PECULIARITIES OF CATALYTIC BEHAVIOR OF BASES IN THE REACTION OF ALIPHATIC CARBOXYLIC ACIDS WITH EPSOXIDE

Yu. N. Bespal'ko, E. N. Shved, and N. M. Oleinik

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A study was carried out on the kinetics of the reaction of 1-chloro-2,3-epoxypropane (epichlorohydrin, ECH) with aliphatic carboxylic acids in the presence of (3-chloro-2-hydroxypropyl)trimethylammonium (CHPTMA) chloride obtained by trimethylammonium chloride and ECH. We compared the catalytic activity of CHPTMA chloride, trialkylamines, and tetraalkylammonium halides and evaluated the effect of their structure. An ab initio quantum-chemical calculation was performed to obtain a detailed analysis of the state of the catalysts in this system in order to understand the peculiarities of catalytic activity of these bases.

Key words: epoxide, monocarboxylic acids, catalysis, ab initio quantum-chemical calculation.

Expoxides are commonly used for the production of adhesives, stabilizers, and polymer surface modifiers [1-3]. The opening of the epoxide ring by carboxylic acids is a model for studying the complex reactions of hardening and the polymerization of epoxide monomers [1] and the metabolism of oxirane compounds in living organisms [4, 5]. Thus, the study of the mechanisms of epoxide ring opening holds importance in both practical and theoretical organic chemistry.

Tertiary amines and quaternary ammonium salts are used as basic catalysts in the reaction of epoxides with carboxylic acids [6]:

\[ R'COOH + O\rightarrow R''\xrightarrow{\text{cat}} R'\text{COO} + R''\text{OH} \]  \hspace{1cm} (1)

Two mechanisms have been proposed to explain the catalytic action of amines and ammonium salts in reaction (1). General base catalysis entails a step involving proton transfer from the acid to the base [2]. The formation of tetraalkylammonium carboxylate, which then catalyzes opening of the epoxide ring, occurs in nucleophilic catalysis.

Our previous study of the effect of the structure of catalysis taken in a broad range of \( pK_a^{H,0} \) values [7] has shown that the nature of the tetraalkylammonium salts and tertiary aliphatic amines has only a slight effect on the rate of acidolysis of epoxides by carboxylic acids. This result has led to a proposal of a single mechanism for the action of such catalysts [7, 8]. In order to support this theory, we used an ammonium salt obtained from an epoxide and a trialkylammonium halide (\( R_3\text{HNX} \)), which upon reaction with a carboxylic acid and epoxide gives a salt \( R_3\text{R''NOOCR'} \) where \( R'' = \text{CH}_2\text{CH(OH)CH}_2R' \), as the initial catalyst of reaction (1) [8].

In the present work, we studied the kinetic behavior and mechanism of the acidolysis of an epoxide, namely, 1-chloro-2,3-epoxypropane (epichlorohydrin, ECH) by aliphatic monocarboxylic acids in the presence of an ammonium salt, namely, (3-chloro-2-hydroxypropyl)trimethylammonium (CHPTMA) chloride.

Donets’k National University, Vul. Universytets’ka, 24, Donet’s’k 83055, Ukraine. E-mail: organica@dongy.donetsk.ua. Translated from Teoreticheskaya i Éksperimental’naya Khimiya, Vol. 44, No. 5, pp. 292-297, September-October, 2008. Original article submitted October 6, 2008.
We studied a reaction series of aliphatic monocarboxylic acids \( R'\text{CO}_2\text{H} \) as reagents in reaction (1), where \( R' \) is \((\text{CH}_3)_2\text{CH} \) (1), \( n\text{-C}_5\text{H}_{11} \) (2), \( n\text{-C}_4\text{H}_9 \) (3), \( n\text{-C}_3\text{H}_7 \) (4), \( \text{CH}_2 \) (6), \( \text{C}_6\text{H}_5\text{CH}_2 \) (7), \( \text{C}_2\text{H}_5\text{OCH}_2 \) (8), \( \text{C}_6\text{H}_5\text{OCH}_2 \) (9), and \( \text{ClCH}_2 \) (10).

The kinetic study was carried out for reaction (1) at 80 ± 0.1 °C with excess ECH. The change in the concentration of the carboxylic acid was monitored by potentiometric acid–base titration [8]. Acids 1-6 were purified by heating at reflux with potassium permanganate and subsequent distillation [9]. Acids 8 and 10 were purified by distillation at reduced pressure [9] and acids 7 and 9 were recrystallized from water [9]. A sample of CHPTMA chloride with mp 187-189 °C was obtained by the reaction of trimethylammonium hydrochloride with ECH [8, 10].

In a previous study [8], we showed that the reaction of carboxylic acids with ECH in the presence of CHPTMA chloride is zero-order relative to the acid reagent. However, first-order kinetics was also found for the epoxide irrespective of its structure [2, 6-8, 11]. Treatment of the experimental was carried out using the following equation:

\[
 k_{\text{obs}} = \frac{x}{(st)} \tag{2}
\]

where \( k_{\text{obs}} \) is the observed reaction rate constant, in s\(^{-1}\), \( x \) is the current concentration of the reaction product, in mol/L, \( s \) is the concentration of ECH, in mol/L, and \( t \) is the elapsed time, in s.

The overall first-order rate constants \( k_{\text{obs}} \) (zero-order relative to the acid and first-order relative to the substrate) remain invariant to high conversions of carboxylic acid (60-75%), i.e., the kinetics relative to the carboxylic acid as the nucleophilic reagent is strictly zero-order for all acids under the conditions of reaction (1). The kinetic curves for the loss of carboxylic acids 1-10 in reaction (1) in plots of \( x \) vs. \( t \) are linear (Fig. 1) \((r = 0.997-0.999)\), which confirms the zero-order kinetics relative to the acid reagent.

Treatment of the experimental data in Table 1 according to the equation

\[
 k_{\text{obs}} = k_0 + k_c b, \tag{3}
\]

where \( b \) is the concentration of the catalyst, gives a linear relationship with satisfactory correlation coefficients (0.991-0.999), indicating first-order kinetics relative to the catalyst. The values of \( k_0 \) calculated using Eq. (3) are on the order of \( 10^{-7} \) s\(^{-1}\) and statistically insignificant. Thus, Eq. (3) may be transformed into

\[
 k_c = \frac{k_{\text{obs}}}{b}. \tag{4}
\]