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Joint Effect of Structure and Temperature on the Rates of the Reactions of 3,5-Dinitrophenyloxirane with Arenesulfonic Acids: Compensation Effect and Isoparametricity

I. V. Shpan'ko and I. V. Sadovaya
Faculty of Chemistry, Donetsk National University, Donetsk, 83055 Ukraine
e-mail: shpanko09@rambler.ru

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Abstract—The joint effect of structure and temperature on the rate and free energy of activation of the reactions of 3,5-dinitrophenyloxirane with arenesulfonic acids $YC_6H_4SO_3H$ in a dioxane–diglyme (1 : 1 vol/vol) mixture is reported. A correlation analysis of the results of a multifactor kinetic experiment has demonstrated the nonadditivity (interaction) of the effects of the substituent Y and temperature for a cross reaction series. The pronounced kinetic enthalpy–entropy compensation effect provided experimental evidence for the isoparametricity phenomenon: at the isoparametric temperature point (isokinetic temperature), the rate of the reaction is independent of the structure of Y. At the isoparametric point for the constant of the substituent Y, the free energy of activation is temperature-independent and the entropy of activation is $\Delta S^{\neq} = 0$. On passing through this point, $\Delta S^{\neq}$ changes its sign. The isoparametric points for the parameters of the varied factors are used in the interpretation of the mechanism of oxirane ring opening.

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The development of the formal theory of interaction and multifactor experiments has led to the discovery of previously unknown properties of physicochemical systems, such as isoparametricity [1]. In the simplest case, isoparametricity shows itself in processes in which there is nonadditivity (interaction) between the simultaneous effects of two cross-varied factors (structure, temperature, solvent, pressure, pH of the medium, and other internal and external factors). These processes are described by polylinearity principle–based relationships with cross terms whose coefficients evaluate the degree of nonadditivity. Isoparametricity manifests itself as a zero value of the sensitivity coefficient for one of the factors in empirical one-parameter correlations (α (β) in the Brønsted equation, ρ in the Hammett equation, coefficient in the Arrhenius equation that is proportional to activation energy, etc.) at the isoparametric value of the parameter of another factor. This value is called the isoparametric point (IPP). Once the IPP is passed, an inversion of the signs of the corresponding sensitivity coefficients takes place—isoparametricity paradox. Because of the unusual properties of the isoparametric relationships, some authors call them mysterious regularities [2] and the IPP is called the magic point [3].

Although isoparametricity reflects the unique properties of physicochemical systems that are in conflict with conventional chemical theory, this phenomenon is still receiving unreasonably little attention. On the one hand, this is due to the high laboriousness of multifactor experiments. On the other hand, this is explained by the fact that, in many series of experiments, IPPs are virtual in character since they fall into a far extrapolation region and are experimentally inaccessible. Because of the latter circumstance, the phenomenon of isoparametricity is a rare occurrence in chemistry. Fortunate exceptions are nucleophilic substitution reactions at the carbonyl, benzyl, and benzhydryl carbon atoms [4, 5]. The systematic study of multifactor effects on the kinetics of these reactions revealed a wide variety of IPPs in cross correlations of the structure–structure, structure–solvent, structure–temperature, and solvent–temperature types. Some of these points were passed through, which is a rare situation in chemical processes, and this was accompanied by the inversion of the signs of the corresponding sensitivity coefficients because of reactivity reorientation.

Isoparametric properties show themselves most frequently in the enthalpy–entropy compensation effect in chemistry, physics, biology, etc. [6–11]. In chemistry, this effect is observed in diverse kinetic and thermodynamic processes in the liquid, solid, and gas phases (various types of chromatography; phase transitions; hydrogen bonds; coordination chemistry; colloid chemistry; chemistry of crown ethers, peptides, lipids, and nucleic acids; etc. [8]). An attribute of the compensation effect is a temperature IPP (T^{IP}), which is conventionally called the isokinetic (isoequilibrium) temperature in the chemical literature. This IPP has long attracted researchers' attention as a reliable test for the existence of a true compensation effect.

It can be determined from the linear dependence between the enthalpy and entropy of activation of the reaction in cross reaction series in which there is nonadditivity of the simultaneous effects of temperature and some other factor j: $\Delta H_J^{\neq} = \Delta H_0^{\neq} + T^{IP}\Delta S_J^{\neq}$ $\left(\Delta H_J = \Delta H_0 + T^{IP}\Delta S_J\right)$, where the subscript 0 stands for the standard value of j. A remarkable property of T^{IP} is that, once this point is reached, the changes in the enthalpic and entropic components of the free energy of activation totally counterbalance one another as the parameter of the factor j is varied. As a consequence, $\delta_J\Delta G^{\neq} = 0$ and $\Delta G_J^{\neq} =$ const ($\delta_J\Delta G = 0$ and $\Delta G_J =$ const) and all reactions of the series proceed at the same rate (all equilibria in the series have the same equilibrium constant). Thus, at the temperature equal to T^{IP}, the slopes of the one-parameter correlations for the effects of the factor j are zero. In graphical representation, T^{IP} is the intersection point of the family of correlation straight lines in the coordinates of the Arrhenius or Eyring (van't Hoff) equation or another temperature dependence describing the kinetics (thermodynamics) of similar processes within one cross series of experiments at a certain set of fixed values of the parameter of the factor j.

Although there have been a great number of publications dealing with the compensation effect in various natural sciences over many decades, experimental observations of T^{IP} are rare [10, 11]. Calculated T^{IP} values typically fall in the region of much higher (much lower) temperatures than are examined in experiments [6, 7].

The purpose of this work is to study the isoparametricity phenomenon and, in particular, its enthalpy–entropy compensation aspect for oxirane ring opening reactions. Here, we will prove that T^{IP} falls within the experimental temperature range. We will demonstrate the realization of one of the two IPPs for the constant σ_Y of the substituent Y and passage through this point for reactions of 3,5-dinitrophenyloxirane with Y-substituted acids $YC_6H_4SO_3H$ (Y = 4-OCH_3, 4-CH_3, H, 4-Cl, 3-NO_2) in a dioxane–diglyme (1 : 1 vol/vol) mixture at 265, 287, and 303 K (reaction (I)). We will show that IPP is usable as a mechanistic criterion for oxirane ring opening.

$$\begin{aligned}&3{,}5\text{-}(NO_2)_2C_6H_3CH(O)CH_2 + YC_6H_4SO_3H\\ &\rightarrow 3{,}5\text{-}(NO_2)_2C_6H_3CH(OH)CH_2OSO_2C_6H_4Y\end{aligned} \qquad (I)$$

EXPERIMENTAL

The product of reaction (I) is a secondary alcohol, specifically, 2-arylsulfonyloxy-1-(3,5-dinitrophenyl)ethanol [12]. Dioxane (analytical grade) and the dimethyl ether of diethylene glycol (diglyme, pure grade) were dried over KOH and were distilled from Na at a reduced pressure. Arenesulfonic acids (pure grade) were dehydrated by ~10-h-long refluxing of their benzene solutions with water removal using a Dean–Stark apparatus. 3,5-Dinitrophenyloxirane was obtained by the reduction of 3,5-dinitrophenacylbromide with aluminum isopropoxide in isopropanol to the corresponding bromohydrin followed by the dehydrobromination of the bromohydrin in an alkali medium [13, 14]. The 3,5-dinitrophenyloxirane content of the product in terms of epoxide groups was at least 98%. The kinetic measurement procedure was described in our earlier publication [12]. Kinetic experiments were performed on reaction mixtures containing a tenfold or even larger excess of an arenesulfonic acid (HA) over the initial 3,5-dinitrophenyloxirane (S) concentration: $[HA]_0 \gg [S]_0 = 0.003–0.007$ mol/l. At these reactant concentrations, reaction (I) is first-order with respect to the oxirane substrate and second-order with respect to the acid and its rate is given by the equation

$$-d[S]/dt = k_{app}[S] = k_3[S][HA]_0^2, \qquad (1)$$

where k_{app} (s^{-1}) and k_3 (l^2 mol^{-2} s^{-1}) are the pseudo-first- and third-order rater constants, respectively. The values of k_3 were determined by extrapolating the linear relationship $k_{app} = k_3[HA]_0^2$ to zero for four, or a larger number of, different HA concentrations (correlation factor of $r \geq 0.995$). The accuracy of kinetic and correlation parameters was estimated in terms of the standard deviation s, which was derived by statistical methods from n experimental data points. Statistical data processing was carried out for a confidence coefficient of 0.95.

RESULTS AND DISCUSSION

The k_3 values for all of the reactions examined here are listed in Table 1. These data indicate that the rates of the reactions at 303 K increases significantly as the electron-donating power of the substituent Y in the arenesulfonic acid decreases and as the electron-withdrawing power of Y increases. As the temperature is lowered, the effect of Y weakens and disappears entirely at 265 K. The reaction rate increases with increasing temperature in all partial reaction series for a given Y, and the temperature effect decreases on passing from electron-withdrawing to electron-donating substituents. Thus, in the cross reaction series (I), there is interaction (nonadditivity) between the structure (substituent Y) and temperature effects. For obtaining a quantitative estimate for this interaction, the results of the multifactor kinetic experiment (Table 1) were subjected to correlation analysis.

One-Parameter Correlations

The effect of substituents Y on the rate of reaction (I) is described by the Hammett equation. The values of the sensitivity parameter ρ_Y^T in this equation for partial

Table 1. Rate constants k_3 and ρ_Y^T values in the Hammett equation for the reactions of 3,5-dinitrophenyloxirane with arenesulfonic acids $YC_6H_4SO_3H$ in a dioxane–diglyme (1 : 1 vol/vol) mixture at different temperatures

$Y(\sigma_Y)$	$k_3 \times 10^3$, $l^2\,mol^{-2}\,s^{-1}$		
	265 K	287 K	303 K
4-OCH_3 (–0.27)	0.212 ± 0.005	0.91 ± 0.01	3.51 ± 0.09
4-CH_3 (–0.17)	0.210 ± 0.007	1.12 ± 0.08	4.74 ± 0.06
H (0)	0.220 ± 0.003	1.58 ± 0.07	6.84 ± 0.04
4-Cl (0.23)	0.219 ± 0.008	2.44 ± 0.09	12.1± 0.4
3-NO_2 (0.71)	0.218 ± 0.007	5.79 ± 0.01	53 ± 2
ρ_Y^T	0	0.81 ± 0.01	1.18 ± 0.05
r	–	0.999	0.998

reaction series at a fixed temperature T are presented in Table 1. The ρ_Y^T value decreases down to zero as the temperature is lowered to 265 K. This behavior of ρ_Y^T is described by the linear equation

$$\rho_Y^T = (9.6 \pm 0.7) + (-2.5 \pm 0.2)10^3/T, \quad s = 0.066,\ r = 0.997,\ n = 3. \tag{2}$$

In the graphical representation of Eq. (2), the slope of the straight line is a measure of the nonadditivity of the simultaneous effects of Y and temperature in the cross reaction series (I). It follows from Eq. (2) that the isoparametric temperature at which the substituents exert no effect on the reaction rate ($\rho_Y^T = 0$) is $T^{IP} =$ 260 K. The data presented in Table 1 indeed indicate that $\rho_Y^T = 0$ at 265 K, a temperature close to the calculated T^{IP} value.

The effect of temperature on the rate of reaction (I) is described by the Eyring equation

$$\log(k_3/T) = A^Y_{T=\infty} + B^Y_T\,10^3/T, \tag{3}$$

where $A^Y_{T=\infty} = \log(k_B/h) + \Delta S^{\neq}_Y/2.3R$, and $B^Y_T = -\Delta H^{\neq}_Y/2.3R$ (k_B is the Boltzmann constant, h is the Planck constant, and R is the gas constant). Equation (3) does not involve the transmission coefficient, which is taken to be unity for heterolytic reactions. Table 2 lists the coefficients of Eq. (3) for partial reaction series and the activation parameters calculated using these coefficients. The variation of these quantities with Y is described by the following linear relationships:

$$B^Y_T = (-3.06 \pm 0.03) + (-2.5 \pm 0.1)\sigma_Y, \quad s = 0.077,\ r = 0.998,\ n = 5. \tag{4}$$

$$\Delta H^{\neq}_Y = (58.6 \pm 0.8) + (48 \pm 2)\sigma_Y, \quad s = 1.78,\ r = 0.997,\ n = 5. \tag{5}$$

$$\Delta S^{\neq}_Y = (-92 \pm 3) + (180 \pm 8)\sigma_Y, \quad s = 6.32,\ r = 0.997,\ n = 5. \tag{6}$$

$$\Delta G^{\neq}_{YT=287} = (84.90 \pm 0.04) + (-4.0 \pm 0.1)\sigma_Y, \quad s = 0.080,\ r = 0.999,\ n = 5. \tag{7}$$

Relationships (2) and (4)–(7) demonstrate the validity of the polylinearity principle in the cross reaction series (I). Another demonstration of this principle is the linear relationship (compensation effect) between $\Delta H^{\neq}_Y$ and $\Delta S^{\neq}_Y$ changing under the action of substituents Y:

$$\Delta H^{\neq}_Y = (83.3 \pm 0.3) \times 10^3 + (268 \pm 3)\Delta S^{\neq}_Y, \quad s = 382,\ r = 0.999,\ n = 5. \tag{8}$$

From the slope angle for Eq. (8), $T^{IP} = 268 \pm 3$ K. With the error of its determination taken into account, this temperature coincides with the experimental value of 265 K.

Cross Correlations

In the quantitative estimation of the joint effect of the substituents Y and temperature on the rate of reaction (I), we used the cross correlation equation for the two-parameter case of the polylinearity principle [1]:

$$\log k_3 = \log k_3^{st} + \rho_Y^{st}\sigma_Y + B_T^{st} \times 10^3/T + q_{YT}\sigma_Y \times 10^3/T, \tag{9}$$

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 the standard reaction series at $T = \infty$ K and $\sigma_Y = 0$, respectively; and q_{YT} is the cross interaction coefficient. Calculation of the coefficients of Eq. (9) using kinetic data presented in Table 1 yielded the following regression:

$$\log k_3 = (8.4 \pm 0.2) + (9.5 \pm 0.6)\sigma_Y + (-3.21 \pm 0.07)10^3/T + (-2.5 \pm 0.2)\sigma_Y\,10^3/T, \tag{10}$$
$$s = 0.048,\ R = 0.997,\ n = 15,\ F = 1141,$$

where R is the multiple correlation factor and F is the F-test value.

Regression (10) provides a rather good fit to the data obtained for the cross reaction series (I). This is indicated by its statistical characteristics and by coincidence of the cross interaction coefficient with the values of this coefficient in Eqs. (2) and (4). Because the cross interaction coefficient differs significantly from zero, regression (10) possesses isoparametric properties, whose quantitative characteristics are the IPPs for the constant of the substituent Y, $\sigma_Y^{IP} = -B_T^{st} q_{YT}^{-1} = -1.28$, and for temperature, $10^3/T^{IP} = -\rho_Y^{st} q_{YT}^{-1} = 3.8$ ($T^{IP} = 263$ K), as well as the same rate constant at both IPPs, $\log k_3^{IP} = \log k_3^{st} - \rho_Y^{st} B_T^{st} q_{YT}^{-1} = -3.8$. At the $\sigma_Y^{IP} = -1.28$ point, the rate of the reaction is temperature-independent ($B_T^Y = 0$) and, therefore, $\Delta H_Y^{\neq} = 0$. It also follows from partial equations (4) and (5) that $B_T^Y = 0$ and $\Delta H_Y^{\neq} = 0$, respectively, at a near-isoparametric value of $\sigma_Y = -1.22$. However, this IPP cannot be realized because of the deficit of powerful electron-donating substituents with $\Sigma\sigma_Y = -1.28$. As for the $T^{IP} = 263$ K point, its value is in agreement with the values calculated via Eqs. (2) and (8) and is nearly equal to the experimental temperature of 265 K. It is at 263 K that, according to the isoparametric relationships, the rate constant k_3 is independent of the structure of the substituent Y in the arenesulfonic acid (Table 1).

In terms of activation parameters, the nonadditive effects of structure and temperature in the cross reaction series (I) can be analyzed using cross correlation equation (11), which describes the joint effect of these factors on the free energy of activation:

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

where $\Delta G_{YT}^{\neq st}$ is the free energy of activation under standard conditions ($\sigma_Y = 0$, $T = 0$ K); a_Y^{st} and b_T^{st} are parameters of the standard reaction series at $T = 0$ K and $\sigma_Y = 0$, respectively; and c_{YT} is the cross interaction coefficient. Calculation of the coefficients of Eq. (11) using the $\Delta G_{YT}^{\neq}$ values presented in Table 2 yielded the following regression:

$$\begin{gathered}\Delta G_{YT}^{\neq} = (60.7 \pm 0.8) + (41 \pm 2)\sigma_Y \\ + (0.084 \pm 0.003)T + (-0.156 \pm 0.008)\sigma_Y T, \qquad (12) \\ s = 0.174,\ R = 0.993,\ n = 15,\ F = 525.\end{gathered}$$

The isoparametric criteria of regression (12) are the temperature IPP $T^{IP(G)} = -a_Y^{st} c_{YT}^{-1} = 263$ K (which is equal to the value calculated via relationship (10)), the above-calculated $\sigma_Y^{IP} = -1.28$ point, and the other substituent Y constant IPP, $\sigma_Y^{IP(G)} = -b_T^{st} c_{YT}^{-1} = 0.54$, as well as the isoparametric value of $\Delta G_{YT}^{\neq IP} = \Delta G_{YT}^{\neq st} - a_Y^{st} b_T^{st} c_{YT}^{-1} = 83$ kJ/mol. At the $T^{IP(G)} = 263$ K point, the free energy of activation, $\Delta G_{YT}^{\neq}$, is independent of the substituent Y (Table 2). This is due to the changes in its enthalpic and entropic components counterbalancing one another: $\delta_Y \Delta H^{\neq} = T^{IP(G)} \delta_Y \Delta S^{\neq}$. As a consequence, $\delta_Y \Delta G_{YT}^{\neq} = 0$ ($\Delta G_{YT}^{\neq} = \Delta G_{YT}^{\neq IP} = \text{const} = 83$ kJ/mol) and, as was mentioned above, $\rho_Y^T = 0$ (Table 1). At the $\sigma_Y^{IP(G)} = 0.54$ point, $\Delta G_{YT}^{\neq}$ is temperature-independent, which is possible if, in the expression $\Delta G_{YT}^{\neq IP} = \Delta H_Y^{\neq} - T\Delta S_Y^{\neq}$, the activation entropy is $\Delta S_Y^{\neq} = 0$ and the free energy of activation is determined solely by its enthalpic term: $\Delta G_{YT}^{\neq IP} = \Delta H_Y^{\neq} = 83$ kJ/mol. This situation is confirmed by Eq. (6), from which it follows that $\Delta S_Y^{\neq} = 0$ at $\sigma_Y = 0.51$, which is close to the isoparametric value (0.54), and by Eq. (8), in which, at $\Delta S_Y^{\neq} = 0$, $\Delta H_Y^{\neq}$ becomes 83.3 kJ/mol, equal to the isoparametric value $\Delta G_{YT}^{\neq IP}$.

Thus, we demonstrated the realization of an IPP with respect to a structure parameter, which is a rare case in chemical processes. For arenesulfonic acids, this point is reached as the electron-donating power of the substituent Y decreases and its electron-withdrawing power increases. Furthermore, we carried out a unique passage through this point using Y = 3-NO_2, with $\sigma_Y > \sigma_Y^{IP(G)}$. According to the regularities of isoparametric relationships, this passage is accompanied by an inversion of the sign of the coefficient b_T^Y, which is a measure of the sensitivity of the free energy of activation, $\Delta G_{YT}^{\neq}$, to temperature in the equation $\Delta G_{YT}^{\neq} = \Delta G_{YT=0}^{\neq} + b_T^Y T$. For Y = 4-$OCH_3$, 4-$CH_3$, H, 4-Cl, and 3-$NO_2$, the value of $b_T^Y \times 10^2$ ($r \geq 0.995$) is 13.2 ± 0.3, 10.6 ± 0.5, 8.0 ± 0.8, 5.2 ± 0.5, and -2.6 ± 0.2, respectively. In addition, according to the polylinearity principle, the following linear relationship between b_T^Y and σ_Y is valid: $b_T^Y = (0.084 \pm 0.002) + (-0.155 \pm 0.007)\sigma_Y$ ($s = 0.00534$, $r = 0.997$, $n = 5$), whose slope coincides with the cross interaction coefficient c_{YT} in Eq. (12). Furthermore, as would be expected based on Eq. (6) in particular, the inversion of the sign at $\Delta S_Y^{\neq}$ takes place on passage through the $\sigma_Y^{IP(G)} = 0.54$ point (Table 2).

Dividing the left- and right-hand sides of regression (12) by T, we obtain the following isoparametric relationship:

$$\begin{gathered}\Delta G_{YT}^{\neq}/\mathrm{T} = (0.084 \pm 0.003) + (60.7 \pm 0.8)/\mathrm{T} \\ + (-0.156 \pm 0.008)\sigma_Y + (41 \pm 2)\sigma_Y/T,\end{gathered} \qquad (13)$$

from which it can be calculated that the temperature IPP is $T^{IP} = 263$ K, the substituent Y IPP is $\sigma_Y^{IP} = -1.48$, and, at these points, $\Delta G_{YT}^{\neq IP}/T = 0.315$ kJ mol^{-1} K^{-1}. These IPP values are in agreement with the values cal-

Table 2. Coefficients of Eq. (4) and the activation parameters $\Delta S^{\neq}_{Y}$, $\Delta H^{\neq}_{Y}$ and $\Delta G^{\neq}_{YT}$ for the reactions of 3,5-dinitrophenyloxirane with arenesulfonic acids $YC_6H_4SO_3H$ in a dioxane–diglyme (1 : 1 vol/vol) mixture at 265, 287, and 303 K

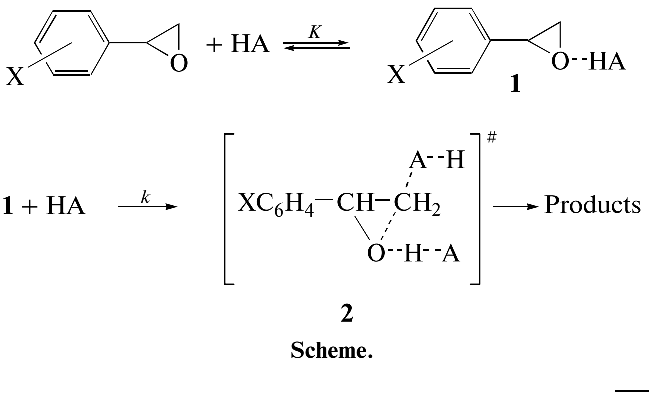
Y	$A^{Y}_{T=\infty}$	B^{Y}_{T}	r	s	$\Delta S^{\neq}_{Y}$, J mol^{-1} K^{-1}	$\Delta H^{\neq}_{Y}$	$\Delta G^{\neq}_{YT=265}$	$\Delta G^{\neq}_{YT=287}$	$\Delta G^{\neq}_{YT=303}$
						kJ/mol			
4-OCH_3	3.0 ± 0.9	−2.4 ± 0.3	0.933	0.0936	−140	46	83	86	88
4-CH_3	4.2 ± 0.9	−2.7 ± 0.3	0.995	0.0907	−117	52	83	85.5	87
H	5.3 ± 0.5	−3.0 ± 0.1	0.999	0.0504	−96	57	83	85	86
4-Cl	7.3 ± 0.3	−3.6 ± 0.1	0.999	0.0296	−58	68	83	84	85
3-NO_2	12.4 ± 0.4	−4.9 ± 0.1	0.999	0.0417	40	94	83	82.5	82

culated for regression (10). At the $\sigma_Y^{IP} = -1.48$ point, $\Delta G^{\neq IP}_{YT}/T$ is temperature-independent, which is possible when, in the expression $\Delta G^{\neq IP}_{YT}/T = \Delta H^{\neq}_{YT}/T - \Delta S^{\neq}_{Y}$, the enthalpic term is $\Delta H^{\neq}_{Y} = 0$; that is, we again arrive at the above conclusion that the free energy of activation at this IPP is completely determined by the entropic term: $\Delta G^{\neq IP}_{YT}/T = -\Delta S^{\neq}_{Y}$.

Thus, in the framework of the compensation effect, owing to the dual nature of $\Delta G^{\neq}_{YT}$, by widely varying substituents Y in arenesulfonic acids it is possible to pass from the extreme state of reaction system (I) in which at the $\sigma_Y^{IP(G)} = 0.54$ point the contribution from the entropic factor to the free energy activation disappears ($\Delta S^{\neq}_{Y} = 0$)—the existence of this state was proved experimentally in the present study—to the equally interesting extreme state at the $\sigma_Y^{IP} = -1.28$ (-1.48) point, at which there should be no contribution from the enthalpic factor ($\Delta H^{\neq}_{Y} = 0$). The variations in the free energy of activation itself ($\Delta G^{\neq}_{YT}$), which are comparatively small as a consequence of the compensation effect, decrease sharply with decreasing temperature and disappear entirely at the $T^{IP(G)} = 263$ K point (Table 2). The sensitivity of $\Delta G^{\neq}_{YT}$ to the substituent Y effect (a^{T}_{Y} $r \geq 0.997$) is -5.9 ± 0.3, -4.0 ± 0.1, and 0 at 303, 287, and 265 K, respectively, and is described by the linear equation $a^{T}_{Y} = (41 \pm 5) + (-0.16 \pm 0.02)T$ ($s = 0.475$, $r = 0.994$, $n = 3$), whose slope coincides with the above values of the cross interaction parameter c_{YT}.

Mechanistic Aspects

The fact that the kinetic and activation parameters of all reactions of the series obey partial and cross correlations of the polylinearity principle is evidence that these reactions proceed via a uniform mechanism under the experimental conditions examined. For interpreting this mechanism, we used the results of cross correlation analysis, including quantitative mechanistic criteria, such as IPPs with respect to the parameters of the factors being varied (σ_Y^{IP}, $\sigma_Y^{IP(G)}$, T^{IP}). The following stepwise mechanism is supposed to be most likely for reaction (I):



Scheme.

This mechanism is consistent with the fact that the reactions examined here are third-order, being first-order with respect to the oxirane substrate ($X = 3,5\text{-}(NO_2)_2$) and second-order with respect to the acid reactant $HA = YC_6H_4SO_3H$. The first, reversible step of this mechanism yields H-bonded complex **1**. In the second, rate-determining step, the thus-activated substrate is attacked nucleophilically by another acid molecule at the less screened, β carbon atom of the oxirane ring to yield transition state (TS) **2**. This step occurs via the concerted nucleophilic substitution mechanism A_ND_N with electrophilic assistance to C–O bond breaking in the oxirane ring.

According to the scheme, k_3 is equal to Kk, and, hence, the parameter of sensitivity to the effects of substituents Y, ρ_Y^T, is a composite quantity: $\rho_Y^T = \rho_1 + \rho_2$. For the first step, $\rho_1 > 0$, because electron-withdrawing substituents Y strengthen the H-bond in complex **1**. The sign and value of $\rho_2 = \rho_{A-C} + \rho_{O-H}$ for the second step are determined by the ratio of $\rho_{A-C} < 0$ and $\rho_{O-H} > 0$ for the formation of the A–C and O–H bonds in TS **2**. The fact that, for the two partial reaction series at 303 and 387 K, the effective sensitivity coefficient is $\rho_Y^T > 0$ (Table 1) indicates that, at these temperatures, the electrophilic properties of the acid HA in both steps of O–H bond formation dominate over its nucleophilic properties in the formation of the A–C in the second step: $\rho_1 + \rho_{O-H} > |\rho_{A-C}|$. The parameter ρ_1 must increase with decreasing temperature because of the strengthening of the H-bond in complex **1**. As this takes place, the effective quantity ρ_Y^T decreases, indicating a larger increase in the absolute value of its negative component ρ_{A-C}. At the isoparametric temperature $T^{IP} = 263$ K, $\rho_Y = 0$, which is possible when $\rho_1 + \rho_{O-H} = |\rho_{A-C}|$. Therefore, the interaction between the effects of the substituent Y and temperature in the reactions examined here occurs at the second stage of oxirane ring opening.

This inference is consistent with the changes in the activation parameters $\Delta H_Y^{\neq}$ and $\Delta S_Y^{\neq}$ caused by substituent Y variation. The reaction mechanism presented in the scheme suggests that $\Delta H_Y^{\neq} = \Delta H_1 + \Delta H_2^{\neq}$, where $\Delta H_1 < 0$ [15] and $\Delta H_2^{\neq} > 0$ [6]; likewise, $\Delta S_Y^{\neq} = \Delta S_1 + \Delta S_2^{\neq}$, where $\Delta S_1 < 0$ [15] and the sign of $\Delta S_2^{\neq}$ depends on the character of TS **2** (see below). Passing from electron-withdrawing substituents Y to electron-donating ones will weaken the H-bond in complex **1** and will decrease $|\Delta H_1|$; accordingly, an increase in the effective activation enthalpy $\Delta H_Y^{\neq}$, should be expected, which is in conflict with the data presented in Table 2. The leads us to the conclusion that, in the reaction series (I), the determining contribution from Y to $\Delta H_Y^{\neq}$, and, accordingly, to the joint effect of structure and temperature is manifested at the TS **2** formation stage due to the large decrease in $\Delta H_2^{\neq}$ because of the electron-donating substituent Y strengthening the nucleophilicity of HA. At the $\sigma_Y^{\text{ИП}} = -1.22$ point, which implies an extremely weak arenesulfonic acid, the H-bond in **1** may be so weak as to make the absolute value of negative ΔH_1 equal to $\Delta H_2^{\neq}$ ($|\Delta H_1| = \Delta H_2^{\neq}$), so we will have $\Delta H_Y^{\neq} = 0$. In this case, the rate of the process will be temperature-independent since, if $\Delta H_Y^{\neq} = 0$, then $B_T^Y = 0$ in Eq. (3).

At the $\sigma_Y^{IP} = 0.54$ point, which implies a strong arenesulfonic acid, the oxirane is effectively protonated, so ΔS_1 for the first stage (formation of H-bonded complex **1**) will have a large negative value. As for the entropy of activation for the second stage, $\Delta S_2^{\neq}$, its value depends on the proportions of A–C bonds ($\Delta S_{A-C}^{\neq} < 0$) and O–H bonds ($\Delta S_{O-H}^{\neq} < 0$) formed in TS **2** and on the proportion of broken C–O bonds ($\Delta S_{C-O}^{\neq} > 0$): $\Delta S_2^{\neq} = \Delta S_{A-C}^{\neq} + \Delta S_{O-H}^{\neq} + \Delta S_{C-O}^{\neq}$. It is expected that, in the case of a strong acid HA, $\Delta S_{O-H}^{\neq} \cong 0$ because the order of the O–H bond in TS **2** differs insignificantly from the order of this bond in **1**. In addition, because of the low nucleophilicity of HA, the S_N1 character of TS **2** will be more pronounced (strong domination of C–O bond breaking over A–C bond formation and an increase in $\Delta S_{C-O}^{\neq}$ will be observed) and it may happen that $\Delta S_{C-O}^{\neq} > \left|\Delta S_{A-C}^{\neq}\right|$ and $\Delta S_2^{\neq} > 0$. This change in the structure of TS **2** will lead to $\Delta S_2^{\neq} = |\Delta S_1|$, and the effective entropy of activation will be zero ($\Delta S_Y^{\neq} = 0$) at the $\sigma_Y^{IP(G)} = 0.54$ point and, hence, $\Delta G_{YT}^{\neq IP} = \Delta H_Y^{\neq}$. Upon passing through the $\sigma_Y^{IP(G)}$ point to more electron-withdrawing substituents Y with $\sigma_Y > 0.54$, the probability of C–O bond breaking in TS **2** will be still higher. This will cause a further increase in $\Delta S_2^{\neq}$, which will possibly lead to $\Delta S_2^{\neq} > |\Delta S_1|$. In this case, there will be the inversion of the sign of the effective entropy of activation ($\Delta S_Y^{\neq} < 0$, Table 1).

The $\sigma_Y^{IP} = -1.22$ point corresponds to a very weak arenesulfonic acid with a powerful electron-donating substituent Y, which will minimize H-bond formation in complex **1** ($\Delta H_1 \approx 0$, $\Delta S_1 \approx 0$) and will weaken the dissociative character of TS **2** by enhancing the nucleophilicity of HA and diminishing the electrophilic assistance to oxirane ring opening. This will result in an increase in the order of the A–C and C–O bonds. Accordingly, $\left|\Delta S_{A-C}^{\neq}\right| + \left|\Delta S_{O-H}^{\neq}\right| > \Delta S_{C-O}^{\neq}$ and $\Delta S_2^{\neq} < 0$, and, as a consequence, there will be a marked increase in the negative value of the effective entropy of activation at this IPP (according to Eq. (6), $\Delta S^{\neq} = -311.6$ J mol^{-1} K at $\sigma_Y^{IP} = -1.22$). In this case, as was noted above, $\Delta H^{\neq} = 0$ and only the entropic component of the free energy of activation determines the rate of the process.

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