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KINETICS OF THE FORMATION OF ALCOHOL AND ALKYL ACID IN THE REACTION OF PROPYLENE WITH AQUEOUS SULFURIC ACID

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A number of works have been devoted to the study of the kinetics of absorption of olefins by sulfuric acid ([1]-[6]). Most of these works have one general fundamental shortcoming: they were carried out under conditions in which the rate of absorption is limited by diffusion processes.

An exception is the work of Kh. R. Rustamov ([5]), in which the true kinetics of the gross absorption of propylene and *n*-butylene by thin films of sulfuric and phosphoric acids was studied in detail under conditions excluding diffusion interference.

We have studied the kinetics of absorption of propylene by 67% H_2SO_4 at 42, 50, 70, 75, 80, and 90° and an initial pressure $P^0_{C_3H_6} \sim 300$ mm Hg. The amount of acid in individual experiments varied from 2.5 to 11 g. The experiments were carried out in an all-glass apparatus (Fig. 1) equipped with a glass circulating pump 1. With the aid of the pump, propylene containing the required amount of water vapor was passed through a reactor filled with sulfuric acid. The reactor was a glass vessel of volume 60 cm^3, inside which a plate of porous glass (Schott No. 2) 20 mm in diameter was sealed in. Propylene passed through the acid, converting the entire mass of it into a continuous foam. The reaction occurred between the gas, the main part of which was in the bubbles, and the film of acid. Under certain conditions we were able to observe the true kinetics of propylene absorption, uncomplicated by diffusion interference.

The progress of the reaction was followed both by the pressure drop in a closed system with a gas volume of 2 l and by analyses of the reaction mixture for the content of alkyl acid and alcohol. The analysis for alkyl acid was carried out acidimetrically ([6],[7]). The alcohol was analyzed by the method of oxidative titration. To separate the alcohol from the alkyl acid, which interfered with its determination, the solution containing water, H_2SO_4, alkyl acid, and alcohol was neutralized with a concentrated KOH solution, and the water together with the alcohol was distilled off in vacuum (about 30 mm) at 35-40°. The first receiver was cooled with ice and salt, the second with liquid air.

The constant of the rate of gross absorption was calculated from the average rate on the initial segment of the kinetic curve (Fig. 2) at 3-4% conversion, assuming that the rate of the reverse reaction at the beginning was negligibly small. The values of the constants calculated in this way are close to the values obtained from the data of Kh. R. Rustamov (^{5}), who deliberately worked in the absence of diffusion interference. Table 1 gives the values of the rate constants gross absorption of propylene by 67% H_2SO_4, reduced to 1 g of acid and 1 liter of the space above the acid.

Table 1

Temperature, °C	42	50	70	75
$K \cdot 10^{-4}$ min^{-1}, our data	3.32	5.71	9.6	11.0
$K \cdot 10^{-4}$ min^{-1}, according to Rustamov	4.46	5.75	11.7	13.8

Confirmation that we were indeed working in the kinetic region is provided by the observed proportionality between the value of the gross absorption rate and the amount of acid (Fig. 3). The fact of proportionality indicates that the entire mass of acid present in the vessel participates simultaneously in the reaction.

Experiments carried out at 70° were interrupted at different times, and the reaction mixture was analyzed for alkyl acid and alcohol content. The data obtained are given in Table 2. As can be seen from the table, the initial rate of alcohol formation is approximately 4 times greater than the rate of alkylation.

Table 2

Kinetics of accumulation of isopropyl alcohol and alkyl acid at 70°
(amount of 67% H_2SO_4 7.7 g, volume of gas phase 2 l)

$P^{\circ}_{C_3H_6}$, mm Hg	Time, min	Absorbed C_3H_6, mmol	Formed u-$C_3H_7SO_4H$, mmol	Formed u-C_3H_7OH, mmol
314.5	60	6.4	1.8	4.6
308.5	101	7.1	0.8	6.3
303.0	139	10.1	2.0	8.4

$P^{\circ}_{C_3H_6}$, mm Hg	Time, min	Absorbed C_3H_6, mmol	Formed *u*-$C_3H_7SO_4H$, mmol	Formed *u*-C_3H_7OH, mmol
306.0	180	12.3	2.9	9.4
305.0	225	13.6	3.0	10.6
306.0	249	12.5	3.5	9.0
310.0	360	12.7	3.2	9.5
312.5	456	14.9	3.8	11.1

Without going into the details of the complex acid-catalytic processes that occur when propylene dissolves in the acid, they may be represented in the form of three reversible reactions:

I. Formation of alkyl acid

$$C_3H_6 + H_2SO_4 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{u-}C_3H_7SO_4H.$$

II. Direct formation of alcohol

$$C_3H_6 + H_2O \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{u-}C_3H_7OH.$$

III. Saponification of the alkyl acid

$$\text{u-}C_3H_7SO_4H + H_2O \underset{k_6}{\overset{k_5}{\rightleftarrows}} \text{u-}C_3H_7OH + H_2SO_4.$$

Fig. 1. Diagram of the apparatus: 1 —glass circulating pump; 2 —pump valves; 3 —reaction vessel; 4 —flask with water; 5 —manometer for observing the course of the reaction; 6 —buffer volume.

In the literature it has not yet been established whether the main amount of alcohol is formed via path II or III. However, the very fact of alcohol accumulation in parallel with the alkyl acid (see the kinetic curves in Fig. 2) excludes the possibility of its formation only by reaction III—by saponification

alkyl acid. Let us compare the experimental curves for the accumulation of products with the theoretical curves obtained on the basis of the scheme written above, under reasonable assumptions about the ratio of the rate constants of the individual steps.

Let us introduce dimensionless concentrations $\alpha = x/a_0$ and $\beta = y/a_0$, where a_0, x, and y are the concentrations of the reactants in the liquid phase: a_0 is the initial concentration of C_3H_6, x is the current concentration of *u*-$C_3H_7SO_4H$, and

Fig. 2. Kinetic curves of gross absorption of propylene in 67% H2SO4. Gas-phase volume 2 l; amount of acid 7.7 g; $P^0_{C_3H_6}$ = 310 mm Hg; 1—42°; 2—50°; 3—70°; 4—80°; 5—90°

Figure 1: Fig. 2. Kinetic curves of gross absorption of propylene in 67% H2SO4. Gas-phase volume 2 l; amount of acid 7.7 g; $P^0_{C_3H_6}$ = 310 mm Hg; 1—42°; 2—50°; 3—70°; 4—80°; 5—90°

y is the current concentration of u-C_3H_7OH. Assuming that the concentrations of H_2SO_4 and H_2O remain unchanged during the process, we write:

$$\frac{d\alpha}{dt} = k'_1(1-\alpha-\beta) - k_2\alpha - k'_5\alpha + k'_6\beta; \tag{1}$$

$$\frac{d\beta}{dt} = k'_1(1-\alpha-\beta) - k_4\beta - k'_5\alpha - k'_6\beta. \tag{2}$$

Here $k'_1 = k_1[H_2SO_4]_0$; $k'_5 = k_5[H_2SO_4]_0$; $k'_6 = k_6[H_2O]_0$.

Solving this system of linear equations, we obtain the law of variation of the concentrations of u-$C_3H_7SO_4H$ and u-C_3H_7OH with time:

$$\alpha = P_1e^{r_1t} + Q_1e^{r_2t} + \frac{\gamma_1}{\rho}; \tag{3}$$

$$\beta = P_2e^{r_1t} + Q_2e^{r_2t} + \frac{\gamma_2}{\rho}, \tag{4}$$

where

$$P_1 = -\frac{k'_1 + r_2\gamma_1/\rho}{r_2 - r_1}, \qquad P_2 = -\frac{k'_3 + r_2\gamma_2/\rho}{r_2 - r_1},$$

$$Q_1 = \frac{k'_1 + r_1\gamma_1/\rho}{r_2 - r_1}, \qquad Q_2 = \frac{k'_3 + r_1\gamma_2/\rho}{r_2 - r_1}.$$

$$r_{1,2} = \frac{(k'_3 + k_4 + k'_6 + k'_1 + k_2 + k_5) \pm \sqrt{(k'_3 + k_4 + k'_6 + k'_1 + k_2 + k_5)^2 - 4\rho}}{2},$$

$$\rho = (k'_1 + k_2 + k_5)(k'_3 + k_4 + k'_6) - (k'_6 - k'_1)(k'_5 - k'_3),$$

$$\gamma_1 = k'_3k'_6 + k_1(k_4 + k'_6),$$

$$\gamma_2 = k_1' k_5' + k_3'(k_2 + k_5).$$

Fig. 2. Kinetic curves of gross absorption of propylene in 67% H_2SO_4. Gas-phase volume 2 l; amount of acid 7.7 g; $P^0_{C_3H_6} = 310$ mm Hg;
1—42°; 2—50°; 3—70°; 4—80°; 5—90°.

Let us find the time dependence of α and β for different ratios between the rate constants of the individual steps. To carry out calculations by the formulas obtained, it is necessary to estimate the rate constants of the individual steps. For this purpose, assuming, in the zero approximation, that the formation of u-$C_3H_7SO_4H$ and u-C_3H_7OH proceeds only by reactions I and II, respectively, we find the constants k_1 and k_3 from the average rate on the initial portions of the kinetic curves for the alcohol and the alkyl acid. The reverse reactions at small degrees of conversion are neglected. Since the absolute amount of dissolved propylene is unknown, the rate constants were found as the quotient obtained by dividing the rate by the partial pressure of propylene. In this case the Henry coefficient is included in the rate constant.

Case 1. The saponification reaction of the alkyl acid is absent, i.e. $k_5' = k_6' = 0$. Taking $k_1' = 1$, we obtain, on the basis of kinetics and the equilibrium condition: $k_2 = 4$, $k_3 = 4$, $k_4 = 6.5$. After substituting the values of the constants into equations (3) and (4), we obtain

$$\alpha = 13.45 \cdot 10^{-2} - 6.1 \cdot 10^{-2} e^{-11.15\tau} - 7.35 \cdot 10^{-2} e^{-7.35\tau},$$

$$\beta = 33.0 \cdot 10^{-2} - 37.8 \cdot 10^{-2} e^{-11.15\tau} + 4.8 \cdot 10^{-2} e^{-7.35\tau}.$$

Taking $k_1' = 7.7 \cdot 10^{-4}$ min^{-1} as unity, we thereby introduce a new time scale $\tau = k_1' t$, where t is the time in minutes.

Case 2. Alcohol is formed both in parallel with u-$C_3H_7SO_4H$ and by saponification of the latter. The true concentration of physically dissolved propylene is evidently much smaller than the concentrations of u-C_3H_7OH and u-$C_3H_7SO_4H$ found by us. Therefore, in order that the rate of saponification be equal to or less than the rate of addition of C_3H_6 to H_2O and H_2SO_4 in reactions II and I, the constants k_5 and k_6 must be smaller than k_1 and k_3. Let again $k_1' = 1$, $k_2 = 4$, $k_3 = 4$, $k_4 = 7$, and $k_5 = k_6 = 0.5$ ($k_5 = k_6$ is adopted for simplicity); then:

$$\alpha = 12.3 \cdot 10^{-2} - 5.3 \cdot 10^{-2} e^{-11.15\tau} - 7.0 \cdot 10^{-2} e^{-5.86\tau},$$

$$\beta = 28 \cdot 10^{-2} - 45 \cdot 10^{-2} e^{-11.15\tau} + 17 \cdot 10^{-2} e^{-5.86\tau}.$$

Fig. 3 and Fig. 4

Figure 2: Fig. 3 and Fig. 4

Having found, from the values of α and β, the corresponding amounts of u-$C_3H_7SO_4H$ and u-C_3H_7OH formed, one can construct the calculated curves for accumulation of the latter and compare them with the experimental ones (Fig. 4). As is seen from the figure, the experimental points lie closer to the curves corresponding to case 1. Taking into account the saponification reaction of the alkyl acid gives a noticeable deviation from the experiment.

Fig. 3. Dependence of the initial rate of the gross absorption reaction of C_3H_6 in 67% H_2SO_4 on the amount of acid. Gas-phase volume 2 l, $P^0_{C_3H_6} = 310$ mm Hg; 1 –42°; 2 –50°; 3 –70°.

Fig. 4. Comparison of experimental data (points) with calculated data (lines): 1 –case 1; 2 –case 2; a and b –kinetic curves of accumulation of u-$C_3H_7SO_4H$ (a) and u-C_3H_7OH (b); v –amount of absorbed propylene.

From the brief analysis presented, one may conclude that the main part of the alcohol, if not all of it, is formed not as a result of saponification of u-$C_3H_7SO_4H$, but in parallel with it in the reaction of C_3H_6 with water.

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CITED LITERATURE

1. H. S. Davis, R. Schuler, *J. Am. Chem. Soc.*, **52**, 721 (1930).
2. V. V. Pigulevskii, N. V. Rudakova, *Materials on Cracking and Chemical Processing of Its Products*, vol. 1, 1933, p. 67.
3. V. G. Moor, *Materials on Cracking and Chemical Processing of Its Products*, vol. 3, 1936, p. 108.
4. M. A. Kerdivarenko, P. K. Migal, M. Kh. Kishinevskii, *ZhPKh*, **28**, 459 (1955).
5. Kh. R. Rustamov, Doctoral dissertation, Institute of Chemical Physics, Academy of Sciences of the USSR, 1954.
6. R. Robey, *Ind. and Eng. Chem.*, **33**, 1077 (1941).

7. R. W. Schrage, E. H. Amick, *Ind. and Eng. Chem.*, **42**, 2550 (1950).

8. A. V. Rakovskii, *Chemical Kinetics and Catalysis*, Moscow–Leningrad, 1932, p. 26.

Note: Figure translations are in progress. See original paper for figures.