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COMBINED EFFECTS of STRUCTURE and TEMPERATURE on KINETICS of REACTIONS between 4-NITRIPHENYLOXIRANE and ARENESULFINIC ACIDS in DIOXANE

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The effects of structure and temperature on the rate and free activation energy of reactions between 4-nitrophenyloxirane and Y-substituted arenesulfinic acids $YC_6H_4SO_2H$ in dioxane at 298, 308, and 323 K have been studied. Cross-correlation analysis of kinetic data was conducted. It was found that as a result of the nonadditivity of the joint effects of substituents Y and temperature, the cross reaction series exhibits isoparametric properties, the quantitative characteristics of which are isoparametrical points with respect to the constant of substituents Y ($\sigma_Y^{IP} = 1.02$; $\sigma_Y^{IP(G)} = -0.58$) and to temperature ($T^{IP} = 367$ K; $T^{IP(G)} = 410$ K). At the isoparametric temperature the rate of the process and the free activation energy should not depend on the effects of substituents Y, due to the full compensation in the change of the enthalpy and entropy components: $\delta_Y \Delta H^\ddagger = T^{IP(G)} \delta_Y \Delta S^\ddagger$, $\delta_Y \Delta G^{\ddagger IP} = 0$, and $\Delta G_{YT}^{\ddagger IP} = \text{const}$ ($\log k_{YT} = \text{const}$, $\rho_Y^T = 0$). At the isoparametrical point $\sigma_Y^{IP} = 1.02$, the rate of the process should not depend on temperature, consequently $\Delta H_Y^\ddagger = 0$. At the isoparametrical point $\sigma_Y^{IP(G)} = -0.58$, free activation energy ΔG_{YT}^{\ddagger} does not depend on a temperature, that is why $\Delta S_Y^\ddagger = 0$ and $\Delta G_{YT}^{\ddagger IP} = \Delta H_Y^\ddagger$. All these isoparametrical points fall outside experimental attainability.

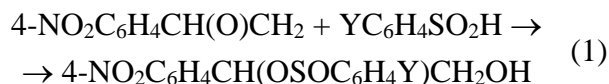
Keywords: 4-nitrophenyloxirane, arenesulfinic acids, correlation analysis, isoparametrical points, compensation effect.

Introduction

It is a topical problem of the chemistry to determine the rate laws of reactions under the action of cross-varied factors (the structures of reactants and catalysts, medium, temperature, pH, pressure etc.). For study of the joint effects of the structure and temperature we chose oxirane ring opening reactions which are of interest from both theoretical and practical viewpoints. The specific organization of the atoms in the oxirane ring, combined with its strain and unsaturated nature, are responsible for a wide variety of practically important reactions of oxirane substrates with compounds from different classes [1-5]. These reactions are widely used in organic synthesis, as well as in production of polymers, pharmaceuticals, and pesticides, and also underlie a number of biochemical processes, in particular, the physiological process of detoxification of metabolites of exogenous substances. The oxirane ring is a structural element of many biologically active substances of both synthetic and natural origin. We showed previously [6, 7] that, in the reactions

of aryloxiranes with arenesulfonic acids, intensive interaction of the effects of the structure of the acid reactant and the temperature is manifested, which allowed the first experimental observation of the isoparametricity phenomenon [8] in its enthalpy–entropy compensation effect (CE) [9].

We report here the results of cross correlation analysis of the kinetic data on the reactions of 4-nitrophenyloxirane with Y-substituted arenesulfinic acids $YC_6H_4SO_2H$ (Y = 4-CH₃, H, 4-Cl) in dioxane at 298, 308, 323 K:



Results and Discussion

The products of reactions (1) were isolated at kinetic conditions as stable ductile yellow-orange oils. The yields of the major products were practically quantitative (90–95 %) by HPLC. Their structures were studied by means of ¹H NMR spectroscopy and found to be in correspondence with 2-arylsulfinyloxy-2-(4-nitro-

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phenyl)ethanol. Analogous 2,2-disubstituted ethanol derivatives (primary alcohols) are also formed in related reactions of aryloxiranes with arenesulfonic acids [6] and HNO₃ [10].

To measure reaction rates, the interaction between reactants was stopped by the addition of an HBr solution in glacial acetic acid to a kinetic sample. After 30 min, the unreacted amount of HBr was determined by potentiometric titration using an AgNO₃ solution. The reaction kinetics was examined using more than tenfold amounts of arenesulfonic acids (HA) with respect to the initial concentrations of 4-nitrophenyloxirane (S): [HA] >> [S] = (3 ÷ 7) 10⁻³ mol dm⁻³. In all cases, the observed pseudo-first-order reaction rate constants (*k*_{obs}, s⁻¹) remained constant up to 70–80 % conversion of the epoxide (determination error was no higher than 5 %). The reaction was found to exhibit the first order with respect to epoxide. At the same, linear relationships between *k*_{obs} and [HA]² were observed (*r* ≥ 0.996), which pass through the origin of coordinates. Thus, the kinetics of the reactions of interest is described by the equation

$$d[S]/dt = k_{obs} [S] = k_3 [S] [HA]^2, \quad (2)$$

where *k*_{obs} (s⁻¹) and *k*₃ (dm⁶ mol⁻² s⁻¹) are pseudo-first-order and third-order rate constants, respectively.

The *k*₃ constants were found from the linear relations *k*_{obs} = *k*₃[HA]² at four or more HA concentrations. Table 1 summarizes the values of *k*₃ for reactions (1) and the ρ_Y^T values calculated by the Hammett equation for partial reaction series (RS) at fixed temperatures. Note that ρ_Y^T decreases with increasing temperature; this fact is indicative of the nonadditivity of combined effects of substituents Y and a temperature factor in cross-reaction series (1). Between ρ_Y^T and reverse temperature (1/*T*, K⁻¹) performed a linear relationship due to the principle of polylinearity (PPL) [8]:

$$\rho_Y^T = (-8.6 \pm 0.9) + (3.2 \pm 0.3) \cdot 10^3/T, \quad (3)$$

$$s = 0.032, r = 0.996, n = 3.$$

In the graphical representation of eqn. (3), the slope of the straight line, which is named as the cross interaction coefficient *q*_{YT}, is a measure of the nonadditivity of the simultaneous effects of Y and temperature in the cross RS (1). It follows

from eqn. (3) that the isoparametric temperature – the isoparametric point (IPP) – at which the substituents Y exert no effects on the reaction rate (ρ_Y^T = 0) is *T*^{IP} = 372 K. The data presented in Table 1 indicate that such a temperature is not attainable in the cross RS (1).

Table 1. Rate constants *k*₃ × 10² (dm⁶ mol⁻² s⁻¹) and ρ_Y^T values in the Hammett equation for the reactions of 4-nitrophenyloxirane with arenesulfonic acids (YC₆H₄SO₂H) in dioxane at different temperatures

Y(σ _Y)	<i>k</i> ₃ · 10 ² (dm ⁶ mol ⁻² s ⁻¹)		
	298 K	308 K	323 K
<i>n</i> -CH ₃ (-0.17)	0.351 ± 0.002	1.07 ± 0.01	3.84 ± 0.01
H (0)	0.92 ± 0.04	2.12 ± 0.02	6.54 ± 0.04
<i>n</i> -Cl (0.23)	2.76 ± 0.02	5.48 ± 0.01	13.4 ± 0.1
ρ _Y ^T	2.2 ± 0.1	1.78 ± 0.01	1.36 ± 0.02
<i>r</i>	0.999	0.999	0.999

To evaluate the effect of temperature on the rate of reactions (1), we used the Eyring equation

$$\log(k_3/T) = A_{T=\infty}^Y + B_T^Y(1000/T), \quad (4)$$

where $A_{T=\infty}^Y = \log(k_B/h) + \Delta S_{Y^\ddagger}/2.3R$, $B_T^Y = -\Delta H_{Y^\ddagger}/2.3R$ (*k*_B is the Boltzmann constant, *h* is the Plank constant and *R* is the gas constant). As a rule, the transmission coefficient is accepted equal to 1 for the heterolytic reactions, so that it was omitted in eqn. (4).

Table 2 summarizes the parameters of eqn. (3) for the reactions of 4-nitrophenyloxirane with arenesulfonic acids, as well as the enthalpies (Δ*H*_{Y[‡]}), entropies (Δ*S*_{Y[‡]}) and free energies (Δ*G*_{YT[‡]}) of activation calculated using these parameters. A change in the slope *B*_{T^Y} in eqn. (4) with Y is consistent with the above-mentioned nonadditive effects of the structure and temperature on the rate of reactions (1) and are described by eqn. (5):

$$B_T^Y = (-3.25 \pm 0.07) + (3.5 \pm 0.4)\sigma_Y, \quad (5)$$

$$s = 0.126, r = 0.992, n = 3.$$

The slope coefficient of eqn. (5) is close to the value of the cross interaction coefficient ρ_{YT} in eqn. (3). As it follows from eqn. (5) the value of *B*_{T^Y} = 0 at IPP σ_{Y^{III}} = 0.93. Almost the same value of this IPP, where Δ*H*_{Y[‡]} = 0, follows from eqn. (6):

$$\Delta H_{Y^\ddagger} = (62 \pm 2) + (-67 \pm 10)\sigma_Y, \quad (6)$$

$$s = 2.87, r = 0.989, n = 3.$$

The change ΔS_Y^\ddagger upon varying substituents Y is described by linear relation

$$\Delta S_Y^\ddagger = (-75 \pm 4) + (-178 \pm 24)\sigma_Y, \quad (7)$$

$$s = 6.83, r = 0.991, n = 3.$$

Table 2. Coefficients of eqn. (3) and activation parameters ΔH_Y^\ddagger , kJ/mol, ΔS_Y^\ddagger , J/(mol K), and ΔG_{YT}^\ddagger , kJ/mol, for the reactions of 4-nitrophenyloxirane with arenosulfonic acids (YC₆H₄SO₂H) in dioxane at different temperatures

Characteristics	Y		
	4-CH ₃	H	4-Cl
$A_{T=\infty}^Y$	8.1 ± 0.6	6.08 ± 0.04	4.36 ± 0.07
$-B_T^Y$	3.9 ± 0.2	3.15 ± 0.01	2.50 ± 0.02
r	0.999	0.999	0.999
s	0.035	0.002	0.004
ΔH_Y^\ddagger	75	60	48
$-\Delta S_Y^\ddagger$	42	81	114
$\Delta G_{YT=298}^\ddagger$	87	84.5	82
$\Delta G_{YT=308}^\ddagger$	87.5	85	83
$\Delta G_{YT=323}^\ddagger$	88	86	84

Relations (3) and (5)–(7) illustrate examples of observing the PPL in a cross RS (1). An important demonstration of the PPL is the linear dependence of the change in ΔH_Y^\ddagger and ΔS_Y^\ddagger under the effect of substituents Y, which reflects the enthalpy-entropy CE:

$$\Delta H_Y^\ddagger = (90.6 \pm 0.5) \cdot 10^3 + (375 \pm 6)\Delta S_Y^\ddagger, \quad (8)$$

$$s = 306, r = 0.999, n = 3.$$

The slope coefficient of eqn. (8) is a measure of the value $T^{IP} = 375$ K, which corresponds to the one calculated using eqn. (3). To estimate the joint effect substituents Y and temperature have on the rate of reactions (1), we used a cross correlation equation for a two-parameter variant of PPL:

$$\log k_3 = \log k_3^{st} + \rho_Y^{st}\sigma_Y + B_T^{st}(1000/T) + q_{YT}\sigma_Y(1000/T), \quad (9)$$

where k_3^{st} is the rate constant under standard conditions ($\sigma_Y = 0$, $T = \infty$ K), ρ_Y^{st} and B_T^{st} are the parameters of standard reactions at $T = \infty$ K and $\sigma_Y = 0$, respectively, and q_{YT} is the cross interaction coefficient. The following polylinear regression was obtained in processing the kinetic data in Table 1 in accordance with eqn. (9):

$$\log k_3 = (9.3 \pm 0.2) + (-9 \pm 1)\sigma_Y + (-3.38 \pm 0.07) \cdot 1000/T + (3.3 \pm 0.4)\sigma_Y \cdot 1000/T, \quad (10)$$

$$s = 0.022, R = 0.999, F = 1368, n = 9.$$

Here, R is the multiple correlation coefficient and F is Fisher's test. Regression (10) describes cross RS (1) to a high degree of accuracy, as is evidenced by its statistical parameters and the correspondence of the value of cross interaction coefficient q_{YT} to its values in eqns. (3) and (5). Because of the difference between this coefficient and zero, regression (10) is characterized by isoparametric properties, the quantitative characteristics of which are IPPs with respect to the constant of substituent $\sigma_Y^{IP} = -B_T^{st}/q_{YT} = 1.02$; to temperature $T^{IP} = (-q_{YT}/\rho_Y^{st}) \cdot 10^3 = 367$ K, the value of which differs negligibly from the ones presented above; and the rate constants at these points: $\log k_3^{IP} = \log k_3^{st} - \rho_Y^{st}B_T^{st}/q_{YT} = 0.10$, $k_3^{IP} = 1.26$, dm⁶·mol⁻²·s⁻¹. At the isoparametric (isokinetic) temperature $T^{IP} = 367$ K, the rate of the process should not be affected by substituents Y in acids ($\rho_Y^T = 0$), while at the IPP $\sigma_Y^{IP} = 1.02$, the rate of the process should not depend on temperature: $B_T^Y = 0$, and thus $\Delta H_Y = 0$. Eqn. (5) shows that $B_T^Y = 0$ at σ_Y corresponding to the isoparametric values, which are 0.93. This IPP cannot be attained, due to the deficit of strong electron-withdrawing substituents Y with $\Sigma\sigma_Y = 1.02$. The IPP with respect to temperature $T^{IP} = 367$ K also falls outside experimental attainability.

In terms of activation parameters, the nonadditive effects of structure and temperature in RS (1) can be analyzed using the equation (11):

$$\Delta G_{YT}^\ddagger = \Delta G_{YT}^{\ddagger st} + a_Y^{st}\sigma_Y + b_T^{st}T + c_{YT}\sigma_Y T, \quad (11)$$

where $\Delta G_{YT}^{\ddagger st}$ is the free activation energy under standard conditions ($\sigma_Y = 0$ and $T = 0$ K); a_Y^{st} and b_T^{st} are the parameters of standard RSEs at $T = 0$ K and $\sigma_Y = 0$, respectively; and c_{YT} is the coefficient of cross interaction. In calculating the coefficients of eqn. (11) using the values of ΔG_{YT}^\ddagger in Table 2, we obtained the regression (12):

$$\Delta G_{YT}^\ddagger = (68 \pm 3) + (-41 \pm 17)\sigma_Y + (0.058 \pm 0.009)T + (0.10 \pm 0.05)T\sigma_Y, \quad (12)$$

$$s = 0.281, R = 0.988, F = 142, n = 9.$$

The following are the isoparametric criteria of regression (12): IPP with respect to temperature $T^{IP(G)} = -a_Y^{st}/c_{YT} = 410$ K, which is consistent with the values of T^{IP} calculated using eqns. (3), (5), and (10); another IPP with respect to the constant of substituent $\sigma_Y^{IP(G)} = -b_T^{st}/c_{YT} = -0.58$, in

addition to the IPP $\sigma_Y^{\text{IP}} = 1.02$ calculated above; and the isoparametric value of $\Delta G_{\text{YT}}^{\neq \text{IP}} = \Delta G_{\text{YT}}^{\neq \text{st}} - a_Y^{\text{st}} b_{\text{T}}^{\text{st}} / c_{\text{YT}} = 92 \text{ kJ/mol}$. At the IPP $T^{\text{IP(G)}} = 410 \text{ K}$, the free activation energy $\Delta G_{\text{YT}}^{\neq}$ should not depend on the effects of substituents Y, due to the full compensation in the change of the enthalpy and entropy components of $\Delta G_{\text{YT}}^{\neq}$ at this temperature: $\delta_Y \Delta H^{\neq} = T^{\text{IP(G)}} \delta_Y \Delta S^{\neq}$, $\delta_Y G^{\neq \text{IP}} = 0$, and $\Delta G_{\text{YT}}^{\neq \text{IP}} = \text{const} = 92 \text{ kJ/mol}$. At the IPP = -0.58, $\Delta G_{\text{YT}}^{\neq}$ does not depend on temperature if the activation entropy $\Delta S_Y^{\neq} = 0$ and free activation energy in the expression $\Delta G_{\text{YT}}^{\neq \text{IP}} = \Delta H_Y^{\neq} - T^{\text{IP}} \Delta S_Y^{\neq}$ is determined by its enthalpic term: $\Delta G_{\text{YT}}^{\neq \text{IP}} = \Delta H_Y^{\neq} = 92 \text{ kJ/mol}$. This is confirmed by eqn. (7), which shows that $\Delta S_Y^{\neq} = 0$ when $\sigma_Y = -0.42$ (close to the isoparametric value) and eqn. (8), where ΔH_Y^{\neq} is 90.6 kJ/mol (i. e., $\Delta G_{\text{YT}}^{\neq \text{IP}}$ is equal to ΔH_Y^{\neq} at $\Delta S_Y^{\neq} = 0$).

Conclusions

Thus, in the framework of the CE, owing to the dual nature of $\Delta G_{\text{YT}}^{\neq}$, by widely varying substituents Y in arenesulfonic acids it is possible to pass from the extreme state of reaction system (1) in which at the $\sigma_Y^{\text{IP(G)}} = -0.58$ point the contribution from the entropic factor to the free energy activation disappears ($\Delta S_Y^{\neq} = 0$) to the equally interesting extreme state at the $\sigma_Y^{\text{IP}} = 1.02$ point, at which there should be no contribution from the enthalpic factor ($\Delta H_Y^{\neq} = 0$). The variations in the free energy of activation $\Delta G_{\text{YT}}^{\neq}$ itself (Table 2) are comparatively small as a consequence of the CE.

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Сумісний вплив структури і температури на швидкість реакцій 4-нітрофенілоксирану з аренсульфінновими кислотами у діоксані

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Вивчено вплив структури і температури на швидкість та вільну енергію активації реакцій 4-нітрофенілоксирану з Y-заміщеними аренсульфінновими кислотами $\text{YC}_6\text{H}_4\text{SO}_2\text{H}$ в діоксані при 298, 308 і 323 K. Проведено перехресний кореляційний аналіз результатів багатофакторного кінетичного експерименту. Встановлено, що завдяки неадитивності сумісних ефектів замісників Y і температури перехресна реакційна серія проявляє ізопараметричні властивості, кількісними характеристиками яких є ізопараметричні точки щодо константи замісників Y ($\sigma_Y^{\text{III}} = 1.02$; $\sigma_Y^{\text{III(G)}} = -0.58$) та температури ($T^{\text{III}} = 367 \text{ K}$; $T^{\text{III(G)}} = 410 \text{ K}$). При ізопараметричній температурі швидкість процесу і вільна енергія активації не залежать від ефектів замісників Y через повну компенсацію у зміні її ентальпійного і ентропійного компонента: $\delta_Y \Delta H^{\neq} = T^{\text{III(G)}} \delta_Y \Delta S^{\neq}$, $\delta_Y \Delta G^{\neq \text{III}} = 0$, $\Delta G_{\text{YT}}^{\neq \text{III}} = \text{const}$ ($\lg k_{\text{YT}} = \text{const}$, $\rho_Y^{\text{T}} = 0$). В ізопараметричній точці $\sigma_Y^{\text{III}} = 1.02$ швидкість процесу не повинна залежати від температури, що можливо, якщо

$\Delta H_{Y^\ddagger} = 0$. В ізопараметричній точці $\sigma_{Y^{IP(G)}} = -0.58$ вільна енергія активації не залежить від температури завдяки тому, що $\Delta S_{Y^\ddagger} = 0$ і $\Delta G_{Y^\ddagger}^{IP} = \Delta H_{Y^\ddagger}$. Усі ці ізопараметричні точки виходять за межі експериментальної досяжності.

Ключові слова: 4-нітрофенілоксиран, аренсульфінові кислоти, кореляційний аналіз, ізопараметричні точки, компенсаційний ефект.

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Совместное влияние структуры и температуры на скорость реакций 4-нитрофенилоксирана с аренсульфиновыми кислотами в диоксане

И. В. Шпанько, И. В. Садовая

Исучено влияние структуры и температуры на скорость и свободную энергию активации реакций 4-нитрофенилоксирана с Y-замещенными аренсульфиновыми кислотами $C_6H_4SO_2H$ в диоксане при 298, 308 и 323 К. Проведен перекрестный корреляционный анализ результатов многофакторного кинетического эксперимента. Выявлено, что вследствие неаддитивности совместных эффектов заместителей Y и температуры перекрестная реакционная серия проявляет изопараметрические свойства, количественными характеристиками которых являются изопараметрические точки по константе заместителей Y ($\sigma_{Y^{IP}} = 1.02$; $\sigma_{Y^{IP(G)}} = -0.58$) и по температуре ($T^{IP} = 367$ К; $T^{IP(G)} = 410$ К). При изопараметрической температуре свободная энергия активации (скорость процесса) не зависит от эффектов заместителей Y из-за полной компенсации в изменении ее энгальпийного и энтропийного термина: $\delta_Y \Delta H^\ddagger = T^{IP(G)} \delta_Y \Delta S^\ddagger$, $\delta_Y \Delta G^\ddagger_{IP} = 0$, $\Delta G_{Y^\ddagger}^{IP} = \text{const}$ ($\lg k_{Y^\ddagger} = \text{const}$, $\rho_{Y^\ddagger} = 0$). В изопараметрической точке $\sigma_{Y^{IP}} = 1.02$ скорость процесса не должна зависеть от температуры, что возможно, если $\Delta H_{Y^\ddagger} = 0$. В изопараметрической точке $\sigma_{Y^{IP(G)}} = -0.58$ свободная энергия активации не зависит от температуры ($\Delta S_{Y^\ddagger} = 0$; $\Delta G_{Y^\ddagger}^{IP} = \Delta H_{Y^\ddagger}$). Все эти изопараметрические точки выходят за пределы экспериментальной достижимости.

Ключевые слова: 4-нітрофенілоксиран, аренсульфінові кислоти, кореляційний аналіз, ізопараметричні точки, компенсаційний ефект.