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Cross correlation analysis of the reactions of 4-nitrophenyloxirane with arylsulfonic acids in dioxane

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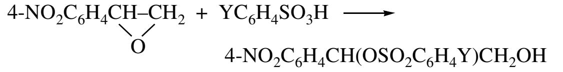
It has been found using cross correlation analysis that the effects of substituents Y and temperature on the rate of oxirane ring opening are nonadditive in the reactions of 4-nitrophenyloxirane with arylsulfonic acids ($YC_6H_4SO_3H$) in dioxane at 286–318 K.

It is a topical problem of the chemistry of oxiranes to determine the rate laws of epoxide ring opening under the action of cross-varied factors (the structures of reactants and catalysts, medium, temperature, *etc.*). We report here the results of cross correlation analysis of the kinetic data on the reactions of 4-nitrophenyloxirane with Y-substituted benzenesulfonic acids (Y = 4-OMe, 4-Me, H, and, in part, 4-Br, and 3-NO_2) in dioxane at 286–318 K:



$$4\text{-}NO_2C_6H_4CH\text{–}CH_2(O) + YC_6H_4SO_3H \longrightarrow 4\text{-}NO_2C_6H_4CH(OSO_2C_6H_4Y)CH_2OH \quad (1)$$

The products of reactions (1) were isolated as stable ductile yellowish orange oils. The yields were very high (90–95%, as found by HPLC). The structures were studied by ^{1}H NMR spectroscopy. The compounds corresponded to 2-arylsulfonato-2-(4-nitrophenyl)ethanols,[1] *e.g.*, 2-(4-methoxyphenylsulfonato)-2-(4-nitrophenyl)ethanol [Y = 4-OMe in equation (1)].[†] Analogous 2,2-disubstituted ethanol derivatives (primary alcohols) were also formed in the related reactions of aryloxiranes with HNO_3.[2]

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 $AgNO_3$ solution. The reaction kinetics was examined using more than tenfold amounts of arylsulfonic acids (HA) with respect to the initial concentrations of 4-nitrophenyloxirane (S): $[HA] >> [S] = (3–7)\times10^{-3}$ mol dm^{-3}. In all cases, the observed pseudo-first-order reaction rate constants (k_{obs}) remained constant in the course of reaction 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 time, linear relationships between k_{obs} and $[HA]^2$ were observed ($r \geq 0.996$), which pass through the origin of coordinates. Thus, the kinetics of the reactions of interest is described by the equation

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

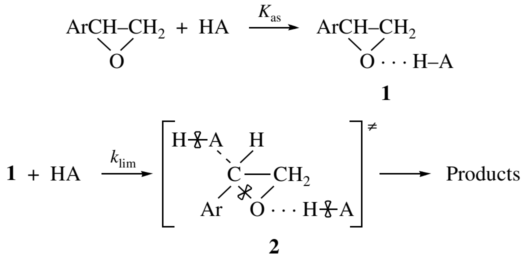
where k_{obs} and k_3 are pseudo-first-order and third-order rate constants, respectively.

The k_3 constants were found from the linear relations $k_{obs} = k_3[HA]^2$ at four or more HA concentrations. Table 1 summarises the values of k_3 for reactions (1) and the ρ_y^T values calculated by the Hammett equation for partial reaction series at fixed temperatures. Note that ρ_y^T dramatically decreases with decreasing temperature; this fact is indicative of the nonadditivity of combined effects of substituents Y and a temperature factor in cross-reaction series (1).

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

$$\lg(k_3/T) = A + BT^{-1}, \quad (3)$$

where $A = \lg(k_B/h) + \Delta S^{\neq}/2.3R$, $B = -\Delta H^{\neq}/2.3R$ (k_B is the Boltzmann constant, h is the Plank constant and R is the gas constant). As a rule, the transmission coefficient was taken equal to 1 for the heterolytic reactions, so that it was omitted in equation (3). Table 2 summarises the parameters of equation (3) for the reactions of 4-nitrophenyloxirane with arylsulfonic acids, as well as the enthalpies ($\Delta H^{\neq}$), entropies ($\Delta S^{\neq}$) and free energies ($\Delta G^{\neq}$) of activation calculated using these parameters. A change in the slope B in equation (3) with Y is consistent with the above nonadditive effects of the structure and temperature on the rate of reactions (1). It was estimated by the equation:



Scheme 1

$$\lg k_3 = \lg k_3^{st} + \rho_Y^{st}\sigma_Y + B_T^{st}\tau_T + q_{YT}\sigma_Y\tau_T, \quad (4)$$

where $\tau_T = (1/T - 1/298)\times10^3$, k_3^{st} is the rate constant under standard conditions ($\sigma_Y = 0$, $T = 298$ K), ρ_Y^{st} and B_T^{st} are the parameters of standard reactions at $T = 298$ K and $\sigma_Y = 0$, respectively, and q_{YT} is the cross interaction coefficient. The following result was obtained using equation (4):

$$\lg k_3 = (-1.06\pm0.01) + (1.96\pm0.06)\sigma_Y + (-3.4\pm0.1)\tau_T + (-5.8\pm0.4)\sigma_Y\tau_T \quad (5)$$

$$N = 13,\ S = 0.027,\ R = 0.998,\ \hat{\sigma}_Y = -0.59,\ \hat{\tau}_T = 0.338\ (\hat{T} = 271\ \text{K})$$

Regression equation (5) adequately describes reactions (1), as follows from the agreement between the experimental and calculated values of k_3 summarised in Table 1.

Because of a statistically significant coefficient of cross interaction ($q_{YT} = -5.8\pm0.4$), regression equation (5) exhibits isoparametric properties, *i.e.*, its attributes are isoparametric points with respect to the constant of substituent $\hat{\sigma}_Y = -B_T^{st}q_{YT}^{-1} = -0.59$ and temperature $\hat{\tau}_T = -\rho_Y^{st}q_{YT}^{-1} = 0.338$ ($\hat{T} = 271$ K). However, these isoparametric points were not attained in practice because, first, the solvent in use (dioxane, mp 284.7 K) is solid at 271 K and, second, an arylsulfonic acid bearing non-amine substituent Y with the constant σ_Y close to an isoparametric value ($\hat{\sigma}_Y = -0.59$) cannot be chosen.

Reactions (1), which are of first or second order with respect to the epoxide substrate and the acid reagent, respectively, most likely proceed *via* a mechanism similar to that proposed for the reactions of ethylene oxide with nitric acid[3] and carboxylic acids (Scheme 1).[4] The first step of the reaction is the formation of association complex **1** by the reversible acid–base interaction. At the second step, this activated epoxide substrate is subjected to a nucleophilic attack by another arylsulfonic acid molecule to form termolecular transition state **2**. This rate-limiting step proceeds *via* the concerted process of nucleophilic substitution A_ND_N with electrophilic assistance to C–O bond rupture in an epoxide ring.

According to Scheme 1, $k_3 = K_{as}k_{lim}$. Therefore, $\Delta H^{\neq} = \Delta H_{as} +$

[†] ^{1}H NMR (200 MHz, [$^2H_6$]DMSO) δ: 3.53 (br. t, 2H, CH_2), 3.84 (s, 3H, OMe), 5.15 (br. t, 1H, OH, exch. D_2O), 5.48 (t, 1H, CH, J 4.3 Hz), 6.96 (d, 2H, arom., J 8.2 Hz), 7.51 (d, 2H, arom., J 7.2 Hz), 7.72 (d, 2H, arom., J 7.5 Hz), 8.08 (d, 2H, arom., J 8.1 Hz).

Table 2 Coefficients of equation (3) and activation parameters of reactions (1).

	4-OMe	4-Me	H
A	2.2±0.5	6.4±0.2	10.2±0.3
B	–1.8±0.1	–2.33±0.05	–3.36±0.03
r	0.994	0.999	0.999
S	0.0378	0.0130	0.0153
$\Delta H^{\neq}$/kJ mol^{-1}	35.5	43.8	63.0
$\Delta S^{\neq}$/J mol^{-1} K^{-1}	–157	–119	–48.8
$\Delta G^{\neq}_{308}$/kJ mol^{-1}	83.7	80.4	78.0

$+ \Delta H^{\neq}_{\text{lim}}$ and $\Delta S^{\neq} = \Delta S_{\text{as}} + \Delta S^{\neq}_{\text{lim}}$; at the first step of association, $\Delta H_{\text{as}} < 0$ and $\Delta S_{\text{as}} < 0$,[5] whereas at the second step (S_N2 substitution) $\Delta H^{\neq}_{\text{lim}} > 0$ and $\Delta S^{\neq}_{\text{lim}} < 0$.[6] The weakening of the electron-donor properties of substituents in the order 4-OMe > > 4-Me > H is favourable for hydrogen transfer in complex **1** to result in a decrease in both ΔH_{as} and ΔS_{as} (an increase in the absolute values). In this case, a decrease in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ should be expected, which is inconsistent with data in Table 2. A decrease in $\Delta G^{\neq}$ on going from Y = 4-OMe to Y = H (Table 2) is indicative of the controlling contribution from an entropy component ($\Delta S^{\neq}_{\text{lim}}$) of free energy of activation at the step of epoxide ring opening to a change in the rate of reactions (1) with varying structures of arylsulfonic acids. The nucleophilicity of a part A in HA decreases with decreasing electron-donor properties of substituents Y. This increases the A–C bond order and decreases the C–O bond order; that is, transition state **2** becomes product-like. This is evidenced from the above decrease in $|\Delta S^{\neq}|$ in the order 4-OMe > 4-Me > H. Thus, the degree of epoxide ring opening considerably increases as the electron-donor properties of Y decrease.

The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are changed with a compensation effect typical of concerted nucleophilic substitution:[7] $\Delta H^{\neq} = (75\pm2)\times10^3 + (260\pm9)\Delta S^{\neq}$, $r = 0.998$, $S = 1092$. The slope of this function characterises an isokinetic temperature ($T_{\text{iso}} = 260$ K), which is consistent with the value calculated by cross correlation (5).

Thus, cross correlation analysis of the reactions of 4-nitrophenyloxirane with arylsulfonic acids is a useful mechanistic tool in the studies of epoxide ring opening.

Table 1 Rate constants $k_3/10^2$ dm^6 mol^{-2} s^{-1} and ρ^T_Y values in the Hammett equation for the reactions of 4-nitrostyrene oxide with arylsulfonic acids $YC_6H_4SO_3H$ in dioxane at different temperatures [the values calculated by equation (5) are given in parentheses].

Y (σ_Y)	*T*/K ($\tau_T\times10^3$)			
	286 (0.141)	298 (0)	308 (–0.109)	318 (–0.211)
4-OMe (–0.268)	1.38 (1.43)	2.5 (2.6)	3.8 (4.1)	7.1 (6.4)
4-Me (–0.17)	1.89 (1.85)	4.02 (4.04)	7.5 (7.4)	12.2 (13.0)
H (0)	2.98 (2.89)	9.16 (8.71)	20.3 (20.4)	—
4-Br (0.23)	4.9 (5.3)	—	—	—
3-NO_2	18.8 (18.7)	—	—	—
ρ^T_Y	1.14±0.03	2.13±0.02	2.7±0.1	
r	0.999	0.999	0.999	

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