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THERMODYNAMIC ASPECTS OF CATALYTIC PHENOLYSIS OF EPICHLOROHYDRIN AND THE REACTION MECHANISM

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The thermodynamic aspects of the epoxide ring-opening reaction in the system «epichlorohydrin (ECH)–4-nitrophenol–tetraethylammonium benzoate/tetrabutylammonium iodide» were studied, and the UV spectra of the initial two- and three-component systems were examined. The catalytic activity of quaternary ammonium salts was studied at temperatures of 333–358 K in a significant excess of ECH, which acts as both a substrate and a solvent. A mixture of ECH and tetrahydrofuran was used as a less polar solvent (1:1, v/v). It has been established that catalysis by tetraalkylammonium benzoate and iodide is described by the same kinetic model. The reaction activation parameters (energy, enthalpy, entropy, and Gibbs energy) corresponding to S_N2-type processes were estimated. A comparison of the studied reaction series and similar ones with different kinetic orders with respect to phenol showed the presence of an enthalpy–entropy compensation effect, which indicates a common reaction mechanism regardless of reagent acidity and, therefore, of the kinetic order with respect to it. Kinetic and thermodynamic models of the reaction are proposed, describing the mechanism of catalysis as a transfer mechanism of the nucleophilic reagent anion by an ion pair, in which, during the multistage process, anion exchange occurs between the acid and the initial ammonium salt, followed by transfer of the reagent anion and formation of the reaction product.

Keywords: epoxide ring opening, acid, quaternary ammonium salt, kinetics, catalysis, activation energy, anion exchange and transfer, mechanism.

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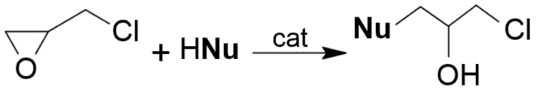
Introduction

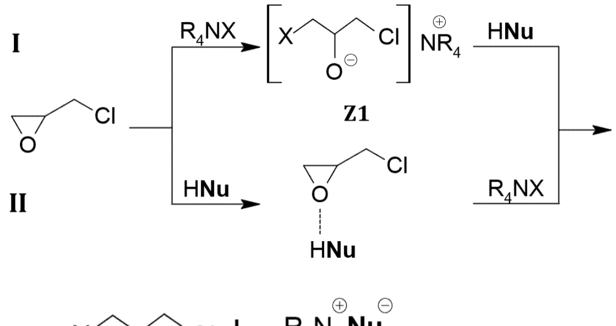
Oxiranes, due to the high strain of the three-membered ring, can interact with a wide spectrum of proton-donor nucleophiles (**HNu**), which opens a route to obtaining various classes of compounds [1–4]. Thus, chlorohydrin esters/ethers act as intermediate products in multistage syntheses, in particular of epoxides for modern composite materials, paint-and-varnish coatings, and adhesives [2,3]; amino alcohols are of critical importance for pharmacology and the development of medicinal drugs [1,4]. The diversity of directions for the use of oxiranes makes the development of predictive reaction models relevant, which will make it possible to selectively obtain products and control their properties depending on the field of application. Predictive modeling of reactions is based on the study of the thermodynamics and kinetics of processes.

A feature of the reaction of chloromethyloxirane (epichlorohydrin, ECH) with such proton-donor nucleophiles as phenols is its regiospecificity [5,6], when the opening of the oxirane ring occurs exclusively according to the Krasusky rule [7] with the formation of the «normal» product according to reaction (1):



(1)

Studies of the kinetic aspects of reaction (1) involving 4-nitrophenol under catalysis by tetrabutylammonium iodide [5] and N,N-dimethylaniline [6,8] showed that, in an excess of oxirane, the reaction has a zero reaction order with respect to the reagent and a first order with respect to the catalyst. This made it possible to establish the kinetic law and to show that the regiospecific phenolysis and regioselective acidolysis of ECH are described by the same kinetic model, where the important role of electrophilic activation by an acidic reagent on the oxirane ring opening process. These findings support the mechanism of the catalytic oxirane ring opening as a mechanism of transfer of the anion of the nucleophilic reagent by an ion pair, where the initial nucleophile leads to the *in situ* formation of a carboxylate/phenolate anion of the reagent, which subsequently reacts with oxirane to form the chlorohydrin ether product (reaction 2) [6,9,10]:



(2)

In the case of catalysis by tetraalkylammonium salts, the formation of the ion pair **IP** is possible by two pathways: **I** without electrophilic assistance by the **HNu** reagent and **II** with electrophilic assistance, when **HNu** forms a complex with oxirane due to a hydrogen bond. The formation of **IP** *in situ* in the reaction system is predicted by the proposed catalytic mechanisms and has been experimentally confirmed by UV spectroscopy [11]. Analysis of the kinetic experiment of the catalytic phenolysis and acidolysis of ECH [8,12] confirms the *in situ* formation of the ion pair **IP** with the anion of the nucleophilic reagent. Therefore, an important stage for the development of a unified model of oxirane phenolysis is the study of tetraalkylammonium carboxylate as the initial catalyst and the comparison of its behavior with tetraalkylammonium halide in analogous reaction series [8]. Since the modeling of the process mechanism is based, first of all, on information about the kinetics and thermodynamics of the reaction, in the present work a study of the thermodynamic aspects of reaction (1) under catalysis by tetraalkylammonium salts, as well as the kinetics of reaction (1) under catalysis by tetraethylammonium benzoate, was carried out. Taking into account that the reaction order for phenols depends on their acidity($pK_a>8$ – first, $pK_a<8$ – zero) [5,6], the study of the thermodynamic aspects of reaction (1) is also necessary for evaluating the unity of the catalysis mechanism for phenols having different kinetic orders.

Experimental

Purification of substances

4-Nitrophenol was purified by crystallization from an aqueous ethanol solution (m.p. 114–115^{0}C (lit. 114^{0}C [13]).

ECH was dried over sodium sulfate for 20 hours, distilled twice, and the fraction with b.p. 116–116.5^{0}C was collected (lit. b.p. 116^{0}C [13]).

Tetraethylammonium benzoate was synthesized using the modified method [14,15]). In a 200 mL beaker, 0.04 mol of benzoic acid was dissolved in 75 mL of water, 25 mL of an aqueous solution of NaOH (0.04 mol) were added. An aqueous solution (25 mL) of $AgNO_3$ (0.04 mol) was added to the resulting solution of PhCOONa. The precipitated PhCOOAg was filtered off, washed on the filter and dried. In a 250 mL flask equipped with a magnetic stirrer, 100 mL of distilled water, PhCOOAg (0.03 mol) and an aqueous solution of Et_4NBr (0.028 mol) were placed. The precipitated AgBr was filtered off, and the filtrate was evaporated until beginning of the salt crystallization. The obtained tetraethylammonium benzoate $Et_4NOOCPh$ was crystallized from benzene (15 mL of solvent were taken per 1 g of substance). The structure of the obtained salt was proven by ^{1}H NMR spectroscopy (298 K, on a Varian Mercury Plus 300 MHz device in deuterated chloroform, chemical shifts were determined on the δ scale from tetramethylsilane as an internal standard), δ, ppm: 1.15 (tr, 12H, CH_3), 3.30 (q, 8H, CH_2), 7.15 (m, 2H), 7.8 (m, 3H).

Tetrahydrofuran (THF) was first purified from peroxides: a 10% aqueous solution of sodium sulfite was added, the mixture was shaken and left for

20–30 minutes. The inorganic layer was separated using a separatory funnel, dry sodium hydroxide was added to the organic layer, and the mixture was left overnight. Tetrahydrofuran was then decanted from the alkali and distilled over sodium at atmospheric pressure, b.p. 65–65.5^{0}C (lit. b.p. 66^{0}C [13]).

Kinetic measurements

The initial solutions of 4-nitrophenol and catalyst were prepared in ECH or in ECH:THF mixture using precisely weighed portions. The reaction was carried out in a flask with two compartments. A solution of 4-nitrophenol (2 mL) was placed in one compartment of the flask, and a catalyst solution (1 mL) was placed in the other compartment. The flask was introduced into a water bath and thermostatted for 10 minutes at a given temperature. The two solutions were then quickly mixed inside the flask and placed back in the water bath for the required reaction time. The initial time of the reaction was defined as the moment of solution mixing. After the required time, the reaction was stopped by adding 10 mL of a cooled (0–5^{0}C) mixture of isopropanol and water (1:1 v/v). The contents of the flask were quantitatively transferred into a titration cell and diluted with water. The amount of unreacted 4-nitrophenol was determined by pH-potentiometric acid-base titration with a 0.1 mol/L NaOH solution.

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Analysis of reaction systems

UV absorption spectra of the initial systems (monitoring the state of 4-nitriphenol, R_4NX, ECH in binary and ternary compositions) were recorded on a Perkin Elmer Lambda 20 spectrophotometer at 20^{0}C.

Results and discussion

The catalytic activity of tetraethylammonium benzoate was studied in the reaction system «ECH–4-nitrophenol» with the significant excess of ECH (30–60-fold), which allowed the studies to be conducted under pseudo-order conditions with respect to oxirane, avoiding complications from association processes. To evaluate the influence of solvent polarity on the reaction rate, ECH and ECH:THF (1:1 v/v), where a significant excess of oxirane remains, were used as solvents.

Since an important characteristic of a kinetic model that depends on its mechanism is the order of the reaction, the primary task of the kinetic studies of the reaction between 4-nitrophenol and epichlorohydrin under catalysis by tetrabutylammonium benzoate is to determine the order of the reaction with respect to the reagent in both solvents. For most reaction series [6,7,9–11], the reaction order is first with respect to the oxirane the catalyst, and zero to first with respect to the phenols depending on the reaction series and the acidity of the reagent.

The kinetics of the reaction of 4-nitrophenol with ECH was investigated at three different concentrations of reagent in ECH as solvent and four different concentrations of tetrabutylammonium benzoate in ECH and ECH :THF (1:1 v/v). The thermodynamic parameters of the reaction were studied for the temperature range of 333–358 K. The progress of the reaction was monitored by changing the concentration of the reagent over time according to the kinetic method described above. Kinetic curves describing the effect of varying the catalyst concentration, and temperature are shown in Fig. 1. The linear relationship observed in the plot of «current reagent concentration» vs. «conversion time» indicates a zero-order reaction with respect to 4-nitrophenol by catalysis of $Et_4NOOCPh$, regardless of the catalyst

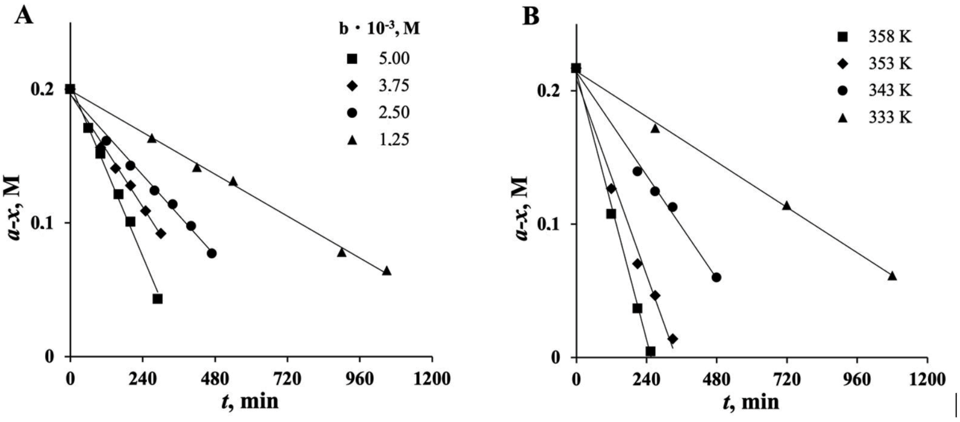


Fig. 1. Plots of the current reagent concentration (a–x) *vs.* time (t) for the reaction of 4-nitrophenol (a=0.2 M) with ECH (s=12.75 M) in the presence of $Et_4NOOCPh$ [b=1.25·10^{-3}–5.00·10^{-3} M (**A**); 5.00·10^{-3} M (**B**)] in ECH as solvent; 353 K (**A**) and 333–358 K (**B**)

concentration and temperature.

The established zero order of the reaction with respect to the reagent and the significant excess of ECH made it possible to calculate the observed reaction rate constants (Table 1) using the following formula:

$$k_{obs}=\frac{a-(a-x)}{st}\ . \tag{3}$$

The zero order of the reaction for 4-nitrophenol is also confirmed by the constancy of the observed rate constants with varying its concentration (*a,* M), $k_{obs}\cdot10^6$, s^{-1}: (0.20) 0.66 ± 0.09; (0.16) 0.65 ± 0.02; (0.11) 0.72 ± 0.06, the average value $k_{obs}\cdot10^6=0.68\pm0.02$.

The reaction order with respect to the catalyst was determined by comparing the observed reaction rate constants with the corresponding catalyst concentrations using the formula:

$$k_{obs}=k_{non}+k_{cat}b\ , \tag{4}$$

where k_{non} and k_{cat} are the rate constants of the noncatalyzed (s^{-1}) and catalyzed (L/(mol·s)) reactions, respectively.

The graphical dependence of the observed rate constants on the catalyst concentration (Fig. 2A) is linear with a correlation coefficient (*r*) close to unity. Taking into account Eq. (4), this corresponds to a first-order reaction with respect to the catalyst. The rate constants of catalytic phenolysis of ECH, calculated by Eq. (4) are given in Table 1. Comparison of the k_{cat} and k_{non} values calculated using Eq. (4) shows that the catalytic process proceeds approximately 4 orders of magnitude faster than the non-catalytic process. Therefore, the following modified equation was used for a number of reaction series:

$$k_{obs}=k_{cat}b\ . \tag{5}$$

The rate constants of the catalytic phenololysis of ECH, calculated using Eqs. (4) and 5, are given in Table 1 and compared with the corresponding constants of the phenololysis of ECH catalyzed by tetrabutylammonium iodide in solvents of ECH and its mixture with THF at temperatures of 333–358 K.

An increase in the catalyst concentration (Fig. 2A) and temperature (Fig. 2B), and a decrease in the polarity of the solvent (Fig. 2A, B) lead to an increase in the rate constants of catalytic reactions for all the reaction series. This effect of changing the solvent polarity is consistent with the behavior of processes occurring *via* an S_N2 mechanism in the case of charged nucleophile. Since the kinetic studies were carried out in the temperature range of 333–358 K, a convenient parameter for evaluating the influence of solvent nature on the phenolysis of ECH is the ratio k'_{cat}/k''_{cat}, which depends primarily on the nature of catalyst rather than on temperature. The average k'_{cat}/k''_{cat} value for $Et_4NOOCPh$ is 0.77, which is comparable with the ratio k'_{cat}/k''_{cat} for *n*-Bu_4NI (0.70). This ratio is virtually independent of the nature of the anion of the salt of the initial catalyst. At the same time, taking into account the structure of the I^- and ^-OOCPh anions, the degree of solvation of the benzoate anion is greater, which means that a change in the polarity of the solvent should have a greater effect on the reactivity of the latter. The ratio k'_{cat}/k''_{cat} is virtually independent of the nature of the anion of the salt of the initial catalyst. This is consistent with the *in situ* formation of the salt R_4NNu during reaction (2), where the anion is the reagent anion HNu. Thus, the phenolysis of oxirane, when the initial catalyst is the base of ionic [5,6] and molecular [6,8] structure, is described by the same kinetic model as the acidolysis of similar reaction systems [6,9,12].

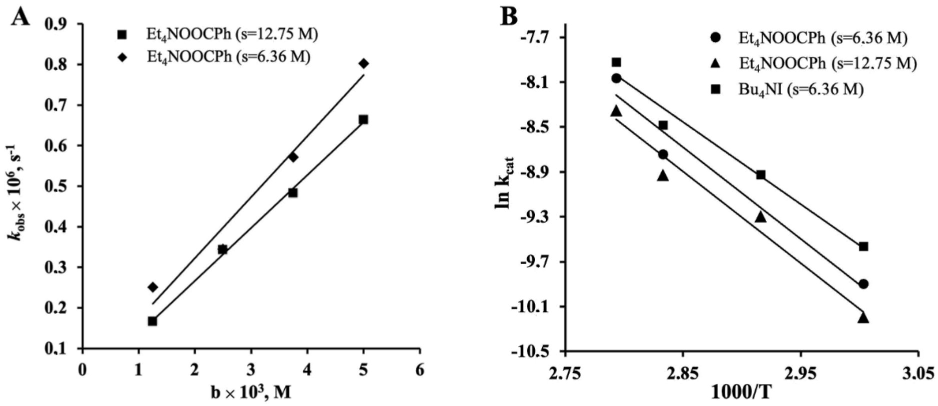


Fig. 2. Plots of the observed reaction rate constants (k_{obs}) *vs.* catalyst concentration ($b=1.25\cdot10^{-3}-5.00\cdot10^{-3}$ M) (**A**) and logarithm of the catalytic reaction rate constant (ln k_{cat}) *vs.* 1000/T (T=333–358 K) (**B**) for the reaction of 4-nitrophenol (*a*=0.2 M) with ECH (*s,* M) in the presence of *n*-Bu_4NI (*s*=6.36 M) and $Et_4NOOCPh$ (*s*=6.36 M, *s*=12.75 M) in ECH (*s*=12.75 M) and ECH:THF (1:1 v/v) (*s*=6.36 M) as solvent; 353 K (**A**) and 333–358 K (**B**)

Important information about the reaction mechanism can be obtained from its thermodynamic parameters. The study of thermodynamic aspects of ECH phenolysis is also necessary to assess the unity of the catalysis mechanism by reagents having different kinetic orders ($pK_a>8$ – first, $pK_a<8$ – zero) [5,6].

The activation parameters of the reaction ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) were calculated by the Eyring equation (6) (Table 2) [6]:

$$\ln\frac{k_{cat}}{T} = A + \frac{B_T}{T}\cdot 1000, \qquad (6)$$

where $A=\ln(k_B/h)+\Delta S^{\neq}/R$; $B_T=-\Delta H^{\neq}/R$; k_B is the Boltzmann constant ($1.38\cdot10^{-23}$ J/K); h is the Planck constant ($6.62\cdot10^{-34}$ J·s); and R is the universal gas constant (8.314 J/(mol·K)).

The activation parameters of the reaction (Table 2) correspond to the processes going *via* the S_N2 and Ad2 mechanisms [6,7]:

Ad2: $\Delta S^{\neq}\approx-70\div-150$ J/(mol·K);

S_N2: $\Delta H^{\neq}\approx48\div72$ kJ/mol;

$\Delta S^{\neq}\approx-100\div-176$ J/(mol·K).

There is a linear relationship between the activation enthalpy and entropy parameters for reaction series with 4-nitrophenol in the studied solvents:

$$\Delta H^{\neq}=(114\pm2)+(366\pm14)\cdot\Delta S^{\neq}\cdot10^{-3}, r=0.999, SD=0.72, N=4. \qquad (7)$$

The similar relationship for seven reaction series also gives the satisfactory correlation with the comparable isokinetic temperature:

$$\Delta H^{\neq}=(106\pm5)+(307\pm44)\cdot\Delta S^{\neq}\cdot10^{-3}, r=0.951, SD=3.59, N=7. \qquad (8)$$

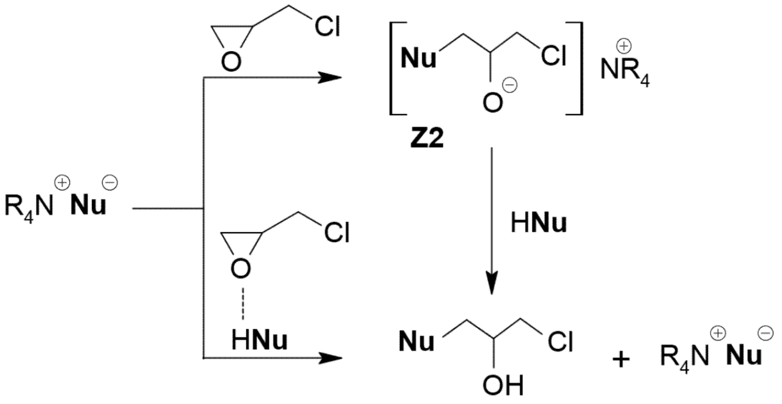
This fact points on the presence of a kinetic enthalpy-entropy compensation effect [12] for the whole reaction series under study. Consequently, there is a single mechanism for the catalytic reaction of epichlorohydrin with phenols of different reaction order with respect to the reagent.

As mentioned earlier [5,6,8,9], these findings support the mechanism of the catalytic oxirane ring opening as a mechanism of transfer of the anion of the nucleophilic reagent by an ion pair. The mechanism described involves two cycles: the *in situ* formation of the **IP – $R_4N^+Nu^-$**, represented by reaction 2, and the transformation of this pair into the epoxide ring opening product, the chlorohydrin ether, represented by reaction (8):

Table 1

The observed (k_{obs}) and catalytic (k_{cat}) rate constants of the reaction of 4-nitrophenol (a=0.2 M) with ECH (s, M) in the presence of n-Bu_4NI (b, M) and $Et_4NOOCPh$ (b, M) in ECH (s=12.75 M) and ECH:THF (1:1) (s=6.36 M) as solvents; 333–358 K

Catalyst	T, K	$b\cdot10^3$, M	$k_{obs}\cdot10^6$, s^{-1}	$k'_{cat}\cdot10^4$, L/(mol·s)	$k_{obs}\cdot10^6$, s^{-1}	$k''_{cat}\cdot10^4$, L/(mol·s)	k'_{cat}/k''_{cat}
			ECH		ECH:THF (1:1)		
$Et_4NOOCPh$	333	5.00	0.187±0.001	0.374±0.002	0.25±0.11	0.50±0.22	0.75
	343	5.00	0.46±0.09	0.92±0.17	–	–	–
	353	5.00	0.66±0.09	1.30±0.05	0.80±0.18	1.50±0.19	0.87
		3.75	0.48±0.03		0.57±0.06		
		2.50	0.34±0.03		0.34±0.04		
		1.25	0.17±0.01		0.25±0.02		
	358	5.00	1.1±0.2	2.2±0,4	1.6±0.3	3.2±0.6	0.69
n-Bu_4NI	333	5.00	–	–	0.353±0.001	0.706±0.001	–
	343	5.00	–		0.67±0.17	1.3±0.3	–
	353	5.00	0.72±0.08	1.4±0.2	1.04±0.08	2.0±0.2	0.70
		3.75	0.56±0.11		–		
		2.50	0.31±0.06		–		
		1.25	0.20±0.03		–		
	358	5.00	–	–	1.8±0.1	3.6±0.2	–



(8)

The formation of the reaction product is accompanied by the regeneration of **IP**. Both cycles include two possible pathways for the transformation of oxirane with and without electrophilic activation of ECH. The formation of the oxirane–4-nitrophenol complex is confirmed by UV spectroscopy data: the absorption maximum of 4-nitrophenol (λ_{max}=290 nm) shifts slightly to the long-wave region (λ_{max}=290–310 nm) upon the addition of ECH, which corresponds to the formation of the complex with H-bond without noticeable ionization of the phenolic group. Analysis of the UV spectra of binary mixtures «4-nitrophenol–R_4NX» shows that in the case of Bu_4NI, there is no sharp transition of the absorption band to the long-wavelength region, while in the case of $Et_4NOOCPh$, the more noticeable shift to 300 nm is observed. This corresponds to the polarization of the H–O bond in phenol (reaction (9)), but the formation of the phenolate anion is not observed.

$$\mathbf{HNu} + R_4NX \rightleftharpoons R_4\overset{\oplus}{N}\overset{-\delta}{X}\cdots H\text{—}\overset{-\delta}{\mathbf{Nu}} \qquad (9)$$

In three-component mixtures «4-nitrophenol–R_4NX–ECH» the more noticeable long-wave shift is observed. In the case of Bu_4NI, a shift of λ_{max} to 300 nm occurs, but the absorption band at 390–400 nm corresponding to the formation of the phenolate anion is not observed. In the case of $Et_4NOOCPh$, in addition to λ_{max}=300 nm, a broad absorption band of 390–400 nm appears, which is characteristic not of a neutral molecule, but of a

Table 2

Activation parameters of the reaction of phenols with epichlorohydrin in the presence of tetraalkylammonium salts in ECH and ECH:THF as solvents, 333–363 K

Reaction system	Reaction order with respect to the phenol	E_a, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J/(mol·K)	$\Delta G^{\neq}_{353}$, kJ/mol
$4\text{-}NO_2C_6H_4OH+Bu_4NI$+(ECH:THF, 1:1)	0	61±7	58±7	151±215	111±14
$4\text{-}NO_2C_6H_4OH+Et_4NOOCPh$+(ECH:THF, 1:1)	0	67±16	64±16	136±47	112±33
$4\text{-}NO_2C_6H_4OH+Et_4NOOCPh$ (ECH)	0	67±8	64±8	139±24	113±17
$4\text{-}NO_2C_6H_4OH+[(CH_3)NCH_2CH(OH)CH_2Cl\}^{+}Cl^{-}$ (ECH) [6]	0	89.5	83.6	82.4	111
$3\text{-}NO_2C_6H_4OH+Pr_4NBr$ (ECH) [6]	0	87±2	84±2	77±6	111±4
$3,5\text{-}(NO_2)_2C_6H_3OH+Pr_4NBr$ (ECH) [6]$^{)}$	0	80±3	79±3	101±7	115±5
$3\text{-}ClC_6H_4OH+Pr_4NBr$ (ECH) [6]	1	81±5	78±5	72±13	103±9

partially ionized form or ionic associate. Thus, in the initial three-component system, even before the start of the reaction, associations between 4-nitrophenol, the catalyst and ECH are established.

It is precisely these nucleophilic-electrophilic interactions that can determine the further reactivity of the system and are consistent with the mechanism of transfer of the anion by the nucleophilic reagent by an ion pair, represented by reactions (2) and (8). The presence of two parallel paths in each cycle explains the dependence of the reaction orders for the proton donor reagent on their acidity. Thus, for the path without electrophilic activation (reactions (2) and (8)), the reaction order with respect to the reagent is zero, since **HNu** participates in the fast stage. The presence of electrophilic activation means that the oxirane–**HNu** complex is involved in the slow stage of oxirane ring opening, and the reagent order with respect is first. The significant excess of ECH relative to **HNu** makes the contribution of the slower path without electrophilic activation greater than with activation. Hence, the reaction of ECH with sufficiently acidic phenols ($pK_a<8$) has a zero order reaction with respect to **HNu**. In the case of phenols with low acidity ($pK_a>8$), the limiting process is the formation of an ion pair $\mathbf{R_4N^+Nu^-}$ with proton transfer to zwitterions **ZI** and **ZII**, $pK_a \approx 13$ [6]. The mechanism under discussion of transfer of the anion of the nucleophilic reagent by an ion pair is consistent with the unified catalytic mechanism for phenolysis and acidolysis of epichlorohydrin.

Conclusions

The study of the reaction series «ECH–4-nitrophenol–tetraalkylammonium benzoate /iodide», including the study of kinetics, thermodynamics, UV spectra, showed comparable catalytic behavior of tetraalkylammonium salts with varying solvent polarity (ECH and the less polar solvent ECH:THF, 1:1 v/v), reaction temperature. It was established that the phenolysis of ECH in excess of the ones has the zero-order reaction with respect to 4-nitrophenol and the first-order reaction with respect to tetraethylammonium benzoate and tetrabutylammonium iodide, regardless of the polarity of the solvent and the reaction temperature. Analysis of thermodynamic data of the studied and similar series with phenols having both zero and first order reactions with respect to the reagent made it possible to calculate the energy, enthalpy, entropy, and Gibbs energy of activation. The activation parameters of the process correspond to reactions of S_N2 characters. The comparison of the enthalpy and entropy of activation of the reaction series studied and similar ones with different kinetic order reaction with respect to phenol showed the presence of the enthalpy–entropy compensation effect, which indicates the single reaction mechanism. The study of the UV spectra of the initial state of the components of the reaction systems showed that the degree of their association is greatest in the three-component system. The obtained data made it possible to propose the unified kinetic and thermodynamic model of the catalytic phenolysis of oxirane, describing the mechanism of catalysis as the mechanism of transfer of the anion of the nucleophilic reagent by an ion pair.

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ТЕРМОДИНАМІЧНІ АСПЕКТИ КАТАЛІТИЧНОГО ФЕНОЛІЗУ ЕПІХЛОРГІДРИНУ ТА МЕХАНІЗМ РЕАКЦІЇ

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Вивчено термодинамічні аспекти реакції розкриття епоксидного циклу в системі «епіхлоргідрин (ЕХГ)–4-нітрофенол–тетраетиламоній бензоат/тетрабутиламоній йодид» та охарактеризовані УФ спектри вихідного стану двох та трикомпонентних систем. Каталітична активність четвертинних амонієвих солей вивчена при температурах 333–358 K у значному надлишку ЕХГ, який є одночасно і субстратом, і розчинником. Як менш полярний розчинник використана суміш ЕХГ з тетрагідрофураном (1:1, об.). Встановлено, що каталіз бензоатом та йодидом тетраалкіламонію описується однаковою кінетичною моделлю. Оцінено активаційні параметри (енергія, ентальпія, ентропія, енергія Гіббса) реакції, які відповідають процесам, що мають S_N2 характер. Зіставленням досліджуваних реакційних серій та аналогічних з різними кінетичними порядками реакції за фенолом показано наявність ентальпійно-ентропійного компенсаційного ефекту, що вказує на єдиний механізм реакції незалежно від кислотності реагенту і, як наслідок, кінетичного порядку за ним. Запропоновані кінетична та термодинамічна моделі реакції, що описують механізм каталізу як механізм переносуаніону нуклеофільного реагенту іонною парою, коли у багатостадійному процесі відбувається обмін аніонами кислотою та вихідною амонієвою сіллю з подальшим перенесенням аніону реагенту та утворенням продукту реакції.

Ключові слова: розкриття циклу епоксиду, кислота, четвертинна амонієва сіль, кінетика, каталіз, енергія активації, обмін та транспорт аніона, механізм.

THERMODYNAMIC ASPECTS OF CATALYTIC PHENOLYSIS OF EPICHLOROHYDRIN AND THE REACTION MECHANISM

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The thermodynamic aspects of the epoxide ring-opening reaction in the system «epichlorohydrin (ECH)–4-nitrophenol–tetraethylammonium benzoate/tetrabutylammonium iodide» were studied, and the UV spectra of the initial two- and three-component systems were examined. The catalytic activity of quaternary ammonium salts was studied at temperatures of 333–358 K in a significant excess of ECH, which acts as both a substrate and a solvent. A mixture of ECH and tetrahydrofuran was used as a less polar solvent (1:1, v/v). It has been established that catalysis by tetraalkylammonium benzoate and iodide is described by the same kinetic model. The reaction activation parameters (energy, enthalpy, entropy, and Gibbs energy) corresponding to S_N2-type processes were estimated. A comparison of the studied reaction series and similar ones with different kinetic orders with respect to phenol showed the presence of an enthalpy–entropy compensation effect, which indicates a common reaction mechanism regardless of reagent acidity and, therefore, of the kinetic order with respect to it. Kinetic and thermodynamic models of the reaction are proposed, describing the mechanism of catalysis as a transfer mechanism of the nucleophilic reagent anion by an ion pair, in which, during the multistage process, anion exchange occurs between the acid and the initial ammonium salt, followed by transfer of the reagent anion and formation of the reaction product.

Keywords: epoxide ring opening; acid; quaternary ammonium salt; kinetics; catalysis; activation energy; anion exchange and transfer; mechanism.

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