

UDC 543.632.542+544.47:547.333.3+544.431.122:544.15

*K.S. Yutilova, E.N. Shved, N.S. Martseniuk***THERMODYNAMIC AND KINETIC ASPECTS OF EPICHLOROHYDRIN ACETOLYSIS UNDER CATALYSIS BY TRIETHYLAMINE IN SOLVENTS OF VARIOUS POLARITIES****Vasyl' Stus Donetsk National University, Vinnytsia, Ukraine**

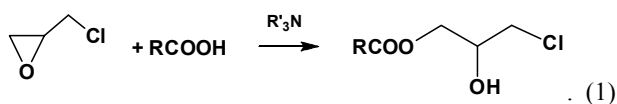
The ring-opening reaction of epichlorohydrin with acetic acid in aprotic solvents under the catalysis by triethylamine in the temperature range of 313–353 K was studied by methods of chemical kinetics. The binary mixtures epichlorohydrin:tetrahydrofuran and epichlorohydrin:nitrobenzene (1:1 vol.) were chosen as solvents, which allowed preserving a significant excess of epichlorohydrin in the reaction system and varying the solvent polarity in the range of $\epsilon=15.1-28.7$. The kinetic law of the reaction was established for the studied reaction series, and the observed and catalytic constants were obtained for epichlorohydrin acetolysis. It was demonstrated that the increase in temperature and solvent polarity accelerates the reaction. The temperature dependences plotted in Arrhenius coordinates exhibited linear behavior. The joint effect of temperature and solvents on activation parameters (energy, enthalpy, entropy, and Gibbs energy) of the reaction was investigated. The values of Gibbs energy of activation were found to be similar in all studied reaction systems. The isokinetic temperature of the epichlorohydrin acetolysis in epichlorohydrin and binary solvents epichlorohydrin:tetrahydrofuran and epichlorohydrin:nitrobenzene was established, and the enthalpy–entropy compensation effect was stated by correlation methods.

Keywords: ring-opening reaction, carboxylic acid, triethylamine, catalysis, solvent polarity, activation energy, isokinetic temperature, enthalpy-entropy compensation effect.

DOI: 10.32434/0321-4095-2023-151-6-213-218

Introduction

Ring-opening reactions of oxiranes with carboxylic acids are widely used in production of alkyd resins, paints, coatings, and acrylate monomer compositions [1,2], antihypertensive [3] and antituberculosis drugs [1]. One of the most widespread synthon for the type of the reactions is epichlorohydrin (2-(chloromethyl)oxirane, ECH) (Eq. (1)) due to its ability to form hydroxyalkyl esters which can further go through the ring-closure reaction resulting in glycidyl esters [4]. The common catalysts of the reaction (1) are organic bases, e.g. tertiary amines, which provide high reaction rate and selectivity [5].



The ring-opening reaction of epichlorohydrin

belongs to the nucleophilic substitution processes. In the presence of tertiary amines, reaction (1) proceeds via S_N2 -like mechanism [5]. One of the fundamental characteristics of the belonging of the reaction to a certain mechanism is its activation barrier. The activation parameters for S_N2 reactions may vary within a range [6]:

$$\Delta H^\ddagger \approx 48-72 \text{ kJ/mol}; -\Delta S^\ddagger \approx 100-176 \text{ J/mol}\cdot\text{K}.$$

An intriguing phenomenon of the organic reactions is the enthalpy-entropy compensation effect [7,8]. The most important quantitative characteristic of this effect is the isokinetic temperature, at which the rate of the reaction remains the same for the entire reaction series. The presence of the compensation effect has been found for the reaction series of substituted carboxylic acids and sulfamides with

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Thermodynamic and kinetic aspects of epichlorohydrin acetolysis under catalysis by triethylamine in solvents of various polarities

aryloxiranes [8]; carboxylic acids with ECH under catalysis by organic bases, where ECH is both substrate and solvent [9]. Considering the mechanism of the ring opening as S_N2 , a significant change of kinetic constants and activation parameters is expected when varying the solvent polarity. Therefore, the influence of the solvent polarity on the oxirane ring opening is an essential task for predicting the reactivity in such systems.

The purpose of the present work was to study the activation parameters and the joint effect of temperature and solvent polarity on oxirane ring opening of epichlorohydrin by acetic acid in different solvents under the catalysis by triethylamine.

Experimental

Purification of substances

ECH was dried over anhydrous sodium sulfate for 20 hours and then distilled twice. The fraction with b.p. 116–116.5°C was collected (lit. b.p. 116°C [10]). Commercially available glacial acetic acid (AcOH) was purified from traces of water by boiling over copper (II) sulfate [10] and further distilled with collecting the fraction with b.p. 117–119°C (lit. b.p. 118°C [10]). Triethylamine (Et_3N) was dried over calcium sulfate for 20 hours and distilled, the fraction with b.p. 89–90°C (lit. b.p. 89.4°C [10]). To remove peroxides, 10% aqueous solution of sodium sulfite was added to tetrahydrofuran (THF), carefully shaken, and allowed to stand for 20–30 minutes. Then the inorganic layer was separated on a separatory funnel, dry sodium hydroxide was added to the organic layer and left overnight. Tetrahydrofuran was decanted from alkali and distilled over sodium under atmospheric pressure, b.p. 65–65.5°C (lit. b.p. 66°C [10]). Nitrobenzene (NB) was purified from nitrotoluene, dinitrothiophene, dinitrobenzene, aniline by distillation with steam in the presence of 20% sulfuric acid, then dried over calcium chloride and distilled at low pressure over P_2O_5 , b.p. 208–211°C, (lit. b.p.=211°C [10]).

Kinetic measurements

Kinetic studies were conducted by the procedure described in ref. [5]. In brief, carboxylic acid and catalyst solutions were prepared in the binary solvents. Then the acid and catalyst solutions were taken in the volume ratio of 2:1 and heated to the reaction temperature separately. Then, the solutions were mixed and heated again during the reaction time. After that, the reaction was stopped by adding cold isopropanol/water mixture (1:1 vol.). The content of the flask was quantitatively transferred to the titration cell and diluted with water. The residual concentration of acetic acid was determined by pH-potentiometric acid-base titration.

Calculation of activation parameters

The activation parameters of ECH acetolysis were estimated by the formulae (2)–(5) [7]:

$$\ln k_{\text{cat}} = \ln A - \frac{E_a}{RT}, \quad (2)$$

$$\Delta H_T^\ddagger = E_a - nRT, \quad (3)$$

$$\Delta S_T^\ddagger = R \cdot \left(\ln A - \ln T - \ln \frac{k_B}{h} - n \right), \quad (4)$$

$$\Delta G_T^\ddagger = \Delta H_T^\ddagger - T\Delta S_T^\ddagger, \quad (5)$$

where k_{cat} is the catalytic rate constant ($M^{-1} \cdot s^{-1}$); A is the preexponential factor ($M^{-1} \cdot s^{-1}$); E_a is the activation energy (kJ/mol); R is the universal gas constant ($8.314 \text{ J mol}^{-1} \cdot K^{-1}$); T is the reaction temperature (K); n is the reaction molecularity; k_B is the Boltzmann constant ($1.38 \cdot 10^{-23} \text{ J/K}$); h is the Planck constant ($6.62 \cdot 10^{-34} \text{ J} \cdot s$); ΔH_T^\ddagger is the enthalpy of activation (kJ/mol); ΔS_T^\ddagger is the entropy of activation ($J \cdot \text{mol}^{-1} \cdot K^{-1}$); and ΔG_T^\ddagger is the Gibbs energy of activation (kJ/mol).

Isokinetic relationships

For the reaction series with different substituents in a substrate or reagent or in different solvents, there is a linear relationship between ΔH^\ddagger and ΔS^\ddagger in the form of the equation (6) [7]:

$$\Delta H^\ddagger = \beta \Delta S^\ddagger + \Delta H_0^\ddagger, \quad (6)$$

where ΔH_0^\ddagger is the enthalpy of activation for the reaction with the unsubstituted compound (kJ/mol).

Considering the Gibbs energy equation ($\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$) in combination with equation (6), one derives the equation (7):

$$\Delta G^\ddagger = \Delta H_0^\ddagger - (T - \beta)\Delta S^\ddagger. \quad (7)$$

Therefore, a sign of the presence of a compensatory effect is the constant Gibbs energy. The proportionality constant (β) is measured in units of temperature and is referred to as the isokinetic temperature for kinetic linear Gibbs energy relationships.

Results and discussion

To investigate the temperature effect on the reaction rate of epichlorohydrin acetolysis catalyzed by triethylamine, this reaction was studied in the temperature range of 313–353 K in binary solvents ECH:THF and ECH:NB (1:1 vol.). It is known that the reactions of ECH with carboxylic acids have the first order by the substrate independently from its structure, while the order by acid reagent in the reaction system with tertiary amines and significant excess of ECH is zero [11]. The observed reaction rate constants, k_{obs} (s^{-1}) were calculated by the following formula [5]:

$$k_{\text{obs}} = \frac{a - (a - x)}{st}, \quad (8)$$

where a is the initial concentration of acetic acid (M); $a-x$ is the current concentration of acetic acid (M) at the reaction time t (s); and s is the initial concentration of ECH (M).

Considering varying the content of the catalyst in the reaction systems, the dependences of the observed reaction rate constants on corresponding catalyst concentrations were plotted (Fig. 1) based on the following equation:

$$k_{\text{obs}} = k_{\text{non}} + k_{\text{cat}}b, \quad (9)$$

where k_{non} is the rate constant of the non-catalytic reaction flow (s^{-1}); k_{cat} is the rate constant of the catalytic reaction flow ($\text{M}^{-1}\cdot\text{s}^{-1}$); and b is the catalyst concentration (M).

The plots in the coordinates of the equation (9) are linear for the reaction systems in both binary solvents. This fact allowed establishing the first reaction order with respect to catalyst (Et_3N) and to calculate the catalytic reaction constants (Table 1) as the slopes of the obtained linear functions.

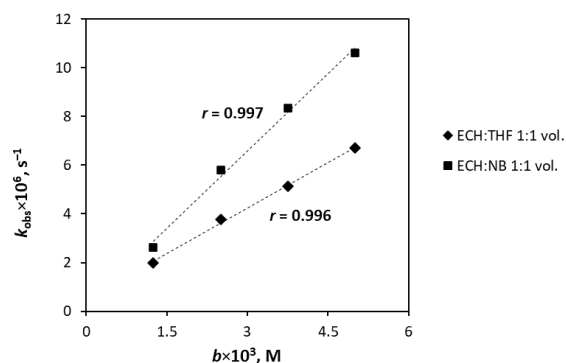


Fig. 1. The dependence of the observed reaction rate constants on Et_3N concentration for the reaction of AcOH ($a=0.2$ M) with ECH ($s=6.36$ M) in binary solvents ECH:THF and ECH:NB (1:1 vol.), 333 K

At 313 and 353 K, reaction (1) was studied in the presence of single concentration of triethylamine ($b\cdot 10^3=5.00$ M). Given that the rate constant of the non-catalytic reaction flow has a negligible value ($k_{\text{non}} \ll k_{\text{cat}}b$), the catalytic rate constants can be approximately calculated from equation (9) as $k_{\text{cat}} = k_{\text{obs}}/b$ (Table 1).

The catalytic rate constants of reaction (1) in the presence of triethylamine demonstrate that the rate increases with the growth in temperature, in accordance with the Arrhenius and Eyring equations [7]. The observed temperature dependencies plotted in Arrhenius coordinates are linear (Fig. 2). This linearity suggests that the mechanism of ECH acetolysis remains constant within the studied temperature range and binary solvents.

The values of activation energy E_a , enthalpy ΔH^\ddagger , entropy ΔS^\ddagger , and Gibbs energy ΔG^\ddagger of activation, calculated using equations (2)–(5), are presented in Table 2.

Table 1

Observed (k_{obs}) and catalytic (k_{cat}) rate constants of the reaction of AcOH ($a=0.2$ M) with ECH ($s=6.36$ M) in the presence of Et_3N (b , M) in binary solvents ECH:THF and ECH:NB (1:1 vol.), 313–353 K

$b \cdot 10^3$, M	T, K	ECH:THF 1:1 vol. ($\epsilon=15.1$)		ECH:NB 1:1 vol. ($\epsilon=28.7$)	
		$k_{\text{obs}} \cdot 10^6$, s^{-1}	$k_{\text{cat}} \cdot 10^4$, $\text{M}^{-1}\cdot\text{s}^{-1}$	$k_{\text{obs}} \cdot 10^6$, s^{-1}	$k_{\text{cat}} \cdot 10^4$, $\text{M}^{-1}\cdot\text{s}^{-1}$
1.25	333	0.258 ± 0.020	0.930 ± 0.058	0.263 ± 0.023	2.12 ± 0.12
2.50		0.378 ± 0.025		0.581 ± 0.073	
3.75		0.514 ± 0.021		0.836 ± 0.054	
5.00		0.600 ± 0.042		1.06 ± 0.01	
5.00	313*	0.162 ± 0.010	0.324 ± 0.020	0.191 ± 0.007	0.382 ± 0.017
5.00	353*	2.25 ± 0.02	4.50 ± 0.045	3.79 ± 0.39	7.59 ± 0.79

Note: * – $k_{\text{cat}} = k_{\text{obs}}/b$.

The calculated activation parameters of ECH acetolysis in binary solvents correspond to the typical values in both A_{d2} and S_N2 processes [6].

The values of E_a , ΔH^\ddagger and ΔS^\ddagger increase from ECH:THF to ECH:NB. The reaction in single ECH exhibits higher values for these parameters than the binary solvents [12]. However, the values of Gibbs energy of activation are similar in all three reaction systems.

According to data in Table 2, the Gibbs energy changes within the error, which indicates that the series is isokinetic. To estimate the presence of the enthalpy–entropy compensation effect in the studied reaction systems, the dependence between enthalpy and entropy of activation of the reaction in ECH and binary solvents was plotted by the equation (6) (Fig. 3) [3,13].

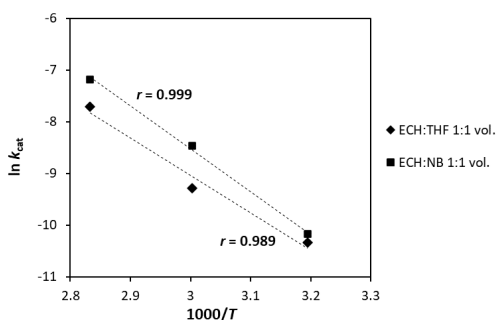


Fig. 2. Arrhenius dependences $\ln k_{cat}$ vs. reciprocal temperature ($1000/T$) for the reaction of AcOH ($a=0.2$ M) with ECH ($s=6.36$ M) in the presence of Et_3N ($b \cdot 10^3=5.00$ M) in binary solvents ECH:THF and ECH:NB (1:1 vol.), 313–353 K

The obtained plot is linear, which allowed determining the isokinetic temperature of the reaction (10):

The isokinetic temperature of ECH acetolysis in ECH and the binary solvents ECH:THF and ECH:NB (1:1 vol.) is determined to be 321 ± 32 K

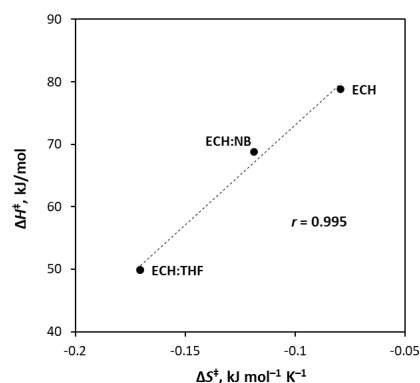


Fig. 3. Isokinetic dependence on enthalpy of activation (ΔH^\ddagger_{333} , kJ/mol) on entropy of activation (ΔS^\ddagger_{333} , $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) for the reaction of AcOH ($a=0.2$ M) with ECH ($s=6.36$ M) in the presence of Et_3N ($b \cdot 10^3=5.00$ M) in binary solvents ECH:THF and ECH:NB (1:1 vol.)

and can be experimentally achieved. Consistency of the dependence (6) indicates the presence of the enthalpy–entropy compensation effect indicates a single mechanism of catalysis for ECH acetolysis by Et_3N in the solvents of different polarities [3,14].

The reaction rate of ECH acetolysis under catalysis by Et_3N depends on the joint effect of various factors in the reaction system. In the studied reaction series, both temperature and solvent polarity were varied. To estimate the contribution of these factors into the system reactivity, the correlation (11) was established:

$$\lg k_{cat} = (5.3 \pm 0.8) - (3.4 \pm 0.3) \cdot 1000/T + (0.8 \pm 0.3) \cdot \lg \epsilon, \quad (11)$$

$$r = 0.990, \text{SD} = 0.090, N = 7.$$

The studied reaction series shows high correlation between the reaction rate and temperature–polarity joint effect. The sensitivity of the series to the change of temperature is higher than the change of solvent. Thus, the kinetic and thermodynamic aspects of ECH acetolysis depend on temperature of the reaction and polarity of the aprotic solvent.

Table 2

Activation energy (E_a), enthalpy (ΔH^\ddagger_{333}), entropy (ΔS^\ddagger_{333}), and Gibbs energy (ΔG^\ddagger_{333}) of activation in the reaction of AcOH ($a=0.2$ M) with ECH ($s=6.36$ M) in the presence of Et_3N ($b \cdot 10^3=5.00$ M) in binary solvents ECH:THF and ECH:NB (1:1 vol.), 313–353 K

Solvent	E_a , kJ/mol	ΔH^\ddagger_{333} , kJ/mol	$-\Delta S^\ddagger_{333}$, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	ΔG^\ddagger_{333} , kJ/mol
ECH:THF 1:1 vol.	53 ± 2	49.8 ± 0.2	170 ± 1	107 ± 3
ECH [12] *	85 ± 3	78.8	79.3	105
ECH:NB 1:1 vol.	69 ± 3	66.0 ± 0.2	119 ± 1	106 ± 2

Note: * – $k_{cat} \cdot 10^4 = 2.02 \pm 0.06 \text{ M}^{-1} \cdot \text{s}^{-1}$; $\epsilon(\text{ECH}) = 22.6$.

Conclusions

The catalytic rate constants for the ring-opening reaction of epichlorohydrin with acetic acid in the presence of Et₃N were determined in the temperature range of 313–353 K in binary aprotic solvents of various polarities. The activation parameters of the ECH acetolysis under the catalysis by triethylamine in different solvents show typical values for both A_D2 and S_N2 processes, with increasing values from ECH:THF to ECH:NB. The isokinetic temperature of the ECH acetolysis reaction in ECH and the binary solvents ECH:THF and ECH:NB was determined. The enthalpy–entropy compensation effect suggests a single mechanism of catalysis for ECH acetolysis by Et₃N in solvents of different polarities. The results of the study contribute to the understanding of the ring-opening reactions of ECH and provide valuable insights for its optimization, prediction, and practical application in epoxy monomer design.

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Received 07.08.2023

ТЕРМОДИНАМІЧНІ І КІНЕТИЧНІ АСПЕКТИ АЦЕТОЛІЗУ ЕПІХЛОРОГІДРИНУ ПРИ КАТАЛІЗІ ТРИЕТИЛАМІНОМ У РОЗЧИННИКАХ РІЗНОЇ ПОЛЯРНОСТІ

Ютілова К.С., Швед О.М., Марценюк Н.С.

Методами хімічної кінетики досліджено реакцію розкриття циклу епіхлоргідрину оцтовою кислотою в аprotонних розчинниках при каталізі триетиламіном в інтервалі температур 313–353 К. Як розчинники були обрані бінарні суміші епіхлоргідрин:тетрагідрофуран та епіхлоргідрин:нітробензол (1:1 об.), що дало змогу зберегти значний надлишок епіхлоргідрину в реакційній системі та варіювати полярність розчинника в діапазоні $\epsilon=15,1-28,7$. Встановлено кінетичний закон реакції для досліджуваної реакційної серії, одержано спостережувані і каталітичні константи ацетолізу епіхлоргідрину. Було показано, що підвищення температури та полярності розчинника прискорюють реакцію. Температурні залежності, побудовані в координатах рівняння Арреніуса, мають лінійний характер. Досліджено спільний вплив температури та розчинників на параметри активації (енергію, ентальпію, ентропію та енергію Гіббса) реакції. Енергія Гіббса активації має близькі значення в усіх досліджуваних реакційних системах. Встановлено ізокінетичну температуру ацетолізу епіхлоргідрину в епіхлоргідрині та бінарних розчинниках епіхлоргідрин:тетрагідрофуран та епіхлоргідрин:нітробензол, кореляційними методами констатовано наявність ентальпійно-ентропійного компенсаційного ефекту.

Ключові слова: реакція розкриття циклу, карбонова кислота, триетиламін, каталіз, полярність розчинника, енергія активації, ізокінетична температура, ентальпійно-ентропійний компенсаційний ефект.

THERMODYNAMIC AND KINETIC ASPECTS OF EPICHLOROHYDRIN ACETOLYSIS UNDER CATALYSIS BY TRIETHYLAMINE IN SOLVENTS OF VARIOUS POLARITIES

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