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1962

SovietRxiv

Abstract

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CORRELATION OF RATE CONSTANTS OF THE ALKALINE HYDROLYSIS OF ESTERS OF AROMATIC SULFONIC ACIDS AS A FUNCTION OF THEIR STRUCTURE

(Presented by Academician V. N. Kondrat' eva, 3 VIII 1961)

It is of interest to consider some problems in the field of the quantitative correlation of reactivity with structure,* on the basis of experimental data ($^{2-7}$) for the rate constants of alkaline hydrolysis of the following series of compounds: 1) $C_6H_5SO_2OAr$, 2) $ArSO_2OC_6H_5$, 3) $ArSO_2OAr'$, and 4) $ArSO_2OC_2H_5$. Here Ar and Ar′ denote mono- or polysubstituted phenyls. In the general case, the dependence of the reactivity of compounds of the type Ar—Y (where Y is the reaction center) on the nature of Ar may be represented in the following form (^{1}):

$$\lg k = \lg k_0 + \rho_0\sigma^0 + \psi + s, \tag{1}$$

where k_0 is the rate constant for C_6H_5—Y, σ^0 is the induction constant of the substituent Ar; C_6H_5 is taken as the standard, for which $\sigma^0 \equiv 0$; ρ_0 is a constant characterizing the sensitivity of the given reaction to the influence of the inductive effect of the substituent Ar; ψ is a term quantitatively characterizing the influence of direct polar conjugation between the substituent X in X—C_6H_4 = Ar and the reaction center; s is the quantitative characteristic of the steric factor (in the case of ortho substituents in Ar).

If the equation given by Yukawa and Tsuno (^{8}) is modified somewhat, replacing in it Hammett' s σ of X by σ^0, then it may be assumed that the value ψ is proportional to the difference $\sigma^+ - \sigma^0 = \sigma_c^+$, where σ^+ are the constants of the corresponding substituents according to Brown and Okamoto (^{9}), i.e. $\psi = \rho_c\sigma_c^+$.

For all meta substituents and those para substituents that cannot enter into direct conjugation with the reaction center, expression (1) reduces to the Hammett equation with the use of the quantities σ^0 instead of σ:

$$\lg k = \lg k_0 + \rho_0\sigma^0. \tag{2}$$

Figure 1 gives the dependences of $\lg k$ on σ^0 for the hydrolysis reactions of esters 1, 2, and 4. The straight lines were drawn through points corresponding

Fig. 1. Dependence of $\lg k$ on the induction constants σ^0 of aromatic substituents: 1—hydrolysis of $C_6H_5SO_2OAr$, 2—hydrolysis of $ArSO_2OC_2H_5$, 3—hydrolysis of $ArSO_2OC_6H_5$

Figure 1: Fig. 1. Dependence of $\lg k$ on the induction constants σ^0 of aromatic substituents: 1—hydrolysis of $C_6H_5SO_2OAr$, 2—hydrolysis of $ArSO_2OC_2H_5$, 3—hydrolysis of $ArSO_2OC_6H_5$

to substituents for which ψ and s are known to be zero. Below are given the results of processing the experimental data according to formula (1). By the method of least squares (^{10}), the values of ρ_0, the correlation coefficients r, and the root-mean-square deviations $\dot{s}$ were calculated.

1. Alkaline hydrolysis of substituted phenyl esters of benzenesulfonic acid in 70% aqueous dioxane. In this case there are no deviations from the linear dependence of $\lg k$ on σ^0, which indicates the practical absence of possible conjugation of para substituents of the $-C^*$ type with the reaction center:

$$C_6H_5—SO_2—O—C_6H_4—NO_2$$

[*] A review of the literature on this question is given in (^{1}).

At 50° C, $\rho_0 = 2.747 \pm 0.041$, $\lg k_{\text{calc}} = -3.36$, $r = 0.9996$, and $s = 0.038$ (based on data for the substituents 4—CH_3, 3—CH_3, H, 4—Cl, 3—NO_2, and 4—NO_2). The value $r \approx 1$ and the small magnitude of s, at a sufficiently large value of ρ_0, make this reaction series very convenient for calculating new values of σ^0 from the formula $\sigma^0 = (\lg k + 3.36)/2.747$. The following new values of σ^0 have been obtained: for 2—CH_3 = −0.19; for $2NO_2$ = +0.91; for 4—(n-$HOC_6H_4SO_2$) = +0.56, and for 4—$C_6H_5SO_2$ = +0.66. The value of σ^0 for ortho-NO_2 is somewhat higher than the literature values σ_{ortho} for this substituent, +0.80 (11) and +0.65 (12). This clearly indicates that in the present case $s = 0$. The last conclusion is not unexpected, since the sulfur atom attacked by the OH^- ion is at a sufficient distance from the substituted benzene ring.

Fig. 1. Dependence of $\lg k$ on the induction constants σ^0 of aromatic substituents: 1—hydrolysis of $C_6H_5SO_2OAr$, 2—hydrolysis of $ArSO_2OC_2H_5$, 3—hydrolysis of $ArSO_2OC_6H_5$

At 0° $\rho_0 = +3.09 \pm 0.059$, $\lg k_{\text{calc}} = -5.63$, $r = 0.999$, $s = 0.096$ (data for 2,6- and 2,4-dinitrophenyl esters and the corresponding sums of the σ^0 values for the ortho- and para-nitro groups were additionally used).

The dependence of ρ_0 on temperature is described by the equation:

$$\rho_0 = +0.20 + 3660/2.3RT.$$

2. Alkaline hydrolysis of phenyl esters of substituted benzenesulfonic acids in 70% aqueous dioxane.

In the present case, direct conjugation with the reaction center is possible for para- and ortho-substituents of the $+C$ type. The values ρ_0' and ρ_c in the equation $\lg k = \lg k_0 + \rho_0'\sigma^0 + \rho_c\sigma_c^+$, calculated by us by the method of least squares from experimental data for the substituents 4—CH_3O, 4—CH_3, H, 4—Cl, 4—Br, 3—NO_2, and 4—NO_2 at 50° C, are equal to: $\rho_0' = +2.24$, $\rho_c = +0.54$; $s = 0.024$, $\lg k_0 = -3.43$.

Since in this case the hydroxyl attack is directed at the sulfur atom directly bonded to the substituted phenyl residue, for ortho-substituents one should assume the presence of steric hindrance and $s \neq 0$. Deviations of the experimental values of $\lg k$ from the straight line $\lg k = -3.43 + 2.24\sigma^0$ give, in the case of ortho-substituted phenyl esters, the value $s = -0.75$ for ortho-NO_2 and $\psi + s = -0.65$ for ortho-Cl (the value $\sigma^0 = +0.31$ for ortho-Cl was estimated by us from data for the reaction series of alkaline hydrolysis of 4—$ClC_6H_4SO_2OAr$ in 70% aqueous dioxane at 0° C). At 0° $\rho_0' = 2.73 \pm 0.15$, $\lg k_{\text{calc}} = -5.64$, $r = 0.990$, and $s = 0.15$.

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* Substituents of the $+C$ type possess an unshared electron pair and are electron donors; substituents of the $-C$ type are electron acceptors by the mechanism of polar conjugation (1).

The dependence of ρ_0' on temperature is described by the equation:

$$\rho_0' = -0.20 + 3660/2.3RT.$$

3. **Alkaline hydrolysis of phenyl benzenesulfonates with substituents in both benzene rings.** This reaction series also includes series 1 and 2. In order to calculate rate constants in this case it is necessary to use methods of "cross" correlation (superposition of several independent correlation equations) (13). Taking this into account, we may write the following equation for this reaction series:

$$\lg k_{ij} = \lg k_{00} + \rho_0 \sum \sigma_i^0 + \rho_0' \sum \sigma_j^0 + \rho^* \sum \sigma_i^0 \sum \sigma_j^0 + \rho_c\sigma_{ci}^0 + s, \qquad (3)$$

where the index i refers to substituents in the benzenesulfonic acid ring, and j to substituents in the phenyl ring. It has been shown (1) that the quantity $\rho^* = (\rho_{0k} - \rho_0)/\sigma_k^0 = (\rho_{0k}' - \rho_0)/\sigma_k$, where ρ_{0k} and ρ_{0k}' refer to the reaction series of hydrolysis of $X_{kC}6H_4SO_2OAr$ and $ArSO_2OC_6H_4X_k$, X_k being any constant substituent. The equality $\rho^* = 0$ means that substitution in one ring does not affect the interaction of the reaction center with substituents in the other ring, and vice versa. The value ρ^*, calculated by the least-squares method from the values of ρ_0, ρ_0', ρ_c, and s given above and from experimental values of $\lg k_{ij}$ at

0°, is $\rho^* = -0.61 \pm 0.06$. The negative value of ρ^* indicates that the presence of electron-withdrawing substituents in one ring decreases the interaction of the reaction center with electron-withdrawing substituents in the other ring, and vice versa.

Neglecting the dependence of ρ_c, ρ^*, and s on temperature, we obtain the following equation for calculating rate constants when substituents are present in both aromatic rings:

$$\lg k_{ij} = 8.35 - 17400/2.3RT + (-0.20 + 3660/2.3RT)\sum \sigma_i^0 + $$
$$+(0.20 + 3660/2.3RT)\sum \sigma_j^0 - 0.61 \sum \sigma_i^0 \sum \sigma_j^0 + 0.54\sigma_{ci}^{0+} + s. \qquad (4)$$

The accuracy of the equation is characterized by the value $s = 0.185$ when $\lg k_{ij}$ varies by more than 6 orders of magnitude.

In calculating rate constants for esters of 2,4,6-trimethylbenzenesulfonic acid, satisfactory agreement with experimental data is obtained only if the term $0.54\sigma_{ci}^{0+}$ is omitted in (4) and $s = 0$ is assumed. This indicates that the two ortho-methyl groups, while not creating steric hindrance to attack by the hydroxyl ion, at the same time disrupt the coplanarity of the system and "switch off" direct conjugation with the reaction center.

4. **Alkaline hydrolysis of substituted ethyl benzenesulfonates in 70% aqueous dioxane.** Direct conjugation of $+C$-type substituents in the para and ortho positions with the reaction center is possible in principle. However, the corresponding deviations from the straight line $\lg k = \lg k_0 + \rho_0\sigma^0$ for the $4-CH_3O$ and $4-CH_3$ groups are small, and for halogens are absent altogether. At least in the case of the latter, the quantity ψ may be neglected.

At 50°, $\rho_0 = +1.425 \pm 0.091$, $\lg k_{(\text{calculated})} = -3.23$, $r = 0.991$, and $s = -0.075$ (calculated from data for the substituents H, $4-Cl$, $4-Br$, $2-NO_2$, $3-NO_2$, $4-NO_2$, and $2,5-Cl_2$). For ortho-NO_2 and ortho-Cl, $s = 0$. This is due to the fact that in this case attack by the hydroxyl ion is directed toward the carbon atom of the ethyl group $^{(14)}$. The deviations for $4-CH_3O$ and $4-CH_3$ are -0.15 and -0.10 logarithmic units, respectively.

It is easily shown that equations of the Hammett or Taft type can be exactly obeyed only for those reaction series in which there exists a linear dependence between the logarithm of the preexponent $\lg A$ (or the entropy) and the activation energy E (heat of reaction). From practice

it is known that the indicated equations are also satisfied in those cases in which there is no linear dependence between the indicated quantities (^{1}). This may be interpreted as an indication of the fundamentally approximate character of these equations.

Fig. 2

Figure 2: Fig. 2

Fig. 2. Linear dependence between the values of $\lg k$ at different temperatures. 1 –hydrolysis of $C_6H_5SO_2OAr$, 2 –hydrolysis of $ArSO_2OC_2H_5$

In the case of reaction series 1 and 4, a linear dependence is observed between the values of $\lg k$ and σ^0–the quantities ψ and s are equal to zero. However, there is no linear dependence between $\lg A$ and E if one uses values calculated from the experimental data by the Arrhenius equation. A specific condition for the exact fulfillment of the Hammett or Taft equations is a linear dependence between the values of $\lg A$ for one and the same reaction series, taken at any two different temperatures, which is equivalent to a linear dependence between $\lg k$ and E. The corresponding plots for the two indicated reaction series are shown in Fig. 2. We see that the linear relations between the values of $\lg k$ at 0° and 50° are satisfied well. Hence it may be concluded that in both cases a linear dependence between the true values of $\lg A$ and E nevertheless exists and cannot be detected directly because small errors in the values of the rate constants lead to large inaccuracies in the values of $\lg A$ and E. On the other hand, it is obvious that good fulfillment of the Hammett or Taft equations at different temperatures for one and the same reaction is equivalent to fulfillment of a linear dependence between $\lg A$ and E. It is easy to show that, if $\rho = a - \mathcal{E}/2.3RT$, then $\lg A = (\lg A_0 - (a/\mathcal{E})E_0) + (a/\mathcal{E})E$, where A_0 and E_0 refer to the standard substituent. For reaction 1 we have: $\lg A = 10.02 - 5.53 \cdot 10^{-5}E$; for reaction 4, $\lg A = 36.33 - 1.50 \cdot 10^{-3}E$. It is interesting to note that, in the case of both reaction series considered, as E decreases the value of $\lg A$ increases–the changes in both factors act in the same direction, and the linear dependence between them does not lead to any "compensation." In the hydrolysis of $C_6H_5SO_2OAr$ the main role is played by changes in the activation energy; in the hydrolysis of $ArSO_2OC_2H_5$, conversely, by the value of $\lg A$.

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Received
29 VII 1961

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Note: Figure translations are in progress. See original paper for figures.