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Abstract

Full Text

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THE RATE OF ABSORPTION OF ETHYLENE AND PROPYLENE BY SULFURIC ACID OF DIFFERENT CONCENTRATIONS

(Presented by Academician V. N. Kondrat' ev on 24 IV 1958)

The absorption of olefins by sulfuric acid, as is known (^{1,9}), is a complex acid-catalytic process, during which the formation of an alcohol and an alkyl acid takes place simultaneously (^{2}). In the case of the absorption of propylene by sulfuric acid, a number of facts indicate that these processes proceed in parallel (^{3}). The question of the order of both reactions has still not been resolved. According to Taft (^{4}), the hydration of olefins is a monomolecular reaction and the order with respect to water is zero; according to Tsvetkova' s data (^{5}), this reaction is of second order—first order with respect to water and to propylene.

The difficulty of experimentally determining the order of the alkylation reaction is connected with the fact that the investigation is always carried out in the presence of an excess of acid, which at the same time is both a reactant and a catalyst. Information concerning the order of the alkylation reaction can be obtained by studying the relation of its rate to the acidity of the medium.

If the dependence of the rates of both reactions on the acidity h_0 is the same, then the dependence of the initial rate of gross absorption w_0 will also be the same ($w_0 = w_{\text{alk}} + w_{\text{sp}}$).

If, however, it is different, then the relation of w_0 to h_0 will, in addition, be determined by the ratio of the absolute values of these terms, which vary with the acid concentration, and the observed relation between $\lg w_0$ and H_0 may assume a complex form.

Knowledge of the dependence between w_0 and H_0 makes it possible to compare absorption rates of different olefins that differ greatly in magnitude under identical conditions.

Since the question of the quantitative difference in the true absorption rates of olefins has been little studied, it was of interest to carry out a comparative study of the absorption rates of propylene and ethylene by acids over a wide range of concentrations. Knowledge of the true absorption rates of propylene and ethylene by aqueous sulfuric acid, besides being of theoretical interest, is of considerable practical importance in carrying out the sulfuric-acid process for obtaining ethyl and isopropyl alcohols.

The data available in the literature on the absorption rates of ethylene and propylene by aqueous sulfuric acid (^{6}) are of no value in this respect, since they were obtained in the diffusion region, where differences in absorption rates are leveled out. An exception is the work of Gel' bshtein and Temkin (^{9}), in which the authors, having made a number of assumptions, obtained from diffusion kinetics the rate constants of the chemical interaction of ethylene and propylene with H_2SO_4.

The study of the true kinetics of the absorption of propylene and ethylene by sulfuric acid was carried out at 70° in the circulating glass apparatus described by us earlier (^{3}), supplemented with a 500 cm^3 gas burette. During the experiment the gas pressure was kept constant, equal to atmospheric pressure. The absorption rate was monitored by the amount of gas lost from the gas burette.

If one confines oneself to the initial portion of the kinetic curve of gross absorption, then, neglecting reversibility, the following equation may be used in the calculations:

$$\frac{d\Delta v}{dt} = k'P, \tag{1}$$

where Δv is the change in volume of the gas phase reduced to normal conditions; P is the gas pressure in the system, and

$$k' = 22.4 \cdot 10^3 kqv_k. \tag{2}$$

The specific rate k' was calculated from equation (1) from the mean rate of absorption of the first 400 cm^3 of gas under the experimental conditions, subsequently reduced to normal conditions. The rate constant k was calculated from equation (2), where q is Henry' s constant in mole/l • mm; v_k is the volume of acid in cm^3. Henry' s constant was found by extrapolating literature data on the solubility of propylene in water (^{7}) to high temperatures (at 70° $q = 3.11 \cdot 10^{-6}$ mole/l • mm). For ethylene the same value was taken.

Table 1

Experiments on the absorption of propylene and ethylene by sulfuric acid of various concentrations at 70°

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H_2SO_4, wt. %	H_0	v_k, cm^3	w_{av}, cm^3/min	P, mm Hg	$k' \cdot 10^3$, cm^3/min mm	k, min^{-1}	$\lg k$	$\lg k + nH_0^{***}$
Propylene	Propylene	Propylene	Propylene	Propylene	Propylene	Propylene	Propylene	Propylene
56.57	−3.70	4.8	0.49*	691.0	0.70	2.11	0.325	−3.24
60.34	−4.18	4.9	1.47	707.0	2.09	6.09	0.785	−3.25
64.92	−4.75	4.6	5.22	710.0	7.36	22.90	1.360	−3.22
67.70	−5.15	4.4	11.80	731.0	16.15	52.30	1.718	−3.25
70.04	−5.45	4.4	18.78	729.0	25.80	84.30	1.926	−3.24
Ethylene	Ethylene	Ethylene	Ethylene	Ethylene	Ethylene	Ethylene	Ethylene	Ethylene
79.51	−6.78	4.1	0.11**	745.5	0.14	0.5	−0.311	−7.91
86.05	−7.69	4.6	1.78	750.5	2.37	8.1	0.908	−7.71
89.39	−8.13	4.3	4.57	741.0	6.17	20.8	1.318	−7.79
91.46	−8.35	3.8	8.58	754.0	11.38	42.7	1.630	−7.72
95.41	−8.83	3.5	28.08	752.0	37.40	151.3	2.180	−7.70

* The value of w_{av} was calculated from the time of absorption of the first 200 cm^3 of C_3H_6.
** The value of w_{av} was calculated from the time of absorption of the first 40 cm^3 of C_2H_4.
*** For propylene $n = 0.97$, for ethylene $n = 1.1$.

Table 1 gives the experimental data on the absorption of propylene and ethylene by sulfuric acid of various concentrations. The values of H_0 of sulfuric acid at 70° were taken from the work of Temkin and co-workers (^{8}). The change in the value of H_0 of sulfuric acid upon dissolution of olefin in it was not taken into account, since the degree of saturation of the acid in the initial portion of the kinetic curve was small.

From the data presented (Fig. 1) it follows that there is a linear relation between the logarithm of the absorption rate constant of the olefin and the acidity function of the medium:

$$\text{for ethylene} \quad \lg k = -1.1H_0 - 7.77, \tag{3}$$

$$\text{for propylene} \quad \lg k = -0.97H_0 - 3.24. \tag{4}$$

In both cases the coefficients of proportionality at H_0 are close to unity; this indicates that in the alcohol-forming reactions

and alkylation, of which the process of olefin absorption by the acid is composed, are preceded in the limiting stage by one and the same process of olefin protonation.

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Fig. 1. Dependence of the absorption rate of propylene (1) and ethylene (2) on the acidity function of the medium

Figure 1: Fig. 1. Dependence of the absorption rate of propylene (1) and ethylene (2) on the acidity function of the medium

In our case, the absorption of ethylene was studied under conditions in which the observed process can almost entirely be attributed to the formation of ethylsulfuric acid, and the obtained dependence of the absorption rate constant on acidity (equation (4)) reflects the dependence of the alkylation constant of sulfuric acid by ethylene.

Fig. 1. Dependence of the absorption rate of propylene (1) and ethylene (2) on the acidity function of the medium

The proportionality between the observed constant and the acidity indicates that the sulfuric acid particle is not included in the activated complex, and the reaction of alkyl acid formation apparently follows first order; that is, the expression for the rate of the alkylation reaction has the form:

$$w_{\text{alk}} = k_0 K h_0 C_{\text{et}}.$$

Here k_0 is the true rate constant of the limiting step, K is the protonation constant of ethylene, C_{et} is the molar concentration of ethylene, a_i are activities, and f_i are activity coefficients.

Extrapolation of the straight lines $\lg k - H_0$ in Fig. 1 into one region of H_0 values makes it possible to compare the true absorption rates of propylene and ethylene. As can be seen from Fig. 1, the absorption rates of these olefins by sulfuric acid of one and the same concentration differ by more than 1000-fold. Such a substantial difference in the true absorption rates of propylene and ethylene by sulfuric acid, realized in the kinetic region or close to it, makes it possible to carry out the quantitative separation of C_3H_6 from C_2H_4 and thereby eliminate the economically disadvantageous stage of gas separation by rectification, currently used in the production of synthetic alcohol.

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