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Abstract

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Kinetics of the Vapor-Phase Hydration of Ethylene on a Phosphoric-Acid Catalyst

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The reaction

$$C_2H_4(g) + H_2O(g) = C_2H_5OH(g) \tag{1}$$

is widely used in industry. The process is carried out at pressures of 60–80 atm and temperatures of 280–300°; the catalyst is phosphoric acid on a porous support consisting mainly of SiO_2. We studied the kinetics of the reaction in a flow system under conditions close to industrial ones, with a catalyst of phosphoric acid on silica gel in the form of grains 2.5 mm in size. Experiments involving variation of the grain size and of the H_3PO_4 content in the catalyst showed that the reaction proceeded in the kinetic region.

It was natural to assume that the mechanism of reaction (1) should be analogous to the mechanism, previously studied in our laboratory (^{1}), of the vapor-phase hydration of C_2H_2 on a phosphoric-acid catalyst, i.e., should correspond to the mechanism of olefin hydration proposed by Taft (^{2}). Then the kinetics of reaction (1) should differ from the kinetics of hydration of C_2H_2 only insofar as it is necessary to take its reversibility into account. As applied to reaction (1), the scheme of the mechanism may be represented as follows:

$$C_2H_4 \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} H_2C \overset{H^+}{\rightleftarrows} CH_2 \rightleftarrows H_3C{-}C^+H_2 \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} C_2H_5O^+H_2 \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} C_2H_5OH. \tag{2}$$

The rate-limiting stage is the conversion of the π-complex

$$H_2C \overset{H^+}{\rightleftarrows} CH_2$$

into the carbonium ion $H_3C{-}C^+H_2$. Scheme (2) leads to the following equation for the rate of the forward reaction:

$$v_1 = k_\pi K_1 s \frac{f_\pi}{f_{C_2H_4} f^{\neq}} P_{C_2H_4} h_0; \tag{3}$$

here k_π is the rate constant of the rate-limiting stage; K_1 is the equilibrium constant of

$$C_2H_4 + H^+ \rightleftarrows H_2C \overset{H^+}{\rightleftarrows} CH_2$$

(in terms of activities); s is the solubility coefficient of C_2H_4 in phosphoric acid $\left(s = a_{C_2H_4}/P_{C_2H_4}\right)$; f_π, $f_{C_2H_4}$, $f^{\neq}$ are, respectively, the activity coefficients of the π-complex, dissolved C_2H_4, and the transition state of the rate-limiting stage; h_0 is the acidity of phosphoric acid $(h_0 = a_{H^+} f_B / f_{BH^+}$, where B is a base); $P_{C_2H_4}$ is the partial pressure of C_2H_4.

Neglecting the change in s and in the ratio $f_\pi / f_{C_2H_4} f^{\neq}$ with change in the composition of the acid, we arrive at the equation

$$v_1 = k_1 h_0 P_{C_2H_4}. \tag{4}$$

Analogously, for the reverse reaction we obtain

$$v_2 = k_2 h_0 \frac{P_{C_2H_5OH}}{P_{H_2O}}. \tag{5}$$

The constants k_1 and k_2 are related to the equilibrium constant of reaction (1) by the equality

$$\frac{k_1}{k_2} = K_P. \tag{6}$$

Hence the observed reaction rate is given by the equation

$$v = k \left(P_{C_2H_4} - K_P^{-1} \frac{P_{C_2H_5OH}}{P_{H_2O}} \right); \tag{7}$$

here

$$k = k_1 h_0. \tag{8}$$

The quantity k must be constant at constant P_{H_2O}. Since the conversions of C_2H_4 and H_2O are small, the change in volume during the reaction may be neglected and one may take $v = dP_{C_2H_5OH}/dt$, where t is the "reaction time," calculated as the ratio of the volume of acid in the catalyst to the volumetric flow rate of the gas mixture (^{1}).

Table 1

Total pressure P, atm	Reaction time t, sec	Partial pressures, atm: C_2H_4	Partial pressures, atm: H_2O	Partial pressures, atm: C_2H_5OH	α/α_∞	$k \cdot 10^2$	P_2O_5, %	h_0	$k_1 \cdot 10^2$	$k' \cdot 10$
81	0,148	50,6	29,9	0,478	0,177	6,85	69,08	2,24	3,06	3,74
71	0,150	40,0	30,4	0,415	0,174	7,53	69,07	2,24	3,36	4,15
61	0,148	30,2	30,5	0,272	0,156	6,54	69,07	2,24	2,92	3,61
51	0,150	20,7	30,1	0,212	0,171	7,50	69,08	2,24	3,35	4,12
71	0,166	29,5	41,2	0,312	0,137	6,60	68,80	2,09	3,16	4,24
61	0,166	29,6	31,0	0,343	0,195	7,75	69,04	2,22	3,49	4,31
51	0,166	29,5	21,1	0,362	0,292	8,61	69,47	2,49	3,46	3,95
41	0,170	29,9	10,6	0,397	0,583	11,60	70,20	3,02	3,84	3,78
36	0,172	30,5	5,1	0,289	0,870	11,80	71,00	3,71	3,19	2,67
81	0,372	49,5	30,2	1,170	0,436	8,14	69,04	2,22	3,66	4,45
71	0,373	40,5	29,5	0,937	0,418	7,87	69,08	2,24	3,51	4,27
61	0,374	30,3	30,0	0,705	0,398	7,82	69,07	2,24	3,49	4,28
51	0,370	20,4	30,1	0,445	0,362	7,20	69,08	2,24	3,21	3,94
41	0,372	10,8	29,9	0,253	0,372	7,80	69,09	2,25	3,46	4,26
71	0,332	29,8	40,5	0,568	0,244	6,50	68,77	2,07	3,14	4,14
61	0,354	29,8	30,5	0,644	0,359	7,48	69,05	2,24	3,34	4,14
51	0,372	30,2	20,0	0,763	0,590	9,78	69,50	2,51	3,89	4,36
41	0,372	30,2	10,2	0,565	0,863	11,05	70,22	3,03	3,65	3,53
71	0,690	30,3	39,6	1,160	0,480	7,58	68,75	2,06	3,68	4,76
61	0,710	30,1	29,7	1,135	0,612	8,20	69,06	2,24	3,66	4,46
51	0,720	30,0	19,9	1,040	0,800	9,90	69,49	2,51	3,95	4,11
41	0,680	29,2	11,0	0,673	0,983	10,75	70,14	3,01	3,58	3,57

Integration of equation (7) at constant $P_{C_2H_4}$ and P_{H_2O} gives

$$k = -\frac{1}{t} K_{PP_{H_2O}} \ln \left(1 - \frac{P_{C_2H_5OH}}{K_{PP_{C_2H_4}} P_{H_2O}} \right). \tag{9}$$

Table 1 gives the experimental data for 290° and the values of k calculated from equation (9). The values of K_P were determined from equilibrium data (^{3}), since it was found that K_P does not depend on the ratio $N_{H_2O}/N_{C_2H_4}$ at given P and T (*). The degree of attainment of equilibrium is characterized by the ratio of the conversion of ethylene α to its equilibrium value α_∞.

As is evident from the table, upon variation of $P_{C_2H_4}$, and also of t, at constant P_{H_2O}, the value of k remains constant within the experimental error. With increasing P_{H_2O} the alcohol yield not only does not increase, but even decreases somewhat (provided that equilibrium is not reached), in qualitative agreement with equation (8).

To verify equation (8), the composition of the acid was calculated from the partial pressure of H_2O using the formula

$$\log \frac{P_{H_2O}}{P^0_{H_2O}} = \left(\frac{1075}{T} - 1.515\right)(72.4 - \%\,P_2O_5), \tag{10}$$

where $P^0_{H_2O}$ is the pressure of H_2O over H_3PO_4 (100%). Equation (10) was derived from previously published (^{5}) and additional data. From the acid composition, the values of h_0 were determined, assuming a linear dependence of $H_0 = -\log h_0$ on temperature (^{6,7}). Table 1 gives $k_1 = k/h_0$; they are approximately constant.

It should be kept in mind that the values of h_0 obtained by extrapolation are approximate. In any case, the fact that the alcohol yield changes little with significant variation of P_{H_2O} indicates a zero order of the reaction with respect to H_2O and confirms the basic initial assumption that H_2O does not participate in the rate-limiting stage of the reaction.

Table 2

°C	270°	290°	310°	330°
$k_1 \cdot 10^2$	1.00	3.46	10.50	25.3
$k' \cdot 10$	2.46	4.24	7.21	9.43

For technological calculations it is convenient to represent the reaction rate as an explicit function of P_{H_2O}. This can be done as follows. Since the catalyst consists of solutions of H_3PO_4 containing little H_2O, then, by analogy with Brand' s result (^{8}) for concentrated solutions of H_2SO_4, it may be assumed that

$$H_0 = \text{const} - \log \frac{X_{H_3PO_4}}{X_{H_2PO_4^-}}, \tag{11}$$

where $X_{H_3PO_4}$ is the mole fraction of H_3PO_4, etc. Considering H_2O as a base, we obtain

$$H_0 = pK - \log \frac{X_{H_3O^+}}{X_{H_2O}}. \tag{12}$$

Taking into account that $X_{H_2PO_4^-} = X_{H_3O^+}$, regarding X_{H_2O} as proportional to P_{H_2O} and $X_{H_3PO_4}$ as practically constant, we arrive at the approximate equality

$$h_0 = \frac{C}{P_{H_2O}^{1/2}}, \tag{13}$$

where C is a constant depending on temperature.

Equations (7), (8), and (13) give

$$v = \frac{k'}{P_{H_2O}^{1/2}} \left(P_{C_2H_4} - K_P^{-1} \frac{P_{C_2H_5OH}}{P_{H_2O}} \right), \tag{14}$$

where $k' = k_1 C$. To calculate k', equation (9) and the equality

$$k' = kP_{H_2O}^{1/2}. \tag{15}$$

were used. The values of k' given in Table 1 are approximately constant. Data analogous to those presented in Table 1 were obtained in experiments at 270, 310, and 330°, covering the same values of $P_{C_2H_4}$, P_{H_2O}, and t. Average values of k_1 and k' at different temperatures and $P_{H_2O} = 30$ atm are given in Table 2 (t in seconds).

The temperature dependence of k_1 and k' is given by the equations

$$\log k_1 = 12.18 - \frac{35\,150}{4.57T}, \tag{16}$$

$$\log k' = 5.39 - \frac{14\,860}{4.57T}. \tag{17}$$

The ethylene used in the experiments contained small amounts of $(C_2H_5)_2O$. The amount of ether in the reaction products differed little from its amount in the initial ethylene. Thus, under the experimental conditions, the ether-formation reaction practically did not occur. This was confirmed by special experiments with ethylene almost free of ether.

In studying the absorption of C_2H_4 and C_3H_6 by solutions of sulfuric acid [9] and the acid hydration of C_2H_2 [1], the conclusion was drawn that the rate-limiting stage is the conversion of the π-complex into a carbonium ion. The results of the present work make it possible to extend this conclusion to the acid hydration of C_2H_4.

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