INVESTIGATION OF THE PROCESS OF AQUEOUS ACID ENOLIZATION OF 2,3;4,6-DI-O-ISOPROPYLIDENE-2-KETO-L-GULONIC ACID

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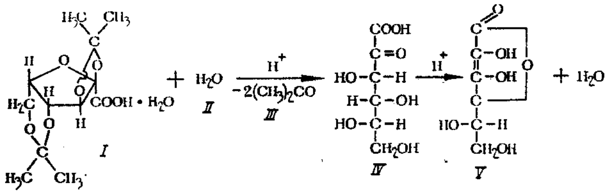
The hydrolysis reaction of the hydrate of 2,3;4,6-di-O-isopropylidene-2-keto-L-gulonic acid (I) and subsequent emolization of the resulting ketoacid serves as the concluding stage in the manufacture of L-ascorbic acid (V).



(1)

Methods of enolization of (I) catalyzed by a mineral acid such as hydrogen chloride are widely used. These methods may be grouped into three main groups. To the first group belong those that are effected in hydrochloric acid of various concentration. The reaction is complete in 6 h and the yield of acid (V) does not exceed 80% according to [2, 3, 6, 10-12]. In the second group are methods of enolization carried out in organic solvents (including such compounds as chloroform, dichloroethane, trichloroethylene, aromatic hydrocarbons, and their halogen substituted derivatives) with the participation of hydrogen chloride dissolved in C_1-C_4 alcohols. The reaction time oscillates between 12 and 48 h and the yield of (V) may vary from 50 to 87% according to [3, 4, 6]. The third group includes enolization processes occurring in the mentioned solvents using concentrated hydrochloric acid. The reaction time in this case was reduced to 6 h, the yield of acid (V) was within the limits 78-85% [2, 9]. In view of the absence in these variants of the method of alcohols to homogenize the reaction mixture the reaction was heterogeneous during the whole process (both the reactants and the majority of the reaction products has low solubility in the solvents used). The role of the solvent is mainly the creation of a continuous phase in the reaction mixture providing favorable conditions for the interaction of reactants present in the dispersed phase. It was also shown in [8] that the application of emulsifying surfactants at 0.05-10 wt.% assigned the breaking up of the dispersed phase which increased the reaction rate. The duration of the process was reduced to 4-6 h and the yield of acid (V) reached 94%. This method may be considered as the most promising for further investigation.

EXPERIMENTAL

Experiments were carried out in a thermostatted 250-ml capacity glass reactor, fitted with an anchor stirrer (rate of rotation 100 rpm) for full stirring and a reflux condenser, under isothermal conditions at 50, 60, and 70°C. Initial ratios of components were $C(I)_0$: $C(II)_0 = 2.3$; $C_K:C_{(I)_0} = 0.379$; $C_T:C(I)_0$ from 1.358 to 6.777. In this $C(I)_0$ and $C(II)_0$ were the initial concentrations of compounds (I) and (II), C_K and C_T the concentrations of hydrogen chloride and trichloroethylene respectively (in moles per liter). Glycerol monostearate was used in an amount of 2.97 g per mole (I). Reaction time was from 5 to 360 min. Each experiment was repeated under the given conditions 1-3 times. Industrial batches of (I) with a content of main substance of 92 wt.%, and concentrated hydrochloric acid and the trichloroethylene of chemically pure grade were used in this work. Before the start of the experiment the mixture of trichloroethylene, (I), and surfactant was heated to the required temperature, then the calculated quantity of hydrochloric acid was added, and counting of the reaction time was begun. At the end of the given time the reaction mixture was rapidly cooled to room

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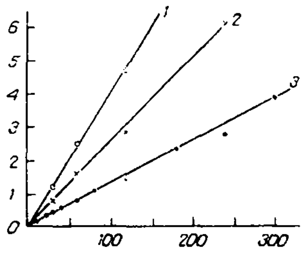

Fig. 1

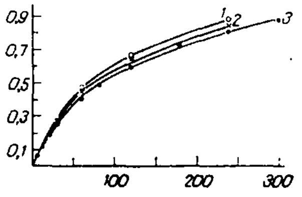

Fig. 2

Fig. 1. Results of processing the experimental results by means of equation [5] at 70°C and various concentrations of trichloroethylene. Time (min) is on the abscissa, values of the left portion $F(C_{(V)})\cdot 10^3$ of equation (5) (liter/mole) on the ordinate. Values of C_T/C_{I_0} were: 1) 6.777; 2) 4.068; 3) 1.358.

Fig. 2. Relationship of the degree of conversion of (I) into (V) at 70°C and various concentrations of trichloroethylene. Time (min) is on the abscissa, degree of conversion $C_{(V)}/C_{(I)_0}$ on the ordinate. Values of $C_T/C_{(I)_0}$ were: 1) 6.777; 2) 4.068; 3) 1.358.

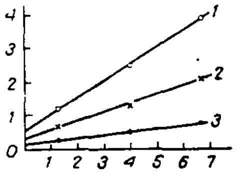

Fig. 3. Dependence of the size of K on concentration of trichloroethylene and temperature. Values of $C_T/C_{(I)_0}$ are on the abscissa, the process constant $K\cdot 10^3$ [in liter/mole•min] on the ordinate. 1) 70°C; 2) 60°C; 3) 50°C.

temperature and distilled water was added, calculated at about 70 moles per mole of initial (I). Then after dissolving the crystals of ascorbic acid the aqueous and organic layers were separated and the content of (V) in each determined by iodometric titration.

RESULTS AND DISCUSSION

As is known the process of enolization is preceded by hydrolysis of (I) to 2-keto-L-gulonic acid (IV) and this was confirmed by us by TLC.

Process (1) corresponds to the empirical equation

$$(I) + (II) \longrightarrow 2(III) + (V). \qquad (2)$$

To describe the kinetics applying to the overall mechanism (2) the following equation was used.

$$\frac{dC_{(V)}}{d\tau} = K\cdot C_{(I)}\cdot C_{(II)}, \qquad (3)$$

where $C_{(I)}$, $C_{(II)}$, $C_{(V)}$ are the running concentrations of compounds (I), (II), and (V), respectively (mole/liter), τ time (min), and K the reaction rate constant [liter/(mole•min)].

Integration of equation (3) using the balance ratios

$$C_{(I)_0} - C_{(I)} = C_{(II)_0} - C_{(II)} = \frac{1}{2} C_{(III)} = C_{(V)} \qquad (4)$$

TABLE 1. Kinetic Constants for the Acid Enolization of the Hydrate of 2,3;4,6-Di-O-isopropylidene-2-keto-L-gulonic Acid (I)

Temperature, °C	$\frac{C_T}{C_{(I)_0}}$	$K \cdot 10^3$, liter/(mole·min)
50	1,358	0,301±0,028
50	4,068	0,512±0,027
50	6,777	0,771±0,059
60	1,358	0,688±0,083
60	4,068	1,320±0,122
60	6,777	2,016±0,201
70	1,358	1,198±0,068
70	4,068	2,535±0,093
70	6,777	3,980±0,130

leads to the relationship

$$F(C_{(V)}) = \frac{1}{C_{(II)_0} - C_{(I)_0}} \ln \left[\frac{C_{(I)_0}(C_{(II)_0} - C_{(V)})}{C_{(II)_0}(C_{(I)_0} - C_{(V)})} \right] = K \cdot \tau . \qquad (5)$$

Here $F(C_{(V)})$ denotes the left portion of equation (5) (in liter/mole).

The experimental data treated according to formula (5) for a temperature of 70°C are shown in Fig. 1 in coordinates $K(C_{(V)})$ and τ. At fixed concentrations of trichloroethylene the values of $F(C_{(V)})$ lay on straight lines passing through the origin of coordinates. Similar relationships were obtained at other temperatures. Thus the size of K is a function of trichloroethylene concentration (see Table 1).

It was established that the reactants and reaction products, with the exception of acetone (III), had a low solubility in trichloroethylene. Reaction proceeded in the dispersed phase which consisted of drops of aqueous solution of reactants and reaction products. In the interaction process the separate components of the dispersed phase will exit from it dissolving in trichloroethylene. First this will be acetone. However allowing for the fact that the volume of the continuous phase significantly exceeds the volume of the dispersed phase, a significant portion of its low solubility components, such as water, may also pass into the continuous phase. Consequently the concentration of components in the reaction zone, apart from the strictly chemical interaction, will be determined by the rate of mass transfer and by the rules of equilibrium distribution between the phases. The presence of a surfactant aids finer dispersion which leads to an increase of interphase surface and a reduction in the resistance to mass transfer. In view of the low reaction rate it may be proposed that the transfer phenomenon is not the limiting influence on interaction. The linearity of the experimental data by means of equation (5) serves as indirect confirmation of this. Thus the distribution of components between the phases in the present case is seemingly mainly determined by the equilibrium rules of a multicomponent reaction system. It should also be noted that the presence of a surfactant may lead to a significant rearrangement of the phase diagrams for the equilibrium [7] including changes and leads to the appearance of new regions of existence of phases. In view of the complexity of determining the true concentrations of the reacting substances in the reaction zone, concentrations were calculated by us in the calculations for the total volume of the reaction mass. In our opinion the dependence of K on trichloroethylene also determines this. In spite of the fact that C_T varies in experiments more than 2 times, the rate of accumulation of ascorbic acid is changed insignificantly (Fig. 2). Some increase in the degree of conversion of (I) into (V), determined by the ratio $C_{(V)}/C_{(I)_0}$, with growth of C_T is probably explained by the drop of the concentration of acetone in the aqueous phase as it passes into the continuous phase.

Analysis of the calculated results showed that the relationships between K and $C_T/C_{(I)_0}$ were linear for the investigated temperatures (Fig. 3) and were described by an equation of the form

$$K = K_{ef} + K_I \cdot \frac{C_T}{C_{(I)_0}} . \qquad (6)$$

The independent term in formula (6) K_{ef} is equal to the size of the segment cut off by the appropriate straight line on the ordinate axis, and may be considered as the effective constant (at a given value of C_K) for the reaction which should take place in the absence of trichloroethylene ($C_T/C_{(I)_0} = 0$). By substituting ratio (6) in equation (3) we obtain

$$\frac{dC_{(V)}}{d\tau} = K_{\text{эф}} \cdot C_{(I)} \cdot C_{(II)} + K_I \cdot \frac{C_T}{C_{(I)_0}} \cdot C_{(I)} \cdot C_{(II)}. \qquad (7)$$

The results of the calculation of K [in liter/(mole•min)] are given in Table 1. When assessing the constants in formula (6) it was found that at 50°C $K_{ef} = 10^{-4} \bullet (1.790 \pm 0.170)$, $K_I = 10^{-4} \bullet (0.881 \pm 0.078)$, at 60°C $K_{ef} = 10^{-4} \bullet (3.450 \pm 0.590)$, $K_I = 10^{-4} \bullet (2.491 \pm 0.271)$, and at 70°C $K_{ef} = 10^{-4} \bullet (5.730 \pm 0.554)$, $K_I = 10^{-4} \bullet (5.218 \pm 0.254)$. The modified least squares method from [1] was used in the calculation of K, but K_{ef} and K_I were found by applying the indicated method in its traditional form. Assessment of the adequacy of the obtained relationships and calculation of the dipsersions was carried out by the known methods of [5]. On finding the dispersions of coefficients K_{ef} and K_I the previously determined dispersion of values of K was considered as caused by the error of the experiment.

On the basis of the obtained results it was established that the carrying out of the enolization reaction by the proposed method was expedient at 70°C, $C_T:C_{(I)_0} = 6.777$ and ratios of components as indicated in the description of the kinetic experiments. An increase in the duration of the process to 8 h showed that after 6 h reaction the rate of accumulating acid (V) fell sharply. As a result of the growth in the rate of destruction processes and resinification, its content in the reaction mixture proved to be less after 8 h than after 7 h. It may therefore be considered that the duration of the reaction must not exceed 6 h. Under the given conditions a yield of 90-93 mole % was achieved.

The developed mathematical model and the found conditions for interaction may be used in selecting an appropriate type of reactor and calculating for it.

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