurements were carried out under pseudo-monomolecular conditions at more than 15 time alkali excess. Rate constants for each phenyl tosylate were measured at 4-14 various hydroxide concentrations. The measurements at each hydroxide concentration were repeated mainly 2-6 times and the arithmetic means of the corresponding pseudo-first order rate constants k_1 were calculated. The second order rate constants were calculated as slopes of the corresponding regression plots of the pseudo-first order rate constants vs. the hydroxide concentration.

When calculating the k_2 values according to the following equation:

$$k_1 = k_2 \cdot C_{OH^-} + \text{const} \qquad (1)$$

both the k_1 values for all parallel measurements at each hydroxide concentration and the corresponding arithmetic means at each hydroxide concentration were applied.

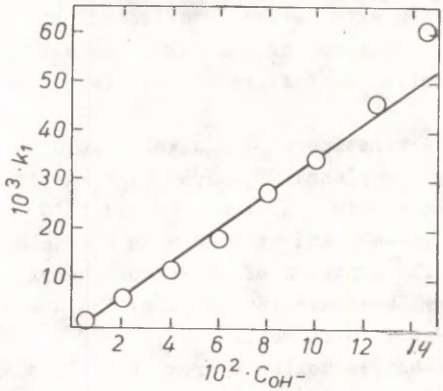


Fig.1. Relationship between k_1 and hydroxide concentration for 3-nitrophenyl tosylate in 80% DMSO at 25°C.

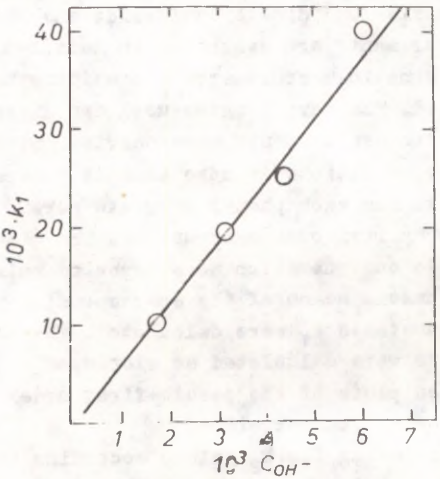


Fig.2. Relationship between k_1 and hydroxide concentration for 3-nitrophenyl tosylate in 80% DMSO at 75°C.

The results of the preliminary kinetic data treatment are given in Table 1: the arithmetic means of the pseudo - first order rate constants at each hydroxide concentration (k_1); number of runs at a certain hydroxide concentration considered (n_1); the values of the second order rate constants calculated according to equation (1), including the k_1 values for all parallel measurements at each concentration ($k_2(1)$), and those of $k_2(2)$ calculated according to Eq. (1) when the corresponding arithmetic means were embraced.

The Figs. 1-6 illustrate the plots of the arithmetic means of the pseudofirst order rate constants k_1 vs. hydroxide concentration for 3-nitrophenyl,3-chlorophenyl and phenyl tosylates at 25 and 75°C.

One can see that at considerably higher hydroxide concentrations the points deviate from the linear plot.

For estimation of "true" rate constants extrapolated to infinite dilution of hydroxide solution the second order rate constants were calculated as follows:

The arithmetic means of the first order rate constants k_1 were divided by the hydroxide concentration; the obtained values of k_2' were treated according to equation:

$$\log k_2' = \log k_2^o + B \cdot C_{OH^-} , \qquad (2)$$

where k_2^o is the second order rate constant for the infinitely diluted solution. Equation (2) is a Setchenow[5,6] type formula for taking into account influence of the neutral electrolyte concentration in case of reactions between ions and neutral molecules.

Table 2 lists the results of the data treatment according to equation (2) for the alkaline hydrolysis of phenyl tosylates in 80% aqueous DMSO.

As it is seen from the data in Table 2 coefficient B before the C_{OH^-} in equation (2) is in general statistically significant and the application of this equation for calculation of the "true" second order rate constants should be considered reasonable.

Both the logarithmic values of the second order rate constants k_2 (1) and $k_2(2)$ found according to equation (1) with-

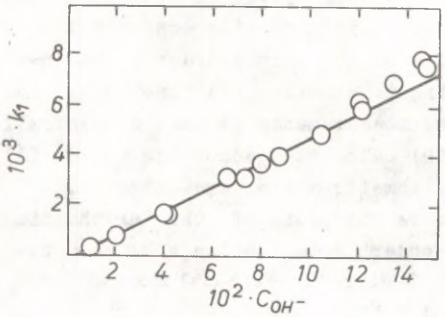


Fig. 3. Relationship between k_1 and hydroxide concentration for 3-chlorophenyl tosylate in 80% at 25°C.

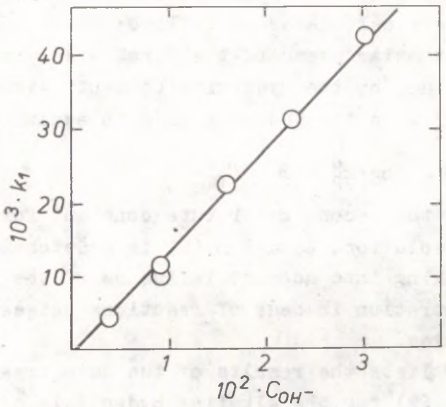


Fig. 4. Relationship between k_1 and hydroxide concentration for 3-chlorophenyl tosylate in 80% DMSO at 75°C.

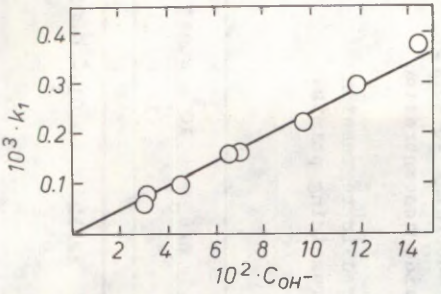


Fig.5. Relationship between k_1 and hydroxide concentration for phenyl tosylate in 80% DMSO at 25°C

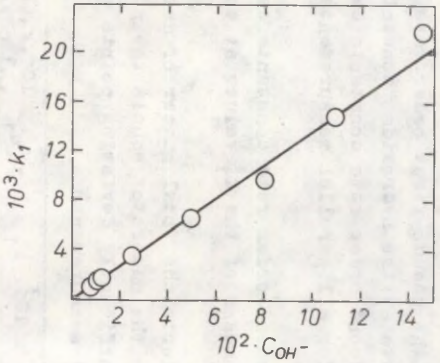


Fig. 6. Relationship between k_1 and hydroxide concentration for phenyl tosylate in 80% DMSO at 75°C.

Table 1

Results of the Preliminary Kinetic Data Treatment According to Eq.(1) $k_1 = k_2 \cdot C_{OH^-} + \text{const}$ for the Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in 80% (v/v) DMSO-Water Mixture

C_{OH^-} - Concentration of hydroxide n-Bu_4NOH

k_1 - Arithmetic means of the pseudo-first order rate constants

n_1 - Number of measurements at the hydroxide concentration considered

$k_2(1)$ - The values of the second order rate constants calculated according to Eq.(1) when the k_1 values for all parallel measurements at each hydroxide concentration are included

$k_2(2)$ - The values of the second order rate constants calculated according to Eq.(1) when the arithmetic means of the k_1 values at each hydroxide concentration are included

n/n_o - The denominator reflects the total number of data, involved in regression data processing and the numerator equals the number of remaining points after excluding significantly deviating points

λ - Wave lengths used at measurements

X and λ	Temperature °C	$10^3 . C_{OH^-}$ (M)	$10^3 . k_1$ (sec^{-1})	n_1	$10^3 . k_2(1)$ and $10^3 . k_2(2)$ ($M^{-1} . sec^{-1}$)	n/n_o	$10^3 .$ const (in Eq.(1))
1	2	3	4	5	6	7	8
H	25	29.30	0.0573±0.0001	1	2.56 ± 0.08	12/12	-0.01 ± 0.01
303							

Table 1 continued

1	2	3	4	5	6	7	8
		30.44	0.0736±0.0090	2	2.58±0.09	7/7	-0.12±0.05
		44.51	0.0965±0.0003	1			
		65.97	0.166 ±0.006	2			
		70.17	0.161 ±0.004	2			
		96.60	0.225 ±0.002	2			
		119.5	0.302 ±0.001	2			
		143.6	0.377 ±0.004*	2			
	50	12.75	0.201 ±0.004	3	23.3 ± 0.2	11/13	-0.10±0.01
		31.58	0.616 ±0.001	2	24.0 ± 0.7	6/6	-0.12±0.05
		59.15	1.28 ±0.02	2			
		89.42	2.02 ±0.02	2			
		118.8	2.90 ±0.03	2			
		144.9	3.26 ±0.02	2			
	75	6.351	0.710 ±0.040	3	132 ± 1	13/20	-0.09±0.02
		10.26	1.23 ±0.04	3	138 ± 1	6/7	-0.18±0.03
		10.33	1.30 ±0.01	1			
		25.67	3.39 ±0.07	4			
		49.50	6.50 ±0.02	2			
		79.88	9.97 ±0.07	3			
		109.8	15.0 ±0.3	4			
		145.9	22.7 ±0.4*	4			

Table 1 continued

1	2	3	4	5	6	7	8
H	75	10.03	0.293±0.010	2	27.3 ± 0.8	5/5	0.03±0.04
(50% DMSO)		49.87	1.42 ±0.01	1	27.3 ± 0.3	3/3	0.03±0.01
299		99.23	2.73 ±0.09	2			
		174.4	5.77 ±0.13*	2			
3-Cl	25	9.838	0.283±0.002	2	47.8 ± 0.4	15/21	-0.23±0.02
308		20.21	0.728±0.025	4	48.1 ± 1.4	9/9	-0.28±0.08
		40.19	1.64 ±0.01	2			
		41.38	1.53 ±0.04	2			
		66.34	3.06 ±0.09	4			
		73.27	3.00 ±0.10	2			
		79.88	3.60 ±0.03	2			
		87.58	3.92 ±0.01	2			
		104.6	4.84 ±0.02	1			
		119.6	6.14 ±0.01*	2			
		119.7	5.73 ±0.03*	1			
		132.7	7.00 ±0.10*	2			
		145.6	7.93 ±0.05*	2			
		147.6	7.62 ±0.06*	1			
	50	3.917	0.140±0.002	3	275 ± 1	16/22	-0.48±0.03
		5.844	1.14 ±0.04	4	280 ± 3	7/7	-0.56±0.08

Table 1 continued

1	2	3	4	5	6	7	8
		8.014	1.64 ± 0.05	2			
		11.68	2.48 ± 0.12	3			
		29.70	8.06 ± 0.05	1			
		50.03	13.3 ± 0.1	4			
		70.30	19.2 ± 0.4	5			
		89.52	26.9 ± 0.5*	5			
	75	4.030	4.42 ± 0.32	4	1335 ± 17	16/22	-0.18±0.22
		8.016	11.0 ± 0.2	4	1413 ± 18	6/6	-0.87±0.27
		8.030	10.7 ± 0.2	3			
		16.08	21.4 ± 1.3	3			
		22.52	30.7 ± 0.7	5			
		30.09	41.9 ± 1.1	3			
3-NO_2	25	4.972	1.06 ± 0.02	2	311 ± 3	10/15	-0.68±0.08
450		19.88	5.42 ± 0.08	5	314 ± 7	4/4	-0.50±0.01
		39.69	11.3 ± 0.2	4			
		60.01	18.4 ± 0.5	4			
		80.22	27.8 ± 0.4*	5			
		99.33	34.6 ± 0.2*	4			
		123.8	45.6 ± 0.6*	5			
		145.8	60.7 ± 1.7*	5			

Table 1 continued

1	2	3	4	5	6	7	8
	50	3.828	5.50 ± 0.08	5	1693 ± 13	16/20	-1.03±0.16
		9.82	15.7 ± 0.3	3	1709 ± 10	5/5	-1.19±0.17
		16.14	26.2 ± 0.2	4			
		23.73	39.2 ± 0.6	5			
		30.35	51.0 ± 0.8	3			
	75	1.686	10.4 ± 0.7	5	6287 ± 246	13/19	-0.98±0.86
		3.189	19.6 ± 0.5	4	6681 ± 561	4/4	
		4.426	24.9 ± 0.4	5			
		5.977	39.9 ± 0.7	5			
4-NO_2	25	4.101	1.55 ± 0.08	3	505 ± 2	32/48	-0.88±0.06
424		5.035	1.73 ± 0.18	4	497 ± 3	9/13	-0.30±0.01
		8.824	3.46 ± 0.29	2			
		10.01	4.39 ± 0.14	4			
		16.62	7.15 ± 0.24	5			
		19.68	8.70 ± 0.14	4			
		24.52	11.5 ± 0.1	2			
		39.11	17.2 ± 0.4	1			
		40.15	20.3 ± 0.5	4			
		43.90	19.6 ± 0.5	6			
		58.72	28.7 ± 0.3	2			

Table 1 continued

1	2	3	4	5	6	7	8
		77.51	39.7 ± 0.6	6			
		78.82	42.5 ± 0.3*	2			
		95.12	47.4 ± 0.3*	1			
		96.10	46.8 ± 1.4	5			
	50	2.797	6.13± 0.11	3	2460 ± 51	30/35	-1.82±0.60
		4.771	9.35± 0.31	4	2477 ± 59	8/9	-1.80±0.72
		8.053	18.0 ± 0.7	4			
		11.12	24.1 ± 0.4	5			
		12.37	32.4 ± 0.8	5			
		12.71	30.5 ± 0.2	4			
		17.68	43.5 ± 0.8	3			
		19.97	46.5 ± 0.8	6			
		19.98	48.0 ± 0.3	1			
	75	0.5188	3.00± 0.14	4	10710 ± 70	10/17	-2.56±0.13
		1.727	16.2 ± 0.3	4	11380 ± 170	4/4	-3.25±0.40
		2.926	29.4 ± 0.5	5			
		4.016	42.9 ± 1.4	4			
4-F		4.166	1.10± 0.01	2	267 ± 3 (1)	15/20	0.25±0.13
^lo		12.06	3.50± 0.06	2	274 ± 5 (2)	6/6	0.56±0.01
		20.04	6.05± 0.02	1			

Table 1 continued

1	2	3	4	5	6	7	8
		40.12	10.7 ± 0.3	5			
		60.27	16.4 ± 0.2	5			
		80.25	22.4 ± 0.4	5			
		99.97	29.5 ± 0.7*	5			
		124.8	38.1 ± 0.3*	4			
		146.0	41.4 ± 0.8*	5			
4-F	75	10.17	0.154±0.009	2	6.80 ± 0.23	11/11	-0.18±0.04
H_2O		39.99	0.526±0.028	2	6.80 ± 0.16	6/6	0.19±0.03
300		69.70	0.716±0.079	2			
		99.09	1.26 ±0.02	2			
		198.4	1.84 ±0.23	1			
		338.2	2.40 ±0.15	2			
		496.2	3.60 ±0.23	2			
4-CH_3	75	9.93	0.602±0.021	2	67.7 ± 1.0	9/10	-0.09±0.04
312		29.71	1.95 ±0.02	2	69.9 ± 1.4	5/5	-0.15±0.07
		49.81	3.16 ±0.03	2			
		69.74	4.73 ±0.01	2			
		89.49	6.17 ±0.23	2			

* These values were excluded from the calculation of the k_2 values according to Eq.(1) since these points fall on the cleary curved part in the dependence of k_1 on hydroxide concentration at the higher values of the latter.

Table 2

Results of Data Treatment According to Eq.(2)

$\log k_2 = \log k_2^o + B \cdot C_{OH^-}$

for the Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in 80% (v/v) DMSO-Water Mixture

X	Temperature °C	$\log k_2^o$	B	s
H	25	-2.686 ± 0.019	0.799 ± 0.259	0.028
	50	-1.760 ± 0.021	1.079 ± 0.288	0.032
	75	-0.925 ± 0.008	0.667 ± 0.157	0.021
H (50% DMSO)	75	-1.557 ± 0.015	0.331 ± 0.183	0.022
3-Cl	25	-1.448 ± 0.010	1.195 ± 0.113	0.016
	50	-0.714 ± 0.017	2.369 ± 0.291	0.034
	75	-0.083 ± 0.018	2.318 ± 1.274	0.028
3-NO_2	25	-0.627 ± 0.013	1.733 ± 0.189	0.024
	50	0.165 ± 0.008	2.186 ± 0.526	0.011
	75	0.770 ± 0.047	4.775 ± 11.41	0.036
4-NO_2	25	-0.385 ± 0.009	1.060 ± 0.214	0.025
	50	0.315 ± 0.017	3.675 ± 1.432	0.025
	75	0.776 ± 0.042	71.78 ±18.31	0.047
4-F	75	-0.558 ± 0.009	0.167 ± 0.143	0.020
4-F (H_2O)	75	-1.938 ± 0.040	-0.519 ± 0.224	0.098
4-CH_3	75	-1.216 ± 0.007	0.632 ± 0.145	0.009

Table 3

Comparison of the log k_2 Values Calculated by Various Methods

$k_2(1)$ and $k_2(2)$ - See at Table 1.

k_2^o - Values of k_2 calculated according to Eq.(2)

$\log k_2 = \log k_2^o + B \cdot C_{OH^-}$

X	Temperature °C	log k_2 (1)	log k_2(2)	log k_2^o
H	25	-2.592 ± 0.014	-2.588 ± 0.015	-2.686 ± 0.019
	50	-1.633 ± 0.004	-1.620 ± 0.013	-1.760 ± 0.021
	75	-0.880 ± 0.002	-0.860 ± 0.003	-0.925 ± 0.008
H (50% DMSO)	75	-1.564 ± 0.012	-1.564 ± 0.005	-1.557 ± 0.015
3-Cl	25	-1.321 ± 0.003	-1.318 ± 0.013	-1.448 ± 0.010
	50	-0.561 ± 0.002	-0.553 ± 0.005	-0.714 ± 0.017
	75	0.126 ± 0.006	0.150 ± 0.006	0.083 ± 0.018
3-NO_2	25	-0.500 ± 0.004	-0.503 ± 0.009	-0.627 ± 0.013
	50	0.229 ± 0.003	0.233 ± 0.002	0.165 ± 0.008
	75	0.798 ± 0.017	0.825 ± 0.035	0.770 ± 0.047
4-NO_2	25	-0.297 ± 0.002	-0.303 ± 0.002	-0.385 ± 0.009
	50	0.391 ± 0.009	0.394 ± 0.010	0.315 ± 0.017
	75	1.030 ± 0.003	1.056 ± 0.007	0.776 ± 0.042
4-F	75	-0.573 ± 0.005	-0.562 ± 0.008	-0.558 ± 0.009
4-F (H_2O)	75	-2.163 ± 0.015	-2.168 ± 0.011	-1.938 ± 0.040
4-CH_3	75	-1.169 ± 0.008	-1.156 ± 0.009	-1.216 ± 0.007

out taking into account the influence of the hydroxide concentration and the values of log k_2^0 calculated by equation (2) for the infinitely diluted solution are presented in Table 3. As it is seen, taking into account the dependence of k_2 on hydroxide concentration leads to a considerable correctione in this value.

The dependence of log k_2' on C_{OH^-} for the alkaline hydrolysis of 3-chlorophenyl tosylate at 25°C is shown in Fig. 7.

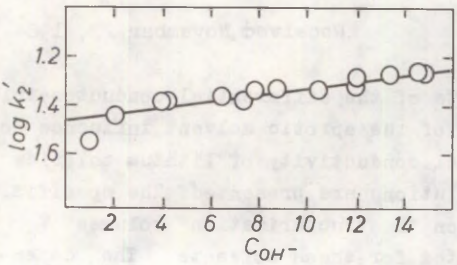


Fig. 7. Dependence of log k_2' on hydroxide concentration for 3-chlorophenyl tosylate in 80% DMSO at 25°C.

Discussion of the obtained kinetic data will be published separately in one of the forthcoming publications.

References

1. T. Püssa, V. Nummert (Maremäe), and V. Palm, Reakts. sposobn.organ.soedin., 9, 697(1972).
2. V. Maremäe and V. Palm, Reakts.sposobn. organ.soedin., I(2) 85(1964).
3. V. Nummert, M. Eek, and M. Piirsalu, Organic Reactivity, 18, 363(1981).
4. S.E. Hazlet, J. Amer. Chem. Soc., 59, 287 (1937).
5. J. Setschenow, Z. phys. Chem., 4, 117(1889)
6. J. Setschenow, Ann. Chim. Phys., 25, 226(1892).

Organic Reactivity
Vol.21. 3(75) 1984

NON-ELECTROLYTE EFFECTS ON THE STRUCTURE OF THE LITHIUM CHLORIDE SOLUTIONS IN ETHANOL. II. APROTIC SOLVENTS.

M.M. Karelson and H. Kuura

Laboratory of Chemical Kinetics and Catalysis, Tartu, Estonian S.S.R., U.S.S.R.

Received November 27, 1984

The results of the differential-conductometric measurements of the aprotic solvent influence on the electrical conductivity of lithium chloride ethanolic solutions are presented. The specific molar solution "restructurization" volumes V_s were calculated for these solvents. The dependence of V_s-parameters on the structure of addition molecules is discussed.

In the previous article of this series[1] the results of the differential-conductometric measurements of the influence of some hydroxylic solvents on the electrical conductivity of lithium chloride ethanolic solutions were given. This article deals with the results of the similar measurements made with various aprotic solvents (acetonitrile, dimethyl sulfoxide, dimethyl formamide, and dicxane).

In the differential conductometry a quantity

$$Y = \frac{k \cdot 10^3}{C_s} \left(\frac{1}{R_o + \Delta R} + \frac{1}{R_x} \right) \qquad (1)$$

is found. In this formula k denotes the conductometric cell constant (cm^{-1}), C_s is the molar concentration of the small addition ($\sim 10^{-2}$ mole/l) of the substance investigated, and R_o and R_x are the resistances (Ω) of the solution before

and after adding this substance, respectively. Quantity ΔR accounts the change of the resistance of the solution due to the dilution in the process of addition. Therefore the quantity Y is the change of the specific conductivity of the solution $\Delta\varkappa$ per mole of added substance, i.e.

$$Y = \frac{\Delta\varkappa}{c_s} \qquad (2)$$

It was shown [2,3] that this quantity is simply related to the specific "restructurization" volume of the substance added, V_s:

$$Y = V_s \cdot \varkappa, \qquad (3)$$

where $\varkappa$ is the specific conductivity of the pure solution at the given electrolyte concentration. Volume V_s is a specific parameter for a given substance and describes its influence on the structure of solvent. Namely it is equal to the statistically mean volume around the molecule of this substance, where the solvent structure is fully perturbed (i.e. transformed either to ideally ordered structure or to the entirely disordered form).

Experimental

Ethanol (grade "Pure for analysis") was dried on the CaO and distilled. The fraction used had b. p. 78.4°C (760 mm Hg) and $d^{25} = 0.7898$.

Dimethyl sulfoxide (grade "Pure for analysis") was dried on the BaO and bidistilled from the mixture with CaH_2 in the argon atmosphere. The fraction used had b.p. 64.0°C (6mm Hg) and $d_{25}^{25} = 1.10105$.

Dimethyl formamide ("grade Pure for analysis") was dried on the CaO and bidistilled. The fraction used had b.p. 39.7-40.0°C (20 mm Hg) and $d_{25}^{25} = 0.9492$.

Acetonitrile (grade "Pure for analysis") was treated with KOH, distilled. The main fraction was treated with CaH_2

and fractionally distilled. The fraction used had b.p.81.5°C (760 mm Hg) and d_{25}^{25} = 0.7791.

Dioxane (grade "Pure for analysis") was treated with HCl and KOH, dried and then boiled with sodium. Finally the fractional distillation was carried out. The fraction used had b. p. 101.5°C (760 mm Hg) and d_4^{20} = 1.0329. The conductometric measurements were carried out on the apparatus described elsewhere[4]. All the measurements were made at the temperature 25.0±0.1°C, hold constant with the precision of ±0.001°C. The conductivity cell was isolated from the surrounding atmosphere with CaO tubes to prevent the absorption of water. The cell constant was k=19.60 cm^{-1}. Constant resistance R_p = 9907.0 Ω was used in parallel joint to the conductivity cell in case of dilute solutions .

Dilution term ΔR in Eq. (1) was calculated according to the procedure, described previously[1].

Discussion

The numerical values of quantity Y for different aprotic compounds in the wide range of lithium chloride concentration in ethanol are given in Tables 1 and 2. The dependence of these quantities on the specific conductivity of the pure electrolyte solutions is illustrated on Fig. 1 (acetonitrile, dioxane, and dimethyl formamide) and Fig. 2. (dimethyl sulfoxide). It is obvious that the linear relationships[6] according to the Eq.(3) are valid for the first three compounde whereas a significant curvature in the region of the concentrated electrolyte solutions is observable for the dimethyl sulfoxide. Therefore the parameter V_s for this compound is estimated from the initial slope of the dependence between Y and specific conductivity $\varkappa$. The values of V_s parameters for all substances investigated are given in Tables 1 and 2 , too.

---

[6] The small intercept for dioxane could be caused by the small uncontrolled ionic admixture in this substance.

Table 1

Differential-conductometric quantities Y for some aprotic solvents in the ethanolic solutions of lithium chloride (25°C).

C_{LiCl} (mole/l)	$\varkappa \cdot 10^2$ ($\Omega^{-1}cm^{-1}$)	Y		
		Dimethyl formamide	Acetonitrile	Dioxane
0.025	0.053	-0.116	-0.111	-0.037
0.087	0.131	-0.282	-0.264	+0.007
0.107	0.154	-0.278	-0.288	0.034
0.146	0.182	-0.402	-0.370	0.037
0.283	0.279	-0.532	-0.512	0.064
0.529	0.390	-0.695	-0.651	0.085
0.717	0.441	-0.747	-0.791	0.119
V_B		-162.1± 9.4	-166.2± 6.9	34.9± 4.0

Table 2

Differential-conductometric quantities Y for the dimethyl sulfoxide in the ethanolic solutions of lithium chloride (25°C).

C_{LiCl} (mole/l)	$\varkappa \cdot 10^2$ ($\Omega^{-1}cm^{-1}$)	Y	C_{LiCl} (mole/l)	$\varkappa \cdot 10^2$ ($\Omega^{-1}cm^{-1}$)	Y
0.0146	0.035	-0.069	0.551	0.397	-0.564
0.0985	0.141	-0.272	0.706	0.437	-0.600
0.133	0.170	-0.316	0.710	0.433	-0.598
0.180	0.212	-0.401	1.127	0.493	-0.482
0.267	0.268	-0.464	1.281	0.501	-0.462
0.340	0.311	-0.529	1.315	0.503	-0.442
			V_B *		-0.190

(* From the initial slope of the Y - $\varkappa$ dependence.

In earlier works simple linear relationships between V_s and intrinsic volume of the molecule(*) were obtained for hydroxylic compounds in hydroxylic solvents (water, ethanol). However, it was noted that in aqueous solutions some compounds - presumably cyclic or aprotic organic substances are characterized by the V_s- values lesser than of the alicyclic hydroxylic compounds of the same intrinsic volume. The same is true for the ethanolic solutions of cyclic (dioxane) or aprotic compounds (dimethyl formamide, acetonitrile, dimethyl sulfoxide). It is interesting that the deviation of the dioxane point from the linear relationship between V_s and intrinsic volumes of molecules defined for the hydroxylic compounds are practically equal in case of aqueous and ethanolic solutions ($\triangle V_s \cong 75 cm^3$/mole) (See Fig.3). The aprotic organic compounds have approximately equal V_s-value in ethanol independently of their intrinsic volume. ($V_s \cong -160 - 190 cm^3$/mole). The negative value of V_s corresponds to the structure-breaking effect of these compounds on the ethanol. Only dioxane has a relatively small structure-making effect ($V_s = +35$). The V_s-value of dimethyl sulfoxide decreases in the more concentrated electrolyte solutions.

This decrease is almost linear from the molar concentration of the electrolyte in solution. (See Fig. 4.) Therefore the relationship (Eq.(3)) can be rewritten as

$$Y = V_s^o (1 + \alpha c) \qquad (4)$$

in case of dimethyl sulfoxide (V_s^o is the restructurization volume at zero electrolyte concentration). The parameter

$$\alpha = -86.1 \pm 2.7 \qquad (5)$$

in Eq. (4)

This exceptional behavior of dimethyl sulfoxide indicates that there is some different mechanism of its influ-

(*) calculated as the sum of corresponding bond refractions in the molecule $(\sum R_D)^5$.

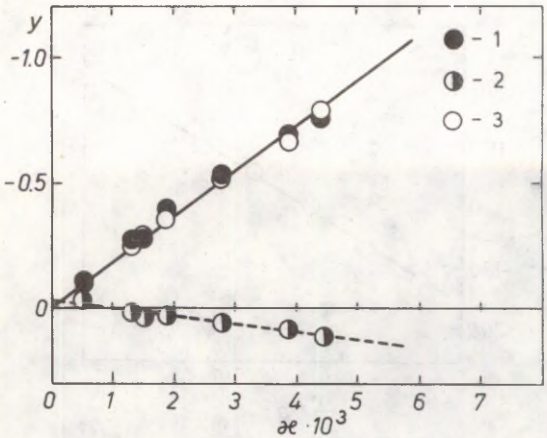


Fig. 1. The linear relationship between the differential - conductometric quantities Y and the specific conductivity $\varkappa(\Omega^{-1}cm^{-1})$ of the pure lithium chloride ethanolic solution. Notations: 1 - dimethyl formamide, 2 - acetonitrile, 3 - dioxane.

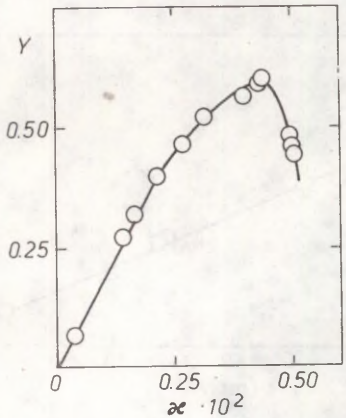


Fig. 2. The dependence of the differential-conductometric quantities Y of dimethyl sulfoxide on the specific conductivity $\varkappa(\Omega^{-1}cm^{-1})$ of the pure lithium chloride ethanolic solution.

II

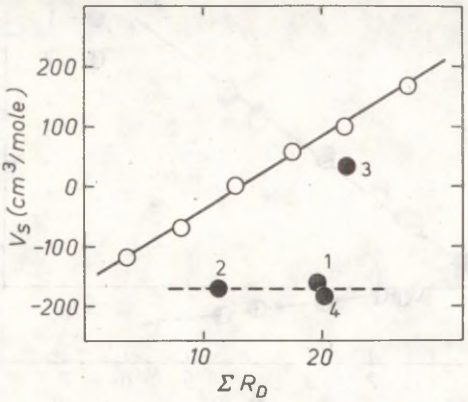


Fig. 3. The dependence of V_s-parameters on the intrinsic volumes of addition molecules in the ethanolic solutions. (⊙-hydroxylic compounds, 1-dimethyl formamide, 2-acetonitrile, 3-dioxane, 4-dimethyl sulfoxide).

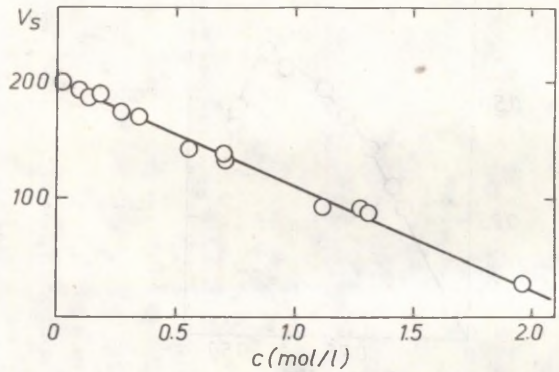


Fig. 4. The dependence of V_s-parameter of dimethyl sulfoxide on the molar concentration of lithium chloride in ethanol.

ence on the structure of ethanol in comparison with other substances. Analogous cases with other compounds are needed for the further investigation of such effects.

References.

1. M.M. Karelson and H. Kuura, This journal, 20,No 3(71), 397 (1983)
2. M.M. Karelson, This journal, 13,No 4(48), 530 (1976)
3. M.M. Karelson, This journal, 14, No 1 (49),74 (1977)
4. Ü. Haldna and V.A. Palm, Dokl. Akad. Nauk. USSR, 135, 667 (1960)
5. Handbook of Chemistry, Part I (in Russian), Moscow-Leningrad, GCHI, 1962

Organic Reactivity
Vol.21. 3(75) 1984

A STRUCTURAL THEORY OF THE ELECTROLYTE SOLUTIONS. II. ACTIVITY COEFFICIENTS OF 1:? ELECTROLYTES IN AQUEOUS SOLUTIONS.

M.M. Karelson and T. Sepp.
Laboratory of Chemical Kinetics and Catalysis, Tartu State University, 202400 Tartu, Estonian S.S.R., U.S.S.R .

Received November 29, 1984

A systematic treatment of the activity coefficients of 1:1 electrolytes in aqueous solutions is proceeded according to the simple lattice theory of electrolyte solutions[1].The statistical parameters of this treatment are favorably compared with the results obtained by the use of extended Debye-Hückel equations.

A preliminary discussion of the ion-solvent interaction parameter B_i structural dependence is also presented. The simple LFER-type dependences are found for the 1:1 electrolyte series with common cation.

The validity of the simple structural theory of the electrolyte solutions was discussed in the previous article [1]. Proceeding from the lattice model of the solutions, a theoretical description of the partial excess molar free energy and therefore, activity coefficients of solutions were finally obtained. The internal structure of the theory predicts no serious limits to the nature of the solution and experimental conditions (temperature, concentration, pressure), at what it is valid in principle. However, the experimental verification of the theory on the basis of the actual experimental data is of paramount importance.

Therefore the present article is the first in the series,

where the data about different properties of electrolyte solutions in the whole range of variability is statistically treated according to the basic equations of the structural electrolyte theory. For the activity coefficients of 1:1-electrolytes the following equation is valid[1]:

$$\ln \gamma_{\pm} = a_t \sqrt[3]{c} + B_i c, \qquad (1)$$

where c is the molar concentration.

The parameter

$$a_t = \frac{\alpha A_M}{\varepsilon RT} \qquad (2)$$

(where A_M is the Madelung constant for the given lattice type in solution, α - energy standardization constant, ε - dielectric permittivity of the solvent, R - universal gas constant and T - absolute temperature), represents the universal multiplier in the theoretical electrostatic interaction term.

The parameter

$$B_i = 2RTV_{s(i)} \qquad (3)$$

characterizes the specific interaction between electrolyte and solvent through the $V_{s(i)}$- constant, which is the volume in solution, where the solvent structure is totally perturbed by the solute (electrolyte ions).

The least-squares treatment of the activity coefficient logarithms was made in two ways.

First, the two parameter equation (1) was used in form

$$\ln \gamma_{\pm} = \Delta \ln \gamma_{\pm} + a_t \sqrt[3]{c} + B_i c, \qquad (4)$$

where a_t and B_i were the parameters to be found. It is essential to use the intercept $\Delta \ln \gamma_{\pm}$. This is only natural, because almost all the published activity coefficients are standardized against the infinite dilution according to some function from square-root of electrolyte concentration on ionic force. Therefore, the expected zero value ($\ln \gamma_{\pm} = 1$), corresponding to Eq. (4) is shifted by a small quantity

Table 1

The Results of the Least-Squares Treatment of the Activity Coefficients of Uni-univalent Electrolyte Aqueous Solutions at 25°C According to Eq. (4)

No	Electrolyte	$\Delta \ln \gamma_{\pm}$	a_t	B_1	r^a	s^b	s^c_o	Reference
1.	LiCl	0.127± 0.026	-0.818± 0.037	0.446± 0.009	0.999	0.0161	0.0096	2.
2.	LiCl	0.062± 0.011	-0.756± 0.020	0.439± 0.007	0.999	0.0095	0.0103	3.
3.	LiCl	0.031± 0.010	-0.654± 0.017	0.392± 0.006	0.999	0.0041	0.0057	4.
4.	LiCl	0.059± 0.017	-0.547± 0.047	0.328± 0.027	0.995	0.1210	0.0245	5.
5.	LiBr	0.199± 0.036	-0.957± 0.051	0.569± 0.012	0.999	0.0221	0.0100	2.
6.	LiBr	0.055± 0.012	-0.712± 0.021	0.477± 0.007	0.999	0.0051	0.0071	6.
7.	LiBr	0.165± 0.064	-0.883± 0.093	0.524± 0.025	0.999	0.0200	0.0194	5.
8.	LiBr	0.032± 0.017	-0.722± 0.031	0.529± 0.020	0.999	0.0251	0.0083	7.
9.	LiI	0.062± 0.031	-0.655± 0.051	0.558± 0.018	0.999	0.0132	0.0132	2.
10.	LiI	0.068± 0.038	-0.691± 0.054	0.570± 0.019	0.999	0.0127	0.0133	4.
11.	$LiNO_3$	0.115± 0.021	-0.803± 0.028	0.436± 0.006	0.999	0.0143	0.0062	8.
12.	$LiNO_3$	-0.069± 0.015	-0.453± 0.022	0.244± 0.005	0.999	0.0098	0.0100	2.
13.	$LiNO_3$	0.028± 0.008	-0.656± 0.014	0.390± 0.002	0.999	0.0036	0.0059	9.
14.	$LiNO_3$	0.067± 0.026	-0.708± 0.033	0.411± 0.007	0.999	0.0047	0.0055	10.
15.	$LiClO_4$	0.161± 0.039	-0.878± 0.063	0.693± 0.020	0.999	0.0184	0.0125	2.
16.	LiOH	-0.013± 0.013	-0.718± 0.019	0.096± 0.005	0.998	0.0075	0.0144	2.

Table 1 continued

1	2	3	4	5	6	7	8	9
17.	LiOH	$0.022^{\pm}_{0.010}$	$-0.714^{\pm}_{0.018}$	$0.097^{\pm}_{0.006}$	0.999	0.0086	0.0127	11
18.	LiOH	$-0.032^{\pm}_{0.013}$	$-0.530^{\pm}_{0.021}$	$0.191^{\pm}_{0.006}$	0.997	0.0066	0.0239	9.
19.	$LiCH_3COO$	$0.054^{\pm}_{0.010}$	$-0.742^{\pm}_{0.012}$	$0.105^{\pm}_{0.002}$	0.999	0.0021	0.0097	10.
20.	NaF	$0.041^{\pm}_{0.005}$	$-0.688^{\pm}_{0.011}$	$0.093^{\pm}_{0.006}$	0.999	0.0010	0.0041	12.
21.	NaCl	$0.071^{\pm}_{0.012}$	$-0.720^{\pm}_{0.017}$	$0.247^{\pm}_{0.004}$	0.999	0.0073	0.0122	2.
22.	NaCl	$0.036^{\pm}_{0.003}$	$-0.663^{\pm}_{0.006}$	$0.229^{\pm}_{0.002}$	0.999	0.0022	0.0082	3.
23.	NaCl	$0.035^{\pm}_{0.005}$	$-0.661^{\pm}_{0.008}$	$0.229^{\pm}_{0.003}$	0.999	0.0023	0.0093	4.
24.	NaCl	$0.044^{\pm}_{0.005}$	$-0.691^{\pm}_{0.009}$	$0.240^{\pm}_{0.003}$	0.999	0.0032	0.0115	13.
25.	NaCl	$0.037^{\pm}_{0.001}$	$-0.655^{\pm}_{0.007}$	$0.198^{\pm}_{0.020}$	0.999	0.0005	0.0027	14.
26.	NaCl	$0.046^{\pm}_{0.007}$	$-0.679^{\pm}_{0.011}$	$0.236^{\pm}_{0.003}$	0.999	0.0035	0.0125	15.
27.	NaCl	$0.043^{\pm}_{0.007}$	$-0.682^{\pm}_{0.012}$	$0.237^{\pm}_{0.003}$	0.999	0.0034	0.0129	16.
28.	NaCl	$0.027^{\pm}_{0.003}$	$-0.607^{\pm}_{0.016}$	$0.207^{\pm}_{0.058}$	0.999	0.0016	0.0084	17.
29.	NaBr	$0.073^{\pm}_{0.012}$	$-0.735^{\pm}_{0.018}$	$0.313^{\pm}_{0.005}$	0.999	0.0076	0.0081	2.
30.	NaBr	$0.038^{\pm}_{0.007}$	$-0.688^{\pm}_{0.011}$	$0.290^{\pm}_{0.003}$	0.999	0.0034	0.0074	6.
31.	NaBr	$0.047^{\pm}_{0.007}$	$-0.692^{\pm}_{0.013}$	$0.300^{\pm}_{0.004}$	0.999	0.0046	0.0105	3.
32.	NaBr	$0.023^{\pm}_{0.021}$	$-0.595^{\pm}_{0.041}$	$0.244^{\pm}_{0.015}$	0.987	0.0156	0.065	18.
33.	NaBr	$0.050^{\pm}_{0.005}$	$-0.692^{\pm}_{0.008}$	$0.300^{\pm}_{0.002}$	0.999	0.0035	0.0052	19.
34.	NaBr	$0.046^{\pm}_{0.008}$	$-0.683^{\pm}_{0.013}$	$0.297^{\pm}_{0.004}$	0.999	0.0038	0.0081	20.
35.	NaI	$0.122^{\pm}_{0.026}$	$-0.816^{\pm}_{0.037}$	$0.430^{\pm}_{0.009}$	0.999	0.0154	0.0106	2.
36.	NaI	$0.040^{\pm}_{0.016}$	$-0.670^{\pm}_{0.026}$	$0.376^{\pm}_{0.008}$	0.999	0.0069	0.0117	6.

Table 1 continued

1	2	3	4	5	6	7	8	9
37.	$NaNO_3$	$0.013^{\pm}_{0.005}$	$-0.647^{\pm}_{0.007}$	$0.044^{\pm}_{0.002}$	0.999	0.0031	0.0040	9.
38.	$NaNO_3$	$0.070^{\pm}_{0.015}$	$-0.759^{\pm}_{0.021}$	$0.129^{\pm}_{0.006}$	0.998	0.0083	0.0085	10.
39.	$NaNO_3$	$0.025^{\pm}_{0.004}$	$-0.656^{\pm}_{0.005}$	$0.045^{\pm}_{0.001}$	0.999	0.0024	0.0033	2.
40.	NaSCN	$-0.017^{\pm}_{0.008}$	$-0.528^{\pm}_{0.011}$	$0.223^{\pm}_{0.003}$	0.999	0.0048	0.0068	2.
41.	NaSCN	$-0.011^{\pm}_{0.006}$	$-0.544^{\pm}_{0.009}$	$0.247^{\pm}_{0.003}$	0.999	0.0027	0.0066	21.
42.	NaOH	$0.058^{\pm}_{0.023}$	$-0.713^{\pm}_{0.033}$	$0.258^{\pm}_{0.008}$	0.997	0.0150	0.0199	2.
43.	NaOH	$0.041^{\pm}_{0.013}$	$-0.668^{\pm}_{0.026}$	$0.259^{\pm}_{0.011}$	0.994	0.0105	0.0390	22.
44.	$NaCH_3COO$	$0.081^{\pm}_{0.024}$	$-0.766^{\pm}_{0.041}$	$0.237^{\pm}_{0.006}$	0.999	0.0059	0.0144	9.
45.	KF	$-0.095^{\pm}_{0.150}$	$-0.457^{\pm}_{0.211}$	$0.158^{\pm}_{0.048}$	0.793	0.0967	0.1690	2.
46.	KF	$0.040^{\pm}_{0.005}$	$-0.682^{\pm}_{0.007}$	$0.219^{\pm}_{0.002}$	0.999	0.0022	0.0088	12.
47.	KCl	$0.050^{\pm}_{0.005}$	$-0.693^{\pm}_{0.008}$	$0.168^{\pm}_{0.002}$	0.999	0.0024	0.0094	2.
48.	KCl	$0.012^{\pm}_{0.014}$	$-0.536^{\pm}_{0.037}$	$0.133^{\pm}_{0.010}$	0.986	0.0193	0.0461	23.
49.	KCl	$0.039^{\pm}_{0.001}$	$-0.672^{\pm}_{0.003}$	$0.164^{\pm}_{0.001}$	0.999	0.0016	0.0034	24.
50.	KCl	$0.035^{\pm}_{0.003}$	$-0.672^{\pm}_{0.005}$	$0.166^{\pm}_{0.001}$	0.999	0.0014	0.0061	25.
51.	KCl	$0.031^{\pm}_{0.002}$	$-0.662^{\pm}_{0.003}$	$0.161^{\pm}_{0.001}$	0.999	0.0009	0.0040	26.
52.	KCl	$0.029^{\pm}_{0.003}$	$-0.658^{\pm}_{0.004}$	$0.161^{\pm}_{0.001}$	0.999	0.0012	0.0053	27.
53.	KCl	$0.026^{\pm}_{0.012}$	$-0.679^{\pm}_{0.017}$	$0.163^{\pm}_{0.004}$	0.998	0.0041	0.0247	5.
54.	KCl	$0.027^{\pm}_{0.003}$	$-0.608^{\pm}_{0.003}$	$0.051^{\pm}_{0.059}$	0.999	0.0017	0.0082	17.
55.	KBr	$0.033^{\pm}_{0.002}$	$-0.662^{\pm}_{0.003}$	$0.187^{\pm}_{0.001}$	0.999	0.0010	0.0038	2.
56.	KBr	$0.030^{\pm}_{0.003}$	$-0.659^{\pm}_{0.005}$	$0.190^{\pm}_{0.002}$	0.999	0.0016	0.0080	20.

Table 1 continued

1	2	3	4	5	6	7	8	9
57.	KBr	0.030± 0.004	-0.661± 0.007	0.184± 0.002	0.999	0.0022	0.0098	6.
58.	KBr	0.037± 0.005	-0.684± 0.009	0.195± 0.003	0.999	0.0033	0.0128	3.
59.	KBr	0.042± 0.009	-0.688± 0.018	0.204± 0.008	0.999	0.0046	0.0195	18.
60.	KI	0.036± 0.005	-0.653± 0.007	0.238± 0.007	0.999	0.0028	0.0050	2.
61.	KI	0.017± 0.004	-0.629± 0.007	0.230± 0.002	0.999	0.0022	0.0067	6.
62.	KI	0.181± 0.025	-1.086± 0.037	0.296± 0.009	0.994	0.0140	0.0308	5.
63.	KNO_3	0.099± 0.003	-0.848± 0.005	-0.049± 0.002	0.999	0.0013	0.0013	2.
64.	KNO_3	0.083± 0.013	-0.836± 0.022	-0.032± 0.008	0.999	0.0050	0.0059	9.
65.	KSCN	-0.005± 0.006	-0.591± 0.009	0.113± 0.002	0.998	0.0038	0.0127	2.
66.	KSCN	0.052± 0.007	-0.705± 0.011	0.166± 0.003	0.999	0.0039	0.0160	21.
67.	KOH	0.038± 0.008	-0.700± 0.011	0.370± 0.011	0.999	0.0051	0.0036	2.
68.	KOH	0.053± 0.008	-0.674± 0.013	0.359± 0.004	0.999	0.0042	0.0053	28.
69.	KOH	0.190± 0.034	-0.854± 0.038	0.393± 0.006	0.999	0.0099	0.0059	10.
70.	KCH_3COO	0.124± 0.028	-0.848± 0.048	0.588± 0.016	0.999	0.0116	0.0127	9.
71.	RbF	-0.060± 0.010	-0.465± 0.017	0.0176± 0.006	0.995	0.0046	0.0308	2.
72.	RbF	-0.046± 0.037	-0.514± 0.060	0.193± 0.008	0.981	0.0153	0.0793	29.
73.	RbCl	0.050± 0.002	-0.719± 0.002	0.167± 0.001	0.999	0.0010	0.0031	2.
74.	RbCl	0.033± 0.005	-0.694± 0.007	0.141± 0.002	0.999	0.0026	0.0084	30.
75.	RbCl	0.041± 0.011	-0.710± 0.007	0.169± 0.004	0.997	0.0060	0.0226	6.
76.	RbCl	0.039± 0.005	-0.700± 0.007	0.163± 0.002	0.999	0.0026	0.0096	4.
77.	RbBr	0.054± 0.002	-0.727± 0.004	0.170± 0.001	0.999	0.0014	0.0048	2.

Table 1 continued

1	2	3	4	5	6	7	8	9
78.	RbBr	0.050± 0.004	-0.725± 0.005	0.170± 0.001	0.999	0.0019	0.0070	30.
79.	RbI	0.083± 0.006	-0.792± 0.009	0.204± 0.003	0.999	0.0034	0.0116	2.
80.	RbI	0.079± 0.006	-0.794± 0.009	0.210± 0.002	0.999	0.0032	0.0113	6.
81.	RbI	0.072± 0.021	-0.774± 0.032	0.210± 0.009	0.999	0.0113	0.0405	30.
82.	$RbNO_3$	0.130± 0.008	-0.921± 0.012	-0.031± 0.004	0.999	0.0039	0.0032	2.
83.	$RbNO_3$	0.098± 0.006	-0.874± 0.011	-0.050± 0.004	0.999	0.0023	0.0027	30.
84.	$RbCH_3COO$	0.049± 0.012	-0.680± 0.021	0.486± 0.007	0.999	0.0052	0.0061	30.
85.	CsF	-0.009± 0.034	-0.593± 0.057	0.292± 0.018	0.996	0.0150	0.0372	29.
86.	CsF	-0.036± 0.009	-0.584± 0.014	0.281± 0.005	0.999	0.0038	0.0129	2.
87.	CsCl	0.112± 0.003	-0.866± 0.004	0.187± 0.001	0.999	0.0019	0.0050	2.
88.	CsCl	0.100± 0.003	-0.858± 0.004	0.186± 0.001	0.999	0.0015	0.0041	4.
89.	CsCl	0.076± 0.008	-0.824± 0.014	0.169± 0.005	0.999	0.0043	0.0096	31.
90.	CsCl	0.080± 0.002	-0.830± 0.003	0.171± 0.001	0.999	0.0009	0.0021	32.
91.	CsBr	0.120± 0.006	-0.883± 0.009	0.195± 0.002	0.999	0.0031	0.0086	2.
92.	CsBr	0.129± 0.011	-0.912± 0.017	0.205± 0.004	0.999	0.0060	0.0166	6.
93.	CsBr	0.123± 0.007	-0.901± 0.011	0.202± 0.003	0.999	0.0038	0.0106	30.

Table 1 continued

1	2	3	4	5	6	7	8	9
94.	CsI	0.090± 0.004	-0.824± 0.00	0.170± 0.002	0.999	0.0015	0.0042	2.
95.	CsI	0.081± 0.023	-0.796± 0.040	0.144± 0.014	0.999	0.0093	0.0199	6.
96.	CsI	0.083± 0.003	-0.820± 0.00	0.169± 0.00	0.999	0.0010	0.0029	30.
97.	$CsNO_3$	0.114± 0.007	-0.891± 0.014	-0.058± 0.008	0.999	0.0017	0.0031	2.
98.	$CsNO_3$	0.106± 0.008	-0.895± 0.017	-0.024± 0.008	0.999	0.0021	0.0041	30.
99.	CsOH	0.062± 0.005	-0.672± 0.011	0.400± 0.006	0.999	0.0013	0.0137	2.
100.	CsOH	0.065± 0.008	-0.721± 0.023	0.437± 0.016	0.998	0.0060	0.0303	31.
101	$CsCH_3COO$	0.106± 0.030	-0.807± 0.050	0.612± 0.018	0.999	0.0123	0.0117	30.

[a] The correlation coefficient

[b] The standard deviation

[c] The normalized standard deviation (See [1]).

($\sim$0.1 units, see Table 1).

The statistical fitness parameters were good for practically every individual electrolyte activity coefficients set (the standard deviation $s < 0.005$ kJ/mol, normalized st. error[1] $s_Q < 0.01$, the correlation coefficient $r > 0.999$), see Table 1.

In some cases (LiBr, $LiNO_3$, or KI, e.g.) a perceptible difference in data sets obtained by different authors or using different experimental methods is noticed.

The a_t-parameter is close to the theoretical value corresponding to the sodium chloride type cubic lattice (A_M=1.748, and a_t = 0.6594 in aqueous solutions at 25°C).

That is why we proceeded the secondary statistical analysis of the activity coefficients according to the equation

$$\delta \ln \gamma_{\pm} = \Delta \ln \gamma_{\pm} + B_1 c \,, \tag{5}$$

where the function is

$$\delta \ln \gamma_{\pm} = \ln \gamma_{\pm} - a_t \sqrt[3]{c}, \tag{6}$$

i.e. the activity coefficients logarithm is corrected by the theoretical electrostatic term. Due to the already mentioned reason (different standardization) the intercept $\Delta \ln \gamma_{\pm}$ is used again. The results of this treatment are given in Table 2. Eq. (5) represents a simple linear relationship, whose validity for some electrolytes is also illustrated in Fig.1. The existence of such relationships was already observed by some earlier authors[32,33], who were using several semiempirical lattice models of electrolyte solutions. Therefore we once more have to underline the definite physical meaning of the B_1- parameter in the present theory.

Obviously the contraction of the number of parameters to be found in treatment does not influence noticeably the characteristics of the statistical fit (cf. Table 1. and 2.) Moreover, the improvement of them can be observed incidentally. Recalling the difference in the different data sets a conclusion, about the fit of the theory almost in the limits of

Table 2

The Results of the Least-Squares Treatment of the Activity Coefficients of Uni-univalent Electrolyte Aqueous Solutions at 25°C According to Eq. (5).

No	Electrolyte	$\Delta \ln \gamma_{\pm}$	B_i	r[a]	s[b]	s_o[c]	References
1	2	3	4	5	6	7	8
1.	LiCl	0.023 ± 0.009	0.411 ± 0.004	0.999	0.0236	0.0090	2.
2.	LiCl	0.017 ± 0.007	0.409 ± 0.004	0.999	0.0165	0.0090	3.
3.	LiCl	0.038 ± 0.002	0.396 ± 0.001	0.999	0.0040	0.0035	4.
4.	LiCl	0.048 ± 0.060	0.437 ± 0.012	0.994	0.1682	0.0261	5.
5.	LiBr	-0.005 ± 0.015	0.500 ± 0.007	0.998	0.0406	0.0130	2.
6.	LiBr	0.028 ± 0.003	0.462 ± 0.002	0.999	0.0062	0.0047	6.
7.	LiBr	0.019 ± 0.017	0.468 ± 0.008	0.999	0.0256	0.0159	5.
8.	LiBr	-0.022 ± 0.015	0.509 ± 0.006	0.999	0.0475	0.0114	7.
9.	LiI	0.068 ± 0.006	0.561 ± 0.004	0.999	0.0126	0.0078	2.
10.	LiI	0.053 ± 0.006	0.561 ± 0.004	0.999	0.0122	0.0084	4.
11.	$LiNO_3$	0.077 ± 0.010	0.291 ± 0.004	0.999	0.0272	0.0134	8.
12.	$LiNO_3$	0.016 ± 0.009	0.407 ± 0.003	0.999	0.0227	0.0067	2.
13.	$LiNO_3$	0.034 ± 0.002	0.392 ± 0.001	0.999	0.0034	0.0027	9.
14.	$LiNO_3$	0.034 ± 0.004	0.401 ± 0.002	0.999	0.0049	0.0037	10.
15.	$LiClO_4$	0.031 ± 0.011	0.628 ± 0.007	0.999	0.0252	0.0117	2.
16.	LiOH	-0.049 ± 0.004	0.083 ± 0.002	0.997	0.0093	0.0205	2.

Table 2 continued

1	2	3	4	5	6	7	8
17.	LiOH	-0.004 ± 0.004	0.081 ± 0.003	0.995	0.0105	0.0304	11.
18.	LiOH	-0.009 ± 0.004	0.090 ± 0.001	0.999	0.0054	0.0154	10.
19.	$LiCM_3COO$	0.004 ± 0.010	0.243 ± 0.003	0.999	0.0129	0.0121	9.
20.	NaF	0.030 ± 0.001	0.080 ± 0.002	0.999	0.0013	0.0220	12.
21.	NaCl	0.034 ± 0.003	0.235 ± 0.002	0.999	0.0095	0.0065	2.
22.	NaCl	0.037 ± 0.001	0.230 ± 0.001	0.999	0.0021	0.0022	3.
23.	NaCl	0.037 ± 0.001	0.230 ± 0.001	0.999	0.0022	0.0025	4.
24.	NaCl	0.030 ± 0.002	0.232 ± 0.001	0.999	0.0044	0.0045	13.
25.	NaCl	0.039 ± 0.001	0.230 ± 0.006	0.998	0.0005	0.0239	14.
26.	NaCl	0.037 ± 0.002	0.232 ± 0.001	0.999	0.0036	0.0037	15.
27.	NaCl	0.033 ± 0.002	0.233 ± 0.001	0.999	0.0036	0.0040	16.
28.	NaCl	0.036 ± 0.015	0.207 ± 0.034	0.939	0.0030	0.1544	17.
29.	NaBr	0.030 ± 0.004	0.296 ± 0.002	0.999	0.0108	0.0059	2.
30.	NaBr	0.036 ± 0.002	0.289 ± 0.001	0.999	0.0033	0.0027	6.
31.	NaBr	0.033 ± 0.003	0.292 ± 0.001	0.999	0.0054	0.0045	3.
32.	NaBr	0.056 ± 0.009	0.269 ± 0.005	0.999	0.0174	0.0182	18.
33.	NaBr	0.034 ± 0.002	0.293 ± 0.001	0.999	0.0035	0.0029	19.
34.	NaBr	0.036 ± 0.002	0.292 ± 0.002	0.999	0.0040	0.0033	20.
35.	NaI	0.020 ± 0.008	0.394 ± 0.004	0.999	0.0225	0.0095	2.

Table 2 continued

1	2	3	4	5	6	7	8
36.	NaI	0.037 ± 0.003	0.375 ± 0.002	0.999	0.0065	0.0051	6.
37.	$NaNO_3$	0.025 ± 0.001	0.048 ± 0.001	0.999	0.0029	0.0083	9.
38.	$NaNO_3$	0.009 ± 0.005	0.052 ± 0.006	0.998	0.0126	0.0193	10.
39.	$NaNO_3$	0.031 ± 0.001	0.047 ± 0.001	0.999	0.0026	0.0084	2.
40.	NaSCN	0.077 ± 0.006	0.254 ± 0.003	0.999	0.0167	0.0102	2.
41.	NaSCN	0.064 ± 0.006	0.282 ± 0.003	0.999	0.0118	0.0103	21.
42.	NaOH	0.039 ± 0.004	0.258 ± 0.003	0.999	0.0099	0.0124	2.
43.	NaOH	0.025 ± 0.006	0.248 ± 0.003	0.999	0.0156	0.0092	22.
44.	$NaCH_3COO$	0.023 ± 0.006	0.318 ± 0.005	0.999	0.0172	0.0148	9.
45.	KF	0.049 ± 0.035	0.204 ± 0.014	0.968	0.0966	0.0667	2.
46.	KF	0.029 ± 0.001	0.214 ± 0.001	0.999	0.0027	0.0029	12.
47.	KCl	0.033 ± 0.001	0.160 ± 0.001	0.999	0.0034	0.0055	2.
48.	KCl	0.048 ± 0.003	0.187 ± 0.004	0.998	0.0097	0.0192	23.
49.	KCl	0.036 ± 0.001	0.162 ± 0.002	0.999	0.0019	0.0026	24.
50.	KCl	0.031 ± 0.001	0.164 ± 0.001	0.999	0.0015	0.0022	25.
51.	KCl	0.033 ± 0.004	0.162 ± 0.001	0.999	0.0009	0.0014	26.
52.	KCl	0.034 ± 0.001	0.163 ± 0.001	0.999	0.0013	0.0020	27.
53.	KCl	0.017 ± 0.012	0.159 ± 0.001	0.999	0.0040	0.0056	5.
54.	KCl	0.036 ± 0.002	0.149 ± 0.034	0.890	0.0030	0.2040	17.

Table 2 continued

1	2	3	4	5	6	7	8
55.	KBr	0.035 ± 0.001	0.188 ± 0.001	0.999	0.0010	0.0011	2.
56.	KBr	0.034 ± 0.001	0.191 ± 0.001	0.999	0.0016	0.0021	20.
57.	KBr	0.033 ± 0.001	0.185 ± 0.001	0.999	0.0021	0.0024	6.
58.	KBr	0.027 ± 0.002	0.189 ± 0.001	0.999	0.0039	0.0051	3.
59.	KBr	0.031 ± 0.003	0.195 ± 0.002	0.999	0.0048	0.0111	18.
60.	KI	0.043 ± 0.001	0.241 ± 0.001	0.999	0.0030	0.0021	2.
61.	KI	0.040 ± 0.002	0.240 ± 0.001	0.999	0.0041	0.0038	6.
62.	KI	-0.081 ± 0.025	0.194 ± 0.008	0.989	0.0465	0.0412	5.
63.	KNO_3	-0.010 ± 0.007	-0.108 ± 0.005	0.989	0.0146	0.0443	2.
64.	KNO_3	-0.015 ± 0.013	-0.092 ± 0.006	0.982	0.0144	0.0661	9.
65.	KSCN	0.045 ± 0.003	0.130 ± 0.001	0.999	0.0093	0.0114	2.
66.	KSCN	0.038 ± 0.002	0.151 ± 0.001	0.999	0.0043	0.0053	21.
67.	KOH	0.022 ± 0.002	0.362 ± 0.001	0.999	0.0064	0.0027	2.
68.	KOH	0.014 ± 0.002	0.357 ± 0.001	0.999	0.0041	0.0025	28.
69.	KOH	0.018 ± 0.002	0.363 ± 0.003	0.999	0.0192	0.0081	10.
70.	KCH_3COO	0.018 ± 0.009	0.377 ± 0.006	0.999	0.0183	0.0119	9.
71.	RbF	0.060 ± 0.007	0.240 ± 0.005	0.997	0.0167	0.0226	2.
72.	RbF	0.046 ± 0.012	0.238 ± 0.006	0.998	0.0205	0.0259	29.
73.	RbCl	0.014 ± 0.002	0.154 ± 0.001	0.999	0.0062	0.0066	2.

Table 2 continued

1	2	3	4	5	6	7	8
74.	RbCl	$0.015^{\pm}_{0.002}$	$0.134^{\pm}_{0.001}$	0.999	0.0040	0.0052	30.
75.	RbCl	$0.012^{\pm}_{0.003}$	$0.157^{\pm}_{0.001}$	0.999	0.0074	0.0089	6.
76.	RbCl	$0.017^{\pm}_{0.002}$	$0.154^{\pm}_{0.001}$	0.999	0.0045	0.0059	4.
77.	RbBr	$0.013^{\pm}_{0.003}$	$0.155^{\pm}_{0.001}$	0.999	0.0065	0.0087	2.
78.	RbBr	$0.011^{\pm}_{0.003}$	$0.155^{\pm}_{0.001}$	0.999	0.0065	0.0079	30.
79.	RbI	$0.002^{\pm}_{0.005}$	$0.181^{\pm}_{0.003}$	0.998	0.0132	0.0155	2.
80.	RbI	$-0.004^{\pm}_{0.006}$	$0.177^{\pm}_{0.003}$	0.999	0.0136	0.0147	6.
81.	RbI	$0.003^{\pm}_{0.007}$	$0.182^{\pm}_{0.003}$	0.998	0.0155	0.0164	30.
82.	$RbNO_3$	$-0.031^{\pm}_{0.010}$	$-0.104^{\pm}_{0.006}$	0.989	0.0241	0.0575	2.
83.	$RbNO_3$	$-0.019^{\pm}_{0.009}$	$-0.126^{\pm}_{0.007}$	0.988	0.0166	0.0575	30.
84.	$RbCH_3COO$	$0.041^{\pm}_{0.003}$	$0.387^{\pm}_{0.004}$	0.999	0.0051	0.0034	30.
85.	CsF	$0.033^{\pm}_{0.009}$	$0.314^{\pm}_{0.005}$	0.999	0.0156	0.0150	29.
86.	CsF	$0.054^{\pm}_{0.006}$	$0.310^{\pm}_{0.004}$	0.999	0.0088	0.0095	2.
87.	CsCl	$-0.024^{\pm}_{0.008}$	$0.140^{\pm}_{0.004}$	0.995	0.0228	0.0265	2.
88.	CsCl	$-0.025^{\pm}_{0.009}$	$0.137^{\pm}_{0.004}$	0.996	0.0206	0.0273	4.
89.	CsCl	$-0.007^{\pm}_{0.009}$	$0.111^{\pm}_{0.006}$	0.998	0.0177	0.0549	31.

Table 2 continued

1	2	3	4	5	6	7	8
90.	CsCl	-0.006 ± 0.009	0.111 ± 0.006	0.988	0.0178	0.0551	32.
91.	CsBr	-0.022 ± 0.009	0.138 ± 0.005	0.992	0.0225	0.0335	2.
92.	CsBr	-0.029 ± 0.012	0.142 ± 0.005	0.993	0.0263	0.0345	6.
93.	CsBr	-0.028 ± 0.011	0.142 ± 0.005	0.994	0.0248	0.0326	30.
94.	CsI	-0.004 ± 0.006	0.117 ± 0.004	0.988	0.0103	0.0571	2.
95.	CsI	0.006 ± 0.007	0.069 ± 0.005	0.979	0.0137	0.0718	6.
96.	CsI	-0.006 ± 0.007	0.116 ± 0.005	0.994	0.0128	0.0404	30.
97.	$CsNO_3$	0.003 ± 0.007	-0.176 ± 0.010	0.988	0.0103	0.0571	2.
98.	$CsNO_3$	-0.008 ± 0.009	-0.177 ± 0.012	0.982	0.0133	0.0863	30.
99.	CsOH	0.047 ± 0.004	0.397 ± 0.001	0.999	0.0012	0.0031	2.
100.	CsOH	0.047 ± 0.004	0.399 ± 0.007	0.999	0.0081	0.0162	31.
101.	$CsCH_3COO$	0.025 ± 0.008	0.406 ± 0.004	0.999	0.0138	0.0097	30.

[a-c] See footnotes [a-c] in Table 1.

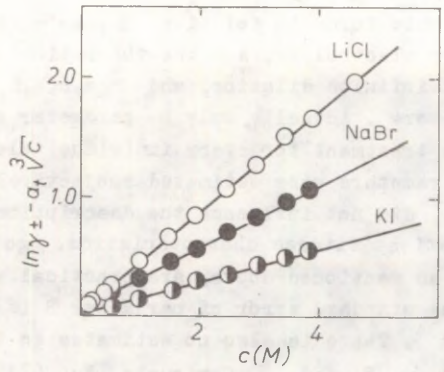


Fig. 1. The linear relationship between function $\delta \ln \gamma_{\pm}$ and molar concentration c for some electrolyte solutions.

experimental error, can be finally set.

However, the comparison with the results of the earlier activity coefficient statistical analyses, based on the use of Debye-Hückel electrostatic solution theory is of utmost interest. Underneath we present an analysis of some published statistical treatments on the basis of the extended Debye--Hückel equations. These treatments are characterized by standard deviations comparable to those obtained from the treatments according to Eq. (4) and (5) in this article. The concentration of electrolyte was varied in the wide range (up to saturated solutions, too.) Proceeding from Eq. (5), the lattice theory of electrolyte solutions has one empirically detected parameter for every electrolyte. In the compilation[34] the following equation was used for activity coefficient analysis:

$$\ln \gamma_{\pm} = \frac{-A/Z_+Z_-/\ I}{1 + \varrho\sqrt{I}} + \frac{(B_o - B)I}{(1+aI)^n} + BI, \qquad (7)$$

where I is the ionic force in solution, Z+, Z- - the ionic charges of binary electrolyte, A - the theoretical Debye--Hückel slope at infinite dilution, and ϱ, a, n, B, B_o - some empirical parameters . Actually, only B- parameter was found by least-squares treatment for every individual electrolyte. The remaining parameters were estimated subjectively, and the value of a, e.g., did not influence the description almost at all. The correlation fitness characteristics, got for Eq. (5) and Eq. (7) as mentioned above, are practically the same. Unfortunately the standard error of parameter B is not given in original work[34]. There is also no estimates to the errors of parameters a, n, B_o and . Obviously, Eq. (7) has less statistical degrees of freedom in comparison with the basic equation of the lattice theory (5). The background of the use of second term in Eq.(7) is vague, too. Therefore the conclusion about the preference of lattice theory over the extended semiempirical Debye-Hückel theory in form of Eq. (7) can be made.

We have to notice, that somewhat better overall characteristics of statistical treatment of activity coefficients were obtained by K.S. Pitzer et al.[35,36]. They used the following equation based on the Guggenheim-Scatchard theory which is also an extensions of the original Debye-Hückel model:

$$\ln \gamma_{\pm} = /Z_+Z_-/f^{elec}(I) + 2\left(\frac{\nu_+\nu_-}{\nu}\right)Bm + \left[(2\nu_+\nu_-)^{3/2}/\nu\right] Cm^2, \qquad (8)$$

where ν_+ and ν_- are the numbers of corresponding ions in electrolyte molecule, respectively, and $\nu = \nu_+ + \nu_-$. The molal concentration m is used in the given equation.

The function

$$f^{elec}(I) = -A\left[\frac{\sqrt{I}}{1 + b\sqrt{I}} + \frac{2}{b}\ln(1 + b\sqrt{I})\right] \qquad (9)$$

has the meaning of the electrostatic interaction energy between ions, and parameter

$$B = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2 I}\left[1-e^{-\alpha\sqrt{I}}\left(1+\alpha\sqrt{I}-\frac{\alpha^2 I}{2}\right)\right] \qquad (10)$$

is a complicated function of ionic force. Three parameters - C, $\beta^{(0)}$, and $\beta^{(1)}$ are found from the least-squares treatment. The quantities α and b have subjectively assumed values. Therefore much less degrees of freedom is present in the treatment by Eq. (8) compared to the lattice theory. the standard errors of parameters are also not given. This leaves opened the question about the reliability of multiparameter correlation parameters.

The underwater stones here can be nicely seen from the results, presented in the compilations[37,39]. The statistical treatment was again performed according to the semiempirical Debye-Hückel-type equations there:

$$\ln \gamma_{\pm} = -\frac{A\sqrt{I}}{1+B\sqrt{I}} + Cm + Dm^2 + Em^3 + \ldots \qquad (11)$$

$$\ln \gamma_{\pm} = -A\sqrt{I} + A_2 I \ln I + \sum_{i=1}^{N} B_i m^{(i+1)/2} \qquad (12)$$

$$\ln \gamma_{\pm} = -A\sqrt{I} + \sum_{i=1}^{N} B_i m^{(i+1)/2} \qquad (13),$$

where A_2, B_i, C, D, E are the empirical parameters. The number of them, to be found in least-squares procedure varied from 3 to 7. However, the standard errors of these parameters are frequently the orders of magnitude greater than the overall standard error of the correlation.This fact indicates that the so-called compensation or overpump effect between different correlation scales is present and there is an excess of empirical parameters. Thus the existence of correlations according to Eq-s (11-13) is only seeming. Fairly enough, the authors do not give any physical significance to separate terms in these expansions. However, the extrapolations of activity coefficient data starting from Eq.-s (11-13) may not be reliable enough for that reason.

Consequently, there is no statistically better description of the experimental activity coefficients of 1:1 electrolyte aqueous solutions on the whole range of concentration on the basis of the Debye-Hückel-type equations in comparison with the simple lattice theory.

For the theoretical extension of the latter the analysis of B_i-parameters (cf. Eq.(4,5)), obtained from the treatment of experimental data could be useful. The recommended values of these parameters are given in Table 3.

Table 3.

Mean values of the B_i-parameters of uni-univalent salts, obtained from the activity coefficients data.

Cation \ Anion	F^-	Cl^-	Br^-	I^-	OH^-	NO_3^-	CH_3COO
Li^+	–	0.403	0.477	0.561	0.086	0.401	0.243
Na^+	0.080	0.232	0.292	0.385	0.253	0.048	0.318
K^+	0.209	0.162	0.189	0.240	0.360	-0.100	0.377
Rb^+	0.239	0.149	0.155	0.180	-	-0.145	0.387
Cs^+	0.312	0.134	0.141	0.117	0.398	-0.176	0.406

One would like to find some regularity between the B_i-parameters and some other properties of electrolytes or their ionic constituents. The main structural characteristics, which according to the lattice theory can describe the influence on the solvent structure, is the size of electrolyte molecule, indeed. Rather badly, it is obvious that there is not any relationship between the B_i-s and the radius of 1:1 electrolyte molecules, calculated as the sum of corresponding crystallographic ionic radiuses (See Fig. 2.).

The well-known fact is, that the thermodynamic properties of ions in solutions (e.g. the free energies, enthalpies and entropies of hydratation, electrostatic free energies etc.) are simple regular functions of their crystallographic radiuses.[39] Therefore the expected linear free energy relationships between the B_i-parameter and ionic thermodynamic prop-

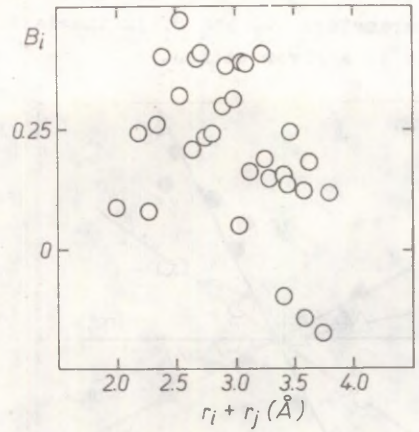


Fig. 2. Nonexistence of the relationship between B_i-parameters and the size of electrolyte molecules.

erties cannot to be observed, either.

However, it is interesting to mention the simple LFER - type relationships between the combinations of B_i- parameters belonging to the two electrolyte series having different common cation. Let's define the difference

$$\Delta B_{ij}\,(Cat_o) = B_{ij} - B_{oj}\,, \qquad (14)$$

where j is the anion index, i and o denote the cation in the given and standard series, respectively. The choice of the reference cation, whose salts form the standard series, is arbitrary indeed. Independently of this choice, the linear relationships are also observable between the quantities B_{ij} and the anion crystallographic radiuses r_j[41]. The examples of such linearities corresponding to the potassium and cesium salts as references, are given in Fig. 3. and Fig. 4.The linear regression parameters of these dependences:

$$\Delta B_{ij} = \alpha_i + \beta_i r_j \qquad (15)$$

for alkali salts (Cs is taken as a reference) are presented in Table 4. The parameters α_i and β_i in the last equation are characteristic to a given cation.

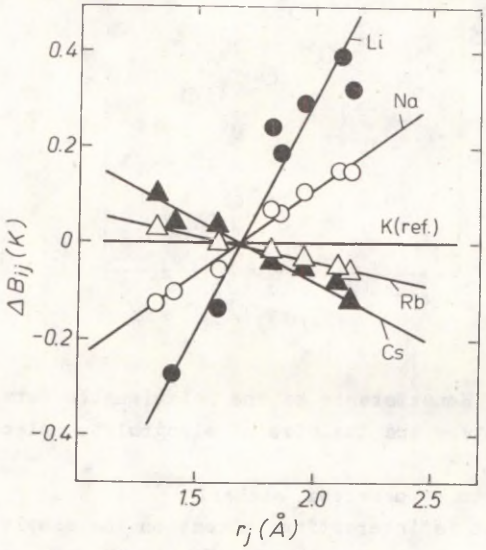


Fig. 3. The relationship between B_{ij} and the anionic crystallographic radiuses (K salts taken as the reference).

The graphs at Fig. 3 and 4. have a singular point at $r_j \approx$ $\approx$1.7 Å, where the straight lines describing the relationship (15) for salts with different alkali cations are crossing one another. This means that at this value of anion radius ΔB_{ij} value becomes insensitive to the size of cation. In the formal LFER theory such point is known as an isoparametric point.[40] It can be an important characteristic of the process or phenomenon the parameters of which have it.

First of all, its presence in case of relationships (15) indicates that B_i- parameters are describing a homogenous

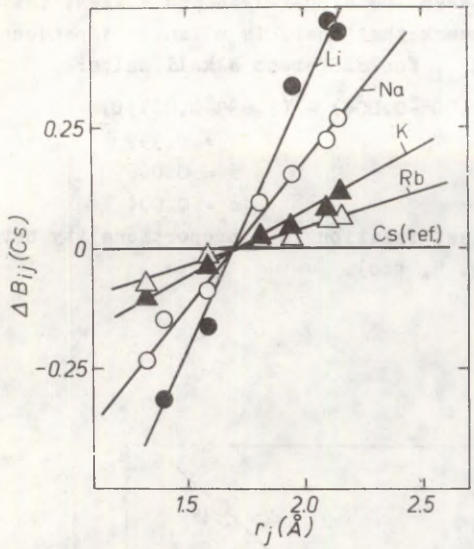


Fig. 4. The relationship between ΔB_{ij} and the anionic crystallographic radiuses (Cs salts taken as the reference).

Table 4

The Linear Regression Parameters of the Data Treatment According to Eq.(15) (Cs salts are the reference).

Cation	α_i	β_i	r[a]	e[b]	s_o[c]
Li	-1.870± 0.156	1.101± 0.084	0.991	0.055	0.075
Na	-0.993± 0.053	0.586± 0.030	0.994	0.024	0.051
K	-0.443± 0.035	0.255± 0.019	0.989	0.014	0.074
Rb	-0.281± 0.028	0.160± 0.015	0.983	0.011	0.092
Cs(ref.)	0	0	-	-	-

[a-c] See footnotes [a-c] in Table 1

interaction between the electrolyte and solvent (water). Formally it also means that there is a linear dependence between numbers α_i and β_i for different alkali salts:

$$\alpha_i = (-0.006 \pm 0.004) - (1.693 \pm 0.007)\beta_i \qquad (16)$$

$$r = 0.999$$

$$s = 0.006$$

$$s_o = 0.004$$

Obviously the last relation is a proportionality between α_i and β_i (See Fig. 5, too).

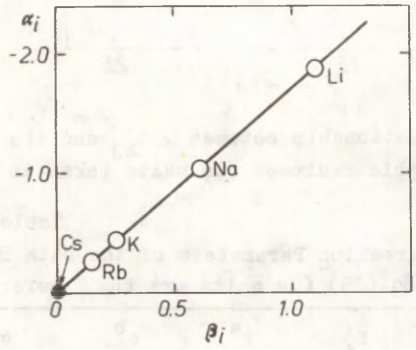


Fig. 5. The proportionality between the α_i and β_i parameters from Eq. (15) for different alkali salt sets. (Cs taken as the reference).

Consequently, quantities ΔB_{ij} are dependent on one cation parameter only (say, the β_i and Eq. (15) could be rewritten as follows:

$$\Delta B_{ij}(Cat_o) = \beta_i(r_j - 1.693) \qquad (17)$$

An important property of β_i - parameters is that they are

approximately linearly dependent on the corresponding cation crystallographic radiuses r_i (See Fig. 6) with the following linear regression parameters:

$$\beta_i = -(0.032 \pm 0.051) + (1.014 \pm 0.087)(1.65 - r_i) \quad (18)$$

$$r = 0.989$$

$$s = 0.074$$

$$s_o = 0.085$$

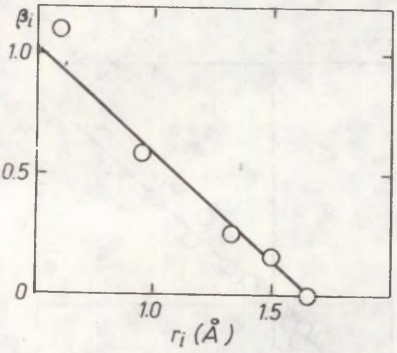


Fig. 6. The relationship between the β_i- parameters (Eq. 15) and the cation crystallographic radiuses r_i.

In a good approximation the last dependence (18) is again a proportionality. The slope of the last relationship, practically equal to unity, has no special physical meaning and depends on the scale of radiuses used. However, in case of present scale (Å), one can write for the ΔB_{ij} (Cs):

$$\Delta B_{ij}(Cs) = (1.65 - r_i)(r_j - 1.693) \quad (19)$$

on for general reference salts

$$\Delta B_{ij}(Cat_o) = (r_o - r_i)(r_j - 1.693), \quad (20)$$

where r_o is the crystallographic radius of the reference cation.

In the general case (scale of radiuses is not specified) the last equation is presented as follows

$$\Delta B_{ij}(Cat_o) = \alpha(r_o - r_i)(r_j - r_{oo}),$$

where α and r_{oo} are some universal constants depending on the choice of the scale or radiuses. There is a good correspondence between the calculated ΔB_{ij} values (from Eq.(19)) and their "experimental" values, obtained from the differences (Eq. 14). (See Fig. 7)

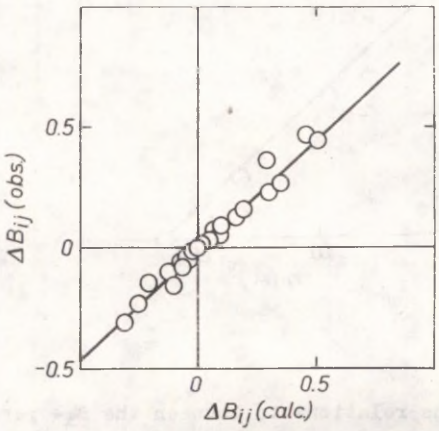


Fig. 7. The relationship between the calculated (Eq.19) and experimental (Eq. 14) values of $\Delta B_{ij}(Cs)$.

The mathematical form of the last two equations (19 and 20) indicates that the influence of ions on the structure of solvent presented by the ΔB_{ij} values is substantially antisymmetrical in case of anions and cations. It is easy to see that cation radius is taken with negative sign in these formula whereas the anion radius is always positive. But

from these data it is difficult to conclude anything about the connexion between this antisymmetry and structure-making and structure-breaking effect of solutes in solution. The Bi parameters of other electrolytes and other electrolyte solution properties in various solvents should be analyzed for this aim.

Keeping in mind the practical equality of constants 1.65 and 1.693 in Eq. (19), the latter can be rewritten as follows:

$$\Delta B_{ij} = A_o + A_1(r_i + r_j) - r_i r_j \qquad (21)$$

or as a linearship:

$$\Delta B_{ij} + r_i r_j = A_o + A_1 (r_i + r_j) \qquad (22)$$

where A_o and A_1 are some universal constants for uni-univalent electrolytes (presumably $A_o = A_1^2$). There is a splendid fit of the latter relationship (22), especially in comparison with the absence of any dependence of primary B_i- parameters from the electrolyte ion size (cf. Fig. 2 and Fig. 8). The linear regression parameters of this relationship are as

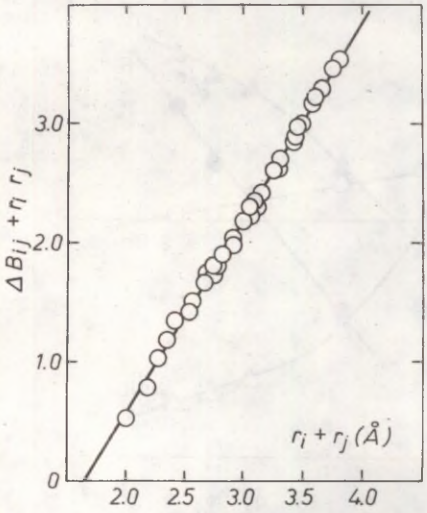


Fig. 8. The linear relationship (22) for uni-univalent electrolytes in water (25°C).

follows:

$$\Delta B_{ij} + r_i r_j = (-2.800 \pm 0.038) + (1.666 \pm 0.012)(r_i + r_j) \quad (23)$$

$$r = 0.999;\ s = 0.030;\ s_o = 0.007$$

By no means this is not the final equation for the calculation of B_i- parameters of 1:1 electrolyte aqueous solutions. The B_i- parameters can be found only by using the reference electrolyte B_i-values. The dependence of the latter on the structural characteristics of electrolytes is the subject of the further discussion which will be published separately. Again more data is needed for the final decisions.

However, it is interesting to notice that the anions have a unique isoparametric radius value (i.e. r_{ip}=1.693 Å), whereas for every electrolyte series with constant cation the isoparametric cation radius is naturally that of the reference cation. Consequently there is no unique isoparametric radius for cations. For that reason the ΔB_{ij} dependences on the cation radius r_i of the electrolyte series with common anion are more complex. (See Fig. 9).

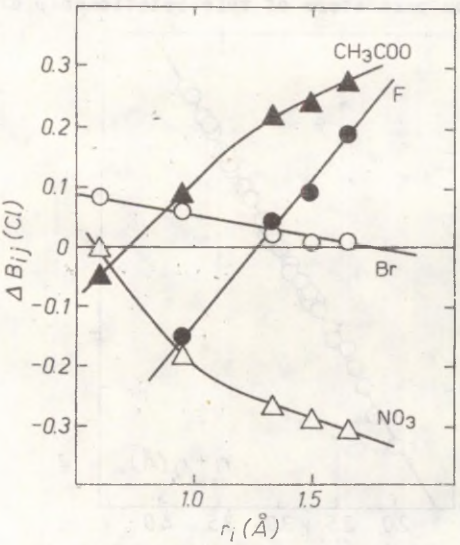


Fig. 9. The relationship between ΔB_{ij} and cation crystallographic radius r_i (Cl salts taken as a reference).

For monoatomic ions they seem to be approximately linear whereas for the polyatomic ions they have a significant curvature in the region of smaller cations. However the $\Delta B'_{ij}$ values for different polyatomic anions are linearly dependent. The physical meaning of such phenomena remains opened in the framework of the present discussion, too. There is no isoparametric point in these functions (See Fig. 9.).

The verification of the structural theory of electrolytes on the basis of more extended experimental data will be presented in the forthcoming communications of this series.

References.

1. M.M. Karelson, This journal, 21, 160(1984).
2. Handbook of Electrochemistry (in Russian), Ed. A.M. Sukhotin, Leningrad, 1981.
3. H.S. Harned, J. Amer. Chem. Soc., 51,(2), 416 (1929)
4. R.A. Robinson and D.A. Sinclair, J. Amer. Chem. Soc.,56. (9), 1830 (1934)
5. J.N. Pearce, J. Amer. Chem. Soc., 54,(9), 3544 (1932)
6. R.A. Robinson, J. Amer. Chem. Soc., 57,(7), 1161 (1935)
7. R.A. Robinson and H.J. McCoach,J.Amer.Chem.Soc.,69,(9), 2244 (1947)
8. R.A. Robinson, J. Amer. Chem. Soc., 68,(11), 2402 (1946)
9. R.A. Robinson, J. Amer. Chem. Soc., 57,(7), 1165 (1935)
10. W. Kangro and A. Groeneveld, Z. phys. Chem. NF, 32, 110 (1962)
11. H.S. Harned and F.E. Swindells, J. Amer. Chem. Soc., 48, (1), 126 (1926)
12. R.A. Robinson, J. Amer. Chem. Soc., 63, (2), 628 (1941)
13. H.S. Harned and L.F. Nims, J. Amer. Chem. Soc., 54,(2), 423 (1932)
14. A.S. Brown and D.A. MacInnes, J. Amer. Chem. Soc., 57. (7), 1356 (1935)
15. R.P.Smith and D.S. Hirtle, J. Amer.Chem. Soc.,61,No 8, 1123(1939)
16. R.A. Robinson and D.A. Sinclair, J. Amer. Chem. Soc.,56, (9), 1834 (1934)

17. T. Shedlovsky, J. Amer. Chem. Soc., 72, (8), 3680 (1950)
18. H.S. Harned and S.M. Douglas, J. Amer. Chem. Soc., 48, (12), 3095 (1926)
19. H.S. Harned and C.C. Crawford, J. Amer. Chem. Soc., 59, (10), 1903 (1937)
20. R.A. Robinson, Trans. Farad. Soc., 35,(2), 1217 (1939)
21. R.A. Robinson, J. Amer. Chem. Soc., 62, (11), 3131(1940)
22. H.S. Harned, Z. phys. Chem., 117,(1), 1 (1925)
23. T. Shedlovsky and D.A. MacInnes, J. Amer. Chem. Soc., 59,(3), 503 (1937)
24. T. Shedlovsky and D.A. MacInnes, J. Amer. Chem. Soc., 59, (3), 504 (1937)
25. V.K. LaMer and E. Noonan, J. Amer. Chem. Soc., 61, No 10, 1487 (1939).
26. H.S. Harned, J. Franklin, Inst. 225, 623 (1938).
27. R. Caramazza, Gazz. chim. Ital., 90, (12), 1721 (1960).
28. H.S. Harned and M.A. Cook, J. Amer. Chem. Soc., 59,(3), 496 (1937)
29. H. Ti Tien, J. Phys. Chem., 67, (2), 532 (1963)
30. R.A. Robinson, J. Amer. Chem. Soc., 59,(1), 84 (1937)
31. H.S. Harned and O.E. Schupp, Jr., J. Amer. Chem. Soc., 52, (10), 3886 (1930)
32. J.E. Desnoyers and B.E. Conway, J. Phys. Chem., 68,(8), 2305 (1964)
33. L. Bahe, J. Phys. Chem. ,76,(7), 1062 (1972)
34. L.A. Bromley, AIChE Journal, 19,(2), 313 (1973)
35. K.S. Pitzer, J. Phys. Chem., 77, (2), 268 (1973)
36. K.S. Pitzer, J. Phys. Chem., 77, (19), 2300 (1973)
37. B.R. Staples and R.L. Nuttall, J. Phys. Chem. Ref. Data, 6,(2), 385 (1977)
38. R.N. Goldberg,and R.L. Nuttall, J. Phys. Chem. Ref.Data, 7,(1), 263 (1978)
39. G.A. Krestov, Thermodynamics of Ionic Processes in Solutions, Leningrad, "Khimiya", 1973
40. V.A. Palm, Fundamentals of the Quantitative Theory of Organic Reactions, Leningrad, "Khimiya", 1977
41. Handbook of Chemistry, Part I (in Russian), M., GCHI, 1962.

C O N T E N T S

РЕАКЦИОННАЯ СПОСОБНОСТЬ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ.
Том. XXI. Вып. 3(75). Ноябрь 1984.
На английском языке.
Тартуский государственный университет.
ЭССР, 202400, г.Тарту, ул.Юликооли, 18.
Ответственный редактор В. Пальм.
Подписано к печати 29.12.1984.
Формат 60x84/16.
Бумага писчая.
Машинопись. Ротапринт.
Условно-печатных листов 6,74.
Учетно-издательских листов 5,64. Печатных листов 7,25.
Тираж 400.
Заказ № 1260.
Цена 85 коп.
Типография ТГУ, ЭССР, 202400, г.Тарту, ул.Пялсона, 14.