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CONTENTS

The Isoparametrical Effect and Multiple Cross-Correlations.

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A geometrical interpretation of the isoparametrical effect (IPE) in the case of the two-parameter cross-correlation is proposed. The effect is not observed for a multiple cross-correlation if its coefficients do not obey the PPL requiremets, i.e. when their values are mutually independent. For such a correlation IPE may be observed only in the case when all variables but two are fixed over experimental conditions.

A. The Isoparametrical Effect (IPE).

Assume that some quantitative characteristics, $f(x_1, x_2)$, of a system can be represented as follows:

$$f(x_1, x_2) = a_0 + a_1 x_1 + a_2 x_2 + a_{12} x_1 x_2 \qquad (1)$$

where x_1 and x_2 are variable parameters (factors) depending on intensity of relevant properties influencing the $f(x_1, x_2)$; a_0, a_1, a_2 and a_{12} are constants depending on accepted x_1 and x_2 scales. In the case of such a correlation the IPE has to be observed. The essence[1] of the effect is as follows:

I. For the variables in Eq.(1), the critical values (CV) $\hat{x}_1 = -a_{12}^{-1} a_2$ and $\hat{x}_2 = -a_{12}^{-1} a_1$, are possible; those are called[1]

the isoparametrical values (IPV's) and denoted as x_1 and x_2 respectively. When one of the variables in Eq.(1) becomes equal (occasionally) to its IPV, function $f(x_1, x_2)$ will be independent of the other variable and $f(\hat{x}_1, x_2) = f(x_1, \hat{x}_2) = a_0 - a_{12}^{-1}a_1a_2$.

II. There is a change of sign of the $f(x_1, x_2)$ dependence upon one of the variables when IPV for another is crossed over.

The inequality $a_{12} \neq 0$ is the formal condition for IPE observance.

It was shown[2-5] recently that IPE exists in effect. IPV's for a temperature[2] and substituent[4] variation were experimentally achieved. The trasitsion[5] through IPV for one of the Eq.(1) variables is really accompanied by a reversal of the function dependence on the other variable.

IPE has to be observed also (see Ref.1) for a multiple correlation if interactions between the properties described by correlational parameters are <u>homogeneous</u>, i.e. if a type (2) expansion[1, 6-8] ⍟) is applicable to any function

$$f(x_1,\ldots, x_i,\ldots, x_n) = a_0 - \alpha^{-1} + \alpha^{-1} \prod_1^n (1 + \measuredangle a_i x_i) \quad (2)$$

The $\measuredangle$ constant characterizes a particular type of interaction between $x_1,\ldots, x_i$ and x_n variables. The number of IPV's equals the number of variables of Eq.(2). The function f for any $x_i = \hat{x}_i = - \measuredangle^{-1}a_i^{-1}$ has to equal $\hat{f} = a_0 - \measuredangle^{-1}$ and be independent of $x_{j\neq i}$ for $1 \leqslant j \leqslant n$. Eq.(2) for $n > 2$, however, is not yet, realized⍟⍟) in practice.

<u>B. Geometrical Interpretation of IPE.</u>

Geometrically, Eq.(1) is a hyperbolic paraboloid (see Fig.1) surface (HPS). Turning and translation of coordinate axes re-

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⍟) Eq.(2) is one of possible representations of PPL (see Ref.1).

⍟⍟) A more complex example of the homogeneous polylinear expansion (for n = 2,3 and 4) was described earlier[9], but IPV is impossible in this case.
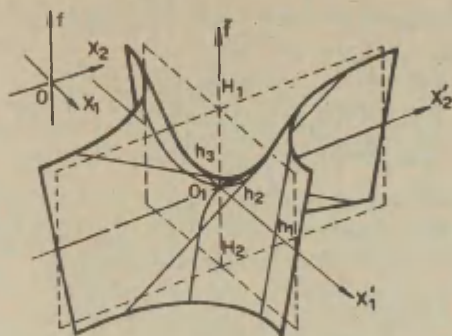
Fig 1. The hyperbolic paraboloid surface. Coordinate
system $x_2 O x_1 f$ corresponds to initial equation (1).
The surface is presented in coordinate system
$\bar{x}_1^1 O_1 \bar{x}_2^1 \bar{f}$. The latter is obtained from the cano-
nical one $\bar{x}_1^1 O_1 \bar{x}_2 \bar{f}$ with the help of turning of
$O_1 \bar{x}_1$ and $O_1 \bar{x}_2$ axis by $45°$ or with the help of
translation of $x_1 O x_2 f$ system to $O_1 (\hat{x}_1, \hat{x}_2, \hat{f})$
point. $x_1 = \{h_1 > h_2 > \bar{x}_1 > h_3\}$ are the surface
sections.
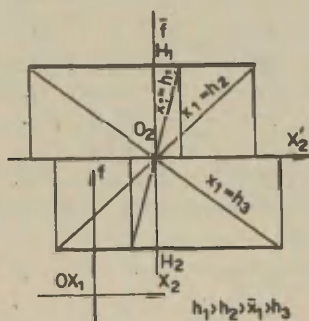
Fig. 2. The projections of HFS generating lines obtained
by $x_1 = \{h_1, h_2, h_3\}$ sections on $\bar{x}_2 O_1 f$ (or $x_2 Of$)
coordinate plane are the straight lines intersec-
ted at the point O_1. The signs and magnitudes of
the slopes for the generating lines depend on the
position of the section planes $x_1 = h$ relative to
the $x_1 = \bar{x}_1$ plane.

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duces Eq.(1) to a canonical form: $x_1^2/b^2 - x_2^2/b^2 = 2f$; $b^2 = |a_{12}^{-1}|$.

The relationship between the two coordinate systems is as follows:

$$\bar{f} = f - (a_0 - a_1 a_2 a_{12}^{-1})$$
$$\bar{x}_1 = 2^{-1/2}(x_1 + x_2) + 2^{-1/2}(a_1 + a_2) a_{12}^{-1}$$
$$\bar{x}_2 = 2^{-1/2}(x_2 - x_1) + 2^{-1/2}(a_1 - a_2) a_{12}^{-1}$$

HPS passes through the origin O_1 in the canonical system (see Fig.1). In the coordinate system of the Eq.(1) this point has as its coordinates the corresponding IPV's:

$$O_1 (\hat{x}_1, \hat{x}_2, \hat{f})$$

HPS is the linear surface[10, 11]. Its generating lines may be formed by the $x_1 = h$ and $x_2 = h$ sections which are parallel to the coordinate planes (two families of generating lines) $x_2 O\hat{f}$ (or $x_1 O\hat{f}$) and $x_1 Of$ (or $X_1^! O_1 \hat{f}$). The section of HPS by $f = \hat{f}$ plane dives two generating lines $O_1 X_2^!$ and $O_1 X_1^!$ (see Fig.1)

$$\begin{cases} f = \hat{f} \\ x_1 = \hat{x}_1, \ \| O x_2 \end{cases} \qquad \begin{cases} f = \hat{f} \\ x_2 = \hat{x}_2, \ \| O x_1 \end{cases}$$

which intersect at O_1 point (see Fig.1). These straight lines are translational from the hyperbolae obtained by the $f \hat{f}$ sections to those obtained by the $f < \hat{f}$ sections. For $f > \hat{f}$ the hyperbolae lie in I and III octants of $X_1^! O_1 X_2^! \hat{f}$ system and are diminishing relative to x_2 for all x_1 values. For $f < \hat{f}$, alternatively, they lie in VI and VIII octants of the latter system, and are increasing relative to x_2 for all x_1 values. Thus, a greater x_1 corresponds to a smaller x_2 in the $f > \hat{f}$ case where as a greater x_1 corresponds to a greater x_2 in the $f < \hat{f}$ case (see Figs.1 and 2).

The generating lines

$$\begin{cases} x_1 = h \\ f = a_0 + a_1 h + (a_2 + a_{12} h) x_2 \end{cases}$$

intersect the $O_1 X_1^!$ axis. When IPV $\hat{x}_1$ is crossed over these lines change their position (and the slope signs):

$$\text{I and VIII octants for } x_1 > \hat{x}_1$$
$$\text{III and VI octants for } x_1 < \hat{x}_1$$

in $x_1' 0_1 x_2' \hat{x}$ (see Figs.1 and 2) coordinate system. Such is the mechanism for the direction change of f dependence on x_2 variable in the case of crossing over IPV $\hat{x}_1$. Generating lines of the second family (i.e. parallel to $0x_1$ axis) behave similarly.

Hence, from the mathematical standpoint, the essence of IPV for type (1) correlations consisting in (i) the existence of IPV's $\hat{x}_1$, $\hat{x}_2$, $\hat{f}$; (ii) the dependence of the f value on Eq.(1) variables; (iii) a sign change for the f dependence on x_1 (or x_2) when IPV $\hat{x}_2$ (or $\hat{x}_1$) is crossed over; is completely determined by the properties of HPS.

C. A Multiple Cross-Correlation For the Case of Three Variables.

When coefficients of a multiple cross-correlation do not obey to the PPL requirements (see Ref.1, 6-8 and Eq.(2)),i.e. when these coefficients are mutually independent[*], IPE with the features described above should not be observed.

Let us consider the equation for some three factors corresponding to three different types of interaction mechanisms (e.g. inductive, resonance, and steric ones) with all possible cross-terms which characterize the interactions[**] (the non-additive influence[14, 15]) between above mechanisms

$$f(x_1, x_2, x_3) = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_{12} x_1 x_2 +$$
$$+ a_{23} x_2 x_3 + a_{13} x_1 x_3 + a_{123} x_1 x_2 x_3 \tag{3}$$

where $a_{ij} \neq \alpha a_i a_j$ and $a_{123} \neq \alpha^2 a_1 a_2 a_3$; i,j = 1, 2, 3 for $i \neq j$. The constants a_i characterize additive contributions of the factors; a_{ij} and a_{123} characterize the contributions of double and triple interactions between these factors to the response function.

[*] Such models have been considered for example, by Miller[12,13] and are used widely in the planning of experiments (e.g., see Ref. 14, 15)

[**] From the physical standpoint, the cross-terms are perturbations which various factors arouse in each other.

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Table 1. The Critical Values (CV's) For Eq.(3) Variables and the Analytical Form of f Values at the Corresponding CV's.

CV type	CV	Analytical form of $f = \hat{f}$ values at CV's
$\hat{x}_1(x_2)$	$-a_2 a_{12}^{-1}$	$a_0 - a_1 a_2 a_{12}^{-1} + (a_3 - a_{13} a_2 a_{12}^{-1})x_3 + (a_{23} - a_{123} a_2 a_{12}^{-1})x_2 x_3$
$\hat{x}_1(x_3)$	$-a_3 a_{13}^{-1}$	$a_0 - a_1 a_3 a_{13}^{-1} + (a_2 - a_{12} a_3 a_{13}^{-1})x_2 + (a_{23} - a_{123} a_3 a_{13}^{-1})x_2 x_3$
$\hat{x}_1(x_2 x_3)$	$-a_{23} a_{123}^{-1}$	$a_0 - a_1 a_{23} a_{123}^{-1} + (a_2 - a_{12} a_{23} a_{123}^{-1})x_2 + (a_3 - a_{13} a_{23} a_{123}^{-1})x_3$
$\hat{x}_2(x_1)$	$-a_1 a_{12}^{-1}$	$a_0 - a_2 a_1 a_{12}^{-1} + (a_3 - a_{23} a_1 a_{12}^{-1})x_3 + (a_{13} - a_{123} a_1 a_{12}^{-1})x_1 x_3$
$\hat{x}_2(x_3)$	$-a_3 a_{23}^{-1}$	$a_0 - a_2 a_3 a_{23}^{-1} + (a_1 - a_{12} a_3 a_{23}^{-1})x_1 + (a_{13} - a_{123} a_3 a_{23}^{-1})x_1 x_3$
$\hat{x}_2(x_1 x_3)$	$-a_{13} a_{123}^{-1}$	$a_0 - a_2 a_{13} a_{123}^{-1} + (a_1 - a_{12} a_{13} a_{123}^{-1})x_1 + (a_3 - a_{23} a_{13} a_{123}^{-1})x_3$
$\hat{x}_3(x_1)$	$-a_1 a_{13}^{-1}$	$a_0 - a_3 a_2 a_{13}^{-1} + (a_2 - a_{23} a_1 a_{13}^{-1})x_2 + (a_{12} - a_{123} a_1 a_{13}^{-1})x_1 x_2$
$\hat{x}_3(x_2)$	$-a_2 a_{23}^{-1}$	$a_0 - a_3 a_2 a_{23}^{-1} + (a_1 - a_{13} a_2 a_{23}^{-1})x_1 + (a_{12} - a_{123} a_2 a_{23}^{-1})x_1 x_2$
$\hat{x}_3(x_1 x_2)$	$-a_{12} a_{123}^{-1}$	$a_0 - a_3 a_{12} a_{123}^{-1} + (a_1 - a_{13} a_{12} a_{123}^{-1})x_1 + (a_2 - a_{23} a_{12} a_{123}^{-1})x_2$

Eq.(2) in the case of only three variables may be reduced to Eq.(4), where $(1 + \alpha a_3 x_3)a_1$, $(1 + \alpha a_3 x_3)a_2$ and $(1 + \alpha a_3 x_3)\alpha a_1 a_2$ are the susceptibility parameters.

$$f(x_1, x_2, x_3) = (a_0 + a_3 x_3) + (1 + \alpha a_3 x_3)a_1 x_1 + (1 + \alpha a_3 x_3)a_2 x_2 + (1 + \alpha a_3 x_3)\alpha a_1 a_2 x_1 x_2 \qquad (4)$$

The signs of all susceptibility parameters in Eq.(4) should be simultaneously changed when IPV $\hat{x}_3 = -\alpha^{-1} a_3^{-1}$ is experimentally crossed over. A similar change of the signs for all susceptibility parameters should also take place when IPV $\hat{x}_1$ or $\hat{x}_2$ is crossed over.

Eq.(3) may be written in the form

$$f(x_1, x_2, x_3) = (a_0 + a_3 x_3) + (a_1 + a_{13} x_3)x_1 + (a_2 + a_{23} x_3)x_2 + (a_{12} + a_{123} x_3)x_1 x_2 \qquad (5)$$

It is evident that the IPV for x_3 variable is not possible in the case of the latter equation. Instead of that, this variable can (see Table 1) take one of the three different critical values[x)] (CV's) $\hat{x}_3(x_1)$, $\hat{x}_3(x_2)$ and $\hat{x}_3(x_1 x_2)$ at which the corresponding susceptibility parameter at the values of arguments x_1, x_2 or $x_1 x_2$ will be equal to zero. However, at any of these CV's for variable, the corresponding f value will be dependent on x_1 and x_2 variables (see Table 1).

It is seen that when CV $\hat{x}_3(x_1)$ is crossed over, the sign at x_1 suspectibility parameter alone is bound to change contrary to that when IPV x_3 for Eq.(4) is crossing over. The change of the sign for the f dependence on x_1 or x_2 variables of Eq.(5) is not the nesessary result of the CV $\hat{x}_3(x_1)$ crossing where as the crossing of IPV $\hat{x}_3$ in the case of Eq.(4) necessarily requires the change of the sign for the f dependence on x_1 variable as well as that on x_2 variable.

[x)] The symbol $\hat{x}_3(x_1)$ designates CV for the variable x_3 at which the susceptibility parameter at x_1 variable of Eq.(5) becomes equal to zero. That is, $\hat{x}_3(x_1)$ is CV for x_3 variable relatively to x_1 variable, etc.

The trasition through CV $\hat{x}_3(x_2)$ or $\hat{x}_3(x_1x_2)$ requires the change of the sign of the susceptibility parameter at the values of arguments x_2 or x_1x_2 alone in Eq.(5).

Three CV's similar to these for x_3, will also exist for each of x_1 and x_2 variables of Eq.(3). All the possible CV's for the equation (3) variables are listed in Table 1. As is seen from the table, these values can be subdivided into two groups, i.e. $\hat{x}_i(x_j)$ and $\hat{x}_i(x_jx_l)$, where i, j, l = 1, 2, 3 at $i \neq j \neq l$.

D. A Comparison with Experiment.

It was recently shown[16] that the velocity the retro-Mannich condensation (at 298°K in H_2O - MeOH system) of the compounds $R_1C_6H_4NHCH_2C(NO_2)_2C_6H_4R_2$ oould be described adequately by means of the following equation:

$$\log K = (2.915 \pm 0.002) + (2.158 \pm 0.001)\,\sigma^o -$$
$$- (2.465 \pm 0.001)\,\sigma^- + (0.509 \pm 0.001)\,Y -$$
$$- (0.428 \pm 0.001)\,\sigma^o\,Y - (0.267 \pm 0.001)\,\sigma^-\,Y +$$
$$+ (0.683 \pm 0.002)\,\sigma^o\,\sigma^-\,Y \qquad (6)$$

where σ^- and σ^o are the constants for substituents R_1 and R_2 respectively, and Y is the solvent parameter. Correlation (6) is the example of a statistically significant non--additive influence of three factors with all possible cross--terms. If the latter correlation is equivalent to Eq.(3) but not to Eq.(2) at n = 3, the IPE has not to be observed. However, there have to exist 9 CV's for σ^o, σ^- and Y variables. All CV's calculated by us for Eq.(6) variables are listed in Table 2.

The comparison of CV's with variation intervals used[16] experimentally for σ^o, σ^- and Y variables shown that three out of nine CV's may be crossed over in experimental conditions of the work cited. The existing CV's belong to the $\hat{x}_i(x_jx_l)$ type only. All CV's of $\hat{x}_i(x_j)$ type are situated beyond the experimental limits of correlation variables (see Table 2).

The tables of experimentally found coefficients for the two-parameter correlations with one cross-term are given in Ref.16. These correlations are obtained if one of σ^o, σ^- and Y variables is fixed at various levels. The tables indicate that

Table 2. Critical Values (CV's) Calculated From Correlation (6)

CV type	CV value	The correlation parameter and the interval of its experimental variation
$\hat{\sigma}^o(\sigma^-)$	-3.64	σ^o
$\hat{\sigma}^o(Y)$	1.19	-0.15 ÷ +0.82
$\hat{\sigma}^o(\sigma^- Y)$	0.39	
$\hat{\sigma}^-(\sigma^o)$	3.18	σ^-
$\hat{\sigma}^-(Y)$	1.91	-0.17 ÷ +0.71
$\hat{\sigma}^-(\sigma^o Y)$	0.63	
$\hat{Y}(\sigma^o)$	5.04	Y
$\hat{Y}(\sigma^-)$	-9.25	-1.05 ÷ +3-56
$\hat{Y}(\sigma^o \sigma^-)$	0.99	

the change of the sign occurs only at the cross-terms.

From Eq.(5) it is seen that this is possible only in the case of the transition through $\hat{x}_i(x_j x_i)$ type CV. The signs for other coefficients of the two-parameter correlations are constant on all levels of the fixed variables. This behavior of the signs proves the absence of IPE; i.e. the equivalence of correlation (6) to Eq.(3) and inaccessibility of any $\hat{x}_i(x_j)$ CV in experimental conditions of Ref.16.

E. Correlations with n Factors and All Possible Cross-Terms.

IPE is not possible in the case of a correlation equation with n factors and all possible cross-terms if the coefficients of the correlation are mutually independent and all factors are variated simultaneously in the experiment. The number of possible CV's for such correlation will be

$$(2^{n-1} - 1) \, n \tag{7}$$

where $n \geqslant 1$. At $n = 2$ 2 CV's are possible; which are simultaneo-

usly IPV's. At $n = 3$, the number of possible CV's is 9 whereas
at $n = 6$ as many as 186 CV's (!) are possible.

On the other hand, the number of possible CV's may be repre-
sented also as the sum

$$n \sum_{k=1}^{(n-1)} \cdot C_{n-1}^{k} \tag{8}$$

where C_{n-1}^{k} is the number of combinations of $(n-1)$ elements ta-
ken k at a time. Formula (8) allows to calculate the number of
CV's of various types. As an example, at $n = 4$ 28 CV's are pos-
sible, i.e. there are 12 CV's $\hat{x}_i(x_j) = -a_j a_{ij}^{-1}$, 12 CV's $\hat{x}_i(x_j x_l) =$
$= -a_{jl} a_{ijl}^{-1}$ and 4 CV's $\hat{x}_i(x_j x_l x_m) = -a_{jlm} a_{ijlm}^{-1}$ at i,j,l,m=
$= 1, 2, 3, 4$ and $i \neq j \neq l \neq m$.

F. IPE For Cross-Correlations When n-2 Factors Are Fixed.

IPE should not be observed for a cross-correlation with n
factors if the coefficients at cross-terms do not obey PPL requi-
rements. However, if n-2 factors are fixed and only two factors
are varied in the conditions of experiment, the initial correla-
tion equation becomes similar to Eq.(1). Thus, in such a case
IPE will be observed as well.

The number of such IPE's will be equal to the number of the
possible combinations C_n^2, since, generally, the choice of factors
experimentally varied is arbitrary. For each of these IPE's two
IPE's are possible for variable factors. But these IPV's depend[*]
upon the accepted values for each of n-2 factors being fixed.

In fact, three different IPE's are possible for Eq.(3): at
fixed values for x_1, x_2 or x_3 variable respectively. As is seen
from Eq.(5) IPV's for $\hat{x}_1$ and $\hat{x}_2$ variables at x_3 value fixed will
be as follows:

$$\hat{x}_1 = - \frac{1 + a_{23}x_3}{a_{12} + a_{123}x_3} \qquad \hat{x}_2 = - \frac{1 + a_{13}x_3}{a_{12} + a_{123}x_3} \tag{9}$$

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[*] In this case the number of possible IPV's for the variable cor-
relation parameter (factor) is practically infinite, since each
parameter being fixed may be fixed any of its theoretically
possible values.

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Hence, to each value of x_3 variable being fixed there should correspond its own IPV's x_1 and x_2. Geometrically, the dependences $\hat{x}_1 = f(x_3)$ and $\hat{x}_2 = f(x_3)$ are hyperbolae with the discontinuity points at $x_3 = \hat{x}_3(x_1 x_2)$. When the condition $x_1 = \hat{x}_1$ or $x_2 = \hat{x}_2$ is fulfilled, the function $f(x_1, x_2, x_3)$ will be also dependent upon the value of a fixed variable x_3. If x_1 variable (or x_2) crosses through IPV $\hat{x}_1$ (or $\hat{x}_2$), a change of the sign will be observed for the $f(x_1, x_2, x_3)$ dependence on x_2 (or x_1). The appearence of IPE (with all properties described above) in the case of fixation of any of the Eq.(6) variable was shown experimentally in Ref.16.

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REACTIVITY OF COMPOUNDS WITH DIARYLMETHYLOL GROUP.
XXVII. IONIZATION CONSTANTS OF I,I-DIARYL-2(N-BENZYLAMINE)
ETHANOL IN ABSOLUTE ALCOHOL.

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Ionization constants of I,I-diaryl-2(N-benzylamine)
ethanols and substituted dibenzylamine in absolute al-
cohol have been determined by the potentiometrie me-
thod. It is shown that intramolecular hydrogen bonds
do not take part in transferring the influence of
substituted phenyls to a reaction center.

Intramolecular hydrogen bonds (IHB) formed in amino alco-
hols can be considered as an example of reactions in which
amine group appears to be a nucleophilic center. $\Delta\nu_{(OH)}$
can be taken as a measure of the amino group nueleophility.
It is well known that the relationship between nucleophili-
ty and basicity of the amines is not always simple.Thus,the
papers [I] demonstrate that with constant substituents at the
nitrogen atom the basicity of the amino group in amino
alcohols is determined by gross electronic and steric effects
of substituents at carbinol atom of carbon as well as by the
length of the carbon chain between the nitrogen atom and the
hydroxyl group. The change in spatial relations at carbinol
carbon upsets the correlation relationship between basicity
and nucleophility of the amine group. However, in case of
changing only polar characteristics of substituents good
correlation between nucleophility $(\Delta\nu_{OH})$ and basicity of
the amine group is evident.[2]

With steric effects being constant, the most convenient

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molecule modele for studying polar effects are amino alco-
hols with diarylmethylol groups, where substituents are
changed in meta and para-positions spaced far enough from
the reaction center. As shewn in the previous report [3],
I,I-diaryl-2(N-benzylamine)ethanels have quality relation-
ship between nucleophility of the amine group expressed by
$\Delta \nu_{(OH)}$ and σ^0 constants of substituted phenyls. It was of
interest to study the influence of substituente on basicity
of the amino group in these compounds.

For this purpose pK_a of I,I-diaryl-2(N-benzylamine)etha-
nols (I-XIII) and substituted dibenzylamine was determined
in the medium of absolute ethanol by the potentiometric
method.

Experimental

The synthesis of compounds I-XIII has been described in
Ref.3. The ionization constants were determined by po-
tentiometric titration of 0.I n $NCIO_4$ as in Ref. 2. Measure-
ments were made by means of a potentiometer LPM-60M. pK_a of
triethylamine being equal to 8.33[4] served as a reference
point for correlation of resultant ionisation constants.

The structure of compounds and pK_a are given in Tables
I and 2.

Results and Discussions

In reaction series where substituted phenyl is a variable
substituent and is not in immediate connection with the
reaction center, the structure-property correlations are
described with the help σ^0 constants assumed to be a measure
of induction effect of substituted phenyls. However, sub-
stituted phenyls cannot be characterised by precise and
universal induction constants because of superimposing the
resonance effect of the substituent the value of which is
not steady and varies when passing from one reaction to ano-
ther. Nevethelese, within the boundaries of one reaction
series when only substituente change in phenyl, σ^0 brought
to one seale with σ^* will apparently be in proportion to
"true" Taft constants.[5] In this case the attenuation factor
will depend on the ability of a molecule fragment, which

Constants of I,I-Diaryl-2(N-benzylamine)ethanols Ionized in Absolute Alcohol

$$\text{(C}_6\text{H}_5)\text{-CH}_2\text{NHCH}_2\overset{\displaystyle R}{\underset{\displaystyle OH}{C}}\text{-R}'$$
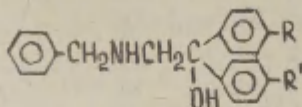
Table I

N comp.	R	R'	pK$_a$
I	H	H	7.01 ± 0.01
II	H	CH$_3$	7.04 ± 0.01
III	H	C$_2$H$_5$	7.02 ± 0.02
IV	H	C$_3$H$_7$	7.01 ± 0.01
V	H	OCH$_3$	7.19 ± 0.01
VI	H	OC$_2$H$_5$	7.10 ± 0.01
VII	H	CI	6.85 ± 0.04
VIII	H	Br	6.71 ± 0.02
IX	Br	CH$_3$	7.01 ± 0.02
X	Br	OCH$_3$	7.03 ± 0.01
XI	Br	CI	6.61 ± 0.01
XII	Br	Br	6.56 ± 0.02
XIII	OCH$_3$	OCH$_3$	7.39 ± 0.02

Constants of Substituted Dibenzylamines Ionized in Absolute Alcohol

$$R-\langle O \rangle-(CH_2)_n\,NH\,CH_2-\langle O \rangle$$

Table 2

№ comp.	n	R	pK_a
XIV	I	H	7.58 ± 0.05
XV	I	CH_3	7.70 ± 0.05
XVI	I	OCH_3	7.85 ± 0.04
XVII	I	CI	$6.95 \pm 0.0I$
XVIII	I	Br	6.90 ± 0.04
XIX	2	H	$7.34 \pm 0.0I$

separatee substituted phenyl from the reaction center, to make electronic effects.

In compounds I-XIII such fragment is a chain of two atoms of carbon which can transfer the induction effect of substituted phenyls. Apparently, there is also possibility to transfer the effects to the reaction center and via the hydrogen bridge

$$\begin{array}{c} C - CH_2 - NH- \\ O - H \end{array}$$

To clear up what are ways for transferring the electronic effects of substituents in compounds I-XIII dissolved in absolute alcohol, the slopes of pK_a vs. σ° correlation for the reaction series of I,I-diaryl-2(N-benzylamine)ethanols (series I) were compared with those of para-substituted dibenzylamines (series 2)(Table 3). In compounds of series 2 substituted phenyl is separated from the reaction center by only one CH_2-group. Apparently, such correlation of ρ° in series I and 2 makes it possible to evaluate the conductivity of one of the carbon atoms in C-C fragment of amino ethanols and if it is overstated, it can denote that IHB are taking part in transferring the influence of substituents to the reaction center.

Parameters of σ° – pK_a Correlation

Table 3

Series №	ρ°	$pK^\circ_{a(est)}$	r	s	$s\rho^\circ$
I	-0.877	7.04	0.958	0.07I	0.083
2	-I.99I	7.45	0.982	0.073	0.I73

From data of Table 3 it is evident that $\rho^\circ_1/\rho^\circ_2 = 0.44$ does not exceed the limits of Z_C^* as noted in the other well-known reaction series. It makes doubts whether IHB take part in transferring the influence of substituents to the amino group under experimental conditions.

Apparently, in the medium of absolute alcohol compounds I-XIII and I,I-diaryl-2-piperidine ethanols [2] do not transfer the influence of substituted phenyl to the reaction center in uniform way. The latter can transfer it not only through the induction mechanism but also with the help of IHB. While in compounds I-XIII which are more prone to solvation as they bear the secondary amino group[6], IHB are practically in full substituted for intramolecular hydrogen bonds with molecules of alcohol.

The results of this study and those obtained earlier [2,3] can be considered as demonstration that with the change of substituents in diarylmethylol group in reaction series of I,I-diaryl-2(N-benzylamine)ethanols nucleophility and basicity change in parallel as it was noted for I,I-diaryl-2-piperidine ethanols.[2] However, in the last case the additional way to transfer the effect of substituents is IHB.

Attention has been drawn to the high value of ρ° for series 2 of compounds (-I.99). If the value of ρ° in absolute alcohol is taken as the reaction constant of secondary amines ionized in water which is equal to 3.23 [7], the estimation of the attenuation of the polar effect gives even in this case $Z^*_{CH_2} = 0.62$. Taking into account the levelling effect of ethanol as a solvent[8], it should be expected that this value in fact may be higher. Indeed, there are some exam-

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ples of reaction series in literature where high values of inductive attenuation factors of the CH_2 group have been observed. Thus,when studying the bonds between spectroscopic and reaction parameters in the eeriee of substituted benzylamines from $\gamma \, \frac{S}{NH_2} = f(\sigma^\circ)$ correlation, the conductivity of electronic effects by CH_2 group was estimated to be 0.60.[8] But, the authors of the cited paper are not prone themselves to consider this result as quite reliable.

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Quantitative Consideration of the Influence of -
Structure, Medium and Temperature on Solvolysis Kine-
tics of β-Polynitroalkylarylamines. I.Kinetic Data.
Multiparameter Correlation with All Cross-Terms.

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The solvolysis reaction of a broad series of
β-polynitroalkylarylamines in aqueous methanol buf-
fer solutions at various temperatures shows the
possibility of using multiparameter correlation
equation with all cross-terms to express the non-
additive influence of several factors, viz. two
variable structural fragments, solvent and tempe-
rature, on the alteration of activation free energy.
    The coefficients of the resulting multiparameter
correlation equation are inter-independent values.

    The estimation of the degree of efficiency of the influ-
ence of different parameters on the system reactivity in va-
rying for one parameter lies on the principle of independence
and additivity (see Ref. 1,2).
    In some instances the additivity approach is not advisable
because of the existence of considerable perturbing influen-
ce among various types of interaction. Therefore the use of
various methods of constructing diverse multiparameter equa-
tions which include cross-terms has been as a logical result
of the intensive development of correlation analysis. This
approach is designed to determine quantitatively the influ-
ence of interacting factors on complicated physico-chemical
processes (see Ref. 1,3,4).
    Mathematical analysis of such equations reveals the pos-
sible existence of the critical value (CV) of any correlated
parameter giving rise to the independence of correlated value
(expanded according

to PPL) of the alternation of all remaining correlation parameters. In other words, in passing through isoparameter values for any parameter the sign of a respective sensitivity constant changes while the mechanism of the reaction remains unchanged (see Ref.5). Also, the problem concerning the experimental attainment of isoparameter points as well as the possibilities of transition "beyond" those points with the change of the sign. of the sensitivity factor has acquired special significance.

Up to now the study of such model reaction series has not been carried out, in which it might be possible to consider the possibility of solving a combined problem as regards the influence of the greatest possible number of independent factors which are responsible for the system reactivity.

For the purpose of formulating the general problem of finding out the mutual influence of various factors on reactivity we studied the solvolysis reaction of a broad series of B-polynitroalkylarylamines which includes simultaneously both the change of structural parameters of a reacting substrate and the influence of changing medium properties and temperature Q on the reactivity of the series studied.

It was shown earlier (see Ref.6-11) that Mannich's solvolysis of polynitrobases in a wide range of changing acid-base properties of the medium (pH=2.5 $\div$ 10.8) is carried out according to the following simple schematic:

$$R_I \text{NHCH}_2 C(NO_2)_2 R_{II} \xrightarrow{k_{solv.}} \left[R_I \text{NH} \cdots \text{CH}_2 \overset{+\delta}{\cdots} \cdots C(NO_2)_2 R_{II} \right]^{\neq} \text{Solv.}$$
$$(I)$$

$$\text{further transformation} \longrightarrow \left[R_I \text{NH} \cdots \text{CH}_2 \right]^{\oplus}_{\text{mSolv}} + \left[C(NO_2)_2 R_{II} \right]^{\ominus}_{\text{nSolv.}}$$
$$(II) \qquad\qquad (III)$$
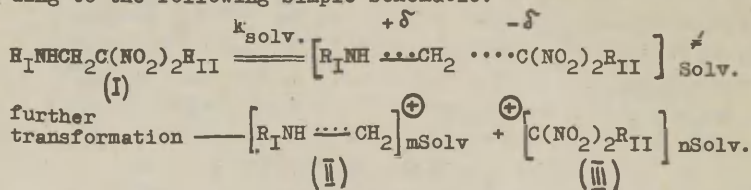
In this paper kinetic data the results on the solvolysis of 42 -dinitroalkylarylamines of the general formula $X_I C_6 H_4 \text{NHCH}_2 C(NO_2)_2 C_6 H_4 X_{II}(I)$, where X_I = p-CH$_3$, H, p-Br, m-Br, p-COOCH$_3$, m-NO$_2$; X_{II}= p-CH$_3$, p-OCH$_3$, H, p-Br, m-Cl, m-NO$_2$, p-NO$_2$ are discussed. The decomposition mechanism of these compounds is given by the above schematic.

The decomposition of (I) has been studied in aqueous metha-
nol buffer solutions (see Ref.12,13) containing 0, 30, 50,
70, 80 and 100 (v/v) of methyl alcohol (MeOH) over a tempera-
ture range from +10°C to +55°C by the spectrophotometric meth-
ods monitoring the intensity increase of the absorption of aryl-
dinitromethane anion evolving during the reaction or monitoring
absorption decrease of the initial compound. Both methods have
given the same results within the experimental error.

Monomolecular constants of the decomposition rate do not
depend on the buffer capacity of the system, the concentra-
tion of a starting material and the ionic strength of a soluti-
on over, the range $\mu = 0.01 \div 1.00$ and the acidity of a medi-
um with pH from 5.4 to 8.2.

The above facts allow solvolysis (I) to be classified as
the reaction of monomolecular nucleophilic substitution (S_N1).

The method of handling experimental data is the same as
that used in Ref.6. The results are tabulated in Tables
1 ÷ 6.

Table 1. Logarithms of Solvolysis Rate Constants[x] of (I) at
Various Temperatures in Water.

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
p-CH$_3$	p-CH$_3$	-1.340	-1.075	-0.571	-0.100	(+0.757)
	p-OCH$_3$	-1.312	-1.053	-0.561	-0.101	(+0.733)
	H	-1.193	-0.962	-0.521	-0.103	(+0.644)
	p-Br	-0.941	-0.767	-0.433	-0.122	(+0.446)
	m-Cl	-0.833	-0.685	-0.397	-0.128	(+0.364)
	m-NO$_2$	-0.513	-0.437	-0.286	-0.146	+0.113
	p-NO$_2$	-0.397	-0.347	-0.246	-0.152	+0.021

[x] Constants are determined from 3-6 parallel runs and
are reproducible within 3-5%.

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Table 1 (continued)

X_I	X_{II}	$283°K$	$288°K$	$298°K$	$308°K$	$328°K$
H	p-CH$_3$	-2.056	-1.761	-1.196	-0.668	(+0.295)
	p-OCH$_3$	-2.017	-1.729	-1.177	-0.661	(+0.278)
	H	-1.862	-1.599	-1.101	-0.636	(+0.211)
	p-Br	-1.517	-1.319	-0.937	-0.579	+0.072
	m-Cl	-1.375	-1.200	-0.867	-0.556	+0.011
	m-NO$_2$	-0.941	-0.844	-0.658	-0.484	-0.169
	p-NO$_2$	-0.783	-0.714	-0.582	-0.459	-0.233
p-Br	p-CH$_3$	-3.038	-2.698	-2.049	-1.443	-0.340
	p-OCH$_3$	-2.984	-2.652	-2.018	-1.426	-0.347
	H	-2.772	-2.468	-1.893	-1.356	-0.379
	p-Br	-2.308	-2.071	-1.623	-1.204	-0.443
	m-Cl	-2.100	-1.903	-1.508	-1.140	-0.468
	m-NO$_2$	-1.521	-1.399	-1.165	-0.947	-0.550
	p-NO$_2$	-1.306	-1.215	-1.040	-0.877	-0.578
m-Br	p-CH$_3$	-3.711	-3.339	-2.634	-1.975	-0.776
	p-OCH$_3$	-3.647	-3.284	-2.595	-1.949	-0.777
	H	-3.394	-3.064	-2.436	-1.849	-0.782
	p-Br	-2.845	-2.587	-2.093	-1.632	-0.792
	m-Cl	-2.613	-2.385	-1.948	-1.540	-0.796
	m-NO$_2$	-1.917	-1.779	-1.513	-1.264	-0.809
	p-NO$_2$	-1.664	-1.559	-1.354	-1.163	-0.815
p-COOCH$_3$	p-CH$_3$	-4.744	-4.328	-3.535	-2.793	-1.443
	p-OCH$_3$	-4.667	-4.259	-3.483	-2.757	-1.436
	H	-4.355	-3.982	-3.273	-2.610	-1.404
	p-Br	-3.677	-3.381	-2.818	-2.291	-1.333
	m-Cl	-3.391	-3.127	-2.626	-2.156	-1.303
	m-NO$_2$	-2.530	-2.365	-2.048	-1.752	-1.213
	p-NO$_2$	-2.219	-2.088	-1.839	-1.605	-1.180

Table 1 (end)

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
m-NO$_2$	p-CH$_3$	-5.056	-4.627	-3.807	-3.041	-1.645
	p-OCH$_3$	-4.977	-4.554	-3.751	-3.000	-1.637
	H	-4.645	-4.259	-3.525	-2.839	-1.592
	p-Br	-3.928	-3.621	-3.037	-2.490	-1.496
	m-Cl	-3.627	-3.352	-2.830	-2.343	-1.457
	m-NO$_2$	-2.715	-2.542	-.2210	-1.900	-1.333
	p-NO$_2$	-2.384	-2.248	-1.935	-1.739	-1.289

Table 2. Logarithms of Solvolysis Rate Constants for (1) at
Various Temperatures in 30% (v/v) Methanol

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
p-CH$_3$	p-CH$_3$	-1.916	-1.648	-1.138	-0.661	(+0.206)
	p-OCH$_3$	-1.873	-1.612	-1.113	-0.647	(+0.203)
	H	-1.709	-1.470	-1.015	-0.589	(+0.186)
	p-Br	-1.354	-1.163	-0.802	-0.464	(+0.146)
	m-Cl	-1.202	-1.033	-0.712	-0.411	(+0.135)
	m-NO$_2$	-0.747	-0.642	-0.441	-0.253	+0.090
	p-NO$_2$	-0.583	-0.500	-0.393	-0.195	+0.073
H	p-CH$_3$	-2.569	-2.272	-1.707	-1.179	-0.219
	p-OCH$_3$	-2.520	-2.230	-1.677	-1.160	-0.219
	H	-2.330	-2.062	-1.555	-1.081	-0.219
	p-Br	-1.913	-1.699	-1.291	-0.910	-0.218
	m-Cl	-1.736	-1.545	-1.180	-0.838	-0.216
	m-NO$_2$	-1.209	-1.084	-0.845	-0.621	-0.215
	p-NO$_2$	-1.017	-0.916	-0.723	-0.543	-0.214
p-Br	p-CH$_3$	-3.459	-3.123	-2.484	-1.886	-0.800
	p-OCH$_3$	-3.401	-3.073	-2.446	-1.859	-0.792
	H	-3.173	-2.870	-2.292	-1.752	-0.770
	p-Br	-2.677	-2.430	-1.959	-1.519	-0.717
	m-Cl	-2.468	-2.244	-1.818	-1.420	-0.696
	m-NO$_2$	-1.839	-1.686	-1.395	-1.124	-0.631
	p-NO$_2$	-1.608	-1.483	-1.242	-1.016	-0.605

Table 2 (continued)

X_I	X_{II}	$283^\circ K$	$288^\circ K$	$298^\circ K$	$308^\circ K$	$328^\circ K$
m-Br	p-CH$_3$	-4.070	-3.707	-3.016	-2.371	-1.196
	p-OCH$_3$	-4.005	-3.650	-2.978	-2.339	-1.187
	H	-3.750	-3.423	-2.797	-2.212	-1.146
	p-Br	-3.200	-2.931	-2.417	-1.936	-1.059
	m-Cl	-2.967	-2.723	-2.256	-1.819	-1.023
	m-NO$_2$	-2.267	-2.099	-1.773	-1.468	-0.912
	p-NO$_2$	-2.016	-1.872	-1.597	-1.341	-0.874
p-COOCH$_3$	p-CH$_3$	-5.008	-4.606	-3.837	-3.118	-1.808
	p-OCH$_3$	-4.937	-4.540	-3.785	-3.073	-1.794
	H	-4.642	-4.276	-3.575	-2.920	-1.728
	p-Br	-4.008	-3.703	-3.122	-2.578	-1.588
	m-Cl	-3.738	-3.461	-2.930	-2.433	-1.529
	m-NO$_2$	-2.934	-2.735	-2.355	-1.999	-1.352
	p-NO$_2$	-2.641	-2.470	-2.145	-1.841	-1.288
m-NO$_2$	p-CH$_3$	-5.295	-4.877	-4.085	-3.343	-1.996
	p-OCH$_3$	-5.219	-4.809	-4.030	-3.301	-1.973
	H	-4.911	-4.533	-3.810	-3.134	-1.904
	p-Br	-4.525	-3.937	-3.335	-2.772	-1.749
	m-Cl	-3.974	-3.684	-3.134	-2.619	-1.683
	m-NO$_2$	-3.134	-2.927	-2.530	-2.159	-1.484
	p-NO$_2$	-2.830	-2.651	-2.311	-1.992	-1.418

Table 3. Logarithms of Solvolysis Rate Constants for (I) at Various Temperatures in 50% (v/v) Methanol.

X_I	X_{II}	$283^\circ K$	$288^\circ K$	$298^\circ K$	$308^\circ K$	$328^\circ K$
p-CH$_3$	p-CH$_3$	-2.376	-2.111	-1.597	-1.115	-0.235
	p-OCH$_3$	-2.328	-2.065	-1.560	-1.088	-0.226
	H	-2.128	-1.881	-1.415	-0.978	-0.185
	p-Br	-1.693	-1.483	-1.100	-0.741	-0.089
	m-Cl	-1.509	-1.314	-0.966	-0.641	-0.049
	m-NO$_2$	-0.959	-0.809	-0.566	-0.340	+0.073
	p-NO$_2$	-0.760	-0.625	-0.421	-0.230	(+0.117)

Table 3 (continued)

X_1	X_{II}	283°K	288°K	298°K	308°K	328°K
H	p-CH$_3$	-2.981	-2.685	-2.121	-1.593	-0.633
	p-OCH$_3$	-2.928	-2.635	-2.081	-1.562	-0.621
	H	-2.708	-2.437	-1.922	-1.441	-0.567
	p-Br	-2.232	-2.006	-1.578	-1.178	-0.450
	m-Cl	-2.032	-1.824	-1.432	-1.066	-0.402
	m-NO$_2$	-1.425	-1.278	-0.996	-0.732	-0.251
	p-NO$_2$	-1.205	-1.079	-0.837	-0.610	-0.197
p-Br	p-CH$_3$	-3.801	-3.467	-2.836	-2.245	-1.172
	p-OCH$_3$	-3.739	-3.413	-2.791	-2.210	-1.153
	H	-3.501	-3.194	-2.614	-2.072	-1.089
	p-Br	-2.977	-2.720	-2.231	-1.773	-0.940
	m-Cl	-2.756	-2.520	-2.069	-1.647	-0.879
	m-NO$_2$	-2.094	-1.918	-1.582	-1.267	-0.694
	p-NO$_2$	-1.853	-1.700	-1.405	-1.129	-0.626
m-Br	p-CH$_3$	-4.360	-4.004	-3.326	-2.692	-1.539
	p-OCH$_3$	-4.297	-3.946	-3.278	-2.654	-1.520
	H	-4.041	-3.713	-3.089	-2.505	-1.443
	p-Br	-3.488	-3.210	-2.678	-2.181	-1.277
	m-Cl	-3.254	-2.996	-2.504	-2.044	-1.208
	m-NO$_2$	-2.553	-2.357	-1.983	-1.634	--0.997
	p-NO$_2$	-2.297	-2.125	-1.794	-1.484	-0.920
p-COOCH$_3$	p-CH$_3$	-5.224	-2.830	-4.081	-3.380	-2.106
	p-OCH$_3$	-5.156	-4.767	-4.029	-3.338	-2.084
	H	-4.877	-4.513	-3.820	-3.172	-1.992
	p-Br	-4.277	-3.964	-3.368	-2.810	-1.798
	m-Cl	-4.024	-3.731	-3.176	-2.657	-1.715
	m-NO$_2$	-3.259	-3.033	-2.602	-2.199	-1.465
	p-NO$_2$	-2.983	-2.780	-2.393	-2.032	-1.376

Table 3 (end)

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
m-NO$_2$	p-CH$_3$	-5.486	-5.080	-4.309	-3.588	-2.277
	p-OCH$_3$	-5.416	-5.015	-4.255	-3.545	-2.255
	H	-5.130	-4.755	-4.041	-3.373	-2.159
	p-Br	-4.517	-4.191	-3.578	-3.000	-1.956
	m-Cl	-4.257	-3.953	-3.379	-2.843	-1.869
	m-NO$_2$	-3.472	-3.238	-2.789	-2.370	-1.606
	p-NO$_2$	-3.191	-2.973	-2.575	-2.198	-1.514

Table 4. Logarithms of Solvolysis Rate Constants for (I) at Various Temperatures in 70 % (v/v) Methanol.

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
p-CH$_3$	p-CH$_3$	-2.972	-2.697	-2.176	-1.689	-0.804
	p-OCH$_3$	-2.908	-2.638	-2.125	-1.645	-0.774
	H	-2.653	-2.401	-1.920	-1.470	-0.652
	p-Br	-2.105	-1.887	-1.476	-1.091	-0.392
	m-Cl	-1.871	-1.670	-1.288	-0.931	-0.281
	m-NO$_2$	-1.173	-1.019	-0.725	-0.450	+0.051
	p-NO$_2$	-0.918	-0.782	-0.520	-0.275	(+0.172)
H	p-CH$_3$	-3.504	-3.207	-2.643	-2.116	-1.158
	p-OCH$_3$	-3.441	-3.147	-2.592	-2.072	-1.128
	H	-3.187	-2.910	-2.386	-1.896	-1.007
	p-Br	-2.633	-2.395	-1.940	-1.516	-0.743
	m-Cl	-2.401	-2.177	-1.752	-1.355	-0.633
	m-NO$_2$	-1.702	-1.523	-1.187	-0.872	-0.301
	p-NO$_2$	-1.445	-1.286	-0.981	-0.696	-0.176
p-Br	p-CH$_3$	-4.230	-3.903	-3.280	-2.698	-1.640
	p-OCH$_3$	-4.166	-3.843	-3.228	-2.654	-1.609
	H	-3.910	-3.604	-3.022	-2.477	-1.487
	p-Br	-3.356	-3.087	-2.574	-2.095	-1.223
	m-Cl	-3.122	-2.868	-2.385	-1.933	-1.111
	m-NO$_2$	-2.419	-2.212	-1.817	-1.448	-0.776
	p-NO$_2$	-2.162	-1.973	-1.611	-1.272	-0.654

Table 4 (end)

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
m-Br	p-CH₃	-4.727	-4.379	-3.717	-3.097	-1.969
	p-OCH₃	-4.664	-4.320	-3.665	-3.053	-1.940
	H	-4.406	-4.080	-3.458	-2.876	-1.819
	p-Br	-3.853	-3.562	-3.009	-2.492	-1.553
	m-Cl	-3.617	-3.342	-2.819	-2.330	-1.440
	m-NO₂	-2.912	-2.684	-2.249	-1.843	-1.104
	p-NO₂	-2.658	-2.445	-2.042	-1.666	-0.983
p-COOCH₃	p-CH₃	-5.496	-5.114	-4.389	-3.712	-2.480
	p-OCH₃	-5.433	-5.054	-4.337	-3.667	-2.451
	H	-5.173	-4.814	-4.129	-3.489	-2.325
	p-Br	-4.617	-4.293	-3.678	-3.104	-2.060
	m-Cl	-4.381	-4.072	-3.488	-2.941	-1.948
	m-NO₂	-3.670	-3.411	-2.915	-2.451	-1.607
	p-NO₂	-3.413	-3.171	-2.707	-2.274	-1.484
m-HO₂	p-CH₃	-5.725	-5.335	-4.593	-3.897	-2.632
	p-OCH₃	-5.662	-5.276	-4.541	-3.853	-2.608
	H	-5.406	-5.035	-4.332	-3.675	-2.480
	p-Br	-4.848	-4.514	-3.881	-3.289	-2.214
	m-Cl	-4.609	-4.293	-3.689	-3.125	-2.099
	m-NO₂	-3.903	-3.631	-3.116	-2.635	-1.762
	p-NO₂	-3.643	-3.390	-2.908	-2.457	-1.637

Table 5. Logarithms of Solvolysis Rate Constants for (I) at
Various Temperatures in 80 % (v/v) Methanol

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
p-CH₃	p-CH₃	-3.365	-3.090	-2.565	-2.074	-1.181
	p-OCH₃	-3.292	-3.022	-2.503	-2.019	-1.137
	H	-3.007	-2.749	-2.259	-1.800	-0.966
	p-Br	-2.385	-2.159	-1.728	-1.326	-0.594
	m-Cl	-2.121	-1.909	-1.504	-1.125	-0.436
	m-NO₂	-1.333	-1.160	-0.831	-0.523	+0.035
	p-NO₂	-1.044	-0.887	-0.586	-0.304	(+0.209)

Table 5 (continued).

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
H	p-CH$_3$	-3.852	-3.557	-2.993	-2.466	-1.507
	p-OCH$_3$	-3.784	-3.491	-2.934	-2.413	-1.467
	H	-3.505	-3.227	-2.697	-2.201	-1.300
	p-Br	-2.901	-2.655	-2.184	-1.742	-0.939
	m-Cl	-2.649	-2.413	-1.966	-1.548	-0.788
	m-NO$_2$	-1.886	-1.688	-1.315	-0.968	-0.332
	p-NO$_2$	-1.606	-1.424	-1.078	-0.754	-0.165
p-Br	p-CH$_3$	-4.519	-4.194	-3.578	-3.002	-1.954
	p-OCH$_3$	-4.450	-4.131	-3.521	-2.951	-1.912
	H	-4.185	-3.879	-3.295	-2.749	-1.755
	p-Br	-3.611	-3.333	-2.805	-2.311	-1.412
	m-Cl	-3.368	-3.102	-2.597	-2.125	-1.268
	m-NO$_2$	-2.635	-2.409	-1.975	-1.569	-0.831
	p-NO$_2$	-2.370	-2.157	-1.749	-1.367	-0.672
m-Br	p-CH$_3$	-4.975	-4.631	-3.979	-3.369	-2.260
	p-OCH$_3$	-4.909	-4.570	-3.924	-3.320	-2.221
	H	-4.650	-4.326	-3.705	-3.124	-2.066
	p-Br	-4.093	-3.798	-3.231	-2.700	-1.734
	m-Cl	-3.861	-3.574	-3.030	-2.521	-1.597
	m-NO$_2$	-3.154	-2.903	-2.428	-1.983	-1.176
	p-NO$_2$	-2.895	-2.659	-2.209	-1.788	-1.022
p-COOCH$_3$	p-CH$_3$	-5.675	-5.304	-4.596	-3.934	-2.729
	p-OCH$_3$	-5.614	-5.246	-4.544	-3.888	-2.693
	H	-5.372	-5.015	-4.337	-3.702	-2.550
	p-Br	-4.879	-4.513	-3.887	-3.301	-2.267
	m-Cl	-4.619	-4.301	-3.696	-3.131	-2.102
	m-NO$_2$	-3.949	-3.664	-3.125	-2.621	-1.705
	p-NO$_2$	-3.704	-3.433	-2.917	-2.435	-1.559

Table 5 (end).

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
m-NO$_2$	p-CH$_3$	-5.890	-5.508	-4.783	-4.105	-2.874
	p-OCH$_3$	-5.828	-5.431	-4.732	-4.059	-2.836
	H	-5.589	-5.223	-4.527	-3.877	-2.695
	p-Br	-5.067	-4.729	-4.085	-3.482	-2.385
	m-Cl	-4.849	-4.521	-3.897	-3.315	-2.256
	m-NO$_2$	-4.186	-3.894	-3.336	-2.813	-1.862
	p-NO$_2$	-3.948	-3.667	-3.131	-2.631	-1.721

Table 6. Logarithms of Solvolysis Rate Constants for (I) at
Various Temperatures in Absolute Methanol.

X_I	X_{II}	283°K	288°K	298°K	308°K	328°K
p-CH$_3$	p-CH$_3$	-4.324	-4.042	-3.507	-3.007	-2.098
	p-OCH$_3$	-4.231	-3.953	-3.422	-2.926	-2.023
	H	-3.864	-3.594	-3.080	-2.600	-1.728
	p-Br	-3.066	-2.817	-2.340	-1.895	-1.084
	m-Cl	-2.730	-2.488	-2.027	-1.597	-0.814
	m-NO$_2$	-1.720	-1.501	-1.088	-0.720	0.000
	p-NO$_2$	-1.350	-1.143	-0.747	-0.376	(+0.298)
H	p-CH$_3$	-4.702	-4.406	-3.843	-3.316	-2.360
	p-OCH$_3$	-4.618	-4.324	-3.765	-3.241	-2.290
	H	-4.284	-3.997	-3.451	-2.942	-2.015
	p-Br	-3.558	-3.287	-2.778	-2.292	-1.418
	m-Cl	-3.251	-2.987	-2.486	-2.017	-1.166
	m-NO$_2$	-2.329	-2.087	-1.625	-1.193	-0.406
	p-NO$_2$	-1.995	-1.760	-1.312	-0.893	-0.131
p-Br	p-CH$_3$	-5.217	-4.902	-4.301	-3.738	-2.716
	p-OCH$_3$	-5.145	-4.831	-4.232	-3.672	-2.655
	H	-4.856	-4.546	-3.958	-3.408	-2.407
	p-Br	-4.226	-3.930	-3.364	-2.834	-1.870
	m-Cl	-3.963	-3.669	-3.112	-2.592	-1.646

Table 6 (end)

X_I	X_{II}	$283^{\circ}K$	$288^{\circ}K$	$298^{\circ}K$	$308^{\circ}K$	$328^{\circ}K$
p-Br	m-NO$_2$	-3.166	-2.887	-2.358	-1.864	-0.966
	p-NO$_2$	-2.876	-2.602	-2.084	-1.599	-0.719
m-Br	p-CH$_3$	-5.571	-5.242	-4.614	-4.028	-2.961
	p-OCH$_3$	-5.507	-5.178	-4.553	-3.968	-2.904
	H	-5.246	-4.923	-4.305	-3.727	-2.675
	p-Br	-4.687	-4.370	-3.768	-3.206	-2.183
	m-Cl	-4.450	-4.136	-3.539	-2.985	-1.973
	m-NO$_2$	-3.736	-3.434	-2.860	-2.323	-1.346
	p-NO$_2$	-3.478	-3.179	-2.613	-2.083	-1.120
p-COOCH$_3$	p-CH$_3$	-6.117	-5.766	-5.098	-4.473	-3.339
	p-OCH$_3$	-6.065	-5.713	-5.046	-4.423	-3.289
	H	-5.850	-5.508	-4.840	-4.219	-3.089
	p-Br	-5.393	-5.048	-4.392	-3.779	-2.661
	m-Cl	-5.198	-4.856	-4.202	-3.591	-2.479
	m-NO$_2$	-4.615	-4.279	-3.634	-3.031	-1.993
	p-NO$_2$	-4.404	-4.069	-3.427	-2.828	-1.736
m-NO$_2$	p-CH$_3$	(-6.282)	-5.924	-5.244	-4.608	-3.453
	p-OCH$_3$	(-6.231)	-5.875	-5.195	-4.560	-3.403
	H	-6.035	-5.679	-5.001	-4.368	-3.216
	p-Br	-5.605	-5.253	-4.580	-3.951	-2.805
	m-CI	-5.425	-5.073	-4.402	-3.774	-2.632
	m-NO$_2$	-4.884	-4.534	-3.868	-3.245	-2.114
	p-NO$_2$	-4.688	-4.337	-3.674	-3.053	-1.926

Note: Logarithms of solvolysis rates constants for (I) in paren-
theses in Tables 1 - 6 were calculated from the equation
of multiparameter cross-correlation.

From the data listed in Tables 1-6 it is seen that the
rate of the reactions depends to a considerable degree on
both the structure of the substituents X_I and X_{II}, and the me
dium properties over the whole range of temperatures studied.
The data can be expressed quite satisfactorily by many linear
regression groups of the same type as Hammett-Taft(see Ref.14),
Grünwald-Winstein (see Ref.15) equations or those of Arrenius.
From the plots in Figures 1-4 it is clearly seen that the
above equations hold true.
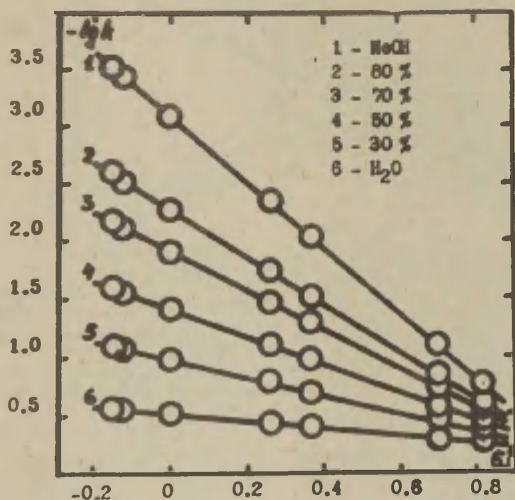
Fig.1. Linear regression in coordinates lg K - $\widetilde{\sigma}^{o}$ with
different compositions of binary mixtures H_2O - MeOH
for solvolysis of $X_I C_6 H_4 NHCH_2 C(NO_2)_2 C_6 H_4 X_{II}$

$$(X_I = p-CH_3 ; \quad T = 298^{o}K)$$
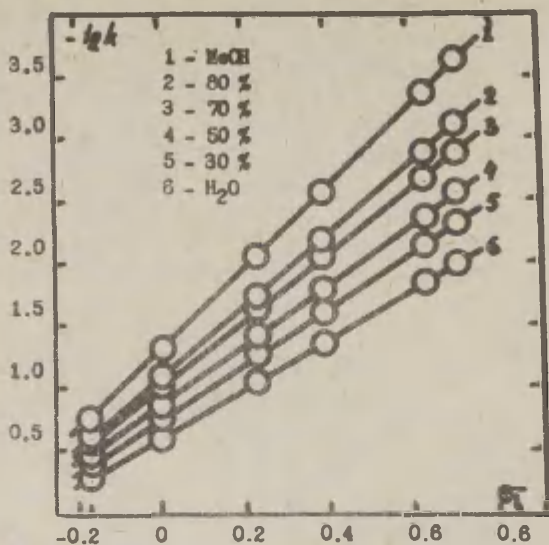
Fig.2. Linear regression in coordinates lg K — σ^- with different compositions of binary mixtures H_2O — MeOH for solvolysis of $X_IC_6H_4NHCH_2C(NO_2)_2C_6H_4X_{II}$

(X_{II} = p-NO_2; T = 298°K)

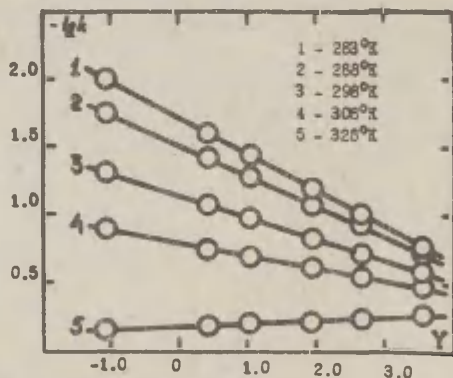Fig.3. Linear regression in coordinates lg K — Y at various temperatures for solvolysis of $X_IC_6H_4NHCH_2C(NO_2)_2C_6H_4X_{II}$
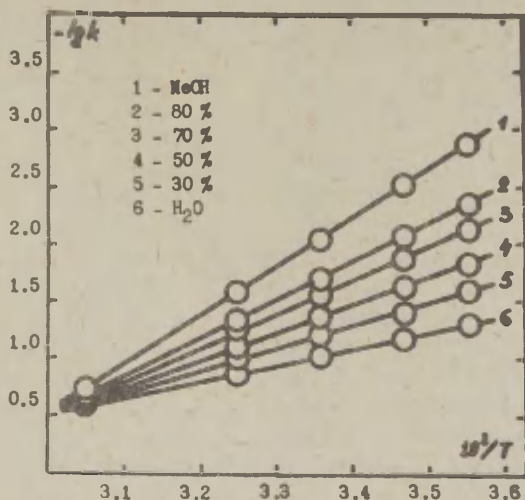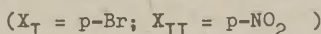
(X_I = H; X_{II} = p-NO_2)

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Fig.4. Linear regression in coordinates lg K - 10^3/T with different compositions of binary mixtures H_2O - MeOH for solvolysis of $X_IC_6H_4NHCH_2C(NO_2)_2C_6H_4X_{II}$

$$(X_I = p-Br; \quad X_{II} = p-NO_2 \quad)$$

As is seen from these plots the sensitivity of particular reaction series towards the influence of various factors is very considerable, which permits the quantitative estimation of the phenomen. All experimental results are brought to a single relationship by the cross-correlation with all cross-terms.

In its general form that kind of equation which includes every possible interaction in a reaction system may be written as follows:

$$f(x_1, x_2, x_3, x_4) = f_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 +$$
$$+ a_{12}x_1x_2 + a_{13}x_1x_3 + a_{14}x_1x_4 + a_{23}x_2x_3 + a_{24}x_2x_4 +$$
$$+ a_{34}x_3x_4 + a_{123}x_1x_2x_3 + a_{124}x_1x_2x_4 + a_{134}x_1x_3x_4 +$$
$$+ a_{234}x_2x_3x_4 + a_{1234}x_1x_2x_3x_4 \qquad (1)$$

True coefficients of equation (1) were obtained by several successive sensitivity parameter correlations of one-parameter

equations with any of fixed parameters, with subsequent cor-
relation of cross-terms obtained with the third parameter and
so on. The method used by us makes it difficult to estimate er-
rors in determinig coefficients of multiparameter cross-cor-
relations, which is immaterial within the range of the reaction
series studied owing to a great number of statistical degrees
of freedom. A general probability analysis made by Student's
t-test (see Ref. 16) has shown that the deviation of the
experimental results from the calculated ones is neglige-
able. An insignificant common error in one-parameter correla-
tions and a high correlation coefficient ($0.013 \leq s \leq 0.048$ and
$0.9987 \leq r \leq 0.9999$) indicate that practically for all particular
reaction series there is almost exact functional relationship.

All attempts to find sensitivity parameters by handling
all experimental data using a polylinear equation with cross-
terms by means of the least squares method in an expanded form
identical with equation (1), have failed. A thorough investi-
gation showed that in the reaction system in question there
is some kind of interdependence between some of interacting
factors in consequence of which there occurs a shift in the
values of sensitivity factors from certain parameters to the
other ones. In this case the solution of an equations is
found to be rather changeable [x]) and the coefficient values
become shifted: in other words, they are incorrect.

Sensitivity parameters of the resulting equation of mul-
typarameter correlation with all cross-terms are given in
Table 7.

The cross-terms in Eq. (1)(see Table 7) characterize
the interaction (non-additivity)of influence among factors
and from the physical point of view are perturbations which
various factors of the reaction system exert one upon another.

Table 7. Sensitivity Parameters Values for the Equation of Multiparameter Linear Regression with all Cross-terms

Parameters of Eq.1	Variable or cross-terms	Sensitivity Factor	Numerical Value
f_0	$lg\ K_0$	-	12.476
x_1	σ^0 a)	a_1	-3.411
x_2	σ^- b)	a_2	3.861
x_3	Y c)	a_3	0.216
x_4	$10^3/T$ d)	a_4	-4.587
x_1x_2	$\sigma^0\ \sigma^-$	a_{12}	1.339
x_1x_3	$\sigma^0\ Y$	a_{13}	-2.478
x_1x_4	$\sigma^0\ 10^3/T$	a_{14}	1.660
x_2x_3	$\sigma^-\ Y$	a_{23}	0.642
x_2x_4	$\sigma^-\ 10^3/T$	a_{24}	-1.885
x_3x_4	$Y\ 10^3/T$	a_{34}	0.088
$x_1x_2x_3$	$\sigma^0\ \sigma^-\ Y$	a_{123}	-1.335
$x_1x_2x_4$	$\sigma^0\ \sigma^-\ 10^3/T$	a_{124}	-0.601
$x_1x_3x_4$	$\sigma^0\ Y\ 10^3/T$	a_{134}	0.610
$x_2x_3x_4$	$\sigma^-\ Y\ 10^3/T$	a_{234}	-0.271
$x_1x_2x_3x_4$	$\sigma^0\ \sigma^-\ Y\ 10^3/T$	a_{1234}	0.601

a) σ^0 - parameter characterizes substituents X_{II}
b) σ^- - parameter characterizes substituents X_I
c) Y - parameter characterizes medium properties, "ionising power of a solvent"
d) $10^3/T$ - temperature, $^\circ K$

In the case of similar multiparameter correlation with single formal interaction mechanism there must exist a definite connection between coefficients which allows Eq.(1) to be simplified (see Ref.1,5).

Our attempts to find the relationship between coefficients by means of the analysis made failed. On the contrary, it appeared that all the coefficients were orthogonal (arbitrary) values and,thus, equation (1) rather resembles Miller's polylinear function (see Ref.3,4) and does not obey any single type of interaction (see Ref.1).

The apparent lack of connection between coefficients presents some additional difficulty when analyzing such multyparameter cross-correlations in detail. Nevertheless, we have attempted to estimate the properties connected with different variable factors which influence the characteristics of a complex system and so to find whether it is possible to give a quantitative definition of interaction intensity between some or other properties responsible for the extent of perturbation exerted by several independent types of interaction upon one another.

We have performed the analysis of the behavior of the whole system in various conditions connected with the independence of some correlated characteristics relative to different interacting parameters. We have shown the possibility of changing the sign of the sensitivity factor not only for cross-terms, which for the most part is not unexpected, but also for any of the varied parameters, and the possibility of principle to find IPV for any correlated parameter.

As it was shown before (see Ref.17), the absence of EIP and the existence of CV of various kinds are typical for Eq.(1). CV of variables calculated from the coefficients of Eq.1 are shown in Table 8. From the comparison of CV given in Table 8 with EIV of correlated parameters it is evident that under the experimental conditions many of those CV may be passed through. In this connection some problems of interest have arisen concerning, one the one hand, the very nature of CV themselves for various interacting parameters and the possible availability of various types of CV within EIV and, on the other hand, the questions which deal with the behavior of those CV in varying parameters of the particular system.

Moreover, it might be interesting to find out the connection between the problems relating to the peculiarities of CV and those which are concerned with different aspects of the reactivity of the system and its sensitivity to the alteration of interacting parameters.

As it is seen from Table 8, the types of CV, the values of

Table 8. CV of Variables σ^0, σ^-, Y and $10^3/T$ Calculated from the Data in Table 7.

Type of CV	Kind of CV	CV	Correlation parameter and experimental interval of its variation
$\hat{\bar{x}}_1(x_j)$	$-a_2a_{12}^{-1}$	-2.883	
	$-a_3a_{13}^{-1}$	0.087	
	$-a_4a_{14}^{-1}$	2.763	
$\hat{x}_1(x_jx_1)$	$-a_{23}a_{123}^{-1}$	0.481	σ^0
	$-a_{24}a_{124}^{-1}$	-3.136	
	$-a_{34}a_{134}^{-1}$	-0.144	-0.15 - +0.82
$\hat{\bar{x}}_1(x_jx_1x_m)$	$-a_{234}a_{1234}^{-1}$	0.451	
$\hat{x}_1(x_j)$	$-a_1a_{12}^{-1}$	2.547	
	$-a_3a_{23}^{-1}$	-0.336	
	$-a_4a_{24}^{-1}$	-2.433	
$\hat{x}_1(x_jx_1)$	$-a_{13}a_{123}^{-1}$	-1.856	σ^-
	$-a_{14}a_{124}^{-1}$	2.762	
	$-a_{34}a_{234}^{-1}$	0.325	-0.17 - +0.71
$\hat{x}_1(x_1x_1x_m)$	$-a_{134}a_{1234}^{-1}$	-1.015	
$\hat{x}_1(x_j)$	$-a_1a_{13}^{-1}$	-1.377	
	$-a_2a_{23}^{-1}$	-6.014	
	$-a_4a_{34}^{-1}$	52.13	
$\hat{x}_1(x_jx_1)$	$-a_{12}a_{123}^{-1}$	1.003	Y
	$-a_{14}a_{134}^{-1}$	-2.721	
	$-a_{24}a_{234}^{-1}$	-6.956	-1.05 - 3.56
$\hat{x}_1(x_jx_1x_m)$	$-a_{124}a_{1234}^{-1}$	1.000	
$\hat{x}_1(x_j)$	$-a_1a_{14}^{-1}$	2.055	
	$-a_2a_{24}^{-1}$	2.048	
	$-a_3a_{34}^{-1}$	2.455	
$\hat{x}_1(x_jx_1)$	$-a_{12}a_{124}^{-1}$	2.228	$10^3/T$
	$-a_{13}a_{134}^{-1}$	4.061	
	$-a_{23}a_{234}^{-1}$	2.369	+3.049 - +3.534
$\hat{x}_1(x_jx_1x_m)$	$-a_{123}a_{1234}^{-1}$	2.221	

6

which are within EIV are not the same for various interacting parameters of the system. Thus, for the parameter which characterizes the substituents in the group moving away (III) – $x_{II}(\sigma^{\circ})$, all the three types of CV: $\hat{x}_i(x_j)$; $\hat{x}_i(x_jx_l)$; $\hat{x}_i(x_jx_lx_m)$ are within EIV. For (Y) which characterizes the medium properties CV are of two latter types only, whereas for the parameter taking into account the properties of substituents in carbonium-immonium cation (II) – $x_I(\sigma^{-})$, only CV of type $\hat{x}_i(x_jx_I)$ are within EIV.

For the last remaining correlation parameter – temperature in our case – all the three types of CV cannot be obtained experimentally.

The above facta apperently point to a considerable difference in perturbation effects of interacting parameters of various kinds on the transition state of a reacting system. One owing to the lack of a unified scale for comparing various kinds of interacting factors a quantitative estimation presents some difficulties.

A thorough analysis of the above-mentioned difference and the comparison of the results of that analysis with experimental data are of interest by themselves and will be dealt with im further reports.

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Quantitative Account of the Influence of Structure,
Medium and Temperature on β-Polynitroalkylarylamines
Solvolysis Kinetics. II. Analysis of Different Vari-
ants of Four-Parameter Cross-Correlation with One

Fixed Parameter.

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The possibility of obtaining a number of dif-
ferent three-parameter cross-correlation equa-
tions with all cross-terms by alternately fi-
xing one of interacting parameters is illustrated
in terms of the solvolysis reaction of a broad se-
ries of β-polynitroalkylarylamines
$X_I O_6 H_4 NHCH_2 C(NO_2)_2 C_6 H_4 X_{II}$. The resulting equations
are the special case of the more general four-
parameter equation which gives all relating dis-
turbing influence possible in a given reaction
system.

The critical values (CV) of varied parameters have
been calculated, on the strength of which an at-
tempt has been made to compare the extent of per-
turbation effect caused by some parameters upon
others. As a quantitative measure of a comparative
effect of perturbation influences it is suggested
to use the ratio of sensitivity coefficients at
appropriate additive or cross-terms in the equ-
ations used.

Earlier [1,2,3] it was shown that in Mannich's reactions of

solvolysis of polynitro-bases the interaction between elec-
tronic effects of X_I and X_{II} substituents is perceptibly di-
splayed, the appreciable perturbating influence of external
factors, viz the solvent and temperature being noted[3].

Theoretically the reaction system which includes several
related factors can be described by the equation of multi-
linear regression with all cross-terms[4,5].In the case of four
parameters (the constants of two variable substituents, the
characteristics of a solvent and temperature) this equation
may be respresented as follows:

$$f(x_1, x_2, x_3, x_4) = f_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 +$$
$$+ a_{12} x_1 x_2 + a_{13} x_1 x_3 + a_{14} x_1 x_4 + a_{23} x_2 x_3 + a_{24} x_2 x_4 +$$
$$+ a_{34} x_3 x_4 + a_{123} x_1 x_2 x_3 + a_{124} x_1 x_2 x_4 + a_{134} x_1 x_3 x_4 +$$
$$+ a_{234} x_2 x_3 x_4 + a_{1234} x_1 x_2 x_3 x_4 \qquad (1)$$

In the above case all the coefficients of such an equati-
on are the arbitrary values (not interrelated)[3]. It is evident
that the susceptibility parameters before cross-terms can
be considered as a measure of perturbations externed by the
interactions of various kinds upon one another[4].

Let us consider Eq. (1) with one of the varied parameters
.e.g. x_4 [*), being fixed.

$$f(x_1, x_2, x_3, x_4) = (f_0 + a_4 x_4) + (a_1 + a_{14} x_4) x_1 +$$
$$+ (a_2 + a_{24} x_4) x_2 + (a_3 + a_{34} x_4) x_3 + (a_{12} + a_{124} x_4) x_1 x_2 +$$
$$+ (a_{13} + a_{134} x_4) x_1 x_3 + (a_{23} + a_{234} x_4) x_2 x_3 +$$
$$+ (a_{123} + a_{1234} x_4) x_1 x_2 x_3 \qquad (2)$$

[*)] We deliberately do not define a fixed parameter as in this
particular case .Its choice is quite arbitrary,and consequen-
tly the conclusions made on such consideration will be al-
so true with respect to other interacting parameters.

It is clear that the coefficients of the equation of that kind are the linear functions of a fixed parameter (x_4). Thus, having written Eq. (2) in the following way:

$$f' = f'_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 +$$
$$+ b_{23} x_2 x_3 + b_{123} x_1 x_2 x_3 \tag{3}$$

$$\text{where} \quad \left. \begin{array}{l} f'_0 = f_0 + a_4 x_4 \\ b_1 = a_1 + a_{14} x_4 \\ b_2 = a_2 + a_{24} x_4 \\ b_3 = a_3 + a_{34} x_4 \\ b_{12} = a_{12} + a_{124} x_4 \\ b_{13} = a_{13} + a_{134} x_4 \\ b_{23} = a_{23} + a_{234} x_4 \\ b_{123} = a_{123} + a_{1234} x_4 \end{array} \right\} \tag{4}$$

we get the series of three-parameter equations of cross-correlation for the reaction system which is acted upon by the same four parameters. If one knows the coefficients (4) of such multiparameter cross-correlations one may calculate very well the CV's for any varied parameter[6], thereby getting an information on mutual disturbing influence (or on its absence) exerted on the reaction system by the interactions of various kinds.

Indeed, the CV for any parameter show, under what conditions the reaction system is not influenced by the perturbing effects of either one or several interacting parameters at the same time (this is shown by the type of CV); under what conditions the direction of the influence changes. They also show by means of what kinds of changes of parameters three are obtained such conditions under which not only the amount of the total interaction effect but also its sign change.

As is shown by Eq. (2) there are 28 CV of parameters for Eq. (1) (see Ref. 3)

$$\begin{cases} 12 \text{ CV's of type} & \hat{x}_i(x_j) = -a_j a_{ij}^{-1} \\ 12 \text{ CV's of type} & \hat{x}_i(x_j x_l) = -a_{jl} a_{ijl}^{-1} \\ 4 \text{ CV's of type} & \hat{x}_i(x_j x_l x_m) = -a_{jlm} a_{ijlm}^{-1} \end{cases} \quad (5)$$

Given the particular influence of x_j with CV type $\hat{x}_i(x_j)$ the sensitivity factor in Eq.(2) is equal to zero. In the transition through this CV the sign of a particular factor will be of opposite sign with any of CV types $\hat{x}_i(x_j x_l)$ the sensitivity factor will be equal to zero under the influence of $x_j x_l$ in Eq.(2) and if there is a change of CV of type $\hat{x}_i(x_j x_l x_m)$ in the experimental interval, the opposite sign will be derived with triple product of interacting factors of Eq.(2).

The analysis of the system of possible three-parameter equations (in our case four systems) derived with fixing any of four interacting parameters on the levels obtained experimentally confirms fully the above considerations.

First, as it is to be expected, all coefficients of cross-correlations do depend linearly upon a parameter being fixed.

Second, according to the change of the value and the sign of sensitivity factors both before additive and cross-terms we are able to find out the most sensitive interacting parameters in a particular reaction system, thereby determining the extent of perturbation effect of different reaction factors.

By a more sensitive parameter in a system we mean such a parameter by fixing of which on different levels within the experimental interval of variation (EIV) there is not only the change of a value but also that of a sensitivity factor in a multiparameter equation (in this particular case in a three-parameter equation). And this, in its turn, is due to the existence of CV for a fixed parameter ih (EIV). It should be noted the more such CV's (of different types if possible) can be reached under the conditions of the experiment, the more sensitive is the parameter towards external perturbations in the reaction systems.

Table 1. Parameters of Correlation Equation $\lg K = \lg K_0 + a_1 \sigma° + a_3 Y + a_4 10^3/T + a_{13} \sigma° Y + a_{14} \sigma° 10^3/T + a_{34} Y 10^3/T + a_{134} \sigma° Y 10^3/T$ and the CV's Computated in Terms of the Values of Correlation Sensitivity Parameters (1)[1].

Type of CV	Kind of CV	CV	X_I	p-CH$_3$	H	p-Br	m-Br	p-COOCH$_3$	m-NO$_2$
			$\lg K_0$	11.820	12.476	13.372	13.986	14.932	15.217
$\hat{x}_1(x_j)$	$\hat{\sigma}^-(\sigma°)$	2.44	$-a_1$	3.638	3.411	3.100	2.887	2.559	2.460
	$\hat{\sigma}^-(Y)$	-0.34	a_3	0.106	0.216	0.365	0.467	0.624	0.672
	$\hat{\sigma}^-(10^3/T)$	-2.43	$-a_4$	4.266	4.587	5.024	5.324	5.785	5.925
$\hat{x}_1(x_j x_1)$	$\hat{\sigma}^-(\sigma° Y)$	-1.86	$-a_{13}$	2.249	2.476	2.785	2.997	3.325	3.423
	$\hat{\sigma}^-(\sigma°10^3/T)$	2.76	a_{14}	1.762	1.660	1.520	1.425	1.278	1.233
	$\hat{\sigma}^-(Y 10^3/T)$	0.33	a_{34}	0.134	0.088	0.025	-0.018	-0.085	-0.105
$\hat{x}_1(x_j x_1 x_m)$	$\hat{\sigma}^-(\sigma° Y 10^3/T)$	-1.02	a_{134}	0.508	0.610	0.750	0.845	0.992	1.037

Note: The CV's underlined are within the experimental interval of the variation of the fixed parameter.

<u>Table 2.</u> Parameters of Correlation Equation $\lg K = \lg K_0 + a_2 \sigma^- + a_3 Y + a_4 \, 10^3/T + a_{23} \sigma^- Y + a_{24} \sigma^- 10^3/T + a_{34} Y \, 10^3/T + a_{234} \sigma^- Y \, 10^3/T$ and the CV's

Computated in Terms of the Values of Correlation Sensitivity Parameters (1)[1].

Type of CV	Kind of CV	CV	X_{II}	p-CH$_3$	p-OCH$_3$	H	p-Br	m-Cl	m-NO$_2$	p-NO$_2$
			$\lg K_0$	12.988	12.885	12.476	11.589	11.214	10.089	9.679
$\hat{x}_1(\hat{x}_j)$	$\hat{\sigma}°(\sigma^-)$	-2.88	a_2	3.660	3.701	3.861	4.209	4.356	4.798	4.959
	$\hat{\sigma}°(Y)$	0.09	a_3	0.587	0.513	0.216	-0.428	-0.700	-1.517	-1.814
	$\hat{\sigma}°(10^3/T)$	2.76	$-a_4$	4.836	4.786	4.587	4.155	3.973	3.425	3.226
$\hat{x}_1(\hat{x}_j \hat{x}_1)$	$\hat{\sigma}°(\sigma^- Y)$	0.48	a_{23}	0.842	0.802	0.642	0.295	0.148	-0.292	-0.452
	$\hat{\sigma}°(10^3/T)$	-3.14	$-a_{24}$	1.795	1.813	1.885	2.041	2.107	2.305	2.377
	$\hat{\sigma}°(Y \, 10^3/T)$	-0.14	a_{34}	-0.004	0.015	0.088	0.246	0.313	0.515	0.588
$\hat{x}_1(\hat{x}_j \hat{x}_1 \hat{x}_m)$	$\hat{\sigma}°(\sigma^- Y \, 10^3/T)$	0.45	a_{234}	-0.361	-0.343	-0.271	-0.115	-0.049	0.150	0.222

Note: The CV's underlined are within the experimental interval of the variation of the
     fixed parameter.

Table 3. Parameters of Correlation Equation $\lg K = \lg K_0 + a_1 \sigma^\circ + a_2 \sigma^- + a_4 \, 10^3/T + a_{12} \sigma^\circ \sigma^- + a_{14} \sigma^\circ \, 10^3/T + a_{24} \sigma^- \, 10^3/T + a_{124} \sigma^\circ \sigma^- \, 10^3/T$ and the CV's Computated in Terms of the Values of Correlation Sensitivity Parameters (1)[1].

Type of CV	Kind of CV	CV	Solvent	H_2O	30%	50%	70%	80%	MeOH
			$\lg K_0$	13.244	13.052	12.896	12.700	12.569	12.250
$\hat{x}_1(x_j)$	$\hat{Y}(\sigma^\circ)$	-1.38	$-a_1$	12.223	10.020	8.238	5.985	4.475	0.811
	$\hat{Y}(\sigma^-)$	-0.01	a_2	6.147	5.576	5.113	4.529	4.137	3.187
	$\hat{Y}(10^3/T)$	-52.1	$-a_4$	4.275	4.353	4.416	4.496	4.549	4.679
$\hat{x}_1(x_j x_1)$	$\hat{Y}(\sigma^\circ \sigma^-)$	1.00	a_{12}	-3.414	-2.226	-1.264	-0.050	0.765	2.740
	$\hat{Y}(\sigma^\circ 10^3/T)$	-2.72	a_{14}	3.831	3.289	2.849	2.294	1.922	1.019
	$\hat{Y}(\sigma^- 10^3/T)$	-6.96	$-a_{24}$	2.849	2.608	2.413	2.166	2.001	1.600
$\hat{x}_1(x_j x_1 x_m)$	$\hat{Y}(\sigma^\circ \sigma^- 10^3/T)$	1.00	a_{124}	1.540	1.005	0.572	0.025	-0.342	-1.232

Note: The CV's underlined are within the experimental interval of the variation of the fixed parameter.

Table 4. Parameters of Correlation Equation $\lg K = \lg K_0 + a_1 \sigma^\circ + a_2 \sigma^- + a_3 Y + a_{12} \sigma^\circ \sigma^- + a_{13} \sigma^\circ Y + a_{23} \sigma^- Y + a_{123} \sigma^\circ \sigma^- Y$ and CV's computated in Terms of the Values of Correlation Sensitivity Parameters (1)[1].

Type CV	Kind of CV	CV	$T,\,^\circ K$	283	288	298	308	328
	$\hat{\ }$		$-\lg K_0$	3.730	3.450	2.916	2.413	1.510
$\hat{x}_1(x_j)$	$10^3/T(\hat{\sigma}^\circ)$	2.06	a_1	2.454	2.353	2.159	1.978	1.650
	$10^3/T(\hat{\sigma}^-)$	2.05	$-a_2$	2.799	2.683	2.463	2.258	1.886
	$10^3/T(\hat{Y})$	2.45	a_3	0.527	0.520	0.510	0.500	0.484
$\hat{x}_1(x_j x_1)$	$10^3/T(\hat{\sigma}^\circ \hat{\sigma}^-)$	2.23	$-a_{12}$	0.784	0.747	0.677	0.612	0.495
	$10^3/T(\hat{\sigma}^\circ \hat{Y})$	4.06	$-a_{13}$	0.321	0.358	0.429	0.495	0.615
	$10^3/T(\hat{\sigma}^- \hat{Y})$	2.37	$-a_{23}$	0.315	0.299	0.267	0.238	0.185
$\hat{x}_1(x_j x_1 x_m)$	$10^3/T(\hat{\sigma}^\circ \hat{\sigma}^- \hat{Y})$	2.22	a_{123}	0.788	0.753	0.683	0.617	0.498

Consequently, the more sensitive is the parameter towards external pertutbations, the less it has the power to cause more or less significant influence on reactivity. On the contrary, the least sensitive parameter causes the greatest disturbances in influencing the reaction system of other interacting factors.

The comparison of the sensitivity coefficients in Tables 1 ÷ 4 with the CV's for fixed parameters made it possible to establish the fact that for our system the most sensitive factor proves to be the influence of the substituents on the reaction center (see Table 2) in the leaving anion (X_{II}). It is in this case that we get full information[*] on various types of interaction in transition state among various factors forming the reaction system.

Indeed, at $\hat{\sigma}^\circ = \hat{\sigma}^\circ = 0.09$ the solvolysis rate of $X_I C_6 H_4 NHCH_2 C(NO_2)_2 C_6 H_4 X_{II}$ (I) remains constant on changing the solvent composition, in other words, the systems reactivity is determined only by the charge of carbonium-immonium cation and by temperature and it is easy to see that the influence of those factors is oppositely directed (cf. $CV\hat{\sigma}^\circ(\sigma^- Y) = 0.48$; $CV\hat{\sigma}^\circ(10^3/T\ Y) = -0.14$ and $CV\hat{\sigma}^\circ (Y) = 0.09$). It follows that if we take into consideration all three interacting factors the value of CV of a particular type will be more than 0.09 (in Table 2 $CV\hat{\sigma}^\circ$ ($\sigma^-\ Y\ 10^3/T$) = 0.45 [**]). It is at these points that the changing of a sign of a particular sensitivity factor takes place (see Tables 1, 2, 3 and Figures

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[*] In (EIV) there are CV's of all the three types possible in this case $\hat{x}_i(x_j)$; $\hat{x}_i(x_j x_l)$; $\hat{x}_i(x_j x_l x_m)$.

[**] It is to be pointed out that tha value of CV of type $\hat{x}_i(x_j x_l x_m)$ is nearly equal in its absolute value to the sum of all other types of CV's in (EIV) given.

1 + 6). It is to be noted that the quantity of a critical value of type $x_i(x_jx_1x_m)$ (see Fig. 4,5,6) remains constant on variation of any pairs of interacting parameters, which confirms once more the independence of a critical value of correlated quantity of any correlated parameter being fixed at the isoparametrical point.Thus, for the first time it has been possible to corroborate experimentally the predicted phenomenon of isoparametricity for multi-parameter correlations[6,7]. Temperature (see Table 4) is the parameter which responds least to perturbations caused by other interacting factors.

The parameter which reasonds least to disturbances caused by other interacting factors is temperature (see Table 4).

The intermediate place between T and σ^o is occupied by the parameters which characterize the changes of medium properties and the carbonium-immonium cation structure (Y and σ^- respectively). This can be represented schematically in this following way:

$$10^3/T \; > \; \sigma^- \; > \; Y \; > \; \sigma^o \qquad (6)$$

Thus, the analysis of critical values of different types for all varied parameters confirmed the assumption as to the effects of various factors being non-equivalent in the system studied.

Also, given the system of three-parameter equations, one might make an attempt to compare one or another types of interaction. It seems possible to compare the extent of disturbing effects caused by various types of interaction on the reaction system using coefficient ratios with appropriate cross terms in the equations of type (1) or (2)(just as the sensitivity parameter ratios before additive terms are the measure of disturbances exerted by one interacting parameter upon another one).For example, the ratios $\gamma = a_{12}/a_{13}$ (see equation (1)) and $\eta = b_{12}/b_{13}$ (see equation (3))may serve as a measure of the intensity of the perturbations between the first and the second type of interaction as compared to

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the first and the third. It is evident that $\acute{\psi} = \eta - \gamma$ reflects the influence of a parameter being fixed upon these types of interaction. For the simultaneous participation of three interacting parameters we get a_{123}/a_{124}, etc.

At the same time, the ratios of sensitivity coefficients before additive terms make it possible to trace the influence of each independent parameter on the reaction system. Also the comparison of sucn relationships of various types as applied to a certain fixed parameter is useful in the quantitative estimation of that influence.

Up to now such estimation presents some difficulty because there is no unified scale for comparing interacting factors which differ in their character.

So it is evident that the picture of interaction of n parameters (e.g. three of them) is specified by the level being fixed of n+ the first (in our case the fourth) parameter on the constant background of which the special cases of mutual influence of the variables chosen may be quantitatively assessed. The dynamics of a reaction system is established by the fact that in considering various fixed levels of one parameter alone, we already get information on when and under what conditions the interaction intensity of the factors considered may change both its quantity and its directions. In other words, the interdependence of coefficients for special cases of general multiparameter dependence does not stimulate a search for the interrelation between the reactivity of the system as a whole and the sensitivity parameters of various few-parameter correlation equations.
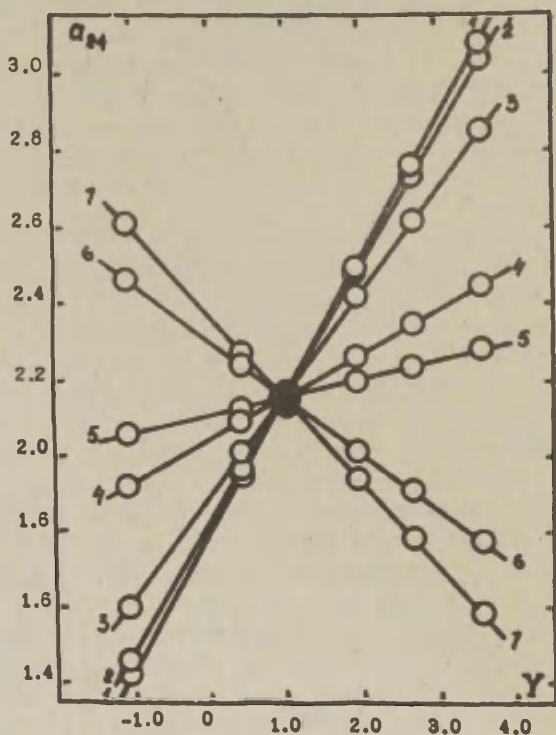
Fig. 1 Changing of the trend of the dependence of a_{24} on the solvent while passing through $\hat{y}$ ($6° 6^- 10^3/T$) for $X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$ series. 1 – p-CH_3; 2 = p-OCH_3; 3 – H, 4 – p-Br; 5-m-Cl; 6 – m-NO_2; 7 – p-NO_2
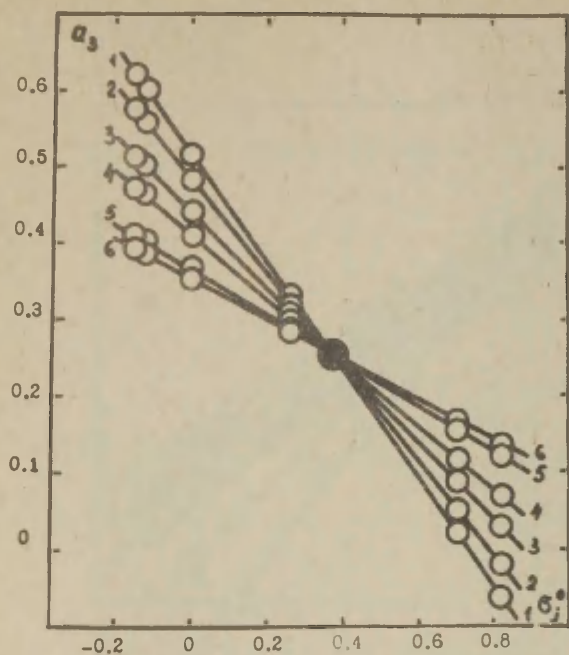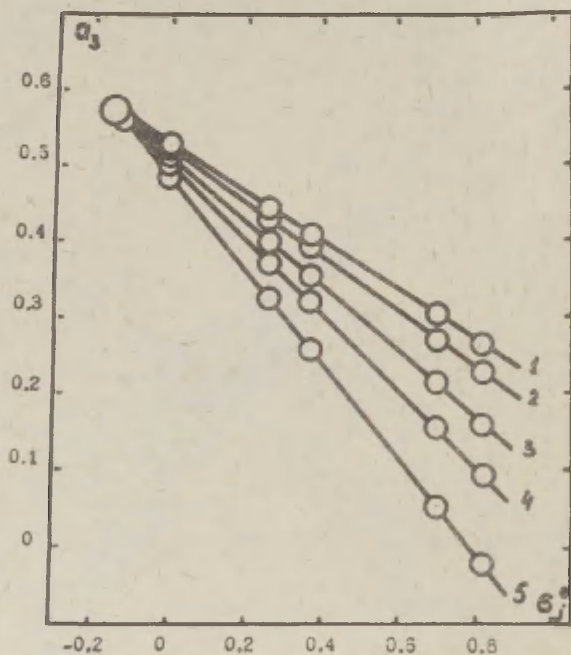
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Fig. 2 Changing of the trend of the dependence of a_3 on X_p structure while passing through $\sigma^o(\sigma^-y)$ for $X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$ at $T=328^oK$. X_1: 1 – p-CH$_3$; 2– H; 3 – p-Br; 4 – m-Br, 5 – p-COOCH$_3$; 6 – m-NO$_2$

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Fig. 3 Changing of the trend of the dependence of
a_3 on X_p structure while passing through
$\theta^\circ (y \ 10^3/T)$ for solvolysis of
$C_6H_5NHCH_2C(NO_2)_2C_6H_4X_p$ at various temperatures.
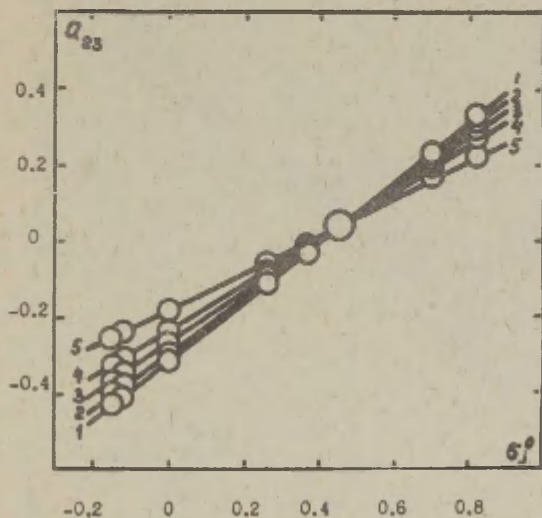$1-283^\circ K$; $2-288^\circ K$; $3-298^\circ K$; $4-308^\circ K$; $5-328^\circ K$

Fig. 4 Changing of the trend of the dependence of
a_{23} on X_p structure while passing through
$\hat{G}^o$ $(G^- y \ 10^3/T)$ for various temperatures
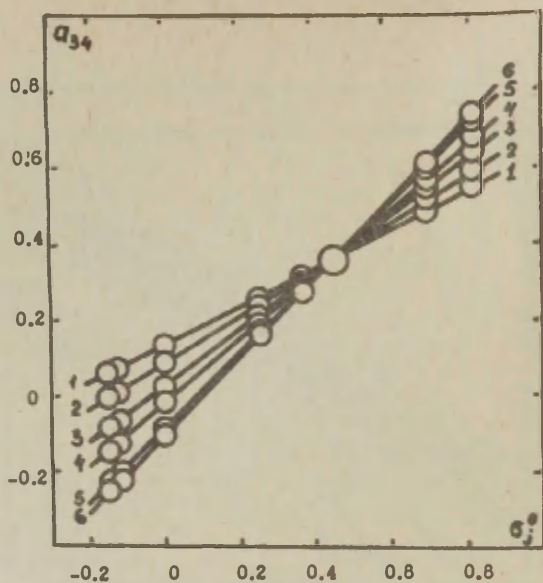1-283°K; 2-288°K; 3-298°K; 4-358°K; 5-328°K

Fig. 5 Changing of the trend of the dependence a_{34}
        on X_p structure while passing through
        $\hat{6}^0(\sigma-\vartheta_{10}^3/T)$ for $X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$
        X_1: 1 - p-CH$_3$; 2 - H; 3 - p-Br; 4 - m-Br;
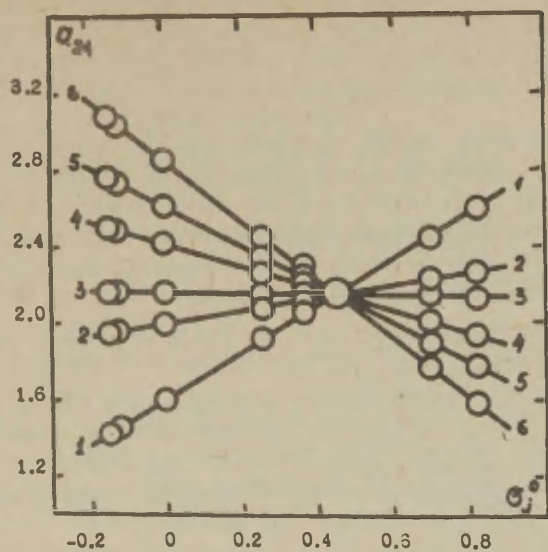   5 - p-COOCH$_3$; 6 - m-NO$_2$

Fig. 6 Changing of the trend of the dependence a_{24}
on X_p structure while passing through
$\hat{\sigma}^\circ(\hat{\sigma} - y_{10}^3/T)$ for different solvents.
1 - MeOH; 2 - 80%(^{V}/v)MeOH; 3 - 70%(^{V}/v)MeOH;
4 - 50%(^{V}/v)MeOH;

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QUANTITATIVE CONSIDERATION OF INFLUENCE OF
STRUCTURE, MEDIUM AND TEMPERATURE ON KINET-
ICS OF SOLVOLYSIS OF β-POLYNITROALKYL-
ARYLAMINES. III. ANALYSIS OF TWO-PARAMETRIC
CROSS-CORRELATIONS

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Kinetics of solvolysis of
$X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X$ (I) in the aqueous methanol at
several temperatures was investigated. Using various
types of two-parametric cross-correlation equations as
an example, the discussion of experimental data is car-
ried on. It's shown that appearing to be special cases
of the general multiparametric dependence such equa-
tions possess characteristics of isoparametrical ef-
fect (IPE). Different formal dependences of isopara-
metric values (IPV) of any parameter varied are anal-
yzed.

The possibility of changing signs of the sensitiv-
ity parameters both before cross- and additive terms
of such equations is shown experimentally.

The real system accounting for mutual perturbing influ-
ence of temperature, medium properties, and substituent ef-
fects on solvolysis of broad series of Mannich β-polynitro-
bases is described with multi-parametric cross- correlation
equation:[1,2]

$$f(x_1, x_2, x_3, x_4) = f_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 +$$
$$+ a_{12}x_1x_2 + a_{13}x_1x_3 + a_{14}x_1x_3 + a_{23}x_2x_3 + a_{24}x_2x_4 +$$
$$+ a_{34}x_3x_4 + a_{123}x_1x_2x_3 + a_{124}x_1x_2x_4 + a_{134}x_1x_3x_4 +$$
$$a_{234}x_2x_3x_4 + a_{1234}x_1x_2x_3x_4 \tag{1}$$

Fixing any two parameters (e.g. x_4 and x_3) out of four interacting in the system, it is obtained by Eq. (1):

$$f(x_1, x_2, x_3, x_4) = (f_0 + a_4x_4) + (a_3 + a_{34}x_4) x_3 +$$
$$+ (a_1 + a_{14}x_4) + (a_{13} + a_{134}x_4) x_3 x_1 + (a_2 + a_{24}x_4) + \tag{2}$$
$$+ (a_{23} + a_{234}x_4) x_3 x_2 + (a_{12} + a_{124}x_4) +$$
$$+ (a_{123} + a_{1234}x_4) x_3 x_1x_2$$

Eq. (2) is a two-parametric equation with a cross-term:

$$f = c_0 + c_1x_1 + c_2x_2 + c_{12}x_1x_2, \tag{3}$$

where

$$c_0 = (f_0 + a_4x_4) + (a_3 + a_{34}x_4) x_3$$
$$c_1 = (a_1 + a_{14}x_4) + (a_{13} + a_{134}x_4) x_3 \tag{4}$$
$$c_2 = (a_2 + a_{24}x_4) + (a_{23} + a_{234}x_4) x_3$$
$$c_{12} = (a_{12} + a_{124}x_4) + (a_{123} + a_{1234}x_4) x_3$$

All coefficients of Eq. (2) are evidently linear functions of x_3 (x_4 being fixed) and of x_4 (x_3 being fixed), whereas function of coefficients of Eq. (3) (parameters x_3 and x_4 being varied at at time) is a hyperbolic paraboloid surface.[3]

Eq. (2) possesses already characteristics of isoparametrical effect (IPE)[3,4] Due to Eq. (3) IPV x_1 and x_2 are:

$$x_1 = - c_2c_{12}^{-1} \quad \text{and} \quad x_2 = - c_1c_{12}^{-1} \tag{5}$$

or
$$x_1 = - \frac{(a_2 + a_{24}x_4) + (a_{23} + a_{234}x_4) x_3}{(a_{12} + a_{124}x_4) + (a_{123} + a_{1234}x_4)x_3} \tag{6}$$
$$x_2 = - \frac{(a_1 + a_{14}x_4) + (a_{13} + a_{134}x_4) x_3}{(a_{12} + a_{124}x_4) + (a_{123} + a_{1234}x_4)x_3}$$

According to Eq. (6), x, and x_2 are hyperbolae relative to
x_3 (x_4 being fixed) or relative to x_4 (x_3 being fixed). But,
if $x_4 = - a_{123}/a_{1234}$ i.e. if x_4 strikes occasionally point
$x_4(x_1,x_2,x_3)$, then functions x_1 and x_2 of x_3 are linear
(point $x_4(x_1 x_2,x_3)$ is a critical value for x_4 variable rel-
ative to x_1, x_2, x_3 variables). Analoguously, the $x_3(x_1 x_2,x_4)$
condition being occasionally realized, functions x, and x_2
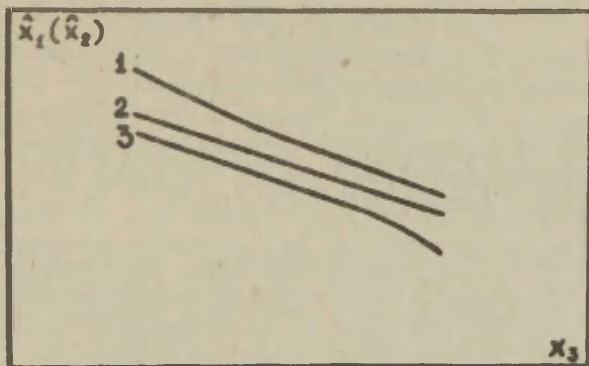of x_4 will be linear as well (see Fig. 1)

Fig. 1   Changing of the trend of the formal dependence
x_1(or x_2) of x_3 at different values of x_4
1 - x_4 x_4 (x_1, x_2, x_3) or x_4 $x_4(x_1,x_2,x_3)$
2 - $x_4 = x_4$ (x_1, x_2, $\bar{x}_3$)
3 - x_4 x_4 (x_1, x_2, x_3) or x_4 $x_4(x_1,x_2,\bar{x}_3)$
Then, according to Eq. (6), at the point

$$x_3 = - \frac{a_{12} + a_{124}x_4}{a_{123} + a_{1234}x_4} \qquad (7)$$

hyperbolic functions $x_1 = (x_3)$ suffer discontinuety (see
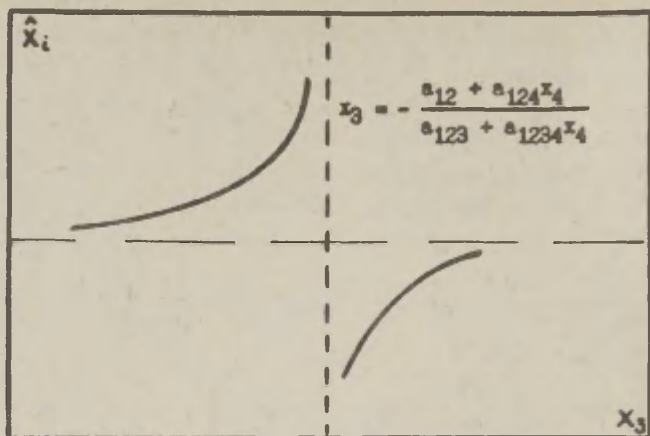Fig. 2).

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Fig. 2   Formal view of the dependence of CV
of any parameter upon x_3

$$x_3 = - \frac{a_{12} + a_{124}x_4}{a_{123} + a_{1234}x_4}$$

Due to formal analysis given above, twoparametric
equations apparently do not work when describing correctly
the influence of a great number of interacting factors on
the system reactivity as both values of sensitivity coeffi-
cients of the equations and values of functions correlated,
depend upon parameters fixed.

Meanwhile, recently the traditional explanation of dif-
ferent reaction mechanisms[5-9] reduces to analysis of experi-
mental data, obtained at the same temperature in a single
solvent only.

With multi-parametric correlation equations[10,10],these
data are utilized to account for the influence of a few
groups of variable substituents in molecules of different
organic compounds upon the rate and equilibrium constants.

However, without taking into consideration all the pos-
sible mutual perturbations in the given system, one cannot
use sensitivity parameters of two-parametric equations for
quantitative estimation of system reactivity even approxi-
mately. The influence of not only internal factors (struc-
ture of substituents) but of external factors (solvent,
temperature, etc.) as well must be taken into account. Mean-

while, it is well known that in a great number of cases namely external factors influence the system reactivity most intensively. Besides, the lack of a cross term in the two-parametric equation isn't a sufficient mark to indicate the absence of perturbing influence between the parameters correlated.A cross term can vansh if the value of parameter fixed strikes occasionally CV zone of a corresponding type. Consequently, varying the earlier fixed parameter, a cross term[17] can appear, its value and sign being determined with corresponding values of the parameters fixed.

We do believe that analysis of mutual influence of substituent effects only, without regard for perturbation caused by temperature (in general, an attempt to generalize one- or twoparametric equations only, without taking into consideration the possible perturbing influence of any parameter fixed) not only leads to the restriction of the use of linear regressions, but reduces artificially the perspectives of more complete description of the behavior of the reaction system under various conditions. Such analysis does not present a complete picture of all possible interactions in the given system. This, in its turn, leads to restricted understanding of phenomenon and may result in erroneous quantitative interpretation.

Formal analysis shows, that if the behavior of the system is determined by four parameters, then a complex dependence of sensitivity coefficients upon the parameters fixed, appears in two-parametric cross- correlations. Therefore, we want to stress again, that as far as different parameters influence the system with different efficiency, the amount of the information about reaction system depends on what parameters are varied and which of them are fixed.

Moreover, due to comparative analysis of different types of CV and sensitivity coefficients in two, three- and four parametric cross-correlation equations, only taking into consideration multiple linear regressions of a higher order, a quantitative relationship between interacting factors can be detected. As to the values of sensitivity coefficients in

cross- correlations, changing of signs and behavior of a
set of different CV, all of them depend on the specific
relationships of a higher order. The singularities of these
relationships (the discontinuity of hyperbolae of CV, linearity
of CV, etc.) can be obtained experimentally only, i.e. in
the case of striking of CV (of a specific kind) of a corres-
ponding parameter into experimental range of variation.

To illustrate this, let's compare the coefficients of the
same equation (see Tables 1 and 2). The only difference is
that sensitivity coefficients are obtained at different tem-
peratures. But without undertaking such an experimental com-
parison, it would be rather hard to assume such a striking
change of the value and sign of a cross term. In fact, if
donor- acceptor properties of x, change (temperature being
constant) the value of interaction between solvent and the
charge of the leaving group changes as well. At another tem-
perature, the change of the structure of x, leads to the
change of the sign and value of a cross-term. It should be
reminded that <u>a single formal mechanism for a reaction se-
ries is analysed</u>

Table 1

Parameters of Correlation Eq.
$\lg k = \lg k_o + a_1{}^o + a_3 Y + a_{13}{}^o y$ at T = 328 K

x_1	$p-CH_3$	H	$p-Br$	$m-Br$	$p-COOCH_3$	$m-NO_2$
$-\lg k_o$	1.176	1.509	1.945	2.246	2.705	2.847
a_1	1.734	1.650	1.534	1.458	1.337	1.299
a_3	0.515	0.484	0.441	0.412	0.365	0.352
a_{13}	-0.700	-0.616	-0.498	-0.421	-0.310	-0.261
Isoparametric Constants						
^{o}	0.74	0.79	0.89	0.98	1.18	1.35
y	2.48	2.68	3.08	3.46	4.31	4.98

Parameters of Correlation Eq.

$$\lg k_o = \lg k_0 + a_1 \sigma^\circ + a_3 Y + a_{13} \sigma^\circ Y \quad \text{at } T = 283 \text{ K}$$

X_1	p-CH$_3$	H	p-Br	m-Br	p-COOCH$_3$	m-NO$_2$
$- \lg K_o$	3.254	3.732	4.381	4.827	5.510	5.719
a_1	2.588	2.455	2.271	2.148	1.957	1.887
a_3	0.579	0.527	0.453	0.403	0.324	0.301
a_{13}	-0.454	-0.321	-0.125	-0.011	0.180	0.241
Isoparametric Constants						
σ°	1.28	1.64	3.62	36.6	-1.80	-1.25
Y	5.70	7.65	18.2	195	-10.9	-7.87

On the other hand, a three-parametric equation is enough
to obtain the value of the parameter fixed (see Ref. 2) at
which the absence of a cross term (for T = 283 K critical
value $\check{\sigma}^-(\sigma^\circ Y) = 0.407$) can be observed. Thus, only uti-
lizing a general threeparametric equation, a quantitative
description of the interaction is possible.

Paramaters of another twoparametric cross - correlation
are given in Tables 3 and 4. It differs from the previous
example in substitution of a parameter varied (Y) for para-
meter fixed (T) in order to stress again how important is
the choice of parameters interacting. The substitution. of
less sensitive parameter (T) for more sensitive one (Y)
changes greatly the substituent effect in the leaving anion
(1). In fact, the relationship between system reactivity and
sensitivity towards structure changes in X_p and variation of
medium properties leads to invariability of direction of the
dependence between lg k_o and a_{13} (see Tables 1 and 2). Hence,
at various temperature points, the interaction between σ°
and Y (i.e. mutual influence of electron effects of substit-
uents of X_p and ionzing power of solvent) results in chan-
ging of sign and sensitivity coefficients before a cross term.

Table 3

Parameters of Correlation Eq.

$$\lg k = \lg k_0 + a_1 \sigma° + a_4\, 10^3/T + a_{14}\, \sigma°\, 10^3/T$$
(In Water)

X_1	$p-CH_3$	H	$p-Br$	$m-Br$	$p-COOCH_3$	$m-NO_2$
$\lg k_0$	12.199	13.244	14.670	15.648	17.154	17.609
$-a_1$	11.643	12.223	13.015	13.558	14.394	14.647
$-a_4$	3.790	4.275	4.936	5.389	6.087	6.298
a_{14}	3.570	3.831	4.189	4.434	4.811	4.925
Isoparametric Constants						
$\sigma°$	1.06	1.12	1.18	1.22	1.27	1.28
$10^3/T$	3.26	3.19	3.11	3.06	2.99	2.97

Table 4

Parameters of Correlation Eq.

$$\lg k = \lg k_0 + a_1 \sigma° + a_4\, 10^3/T + a_{14}\, \sigma°\, 10^3/T$$
(In Methanol)

X_1	$p-CH_3$	H	$p-Br$	$m-Br$	$p-COOCH_3$	$m-NO_2$
$\lg k_0$	11.708	12.250	12.989	13.496	14.277	14.513
a_1	-1.277	-0.811	-0.176	-0.260	0.932	1.134
$-a_4$	4.407	4.679	5.050	5.304	5.696	5.815
a_{14}	1.229	1.019	0.734	0.538	0.236	0.145
Isoparametric Constants						
$\sigma°$	3.59	4.59	6.89	9.87	24.2	40.2
$10^3/T$	1.04	0.80	0.24	-0.48	-3.95	-7.85

On the contrary, if σ° interacts with T (see Tables 3 and 4) we observe the change of perturbing influence of both parameters varied upon the system. (The given influence being a function of solvent ionizing power). So, substituting water $(Y = +3.56)$ for methanol $(Y = -1.05)$, the direction of dependence between system reactivity $(lg\ k_0)$ and sensitivity towards structure changes in the leaving group (X_p) turns to be reverse. Moreover, here, the sign of sensitivity coefficient changes before an additive ( ) term too. (see Table 4) Formerely it was considered to be an unequivocal evidence of the change of the interaction mechanism of the system.

Comparing now IPV for the examples given with the CVS calculated by sensitivity coefficients of three-parametric equations (see Tables 5-8), the evident relation between them can be observed.

T a b l e   5

CV of the Parameters Calculated by Eq. $lg\ k =$
$= lg\ k_0 + a_1\ \sigma° + a_3 Y + a_4\ 10^3/T + a_{13}\ \sigma° Y + a_{14}\ \sigma°$
$10^3/T + a_{34}\ Y\ 10^3/T + a_{134}\ \sigma°\ 10^3/T$

Parameter and its ERV	Type of CV X_1	p-CH$_3$	H	p-Br	m-Br	p=COOCH$_3$	m-NO$_2$
σ°	σ°(Y)	0.06	0.09	0.13	0.16	0.19	0.20
-0.15 ±	σ°(10³/T)	2.40	2.76	3.30	3.74	4.53	4.81
+0.82	σ°(Y 10³/T)	-0.26	-0.14	-0.03	0.02	0.09	0.10
Y	Y (σ°)	-1.62	-1.38	-1.11	-0.96	-0.77	-0.72
-1.05 ÷	Y (10³/T)	31.8	52.1	201	-296	-68.1	-56.4
+3.56	Y (σ°10³/T)	-3.47	-2.72	-2.03	-1.69	-1.29	-1.19
10³/T	10³/T(σ°)	2.07	2.06	2.04	2.03	2.00	1.99
+3.05 +	10³/T(Y)	-0.79	-2.46	-14.6	25.9	7.34	6.40
+3.53	10³/T(σ°Y)	4.43	4.06	3.71	3.55	3.35	3.30

CV of Parameters Calculated by Eq. $\lg k = \lg k_o + a_2{}^- + a_3 Y + a_4\ 10^3/T + a_{23}{}^{-Y} + a_{24}{}^-\ 10^3/T + a_{34} Y\ 10^3/T + a_{234}{}^{-Y}\ 10^3/T$

Parameter and its ERV	CV Type X_p	p-CH$_3$	n-OCH$_3$	H	p-Br	m-Cl	m-NO$_2$	p-NO$_2$
$^-$	$^-(Y)$	−0.70	−0.64	−0.34	1.45	4.73	−5,20	−4.01
−0.17 ÷ +0.71	$^-(10^3/T)$	2.69	2.64	2.43	2.04	1.89	1.49	1.36
	$^-(Y,\ 10^3/T)$	−0.01	0.04	0.33	2.14	6.39	−3.43	−2.65
Y	$Y (^-)$	−4.35	−4.62	−6.01	−14.3	−29.4	16.4	10.9
−1.05 ÷ +3.56	$Y (10^3/T)$	−1209	319	52.1	16.9	12.7	6.65	5.49
	$Y (^-,\ 10^3/T)$	−4.97	−5.29	−6.96	−17.7	−43.0	15.4	10.7
$10^3/T$	$10^3/T(^-)$	2.04	2.04	2.05	2.06	2.07	2.08	2.09
+3.05 ÷ + 3.53	$10^3/T(Y)$	147	−34.2	−2.45	1.74	2.24	2.95	3.09
	$10^3/T(^-,\ Y)$	2.33	2.34	2.37	2.58	3.02	1.95	2.04

CV of Parameters Calculated by $\lg k = \lg k_0 + a_1{}^{\circ} + a_2{}^{-} + a_4 10^3/T + a_{12}{}^{\circ-} + a_{14}{}^{\circ} 10^3/T + a_{24}{}^{-} 10^3/T + a_{124}{}^{\circ-} 10^3/T$

Parameter and its ERV	CV Type	MeOH in mixture	0	30	50	70	80	100
$\circ$	$^{\circ}(\,^{-})$		1.80	2.51	4.05	90.6	-5.41	-1.16
- 0.15 ÷ + 0.82	$^{\circ}(10^3/T)$		1.12	1.32	1.55	1.96	2.37	4.59
	$^{\circ}(\,^{-},\,10^3/T)$		1.85	2.60	4.22	86.6	-5,85	-1,30
	$^{-}(\,^{9})$		-3,58	-4,50	-6,52	-120	5.85	0.30
- 0.17 ÷ + 0.71	$^{-}(10^3/T)$		-1.50	-1.67	-1.83	-2.08	-2,27	-2,92
	$^{-}(\,^{\circ},\,10^3/T)$		-2,49	-3.27	-4.98	-91.8	5.62	0.83
$10^3/T$	$10^3/T(\,^{\circ})$		3.19	3,05	2.89	2.61	2.33	0.80
+ 3.05 ÷ + 3.53	$10^3/T(\,^{--})$		2.16	2.14	2.12	2.09	2.07	1.99
	$10^3/T(\,^{\circ}\,^{-})$		2.22	2.22	2.21	2.20	2.24	2.22

CV of Parameters Calculated by $\lg k = \lg k_0 + a_1 6^\circ + a_2 6^- + a_3 Y + a_{12} 6^\circ 6^- + a_{13} 6^\circ Y + a_{28} 6^{-Y} + a_{123}$

Parameter and its ERV	CV Type T°K	283	288	298	308	328
6°	$6^\circ(6^-)$	-3.57	-3.59	-3.64	-3.69	-3.80
$-0.15 \div + 0.82$	$6^\circ(Y)$	1.64	1.45	1.19	1.01	0.79
	$6^\circ(6^-, Y)$	0.40	0.40	0.39	0.39	0.37
6^-	$6^-(6^\circ)$	3.13	3.15	3.19	3.23	3.34
$-0.17 \div + 0.71$	$6^-(Y)$	1.67	1.74	1.91	2.19	2.62
	$6^-(6^\circ, Y)$	0.41	0.48	0.63	0.80	1.24
Y	$Y(6^\circ)$	7.64	6.57	5.03	3.99	2.68
$-1.05 \div + 3.56$	$Y(6^-)$	-8.89	-8.97	-9.23	-9.49	-10.2
	$Y(6^\circ, 6^-)$	0.99	0.99	0.99	0.99	0.99

Moreover, only two parameters interacting, CV of different types (see Table 5-8) help one to perfectly understand the possible effects observed. Hyperbolae, illustrating the change of IPV .

Y as the function of the parameter fixed (6^-) are represented in Fig. 3. Discontinuity boundaries of the hyperbolae are marked with a dotted line[x]. The temperature inreasing, the hyperbolae turn to be straight lines. Therefore for T=328 K (e.g.) the experimental determination of the discontinuity point is impossible, though namely in this point system reactivity.

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[x] CV $6^-(6^\circ, Y)$ determining the discontinuity point, for all temperatures are given in Table 8. CV underlined holds within an ERV and can be de detected experimentally.
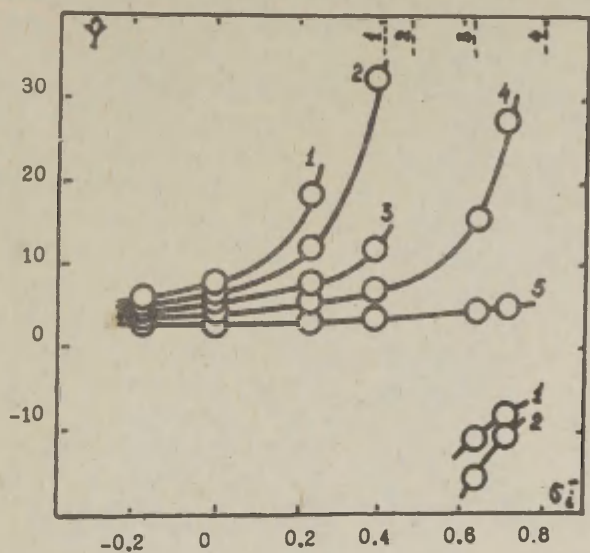
Fig. 3   Changing of the trend of function
$Y = f(6^-_1)$ at varions temperatures
1 – 283°K; 2 – 288°K; 3 – 298° K;
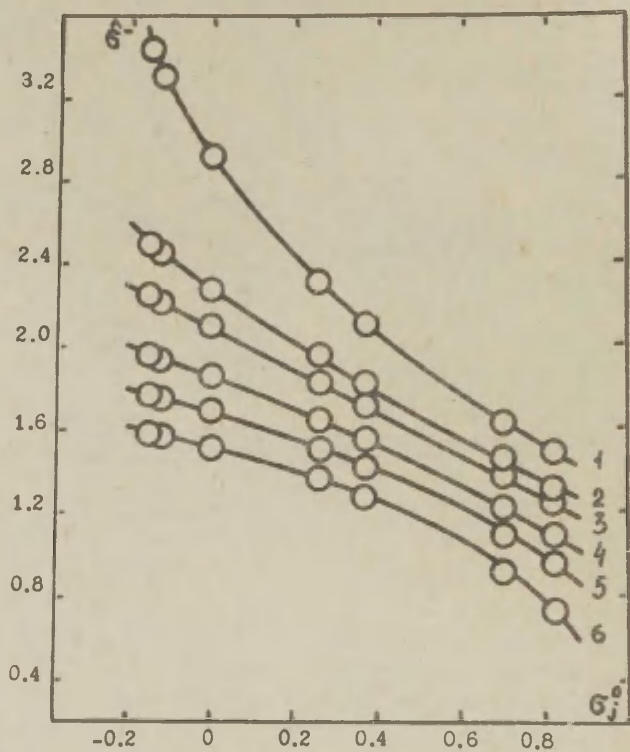4 – 308°K; 5 – 328°K

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Fig. 4 Changing of the trend of function
$\hat{\sigma}_i^- = f(\sigma_j^o)$ in binary mixtures MeOH-H$_2$O
1 - MeOH; 2 - 80%($^V/_V$)MeOH; 3 - 70%($^V/_V$)MeOH;
4 - 50%($^V/_V$)MeOH; 5 - 30%($^V/_V$)MeOH; 6 - H$_2$O

is independent of the influence of σ^o and Y and the direction of the dependence turns to be reverse in "reactivity – sensitivity" plots. Consequently, confining oneself to a single value of the parameter fixed, the interpretation of the physical phenomenon may be absolutely erroneous.

Fig. 4 demonstrates another case of the transformation of hyperbolic dependence . It should be compared with Fig. 1. Here, IPV for the parameter correlated is determined by the presence of CV of the equation of a higher order. (Data of Table 6 and CV of a corresponding type for three-, and four-parametric equations[1,2] should be compared).

Thus, different types of relationship between critical values and isoparametric ones of any parameter interacting, correspond to different types of equations (four, – three, – and twoparametric). The less sensitive is parameter towards the influence of the rest reaction parameters, the simplier type of CV corresponds it within experimental range of variation; but it works only for simple (two-parametric) equations. On the contrary, for more sensitive parameters all types of CV can be obtained experimentally, beginning with four parametric equation (CV for four[1]– three[2]– and two-parametric equations should be compared. See Tables 1–11).

Moreover, due to the analysis of CV of multiparametric equations[1,2,3] if as great number of interacting factors as possible is used to describe the system reactivity, the sign changes both before cross- and additive term[3] in twoparametric equation, which at a first glance is absolutely unexpected. As to the sensitivity coefficients, their behavior is not always unambiguously determined by mutual influence of the parameters, interacting in the system. For example, the influence of structural parameters leads to the change of the sign[9] of a cross-term of a corresponding equation. However, for the interaction of such "insensitive" parameters as T and σ^-_i with solvent or σ^o_j, the direction of the charge of coefficients (but not the sign of the coefficients) changes. (The changes of lg k_o and a_4; lg k_o and a_2 should be compared. See Tables 10 and 11).

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Parameters of Correlation Eq. $\lg k = \lg k_o + a_1 \sigma° + a_2 \delta^- + a_{12} \sigma° \delta^-$ at T=328 K in Aqueous Methanol

v/v MeOH	$\lg k_o$	a_1	$-a_2$	a_{12}	$\sigma°$	δ^-
0	0.210	-0.543	2.539	1.281	1.98	0.43
30	-0.219	0.007	2.375	0.838	2.82	-0.01
50	-0.567	0.448	2.244	0.480	4.68	-0.93
70	-1.007	1.009	2.075	0.026	79.8	-38.8
80	-1.300	1.385	1.964	-0.277	-7.09	5.00
100	-2.015	2.296	1.691	-1.016	-1.66	2.26

T a b l e   10

Parameters of Correlation Eq. $\lg k = \lg k_o + a_2 \delta^- + a_4 \, 10^3/T + a_{24} \delta^- \, 10^3/T$ (Solvent-Water)

X_p	$\lg k_o$	a_2	$-a_4$	$-a_{24}$	δ^-	$10^3/T$
p-CH$_3$	15.078	6.659	4.849	3.080	-1.57	2.16
p-OCH$_3$	14.711	6.557	4.734	3.034	-1.56	2.16
H	13.224	6.147	4.275	2.849	-1.50	2.16
p-Br	10.066	5.260	3.388	2.449	-1.38	2.15
m-Cl	8.721	4.884	2.858	2.280	-1.25	2.14
m-NO$_2$	4.688	3.758	1.593	1.772	-0.90	2.12
p-NO$_2$	3.221	3.348	1.133	1.587	-0.71	2.11

T a b l e   11

(Solvent-Methanol)

X_p	$\lg k_o$	a_2	$-a_4$	$-a_{24}$	δ^-	$10^3/T$
p-CH$_3$	12.372	2.776	4.832	1.415	-3.41	1.96
p-OCH$_3$	12.347	2.858	4.801	1.452	-3.31	1.97
H	12.250	3.187	4.679	1.600	-2.92	1.99
p-Br	12.039	3.899	4.414	1.921	-2.30	2.03
m-Cl	11.950	4.201	4.302	2.056	-2.09	2.04
m-NO$_2$	11.682	5.105	3.965	2.463	-1.61	2.07
p-NO$_2$	11.585	5.434	3.843	2.610	-1.47	2.08

We want to stress again, that different parameters influence the system with different intensity and only utilizing cross‑correlations of a higher order, the quantitative relationship between parameters fixed and parameters varied can be detected.

Due to such analysis, it's possible both to explain the effects observed (e.q., to confirm the presence of isoparametric relationships and to estimate quantitatively the influence of substituents and solvent upon the system reactivity while transition through IPV takes place (see Tables 7 and 8) and to predict the phenomena not yet detected. In particular, Table 7 represents $CV\,\sigma^{\circ}(10^3/T)$ which, probably, will work in attempts to detect the inversion of the temperature influence ($/$) upon the system reactivity. In fact, the introduction of a few electronoaccepting groups into a leaving group is estimated by $\sigma^{\circ}=1.40$ (for two NO_2 groups, e.g.), whereas $\sigma^{\circ}=1.12$ (see Table 7) is enough for transition through IPV in water.

Consequently, undertaking such an experiment, it's possible to predict the existence of a <u>negative activation energy</u> (!?) for solvolysis.

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QUANTITATIVE CONSIDERATION OF INFLUENCE OF STRUCTURE, MEDIUM AND TEMPERATURE ON THE KINETICS OF SOLVOLYSIS OF β-POLYNITROALKYLARYLAMINE IV. ANALYSIS OF ONE-PARAMETRIC CORRELATIONS

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The perfect description of experimental data with the one-parametric linear regressions is obtained by the kinetic investigation of solvolysis of series of Mannich -polynitrobases at different temperatures. The equations obtained are shown to be special cases of the general multiparametric cross-correlation.

Different formal dependences determining the behavior of sensitivity factors of one-parametric equations under conditions of variation of interacting parameters have been investigated.

It is shown, that even utilizing a set of one-parametric equations, the rigorous quantitative estimate of all effects of the reaction system is impossible.

It was shown earlier[1-5] that the rate of solvolysis of Mannich polynitrobases depends essentially upon all the parameters interacting in the system.

The phenomenon observed is described[1] with multiparametric linear regression with all cross terms:

$$f(x_1, x_2, x_3, x_4) = f_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 +$$
$$+ a_{12} x_1, x_2 + a_{13} x_1 x_3 + a_{14} x_1 x_4 + a_{23} x_2 x_3 + a_{24} x_2 x_4 + \quad (1)$$
$$+ a_{34} x_3 x_4 + a_{123} x_1 x_2 x_3 + a_{124} x_1 x_2 x_4 + a_{134} x_1 x_3 x_4 +$$
$$+ a_{234} x_2 x_3 x_4 + a_{1234} x_1 x_2 x_3 x_4$$

II

One-parametric equation, i.e. an equation depending, e.g., on x_1 (x_4, x_3, and x_2 being fixed) is easily obtained from Eq.(1)

$$f(x_1, x_2, x_3, x_4) = (a_0 + a_4 x_4) + (a_3 + a_{34} x_4) x_3 +$$
$$+ (a_2 + a_{24} x_4) + (a_{23} + a_{234} x_4) x_3 x_2 + (a_1 + a_{14} x_4) + \qquad (2)$$
$$+ (a_{13} + a_{134} x_4) x_3 + (a_{12} + a_{124} x_4) + (a_{123} + a_{1234} x_4) x_3 x_2 x_1$$

or, the same

$$f = d_0 + d_1 x_1 \qquad (3)$$

where

$$d_0 = (a_0 + a_4 x_4) + (a_3 + a_{34} x_4) x_3 + (a_2 + a_{24} x_4) + \qquad (4)$$
$$+ (a_{23} + a_{234} x_4) x_3 x_2$$

$$d_1 = (a_1 + a_{14} x_4) + (a_{13} + a_{134} x_4) x_3 + (a_{12} + a_{124} x_4) + \qquad (5)$$
$$+ (a_{123} + a_{1234} x_4) x_3 x_2$$

Due to Eq. (3), d_0 and d_1 are linear functions of x_4 (x_3 and x_2 being fixed); x_3 (x_4 and x_2 being fixed), or x_2 (x_4 and x_3 being fixed).

The dependence of d_0 and d_1 upon two variables (the third value being fixed) is a hyperbolic paraboloid surface.[4] The dependence of d_0 and d_1 upon x_4, x_3 and x_2 varied at a time, is a surface of a higher order.

Thus, taking into consideration one-parametric dependences without regard for the influence of all perturbing factors, the rigorous quantitative description of the system is impossible. Also the explanation of the change of trends of dependences, positive or negative values of coefficients, and the interpretation of the results to explain system reactivity or interaction mechanism is impossible.

In fact, due to Eq. (5), if

$$x_2' = x_2 = -\frac{(a_1 + a_{14} x_4) + (a_{13} + a_{134} x_4) x_3}{(a_{12} + a_{124} x_4) + (a_{123} + a_{1234} x_4) x_3} \qquad (6)$$

then $d_1 = 0$. If $x_2 > \hat{x}_2$ and $x_2 < \hat{x}_2$, signs of d_1 differ. The formula, which describes the behavior of d_1 as dependent on x_4, x_3 and x_2 can be obtained by substitution of coefficients a_1, a_{1j}, a_{1j1} and a_{1234} into Eq. (5)

Also for d_0 the conclusion is valid. The equation for d_0 (lg k_0) at isoparametric point, i.e. when $x_2 = \hat{x}_2$, is as follows:

$$d_0 = (a_0 + a_4 x_4) + (a_3 + a_{34} x_4) x_3 -$$
$$- \frac{(a_2 + a_{24} x_4) + (a_{23} + a_{234} x_4) x_3 \, (a_1 + a_{14} x_4) + (a_{13} + a_{134} x_4) x_3}{(a_{12} + a_{124} x_4) + (a_{123} + a_{1234} x_4) x_3}$$

$$(7)$$

Thus, the complexity of equations for the description of system reactivity (d_0) and its sensitivity (d_1) towards the change of a number of interacting parameters is evident. Nevertheless, the opinion exists, that quantitative description in the "reactivity – sensitivity" plot (lg k_0 vs. ρ) is enough to assign an interaction mechanism to a particular type. As an example, small changes of ρ values in Hammett Taft and Grünwald-Winstein equations or changes of "reactivity – sensitivity" relationship are used this way.

But the matter is much more complicated. As an example, let us try to determine the relationship between system reactivity (lg k_0) and sensitivity (ρ) towards one of the parameter varied in order to observe the possible changes of the dependence under parameter variation condition.

x_2 can be obtained from Eq. (4)

$$x_2 = \frac{d_0 - (a_0 + a_4 x_4) + (a_3 + a_{34} x_4) x_3}{(a_2 + a_{24} x_4) + (a_{23} + a_{234} x_4) x_3}$$

$$(8)$$

This result is substituted into (5), the equation for d_1 follows:

$$d_1 = (a_1 + a_{14}x_4) + (a_{13} + a_{134}x_4)x_3 +$$

$$\div \frac{(a_{12} + a_{124}x_4) + (a_{123} + a_{1234}x_4)x_3}{(a_2 + a_{24}x_4) + (a_{23} + a_{234}x_4)x_3} \quad do -$$

$$- \frac{(a_0 + a_4 x_4) + (a_3 + a_{34}x_4)x_3}{(a_2 + a_{24}x_4) + (a_{23} + a_{234}x_4)x_3}$$

or

$$d_1 = (a_1 + a_{14}x_4) + (a_{13} + a_{134}x_4)x_3 -$$

$$- \frac{(a_0 + a_4 x_4) + (a_3 + a_{34}x_4)x_3}{(a_2 + a_{24}x_4) + (a_{23} + a_{234}x_4)x_3} \quad +$$

$$+ \frac{(a_{12} + a_{124}x_4) + (a_{123} + a_{1234}x_4)x_3}{(a_2 + a_{24}x_4) + (a_{23} + a_{234}x_4)x_3} \quad do \tag{9}$$

-i.e., d_1 and d_o are connected by the linear equation:

$$d_1 = A + Bdo, \quad \text{where} \tag{10}$$

$$A = (a_1 + a_{14}x_4) + (a_{13} + a_{134}x_4)x_3 -$$

$$- \frac{(a_0 + a_4 x_4) + (a_3 + a_{34}x_4)x_3}{(a_2 + a_{24}x_4) + (a_{23} + a_{234}x_4)x_3};$$

$$B = \frac{(a_{12} + a_{1234}x_4) + (a_{123} + a_{1234}x_4)x_3}{(a_2 + a_{24}x_4) + (a_{23} + a_{234}x_4)x_3}$$

It's seen now, that even the qualitative interpretation of
the linear dependence obtained for the system, including four
parameters is hindered. And to elucidate physical content of
such a dependence and to estimate it quantitatively seems for
us next to impossible.

Investigating the solvolysis of broad series of β-poly-
nitroalkylarylamins in various binary mixtures $H_2O-MeOH$, it's
possible, however, to observe the theoretically predicted[7,8]
inversion of influence of some parameters interacting, if the
choice of experimental range of variation of parameters is
successful. Practically, investigating the dependence of the
value correlated upon one of the parameter varied and plot-
ting then the family of straight lines for the set of values
of another parameter[6,8] the isoparametric function can be
obtained.

Direct experiments have shown the existence of the com-
pensation effect (isoparametric dependences) for a set of
parameters interacting (experimental data are given in Ref.1).
Thus, the predicted[1,3] change of signs of the sensitivity
coefficients in one-parametric equations (see Fig. 1÷4) while
passing through IPV is confirmed.

Tables 1-4 represent the parameters of correlation equa-
tions for a set of separate reaction series. These examples
give the comprehension of the perturbing influence of dif-
ferent factors on the system reactivity and, in particular,
illustrate the conditions under which the sign of some sen-
sitivity factors changes.

Moreover, due to the given values of coefficients one
might suggest, that IPV of one of the structural parameters
(see Fig. 5) can be obtained experimentally, which leads to
the inversion of temperature effect on the system reactivity.
Thus, at isoparametric point the activation energy should
equal zero, and while passing through such a point, the
activation energy should become negative.(!?) According to
the calculations,[3] such a case can be realized experimentally.

Due to examples given the relationships in multiparametric
non-homogenous reaction systems are rather complicated. This
makes one revize the way of describing reactivity and reaction
mechanisms with one-parametric (two-parametric) dependences.

These dependences are, evidently, special cases of the
general multiparametric linear regressions. So, utilizing
them, it's impossible to give quantitative description of all

interactions within a system.

The authers believe that general multiparametric dependences have to be used for the description of the system reactivity. The more reaction system will be described with such dependences, sooner the physical content of predictions and determinations used in correlations will be elucidated.

Correlation Parameters of Eq. $\lg k = \lg k_0 + a_2$
for Solvolysis of $X_1, C_6H_4NHCH_2C(NO_2)_2C_6H_4Xp$ at T=298 K

X_p	$v/_v$ MeOH	0	30	50	70	80	100
$p-CH_3$	$-\lg k_0$	1.196	1.707	2.120	2.642	2.993	3.842
	$-a_2$	3.677	3.348	3.082	2.746	2.521	1.974
$p-OCH_3$	$-\lg k_0$	1.176	1.676	2.080	2.591	2.933	3.764
	$-a_2$	3.625	3.314	3.063	2.745	2.532	2.016
H	$-\lg k_0$	1.100	1.554	1.921	2.385	2.696	3.451
	$-a_2$	3.414	3.177	2.984	2.741	2.578	2.184
$p-Br$	$-\lg k_0$	0.936	1.290	1.577	1.940	2.183	2.773
	$-a_2$	2.958	2.879	2.814	2.732	2.678	2.546
$m-Cl$	$-\lg k_0$	0.866	1.179	1.432	1.751	1.966	2.486
	$-a_2$	2.765	2.752	2.742	2.729	2.720	2.699
$m-PO_2$	$-\lg k_0$	0.652	0.844	0.995	1.186	1.314	1.625
	$-a_2$	2.187	2.374	2.526	2.718	2.846	3.159
$p-PO_2$	$-\lg k_0$	0.581	0.722	0.836	0.980	1.077	1.311
	$-a_2$	1.976	2.237	2.447	2.714	2.892	3.327

Footnote:

1) In all reaction series correlation coefficient
   is $0.9978 \geqslant V \leqslant 0.9999$

2) Standard deviation for all series is within
   $0.015 \geqslant S \leqslant 0.034$

3) While handling data with a least squares method,
   6 points were always used.

Correlation Parameters of Eq. $\lg k = \lg k_0 + a_4 10^3/T$
for Hydrolysis of $X_1 C_6 H_4 NHCH_2 C(NO_2)_2 \; C_6 H_4 Xp$

X_p	X_1	$p-CH_3$	H	$p-Br$	$m-Br$	$p-COOCH_3$	$m-NO_2$
$p-CH_3$	$\lg k_0$	13.946	15.078	16.623	17.681	19.313	19.806
	$-a_4$	4.326	4.849	5.564	6.054	6.808	7.036
$p-OCH_3$	$\lg k_0$	13.596	14.711	16.232	17.275	18.881	19.366
	$-a_4$	4.219	4.734	5.438	5.921	6.664	6.889
H	$\lg k_0$	12.199	13.244	14.670	15.648	17.154	17.609
	$-a_4$	3.790	4.275	4.936	5.389	6.087	6.298
$p-Br$	$\lg k_0$	9.172	10.066	11.286	12.123	13.411	13.800
	$-a_4$	2.862	3.278	3.847	4.236	4.836	5.017
$m-Cl$	$\lg k_0$	7.891	8.721	9.855	10.631	11.828	12.189
	$-a_4$	2.469	2.857	3.386	3.748	4.307	4.476
$m-PO_2$	$\lg k_0$	4.049	4.688	5.560	6.157	7.078	7.386
	$-a_4$	1.291	1.593	2.104	2.285	2.719	2.850
$p-PO_2$	$\lg k_0$	2.652	3.221	3.998	4.530	5.350	5.598
	$-a_4$	0.863	1.133	1.501	1.753	2.142	2.259

Footnote:

1. In all reaction series correlation coefficient is
   $0.9973 \geqslant \nabla \leqslant 0.9999$

2. Standard deviation for all series is within
   $0.021 \geqslant S \leqslant 0.043$

3. While handling data with a least squares method,
   5 points were always used with the exception of
   $(p-CH_3) \; C_6 H_4 NHCH_2 C(NO_2)_2 - C_6 H_4 (p-NO_2)$ and
   $(m-NO_2) C_6 H_4 NHCH_2 C(NO_2)_2 C_6 H_4 - (p-CH_3)$, where four
   values of temperature were used.

Correlation Paramaters of Eq. $\lg k = \lg k_o + a_3 Y$
for Solvolysis of $X_1 C_6 H_4 NHCH_2 C(NO_2)_2 C_6 H_4 X_p$ ($X_p = p-NO_2$)

T, °K	X_1	p-CH$_3$	H	p-Br	M-Br	p-COOCH$_3$	m-NO$_2$
283	$-\lg k_o$	1.145	1.720	2.516	3.062	3.908	4.165
	a_3	0.205	0.264	0.339	0.391	0.474	0.500
288	$-\lg k_o$	0.961	1.521	2.285	2.809	3.617	3.860
	a_3	0.173	0.227	0.301	0.352	0.430	0.453
298	$-\lg k_o$	0.632	1.145	1.845	2.325	3.065	3.288
	a_3	0.111	0.159	0.226	0.273	0.345	0.366
308	$-\lg k_o$	0.325	0.794	1.434	1.873	2.549	2.753
	a_3	0.049	0.094	0.157	0.199	0.265	0.285
328	$-\lg k_o$	-0.223	0.156	0.685	1.049	1.611	1.782
	a_3	-0.061	-0.021	0.029	0.068	0.121	0.138

Footnote:

1. In all reaction series correlation coefficient is
   $0.9980 \geqslant V \leqslant 0.9999$

2. Standard deviation for all series is within
   $0.013 \geqslant S \leqslant 0.032$

3. While handling data with a least squares method,
   6 points were used.

Correlation Parameters of Eq. $\lg k = \lg k_o + a_1 \sigma$

of Hydrolysis of $X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4Xp$

X_1		283	288	298	308	328	T, ^oK
p-CH$_3$	$-\lg k_o$	1.193	0.961	0.520	0.107	-0.644	
	a_1	0.972	0.751	0.336	-0.054	-0.759	
H	$-\lg k_o$	1.882	1.598	1.100	0.635	-0.211	
	a_1	1.314	1.080	0.634	0.216	-0.544	
p-Br	$-\lg k_o$	2.772	2.467	1.893	1.355	0.379	
	a_1	1.787	1.528	1.041	0.584	-0.244	
m-Br	$-\lg k_o$	3.394	3.063	2.435	1.849	0.782	
	a_1	2.110	1.836	1.320	0.836	-0.040	
p-COOCH$_3$	$-\lg k_o$	4.355	3.981	3.279	2.609	1.404	
	a_1	2.606	2.309	1.749	1.225	0.273	
m-HO$_2$	$-\lg k_o$	4.645	4.258	3.525	2.839	1.592	
	a_1	2.755	2.453	1.879	1.342	0.368	

Footnote:

1. In all reaction series correlation coefficient is
   $0.9975 \geqslant V \leqslant 0.9999$

2. Standard deviation for all series is within
   $0.017 \geqslant S \leqslant 0.038$

3. While handling data with a least squares method
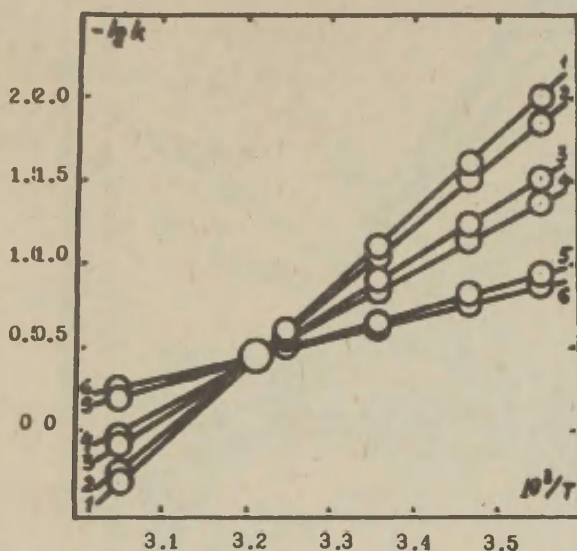   7 points were used.

Fig. 1   Inversion of the trend of the dependence
of lg k = f (10^3/T) for hydrolysis of
$X_p C_6 H_4 C(NO_2)_2 CH_2 NHC_6 H_5$ while passing through IPV
x_p: 1 - p-CH$_3$; 2 - H; 3 - p-Br; 4 - m-Cl;
5 - m-NO$_2$; 6 - p-NO$_2$;
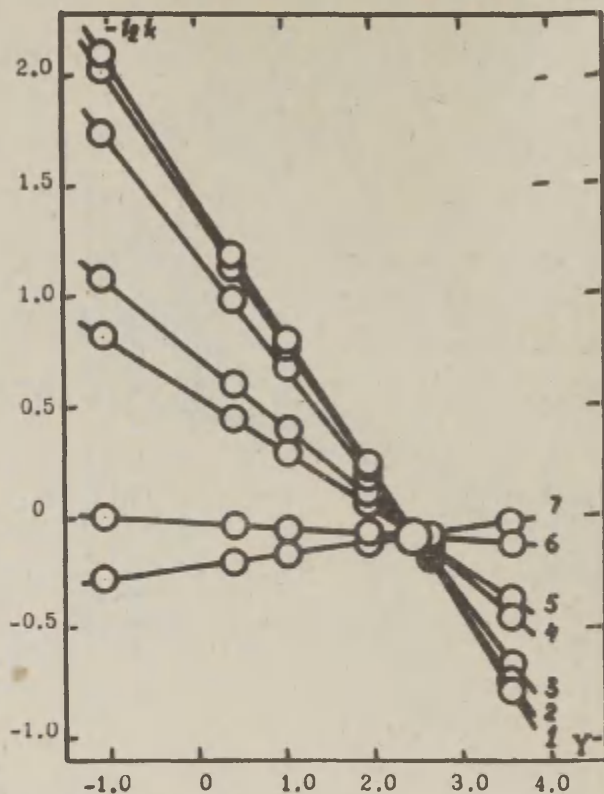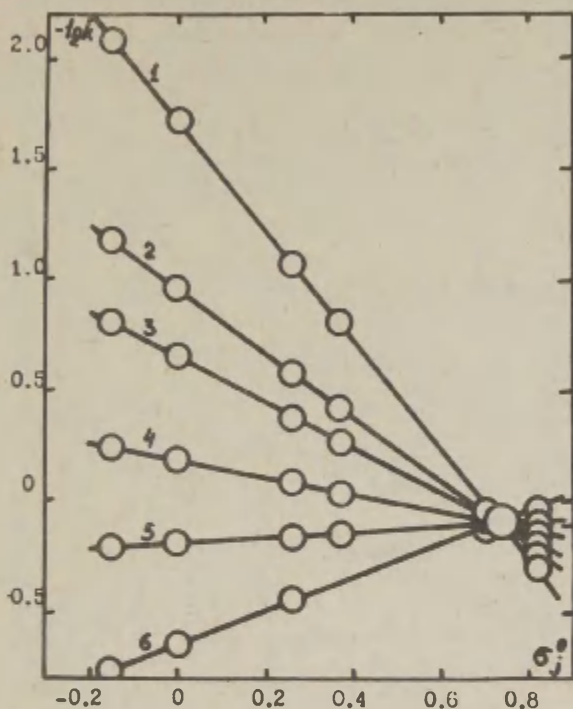10 ^{3}/T = 3.190 (β = 313 . 5°K)

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Fig. 2   Inversion of the trend of the function of
          lg k = f (Y) for solvolysis of
          $X_pC_6H_4C(NO_2)_2CH_2NHC_6H_4(p-CH_3)$ at $T = 328°K$
          while passing through IPV
          X_p: 1 – p–CH$_3$; 2 – H; 3 – p–Br; 4 – m–Cl;
          5 – m–NO$_2$; 6 – p–NO$_2$
          $\hat{Y}$ $(6°)$ = 2.477

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Fig. 3　Inversion of the trend of the function of
$\lg k = f(G^0)$ for solvolysis of
$X_p C_6 H_4 C(NO_2)_2 CH_2 NHC_6 H_4(p\text{-}CH_3)$ at $T = 328^0 K$
while passing through IPV
1-MeOH; 2-80%($^V/v$)MeOH; 3-70%($^V/v$)MeOH
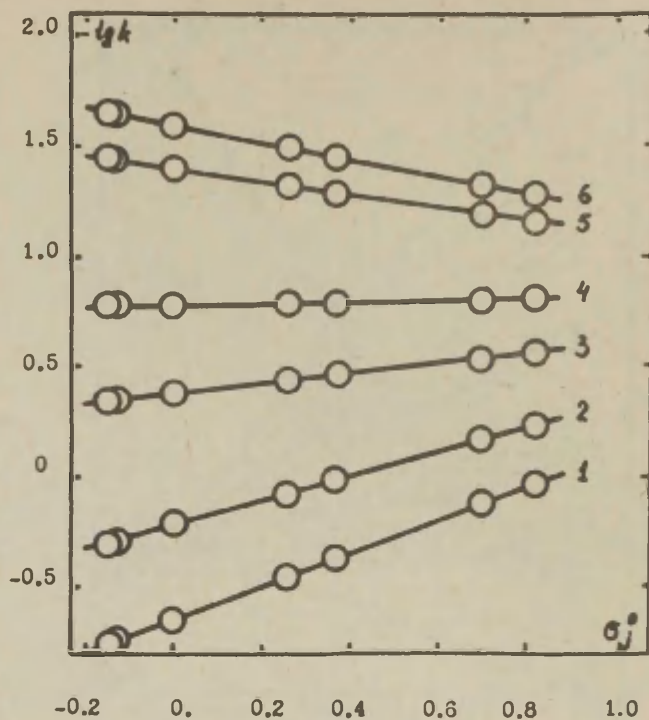4 - 50%($^V/v$) MeOH; 5-30% ($^V/v$) MeOH;
6 - H_2O.　$^0(Y) = 0.736$

·Fig. 4   Inversion of the trend of the dependence of
rate cont. log. of hydrolysis of
$X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$ at $T = 328^{\circ}K$
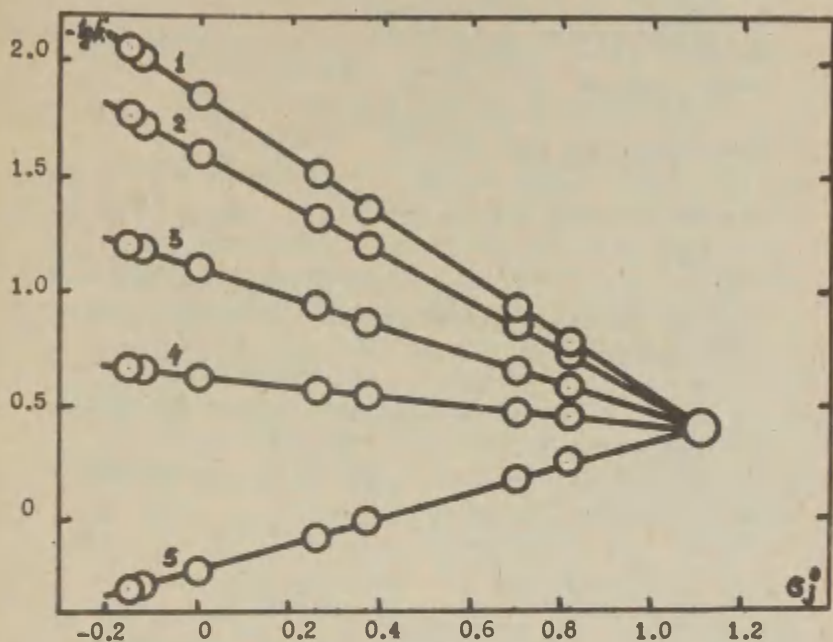X_1: 1 – p-CH$_3$; 2 – H; 3 – p-Br; 4 –m-Br;
5 – p-COOCH$_3$; 6 – m-NO$_2$

Fig. 5 Inversion of the trend of the function of
lg k = f(σ^o) for hydrolysis of
$C_6H_5NHCH_2C(NO_2)_2C_6H_4X_p$ at different temperatures:
1 - 283°K; 2 - 288°K; 3 - 298°K; 4 - 308°K;
5 - 328°K
$\sigma^o(10^3/T) = + 1.12$

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QUANTITATIVE CONSIDERATION OF INFLUENCE OF STRUCTURE,
MEDIUM AND TEMPERATURE ON THE KINETICS OF SOLVOLYSIS
OF β-POLYNITROALKYLARYLAMINS. V. REACTION THERMO-
DYNAMICS. REALIZATION OF ENTROPY AND ENTHALPY CONTROL
FOR A PARTICULAR PROCESS

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The activation parameters of solvolysis of -poly-
nitroalkylarylamins series are determined in aqueous-
methanol buffer solutions. Utilizing the multiparametric
cross-correlation equation, the formal dependence of acti-
vation parameters upon the structure of
$x_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$ and medium properties is ob-
tained. The possible entropy and enthalpy control is
shown within a reaction system under conditions of in-
variability of the reaction mechanism.

It was established earlier[1] that equation
lg k = lg H − $E_a 10^3$/T.2.3 K   holds

(I)

for solvolysis of $x_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$ where
x_1=p-CH_3, H, p-Br, m-Br, p-COOCH$_3$, m-NO$_2$; x_p=p-CH_3,p-OCH_3,
H, p-Br, m-Cl, m-NO$_2$, p-NO$_2$, over the whole range of varia-
tion of structural and medium factors. On the other hand the
system can be described with the cross-correlation equation
with all the cross terms[1] as follows:

$$lgk\,(x_1,x_2,x_3,x_4)=lgk_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 +$$
$$+ a_{12}x_1x_2 + a_{13}x_1x_3 + a_{14}x_1x_4 + a_{23}x_2x_3 + a_{24}x_2x_4 + \quad (2)$$
$$+ a_{34}x_3x_4 + a_{123}x_1x_2x_3 + a_{124}x_1x_2x_4 + a_{134}x_1x_3x_4 +$$
$$+ a_{234}x_2x_3x_4 + a_{1234}\,x_1x_2x_3x_4$$

where x_1= °, x_2= ¯, x_3 = Y, x_4=10^3/T
Grouping addends, equation (2) takes the form:

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$$\lg k = \lg k_o + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_{12} x_1 x_2 + a_{13} x_1 x_3 +$$
$$+ a_{23} x_2 x_3 + a_{123} x_1 x_2 x_3 + \boxed{a_4 + a_{14} x_1 + a_{24} x_2 + a_{34} x_3 +} \quad (3)$$
$$+ a_{124} x_1 x_2 + a_{134} x_1 x_3 + a_{234} x_2 x_3 + a_{1234} x_1 x_2 x_3 \boxed{} \; x_4$$

The identity of Eq.(3) and Eq.(1) is evident. Hence:
$$\lg A = \lg k_o + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_{12} x_1 x_2 + a_{13} x_1 x_3 + \quad (4)$$
$$+ a_{23} x_2 x_3 + a_{123} x_1 x_2 x_3$$

$$-E_a/2.3 \, R = a_4 + a_{14} x + a_{24} x_2 + a_{34} x_3 + a_{124} x_1 x_2 + \quad (5)$$
$$+ a_{134} x_1 x_3 + a_{234} x_2 x_3 + a_{1234} x_1 x_2 x_3$$

Fixing any two parameters out of three $(x_1, x_2$ or $x_3)$ in equations (4) or (5), the linear dependence of the activation energy and log of the preexponential factor upon the third parameter is obtained: Thus, fixing in their turn x_1, and x_2 in equation (4), the linear dependence upon x_3 will take the form:

$$\lg A = (\lg k_o + a_1 x_1) + (a_2 + a_{12} x_1) x_2 +$$
$$+ (a_3 + a_{13} x_1) + (a_{23} + a_{123} x_1) x_2 \; x_3 \quad (6)$$
$$\lg A = (\lg k_o + a_2 x_2) + (a_1 + a_{12} x_2) x_1 + (a_3 + a_{23} x_2) + \quad (6\text{-}a)$$
$$+ (a_{13} + a_{123} x_2) x_1 \; x_3$$

As far as $S^{\neq}$ is unambiguously defined with the log of the preexponential factor then, due to Eq. (6) and (6-a) the isoentropic phenomenon (invariability of the entropy component of the system) can be observed in the case of the indenpendence of the log A of the parameter variated (e.g. x_3) i.e. at the following critical values of the parameters fixed:

$$x_1 = - \frac{a_3 + a_{23} x_2}{a_{13} + a_{123} x_2} \quad (7) \qquad x_2 = - \frac{a_3 + a_{13} x_1}{a_{23} + a_{123} x_1} \quad (7\text{-}a)$$

Invariability condition of enthalpy component can be obtained analogously. Fixing in turn x_1 and x_2 in Eq. (5), the linear

Values of Solvolysis Activation Energy
E_a (kcal/mol)

X_1	X_p	H_2O	30	50	70	80	MeOH
p-CH$_3$	p-CH$_3$	19.79	20.03	20.22	20.46	20.62	21.01
	p-OCH$_3$	119.30	19.60	19.84	20.15	20.35	20.84
	H	17.34	17.89	18.33	18.89	19.26	20.17
	p-Br	13.10	14.18	15.06	16.16	16.90	18.70
	m-Cl	11.30	12.61	13.67	15.01	15.91	18.09
	m-NO$_2$	5.91	7.90	9.51	11.55	12.92	16.23
	p-NO$_2$	3.95	6.19	8.00	10.29	11.83	15.56
H	p-CH$_3$	22.19	22.17	22.16	22.15	22.14	22.11
	p-OCH$_3$	21.66	21.72	21.77	21.83	21.87	21.97
	H	19.56	19.92	20.21	20.57	20.82	21.41
	p-Br	15.00	16.01	16.82	17.84	18.53	20.20
	m-Cl	13.07	14.35	15.38	16.69	17.56	19.69
	m-NO$_2$	7.29	9.38	11.08	13.22	14.66	18.15
	p-NO$_2$	5.18	7.58	9.52	11.96	13.60	17.59
p-Br	p-CH$_3$	25.46	25.10	24.82	24.45	24.21	23.61
	p-OCH$_3$	24.89	24.62	24.41	24.13	23.95	23.51
	H	22.59	22.69	22.77	22.87	22.94	23.11
	p-Br	17.60	18.50	19.22	20.14	20.75	22.36
	m-Cl	15.49	16.72	17.72	18.98	19.82	21.87
	m-NO$_2$	9.17	11.41	13.22	15.50	17.04	20.76
	p-NO$_2$	6.87	9.47	11.58	14.24	16.03	20.36
m-Br	p-CH$_3$	27.70	27.11	26.63	26.03	25.62	24.64
	p-OCH$_3$	27.09	26.61	26.21	25.71	25.38	24.57
	H	24.66	24.58	24.52	24.45	24.40	24.27
	p-Br	19.38	20.20	20.87	21.71	22.27	23.63
	m-Cl	17.15	18.35	19.32	20.55	21.37	23.36
	m-NO$_2$	10.46	12.79	14.68	17.07	18.67	22.55
	p-NO$_2$	8.02	10.77	12.99	15.80	17.69	22.26

X_1	X_p	H_2O	30	50	70	80	MeOH
p-COOCH$_3$	p-CH$_3$	31.16	30.20	29.44	28.46	27.81	26.23
	p-OCH$_3$	30.49	29.66	28.99	28.15	27.58	26.20
	H	27.85	27.51	27.23	26.88	26.64	26.07
	p-Br	22.13	22.84	23.41	24.13	24.61	25.79
	m-Cl	19.71	20.86	21.79	22.97	23.75	25.67
	m-NO$_2$	12.44	14.93	16.94	19.48	21.18	25.31
	p-NO$_2$	9.80	12.77	15.17	18.21	20.24	25.18
m-NO$_2$	p-CH$_3$	32.20	31.14	30.28	29.20	28.47	26.71
	p-OCH$_3$	31.52	30.59	29.83	28.88	28.24	26.69
	H	28.82	28.39	28.05	27.61	27.32	26.61
	p-Br	22.96	23.63	24.17	24.86	25.32	26.44
	m-Cl	20.48	21.62	22.54	23.70	24.48	26.36
	m-NO$_2$	13.04	15.57	17.62	20.21	21.94	26.15
	p-NO$_2$	10.34	13.37	15.83	18.94	21.02	26.07

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$H^{\neq}_{25}$ Values (kcal/mol) for Solvolysis of (I)

X_1	X_p	H_2O	30	50	70	80	MeOH
p-CH$_3$	p-CH$_3$	19.20	19.44	19.63	19.87	20.03	20.42
	p-OCH$_3$	18.71	19.01	19.25	19.55	19.76	20.25
	H	16.75	17.30	17.74	18.29	18.67	19.57
	p-Br	12.51	13.59	14.46	15.57	16.31	18.11
	m-Cl	10.71	12.02	13.08	14.42	15.32	17.49
	m-NO$_2$	5.32	7.31	8.92	10.96	12.32	15.64
	p-NC$_2$	3.36	5.60	7.41	9.70	11.24	14.96
H	p-CH$_3$	21.60	21.58	21.57	21.55	21.54	21.52
	p-OCH$_3$	21.07	21.13	21.18	21.24	21.28	21.38
	H	18.97	19.33	19.61	19.98	20.22	20.82
	p-Br	14.41	15.41	16.22	17.25	17.94	19.61
	m-Cl	12.48	13.76	14.79	16.10	16.97	19.09

X_1	X_p	H_2O	30	50	70	80	MeOH
	$m-NO_2$	6.70	8.79	10.49	12.63	14.07	17.55
	$p-NO_2$	4.59	6.99	8.92	11.37	13.01	16.99
p-Br	$p-CH_3$	24.87	24.51	24.22	23.86	23.61	23.02
	$p-OCH_3$	24.29	24.03	23.81	23.54	23.36	22.92
	H	21.99	22.09	22.18	22.28	22.35	22.52
	p-Br	17.01	17.90	18.63	19.54	20.16	21.64
	m-Cl	14.90	16.13	17.13	18.30	19.23	21.28
	$m-NO_2$	8.58	10.81	12.62	14.91	16.45	20.17
	$p-NO_2$	6.28	8.88	10.99	13.65	15.44	19.76
m-Br	$p-CH_3$	27.11	26.52	26.04	25.44	25.03	24.05
	$p-OCH_3$	26.50	26.01	25.62	25.12	24.79	23.98
	H	24.07	23.99	23.93	23.86	23.80	23.68
	p-Br	18.79	19.61	20.28	21.12	21.68	23.04
	m-Cl	16.56	17.76	18.73	19.96	20.78	22.77
	$m-NO_2$	9.87	12.20	14.09	16.48	18.08	21.96
	$p-NO_2$	7.43	10.18	12.40	15.21	17.09	21.66
$p-COOCH_3$	$p-CH_3$	30.56	29.61	28.84	27.87	27.22	25.64
	$p-OCH_3$	29.90	29.07	28.40	27.55	26.98	25.60
	H	27.26	26.92	26.64	26.28	26.05	25.48
	p-Br	21.54	22.24	22.81	23.54	24.02	25.19
	m-Cl	19.12	20.27	21.20	22.37	23.16	25.08
	$m-NO_2$	11.85	14.34	16.35	18.89	20.59	24.72
	$p-NO_2$	9.21	12.18	14.58	17.62	19.65	24.59
$m-NO_2$	$p-CH_3$	31.61	30.55	29.69	28.61	27.88	26.12
	$p-OCH_3$	30.93	30.00	29.24	28.29	27.65	26.10
	H	28.23	27.80	27.45	27.02	26.73	26.02
	p-Br	22.37	23.04	23.58	24.27	24.73	25.84
	m-Cl	19.89	21.02	21.94	23.10	23.86	25.77
	$m-NO_2$	12.45	14.98	17.03	19.61	21.35	25.55
	$p-NO_2$	9.75	12.78	15.24	18.34	20.43	25.48

$S^{\neq}_{25}$ Values (e.u.) for Solvolysis of (I)

X_1	X_D	H_2O	30	50	70	80	MeOH
p–CH$_3$	p–CH$_3$	5.27	3.47	2.02	0.15	−1.08	−4.09
	p–OCH$_3$	3.67	2.14	0.92	−0.67	−1,72	−4,27
	H	−2,72	−3,15	−3,51	−3,95	−4.25	−4,97
	p–Br	−16.57	−14.63	−13.09	−11.06	−9.72	−6,49
	m–Cl	−22.43	−19.48	−17,15	−14.07	−12.04	−7.13
	m–NO$_2$	−40.02	−34.04	−29.32	−23.09	−19.00	−9.06
	p–NO$_2$	−46.41	−39.33	−33.74	−26.38	−21.52	−9.76
H	p–CH$_3$	10.45	8.06	6.13	3.68	2.05	−1,93
	p–OCH$_3$	8.78	6.69	4.99	2.86	1.43	−2.04
	H	2.06	1.18	0.47	−0.43	−1.03	−2,49
	p–Br	−12.48	−10.74	−9.33	−7.55	−6.35	−3.45
	m–Cl	−18.63	−15.78	−13.48	−10.56	−8.60	−3.86
	m–NO$_2$	−37.09	−30.91	−25.92	−19.60	−15.36	−5,09
	p–NO$_2$	−43.80	−36.42	−30.44	−22.89	−17.82	−5,53
p–Br	p–CH$_3$	17.52	14.34	11.76	8.50	6.32	1.02
	p–OCH$_3$	15.74	12.89	10.58	7.67	5.73	0.99
	H	8.59	7.10	5.90	4.38	3.37	0.90
	p–Br	−6,90	−5.43	−4,25	−2,75	−1,75	0.69
	m–Cl	−13.45	−10.74	−8.55	−5.77	−3,91	0.60
	m–NO$_2$	−33.00	−26.65	−21.43	−14.83	−10.40	0.34
	m–NO$_2$	−40.25	−32.43	−26.11	−18.12	−12.76	0.24
m–Br	p–CH$_3$	22.37	18.64	15.61	11.80	9.24	3.04
	p–OCH$_3$	20.51	17.14	14.41	10.97	8.67	3.07
	H	13.06	11.16	9.61	7.68	6.38	3.22
	p–Br	−3.07	−1.80	−0.77	0.53	1.41	3.53
	m–Cl	−9,89	−7.28	−5.17	−2,49	−0.70	3.66
	m–NO$_2$	−30.37	−23.72	−18.35	−11.56	−7.00	4.05
	p–NO$_2$	−37.81	−29.70	−23.15	−14.86	−9.29	4.19

X_1	X_p	H_2O	30	50	70	80	MeOH
p-COOCH$_3$	p-CH$_3$	29.83	25.26	21.56	16.88	13.75	6.15
	p-OCH$_3$	27.86	23.69	20.31	16.06	13.20	6.28
	H	19.95	17.41	15.35	12.75	11.01	6.79
	p-Br	2.83	3.81	4.59	5.60	6.27	7.90
	m-Cl	−4.42	−1.95	0.04	2.57	4.26	8.37
	m-NO$_2$	−26.16	−19.22	−13.61	−6.52	−1.76	9.77
	p-NO$_2$	−34.06	−25.50	−18.58	−9.82	−3.95	10.28
m-NO$_2$	p-CH$_3$	32.09	27.26	23.35	18.42	15.11	7.09
	p-OCH$_3$	30.08	25.67	22.10	17.59	14.58	7.25
	H	22.04	19.30	17.08	14.29	12.42	7.87
	p-Br	4.61	5.50	6.21	7.13	7.74	9.22
	m-Cl	−2.76	−0.34	1.62	4.10	5.76	9.79
	m-NO$_2$	−24.88	−17.86	−12.18	−5.00	−0.18	11.50
	p-NO$_2$	−32.93	−24.23	−17.20	−8.30	−2.34	12.12

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$G^{\neq}_{25}$ Values (kcal/mol) for Solvolysis of (I)

X_1	X_p	H_2O	30	50	70	80	MeOH
p-CH$_3$	p-CH$_3$	17.63	18.40	19.02	19.82	20.35	21.64
	p-OCH$_3$	17.62	18.37	18.98	19.75	20.27	21.52
	H	17.56	18.24	18.78	19.47	19.93	21.05
	p-Br	17.44	17.95	18.37	18.87	19.21	20.04
	m-Cl	17.39	17.82	18.19	18.61	18.90	19.62
	m-NO$_2$	17.24	17.45	17.66	17.84	17.99	18.34
	p-NO$_2$	17.19	17.32	17.47	17.56	17.65	17.87
H	p-CH$_3$	18.48	19.18	19.75	20.46	20.93	22.09
	p-OCH$_3$	18.46	19.14	19.69	20.39	20.85	21.99
	H	18.35	18.97	19.47	10.11	20.53	21.56
	p-Br	18.13	18.61	19.01	19.50	19.83	20.63
	m-Cl	18.03	18.46	18.81	19.24	19.53	20.24
	m-NO$_2$	17.75	18.00	18.21	18.47	18.65	19.07
	p-NO$_2$	17.65	17.84	17.99	18.19	18.32	18.64

X_1	X_p	H_2O	30	50	70	80	MeOH
p-Br	p-CH$_3$	19.65	20.24	20.72	21.33	21.73	22.72
	p-OCH$_3$	19.60	20.19	20.66	21.26	21.66	22.62
	H	19.43	19.98	20.42	20.97	21.35	22.35
	p-Br	19.07	19.52	19.90	20.36	20.68	21.44
	m-Cl	18.91	19.33	19.67	20.11	20.39	21.10
	m-NO$_2$	18.41	18.76	19.01	19.33	19.55	20.07
	p-NO$_2$	18.27	18.55	18.77	19.05	19.24	19.69
m-Br	p-CH$_3$	20.44	20.97	21.39	21.92	22.28	23.14
	p-OCH$_3$	20.39	20.91	21.32	21.85	22.20	23.06
	H	20.17	20.67	21.07	21.57	21.90	22.72
	p-Br	19.77	20.15	20.50	20.96	21.26	21.99
	m-Cl	19.51	19.93	20.27	20.70	20.98	21.68
	m-NO$_2$	18.92	19.27	19.56	19.92	20.16	20.75
	p-NO$_2$	18.70	19.03	19.30	19.64	19.86	20.42
p-COOCH$_3$	p-CH$_3$	21.67	22.08	22.42	22.84	23.12	23.81
	p-OCH$_3$	21.60	22.01	22.34	22.77	23.05	23.73
	H	21.32	21.73	22.06	22.46	22.77	23.45
	p-Br	20.69	21.11	21.45	21.87	22.15	22.84
	m-Cl	20.43	20.85	21.18	21.61	21.89	22.58
	m-NO$_2$	19.65	20.06	20.40	20.83	21.11	21.81
	p-NO$_2$	19.36	19.78	20.12	20.54	20.83	21.53
m-PO$_2$	p-CH$_3$	22.04	22.42	22.73	23.12	23.37	24.00
	p-OCH$_3$	21.97	22.35	22.66	23.05	23.31	23.94
	H	21.66	22.05	22.36	22.76	23.03	23.67
	p-Br	20.99	21.40	21.73	22.15	22.42	23.10
	m-Cl	20.71	21.13	21.46	21.88	22.17	22.86
	m-NO$_2$	19.87	20.30	20.66	21.10	21.40	21.86
	p-NO$_2$	19.56	20.00	20.36	20.83	21.12	21.86

dependence of activation energy upon x_3 will take the form:

$$- E_a/2.3 \ R= (a_4 + a_{14}x_1) + (a_{24} + a_{124}x_1)x_2 +$$
$$+ \ (a_{34} + a_{134}x_1 + (a_{234} + a_{1234}x_1)x_2 \ x_3 \tag{8}$$

or

$$- E_a/2.3 \ R = (a_4 + a_{24}x_2) + (a_{14} + a_{124}x_2)x_1 +$$
$$+ \ (a_{34} + a_{234}x_2) + (a_{134} + a_{1234}x_2)x_1 \ x_3 \tag{8-a}$$

Isoenthalpic phenomenon is evidently to be observed
in the case of E_a being independent of x_3, i.e. when the fol-
lowing equalities are realized:

$$x_1 = - \frac{a_{34} + a_{234}x_2}{a_{134} + a_{1234}x_2} \tag{9}$$

$$x_2 = - \frac{a_{34} + a_{134}x_1}{a_{234} + a_{1234}x_1} \tag{9-a}$$

The condition of isoentropic and isoanthalpic phenomena of
the system for the rest of the fixed parameters can be de-
rived analogously. The principle condition remains the same:
two parameters being fixed, the third one is varied. Using
the evidence available[1],[2] we calculated activation parameters
for all separate reaction series within the whole system in-
vestigated $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ values, assigned to 25°C were
calculated due to the formulae known.[3] Tables 1 ÷ 4 give the
data.

Due to analysis of data given in Tables 1 ÷ 4, isokinetic
dependence (ID) holds over the whole range of structure pro-
perties of the system and in all the solvents investigated.
Fig. 1 shows the realization of the isokinetic dependence
according to Petersen method.[4]

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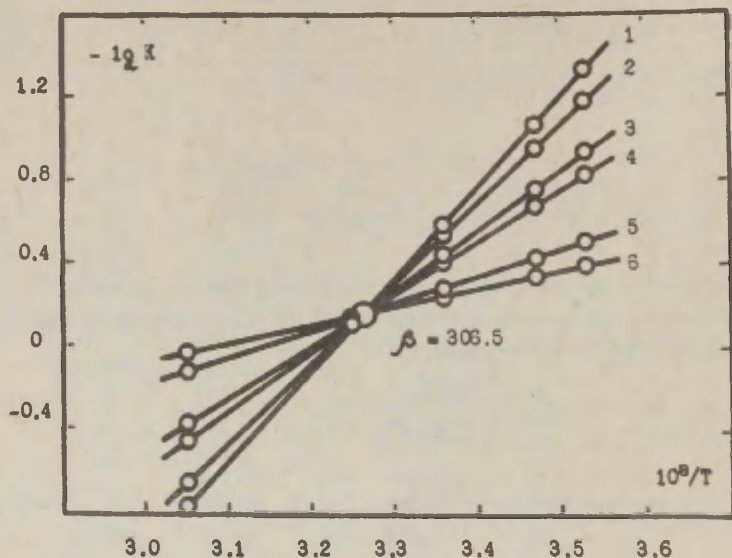
Fig. 1   The lg k vs. 10^3/T   plots for the correlation for
hydrolysis of (p-CH$_3$) - C$_6$H$_4$NHCH$_2$C(NO$_2$)$_2$C$_6$H$_4$X$_p$

X$_p$: 1 - p-CH$_3$; 2 - H; 3 - p-Br; 4 - m-Cl;
5 - m-NO$_2$; 6 - p-NO$_2$

The presence of such dependences is confirmed by
linear dependence for all separate reaction series in
Δ H$^{\neq}_{25}$ vs. Δ S$^{\neq}_{25}$ plots (see Tables 2, 3 and Fig. 2).
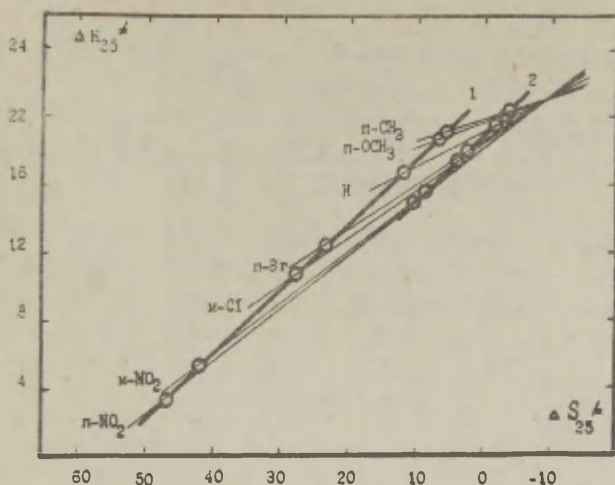
Fig. 2 The $\Delta H_{25}^{\neq}$ vs. $\Delta S_{25}^{\neq}$ plots for the solvolysis
of $(m-Br)$ $C_6H_4PHCH_2C(HO_2)_2C_6H_4X_p$ in various
binary mixtures.

1 - H_2O; 2 - MeOH

Besides, we calculated the values of isokinetic temper-
atures (β) using linear relations between const. log k for
the solvolysis of (I) at various temperatures. Analysis of
the lg k_{T_1} = (lg K_{T_2}) relationship where T, and T_2 are dif-
ferent temperatures, to which the rate constants of the re-
action assigned, is preferable because we deal with abso-
lutely independent experimental values.[5,6]

$\varkappa$ [*] values and isokinetic temperatures β [**] calculated
are presented in the Tables (5) and (6)

---

[*] $\varkappa$-is a slope of the straight line
  lg k_{T_2} = const + lg k_{T_1}, where T_2 T_1
[**] β values are calculated by $= \dfrac{T_1T_2(\varkappa-1)}{T_2 - T_1}$

Values Calculated by Equation: $\lg k_{328} = \text{const} +$
$\lg k_{283}$ (0.9987   r   0.9999;   0.008   s   )

X_1	(v/v) MeOH	0	30	50	70	80	100
p-CH$_3$		-0.789	-0.101	0.199	0.475	0.599	0.806
H		-0.414	-0.002	0.245	0.476	0.598	0.823
p-Br		-0.138	0.104	0.279	0.476	0.596	0.853
m-Br		-0.020	0.157	0.299	0.477	0.596	0.879
p-COOCH$_3$		0.104	0.189	0.326	0.478	0.594	0.935
m-NO$_2$		0.133	0.203	0.333	0.478	0.593	0.957

X_p	(v/v) MeOH	0	30	50	70	80	100
p-CH$_3$		0.647	0.652	0.657	0.664	0.670	0.692
p-OCH$_3$		0.647	0.652	0.657	0.664	0.670	0.691
H		0.650	0.654	0.658	0.664	0.669	0.686
p-Br		0.651	0.657	0.659	0.664	0.668	0.677
m-Cl		0.652	0.658	0.660	0.664	0.667	0.675
m-NO$_2$		0.658	0.660	0.662	0.664	0.665	0.668
p-NO$_2$		0.659	0.661	0.662	0.664	0.665	0.666

X_p	X_1	p-CH$_3$	H	p-Br	m-Br	p-COOCH$_3$	m-NO$_2$
p-CH$_3$		0.957	1.003	1.090	1.174	1.380	1.471
p-OCH$_3$		0.944	0.987	1.067	1.144	1.326	1.407
H		0.887	0.919	0.973	1.022	1.126	1.168
p-Br		0.720	0.730	0.744	0.755	0.774	0.780
m-Cl		0.621	0.627	0.633	0.641	0.652	0.654
m-NO$_2$		0.092	0.172	0.253	0.295	0.346	0.359
p-NO$_2$		-0.173	-0.070	0.088	0.169	0.254	0.275

Values of Isokinetic Temperatures (β) for the Solvolysis of $X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$

X_1	v/v MeOH	0	30	50	70	80	100
p-CH$_3$		306.5	323.3	341.5	383.1	430.0	962.1
H		313.4	328.1	345.8	383.3	429.5	1256
p-Br		321.8	334.2	349.5	383.5	428.7	4177
m-Br		327.0	338.0	351.9	383.6	428.2	-2066
p-COOCH$_3$		334.2	343.4	355.3	383.9	427.3	-253.0
m-NO$_2$		336.2	344.9	356.3	383.9	427.0	-127.3

X_p	v/v MeOH	0	30	50	70	80	100
p-CH$_3$		462.6	466.9	471.2	478.4	484.7	509.8
p-OCH$_3$		462.7	467.0	471.3	478.4	484.5	508.1
H		463.5	467.8	471.9	478.3	483.7	502.1
p-Br		465.6	469.6	473.3	478.3	482.0	492.5
m-Cl		466.7	470.6	473.9	478.3	481.4	489.4
m-NO$_2$		471.4	474.1	476.0	478.2	479.5	482.4
p-NO$_2$		473.9	475.7	476.8	478.2	478.9	480.4

X_p	X_1	p-CH$_3$	H	p-Br	m-Br	n-COOCH$_3$	m-NO$_2$
p-CH$_3$		-129.8	6.474	112.0	158.3	208.0	219.2
p-OCH$_3$		-194.0	-29.29	93.22	144.8	199.2	211.7
H		-1276	-406.8	-68.02	39.21	135.7	155.9
p-Br		555.8	575.5	611.0	644.3	720.9	754.7
m-Cl		443.4	447.5	452.0	458.4	467.1	468.9
m-NO$_2$		333.4	339.2	346.7	351.4	358.1	360.1
p-NO$_2$		316.7	324.0	333.1	339.0	346.8	349.1

It should be noted that the observance of the linear dependence in lg k_{T_2} vs lg k_{T_1} plots is a direct condition[5] of realization of Hammett-Taft equation at different temperatures. Hence, in this case, the isokinetic dependence (ID) must occur in a_i – $10^3/T$ plots as well. The point, where $a_i = 0$ will correspond the isokinetic temperature (β). (see Fig. 3,4).
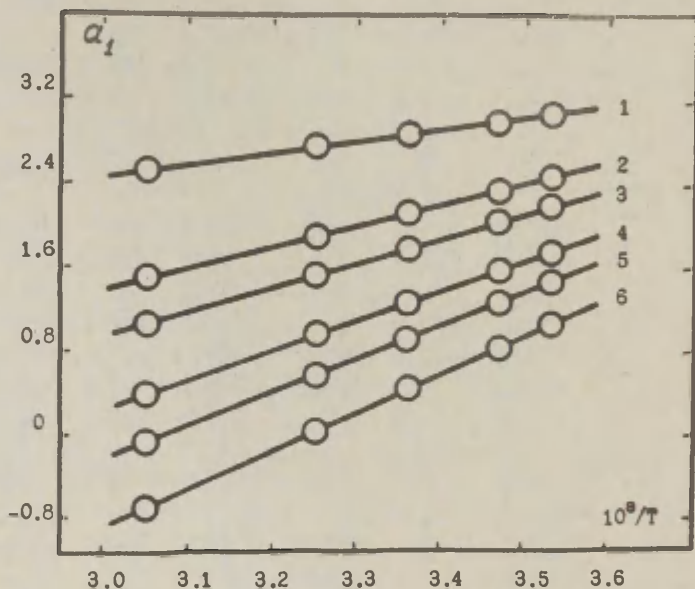
Fig. 3   Linear plot of a_1 – $10^3/T$ for solvolysis of $X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$ in various binary mixtures

1 – MeOH; 2 – 80% ($^V/v$) MeOH; 3 – 70% ($^V/v$) MeOH; 4 – 50% ($^V/v$) MeOH; 5 – 30% ($^V/v$) MeOH; 6 – H_2O
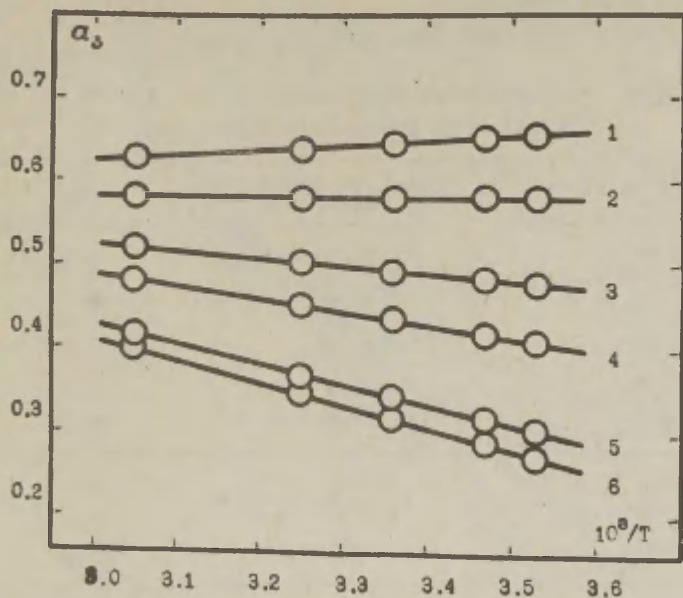
Fig. 4. Linear regression for the solvolysis of
$X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4(p-CH_3)$ in water.
X_1: 1 – p-CH$_3$; 2 – H; 3 – p-Br; 4 – m-Br;
5 – p-COOCH$_3$; 6 – m-NO$_2$

Values of isokinetic temperatures obtained by linear
plots lg k vs. $10^3/T$, a_i vs $10^3/T$, $H^{\neq}_{25}$ vs $S^{\neq}_{25}$ coincide
with those of ( ), (see Table 6) calculated by $\mathscr{L}$ values
(see Table 5), within 1°-$2^\circ K$. Thus, four independent methods
of data processing give the self-consistent results. Analysing
values, it is clear, that the set of parameters, where both
entropy and enthalpy control is possible, exist in the sys-
tem investigated. Due to the experimental range of variation

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being rather wide, all the change zones of $æ$ and β [*] are
practically monitored (see Tables 5, 6 and 7).

T a b l e   7

Values of Parameters Correlated in the Case of
Isoentropic Phenomenon ($\beta = \pm \infty$)

Parameter fixed	Value of parameter correlated	$S^{\neq}_{25}$
X_1: $p-CH_3$	0.06	-5.2
H	0.09	-2.8
$p-Br$	0.13	+0.8
$m-Br$	0.16	+3.4
$p-COOCH_3$	0.19	+7.6
$m-NO_2$	0.20	+9.0
X_1: $m-Br$	-0.96	+3.4
$p-COOCH_3$	-0.77 Y	+7.6
$m-NO_2$	-0.72	+8.8
Solvent 100% MeOH	0.30 –	+1.8

T a b l e   8

Values of Parameters Correlated in the Case of
Isoenthalpic Phenomenon ($\beta = 0$)

Parameter fixed	Values of parameter correlated	$H^{\neq}_{25}$ (kcal/mol)
X_1: H	-0.14	21.45
$p-Br$	-0.03	22.60
$m-Br$	0.02	23.60
$p-COOCH_3$	0.09	25.30
$m-NO_2$	0.10	25.90
X_p: $p-CH_3$	-0.01	21.45
$p-OCH_3$	0.04 –	21.60
H	0.33	23.25

[*]Special cases of changing of $æ$ and β values fit the
classification suggested by Exner and Palm[5].
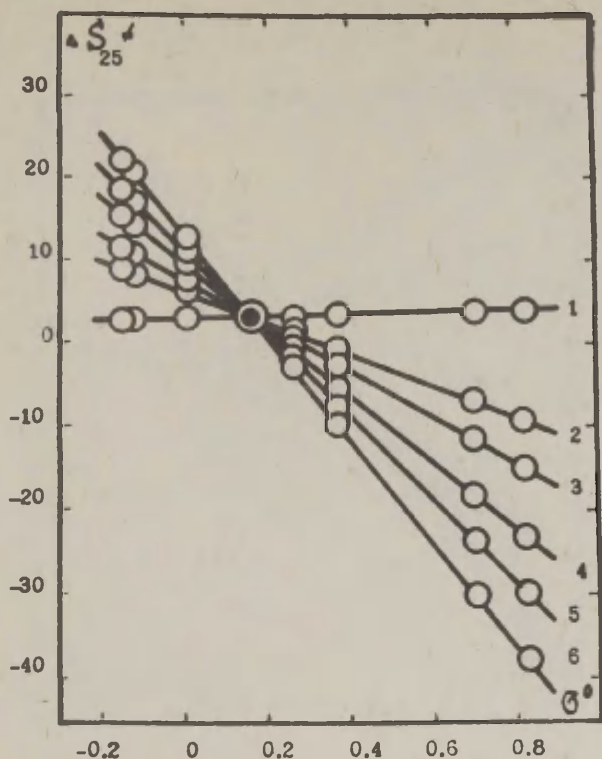
Fig. 5 Changing of the trend of the relationship
$\Delta S_{25}^{\neq}$ vs. σ° for solvolysis of (m-Br)
$C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$ in various binary
mixtures
1 - MeOH; 2 - 80% (^{V}/v) MeOH; 3 - 70% (^{V}/v) MeOH;
4 - 50% (v/v) MeOH; 5 - 30% (^{V}/v) MeOH; 6 - H_2O.
$\Delta S_{25}^{\neq}$ value at isoparametric point (σ° =0.16)
equals + 3.4

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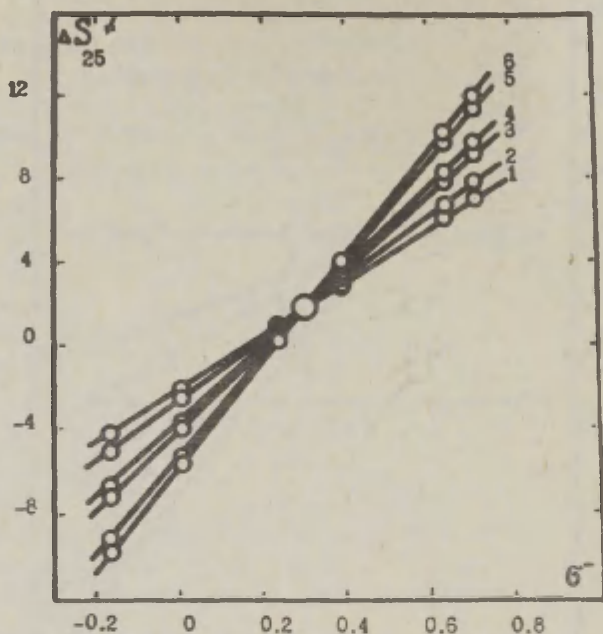
Fig. 6 Changing of the trend of relationship $\Delta S_{25}^{\neq}$ vs. σ^- for methanolysis of

$X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$

X_p: 1-p-CH_3; 2-H; 3 = p-Br; 4 - m-Cl; 5 - m-PO_2;

6 - p-NO_2

$\Delta S_{25}^{\neq}$ value at isoparametric point (σ^-=0.30) equals + 1.18.
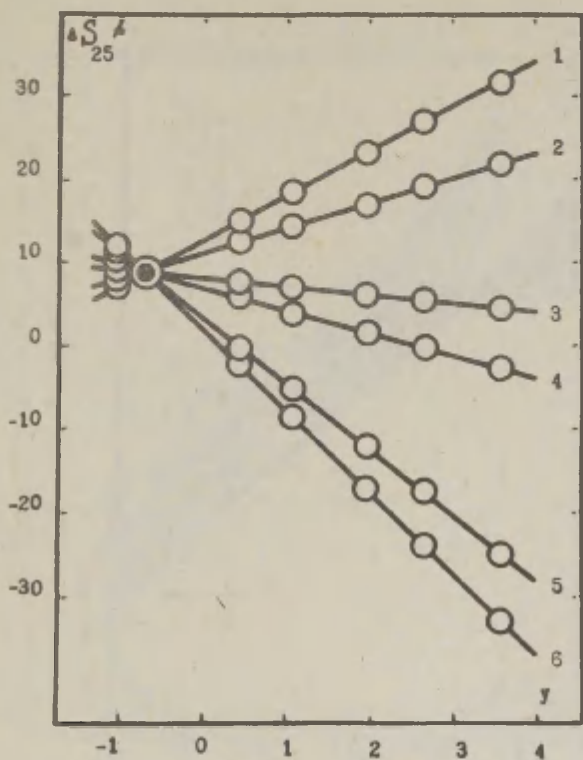
Fig. 7   Changing of the trend of the relationship
$\Delta S_{25}^{\neq}$ vs. Y for solvolysis of
$(m - NO_2)C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$
X_p: 1 - p-CH$_3$; 2 - H; 3 - p-Br; 4 - m-Cl
       5 - m-PO$_2$; 6 - p-NO$_2$
$\Delta S_{25}^{\neq}$ value at isoparametric point (Y=-0.72)
equals + 3.8
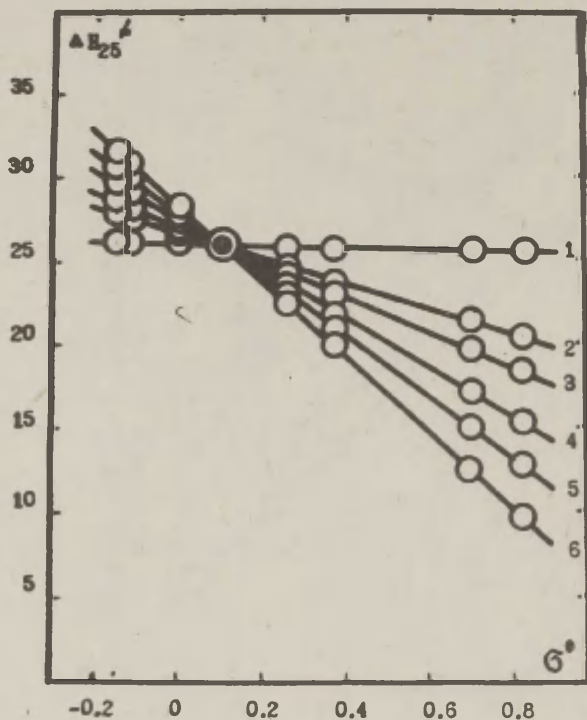
'Fig. 8 Changing of the trend of the relationship $\Delta H^{\neq}_{25} - \sigma^0$
for solvolysis of $(m - NO_2)C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$
in various binary mixtures.
1 - MeOH; 2 - 80% ($^V/v$)MeOH; 3 - 70% ($^V/v$) MeOH
4 - 50% ($^V/v$) MeOH; 5 - 80% ($^V/v$) MeOH; 6 - H_2O
$\Delta H^{\neq}_{25}$ value at isoparametric point ($\sigma^0 = 0.10$)
equals 25.90
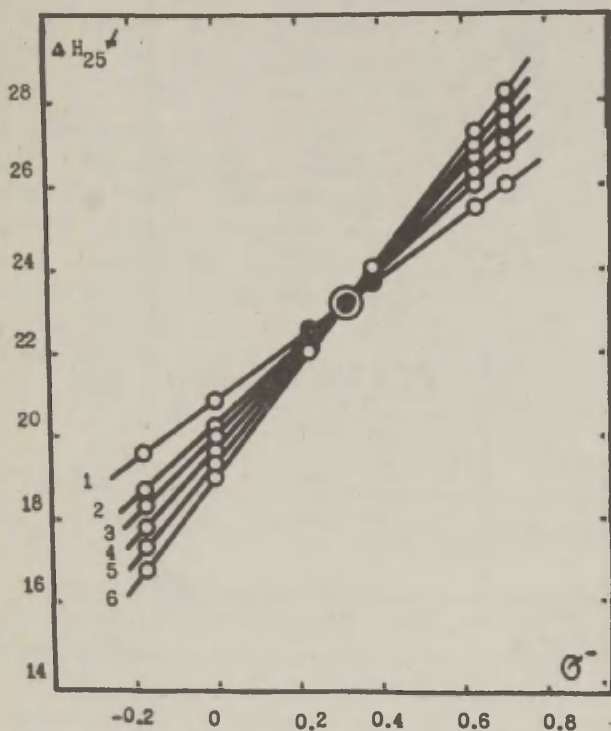
Fig. 9 Changing of the trend of the relationship $\Delta H_{25}^{\neq}$ -
         $-\sigma^-$ for solvolysis of $X_1C_6H_4NHCH_2C(NO_2)_2C_6H_5$ in
         various binary mixtures
         1 - MeOH; 2 - 80% (^{V}/v) MeOH; 3 - 70% (^{V}/v) MeOH
         4 - 50% (^{V}/v) MeOH; 5 - 30% (^{V}/v) MeOH; 6 - H_2O
         $\Delta H_{25}^{\neq}$ value at isoparametric point (σ^- = 0.33)
         equals 23.25

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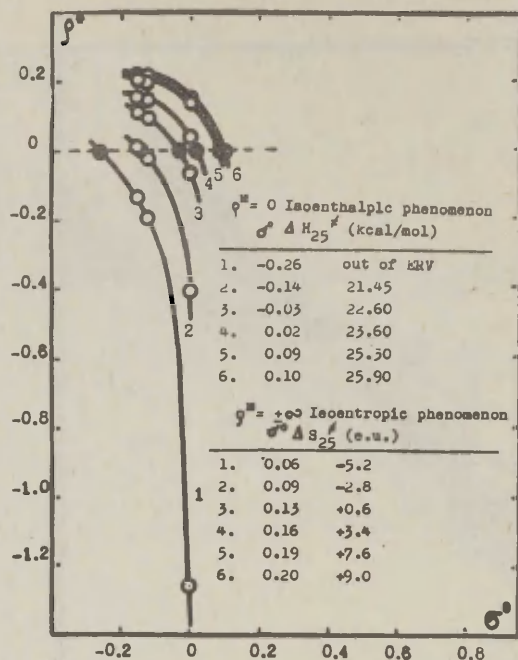
Fig. 10 Changing of the trend of the dependence of secondary function $\rho^{\ast} - \sigma^0$ ($\rho^{\ast}$ is the slope of the $-E_a/2.3\,R = f(\lg A)$ plots) for solvolysis of $X_1C_6H_4NHCH_2C(NO_2)_2C_6H_4X_p$
X_1: 1 – p-CH$_3$; 2 – H; 3 – p-Br; 4 – m-Br; 5 – p-COOCH$_3$; 6 – m-NO$_2$

Values of fixed parameters at which $\beta = \pm \infty$ or $\beta = 0$ can be obtained both graphycally and analytically.

In fact, if $\beta = 0$ the slope of the "reactivity-sensitivity" plots ($\lg k_o$ vs a_i) for parameters of Arrhenius equation ($\lg A$ vs $E_a/2.3$ R) equals zero, i.e. $tg\alpha = 0$ and the straight line runs parallel to ($\lg k_o$) axis.[2] The system sensitivity[1] in such points is evidently invariant of the temperature.

Hence, the system itself will be isoenthalpic and all straight lines $\Delta H_{25}^{\neq} = const. + \rho^{\text{#}} \sigma^o$ will cross at a single point for each value of the parameter fixed (see Fig.8,9,10) In those points, where entropy control exists, $\beta = \pm \infty$, i. e. system reactivity is constant and independent of the temperature (see Fig. 5,6,7,10).

In Fig. 10 it is demonstrated that at different values of the same parameters, the system can be both isoenthalpic (hyperbolae $\rho^{\text{#}} = F(\sigma^o)$ cross 0) and isoentropic (hyperbolae $\rho^{\text{#}} = F(\sigma^o)$ suffer discontinuity).

With substitution of values of sensitivity factors from Eq.(2) into formulae for critical values of parameters fixed (Eq. (7) and (7-a), (9), and (9-a), analytical calculation is realized.

It's of a certain interest that while isokinetic temperature is defined by equality $a_i = 0$ (where a_i are values from monoparametric equations of Hammett-Taft type in a_i vs $1/T$), plots then, secondary function $\rho^{\text{#}}$ equaling 0 or going into $\pm \infty$, we obtain an unambiguous criterion of the observance of the isoenthaplic or isoentropic phenomenon.

#The figure represents the left lower branches of hyperbolae only. The right top branches of these hyperbolae contact in a point, which corresponds to CV of the parameter of the most complicated type.

#For comparison see CV for three-parametric equations[7], including always temperature as a variable. Evidently, CV of different types determines the criteria for monitoring the isoenthalpic or isoentropic phenomenon.

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KINETICS OF γ - RADIATION INITIATED OXYDATION OF POLYCYCLIC AROMATIC HYDROCARBONS

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Rate constants of γ-radiation initiated oxydation reaction for 10 polycyclic aromatic hydrocarbons (PAH) have been determined in n-octane. The correlations of the rate constants with MO-indices, and Streitwiesers σ_r constants have been established. The reaction rate is weakly sensitive to the changes in electron density at the reaction center. The similarity between the mechanisms of the oxydations initiated by UV- and γ-radiations has been pointed out.

To find the rational ways to natural or compulsory environment cleaning from carcinogenic pollutants it is necessary to possess thorough information about the reactivity of relevant polycyclic aromatic hydrocarbons (PAH), first of all, in their oxydation reactions. It also concerns the data for their oxydative radiolysis which has been investigated insufficiently.[1]

Earlier[2], basing on the kinetic data for 27 PAH, we established the dependence of the reactivity of PAH in UV induced oxydation reaction on some characteristics of their structure. The latters were free valency MO-indices F_r^{max}, and of minimal localization energy, L_r^{min}, for the most reactive carbon in PAH.[3-5] Also the empirical polar constants σ_r proposed by Streitwieser by analogy with well known Hammett equation have been used.

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In this paper we present the results of a kinetic investigation on oxydative destruction of PAH initiated by γ - radiation, and that of our attempt to compare quantitatively the obtained kinetic data with the MO-indices and σ_r constants.

Experimental

A set of 10 PAH (listed in Table 1) was subjected to experimental investigation in 2×10^{-4} M n-octane solution. The capacity of γ-Co^{60} radiation source was 240 rad/sec. The experimental techniques is described elsewhere.[6]

The variation of the concentration of initial substances during the reaction was followed by spectrophotometric analysis of samples worked up by thin layer chromatography on aluminium oxyde of second grade activity (eluation by mixed solvent white spirit - chloroforme 9:1, chromatograms are developed by UV-light or by sulphuric acid).

The rate constants of the reaction were calculated from the decrease of the concentration of PAH according to the pseudo-zeroeth-order reaction law. In order to eliminate the influence of inevitable fluctuations of the radiation intensity in various runs all the kinetic determinations were paralleled with the corresponding experiment with benz(a)pyrene (BP). The rate constant of decomposition of PAH, k, was then devided by the rate constant of decomposition of BP, k_o, in the same run. The relative rate constants, k/k_o, are listed in Table 1.
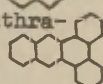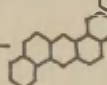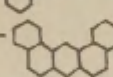
Discussion
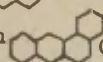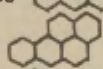
The experimental data from Table 1 were treated with the following equation:

$$\log k_i/k_o = x_{ij} y_j,$$

where k_i and k_o are the oxydation rate constants of the i-th PAH and BP correspondingly, y_j is the susceptibility factor of the reaction and x_{ij} are the values of MO-indices F_r^{max} or

Rate Constants of Radiation-Initiated Oxydation of PAH,
the Values of MO-Indices, and σ_r

Substance	$\lg(k/k_o)+1$	F_r^{max}[e]	L_r^{min}[b]	σ_r^c	r^d
1. Phenanthrene[f]	0.39	0.452	2.3	0.5	1
2. Triphenylene[f]	0.23	0.439	2.37	0.8	1
3. Pyrene[f]	0.49	0.469	2.19	2.9[e]	1
4. Chrysene[g]	0.49	0.457	2.24	2.6	6
5. Benz(a)anthracene[h]	0.87	0.514	2.04	8.2[e]	7,12
6. Benz(a)pyrene[i]	1.00	0.529	1.94	11.1	6
7. Benz(e)pyrene[k]	0.44	0.460	...	1.8[e]	6
8. 1,2,3, 4-dibenzanthra-cene[k]	0.75	0.499	2.12	6.4[e]	5
9. 1,2,5,6- - " -	0.77	0.498	2.13	6.5	7
10. 1,2,7,8- - " -	0.88	0.510	2.08	7.7[e]	7

[a]Ref. 4 [b]Refs. 4,5 [c]Refs. 3,6 [d]Position in PAH [e]Estimated in previous work[2] [f]Soyuzkhimreaktiv [g]Austrowaren [h]British Drug Houses Ltd. [i]Fluka AG Buchs SG. [k]Gee Lawson Chemicals.

Correlation Equations for the Reactivity of PAH in Oxydations Initiated by
UV- and γ -Radiations

N$\underline{o}$	Correlation equation[a]	r	s	Number of points
1.	$\log k/k_o = -(4.32 \pm 0.18) + (8.18 \pm 0.36)\ F_r^{max}$	0.992	0.033	9
2.	$\log k/k_o = (3.74 \pm 0.35) - (1.89 \pm 0.16)\ L_r^{min}$	0.976	0.061	8
3.	$\log k/k_o = -(0.68 \pm 0.02) + (0.066 \pm 0.033)\ \sigma_r$	0.992	0.034	9
4.[b]	$\log k/k_o = -(0.64 \pm 0.04) + (0.058 \pm 0.006)\ \sigma_r$	0.950	0.074	12

[a]
k/k_o - ratio of rate constants for PAH and benz(a)pyrene.
[b]
Photolysis, data from previous work.[2]

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L_r^{min}, or of σ_r constants. The obtained correlation equations are given in Table 2 (Eqs.1-3). It follows, as in the case of the light-initiated oxydation[2], that reactivity of PAH is determined not only by the value of the free valency of the most active carbon atom, but also, in view of the good interdependence[5] of these parameters, by localization energy or by Streitwieser's σ_r constant. In the correlations with the latter constants the values of σ_r estimated in our previous work[2] from the correlations between σ_r and F_r^{max} or L_r^{min} were used for five PAH (see Table 1). The fact that the points for these PAH keep close to the total regression line (Fig. 1) is an evidence for the reliability of the estimated σ_r values.
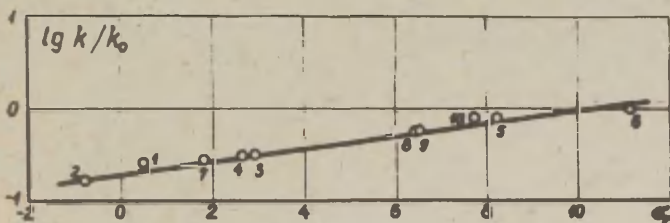
Fig. 1. Dependence of the relative rate of oxydative γ-radiolysis of PAH upon the values of Streitwieser σ_r constants. For the numbering of the points see Table 1.

A special attention must be paid to the fact, that the correlation relations between the reactivity of PAH and σ_r constants for photooxydation (Eq. 4, Table 2) and for radiolysis (Eq.3, ibid.) coinside practically. Naturally, corresponding equations including F_r^{max} or L_r^{min} also coinside. This evidences of the similarity of the mechanisms of both the initiated oxydations. One can assume that under the reaction conditions kept in our experiments both the UV- and γ-radiations generate the same active particles which attack the most reactive center of PAH in the rate-limiting step of the reaction.

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Investigation of 1,4-Dioxane Structure and Properties by Dielcometric and Spectroscopic Methods.

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The structure and properties of 1,4-dioxane have been studied in terms of Onsager model by dielcometric and spectroscopic methods. Some thermodynamic characteristics have been obtained by dielcometric method. The free energy of transition ($\triangle F_{c-b}$) has been determined on the bases of investigating of shifts of absorption bands of molecules including dioxane and with the use of the spectroscopic theory of intermolecular interactions. The $\triangle F_{c-b}$ values obtained by the two independent methods are found to be very close. The spectroscopic investigations have also shown the possibility of conformation reconstruction of dioxane molecule using the energy of electrostatic field of molecules dissolved in dioxane.

Among urgent problems of modern chemistry connected with the molecule's reactivity in solutions is the problem of prediction of the properties of solvents which consist of nonrigid molecules passing from one conformer's form into another. As a typical example of such solvents we may take 1,4-dioxane which has attracted the attention of many scientists /1-19/. We have carried out comprehensive investigation of the properties of dioxane by spectroscopic and dielcometric methods using the concepts of universal intramolecular interaction theory (UII)

The 1,4-dioxane molecule can exist in the form of several conformers:

Symmetric forms   asymmetric forms

cnair   boat   chair   boat

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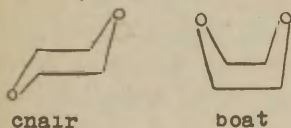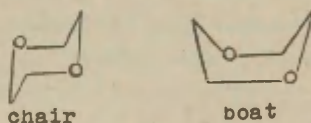
To simplify calculations as it was adopted earlier /17, 18/, we assume that the main dioxane properties as a solvent can be described fairly well by reducing the number of probable conformers to two, namely to the symmetric forms of chair and boat. Let us consider the problem of the dielectric properties of dioxane supposing that the latter is a mixture of the above-mentioned conformers. In terms of physics of dielectrics, the dielectric permittivity (ε) of a binary solvent having no specific and local interactions between molecules (which form dielectric) can be expressed by dielectric permittivities of the components (or conformers in our case) as:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\varepsilon_b - 1}{\varepsilon_b + 2} \cdot V_b + \frac{\varepsilon_c - 1}{\varepsilon_c + 2} \cdot V_c \qquad (1)$$

where V_b and V_c are the volume fractions, ε_b and ε_c are the dielectric permittivities the boat and chair forms of dioxane, respectively. Taking into consideration that the final precission of the model used does not exceed 15–25% one might transform (1) into the following form:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\varepsilon_b - 1}{\varepsilon_b + 2} \cdot N_b + \frac{\varepsilon_c - 1}{\varepsilon_c + 2} \cdot N_c \qquad (2)$$

where N_b and N_c are mole fractions of corresponding conformers. This expression will give the percentage of the polar form of dioxane in pure dioxane, provided that the $\frac{\varepsilon_b - 1}{\varepsilon_b + 2}$ and $\frac{\varepsilon_c - 1}{\varepsilon_c + 2}$ values are known. The value of $\frac{\varepsilon_b - 1}{\varepsilon_b + 2}$ is determined by the sum of electronic (P_E) and nuclear (P_N) polarizations. The P_E value may be obtained using conventional methods by means of investigation of the dependence of the refractive index function on the light frequency in optical region. Thus extrapolation of the $\frac{n^2 - 1}{n^2 + 2}$ function vs. V^2 up $V = 0$ yielded $P_E = 21,0$ cm^3 which is in fair agreement with the value given in /6/. The $P_N = 2,6$ cm^3 value was taken from literature /20/. In Ref. /20/ the P_N value was determined by measuring the refractive index of pure dioxane in the IR-range. In order to estimate ε_b we used the well-known Onsager

equation /21/:

$$\frac{\mu^2}{a^3} = \frac{(\varepsilon_\beta - \varepsilon_\infty)(2\varepsilon_\beta - \varepsilon_\infty)3\kappa T}{(\varepsilon_\infty + 2)^2 \varepsilon_\beta} \tag{3}$$

The data needed for calculations were obtained as follows: the dipole moment of the boat form of dioxane was found by the vector scheme, and the calculated μ_β = 2,4 D value coincided with that obtained in Ref./17/. The dielectric permittivity ε_∞ associated with electronic and nuclear polarizations of the polar form of dioxane was assumed to be close to static dielectric permittivity for its nonpolar form, i.e. $\varepsilon_\infty \approx$ $\approx \varepsilon_c$. The structural radius of the dioxane molecule (r) was determined as a volume per one molecule in solution. Table 1 gives experimental values of ε and $\frac{\varepsilon - 1}{\varepsilon + 2}$ at different temperatures; $\frac{\varepsilon_c - 1}{\varepsilon_c + 2}$ and $\frac{\varepsilon_\beta - 1}{\varepsilon_\beta + 2}$ values obtained by the method described above; the mole fraction values of the boat form N_β and equilibrim constants for chair-boat transition K_ρ. It should be noted that the conformation equilibrim constant K_ρ practically does not depend on temperature, which testifies that enthalpy of chair-boat transition in pure dioxane is close to zero. If we use the well-known equation of the isotherm of the chemical reaction, one can determine the standard free energe value of this transition (ΔF^{o}_{c-b}). It was found to be equal to 2,3 kcal/mole.

Table 1.

t°C	ε	$\frac{\varepsilon - 1}{\varepsilon + 2}$	$\frac{\varepsilon_c - 1}{\varepsilon_c + 2}$	$\frac{\varepsilon_\beta - 1}{\varepsilon_\beta + 2}$	$N\%$	K_p
25	2,2058	0,287	0,276	0,806	2,1	0,021
30	2,2008	0,286	0,274	0,801	2,1	0,021
40	2,1818	0,283	0,272	0,793	2,1	0,021
50	2,1638	0,279	0,268	0,784	2,1	0,021

The theory of the spectroscopy of intermolecular interactions for the case of binary solvents was used to obtain additional information on the structure and properties of dioxane. Solvate shell composition of a polar molecule is known to

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differ essentially from the ratio of components forming solvent (usually polar + nonpolar) /22-24/. Besides the excess concentration of the polar component of the solvent in the nearest surrounding of the molecule rises with the increasing energy of orientation - induction interaction; the solvate shell composition will try to attain one consisting entirely of molecules of the polar component in the mixed solvent. In our presentation the ratio $\frac{\mu^2}{a^3}$, where a is Onsager radius of molecule, is a parameter which determines the energy of the orientation-induction interaction of the molecule with the medium. It was interesting to determine first the local dielectric characteristics and then the solvate shell composition of some preselected molecules with different ratios $\frac{\mu^2}{a^3}$ in dioxane using the methods of the spectroscopy of intermolecular interaction. Let us consider this problem in more detail.

The expression describing the displacement of electron absorption band of the molecule as a function of the solvent /25/ is as follows:

$$\widetilde{\gamma}^a = \left(\frac{n^2-1}{n^2+2} + 1\right) \frac{\varepsilon-1}{\varepsilon+2} \, C_1^a + \frac{n^2-1}{n^2+2}\left(\frac{n^2-1}{n^2+2} + 1\right) \cdot$$
$$\cdot \left(C_2^a - C_1^a\right) + \frac{n^2-1}{n^2+2} \, C_3^a + \frac{n^2-1}{2n^2+2} \, C_4^a \tag{4},$$

where C_1^a, C_2^a, C_3^a, C_4^a - are respective molecular parameters from Ref./25/. In the case of multicomponent solvents it as necessary to substitute the local values of refractive index n_ℓ and dielectric permittivity ε_ℓ of the solvents determining the optical and dielectric properties of the latter in the proximity of the molecule under study. Expression (4) can be simplified considerably by choosing solvents with nearly equal refractive indices. For one component solvents the expression (4) transforms in (5)

$$\widetilde{\gamma}^a = \left(\frac{n^2-1}{n^2+2} + 1\right) \frac{\varepsilon-1}{\varepsilon+2} \, C_1^a + \widetilde{\gamma}_0^a \tag{5},$$

which for multicomponent solvents has the form

$$\widetilde{\gamma}^a = \left(\frac{n^2-1}{n^2+2} + 1\right) \frac{\varepsilon_\ell-1}{\varepsilon_\ell+2} \cdot C_1^a + \widetilde{\gamma}_0^u \tag{6},$$

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where $\widetilde{\nu}_o^a$ is the frequency of transition of the molecule when $\frac{\varepsilon - 1}{\varepsilon + 2} = 0$. Equation (5) was used to determine the molecular parameters c_1^a and $\widetilde{\nu}_o^a$. Then substituting the c_1^a and $\widetilde{\nu}_o^a$ values obtained from (5) in (6) we may find the desired values of the function $\frac{\varepsilon_\ell - 1}{\varepsilon_\ell + 2}$ for dioxane. A well-studied series of p-substituted nitrobenzenes was choosen as an object of our investigation. Table 2 shows that the $\frac{\varepsilon_\ell - 1}{\varepsilon_\ell + 2}$ values increase with the growing $\frac{\mu^2}{a^3}$ values trying to attain the limiting value of $\frac{\varepsilon_g - 1}{\varepsilon_g + 2}$ which equals approximately 0,8 for a pure polar dioxane form (compare with Table 1).

Table 2.

The Values of the Parameters c_1^a (cm^{-1}), $\frac{\mu^2}{a^3} \cdot 10^{12}$ (erg and $\widetilde{\nu}_o^a$ (cm^{-1}) for the Selectedd Series of Molecules and the Value of the Function $\frac{\varepsilon_\ell - 1}{\varepsilon_\ell + 2}$ for Solvent Dioxane.

Compound	$c_1^a (cm^{-1})$	$\frac{\mu^2}{a^3} \cdot 10^{12}$ (erg)	$\widetilde{\nu}_o^a (cm^{-1})$	$\frac{\varepsilon_\ell - 1}{\varepsilon_\ell + 2}$
1. nitrobenzene	1700±100	0,38	40000±100	0,70±0,07
2. p-nitrotoluene	2900±400	0,40	38900±300	0,70±0,10
3. p-nitroaniline	4800±700	0,54	32500±600	0,70±0,12
4. p-nitrophenol	4200±800	0,35	36300±500	0,66±0,13
5. p-dimethylamine-nitrostilbene	3500±300	0,10	26600±300	0,61±0,06
6. p-dimethylamine-nitrostyrene	1800±300	0,27	25200±300	0,61±0,11
7. p-dimethylamine-benzylidene-p'-nitroaniline	2700±200	0,11	27600±200	0,53±0,04

A typical relation between the displacement of the absorption band of the substance and universal intermolecular interaction function $F(\varepsilon) = \frac{\varepsilon - 1}{\varepsilon + 2}\left(\frac{n^2 - 1}{n^2 + 2} + 1\right)$ is presented in Fig. 1.

The experimental relations $\widetilde{\nu} = f[F(\varepsilon)]$ were processed using expression (5) by the method of least squares. The confidence level of c_1^a and $\widetilde{\nu}_o^a$ values was obtained for 9% probability. Fig. 1 shows that the deviation of the dioxane

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point from a general relationship exceeds the confidence interval several times.

The results obtained allow to determine the mole fraction of the polar component in pure dioxane. As it was shown earlier /26/, the mole fraction of the polar component of binary solvent in the solvate shell of the molecule (x_β) may be represented in the following manner:

$$x_\beta = \frac{1}{N_c / N_\beta \cdot exp\,(-\Delta\Delta F/RT + 1)} \qquad (7)$$

where N_c and N_β are the mole fractions of the polar and non-polar forms of dioxane, $\Delta\Delta F$ is the difference of changes in free energy of the molecule for vapor-dioxane solution phase transition when all the molecules are in the chair form and when all the molecules are in the boat form. Taking into account that $ln\ N_c / N_\beta = \Delta F_{c-\beta} \cdot RT$, we shell transform expression (6):

$$x_\beta = \frac{1}{exp\,[\Delta F_{c-\beta}^\circ - \Delta\Delta F/RT] + 1} \qquad (8)$$
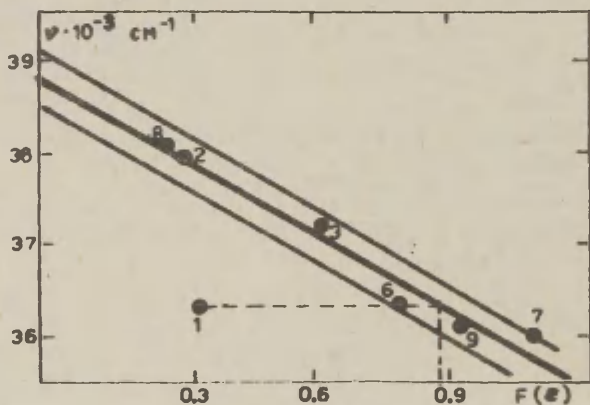
Fig. 1. Position of maximum of longwave absorption band in electronic absorption spectrum of nitrotoluene vs. universal interaction function of solvent $F(\mathcal{E})$. 1. Dioxane.
2. Cyclohexane. 3. Diethyl ether. 4. Acetone. 5. Nitrometha-

ne. 6. Methylacetate. 7. Acetonitril. 8. n-Hexane. 9. 1,2-
Dichlorethane. 10. Ethanol. 11. n-Propanol. 12. n-Buthanol.
Correlation coefficient 0,96.

As was shown in /26/ the $\Delta\Delta F$ value may be determined
using the following expression:

$$\Delta\Delta F = \frac{\mu^2}{a^3}\left(\frac{\varepsilon_\delta - 1}{\varepsilon_\delta + 2} - \frac{\varepsilon_c - 1}{\varepsilon_c + 2}\right) + \Delta W_g + \Delta W_n \quad (9)$$

The first term of this expression includes variations in the
free energy of orientation-induction interaction between the
molecule and the medium when the dioxane solvent in the boat
form is replaced by that in the chair form; the second and
the third terms include changes in the dispersive and
cavitation energies in the process considered. Assuming $\Delta W_g =$
0, we shall have:

$$\Delta\Delta F = \frac{\mu^2}{a^3}\left(\frac{\varepsilon_\delta - 1}{\varepsilon_\delta + 2} - \frac{\varepsilon_c - 1}{\varepsilon_c + 2}\right) + \Delta W_n \quad (10)$$

The ΔW_n value was calculated by the method described in Ref.
/24/ and was found to be equal to 0,26 $\frac{kcal}{mole}$. On the other hand,
in the case when there are no pronounced specific interacti-
ons between a given molecule and a dioxane molecule the mole
fraction of the polar form of the dioxane in the solvate
shell of the molecule (x_δ) may be calculated from expression
(2) using the $\frac{\varepsilon_\delta - 1}{\varepsilon_\delta + 2}$ value obtained earlier.

The values of $\Delta\Delta F$ and ΔF_{c-b} calculated by the above-
described method for the molecules which do not form strong
H-bonds with dioxane molecules are given in Table 3.

Table 3.

Compound	x_b	$\Delta\Delta F$ (kcal/mole)	ΔF_{c-b} (Kcal/mole)
1. nitrobenzene	0,80	2,7	1,9
2. nitrotoluene	0,80	2,8	2,0
3. p-dimethylamine- - nitrostyrene	0,63	1,9	1,6
average value			1,8

The agreement between the chair-boat transition free ener-
gy values ΔF_{c-b} determined by dielcometric ($\Delta F_{c-b} = 2,3$
kcal/mole) and spectroscopic ($\Delta F_{c-b} = 1,8$ kcal/mole) methods
is quite fair. It is important to note that the $\Delta\Delta F$ value
exceeds appreciably the chair-boat transition free energy for
dioxane (see Fig. 2), which suggests that the polar molecule
of the substance has an ability for conformation reconstruction
of dioxane molecules composing its solvate shell. To verify
this hypothesis, "model dioxane" was prepared consisting of a
mixture of polar and nonpolar solvents and possesing electri-
cal properties similar to natural dioxane. Cyclohexane and
1,2-dichlorethane were choosen as solvents to obtain such a
system (see Table 4).

Table 4.

Solvent	$\dfrac{n^2 - 1}{n^2 + 2}$	$\dfrac{\varepsilon - 1}{\varepsilon + 2}$
1. 1,2-Dichlorethane	0,263	0,750
2. Cyclohexane	0,256	0,256
3. Model dioxane	0,256	0,287
4. 1,4-Dioxane	0,253	0,287

It should be noted that the content of the polar compo-
nent ($N_\varepsilon \approx 0,8$ m.d.) in "model dioxane" exceeds essentially
that in real dioxane. Model dioxane was used for obtaining
relations between the shifts of dioxane longwave absorption
band in the electronic spectrum of nitrobenzene and the volume
composition of multicomponent solvents such as heptane-dioxane
and heptane-model dioxane (see Fig. 2).

It was found /24/ that the shifts of the absorption band
as a function of the composition of binary solvent are usual-
ly non-linear, the degree of nonlinearity being governed both
by the energy of universal untermolecular interaction with
the solvent components and by the ratio of the components in
the solvent. When the macrocharacteristics of the components
and the composition of binary solvent are in close agree-
ment the character of the displacement of the absorption bands
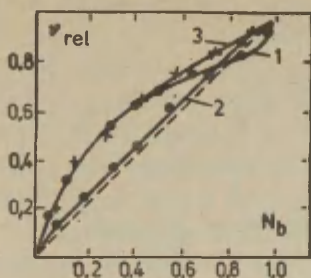of the molecules must be analogous. A comparison of the ob-

Fig.2. Relative shifts of absorption band of nitroben-
zene vs. volume percentage of polar solvent. 1.Dio-
xane-n-heptane. 2. Model dioxane-n-heptane. 3.1,2-
Dichlorethane-n-heptane.

tained relations between the displacement of spectra and the
composition of the binary solvent shows substantial distincti-
on (see Fig.2). Thus in the case of a heptane-dioxane mixture
the solvate shell of the molecules is enriched by polar mole-
cules to a greater extent than in the case of heptane-model
dioxane. It is important to note that the shape of the curve
($\nu_{OTH.}$) vs. N_b in the heptane -1,2-$C_2H_4Cl_2$ system is similar
to that in the case of binary mixture of heptane-dioxane. The
comparison carried out allowed to conclude that about 80% of
polar molecules of dioxane in the solvate shell were accoun-
ted for not by diffusion but by their conformational recon-
struction. Hence it may be concluded that anomalies noted in
the behavior of solvent dioxane are due to not only the exi-
stence of polar conformers in dioxane solvent but also to
the ability of dioxane to undergo conformational reconstruc-
tions under the influence of the intermolecular interaction
energy of dissolved molecules.

Our investigations by no means diminish the significance
of the formation of the H-bonds between proton-donor and dio-
xane molecules in many processes. They neither exclude the
fact that in certain cases H-bonds may have decisive influen-
ce on the rate and mechanism of chemical reactions. Apparent-

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ly the so-called "dioxane effect" (when the dipole moments of molecules measured in pure dioxane by the dielcometric method are usually greater than those measured in benzene) is mainly associated with specific interactions in dioxane. Our findings elucidating the effect of universal intermolecular interactions on dioxane properties emphasize the necessity to consider the problem of dioxane effect both as regards specific and universal intermolecular interactions.

In conclusion the writers wish to express their gratitude to Prof. N.G. Bakhshiev for his valuable comments in the process of discussion of the paper.

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INTERACTION OF ORGANOPHOSPHORUS COMPOUNDS WITH
α-CHYMOTRYPSIN. X. THE INFLUENCE OF THE HYDRO-
PHOBICITY OF THE ACID PORTION OF THIOPHOSPHONATES

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The second-order rate constants k_1 of the reaction bet-
ween α-chymotrypsin and its organophosphorus quasisub-
strates $(RO)(CH_3)P(O)SC_4H_9$-n where R is a normal or ϲ
branched-chain hydrocarbon radical (25.0°C, pH 7.6,
0.04 M Na-veronal - HCl buffer) have been determined.
The reactivity of the quasisubstrates depends on the
hydrophobicity of the radical R and is described by the
equation $\log k_1 = const + \varphi'\pi$ up to $\pi = 3$ ($\varphi' = 1.49 \pm$
± 0.12) irrespective of the type of the branching of R
(13 compounds); in the case of $\pi > 3$ $\log k_1$ fall on a
separate straight line with the slope -0.54 ± 0.12
(6 compounds). The conclusion has been drawn that the
break   in the $\log k_1$ versus π plot is determined
by a border length of the main chain of alkoxyl radi-
cal while the change of the reactivity of the quasi-
substrates with "allowed" extent of the radical is
completely determined by the hydrophobicity of R which is
accounted for by its π-constant.

In the case of the reaction between   α-chymotrypsin
(CT) and O-alkyl methylthiophosphonic acid n-butyl esters,

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$(RO)(CH_3)P(O)SC_4H_9-n$, iso-branching of the hydrocarbon
radical $R = -(CH_2)_mCH(CH_3)_2$ in acid portions of the qua-
sisubstrates did not cause considerable changes in their
second-order rate constants (k_1) compared with the quasi-
substrates with normal hydrocarbon radicals[1,2].At the same
length of main chain the compounds with branched hydrocar-
bon radicals in O-alkyl substituents had somewhat greater
values of k_1 than the quasisubstrates with normal radicals
which is analogous to the influence of branching on the
competitive inhibitory effectiveness of aliphatic alcohols
on CT[3]. It was shown[3,4] that independently of the alcohol
hydrocarbon chain branching,their log K_1 were in correla-
tion with the logarithms of the partition coefficients
(log P) in non-aqueous solvent (octanol) - water system.

On the basis of these data one can assume that the in-
fluence of the structure of alkoxyl radical in the acid
portion of the compounds $(RO)(CH_3)P(O)SX$ upon their k_1 in
the reaction with CT can entirely be described by π-cons-
tant[5,6] of R which characterizes the hydrophobicity of the
substituent. In order to prove this assumption the second-
-order rate constants of the reaction between CT and a num-
ber of quasisubstrates $(RO)(CH_3)P(O)SC_4H_9-n$ with highly
branched O-alkyl substituents have been determined in this
work in addition to the data mentioned above[1].We have used
the reaction series in which π-conctants of R varied
within 1.5 units at the same length of the main chain of
the substituent.

Experimental section

α-Chymotrypsin was a crystallized sample from Leningrad
Meat Packing Plant Medical Preparation Works.

Synthesis and the physical properties of the organophos-
phorus inhibitors (OPI) were described ealier[7-9].

N-Acetyl-L-tyrosine ethyl ester (ATEE) was a prepara-
tion of Reanal.

Na-veronal was recrystallized from double-distilled wa-

ter and dried at 110°C.

Acetonitrile was dried over P_2O_5 and rectified.Before the final distillation the sample was dried over K_2CO_3. The fraction with b.p. 81.8°C at 759 mm Hg was collected.

HCl - "chemically pure" grade.

KOH - Reinst,VEB chem.Werke, Buna.

1-octanol - "analytically pure" grade.

Double-distilled water was used.

The reaction of CT with organophosphorus quasisubstrates was conducted at 25.0 $\pm$ 0.1° C,pH 7.60 $\pm$ 0.02 in 0.04 M Na-veronal - HCl buffer.CT stock solutions were prepared in 10^{-3}M HCl, OPI and ATEE stock solutions - in acetonitrile.

The rate of the reaction of OPI with CT was determined on pH-stat ("Radiometer" TTT1d/SBR2c/ABU1c) by the residual activity of the enzyme.ATEE was used as substrate. The reactions were conducted under the condition that $[Q]_o \gg [E]_o$ to the extent of inhibition not less than 40 - 60%. Detailed technique of the kinetic measurements has been described earlier[10].

The second-order rate constants were calculated from the relationships between the observed first-order rate constants k_I and $[Q]_o$, according to the equation:

$$k_I = k_{I,o} + k_1[Q]_o \quad , \tag{1}$$

where $k_{I,o}$ is the rate constant of the spontaneous inactivation of the enzyme in the course of the reaction with quasisubstrate[11].

In the case of OPI with $k_1 < 10^{-2}$ $M^{-1}sec^{-1}$ the rate of the spontaneous inactivation of CT in the experimental conditions was comparable in magnitude to the rate of the reaction between CT and OPI. Disregarding this matter the heightened values of the second-order rate constants for the compounds $(C_nH_{2n+1}O)(CH_3)P(O)SC_4H_9$-n with n = 1 - 3 were published ealier[1,2].In the present work the corrected values of k_i obtained from the relationships (1) are given (the compounds 1 - 4 in Table 1).

Results and discussion

The second-order rate constants of the reaction between CT and n-butyl esters of O-alkyl methylthiophosphonic acids which contain normal and branched O-alkyl substituents in acid portion are listed in Table 1. The hydrophobicity constants for normal hydrocarbon radicals were calculated on the assumption that each methyl group makes an additive contribution of 0.5 units to the π of the radical[5,6].

Chain branching in aliphatic compounds generally leads to the reduction of its π as compared to the normal hydrocarbon radical with the same number of methylene groups (see[6,12,13]). It can be concluded from the comparison of log P for normal and branched-chain alcohols[6,12,13] given in Table 2. It is evident from the Table that the chain branching in α-position with respect to functional group decreases log P about 0.3 units and branching in the more distant positions - about 0.2 units. Therewith, in the case of 2,2-dimethylpropyl radical there is practically no branching effect. Determination[*] of the partition coefficients for the OPI $\{[(CH_3)_3CCH(CH_3)O](CH_3)P(O)SC_2H_4\overset{+}{S}(CH_3)C_2H_5\}CH_3SO_4^-$ and $[(n-C_6H_{13}O)(CH_3)P(O)SC_2H_4\overset{+}{S}(CH_3)C_2H_5]CH_3SO_4^-$ in octanol - - water system enabled us to draw the same conclusion for another highly branched radical, $(CH_3)_3CCH(CH_3)-$ (log P for the above-mentioned OPI have the same value, -2.63).

Figure 1 gives the dependence of log k_i from Table 1 upon π for hydrocarbon radicals R. The figure shows that log k_i is proportional to the hydrophobicity of the substituent up to $\pi = 3$ (the parameters of the correlation are listed in Table 3).Excluding from the series the derivati-

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[*] The technique of the determination of log P has been described elsewhere[14].

Table 1

The Second-order Rate Constants of the Reaction Between α-Chymotrypsin and n-Butyl Esters of O-alkyl Methylthiophosphonic Acids, $(RO)(CH_3)P(O)SC_4H_9$-n. Temperature 25.0°C, pH 7.6, 0.04 M Na-veronal - HCl buffer, 0 - 0.5% (v/v) acetonitrile.

N°	R	$k_1 [M^{-1}sec^{-1}]$	π [a]
1	CH_3	$(4.73 \pm 0.29) \cdot 10^{-4}$	0.5
2	C_2H_5	$(7.26 \pm 0.01) \cdot 10^{-4}$	1.0
3	$n-C_3H_7$	$(9.16 \pm 1.25) \cdot 10^{-3}$	1.5
4	$(CH_3)_2CH$	$(8.64 \pm 1.67) \cdot 10^{-4}$	1.2
5	$n-C_4H_9$	$(1.02 \pm 0.03) \cdot 10^{-1}$ [b]	2.0
6	$(CH_3)_2CHCH_2$	$(4.68 \pm 0.34) \cdot 10^{-2}$ [c]	1.8
7	$CH_3CH_2CH(CH_3)$	$(3.48 \pm 0.50) \cdot 10^{-2}$ [c]	1.7
8	$n-C_5H_{11}$	$(2.84 \pm 0.18) \cdot 10^{-1}$ [b]	2.5
9	$(CH_3)_2CH(CH_2)_2$	$(2.85 \pm 0.06) \cdot 10^{-1}$ [c]	2.3
10	$(CH_3)_3CCH_2$	$(7.15 \pm 0.90) \cdot 10^{-2}$	2.5
11	$n-C_6H_{13}$	1.66 ± 0.05 [b]	3.0
12	$(CH_3)_2CH(CH_2)_3$	$(5.10 \pm 0.29) \cdot 10^{-1}$ [c]	2.8
13	$(CH_3)_3CCH(CH_3)$	1.36 ± 0.14	3.0
14	$n-C_7H_{15}$	1.51 ± 0.05 [b]	3.5
15	$(CH_3)_2CH(CH_2)_4$	2.47 ± 0.06 [c]	3.3
16	$n-C_8H_{17}$	$(9.61 \pm 0.50) \cdot 10^{-1}$ [b]	4.0
17	$(CH_3)_2CH(CH_2)_5$	1.16 ± 0.07 [c]	3.8
18	$CH_3(CH_2)_5CH(CH_3)$	2.16 ± 0.07	3.7
19	$n-C_9H_{19}$	$(5.40 \pm 0.43) \cdot 10^{-1}$ [b]	4.5
20	$(CH_3)_3CCH(CH_3)$ [d]	2.73 ± 0.13	3.0
21	$n-C_6H_{13}$ [d]	4.63 ± 0.25 [b]	3.0

[a] Calculation of π-constants see text. [b] Taken from literature[2]. [c] Taken from literature[1]. [d] The leaving group is $-SC_2H_4SC_2H_5$.

Table 2

Comparison of log P for Normal and Branched-chain
Alcohols

Compound	log P [a]	$\Delta\pi$ for one branching
$CH_3CH_2CH(CH_3)OH$	0.61	
$n\text{-}C_4H_9OH$	0.88	-0.27
$(CH_3)_3COH$	0.37	
$n\text{-}C_4H_9OH$	0.88	-0.26
$CH_3CH_2C(CH_3)_2OH$	0.86	
$n\text{-}C_5H_{11}OH$	1.40	-0.27
$(CH_3)_2CHCH_2OH$	0.65	
$n\text{-}C_4H_9OH$	0.88	-0.23
$(CH_3)_2CH(CH_2)_2OH$	1.16	
$n\text{-}C_5H_{11}OH$	1.40	-0.24
$(CH_3)_3CCH_2OH$	1.36	
$n\text{-}C_5H_{11}OH$	1.40	-0.04

[a] The logarithms of the partition coefficients in
octanol – water system[6,12,13].

Fig. 1. Dependence of the logarithms of the second-order
rate constants of the reaction between α-chymo-
trypsin and the compounds $(RO)(CH_3)P(O)SC_4H_9$-n upon
the π of the hydrocarbon radical R. ●, normal
radicals; ○, branched radicals. The calculation
of π-constant see in text; experimental conditions
see Table 1.

ves with branched hydrocarbon substituents (1b in Table 3)
as well as replacing the leaving group $-SC_4H_9$-n by
$-SC_2H_4SC_2H_5$[15,16] (series II) or by $-SC_2H_4\overset{+}{S}(CH_3)C_2H_5$[15] (se-
ries III) did not change the slope of the straight line. It
is as well evident from the Figure 1 that log k_1 for the
quasisubstrates where the π of hydrocarbon radical exceeds
the value 3 fall on a separate straight line with a negative

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Table 3

Dependence of the Reactivity of the Chymotrypsin Quasisubstrates $(RO)(CH_3)P(O)SX$ upon the Hydrophobicity of the Hydrocarbon Radical R in Their Acid Portion. The Results of Correlation between the Logarithms of the Second-order Rate Constants, $\log k_1$, and π-constants of the Substituents According to the Equation $\log k_1 = $ const $+ \varphi'\pi_R$.

N°	R	X	Slope[a) φ'	r	e	Ref.
I	C_nH_{2n+1}, n = 1 – 6 [b)	$-C_4H_9-n$	1.49 ± 0.12	0.965	0.332	
Ia	C_nH_{2n+1}, n = 6 – 9 [b)	$-C_4H_9-n$	-0.54 ± 0.11	0.930	0.100	
Ib	$n-C_nH_{2n+1}$, n = 1 – 6	$-C_4H_9-n$	1.52 ± 0.12	0.988	0.251	
II	$n-C_nH_{2n+1}$, n = 1 – 6	$-C_2H_4SC_2H_5$	1.33 ± 0.08	0.993	0.165	15,16
III	$n-C_nH_{2n+1}$, n = 1 – 6	$-C_2H_4\overset{+}{S}(CH_3)C_2H_5$ [c)	1.34 ± 0.08	0.993	0.170	15

[a) At the 95% confidence level.

[b) Both normal and branched hydrocarbon radicals included, see text.

[c) The compounds were used as salts with $CH_3SO_4^-$.

elope (series Ia in Table 3).

Up to the break that is observed in the plot of log k_i versus π at $\pi = 3$ only the 2,2-dimethylpropyl derivative deviates from the correlation line. It cannot be explained by steric effect of the substituent since all the points for the rest of compounds with branched and normal substituents fall on common straight line. In the limits of $\pi \leqslant 3$ the length of the main chain of the hydrocarbon radical seems not to be essential for the reactivity of the quasisubstrates. This statement follows from the comparison between the k_i for the compounds which have equal length of the main chain of radical R, particulary from the comparison of k_i for n-propyl, iso-butyl, sec-butyl, 2,2-dimethylpropyl and 1,2,2-trimethylpropyl derivatives.It is seen from Table 1 that the k_i values for the compounds vary for two orders of magnitude according to the variation in the π of R. Concequently, up to the break at $\pi = 3$ the change of the reactivity of the studied quasisubstrates, n-butyl esters of O-alkyl methylthiophosphonic acids,depends only upon the hydrophobicity of the hydrocarbon radical.Most likely the same holds for the quasisubstrates of the series II (Table 3) where k_i for n-hexyl and 1,2,2-trimethylpropyl derivates are close to one another (see N° 20 and 21 in Table 1).

After the break at $\pi = 3$ log k_i decrease by increasing of π (see Figure 1) irrespective of the branching of radical R. This is not inconsistent with the conclusion made above which concerns the dependence of log k_i upon the hydrophobicity of R. But the question whether the break is determined by high π value or by the extent (the length of the main chain) of the substituent, or by both, remains unsolved on the basis of the data. To deal with this problem it is necessary to have quasisubstrates with π that substantially exceed the value 3 at "permitted" length (not exceeding the length of n-hexyl radical), for example, the quasisubstrates with the radicals $(CH_3)C(CH_2)n^-$, where n = 3 and 4.

It should be noted that concerning the reaction between

CT and N-acetyl-L-amino acid methyl esters, $CH_3C(O)NHCH(R_2)C(O)OCH_3$, the data to comply with this requirement can be found in literature[18-21]. In Figure 2 a linear correlation between $\log(k_{cat}/K_m^{app})$ and π for aliphatic amino acid side chain R_2 is presented. At $R = n\text{-}C_5H_{11}$, which has $\pi = 2.5$ a break is observed in this plot. The value of $\log(k_{cat}/K_m^{app})$ for the substrate with $R_2 = n\text{-}C_6H_{13}$ ($\pi = 3.0$) is for 0.6 units smaller than $\log(k_{cat}/K_m^{app})$ for n-pentyl derivative[18]. At the same time the

Fig. 2. Dependence of the logarithms of second-order rate constants of the reaction between α-chymotrypsin and substrates $CH_3C(O)NHCH(R_2)C(O)OCH_3$[18,19,22,24] upon the π of R_2. Temperature 25°C, pH 7.8 - 8.0, 0.1 M NaCl or KCl. The calculation of π-constants see text.

$\log(k_{cat}/K_m^{app})$ for phenylalaline[18,19,22] ($\pi = 2.63$)[*] and β-cyclohexylalaline[18] ($\pi = 2.89$)[**] derivatives are more than the order of magnitude higher than $\log(k_{cat}/K_m^{app})$ for the derivative with $R_2 = n\text{-}C_6H_{13}$, and fall on the extention of the straight line conducted through the points for the $\log(k_{cat}/K_m^{app})$ of the compounds which have the main chain length not over five methylene groups. From this the conclusion can be made that in the given series of substrates and probably as well in the series of the OPI studied in the present work the break observed in the logarithm of the second-order rate constant versus π plot is determined by the sizes (the length of the main chain) of appropriate substituent.

It can be seen from Figure 2 that in the case of substrates $CH_3C(O)NHCH(R_2)C(O)OCH_3$ the k_{cat}/K_m^{app} for valine and isoleucine derivatives which have "permitted" length of the radical R_2 sharply fall out from the correlation line[***]. At the same time the k_{cat}/K_m^{app} for N-acetyl-L-leucine methyl ester[18,24] falls on the line. Such a specific influence of branching in β-position with respect to the reaction centre of amino acid substrates[25-27] and the absence of the effect in the case of n-butyl esters of O-alkyl methylthiophosphonic acids is apparently connected with the differences in the orientation of the substituents at carbonyl carbon in amino acid esters and at tetrahedral phosphorus in phosphonates.

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[*] The π is calculated from the data given in literature[6]: $\pi_{C_6H_5CH_2} = \log P_{C_6H_6} + \pi_{-CH_2-}$.

[**] Data from literature.[17]

[***] The falling out of $\log(k_{cat}/K_m^{app})$ for the derivatives of valine and isoleucine is mainly due to the low values of enzyme acylation rate constants (see[23]).

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KINETIC INVESTIGATION OF ALCOHOLYSIS OF SOME ESTERS ON CATION EXCHANGE RESIN KU-2-8

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The substituent effects on the kinetics of alcoholysis of some esters has been investigated with cation exchange resin KU-2-8 as a catalyst. The linearity between energies and entropies of activation was observed for three reaction series that permits treat them as isokinetic. The equilibrium constants of investigated reactions correlate with the Taft substituent constants. The similar curves for rate constants and sorption constants of components of reaction mixture have a peak when passing from electron-donating to electron-accepting substituents, i.e., $\rho^{\ast}$ changes its sign. Due to the analysis of relationships obtained, the cation catalysis is similar to that of homogeneous acid catalysis, posessing, however, singularities resulting in anomaly of relationship between rate constants and substituent constants.

Investigation in the field of ion exchange resin catalysis[1,2] has shown the cation exchange resins to be typical acid catalyst. However, their peculiarities cause certain difficulties in establishing quantitative relationships between reagent structure and their reactivity, medium characteristics and reaction kinetics on cation exchange resins, etc.[3,4] As it was shown earlier[5,6] these difficulties are caused mainly by selective sorption of the components of reaction mixture and by the complexity of determination of the true concentrations of reagents.

Developing the proper techniques of kinetic measure-ments[5] we investigated the reagent structure effect on the parameters of alcoholysis of esters catalyzed by cation ex-change resin KU-2-8. The kinetic investigation of alcoholy-sis was carried out at 70, 80, 90 and 100°C for the follow-ing reaction series:

1. $ROH + C_2H_5OOC-CH=CH_2 \rightleftharpoons C_2H_5OH + HOOC - CH=CH_2.$

   $R:-CH_3; -C_4H_9; -i-C_5H_{11}; -C_2H_4OC_2H_5; -CH_2CH=CH_2; -CH_2-C_6H_5;$

2. $C_4H_9OH + R'OOC-CH=CH_2 \rightleftharpoons R'OH + C_4H_9OOC-CH=CH_2.$

   $R':-CH_3; -C_2H_5; -i-C_3H_7; -C_2H_4OCH_3; -CH_2CH=CH_2;$

3. $C_4H_9OH + C_2H_5OOC-R'' \rightleftharpoons C_2H_5OH + C_4H_9OOC-R''.$

   $R'':-CH_3; -C_2H_5; -iC_3H_7; -CH_2CL; -CF_3; -CH=CH_2;$
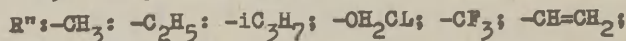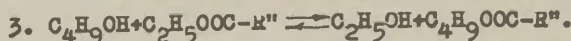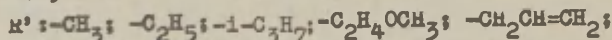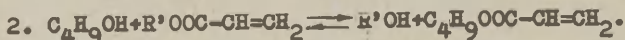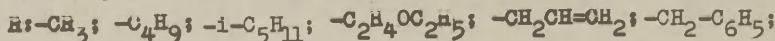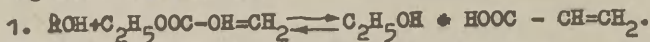
The rate and equilibrium constants, the energy and entropy of activation were calculated from the experimental data. Also the ability of components from the reaction mixture to be sorbated(defined as a ratio of the quantity of compo-nent in ion exchange resin phase to the total quantity of this component in the reaction mixture ($\Gamma_i^{r.m.}$)) was deter-mined.

The experimental data are represented in Table 1 and in Figures 1-4.

The dependence between activation energy and entropy being linear, (Fig.1), the series can be treated as isokine-tic. Applying of Taft equation[7,8] can be expected due to re-lationship represented in Fig.1. Correlation of rate con-stants with Taft substituent constants (Fig.2) proves it. However, if the $\lg K_p$ vs. σ^* plot (Fig.2) is linear within the whole range of variation it is not the case for the rate constants where the curve has a peak passing from electron-donating substituents to electron-accepting ones, ρ^* changing its sign. It should be noticed that experi-mental points for $CH_2=CH-$(curve 3, Fig.3) and $C_2H_5CH_2-$ (curve 1, Fig. 3) substituents did not fit the main rela-tionship. It might be due to their interaction with the

Table 1

Parameters of Kinetics of Alcoholysis. (Reesterification) of Esters on Cation Exchange Resin KU-2-8. The Concentration of Cation Exchange Resin Is 26.1 $g_{res.}$/mol $_{mixt}$

Series		Substituent	6^*	E kcal/mol	$S\neq$ e.u.	$Kp^{x)}$	$k\cdot10^2$ min^{-1}	α^{rm}_i
$KOH+C_2H_5OOCCHCH_2$	$C_2H_5OH+ROOCCHCH_2$	$-CH_3$	0,00	16,8	-28,2	0,99	2,39	0,740
		$-C_4H_9$	-0,130	14,9	-36,6	0,76	0,446	0,356
		$-i-C_5H_{11}$	-0,162	14,6	-37,6	0,69	0,392	0,322
		$-C_2H_4OC_2H_5$	0,25	14,0	-39,4	1,67	0,328	0,270
		$-CH_2-CH=CH_2$	0,18	15,1	-35,5	1,32	0,538	0,398
		$-CH_2-C_6H_5$	0,215	12,8	-46,4	1,58	0,144	0,156
$C_4H_9OH+R'OOCCHCH_2$	$R'OH+C_4H_9OOCCHCH_2$	$-CH_3$	0,00	15,9	-31,5	0,66	0,901	0,245
		$-C_2H_5$	-0,1	14,9	-36,6	0,76	0,446	0,128
		$-i-C_3H_7$	-0,115	15,6	-34,4	0,94	20,370	0,138
		$-C_2H_4OOH_3$	0,25	15,8	-32,1	0,37	0,851	-
		$-CH_2-CH=CH_2$	0,18	15,7	-33,4	0,44	0,807	0,206
$C_4H_9OH+C_2H_5OOC$ R''	$C_2H_5OH+C_4H_9OOC$ R''	$-CH_3$	0,00	13,7	-35,5	0,97	6,65	0,215
		$-C_2H_5$	-0,1	15,0	-32,4	0,83	2,58	0,149
		$-iC_3H_7$	-0,19	14,0	-37,6	1,03	0,55	0,073
		$-CH_2Cl$	1,05	11,3	-42,0	0,68	5,47	0,120
		$-CF_3$	2,6	9,4	-47,6	0,51	4,91	0,096
		$-CH=CH_2$	0,653	14,9	-36,6	0,76	0,446	0,128

x) Equilibruim conctants (Kp) and rate constante (k) are taken at $T=343^{o}K$.
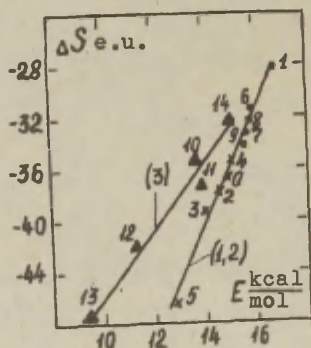
Fig.1. Relationship between energy and entropy
of activation.

(1) **x** Series $ROH+C_2H_5O_2CCH=CH_2 \rightleftarrows$; r=0,995; s=0,62

$0-C_4H_9$; $1-CH_3$; $2-i-C_5H_{11}$; $3-C_2H_4OC_2H_5$; $4-CH_2CHCH_2$;

$5-CH_2C_6H_5$;

(2)●Series $C_4H_9OH+R'O_2CCH=CH_2 \rightleftarrows$; r=0,952; s=0,71

$0-C_2H_5$; $6-CH_3$; $7-C_3H_7$; $8-C_2H_4CCH_3$; $9-CH_2CH=CH_2$;

(3)▲Series $C_4H_9OH+C_2H_5O_2CR'' \rightleftarrows$; r=0,955; s=0,18

$0-CH=CH_2$; $10-CH_3$; $11-i-C_3H_7$; $12-CH_2Cl$; $13-CF_3$;

$14-C_2H_5$;

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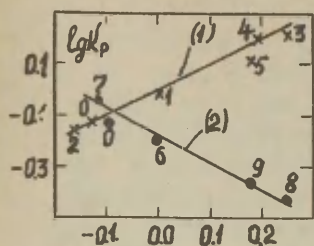
Fig.2. The relationship bet-
        ween equilibrium con-
stants and Taft substituent
constants

r=0.957-0.996;

s=0.65-0.82;
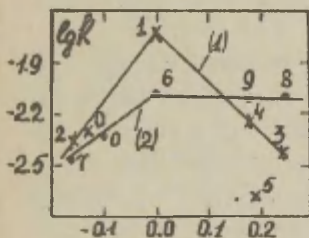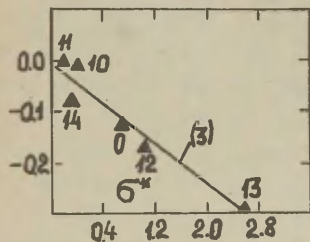
See Fig. 1, for symbols.
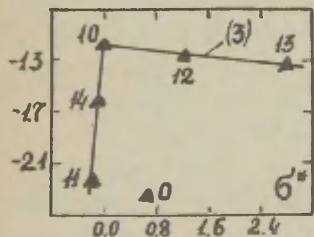

Fig.3. The relationship bet-
        ween the rate con-
stants for direct reaction
and Taft substituent con-
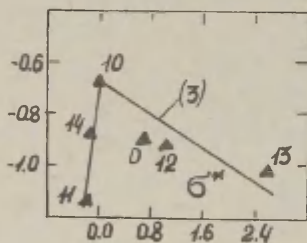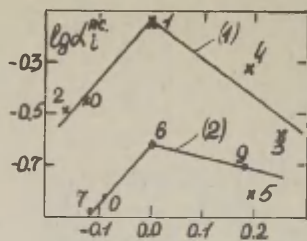stans.

See Fig. 1 for symbols.

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Fig. 4. The relationship between abilities of the components from reaction mixture to be sorbate and Taft substituent constants.
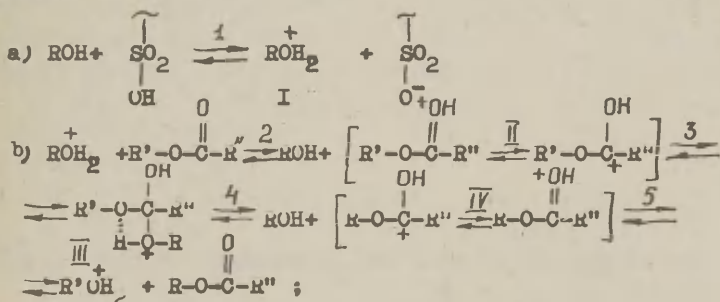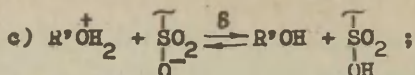See Fig. 1. for symbols.

reaction center that causes the delocalization of electrons and, hence, decreases the reactivity.

Changing of ρ^{*} sign is normally interpreted as the change of the mechanism of the reaction. But for the case it isn't so, as the same peak must have been presented on the curve $\lg Kp = f$ (σ^{*}) which in reality did not take place. The anomaly of function $\lg K = f$ (σ^{*}) depends, apparenfly. on the transformations in the ionite phase and interaction of the cationite with components of reaction mixtures. Such an assumption is probable, if the fact, that Taft equation is based on relationships obtained by investigation of kinetics and equilibrium of hydrolysis of esters and,consequently, on the realization of correlations of homogencous acid catalysis, is taken into consideration. The same conclusion may be reached from comparison of ability of cation exchange resin to sorbate the components (with variable substituents of the reaction mixture with substituent constants of the same components (Fig.4). Fig.4.shows the relationship $\lg \alpha_{i}^{r.m.} = f$ (σ^{*}) to be similar to the relationship demonstrated on Fig. 3.

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From the analysis of experimantal data (see Fig. 1-4) and relationships for homogenous acidic hydrolysis of esters it may be inferred that intermediate states in the catalysis with soluble acids and with cation exchange resins are identical. Hence, one may suggest that the mechanism of cation exchange resin catalysis is similar to that of homogenous catalysis. According to the generally accepted mechanism[10] the reesterification is going through protonization of carbonyl oxygen with subsequent nucleaphilic attack of alcohol molecule on the newly developed cation. But due to the comparativly low ability of cation exchange resins to sorbate esters, their direct protonization in this case is hindered. Consequently we suggested[11] that a special carrier is needed to trasport the proton cation exchange resin to ester. Molecules of alcohol may obviously serve such carriers; their ability to sorbate[11] limits the rate of reesterification on cation exchange resins.

The earlier[12] suggested mechanism of reesterfication may be defined more precisely due to obtained identity of intermediate states in homogeneous and cation exchange resin catalysis and due to some peculiarities of alcoholysis reaction with the cation exchange resin. The increased number of objects of investigation, makes it possible to suggest that the substituent effect on the reaction rate may be defined not only by structure of reaction state but by the rates of different stages of the alcoholysis reaction on cation exchange resin as well:

a) $ROH + \widetilde{SO_2} \overset{1}{\rightleftharpoons} R\overset{+}{OH_2} + \overline{SO_2}$

b) $R\overset{+}{OH_2} + R'-O-\overset{\|}{\underset{OH}{C}}-R'' \overset{2}{\rightleftharpoons} ROH + \left[R'-O-\overset{\|}{\underset{OH}{C}}-R'' \overset{II}{\rightleftharpoons} R'-O-\overset{OH}{\underset{+OH}{\overset{|}{C}}}-R'' \right] \overset{3}{\rightleftharpoons}$

$\rightleftharpoons R'-O-\overset{|}{\underset{III}{\underset{H-O-R}{C}}}-R'' \overset{4}{\rightleftharpoons} ROH + \left[R-O-\overset{|}{\underset{+}{C}}-R'' \overset{IV}{\rightleftharpoons} R-O-\overset{\|}{C}-R'' \right] \overset{5}{\rightleftharpoons}$

$\rightleftharpoons R'\overset{+}{OH_2} + R-O-\overset{\|}{C}-R'' ;$

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c) $R'\overset{+}{O}H_2 + \overset{\displaystyle\frown}{\underset{O^-}{SO_2}} \overset{\text{B}}{\rightleftharpoons} R'OH + \overset{\displaystyle\frown}{\underset{OH}{SO_2}}$;

In the first step (a) the alcohol is sorbated by cation exchange resin and then is protonized forming the cation I. Then (stage b) alcohol transports a proton to carbonyl oxygen of esters, thus forming the cation II which, in its turn, interacts with alcohol and forms intermediate III. In the intermediate state the proton, certainly, can migrate from the oxygen of one ester to the oxygen of another ester. The decomposition of intermediate state results in forming an alcohol molecule and cation IV which as well as cation II is oksonium salt of ester. The reaction ends with trasportation of proton from esters to newly formed alcohol with the result of forming of cation V and with subsequent transportation of proton to sulphonic-acid group of cation exchange resin (c).

From the scheme it can be easily seen that the energy and the entropy of activation are possibly defined by the easiness of forming the intermediate III and the rate constatnts must depend on the distribution of charge over the ester oxy gen atoms of the coming and leaving alcohol groups. To discuss relationships between the rate and the reagent structure based on the suggested mechanism scheme is much more difficult. The reaction is multistaged, all stages (except the one or de composition of the intermediate) being bimolecular and differ on attacks: electrophilic attack of cation I on the ester molecule (2) nucleophilic attack of alcohol molecules on the cation II, etc. According to that and taking into account Fig. 3, showing the change of ρ^{*} sign and the change of character of attack from electrophylic to nucleophilic, one might suggest that we are dealing with transition from one stage limiting the reaction rate (2) to another (3).

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DETERMINATION OF pK_a VALUES OF FORMOCHOLINE AND CHOLINE CHLORIDES, AND BIS-(DIETHYLAMINO)-METHANE

V.M. Nummert, V.A. Palm, and M.K. Uudam

Chemistry Department, Tartu State Universtiy,
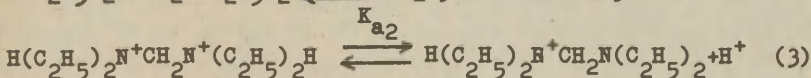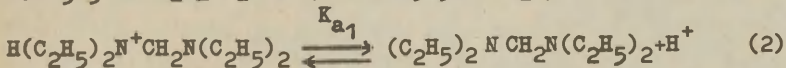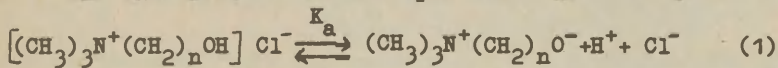Estonian S.S.R., U.S.S.R.

The pK_a values of formocholine and choline chlorides, and bis-(diethylamino)-methane have been determined in water at $25^{\circ}C$ potentiometrically.

The $\sigma^{\ast}$ values for charged substituents NMe_3^+, NMe_2H^+, and NEt_2H^+ with and without electrostatic correction were calculated making use of these and literature pK_a values for alcohols and ammonium ions, and also the $\lg(k_{OH}/k_H)$ data for phenyl benzoates hydrolysis.

The $\sigma^{\ast}$ values for NMe_3^+, NMe_2H^+ and NEt_2H^+ rather close to each other were obtained.

The purpose of this work was to determine the pK_a values of formocholine chloride $[(CH_3)_3N^+CH_2OH]Cl^-$, choline chloride $[(CH_3)_3N^+CH_2CH_2OH]Cl^-$ and the pKa_2 value of bis-(diethylamino)- methane $(C_2H_5)_2NCH_2N(C_2H_5)_2$. As far as we are aware corresponding literature values are absent. The pK_a data of these compounds enable to estimate the $\sigma^{\ast}$ constants for charged substituents of type $R_1R_2R_3N^+$.

One can write the studied processes as follows:

$$\left[(CH_3)_3N^+(CH_2)_nOH\right]Cl^- \xrightleftharpoons{K_a} (CH_3)_3N^+(CH_2)_nO^- + H^+ + Cl^- \quad (1)$$

$$H(C_2H_5)_2N^+CH_2N(C_2H_5)_2 \xrightleftharpoons{K_{a_1}} (C_2H_5)_2NCH_2N(C_2H_5)_2 + H^+ \quad (2)$$

$$H(C_2H_5)_2N^+CH_2N^+(C_2H_5)_2H \xrightleftharpoons{K_{a_2}} H(C_2H_5)_2N^+CH_2N(C_2H_5)_2 + H^+ \quad (3)$$

The processes (1) and (3) are dependent on the intra-molecular ion-ion interaction between reaction center and substituent: "plus-minus" interaction in the case of disso-ciation of cholines (equilibrium 1) and "plus-plus" inter-action in the case of bis-(diethylamino)-methane (equilib-rium 3). Evidently both are strengthening the acidity of compounds considered.

Experimental

Formocholine chloride $Cl^-(CH_3)_3N^+CH_2OH$ was obtained by acidic hydrolysis of acetyl formocholine chloride in an-hydrous ethanolic solution,[1] Recrystallization from anhy-drous ethanol gave hygroscopic colorless crystals. After keeping 3 days over P_2O_5 the chlorine content was deter-mined by the Volhard method. Found: 28.59%, calculated: 28.23%

Acetyl formocholine chloride was prepared from mono-chloro methyl acetate and trimethylamine in anhydrous EtOH solution,1

Choline chloride $Cl^-(CH_3)_3N^+CH_2CH_2OH$ was obtained from commercial pharmaceutical 20% aqueous solution after distil-lation of water as azeotrope with benzene.

For the purpose of comparision the pK_a value of cho-line iodide ("Chemapol", "Pure" grade) was measured, too, considering choline iodide less hygroscopic than choline chloride.

Bis-(diethylamino)-methane $(C_2H_5)_2NCH_2N(C_2H_5)_2$ was prepared and kindly delivered by Dr. A.S. Dneprovskii (Chem-istry Department, Leningrad State University).

B.p. 168°C/760 mm Hg.[2]
The pK_a values were determined by the potentiometric titra-tion using LPU-01 Type pH-meter equipped with a glass and silver chloride electrodes. The measurements were ascer-tained to be correct within $\pm$ 0.04 pH units. 50 ml aliquots of 0.01 M aqueous solution of compound studied were titrated with 0.1n KOH solution or 0.1 n HCl solution, respectively.

Experimental pK_a Values for Dissociation of Formocholine Chloride, Choline
Chloride, Choline Iodide, and bis-(Diethylamino)-Methane in Water at $25^{o}C$ *

Compound	Experimental pK_a values obtained by different measurements				$(pK_a)_{av}$
	I	II	III	IV	
$Cl^-(CH_3)_3N^+CH_2OH$	10.09 ± 0.05	10.08 ± 0.04	10.09 ± 0.09	10.12 ± 0.10	10.10 ± 0.02
$Cl^-(CH_3)_3N^+CH_2CH_2OH$	12.12 ± 0.09	12.08 ± 0.10	12.08 ± 0.08	12.12 ± 0.09	12.10 ± 0.02
$J^-(CH_3)_3N^+CH_2CH_2OH$	12.10 ± 0.15	12.15 ± 0.10	12.06 ± 0.13	12.03 ± 0.12	12.09 ± 0.06
$(C_2H_5)_2NCH_2N(C_2H_5)_2$ pK_{a_2}	2.89 ± 0.01	$2.92 \quad 0.06$			2.91 ± 0.02

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* Maximum errors are shown

The measurements were performed at 25°C under argon. The
pH-meter was calibrated and checked with the standard buffer
solutions: 0.05 M potassium tetraoxalate (pH=1.68 at 25°C)
and 0.01 M sodium tetraborate (pH=9.18 at 25°C). KOH solu-
tion was freed from carbonate ions according to Albert and
Sergeant.[3]

In order to check up the method for pK_a measurements the
pK_a values of phenylacetic acid of "Pure" grade and α-naph-
thol (Analytical grade) were determined:

	pK_a	pK_a(Lit.)
Phenylacetic acid	4.29($\pm$0.02)	4.31[3]
α-Naphthol	9.86($\pm$0.04)	9.85[3]

The measured pK_a values of formocholine chloride, chol-
ine chloride, choline iodide and bis-(diethylamino)-methane
at 25°C are given in Table 1. The maximum errors are shown.
The activity coefficients of ions were taken into account.[3]

Discussion

Recently some attempts to interpret different chemical
processes including reagents with ionic charge have been
made making use of the electrostatic model. It appeared that
the electrostatic model enables us to interpret most of the
observed salt effects quantitatively.[4-6] On the other hand,
electrostatic model based on the electrostatic interaction
between charged substituent and reaction center cannot ex-
plain the presence or absence of a salt effect depending
upon the specific nature of a reaction.[7-9] It was found[5,7,9,10]
that sometimes in the case of reaction involving ionic rea-
gents salt effect was observed. But in the case of another
ionic reaction of the same type the salt effect was absent.

Recently[11] the constancy of the inductive attenuation
factor of carbon atom Z_c^{π}, within a given reaction series,
has been checked up in the case of neutral and charged substi-
tuents. The treatment of the pK_a values of carboxylic acids

and ammonium ions in coordinates pK_{n+1} vs. pK_n gave the evidence that the introduction of the electrostatic correction into gross pK_a values for acids with charged substituents results in an inductive attenuation factor of carbon atom, $Z_c^{\times}$, common for acids with uncharged and charged substituents, but different for every reaction series. Unfortunately, the results of the treatment of the pK_a values in the same coordinates without introduction of the electrostatic correction for charged substituents have not been given.

The regression analysis of the pK_a values of substituted ammonium ions $X(CH_2)_nNH_3^+$, $X(CH_2)_nNMe_2H^+$ and $X(CH_2)_2NEt_2H^+$ at 25^oC in water according to equation

$$pK_{n+1}=a+Z_c^{\times}pK_n \qquad (1)$$

has been carried out in the case of neutral and charged substituents, with and without electrostatic correction for charged substituents. The pK_a values given in Ref. 11 were used.

The results of the statistical treatment of data according to Eg. (1) are listed in Table 2.

One can see (Table 2) that the values $Z_c^{\times}$ found with and without the introduction of the electrostatic correction for compounds with charged substituent are very close to each other. The introduction of the electrostatic correction also does not improve the results of regression analysis. On the other hand, the values of $Z_c^{\times}$ calculated including the data for charged substituents with or without electrostatic correction do not differ from the $Z_c^{\times}$ values found only for compounds with neutral substituents. Hence the treatment of the pK_a data of ammonium ions according to Eq. 1 cannot demonstrate unambigously the necessity for the introduction of the electrostatic correction in the case of charged substituents.

Therefore, it is interesting to check up wheather the electrostatic correction is indispensable in the case of

Results of Correlation of pK_a Values of Substituted Ammonium Ions According to Equation $pK_{n+1} = a + Z_c^{\ast} pK_n$

Data correlated	Substituents[*]	Attenuation factor $Z_c^{\ast}$	r	s
1. Dissociation of substituted ammonium ions, $X(CH_2)_n NH_3^+$, H_2O, 25^oC	Neutral substituents: H, C_6H_5, OH, OCH_3, $COOCH_3$, NH_2, CN, $SiMe_3$	0.552 ± 0.009	0.999	0.084
	Neutral substituents and charged substituents: COO^-, NH_3^+	0.560 ± 0.012	0.997	0.113
	The same, the electrostatic correction included for charged substituents	0.553 ± 0.008	0.998	0.078
2. Dissociation of substituted ammonium ions, $X(CH_2)_n NMe_2H^+$, H_2O, 25^oC	Neutral substituents: OCH_3, $C{\equiv}CH$, CN	0.492 ± 0.045	0.983	0.19
	Neutral substituents and charged substituent NMe_2H^+	0.482 ± 0.040	0.984	0.18
	The same, the electrostatic correction included for charged substituent	0.479 ± 0.051	0.973	0.22

Data correlated	Substituents[※]	Attenuation factor $Z_c^※$	r	s
3. Dissociation of substituted ammonium ions, $X(CH_2)_n NEt_2 H^+$, H_2O, $25^{\circ}C$	Neutral substituents: NEt_2, CN	0.487 ± 0.008	0.999	0.082
	Neutral substituents and charged substituent $NEt_2 H^+$	0.490 ± 0.010	0.999	0.116
	The same, the electrostatic correction included for charged substituent	0.487 ± 0.006	0.999	0.06

[※] The pK_a data given in Ref. 11 were used.

Table 3

Values of $\sigma^{\boldsymbol{x}}$ Constants for Charged Substituents of Type $R_1R_2R_3N^+$

Data used for calculation of $\sigma^{\boldsymbol{x}}$ [a] constants for charged substituents	pK_o	$\rho^{\boldsymbol{x}}$	[b] Charged substituent X	$\sigma^{\boldsymbol{x}}_{(x)}$ Electrostatic correction no included	Electrostatic correction included
1	2	3	4	5	6
1. pK_a of alcohols, XOH, H_2O, $25°C$; X=H, OH, OMe, NH_2, Cl, Br[3,12-16]	15.94 ± 0.41	2.99 ± 0.22	NMe_3^+	3.79	3.09
2. pK_a of alcohols, XCH_2OH, H_2O, $25°C$; X=H, OH, CCl_3, CF_3[3,17]	15.29 ± 0.32	1.21 ± 0.17	NMe_3^+	4.30	3.18
3. pK_a of alcohols, $X(CH_2)_2OH$, H_2O, $25°C$; X=H, OH, OMe, Cl[3,16]	16.14 ± 0.30	0.96 ± 0.18	NMe_3^+	4.20	3.33
4. $lg(k_{OH}/k_H)$ of hydrolysis of benzoates, $C_6H_5COOCH_2X$, H_2O, $50°C$[18,g]	4.18 ± 0.01	2.08 ± 0.01	NMe_3^+	4.31^o	2.66^c
5. pK_a of substituted acetic acids, XCH_2COOH, H_2O, $25°C$[19,c]	4.75 ± 0.03	1.81 ± 0.03	NMe_3^+	4.15^{19}	2.92
				av.=4.16	av. 3.04

1	2	3	4	5	6
			NEt_2H^+	3.98	2.82
6. pK$_a$ of substituted ammonium ions, $XCH_2NEt_2H^+$, H_2O, 25°C; X=H, Ph, CN[20]	10.53±0.09	1.88+0.05	NEt_2H^+	4.00	3.23
7. pK$_a$ of substituted ammonium ions, $X(CH_2)_2NEt_2H^+$, H_2O, 25°C; X=H, OH, COCH$_3$Cl, CN[20]	10.81±0.28	0.89±0.13	NEt_2H^+	4.28	3.37
				av.=4.14	av.=3.13
8. pK$_a$ of substituted ammonium ions, $X(CH_2)_2NMe_2H^+$, H_2O, 25°C; X=H, OH, COCH$_3$, ON[20]	10.26±0.26	1.00±0.13	NMe_2H^+	4.30	3.49
9. Reaction series Nr. 5			NMe_2H^+	4.03	2.78
				av. 4.17	av. 3.14

a) For reaction series 1,2,3,6,7 ûnd 8 for H $\overset{\neq}{\sigma}$=0 was used

b) The pK$_a$ values for compounds with charged substituent are given in Table 4

c) For acidic hydrolysis of $C_6H_5CO_2CH_2NMe_3^+$ the electrostatic correction was not included (salt effect was not observed)

d) Attenuation factor $Z_c^{\neq}$=0.388 [18] was used

e) Attenuation factor $Z_c^{\neq}$=0.384[19] was used

the σ^{x} calculations for charged substituents of type $R_1R_2R_3\overset{+}{N}$. The σ^{x} values for substituents NMe_3^+ , NMe_2H^+ and NEt_2H^+ calculated making use of the data for different reaction series with and without electrostatic correction are given in Table 3. The pK_a values used for compounds with charged substituents are listed in Table 4.

One can see(Table 3) that the σ^{x} values for NMe_3^+ substituent found from the pK_a data of alcohols and $lg(k_{OH}/k_H)$ of hydrolysis of benzoates without introduction of the electrostatic correction do not differ from the σ^{x} value for NMe_3^+ estimated making use of the pK_a values of substituted acetic acids.[19]

T a b l e 4

Experimental pK_a Values for Compounds with Charged Substituent

Compound	pK_a	References
Me_3N^+OH	4.65	20
$Me_3N^+CH_2OH$	10.10 ± 0.02	This work
$Me_3N^+CH_2CH_2OH$	12.10 ± 0.02	This work
$Me_3N^+CH_2COOH$	1.83	21
$Me_2NH^+CH_2COOH$	1.95	22
$Et_2NH^+CH_2NEt_2H^+$	3.21 ± 0.02 [x]	This work
$Et_2NH^+CH_2CH_2NEt_2H^+$	7.00 [x]	20
$Me_2NH^+CH_2CH_2NMe_2H^+$	6.00 [x]	20

[x] Statistical correction included.

The σ^{x} values for substituents NMe_3^+, NMe_2H^+ and NEt_2H^+ calculated with and without electrostatic correction are different from each other by about one σ^{x} unit. In both

cases the values of $\sigma^{\text{¤}}$ found from different reaction series coincide quite well.

Besides one can conclude that the $\sigma^{\text{¤}}$ values for substituents NMe_3^+, NMe_2H^+ and NEt_2H^+ are practically equal.

Consequently, the $\sigma^{\text{¤}}$ values for these charged substituents calculated making use of the data for different reaction series are close to each other even without the introduction of the electrostatic correction.

On the other hand, it is necessary to mention that such a conclusion cannot be valid in the case of the calculation of $\sigma^{\text{¤}}$ constant for CO_2^- substituent from the pK_a values of substituted acetic acids. Probably the same is valid for NH_3^+ substituent.

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THE STUDY OF POSSIBLE APPLICATION OF ATOMIC ORBITAL ENERGY MODEL.
I. The Modification of the Orbital Electronegativity Concept and Bond Polarity Model

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The modiffied orbital energy (electronega-
tivity) concept is formulated. The relationship between
atomic orbitals population levels and the orbital ener-
gies for two orbitals involved in the formation of the
covalent bond has been developed as well that for atomic
charges.

The widely known concept of the electronegetivity of ele-
ments has been proved to be useless for construction of physi-
cal models distinquishable from the formal ones so far as the
quantitative description of some molecules properties is aimed.
Therefore this concept is thoroughly criticized (see Ref. 1
and 2).

The shortcomings of Pauling-Mulliken concept[3],[4] are due
to the attempt to introduce a definite quantitative charac-
teristics for elements independently of their valence states
and the nature of the orbitals forming the bond being consi-
dered.Moreover,there is no reason to believe that any given atom
can be charactarized using a single parameter (the electro-
negativity) because such an approach completely ignores the
real conditions of the interaction between electrons occupy-
ing the same orbital[5]:

An attempt to overcome the shortcomings of the classical
concept of electronegativity of elements has been made by Hinze
and Jaffe[5-8]. These authors introduced the so called orbital
electronegativity which is considered to be characteristic
of a definite orbital for definite valence state of the ele-

ment. Besides, the orbital electronegativity is not considered to be a constant but is represented by function of the level of the electron population of the orbital considered. The value of orbital electronegativity is equalized to the derivative of the energy of the system orbital – electrons on the population level. According to the Pauly principle the last quantity can change from 0 to 2.

As the relationship between orbital energy and the respective population level is not considered to be known a priori the concrete solution of the problem has been suggested postulating the parabolic nature of this relationship.Three empirical parameters of the parabolic equation for any given orbital have been suggested to be evaluated using three known energy levels at definite occupation levels equaling zero (energy equals zero, too), unity (energy is defined by ionization potential), and two (energy is defined by the sum of the ionization potential and the electron affinity).

Unfortunately, the parametrization of those parabolic relationships used in the papers cited above is connected with a principal miscalculation. At the population level equaling to the unity, the coefficient before the second power of population has not been equalized to zero. Such a procedure leads to the lack of any concrete physical meaning attributed to this parabolic relation. The reason is that the decrease of the orbital electronegativity accompanying the rise of the population level can be attributed to the repulsion between electrons, only. So the occupation level can affect the electronegativity if it is constituted by two electrons (an electron pair) responsible for a covalent bond. For a single electron the linear dependence between orbital energy and the occupation level should be assumed as the repulsion of the electron from itself is obviosly physically meaningless.

When parametrisizing their parabolic relationship, the unity population level was attributed to the ionization potential connected with the occupation of the orbital under consideration by a single electron. Therefore this parametri-

zation and all results obtained on this basis should be considered as practically depreciated.

The orbital electronegativity functions were suggested by authors as a basis for the evaluation of the population levels of atomic orbitals forming covalent bonds and calculation of respective atomic charges(bond polarities).The procedure applied by them makes use from the energy minimization principle for two bond-making atomic orbitals transformed into the mathematically equivalent electronegativity equalization principle. This procedure is considered by us to be a correct one and will be used in this study, also.

For real calculations the numerical values of ionization potentials and electron affinities for valent orbitals of atoms valence (hybridizied) states are needed.One can conclude that in papers[5-8] this problem gets no satisfactory solution and its additional study is needed. Therefore the following papers of this series are devoted to this problem, and the possibility of the empirical evaluation of orbital energies will   be tested.

This paper deals with the derivation of the correct relationship between the characteristic of atomic orbitals and the polarity of covalent bonds formed by those orbitals. The correct modification of the orbital energy model considered to be the further evolution of the electronegativity concept,has to be proposed.

Starting postulates

Following assumption will be taken as granted:

i. Any atomic orbital can be characterized by two constants – by the orbital energy equaling the ionization potential taken with the sign "minus" and by the coefficient of the orbital electron repulsion (R) being equal to the difference $(I - \varepsilon)$ of the ionization potential and electron affinity.

ii. The mean effective distance between two electrons occupying the same atomic orbital does not depend on the population level of this orbital.

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iii. The distribution of the electron pair between two orbitals constituting a covalent bond depends only on the I and R values of those orbitals and can be uniquely defined using the total energy minimization principle.

iv. The electron charge-distribution for the atomic orbital is center-symmetrized. This means that the mass-center of the respective negative charge cloud is localized on the atomic nucleous.

Development of Equations for the Equilibrium
Orbitals Population Levels and Atomic Charges

Making use of the postulates i. and ii. the total energy U of the system "atomic orbital - electrons" depends on the occupation levels x_1 and x_2 related to the first and second electrons, respectively, as follows:

$$U = - I(x_1 + x_2) + Rx_1x_2 \qquad (1)$$

If the orbital involved into the covalent bond formation is considered, it is possible to consider the occupation level by the electron pair, only. Due to the electrons indistingulishability principle one can conclude that $x_1 = x_2 = x$ and Eq.(1) can be rewritten as follows:

$$U = - 2Ix + Rx^2 \qquad (2)$$

Let us denote the two atomic orbitals forming a covalent bond using subscripts "a" and "b". If the occupation level of the orbital "a" equals x_a, the respective quantity for the orbital "b" equals $x_b = 1 - x_a$. The total energy for the model system which consists from those two orbitals and the electron pair distributed between them can be now expressed by the relationship:

$$U_{a_b} = - 2I_ax + R_ax^2 - 2I_b(1 - x) + R_b(1 - x)^2 \qquad (3)$$

Applying the energy minimization conditions

$$dU_{a_b}/dx = 0 \quad \text{and} \quad d^2U_{a_b}/dx^2 < 0$$

the following equilibrium value for the occupation level x_s is obtained:

$$x_a = (I_a - I_b + R_b)/(R_a + R_b) =$$
$$= (I_a - \mathcal{E}_b)/(I_a - \mathcal{E}_a) + (I_b - \mathcal{E}_b) \qquad (4)$$

For x_b an analogical expression can be derived.

Due to postulate iV. the charge qa (in elementary charge units) on the atom a can be expressed via the respective occupation level x_a:

$$q_a = 2(0.5 - x_a) \qquad (5)$$

After substitution the x_a value from Eq.(4) the follow-ing final expressions are obtained:

$$q_a = 1 - 2(I_a - I_b + R_b)/(R_a + R_b) \qquad (6)$$

or

$$q_a = -\left[(I_a + \mathcal{E}_a) - (I_b - \mathcal{E}_b)\right]/\left[(I_a - \mathcal{E}_a) + (I_b - \mathcal{E}_b)\right] \qquad (7)$$

The quantity q_a represents the fraction of the atomic charge caused by the polarity of the covalent bond between atoms a and b considered. One can see that numerator of the fraction on the right side of Eq.(7) is equivalent to the Pauling relationship according to which the bond polarity is defined by the difference of electronegativies ($\chi_a - \chi_b$) meaning that for the electronegativities the Mulliken de-finition ($\chi = I + \mathcal{E}$) is accepted. Sure, it should be kept in mind that the original Pauling–Mulliken's conception deals with the electronegativities of elements but not of orbitals.

The principal inaccuracy of this concept is reflected by the denumerator of the fraction on the right side of Eq.(7). This quantity also depends on I and $\mathcal{E}$ values and therefore does not remain constant for different pairs of bondforming atomic orbitals. This is the reason why the influence of the nature of the orbital on the polarity of bonds formed by its participation can not be expressed by a single parameter (electronegativity) characterizing this orbital.

If the orbital electronegativity is defined as a function of its occupation level as it was in principle suggested by Hinze and Jaffe[5] one can make use of Eq.(2) to obtain the expression as follows:

$$\chi(x) = -0.5 \, dU/dx = I - Rx \qquad (8)$$

According to Eq.(8) $\chi(x)$ is defined as the specific energy of the removal of the infinitly small fraction of the electronic charge from the orbital (recalculated for the elementary charge unity). At the population level $x = 0$ (population by electron pair) $\chi(x) = I$ and at $x = 1$,

$\chi(x) = I - R = \mathcal{E}$ in well agrement with the physical meaning of quatities I and $\mathcal{E}$.

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THE STUDY OF POSSIBLE APPLICATIONS OF ATOMIC ORBITAL ENERGY MODEL.

2. Empirical Dependence of Orbital Energies on Nuclear Charge and Electronic Configuration. The Additivity of Screening and Nonscreening Interactions between Electrons.

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It is shown that after addition of a term (potential) representing the nonscreening interaction of the electron considered with all other electrons of the given atom to the right side of the Moseley equation one can obtain a relationship which adequately represents the ionization potentials for s- and p-orbitals of first three electron shells. In good approximation the potentials of the non-screening interaction depend linearly on the nuclear charge. The additivity of the screening constants as well as the potentials of nonscreening interaction is demon-strated. The second approximation is considered assuming that the potential of nonscreening interaction contains a term proportional to the square of the nuclear charge. The roughly proportional relationship between the poten-tial of the nonscreening interaction and the difference between the number of screening electrons and the screen-ing constant holds.

In theoretical and quantum chemistry the term "screening constant" representing the decrease of the effective nucleus charge affecting the electron considered, due to the influ-ence of all other electrons of a given atom, is widely used. Originally the concept of screening was introduced in the Moseley equation (for a review see Ref. 1). Using the results of the hydrogen-like atom theory, this equation can be repre-

sented as follows:

$$1_j = (I_H/n^2)(z - \widetilde{G}_j)^2 = (I_H/n^2)z^2 - 2(I_H/n^2)\widetilde{G}_j z + (I_H/n^2)\widetilde{G}_j^2 \tag{1}$$

where by I_j the ionization potential of the outer shell electron for a given atom or ion with the nuclear charge z is denoted, j is the sequence number of its energetical level, I_H denotes the hydrogen atom ionization potential and by $\widetilde{G}_j$ the respective screening constant is denoted.

It is well known that Eq. (1) does not lead to the adequate quantitative description of I_j-values. For isoelectronic series the parabolic equation is proposed[2,3] as follows:

$$I_j = a_j + b_j z + c_j z^2 \tag{2}$$

where coefficients a_j, b_j and c_j are considered to be independent empirical constants characteristic for the jth electronic configuration.

The use of Eq. (2) by itself does not lead to the concept of screening. But it is simple to notice that the fully developed right side of Eq. (1), too, represents a polynomial of a second power on z with the only difference that the coefficient before z and the intercept are not independent of each other and the coefficient before z^2 equals the theoretical value of I_H/n^2.

We are not aware about any attempts to perform a statistical test of Eq. (2). For the extrapolations along the isoelectronic series (to obtain the values of electron affinities) the coefficients estimated from values of I_H at three different t-values were used.

If it would be observed and in fact it is that the difference between c_j and I_H/n^2 values is almost insignificant, the linear dependence between the difference $W_j = I_H/n^2 - I_j$ and the nuclear charge z has to be observed as follows:

$$W_j = -A_j + B_j z \tag{3}$$

By the definition, W_j equals the total interaction energy between given (j^{th}) and all other electrons if this

interaction and the interaction between j^{th} electron and the atomic nucleus are independent and additive.

In this study the statistical test of Eq. (3) has been performed using the ionization potentials from handbook[4]. The linear regression parameters in coordinates of Eq. (3) were calculated using respective program on computer "Nairi-2". Additionally , the two-parameter regression analysis in coordinates of Eq. (2) has been carried out.

With the aim to enhance the statistical weight of the points for neutral atoms (for which ones the I_j- values are assumed to be most accurate) the regression lines were forced to cross these points. Therefore,the actual treatment of data was made according to the proportionality-relationship as follows:

$$W_j - W_j^o = B_j(z - z^o) \tag{4}$$

where W_j^o and z^o are related to the electroneutral atom.

The A_j-values were calculated using obtained B_j-values and I_j tabulated.

The results of the regression analysis of the data are represented in Table 1.

As one can conclude from the data listed in Table 1 Eq. (2) leads to slightly more precise description of the ionization potentials as compared with Eq. (3). In the same time the c_j-values are indeed very close to respective I_H/n^2- -values as demonstrated by rather small values of Δ_j. Nevertheless, the last ones exceed the uncertainties in c_j-values. Besides of that, the nearly constancy of Δ_j-values for a given n-value (orbital-shell) can be detected with the possible exceptions for $j = 3$ and $j = 4$.

From the viewpoint of the further use of the coefficients of Eq. (3) or Eq. (2) the problem of their additivity is of importance. Such an additivity can be proved if from differences of respective coefficients for different pairs of j-values, the same term can be evaluated, only. If one assumes that those coefficients represent characteristics of the interaction between given (j^{th}) and all other electrons,

Table 1

The Results of Regression Analysis of the Ionization Potentials Data for Electronic Configurations Corresponding to First Three Rows According to Eqs. (3) and (4) and Eq. (2).

Standard deviations for coefficients are listed. By s the mean root square deviation is denoted.

In last column differences $\Delta_j = c_j - I_H/n_j^2$ are listed. By j the sequence number of the ionized electron is denoted. It equals numerically the nuclear charge for the neutral atom.

j	Orbital	Eqs. (3) and (4)			Eq. (2)				Δ_j
		A_j	B_j	s	a_j	b_j	c_j	s	
1	2	3	4	5	6	7	8	9	10
2^a	$1s^2$	3.81 ± 0.06	16.80 ± 0.03	0.45	4.68 ± 0.43	17.22 ± 0.15	13.633 ± 0.011	0.25	0.038
3	$2s$	7.28 ± 0.04	10.81 ± 0.01	0.22	7.66 ± 0.22	11.03 ± 0.06	3.415 ± 0.004	0.10	0.016
4	$2s^2$	13.22 ± 0.07	14.57 ± 0.02	0.30	14.27 ± 0.37	14.95 ± 0.09	3.423 ± 0.005	0.13	0.024
5	$2p$	28.25 ± 0.14	20.98 ± 0.03	0.47	30.45 ± 0.74	21.61 ± 0.16	3.436 ± 0.009	0.20	0.037
6	$2p^2$	41.62 ± 0.21	25.45 ± 0.03	0.59	45.32 ± 0.56	26.36 ± 0.11	3.446 ± 0.005	0.12	0.047
7	$2p^3$	58.24 ± 0.23	30.03 ± 0.03	0.55	62.79 ± 3.48	31.03 ± 0.63	3.443 ± 0.027	0.63	0.044
8	$2p^4$	83.66 ± 0.23	35.79 ± 0.03	0.49	87.26 ± 0.86	36.68 ± 0.14	3.432 ± 0.006	0.13	0.033
9	$2p^5$	107.06 ± 0.26	40.55 ± 0.03	0.50	112.56 ± 0.48	41.52 ± 0.07	3.438 ± 0.003	0.06	0.039
10^b	$2p^6$	132.46 ± 0.43	45.08 ± 0.04	0.72	141.50 ± 1.16	46.54 ± 0.16	3.453 ± 0.006	0.13	0.054

1	2	3	4	5	6	7	8	9	10
11	$3s$	86.95 ± 0.65	24.05 ± 0.06	1.00	101.45 ± 1.68	26.23 ± 0.22	1.586 ± 0.007	0.16	0.070
12	$3s^2$	100.5 ± 0.7	25.86 ± 0.06	0.95	117.43 ± 1.39	28.20 ± 0.17	1.586 ± 0.005	0.12	0.070
13[c]	$3p$	137.1 ± 1.4	29.72 ± 0.11	1.83	154.27 ± 3.79	32.01 ± 0.45	1.584 ± 0.013	0.23	0.068
14	$3p^2$	151.0 ± 0.9	31.35 ± 0.07	1.14	174.2 ± 4.6	34.17 ± 0.50	1.592 ± 0.013	0.31	0.076
15	$3p^3$	164.9 ± 1.2	32.95 ± 0.08	1.36	195.9 ± 9.5	36.48 ± 0.99	1.607 ± 0.025	0.58	0.091
16	$3p$	193.2 ± 1.0	35.59 ± 0.06	1.10	223.0 ± 6.7	38.79 ± 0.66	1.593 ± 0.016	0.37	0.077
17	$3p^5$	213.0 ± 1.1	37.44 ± 0.06	1.07	242.2 ± 9.2	40.42 ± 0.86	1.584 ± 0.020	0.46	0.068
18	$3p^6$	231.0 ± 1.1	39.15 ± 0.06	1.05	268.5 ± 5.1	42.75 ± 0.46	1.594 ± 0.010	0.10	0.078

[a] On the 0.95 level of Student's test the point for F^{7+} is excluded.

[b] Using the same criterion the point for Mg^{2+} is excluded.

[c] Using the same criterion the points for Ca^{7+} and Ti^{9+} are excluded.

the additivity hypothesis can be represented as follows:

$$K_j = \sum_{i=1}^{j-1} K_{j(i)} \tag{5}$$

where by K_j the A_j or B_j (a_j or b_j) for the last occupied (j^{th}) configuration is denoted and $K_{j(i)}$ represents an additive increment related to the interaction between j^{th} and i^{th} electrons.

It is easy to show that the differences $\Delta K_j = K_j - K_{j-1}$ as considered in sequence of the increasing j – values beginning from $j = 2$ and up to $j = 5$ are related to different interactions and could not be compared when the proof of the additivity is attempted. But the differences ΔK_j for the j-values equaling 6, 7, 9 and 10 are related to the interaction between two electrons occupying different 2p-orbitals. Consequently, these differences should equal each other if the additivity is really held. Analogical situation is expected for ΔK_j-values if j equals 14, 15, 17 and 18, because those differences could be related to the interaction between two electrons occupying different 3p-orbitals.

It is easy to demonstrate that for coefficients a_j from Eq. (2) and A_j from Eq. (3) this additivity is not held. But, when comparing these equations with Eq. (1) one can conclude that a_j or A_j can be identified with the value of $I_H/n^2 \sigma_j^2$ being proportional to the square of the screening constant σ_j. If one would assume that the inaccuracy of the Moseley equation does not touch this term in the right side of (the developed form) Eq. (1), the additivity should be assumed not for the coefficients a_j or A_j itself but for respective square roots. Indeed, the additivity is held namely for $\sqrt{a_j}$ or $\sqrt{A_j}$ and for coefficients b_j or B_j, also. Respective data are represented in Table 2.

One can see that from the viewpoint of the degree of accuracy this additivity is held, the coefficients a_j and b_j of Eq. (2) possess no advantages when compared with coeffi-

cients A_j and B_j calculated from Eqs. (3) and (4) (first three orbital-shells are considered).

Mean Values and Mean Square Deviations for A_j and B_j from Eqs. (3) and (4) and for a_j and b_j from Eq. (2) Representing the Interactions Between Two Electrons Occupying Different 2p- of 3p - Orbitals.

j	Interaction	A_j	B_j	a_j	b_j
6,7,9,10	2p - 2p	$\pm$ 1.172 0.024	$\pm$ 4.585 0.108	$\pm$ 1.24 0.04	$\pm$ 4.82 0.13
14,15,17,18	3p - 3p	$\pm$ 0.610 0.053	$\pm$ 1.70 0.10	$\pm$ 0.77 0.09	$\pm$ 2.16 0.33

Additivity of quantities $\sqrt{A_j}$ (or $\sqrt{a_j}$) can be accepted as a proof that the deviations from Eq. (1) really do not touch the zeroth order term in the right side of this equation. As a consequence, the true value of the screening constant can be calculated from the value of A_j (or a_j) as follows:

$$\sigma_j = n\sqrt{A_j/I_H} \tag{6}$$

Besides, it seems to be useful to introduce constants β_j defined as the differences:

$$\beta_j = B_j - 2(I_H/n^2)\,\sigma_j = B_j - 2\sqrt{I_H A_j}/n \tag{7}$$

Numerical values of the constants σ_j and β_j are listed in Table 3.

The parameters A_j and B_j can be expressed via σ_j and β_j and for I_j-value the equation is obtained as follows:

$$I_j = (I_H/n^2)\,(z - \sigma_j)^2 - \beta_j z \tag{8}$$

Analogically, from Eq. (2) the following equation can be derived:

$$I_j = (I_H/n^2)(z \cdots \sigma_j)^2 - \beta_j z + \Delta_j z^2 \tag{9}$$

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The Values of Screening Constants (σ_j) and
Constants of Nonscreening Interaction (β_j) for

First Three Electron Shells

The σ_j- and β_j- values are calculated proceeding
from A_j- and B_j- values

J	Orbit-al screen-ed	Screening configuration	β_j	σ_j		
				This study	From Ref.5	According to the Slater's rules
1	1s	1s	2.42±0.14	0.529±0.005	0.3125	0.30
2	2s	$1s^2$	0.896±0.040	1.458±0.005	1.7208	1.70
3	2s	$1s^2 2s$	1.16±0.05	1.973±0.006	2.0880	2.05
4	2p	$1s^2 2s^2$	1.39±0.06	2.883±0.009	2.5786	2.40
5	2p	$1s^2 2s^2 2p$	1.66±0.09	3.499±0.010	2.8642	2.75
6	2p	$1s^2 2s^2 2p^2$	1.89±0.09	4.140±0.010	3.1660	3.10
7	2p	$1s^2 2s^2 2p^3$	2.22±0.07	4.962±0.008	3.5468	3.45
8	2p	$1s^2 2s^2 2p^4$	2.40±0.08	5.613±0.008	3.9000	3.80
9	2p	$1s^2 2s^2 2p^5$	2.64±0.11	6.243±0.012	4.2416	4.15
10	3s	$1s^2 2s^2 2p^6$	1.13±0.14	7.587±0.034	8.4926	8.80
11	3s	$1s^2 2s^2 2p^6 3s$	1.22±0.14	8.157±0.033	8.6835	9.15
12	3p	$1s^2 2s^2 2p^6 3s^2$	0.95±0.17	9.522±0.039	8.9344	9.50
13	3p	$1s^2 2s^2 2p^6 3s^2 3p$	1.15±0.16	9.998±0.038	9.7148	9.85
14	3p	$1s^2 2s^2 2p^6 3s^2 3p^2$	1.38±0.20	10.449±0.046	10.1136	10.20
15	3p	$1s^2 2s^2 2p^6 3s^2 3p^3$	1.43±0.16	11.31±0.04	10.5181	10.55
16	3p	$1s^2 2s^2 2p^6 3s^2 3p^4$	1.57±0.15	11.87±0.04	10.8759	10.90
17	3p	$1s^2 2s^2 2p^6 3s^2 3p^5$	1.79±0.15	12.37±0.04	11.2359	11.25

Proceeding from the additivity of $\sqrt{A_j}$ ($\sqrt{a_j}$) and B_j (b_j) it can be concluded that analogical additivity is held for screening constants $(\tilde{\sigma}_j)$ and β_j-values:

$$\tilde{\sigma}_j = \sum_{i=1}^{j-1} \tilde{\sigma}_{j(i)} \tag{10}$$

$$\beta_j = \sum_{i=1}^{j-1} \beta_{j(i)} \tag{11}$$

By $\tilde{\sigma}_{j(i)}$ and $\beta_{j(i)}$ the additive terms are denoted, related to the interactions between screened (j^{th}) and screening (i^{th}) electrons. So these constants are related to respective orbital-orbital interactions.

Simple straightforward processing of ionization potential values does not allow to separate all these interaction constants. Part of them is obtained as some combinations, only. The values of orbital-orbital interaction constants so obtained, are listed in Table 4.

It is worthy to underline that the screening constants obtained in this study differ considerably from those reported up to date. For a sake of comparision, in Table 3 the values from paper by Clementi and Raimondi are listed as well as the numbers obtained using the Slater's rules.

Acception for $\tilde{\sigma}_j$-values the physical meaning of screening constants leads to the interpretation of β_j-values as the constants of the nonscreening interaction of the given (j^{th}) electron with all remaining electrons. The product $n^2\beta_j$ can be, consequently, named the nonscreening potential of remaining electrons. The portion of the electronic charge of the last ones not involved in the screening of the jth electron equals $N - \tilde{\sigma}_j$, where N is the total number of screening electrons ($N=j-1$). As it is demonstrated in Fig.1 roughly proportional relationship between quantities $n^2\beta_j$ and $N - \tilde{\sigma}_j$ is held which for 3p-orbitals is represented by practically strict proportionality.

Additive Constants for Orbital-orbital Interactions.

In the first column the screened (j^{th}) orbital and in the second column the screening electronic configuration are shown.

For the interaction of two electrons occupying the same p-orbital no subscript for symbol "p" is used. Symbols "p_1" and "p_2" refer to the interaction between two electrons occupying different p-orbitals of the same shell.

Screened orbital j	Screening orbital or configuration i	$\sigma_{j(i)}$	$\beta_{j(i)}$
1s	1s	0.529 ± 0.003	2.42 ± 0.14
2s	1s	0.7782 ± 0.0024	0.448 ± 0.020
2s	2s	$0.5141\pm$	0.2495 [a]
$2p_1$	$2p_2$	0.6343 ± 0.0210	0.2495 [a]
2p	2p [b]	0.8224	0.2495 [a]
2p	$1s^2 2s^2$	2.8829 ± 0.0085	1.3874 ± 0.0600
3s	$1s^2 2s^2 2p^6$	7.5869 ± 0.0340	1.1326 ± 0.1447
3s	3s	0.570	0.089
$3p_1$	$3p_2$	0.497 ± 0.043	0.200 ± 0.038
3p	3p [b]	0.858	0.048

[a] The mean value of difference $\beta_j - \beta_{j-1}$ for the second orbital shell. The scatter of these differences is statistically not significant.

[b] Strictly speaking, these constants reflect not only the interaction between electrons occupying the same 2p- or 3p-orbital but also the difference of interactions between the given p-electron and two p-electrons, occuying other p-orbitals, caused by the reversion of the spins for latters.

The nonscreening interaction can be interpreted as Coulonbic repulsion between the charge of the jth electron and the part of the charge of the remaining electrons in condition that the jth electron occupies the position closer to the nucleus than electron interacting with it.
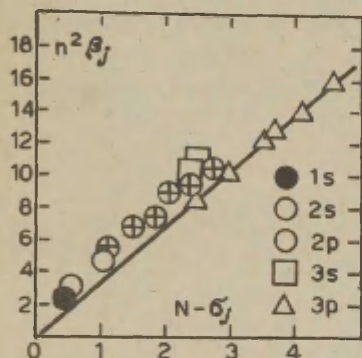

Fig. 1   The dependence between $n^2\beta_j$ and $N - \sigma_j$.

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