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Nonadditive Effects of Structural Factors in Reactions of Aryloxiranes with Arenesulfonic Acids. Observation of Isoparametricity Phenomenon

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Abstract—In reactions of aryloxiranes $XC_6H_{4(3)}CH(O)CH_2$ with arenesulfonic acids $YC_6H_4SO_3H$ in a mixture of dioxane with diglyme (1 : 1) at 265 K the nonadditive effects of substituents X and Y were strongly revealed, therefore it was possible to observe experimentally the isoparametricity phenomenon: In the isoparametric point $\sigma_X^{IP} = 1.42$ with respect to the X substituent constant the rate of the oxirane ring opening did not depend on the structure of Y ($\rho_Y^X = 0$).

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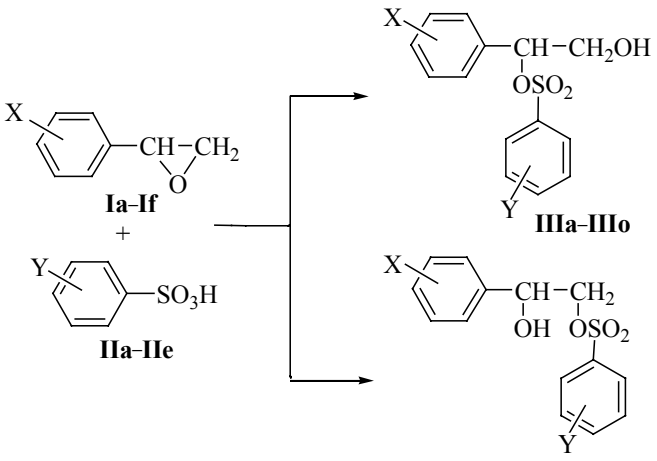
The versatility and features of the mechanisms of oxirane reactions, their unique synthetic possibilities and practical value have attracted the attention of researchers for several decades. The interest in oxirane chemistry is still strong nowadays as show the numerous recent publications (see, e.g., [1]). However although the research on oxiranes is very versatile, the quantitative aspects of their reactions are still poorly understood. The establishment of quantitative laws taking into account the effect of the structure, solvent, temperature, pH of the medium and the other internal and external factors on the rate and regioselectivity of reactions of oxirane substrates with reagents of diverse character is a topical problem. In this respect a special attention should be paid to cross reaction series where occurs the interaction (nonadditivity) of effects of mutually varied factors. These series should be described with the use of polylinear equations with cross terms whose coefficients take into account such interactions and therefore their prognostic value significantly grows [2].

The goal of this work is the study of the combined effect of substituents X and Y on the reaction rate of substituted aryloxiranes with substituted arenesulfonic acids in a mixture dioxane–bis(2-methoxyethyl) ether (diglyme), 1:1 (Scheme 1).

Scheme 1.



I, X = H (**a**), 3-Br (**b**), 4-Br (**c**), 4-NO_2 (**d**), 4-Br-3-NO_2 (**e**), 3,5-$(NO_2)_2$ (**f**); **II,** Y = 4-OMe (**a**), 4-Me (**b**), H (**c**), 4-Cl (**d**), 3-NO_2 (**e**); **III**, X = H, Y = 4-OMe (**a**), 4-Me (**b**), H (**c**); X = 3-Br, Y = 4-OMe (**d**), 4-Me (**e**), H (**f**), 4-Cl (**g**); X = 4-Br, Y = 4-OMe (**h**), 4-Me (**i**), H (**j**), 4-Cl (**k**); X = 4-NO_2, Y = 4-OMe (**l**), 4-Me (**m**), H (**n**), 4-Cl (**o**), 3-NO_2 (**p**); **IV**, X = 4-Br-3-NO_2, Y = 4-OMe (**a**), 4-Me (**b**), H (**c**), 4-Cl (**d**), 3-NO_2 (**e**); X = 3,5-$(NO_2)_2$, Y = 4-OMe (**f**), 4-Me (**g**), H (**h**), 4-Cl (**i**), 3-NO_2 (**j**).

In this mixed solvent the reaction rate proved to be convenient for measurement in a wide range of variation of substituents at 265 K. In reactions of aryloxiranes **Ia–Id** with arenesulfonic acids **IIa–IIe** products formed resulting from the α-opening of the oxirane ring, primary alcohols 2-aryl-2-arylsulfonyloxyethanols **IIIa–IIIp** [3]. The formation of 2,2-disubstituted ethanol derivatives was also observed in the reactions of these aryloxiranes with benzoic acids [4], HNO_3 [5], and the other acid reagents [6]. However with aryloxiranes **Ie, If** with electron-acceptor substituent X more powerful than 4-NO_2 according to the ^{1}H NMR data (see below) the products of the β-opening of the oxirane ring, secondary alcohols 1-aryl-2-arylsulfonyloxyethanols **IVa–IVj** were obtained. The observed change I in the reaction regioselectivity is in agreement with the stated in a number of publications [7] β-opening of the oxirane ring in the presence in the aryloxiranes of strong electron-acceptor substituents.

All reactions have the overall third order, first with respect to oxirane and second for the acid. The values of the rate constants k_{XY} l^2 mol^{-2} s^{-1} of these reactions are compiled in Table 1. To evaluate quantitatively the effect on the rate of substituents X and Y were used the respective equations:

$$\log k_{XY} = \log k_{HY} + \rho_X^Y\sigma_X \quad (1)$$

$$\log k_{XY} = \log k_{XH} + \rho_Y^X\sigma_Y. \quad (2)$$

Equation (1) describes the partial reaction series with variable substituents X and fixed subsstituents Y, and equation (2), with variable substituents Y and fixed substituents X. The results of processing kinetic data (Table 1) using these equations are compiled in Table 2. They show that in going from one fixed substituent X (Y) to another the sensitivity factors ρ_Y^X (ρ_Y^X) considerably change. This shows the interaction of mutual effects of substituents X and Y in the studied reactions, i.e., their nonadditive influence on the process. However the uniformity of such interaction is not retained within the total range of variation of substituents X in the oxirane substrate, as is demonstrated in Fig. 1 where the deviation is shown of the kinetic data of oxirane **Ie, If** reactions from the linear correlations in the coordinates of equation (1). Consequently, the reactions involving these substrates cannot be included into the main cross reaction series (CRS 1). This is due to the above mentioned change in the regioselectivity of the opening of the oxirane ring effected by strong electron-acceptor substituents X = 4-Br-3-NO_2, 3,5-$(NO_2)_2$.

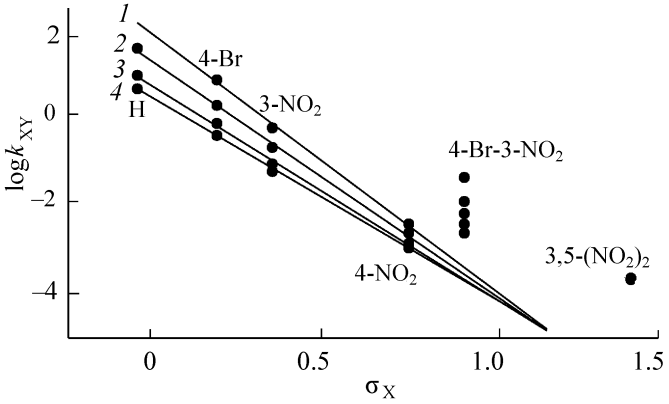


Fig. 1. Dependence of log k_{XY} on σ_X of substituents X for reactions of aryloxiranes $XC_6H_{4(3)}CH(O)CH_2$ with arenesulfonic acids $YC_6H_4SO_3H$ [Y = 4-Cl (*1*), H (*2*), 4-Me (*3*), 4-OMe (*4*)] in the mixture of dioxane with diglyme, 1 : 1, at 265 K.

The quantitative estimation of the mutual effects of substituents X and Y in CRS 1 was performed applying the equation of the cross correlation for two-parametric polylinear principle [2]:

$$\log k_{XY} = \log k_{HH} + \rho_X^{Y=H}\sigma_X + \rho_Y^{X=H}\sigma_Y + \rho_{XY}\sigma_X\sigma_Y, \quad (3)$$

where k_{HH} is the rate constant of the standard reaction of oxirane **Ia** with acid **IIc** (X = Y = H, $\sigma_X = \sigma_Y = 0$), $\rho_Y^{X=H}$ and $\rho_Y^{X=H}$ are the sensitivity factors of the standard reaction series, ρ_Y^X is the factor of the cross interaction. The performance of the cross correlation analysis of the results of the multifactor kinetic experiment according to equation (3) along the program of multilinear regression analysis furnished the following result:

$$\log k_{XY} = (1.47 \pm 0.03) - (5.35 \pm 0.06)\sigma_X + (3.1 \pm 0.2)\sigma_Y - (2.9 \pm 0.2)\sigma_X\sigma_Y \quad (4)$$

$$R\ 0.998,\ s\ 0.066,\ F\ 2418,\ n\ 16.$$

Table 1. Rate constants $k_{XY} \times 10^2$ (l^2 mol^{-2} s^{-1}) of reactions between aryloxiranes **Ia–If** and arenesulfonic acids **IIa–IIe** in the mixture of dioxane with diglyme (1 : 1) at 265 K

Acid	Oxirane					
	Ia	**Ib**	**Ic**	**Id**	**Ie**	**If**
IIa	415	39.4	6.06	0.112	0.24	0.0212
IIb	840	72	8.46	0.140	0.365	0.021
IIc	3520	183	20.3	0.23	0.644	0.022
IId	–	700	55.2	0.38	1.24	0.0219
IIe	–	–	–	0.84	4.26	0.0218

Table 2. Values of sensitivity factors ρ_X^Y and ρ_Y^X in equations (1) and (2) for reactions of aryloxiranes $XC_6H_{4(3)}CH(O)CH_2$ with arenesulfonic acids $YC_6H_4SO_3H$ in the mixture of dioxane with diglyme, 1 : 1, at 265 K

Y (σ_Y)	ρ_X^Y	*r*	X (σ_X)	ρ_Y^X	*r*
4-OCH_3 (–0.27)	–4.59 ± 0.07	0.999	H (0)	3.5 ± 0.2	0.999
4-CH_3 (–0.17)	–4.9 ± 0.1	0.999	4-Br (0.23)	2.48 ± 0.02	0.999
H (0)	–5.4 ± 0.1	0.999	3-Br (0.39)	1.96 ± 0.07	0.999
4-Cl (0.23)	–5.9 ± 0.3	0.999	4-NO_2 (0.78)	0.89 ± 0.07	0.993
3-NO_2 (0.71)	–	–	4-Br-3-NO_2 (0.94)	1.25 ± 0.060	0.997
			3,5-$(NO_2)_2$ (1.42)	0	–

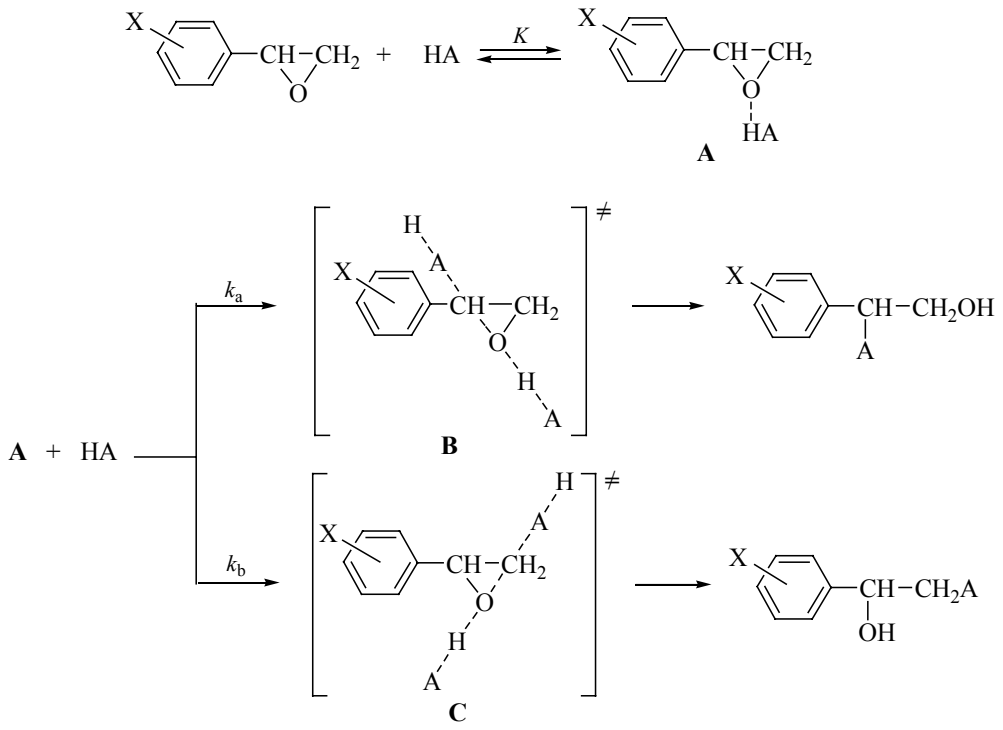
Owing to the statistically valid factor of the cross interaction ρ_{XY} regression (4) exhibits the isoparametric properties. Its attributes are isoparametric points (IPP) corresponding to substituents constants, for X ($\sigma_X^{IP} = -\rho_Y^{X=H}\rho_{XY}^{-1} = 1.07$) and Y ($\sigma_Y^{IP} = -\rho_X^{Y=H}\rho_{XY}^{-1} = -1.84$), and also the same rate constant value k_{XY} in both IPP ($\log k_{XY}^{IP} = \log k_{HH} - \rho_Y^{X=H}\rho_Y^{X=H}\rho_{XY}^{-1} = -4.25$). As seen from the calculation data, IPP fall to the region of low reactivity of the system. The experimental attainment of IPP σ_Y^{IP} where the process rate should not depend on the structure of substituents X ($\rho_Y^X = 0$) is not possible for it requires the introduction into the molecule of arenesulfonic acid improbably powerful electron-donor substituents Y with $\Sigma\sigma_Y$ –1.84. As to IPP σ_X^{IP} where the rate should not be affected by the changes in the structure of substituents Y ($\rho_Y^X = 0$) we attempted to test the possibility of its existence using as the substrate oxirane **Ie** with summary value of constants of substituent X ($\Sigma\sigma_X$ 0.94) close to isoparametrical. However the reactions involving this oxirane showed abnormally high sensitivity to the change of substituents Y (Table 2). This is due to the distortion of the uniformity of the interaction of structural factors because of the changed regioselectivity of reactions (Scheme 1), therefore the experimental test of this IPP failed. Yet we succeeded to prove a complete absence of the effect of substituent Y on the opening rate of oxirane ring involving oxirane **If** where $\rho_Y^X = 0$. Evidently the value $\Sigma\sigma_X$ 1.42 of constants of substituent X = 3,5-$(NO_2)_2$ corresponds to the value of the experimentally attainable IPP σ_X^{IP} 1.42 in another cross reaction series partially investigated in this work (CRS 2) that includes the formation of secondary alcohols **IVa–IVj** involving oxiranes **Ie, If**. From the data of Table 2 it is possible to calculate for CRS 2 the approximate value of the factor of the cross interaction: $\rho_{XY} = \Delta\rho_Y^X/\Delta\sigma_X = -2.6$.

For the described regressions (4) of the reactions of oxirane ring opening with the formation of primary alcohols **IIIa–IIIp** in CRS 1 we suggest a stage mechanism (Scheme 2) that is in agreement with the overall third order of these reactions, partial first with respect to oxirane substrate and partial second with respect to acid reagent HA ($YC_6H_4SO_3H$). This mechanism involves the formation in the first reversible stage of complex **A** with an H-bond. In the second stage limiting the rate k_α the activated substrate suffers the nucleophilic attack of the second acid molecule on the α-carbon atom of the oxirane ring, located in the benzyl position, to form the trimolecular transition state **B**. Just this direction of the oxirane ring opening corresponds to the formation of primary alcohols **IIIa–IIIp** in reactions involving aryloxiranes **Ia–Id**.

In keeping with the two-stage mechanism $k_{XY} = Kk_\alpha$ that means $\rho_Y^X = \rho_Y^1 + \rho_X^2$. Taking into account the nature of the first stage a conclusion is possible that $\rho_X^1 < 0$. The second stage proceeds along the mechanism of concerted nucleophilic substitution A_ND_N with the electrophilic assistance to the C–O bond cleavage in the oxirane ring. The transition state **B** is by its character dissociative. There the cleavage of the C–O bond largely surpasses the formation of the O–C bond leading to the appearance of a positive charge on the α-carbon atom of the oxirane ring, and consequently $\rho_X^2 < 0$ (the strengthening of the electron-acceptor properties of substituents X destabilizes the transition state **B**). Inasmuch as both stages of the process are characterized by negative values of the sensitivity factor with respect to the effect of substituents X, the effective value ρ_Y^X is expressed by large negative values for the studies partial reaction series (Table 2).

The sensitivity parameter ρ_Y^X is also a combined value: $\rho_Y^X = \rho_Y^1 + \rho_Y^2$, where $\rho_Y^1 > 0$, and the sign and magnitude of ρ_Y^2 is determined by the prevalence of either the formation of the O–C bond or the cleavage of the C–O bond in

Scheme 2.



the transition state **B**. The electron-acceptor substituents Y impede the formation of the O–C bond ($\rho_{O-C} < 0$) and facilitate the cleavage of the C–O bond ($\rho_{C-O} > 0$) by the electrophilic assistance to this process in the transition state **B**, therefore $\rho_Y^2 = (-\rho_{O-C}) + \rho_{C-O}$. Since as already mentioned the transition state **B** is dissociative it is presumable that $|\rho_{A-C}| < \rho_{C-O}$ and $\rho_Y^2 > 0$. Inasmuch as both sensitivity parameters ρ_Y^1 and ρ_Y^2 with respect to the effect of substituents Y prove to be positive for both stages, it is reasonable that the observed effective ρ_Y^X value for the partial reaction series forming CRS 1 is also positive (Table 2).

The stage character of the process governs also the sign and the magnitude of the factor of cross interaction ρ_{XY}. In the first stage of the process the increase in the electron-acceptor properties of substituents X ($\Delta\sigma_X > 0$) would result in the decrease in the electron density on the oxygen atom of the oxirane ring and therefore to the weakening of the H-bond in complex **A** resulting in the diminishing of ρ_Y^1 ($\Delta\rho_Y^1 < 0$), hence $\rho_{XY}^1 = \Delta\rho_Y^1/\Delta\sigma_X < 0$. On the other hand, the strengthening of the electron-acceptor properties of substituents Y ($\Delta\sigma_Y > 0$) would favor the strengthening of the H-bond and consequently would increase the negative value of ρ_X^1 ($\Delta\rho_X^1 < 0$) and, as a result, $\rho_{XY}^1 = \Delta\rho_X^1/\Delta\rho_Y < 0$. Taking into account the above reasoning it is possible to conclude that in the stage of the formation of complex **A** to IPP with respect to the constants of substituents X ($\sigma_X^{IP(A)} = -\rho_Y^1/\rho_{XY}^1 > 0$) and Y ($\sigma_Y^{IP(A)} = -\rho_X^1/\rho_{XY}^1 < 0$) would correspond respectively weak proton acceptors (aryloxiranes with the electron-acceptor substituents X) and inactive proton donors (arenesulfonic acids with electron-donor substituents Y). In this event the H-bond can become so weak that it would result in parameters ρ_X^1 and ρ_Y^1 equal zero in IPP $\sigma_Y^{IP(A)}$ and $\sigma_X^{IP(A)}$ respectively. Just this situation is characteristic of the cross reaction series under consideration, whose attribute is IPP σ_X^{IP} 1.07 and σ_Y^{IP} –1.84 corresponding to low reactivity of the system (log k_{XY}^{IP} –4.25). A similar relationship in the interaction of mutual structural effects was observed in the acid-base interaction of substituted pyridines with substituted phenols with the formation of H-complexes [8].

The $A_N D_N$ mechanism of the second limiting stage is resembling that of the nucleophilic substitution at the benzyl carbon atom where the negative values of ρ_{XY} and IPP corresponding to maximum reactivity of the substrate and the nucleophile are characteristic [9]. Since in CRS 1 the cleavage of the oxirane ring occurs involving the α-carbon atom located in the benzyl position, analogously to the benzyl systems we should expect $\rho_{XY}^2 < 0$ for this

stage. At the same time the contribution of ρ_{XY}^2 into the effective value ρ_{XY} in equation (4) should be insignificant, for in the opposite case the calculated values of IPP σ_X^{IP} and σ_Y^{IP} for CRS 1 would not correspond to the minimum of reactivity.

Hence from the above reasoning it is possible to conclude that in the studied CRS 1 the nonadditive effect of substituents X and Y on the rate of the process is due mainly to the interaction of their electronic effects in the stage of the formation of H-complex **A**.

As to the reactions involving aryloxiranes **Ie, If** forming CRS 2, their first stage consists in appearance of H-complex **A** similar to that in CRS 1, which in the second limiting stage k_β suffers the nucleophilic attack of the second acid molecule on the spatially more accessible β-carbon atom of the methylene group of the oxirane ring with the formation of the transition state **C**. The similarity of the first stage of both types of the oxirane ring opening results in same sign and close values of the factor of cross interaction in CRS 1 (ρ_{XY} –2.9) and CRS 2 (ρ_{XY} –2.6), confirming for another time the conclusion of the appearance just in this stage of the nonadditive effects of substituents X and Y.

The β-opening of the oxirane ring caused by the powerful electron-acceptor substituents X results in significant acceleration of the oxirane ring opening (Fig. 1) compared with the rate extrapolated for the α-opening. Thus in the case of oxirane **If** the experimental value of the rate constant of the formation of secondary alcohol **IVh** involving acid **IIc** (Table 1) is 295-fold larger than that calculated by equation (4) for the α-opening of the oxirane ring to form the primary alcohol (log k_{XY} = –6.127, k_{XY} 7.46 × 10^{-7} l^2 mol^{-2} s^{-1}). This significant decrease in the rate of α-opening of the oxirane ring is caused by the destabilizing effect of powerful electron-acceptor substituents X in the process of formation of the transition state **B** of the carbocation character with a significant part of the positive charge on the benzyl carbon atom.

The transition from the α-opening of the oxirane ring to the β-opening at introduction into the molecule of aryloxirane of powerful electron-acceptor substituents X = 4-Br-3-NO_2 and 3,5-$(NO_2)_2$ is accompanied by abnormally large growth of the thermodynamic stability of the forming in CRS 2 secondary alcohols compared with the stability of the products of the α-opening (primary alcohols) in CRS 1. This statement is illustrated by Fig. 2 where versus σ_X is plotted the difference between the calculated by semiempirical method PM3 (Mopac 97) ehthalpy of formation in reaction of aryloxiranes with acid **IIc** of secondary alcohols $XC_6H_{4(3)}CH(OH)CH_2OSO_2C_6H_5$ [$-\Delta H^{II}$ = 597.7, 477.7, 438.6, 406.7, 466.7, 406.7, 477.5, 430.0, 501.6 kJ mol^{-1} in the series of X = 4-OCH_3, 4-CH_3, H, 4-Br, 3-Cl, 3-Br, 4-NO_2, 4-Br-3-NO_2, 3,5-$(NO_2)_2$] and their isomers primary alcohols $XC_6H_{4(3)}CH(OSO_2C_6H_5)CH_2OH$ ($-\Delta H^{I}$ = 596.1, 476, 436.6, 404.3 463.9, 403.8, 473.5, 421.7, 490.9 kJ mol^{-1} respectively in the same series of substituents X). As seen from Fig. 2, the difference $\delta_X\Delta H = \Delta H^{II} - \Delta H^{I}$ is in a fair linear dependence on constants σ_X in the range of σ_X from –0.27 (X = 4-OCH_3) to 0.78 (X = 4-NO_2):

$$\delta_X\Delta H = (2.08 \pm 0.07) + (2.2 \pm 0.2)\sigma_X \quad (5)$$

$$r\ 0.983,\ s\ 0.167,\ n\ 7.$$

The points for substituents X = 4-Br-3-NO_2 and 3,5-$(NO_2)_2$ deviate from this correlation. The comparison for them the values $\delta_X\Delta H$ (4.1 and 5.3) obtained by equation (5) and calculated from the difference $\delta_X\Delta H = \Delta H^{II} - \Delta H^{I}$ (8.3 and 10.7) shows that the secondary alcohols **IVc, IVh** formed at the β-opening of oxiranes are by 4.2 and 5.4 kJ mol^{-1} respectively more stable than the corresponding primary alcohols if they would have formed by the α-opening of the oxirane ring. It is therefore not surprising that in the presence of powerful electron-acceptor substituents X in the oxirane substrate the regioselectivity of reactions changes to the forma-

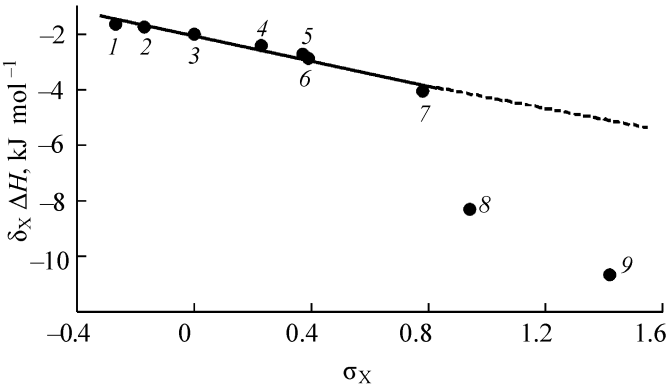


Fig. 2. Plot vs. σ_X of the difference $\delta_X\Delta H = \Delta H^{II} - \Delta H^{I}$ between calculated values of enthalpy of formation in reactions of aryloxiranes $XC_6H_{4(3)}CH(O)CH_2$ with benzenesulfonic acid $PhSO_3H$ of secondary alcohols $XC_6H_{4(3)}CH(OH)CH_2OSO_2C_6H_5$ (ΔH^{II}, kJ mol^{-1}) and isomeric primary alcohols $XC_6H_{4(3)}CH(OSO_2C_6H_5)CH_2OH$ (ΔH^{I}, kJ mol^{-1}) in the series X = 4-OMe (*1*), 4-Me (*2*), H (*3*), 4-Br (*4*), 3-Cl (*5*), 3-Br (*6*), 4-NO_2 (*7*), 4-Br-3-NO_2 (*8*), 3,5-$(NO_2)_2$ (*9*).

tion of the thermodynamically significantly more stable secondary alcohols.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Bruker Avance-400 (400 MHz) in $CDCl_3$, internal reference TMS. Dioxane of "pure for analysis" grade and diglyme of "pure" grade were dried with KOH and distilled over Na (diglyme at reduced pressure). Commercial (Merck) phenyloxirane (98% of the main substance) was used without additional purification. Technical 4-nitrophenyloxirane was twice recrystallized from hexane, mp 85–86°C [10]. The other aryloxiranes were obtained from the corresponding phenacyl bromides by known procedures [11]. Arenesulfonic acids of "pure" grade were dried by long (10 h) boiling of their benzene solutions with water separation on a Dean–Stark trap and were stored in a vacuum desiccator over P_2O_5.

The measurement of the reaction rate was carried out by sampling, the addition to the sample of HBr solution in glacial acetic acid to stop the process. Then the mixture was cooled to 265 K and after 180 min the excess HBr unreacted with residual oxirane was determined by potentiometric titration with water solution of $AgNO_3$ [3]. The reaction kinetics were studied at 10-fold and over excess of arenesulfonic acids with respect to the initial concentrations of aryloxiranes (S): $[HA]_0 >> [S]_0 = 0.001 - 0.008$ mol l^{-1}. Under these concentration conditions the reaction is of the first order with respect to oxirane substrate and of the second order with respect to acid reagent, and the process rate is described by the equation

$$-d[S]/dt = k[S] = k_{XY}[S][HA]_0^2, \quad (6)$$

where k (s^{-1}) and k_{XY} (l^2 mol^{-2} s^{-1}) are rate constants of pseudofirst and third order respectively. In all kinetic runs the apparent rate constants k remained constant in the course of the process till the conversion of oxirane was 70–80% (the error in the constant measurement did not exceed 5%). The constants k_{XY} characterizing the combined effect of substituents X and Y on the rate of the process were evaluated by extrapolation to zero of linear dependences $k = k_{XY}[HA]_0^2$ for four and more different concentrations of HA ($r \geq 0.995$). The statistical processing of experimental data was performed at the confidence range 0.95.

The homogeneity of compounds obtained was checked by TLC on Silufol UV-254 plates (development in iodine vapor, eluent cyclohexane–dichloromethane, 7:3). The products of reactions between oxiranes **Ie, If** and acids **IIb,IIc** were synthesized in conditions similar to the kinetic runs.

1-(4-Bromo-3-nitrophenyl)-2-tosyloxyethanol (IVb). A solution of 0.122 g (0.5 mmol) of oxirane **Ie** and 0.860 g (5 mmol) of acid **IIb** in 50 ml of a mixture of dioxane with diglyme, 1 : 1, was maintained for 72 h at –8°C till the disappearance of oxirane (TLC monitoring, the absence of reaction with HBr). Then the reaction mixture was diluted with 100 ml of water, the reaction product was extracted with ether (3 × 20 ml), the combined ether extracts were washed with water till neutral reaction of washings, and dried with anhydrous $MgSO_4$, the solvent was distilled off at a reduced pressure. Yield 0.198 g (95%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 2.38 s (3H, CH_3), 3.54 d.d (1H, CH_2, ^3J 7.0, ^2J 11.2 Hz), 3.62 d.d (1H, CH_2, ^3J 4.1, ^2J 11.2 Hz), 3.86 d.d (1H, CH, $^3J_1$ 7.0, ^3J 4.1 Hz), 7.33 d (2H, $H^{3,5}$, C_6H_4, J 8.0 Hz), 7.73 d (2H, $H^{2,6}$ C_6H_4, J 8.0 Hz), 9.06 d.d (1H, H^6, C_6H_3, $J_{6,2}$ 2.1, $J_{6,5}$ 9.0 Hz), 9.42 d (1H, H^5, C_6H_3, $J_{6,5}$ 9.0 Hz), 9.45 d (1H, H^2 C_6H_3, $J_{6,2}$ 2.1 Hz). Found, %: C 43.45; H 3.28; Br 19.11; N 3.43; S 7.83. $C_{15}H_{14}BrNO_6S$. Calculated, %: C 43.27; H 3.36; Br 19.23; N 3.36; S 7.69.

1-(3,5-Dinitrophenyl)-2-phenylsulfonyloxyethanol (IVh) was similarly obtained from 0.105 g (0.5 mmol) of oxirane **If** and 0.791 g (5 mmol) of acid **IIc**. Yield 0.171 g (93%), light yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 4.17 d.d (1H, CH_2, ^3J 6.8, ^2J 10.9 Hz), 4.27 d.d (1H, CH_2, ^3J 3.9, ^2J 10.9 Hz), 5.22 d.d (1H, CH, ^3J 3.9, ^3J 6.8 Hz), 7.45–7.83 m (5H, Ph), 8.42 d (2H, $H^{2,6}$, C_6H_3, J 4.3 Hz), 8.93 t (1H, H^4, C_6H_3, J 4.3 Hz). Found, %: C 45.93; H 3.19; N 7.79; S 8.53. $C_{14}H_{12}N_2O_8S$. Calculated, %: C 45.65; H 3.26; N 7.61; S 8.69.

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