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Kinetics of Chlorohydrination of Allyl Chloride

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Abstract—The chlorohydrination of allyl chloride with chlorine in water was studied at 20–80°C. The effect of the concentration of chloride ions within the range 0–3.6 mol/l on the selectivity of formation of glycerol dichlorohydrins was studied. An equation that relates the selectivity and the concentration of Cl^- was derived, which adequately describes experimental data. The schemes of parallel and consecutive reactions occurring in the system were suggested. The ratios between the rate constants of the following reactions were found: the reactions of chlorine with water and allyl chloride dissolved in water ($k_1/k_4 = 4.1 \times 10^{-4}$), the reaction of allyl chloride with hypochlorous acid and the decomposition of hypochlorous acid ($k_2/k_3 = 1.7 \times 10^3$), and the reactions of the allyl chloride–chlorine complex with a water molecule and Cl^- ($k_5/k_6 = 2.9 \times 10^{-2}$).

INTRODUCTION

The chlorohydrination of allyl chloride forms the basis for the preparation of glycerol dichlorohydrins in the commercial production of epichlorohydrin and synthetic glycerol. The process is performed by the interaction of allyl chloride with hypochlorous acid (HOCl) or chlorine in water. In this case, hydrogen chloride and 1,2,3-trichloropropane (a product of chlorine addition at a double bond) are primarily formed as by-products.

The process of allyl chloride chlorohydrination is poorly understood; the available information is mainly restricted to patent data [1–9] and technical feasibility studies [10, 11]. The cited studies and works [12, 13] devoted to the chlorohydrination of other olefins lead to the important conclusion that the selectivity of these processes significantly depends on the concentration of chloride ions, which are formed simultaneously with the target product chlorohydrin, and on the presence of an organic phase in the reaction medium. The role of the organic phase is easy to explain by chlorine and allyl chloride absorption, which is favorable for increasing the amount of 1,2,3-trichloropropane [14] and, hence, for decreasing selectivity. However, the reasons for the effect of the concentration of chloride ions remain unclear.

Note that an adverse effect of chloride ions on the selectivity of the process dramatically restricts the possibility of obtaining highly concentrated solutions of glycerol dichlorohydrins. Therefore, low-concentration aqueous solutions (<0.4 mol/l) should be used in the production cycles of large-scale epichlorohydrin and propylene oxide manufacturing.

The aim of this work is to study and quantitatively assess the role of chloride ions in the production of glycerol dichlorohydrins and to determine the mechanisms of formation of the target product and by-products of the reaction. Most attention was focused on the effect of the concentration of chloride ions on the selectivity of the process in the absence of a liquid organic phase. To preclude the entry of an organic phase into the system, a vapor–gas mixture containing 60–70 vol % allyl chloride vapor and 30–40 vol % nitrogen as an inert gas was fed into the reactor.

EXPERIMENTAL

The reactor consisted of a jacketed glass column 1 m in height and 46 mm in diameter. The column was equipped with inlet pipes for supplying water, chlorine, and the vapor–gas mixture (through Schott filters) and outlet pipes for withdrawing the reaction mixture (both at the top and at the bottom) and waste gases (gases not absorbed by an aqueous solution).

To perform the synthesis, required amounts of chlorine and a vapor–gas mixture containing allyl chloride were continuously passed through the column filled with distilled water at a temperature of 20–80°C. To study the effect of the concentration of chloride ions on the course of the reaction, the reactor was filled with either hydrochloric acid or an aqueous NaCl solution, which contained Cl^- in a concentration of 0.09, 0.24, 0.78, 1.31, 1.88, or 3.54 mol/l. The reaction solution was sampled at regular intervals; the concentrations of chloride ions and organic components were determined by chemical analysis [15] and a specially developed chromatographic procedure [16], respectively.

RESULTS AND DISCUSSION

Figure 1 demonstrates the formation selectivity for glycerol dichlorohydrins as a function of reaction time at various temperatures.

It is important to note that the curves exhibit a broad and flat maximum at all temperatures. The highest

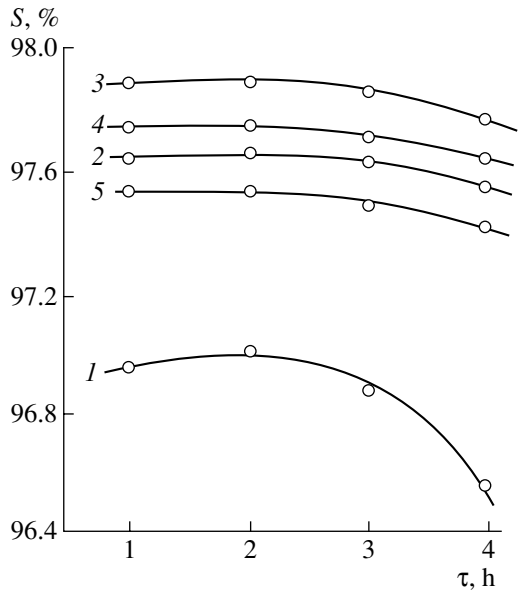


Fig. 1. Selectivity of formation of glycerol dichlorohydrins as a function of reaction time at a temperature (°C) of (*1*) 20, (*2*) 40, (*3*) 50, (*4*) 60, or (*5*) 80.

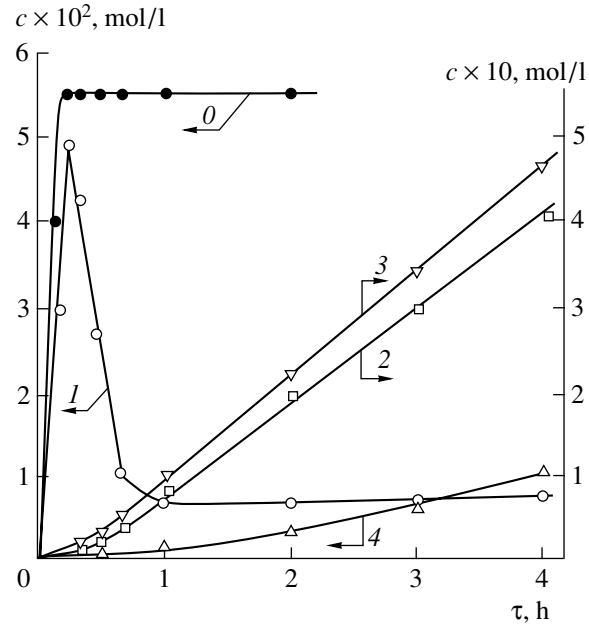


Fig. 2. Changes in the concentrations of (*0, 1*) allyl chloride, (*2*) glycerol dichlorohydrins, (*3*) HCl, and (*4*) 1,2,3-trichloropropane as functions of time at 50°C.

selectivity was attained at 50°C; therefore, the subsequent experiments were performed at this temperature.

Figure 2 demonstrates the time dependence of the concentrations of allyl chloride, glycerol dichlorohydrins, HCl, and 1,2,3-trichloropropane in the reaction medium. The complex shape of curve *1*, which characterizes the concentration change of allyl chloride, clearly indicates that several simultaneous and consecutive reactions rather than a single reaction occurred in this system. Initially, the concentration of allyl chloride in water rapidly increased to a certain value (in this case, a concentration of 4.9×10^{-2} mol/l was attained in 15 min). Thereafter, it decreased at almost the same rate to ~0.7×10^{-2} mol/l and remained unchanged in the subsequent period of time.

A special blank experiment (curve *0*) was performed, in which a vapor–gas mixture containing 60 vol % allyl chloride vapor was passed through the chemical reactor in the absence of chlorine. It was found that the aqueous solution was saturated with allyl chloride to a constant value of 5.5×10^{-2} mol/l in 15 min after the onset of the reaction. It is likely that the above value is the solubility limit under these conditions.

It is believed that, initially, allyl chloride is accumulated due to its dissolution in water; thereafter, its simultaneous consumption comes into play. This consumption, which is initially slow, then rapidly intensifies and attains a certain constant level when the rates of allyl chloride dissolution and consumption become equilibrated. Of course, the consumption of allyl chloride depends on its reaction with chlorine, which is also simultaneously absorbed by an aqueous solution (dissolves).

The change in the slope of curve *2*, which corresponds to the accumulation of glycerol dichlorohydrins, suggests that the chlorohydrination reaction began not immediately but after a certain time had elapsed. Thereafter, the rate of accumulation of glycerol dichlorohydrins became constant and its concentration linearly increased with time.

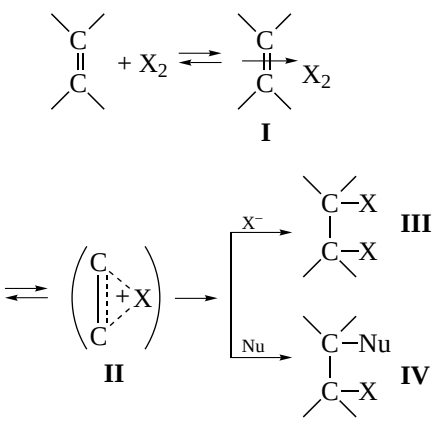
The concentration of HCl (curve *3*) changes in a similar manner. This product was obtained simultaneously with glycerol dichlorohydrins; however, its concentration was higher than an equimolar amount of glycerol dichlorohydrins by 10–15%. This fact suggests that another reaction afforded an additional amount of Cl^-.

It was noted in early works that a certain time should be spent on the formation of a reaction medium for the beginning of a chlorohydrination reaction. Thus, to attain a high yield of the target product, it is usually recommended to perform chlorohydrination with specially prepared chlorine water. Ioffe and Yampol'skaya [17] supposed that a product of chlorine addition to a double bond was formed in the direct contact of an olefin with free chlorine, whereas another portion of chlorine is hydrolyzed in water to hypochlorous acid and hydrochloric acid. In turn, hypochlorous acid added to an olefin dissolved in water forms a corresponding chlorohydrin.

However, it should be kept in mind that the equilibrium constant K_p of chlorine hydrolysis in water is very low. According to various published data, it is as low as

(3.9–4.5) × 10^{-4} at 25°C [18]. Moreover, HOCl readily decomposes on heating [19, 20] to form an additional amount of chloride ions, which are favorable for an additional shift of the equilibrium to the left. This suggests that the chlorohydrination process cannot involve the hydrolysis of chlorine in water as a slow step (the rate-limiting step of the hydrolysis of chlorine is its diffusion in water, the rate constant of which is very low and equals 3.1 × 10^{-5} cm^2/s [21]).

On the other hand, it is well known [22] that a π-complex (**I**) is initially formed on the electrophilic addition of halogens to olefins. In strongly solvating media, this π-complex dissociates into two solvated ions, an X^- anion and a cation (**II**). The subsequent transformations of this cation involve its reaction with nucleophilic agents (Nu) present in the reaction medium:



Addition products (**III**) and chlorohydrin (**IV**) (when water is a nucleophilic agent) are formed simultaneously, and the ratio between these products primarily depends on the relative activity of nucleophilic agents and on their concentration in solution [12].

The accumulation of 1,2,3-trichloropropane in solution (Fig. 2, curve *4*) was almost linear, and its amount after a 4-h experiment was as high as ~1 × 10^{-2} mol. Note that the reaction mixture remained homogeneous during this period; that is, an organic phase was absent from the system. However, an organic phase appeared in the reaction medium (the water solubility of 1,2,3-trichloropropane is 1.3 × 10^{-2} mol/l under ordinary conditions [23]) and the course of the process dramatically changed when the experiment was performed further (this period is not shown in the figures). The course of this process under these conditions is beyond the scope of this paper; this problem was partially considered previously [14].

Thus, based on the above consideration, the following simplified scheme of simultaneous and consecutive chemical reactions occurring in the system can be proposed:

$$Cl_2 + H_2O \xrightarrow{k_1} HOCl + Cl^- \quad \text{(I)}$$

$$HOCl + \text{Allyl chloride} \xrightarrow{k_2} \text{Glycerol dichlorohydrins} \quad \text{(II)}$$

$$HOCl \xrightarrow{k_3} Cl^- \quad \text{(III)}$$

$$Cl_2 + \text{Allyl chloride} \xrightarrow{k_4} [M] \quad \text{(IV)}$$

$$[M] + H_2O \xrightarrow{k_5} \text{Glycerol dichlorohydrins} + Cl^- \quad \text{(V)}$$

$$[M] + Cl^- \xrightarrow{k_6} \text{1,2,3-Trichloropropane} + Cl^- \quad \text{(VI)}$$

According to this scheme, glycerol dichlorohydrins are formed both via hypochlorous acid by reaction (II) and by the interaction of the intermediate complex [M] with water in reaction (V); 1,2,3-trichloropropane is formed in reaction (VI) by the interaction of [M] and Cl^-; and Cl^- is formed in reactions (I), (III), and (V).

Thus, the rate equations for the formation and accumulation of the above reaction products have the forms

$$d[\text{Glycerol dichlorohydrins}]/d\tau = w_2 + w_5 = k_2'[HOCl] + k_5'[M], \quad (1)$$

where $k_2' = k_2[\text{Allyl chloride}]$ and $k_5' = k_5[H_2O]$;

$$d[\text{1,2,3-Trichloropropane}]/d\tau = w_6 = k_6[M][Cl^-]; \quad (2)$$

$$d[Cl^-]/d\tau = w_1 + w_3 + w_5 = k_1[Cl_2][H_2O] + k_3[HOCl] + k_5'[M]. \quad (3)$$

In a quasi-steady state,

$$d[HOCl]/d\tau = w_1 - k_2'[HOCl] - k_3[HOCl] = 0$$

and the intermediate concentration $[HOCl] = w_1/(k_2' + k_3)$. Similarly,

$$d[M]/d\tau = w_4 - k_5'[M] - k_6[M][Cl^-]$$

and $[M] = w_4/(k_5' + k_6[Cl^-])$.

The ratios between the reaction products are determined by the equations

$$\frac{d[\text{glycerol dichlorohydrines}]}{d[\text{1,2,3-Trichloropropane}]} = \frac{k_2'[HOCl]}{k_6[M][Cl]} + \frac{k_5'}{k_6[Cl^-]},$$

$$\frac{d[Cl^-]}{d[\text{1,2,3-Trichloropropane}]} = \frac{w_1}{k_6[M][Cl^-]} + \frac{k_3[HOCl]}{k_6[M][Cl^-]} + \frac{k_5'}{k_6[Cl^-]}.$$

Inserting the concentrations of intermediate species [HOCl] and [M] into these equations and upon rearrangement, we obtain

$$\frac{[\text{glycerol dichlorohydrines}]}{[\text{1,2,3-Trichloropropane}]} = \frac{w_1}{w_4(1 + k_3/k_2')} + \left(1 + \frac{w_1}{w_4(1 + k_3/k_2')}\right)\frac{k_5'}{k_6[Cl^-]}, \quad (4)$$

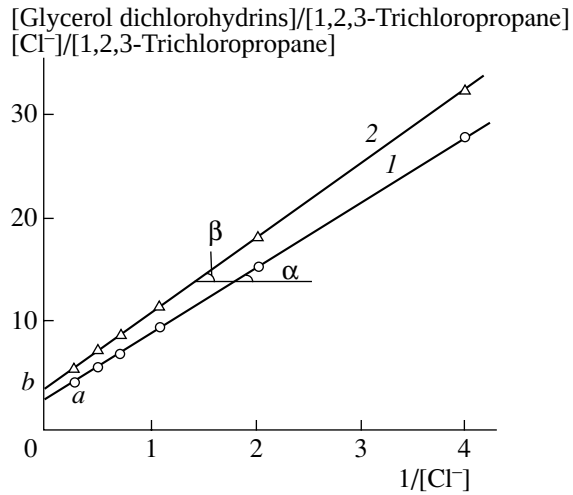


Fig. 3. (*1*) [Glycerol dichlorohydrins]/[1,2,3-Trichloropropane] and (*2*) [Cl^-]/[1,2,3-Trichloropropane] ratios as functions of 1/[Cl^-].

$$\frac{[Cl^-]}{[1,2,3\text{-Trichloropropane}]} = \frac{w_1}{w_4}\left(1 + \frac{k_3/k_2'}{1 + k_3/k_2'}\right) + \left[1 + \frac{w_1}{w_4}\left(1 + \frac{k_3/k_2'}{1 + k_3/k_2'}\right)\right]\frac{k_5'}{k_6[Cl^-]}. \quad (5)$$

It follows from Eqs. (4) and (5) that the ratios [Glycerol dichlorohydrins]/[1,2,3-Trichloropropane] and [Cl^-]/[1,2,3-Trichloropropane] linearly depend on the reciprocal of chloride ion concentration (1/[Cl^-]), and the respective slopes are

$$\tan\alpha = \left(1 + \frac{w_1}{w_4(1 + k_3/k_2')}\right)\frac{k_5'}{k_6}, \quad (6)$$

$$\tan\beta = \left[1 + \frac{w_1}{w_4}\left(1 + \frac{k_3/k_2'}{1 + k_3/k_2'}\right)\right]\frac{k_5'}{k_6}. \quad (7)$$

The intercepts on the axis of ordinates correspond to the first members of Eqs. (4) and (5), that is,

$$a = \frac{w_1}{w_4(1 + k_3/k_2')}, \quad (8)$$

$$b = \frac{w_1}{w_4}\left(1 + \frac{k_3/k_2'}{1 + k_3/k_2'}\right). \quad (9)$$

A combined solution of Eqs. (6) and (8) demonstrates that $k_5'/k_6 = \tan\alpha/(1 + a)$, and it follows from Eqs. (7) and (9) that $k_5'/k_6 = \tan\beta/(1 + b)$. Next, we find from Eqs. (8) and (9) that $b/a = 1 + 2k_3/k_2'$ or $k_3/k_2' = (b - a)/2a$. According to Eq. (8), $w_1/w_4 = (1 + k_3/k_2')a = (a + b)/2$.

Figure 3 demonstrates experimental data on the ratios [Glycerol dichlorohydrins]/[1,2,3-Trichloropropane] and [Cl^-]/[1,2,3-Trichloropropane] as functions of 1/[Cl^-], which were obtained upon filling the reactor with hydrochloric acid. The following values were obtained from the presented graphs: $a = 3.0$, $b = 3.5$, $\tan\alpha = 6.25$, and $\tan\beta = 7.25$.

Knowing these parameters and taking into account that the constant reactant concentrations in the course of stable operation of the system are [Allyl chloride] = 0.7×10^{-2} and [H_2O] = 55.5 mol/l, the following ratios between the rate constants of the corresponding reactions were found: $w_1/w_4 = 3.25$, $k_1/k_4 = 4.1 \times 10^{-4}$, $k_3/k_2' = 8.3 \times 10^{-2}$, $k_3/k_2 = 5.8 \times 10^{-4}$, $k_5'/k_6 = 1.6$, and $k_5/k_6 = 2.9 \times 10^{-2}$.

It follows that, first, the actual rate of HOCl formation by reaction (I) is higher than the rate of formation of complex [M] by a factor of 3.25 ($w_1/w_4 = 3.25$), although the true reaction rate constant of formation of this complex (k_4) is higher than the reaction rate constant of HOCl formation (k_1) by at least three orders of magnitude. This implies that the concentration factors play the major role in this case.

Second, the relative reactivity of the chloride ion in the chlorohydrination of allyl chloride in water at 50°C (k_6) is higher than the activity of the water molecule (k_5) by a factor of ~35: $k_5/k_6 = 2.9 \times 10^{-2}$. It is of interest that converting the published data [24] on the nucleophilic activities of chloride ions and water molecules toward free chlorine gave a value that was higher by an order of magnitude (3.1×10^2 in place of 35).

Third, the rate constant of the reaction between allyl chloride and HOCl (k_2) is higher than the rate constant of HOCl decomposition (k_3) under these conditions by four orders of magnitude. Using published data [19, 20], according to which $k_3 \cong 10^{-4}$ l mol^{-1} s^{-1}, the rate constant of formation of glycerol dichlorohydrins from HOCl and allyl chloride can be estimated: $k_2 = k_3/5.8 \times 10^{-4} = 1.7 \times 10^{-1}$ l mol^{-1} s^{-1}. Thus, it is unlikely that the reaction of formation of glycerol dichlorohydrins from allyl chloride and HOCl can be classified under fast reactions [25].

The relative contributions to the formation of glycerol dichlorohydrins from reactions (II) and (IV) can be found theoretically using the corresponding differential equation

$$\frac{d[\text{glycerol dichlorohydrines}]_2}{d[\text{glycerol dichlorohydrines}]_5} = \frac{k_2'[HOCl]}{k_5'[M]} = \frac{w_1}{w_4(1 + k_3/k_2')}\left(1 + \frac{k_6[Cl^-]}{k_5'}\right).$$

Substituting experimental ratios between the reaction rates and rate constants into this equation gives

$$[\text{Glycerol dichlorohydrins}]_2/[\text{Glycerol dichlorohydrins}]_5 = 3.0 + 1.9[Cl^-].$$

The physical meaning of this expression is that glycerol dichlorohydrins are formed both via HOCl by reaction (II) and via intermediate complex [M] by reaction (V). The fraction of glycerol dichlorohydrins produced via HOCl linearly increased as the degree of reaction increased, that is, with an increase in the concentration of chloride ions in the system. The maximum amount (~25%) of glycerol dichlorohydrins was formed through the intermediate complex at the beginning of the process when the concentration of chloride ions was minimum ($[Cl^-] \longrightarrow 0$). In the experiments with a maximum concentration of chloride ions (3.6 mol/l), the fraction of glycerol dichlorohydrins formed through HOCl was ~90%. At a chloride ion concentration of 0.4 mol/l, which was recommended for industrial processes [11], 80% glycerol dichlorohydrins was formed through hypochlorous acid by reaction (II).

In summary, note that Eq. (4) describes the theoretical dependence of the process under consideration on the concentration of chloride ions in the reaction medium. That is, a maximum yield of the target product in the chlorohydrination of allyl chloride with chlorine in water can be practically attained only in a very dilute solution. Because the subsequent processing of a very dilute solution of glycerol dichlorohydrins is energy consuming, the optimum concentration of glycerol dichlorohydrins (and Cl^-) should be determined (calculated) in each specific case in order to provide continuous operation of the relevant plant.

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