

Structure and Temperature Effects on the Reaction Rate of Aryloxiranes with 3,5-Dinitrobenzoic Acid in Acetonitrile

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Abstract—The effects of temperature and structure of aryloxiranes on the rate of their reaction with 3,5-dinitrobenzoic acid in acetonitrile are additive, and the process is entropy-controlled.

Reactions accompanied by opening of oxirane ring have long attracted researchers' attention due to their diversity, specificity of their mechanisms under catalytic and noncatalytic conditions, and wide application in organic synthesis (in particular, in the preparation of polymeric epoxy compounds [1–6]). An important problem in the chemistry of oxiranes is to reveal quantitative relations holding in opening of the oxirane ring upon variation of internal (structure of the reactants and catalysts) and external factors (reaction medium, temperature).

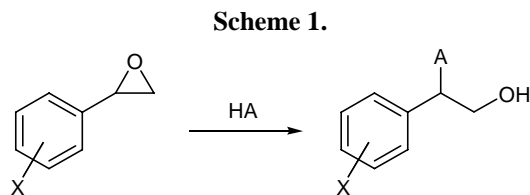
We previously [6, 7] made an attempt to simulate the reactivity of the system epoxy substrate–acid reagent by mathematical modeling with the aid of cross correlation analysis of the results of multifactor kinetic experiments. While studying the joint effect of the structure of arenesulfonic acids ($\text{YC}_6\text{H}_4\text{SO}_3\text{H}$) and temperature on the kinetics of oxirane ring opening in 4-nitrophenyloxirane in dioxane, we showed that quantitative estimation of the reactivity in terms of a polynomial regression model (which includes statistically significant cross correlation coefficient $\rho_{YT} = -5.8 \pm 0.4$ [6]) requires that nonadditive effects of factors being varied be taken into consideration. Nonadditive effect of structural factors was found in reactions of X-substituted phenyloxiranes with Y-substituted benzoic acids in acetonitrile at 343 K ($\rho_{XY} = -1.1 \pm 0.2$ [7]).

The goal of the present work was to examine joint effect of temperature and structure of aryloxiranes on the rate of their reactions with 3,5-dinitrobenzoic acid (HA) in acetonitrile. The products of these reactions are primary alcohols, 1-aryl-2-hydroxyethyl 3,5-dinitrocarboxylates (Scheme 1) [7]. The kinetic relations holding in the process were studied using more than tenfold excess of the oxirane substrate (S) with respect to 3,5-dinitrobenzoic acid $[\text{S}]_0 \gg [\text{HA}]_0$, 0.08–0.17 M, according to the procedure described in [7]. The procedure is based on acid–base titration of the unreacted acid reagent with an aqueous solution of sodium hydroxide. Under the given conditions, the reaction was of first order with respect to the substrate and of second order with respect to HA, in keeping with the following kinetic equation:

$$-\partial[\text{HA}]/\partial t = k_2[\text{HA}]^2 = k_3[\text{S}]_0[\text{HA}] \quad (2)$$

In all cases, the apparent pseudosecond rate constants k_2 ($\text{lmol}^{-1}\text{s}^{-1}$) remained unchanged during the process until an acid reagent conversion of 70–80% (the error in the determination of k_2 did not exceed 7%). The third-order rate constants ($k_3 = k_2/[\text{S}]_0$; Table 1) increased as the temperature rose, as well as the electron-acceptor power of the X substituent decreased. The latter relation is consistent with the negative sign of ρ^+ . The ρ^+ (r) values calculated for particular reaction series at 323, 333, and 343 K are, respectively, -3.0 ± 0.2 (0.999), -2.9 ± 0.1 (0.998), and -3.1 ± 0.2 (0.993). The given ρ^+ values do not depend on temperature, indicating additivity in the effects of temperature and substituent X on the reaction rate.

The effect of temperature on the reaction rate was taken into account in terms of the Eyring equation



$$\log(k_3/T) = A + B(1000/T), \quad (3)$$

where $A = \log(k_B/h) + \Delta S^\ddagger/2.3R$, $B = -\Delta H^\ddagger/2.3R$, k_B is the Boltzmann constant, h is the Planck constant, and R is the universal gas constant. Equation (3) lacks transmission coefficient which is usually assumed to be equal to unity for heterolytic reactions. Table 2 contains values of the coefficient B in Eq. (3) for particular reaction series; these values may be regarded as roughly constant (within the error in their determination) in going from one X substituent to another. These data provide one more support for the additive character of the effects of the examined factors.

Thus the joint effect of the substituent in aryloxiranes and temperature on the rate of the process can be estimated using Eq. (4) which is based on the additivity principle.

$$\log k_3 = \log k_3^0 + \rho^0 \sigma^+ + B^0 \tau. \quad (4)$$

Here, the index "0" refers to standard conditions ($X = H$, $T = 333$ K), and $\tau = (1/T - 1/333) \times 10^3$ is an arbitrary internal temperature scale. Calculation of the parameters in Eq. (4) by multilinear regression analysis (with a confidence probability of 95%) gave the following result:

$$\log k_3 = -(2.42 \pm 0.04) - (2.99 \pm 0.08) \sigma^+ - (4.3 \pm 0.3) \tau; \quad (5)$$

$$S = 0.0741, R = 0.996, n = 13.$$

The coefficients in regression (5) coincide (within the error in their determination) with the parameters characterizing the sensitivity of reaction series to the substituent effect and temperature, $\rho^+ = -(2.9 \pm 0.1)$ at 333 K and $B = 4.4 \pm 0.5$, for the reaction with phenyloxirane (Table 2), as well as with the rate constant of the reference reaction, i.e., the reaction of phenyl-

oxirane with 3,5-dinitrobenzoic acid at 333 K, $\log k_3 = -2.40$ (Table 1).

Most probably, the reaction under study follows a mechanism analogous to that proposed in [8] for the reaction of oxirane with carboxylic acids (Scheme 2). This mechanism implies initial formation of H-complex **A**. In the next rate-determining stage, the activated substrate undergoes nucleophilic attack by the second acid molecule at the α -carbon atom of the oxirane ring (in the benzylic position) to give trimolecular transition state **B**. This stage may be regarded as concerted nucleophilic substitution ($A_N D_N$) with electrophilic assistance to rupture of the oxirane C–O bond. According to Scheme 2, $k_3 = Kk$; therefore, the sensitivity parameter ρ^+ is a complex quantity: $\rho^+ = \rho_1 + \rho_2$. In the first stage, ρ_1 has a negative sign, for electron-acceptor substituents X hamper formation of hydrogen bond in complex **A**. The sign of ρ_2 (second stage) is determined by the character of transition state **B**. Judging by the large negative apparent values of ρ^+ for particular reaction series ($(\rho^+)_{av} = -3.0$, transition state **B** should be dissociative (cleavage of the C–O bond is faster than formation of the A–C bond), i.e., $\rho_2 < 0$. Taking into account that the substituent X is more distant from the reaction center (oxygen atom) in complex **A** than from the reaction center (benzylic carbon atom) in transition state **B**, we presume that $|\rho_1| < |\rho_2|$. Although reduction of the temperature favors transfer of hydrogen atom to oxygen in complex **A**, it should not lead to an appreciable increase of $|\rho_1|$ due to remoteness of the proton-acceptor ring oxygen atom from the benzene ring of the substrate. On the other hand, decrease in the temperature should induce shift of transition state **B** along the reaction coordinate toward the products, which should result in increase of the order of the A–C bond ($\Delta\rho^{A-C} > 0$) and reduction of the order of the C–O bond ($\Delta\rho^{C-O} < 0$). However, it is unlikely that $\rho_2 = \rho^{A-C} (-\rho^{C-O})$ will change to an ap-

Table 1. Rate constants $k_3 \times 10^4$ ($l^2 \text{mol}^{-2} \text{s}^{-1}$)^a for reactions of substituted aryloxiranes with 3,5-dinitrobenzoic acid in acetonitrile

X (σ^+)	Temperature, K		
	323	333	343
H (0)	18.3	39.4	120
4-Cl (0.11)	6.17	13.8	30.5
3-NO ₂ (0.67)	–	0.488	0.861
4-NO ₂ (0.79)	0.067	0.166	0.323

^a For the reactions with 2-(3-bromophenyl)oxirane ($\sigma^+ = 0.41$) and 2-(4-bromophenyl)oxirane ($\sigma^+ = 0.15$), the rate constants $k_3 \times 10^4$ are 3.13 and 29.3, respectively, at 343 K.

Scheme 2.

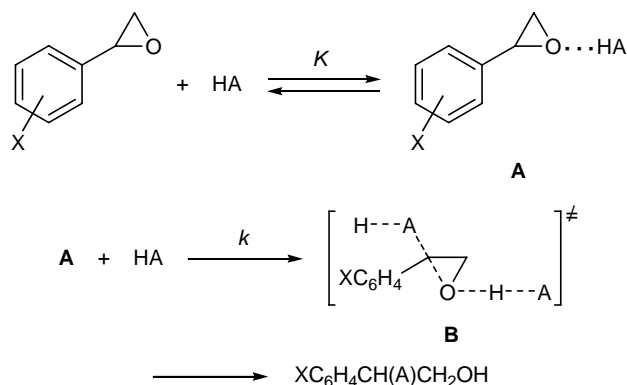


Table 2. Coefficients in Eq. (3) and activation parameters of reactions of substituted aryloxiranes with 3,5-dinitrobenzoic acid in acetonitrile

X	A	-B	r	S	ΔH^\ddagger , kJ/mol	$-\Delta S^\ddagger$, J mol ⁻¹ K ⁻¹	ΔG^\ddagger_{333} , kJ/mol
H	8.3±0.4	4.4±0.5	0.994	0.061	84	39	97
4-Cl	5.8±0.1	3.72±0.03	0.999	0.004	71	87	100
4-NO ₂	3.3±0.2	3.6±0.3	0.996	0.041	68	134	112

preciable extent due to the opposite temperature effect on its constituents ($\Delta\rho^{A-C} \approx |\Delta\rho^{C-O}|$). Then the sensitivity parameters ρ_1 and ρ_2 at both stages should not depend considerably on the temperature, which is consistent with the observed additivity in the effects of these factors on the rate of the process.

According to the data in Table 2, increase in the electron-acceptor power of the X substituent in the series X = H, 4-Cl, 4-NO₂ leads to reduction in the enthalpy of activation ΔH^\ddagger ($\Delta\Delta H^\ddagger < 0$, acceleration) and increase (in absolute value) of the entropy of activation ΔS^\ddagger ($\Delta\Delta S^\ddagger < 0$, deceleration). It is seen that just increase in $|\Delta S^\ddagger|$ induces increase in ΔG^\ddagger , i.e., the contribution of the entropy factor to ΔG^\ddagger and hence to the rate of the process on the whole is determining. While analyzing the effect of substituent X on ΔS^\ddagger , it should be kept in mind that $\Delta S^\ddagger = \Delta S_1^\ddagger + \Delta S_2^\ddagger$ and that $\Delta S_1^\ddagger \ll 0$ in the formation of associative complex **A** [9]; in the second stage (S_N2 reaction), ΔS_2^\ddagger should also be negative [10].

Increase in the electron-acceptor power of substituent X should favor weakening of the hydrogen bond in complex **A**, which should lead to reduction of $|\Delta S_1^\ddagger|$ ($\Delta\Delta S_1^\ddagger > 0$). This tendency in variation of ΔS_1^\ddagger contradicts the observed behavior of ΔS^\ddagger (Table 2): the latter parameter increases in absolute value in going from X = H to X = 4-NO₂ ($\Delta\Delta S^\ddagger < 0$). Therefore, the effect of substituent X on the apparent value of ΔS^\ddagger should be determining in the stage of formation of transition state **B**. As noted above, increase in the electron-acceptor power of substituent X favors more product-like character of transition state **B** with a more ordered structure (ΔS_2^\ddagger should decrease due to strengthening of the A–C and O–H bonds). By contrast, opening of the oxirane ring via extension of the C–O bond should lead to reduced ordering of transition state **B** and increase of ΔS_2^\ddagger . However, the latter factor has no appreciable effect on the behavior of ΔS^\ddagger (Table 2) upon variation of substituent X.

Thus the determining effect of the electronic factor (substituent X) on the Gibbs energy of activation ΔG^\ddagger and hence on the rate of the process originates from the entropy contribution to formation of the A–C and O–H

bonds in transition state **B**. To conclude, it should be noted that ΔG^\ddagger values and substituent constants σ^+ give rise to an excellent linear correlation:

$$\Delta G^\ddagger = (97.4 \pm 0.4) + (19.8 \pm 0.9)\sigma^+, \\ r = 0.999, s = 0.582.$$

Commercial phenyloxirane (purity 98%) and acetonitrile (Merck) were used without additional purification. 4-Nitrophenyloxirane of technical grade was recrystallized twice from hexane, mp 85–86°C [11]. The other substituted phenyloxiranes (X = 3-Br, 4-Br, 4-Cl, 3-NO₂) were synthesized from the corresponding phenacyl bromides as described in [3, 12].

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