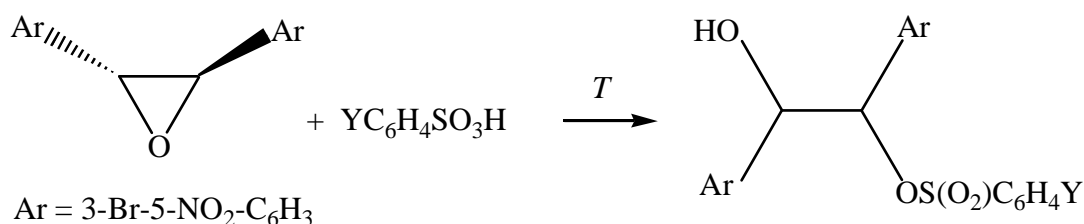


**COMBINED EFFECTS of STRUCTURE and TEMPERATURE on
KINETICS and FREE ACTIVATION ENERGY of REACTIONS
BETWEEN *trans*-2,3-bis(3-BROMO-5-NITROPHENYL)OXIRANE and
ARENESULFONIC ACIDS**

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The combined effects of structure and temperature on the rate and free activation energy of reactions between *trans*-2,3-bis(3-bromo-5-nitrophenyl)oxirane and Y-substituted arenesulfonic acids (Y = 4-OCH₃, 4-CH₃, H, 4-Cl) in a mixture of dioxane with 1,2-dichloroethane (7:3, v/v) at 265, 281, and 298 K have been studied.



Cross-correlation analysis of kinetic data was conducted. It was found the nonadditivity of the joint effect of substituents Y and temperature on the rate and free activation energy of the process of oxirane ring opening. The cross-reaction series is described by the polylinear equations:

$$\lg k_{YT} = (11.7 \pm 0.1) + (8.4 \pm 0.7)\sigma_Y + (-4.61 \pm 0.04) \cdot 10^3/T + (-2.2 \pm 0.2)\sigma_Y \cdot 10^3/T, \quad (1)$$

$$R = 0.999, s = 0.021, F = 5062, n = 12.$$

$$\Delta G_{YT}^\ddagger = (83 \pm 1) + (47 \pm 5)\sigma_Y + (0.036 \pm 0.003)T + (-0.18 \pm 0.02)\sigma_Y T, \quad (2)$$

$$R = 0.983, s = 0.152, F = 151, n = 12.$$

Regressions (1) and (2) describe the cross-reaction series to a high degree of accuracy, as is evidenced by their statistical parameters. Because of the difference between cross interaction coefficients and zero, these regressions are characterized by isoparametric properties, the quantitative characteristics of which are isoparametric points with respect to the constant of substituents Y ($\sigma_Y^{\text{IP}} = -2.0$; $\sigma_Y^{\text{IP(G)}} = 0.2$) and to temperature ($T^{\text{IP}} = 262$ K; $T^{\text{IP(G)}} = 261$ K). At the isoparametric temperature, that is close to the temperature in the experiment ($T = 265$ K), the rate of the process and the free activation energy ΔG_{YT}^\ddagger are not depend on the effects of substituents Y, due to the full compensation in the change of the enthalpy and entropy components: $\delta_Y \Delta H^\ddagger = T^{\text{IP(G)}} \delta_Y \Delta S^\ddagger$, $\delta_Y \Delta G^{\ddagger \text{IP}} = 0$, and $\Delta G_{YT}^{\ddagger \text{IP}} = \text{const}$ ($\log k_{YT} = \text{const}$, $\rho_Y^T = 0$). At the isoparametric point $\sigma_Y^{\text{IP}} = -2.0$, the rate of the process should not depend on temperature, consequently $\Delta H_Y^\ddagger = 0$. At the isoparametric point $\sigma_Y^{\text{IP(G)}} = 0.2$, free activation energy $\Delta G_{YT}^\ddagger = \Delta H_Y^\ddagger - T \Delta S_Y^\ddagger$ does not depend on a temperature, that is why $\Delta S_Y^\ddagger = 0$ and $\Delta G_{YT}^{\ddagger \text{IP}} = \Delta H_Y^\ddagger$. The isoparametric points $T^{\text{IP}} = 262$ K, $T^{\text{IP(G)}} = 261$ K, and $\sigma_Y^{\text{IP(G)}} = 0.2$ fall inside experimental attainability.

Thus, intensive interaction of the effects of the structure (substituents Y) and the temperature in the investigated cross-reaction series allowed the rare experimental observation of the isoparametricity phenomenon in its enthalpy–entropy compensation effect.

The possibility of using isoparametric points as quantitative mechanistic criteria is demonstrated.