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Kinetics and Adsorption on Acid Catalysts

I. Gas-Phase Reesterification of Esters with Alcohols on Sulfonated Ion Exchanger

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Kinetics of the reesterification of ethyl acetate with methanol, 1-propanol, and 2,2-dimethylpropanol and of ethyl formate and ethyl isobutyrate with 1-propanol was investigated. The reaction was carried out at 120°C in gaseous phase using sulfonated styrene–divinylbenzene copolymer as catalyst. The results of kinetic analysis performed by means of the method of initial reaction rates as well as confrontation with the mechanisms accepted for similar reactions in solutions show that the reaction proceeds by a bimolecular mechanism, both reaction components being adsorbed on the surface of the catalyst. The constancy of adsorption coefficients of ethyl acetate or 1-propanol determined by kinetic analysis of their reactions with series of substances of different reactivity indicates that physical meaning can be ascribed to these coefficients.

The question whether the surface of catalyst can be regarded as homogeneous or whether its heterogenity has to be reckoned with still remains one of the controversial problems of kinetics of heterogeneous catalytic reactions [for detailed discussion see (*1*)]. The frequent consistency of the Langmuir-Hinshelwood kinetic model with experimental data cannot be taken as evidence of its theoretical justification. With the majority of catalysts used, one has, in fact, no possibility to verify whether catalytically (and not adsorptionally) active sites are equivalent and whether the circumstance that the Langmuir-Hinshelwood model fits experimental data is not only an approximation. Consequently, we found it useful to perform kinetic analysis of a catalytic reaction using a catalyst which would posses sites of single kind and activity. For this purpose we have chosen a sulfonated styrene-divinylbenzene copolymer containing the $-SO_3H$ groups bound to the benzene ring as the only sites of catalytic activity.

It turned out that reesterification of esters of organic acids with alcohols in the gaseous phase [Eq. (I)] is a suitable acid catalyzed model reaction. This reaction takes place within the region of thermal stability of ion exchangers with sufficient rate.

$$\underset{A}{RCOOR^1} + \underset{B}{R^2OH} \rightarrow \underset{C}{RCOOR^2} + \underset{D}{R^1OH}. \quad (I)$$

It was the aim of the present study to appreciate physical meaning of the so-called adsorption coefficients by studying reaction kinetics of a certain compound with several differently reactive components. If Langmuir-Hinshelwood kinetics is valid, in all cases the same values of adsorption coefficient, within the range of experimental error, of a common reaction component should be obtained.

For this purpose we performed kinetic analysis of reesterification of ethyl acetate with methanol, 1-propanol, and 2,2-dimethylpropanol and, in addition, extended our study to the reaction of ethyl formate and ethyl isobutyrate with 1-propanol. The data obtained were treated statistically and for equations giving the best correlations the values of rate constants and adsorption coefficients were calculated. This made it possible to draw also some conclusions concerning mechanism of gas-phase re-esterification of esters on acid ion exchange resins.

Ion exchangers containing acid functional groups have been already employed as heterogeneous catalysts in a great number of cases [e.g., reviews (*2*)], however, mostly only for preparative purposes. There are only a few kinetic studies of reactions on the surface of ion exchange resins, and, furthermore, these deal predominantly with the reactions in liquid phase, the course of which is strongly influenced by the nature of solvent and by swelling of ion exchanger and in which mass transport plays an important role. Kinetics of decomposition in gaseous phase of formic acid and of esterification of acetic acid with ethanol and butanol were studied by Andrianova (*3, 4*) and that of the hydration of ethylene oxide and isobutylene was investigated by Metzner and collaborators (*5–8*). Kinetic study of isomerization of *n*-butenes was performed by Kalló and Preszler (*9*). Dehydration of isopropanol and esterification of acetic acid with isopropanol was in terms of Langmuir-Hinshelwood type equations described by Gottifredi *et al.* (*10, 11*). Langmuir-Hinshelwood relations were also applied by Johanson and co-workers (*12–14*) to the description of gas-phase reactions on ion exchangers; in addition they have compared adsorption coefficients found by kinetic analysis with those obtained by measuring adsorption of reaction components. The mutual agreement, though approximate, led the authors to conclude that these quantities have the same physical meaning and, as a consequence, that this finding may be taken as a further support of the validity of the Langmuir-Hinshelwood model.

NOMENCLATURE

F/W	space velocity (mole/hr kg)
k_{adsA} k_{adsB}	rate constants of adsorption of compounds A and B, respectively
k_s	rate constant of surface reaction
k_{desR}	rate constant of desorption of product R
K'_3	equilibrium constant of surface reaction [Eq. (II-3)]
K_A, K_B, K_D	adsorption coefficients of compounds A, B, and D, respectively
n	number of moles
p_A, p_B	initial partial pressure of starting compounds A and B, respectively (atm)
r	initial reaction rate (mole/hr kg)
Q	sum of squares of deviations between experimental and calculated reaction rates
Q_{crit}	critical value of sum of squares of deviations
x	conversion
ρ	correlation coefficient

Indices

A	starting ester
B	starting alcohol
C	ester formed
D	alcohol formed

EXPERIMENTAL METHODS

Materials

Ethyl acetate, ethyl formate, methanol, 1-propanol, and 2,2-dimethylpropanol, commercial products of analytical or technical purity (Lachema), were dried by standing over anhydrous magnesium sulfate and then purified by rectification. Using this procedure pure compounds were obtained, except 1-propanol which was contaminated by a small amount of 2-butanol. To remove this impurity the alcohol was partially dehydrated in gas phase on acid ion exchange resin (see below) at 120°C. The reaction brought about the quantitative dehydration of the secondary butanol, while 1-propanol reacted only to about 20%. After drying, rectification yielded pure 1-propanol. Ethyl isobutyrate was prepared by esterification of isobutyric acid with ethanol in liquid phase using a little amount of sulfuric acid as catalyst. After isolation and drying, the ester obtained was purified by rectification. In all the alcohols and esters under study the content of water was checked using Fischer method (the water content was below 0.3%). Gas-chromatographic analysis did not reveal any admixtures in the compounds studied.

Nitrogen (oxygen content lower than 200 ppm) from pressure cylinder was dried by potassium hydroxide and its flow rate was measured by differential capillary flow meter.

Sulfonated macroreticular styrene-divinylbenzene copolymer containing 25% of divinylbenzene (Research Institute of Synthetic Resins and Varnishes, Pardubice) was used as catalyst; it was dried at 90°C (14 Torr) before use. Particle size 0.16–0.3 mm was used. The BET specific surface area in dry state, measured by means of nitrogen adsorption, amounted to 49 m^2/g, the average pore diameter being, according to the producer, around 100 Å. The capacity (i.e., number of acid groups accessible from the gas phase) in dry state, determined by measuring ammonia adsorption (*15*) at 125°C, was 2.31 meq/g. The catalyst was thermally stable within the range of temperatures chosen, no appreciable weight loss being detected by thermogravimetric analysis on heating dried sample of the resin up to 150°C for 60 hr.

Apparatus and Procedure

A glass flow reactor was used. After placing into the reactor, the catalyst was heated to reaction temperature (120°C) for 1–2 hr in a stream of dry nitrogen. Liquid reactants were charged at constant rate into an evaporator by means of a 5-ml syringe, operated by a synchronous electromotor provided with adjustable gears. In the evaporator the vapors were mixed with nitrogen and then led through the catalyst bed (0.01–1.0 g) placed in the U-shaped reactor. The reactor (9-mm i.d.) was provided with a thermocouple well (5-mm o.d.) and was placed in a silicone oil bath kept at 120 ± 0.5°C. Liquid reaction products were separated from the stream of nitrogen by condensation in a trap cooled to −78°C.

Analytical Methods

Liquid reaction products were analyzed gas chromatographically (Chrom II chromatograph (Laboratorní přístroje, Prague) with flame-ionization detector) using nitrogen as carrier gas. Products of reaction of ethyl acetate and ethyl isobutyrate with 1-propanol were separated on dinonyl sebacate (15%) on Celite (340-cm column length, 88°C), products of reaction of ethyl acetate with methanol and 2,2-dimethylpropanol and of ethyl formate with 1-propanol on polyethylene glycol 400 (15%) on Celite (340-cm column length, 80°C). Chromatograms were evaluated on the basis of chromatographic peak areas. For each compound a calibration curve was constructed.

Kinetic Measurements

Initial reaction rates were determined graphically as slopes of the dependence x vs. W/F at $x = 0$; in most cases these dependences were linear within the range of the conversions used. Conversion x, related to ester, was defined as the ratio of molar amount of the formed ester to total molar amount of the starting and the formed ester: $x = n_C/(n_C + n_A)$. Preliminary experiments carried out with varying feed rate at constant space velocity revealed that the influence of external diffusion is negligible. Catalyst activity remained sufficiently constant during the reaction so that it was possible to determine conversions at several (usually three) space velocities on each sample of catalyst.

For each of the reesterification reactions under study 30 initial reaction rates at varying initial partial pressures of reactants were measured, the partial pressures being changed within 0.02–0.81 atm and the total pressure being 0.1–0.9 atm (lowering of the pressure was achieved by diluting vapors of reactants with nitrogen, which is not adsorbed on the catalyst).

RESULTS AND DISCUSSION

Selection of Catalyst, Model Reaction, and Reaction Conditions

In preliminary investigation of the catalysts suitable for studying kinetics of acid catalyzed bimolecular reaction in gas phase we tried a number of commercial ion exchange resins, copolymers of styrene–divinylbenzene type and polycondensates

TABLE 1

DEPENDENCE OF CONVERSION ON PARTICLE SIZE OF DUOLITE C 10 CATALYST IN ESTERIFICATION OF ACETIC ACID WITH ETHANOL

Molar ratio of reacting compounds 1:1; temp 120°C; W/F of acetic acid 0.22 hr $kg_{catalyst}$ $mole^{-1}$.

Fraction	Particle size (mm)	Conversion (%)
1	1.25–1.60	8.0
2	0.40–0.80	9.3
3	0.25–0.40	10.7
4	<0.25	23.5
5	Powder[a]	63.1

[a] Obtained by fine powdering of fraction 4.

of phenol–formaldehyde type, containing $-SO_3H$ or $-PO(OH)_2$ groups. Esterification of acetic acid with ethanol in the gas phase at 120°C served as test reaction with the result that on most of the catalysts used (in dry state) the reaction practically does not proceed. Only Dowex 50 W-X 8, Allasion CSH, and Duolite C 10 were active, however, the conversion was strongly dependent on the size of particles. This finding indicates that internal surface is utilized only to a small extent and that there is a danger of limitation of the rate by internal difusion. In the case of Duolite C 10 this dependence is shown in Table 1. Therefore, in the following stage, attention was paid to macroreticular ion exchangers and a set of samples containing $-SO_3H$ or $-PO(OH)_2$ groups was investigated. From a certain degree of cross-linking (the divinylbenzene content above 8%), activity of these samples is not affected by particle size. Of these samples sulfonated styrene–divinylbenzene copolymer containing 25% divinylbenzene (see Experimental Methods) was selected, due to its suitable activity, as catalyst for intended kinetic study. The dependence of conversions of the two test reactions on the catalyst particle size is presented in Table 2. The results show that macroreticular ion exchange resins have sufficiently accessible internal surface even in dry state [cf. (*16*)]. It can be further concluded that the results of kinetic measurements performed on common types of exchangers should be regarded as disputable.

Using a selected catalyst, we began to study kinetics of the esterification of acetic acid with ethanol. However, we have found that the reaction rate increased with conversion (Fig. 1, curve 1), probably due to modification of the catalyst by water. It was reported (*17*, *18*) that water may hydrate the $-SO_3H$ groups of an ion exchanger or of sulfonated polystyrene films to different degrees. Thus the mobility of a proton of the $-SO_3H$ group and also the catalytic activity may change. This assumption is substantiated by results illustrated in Fig. 1 (curve 2); water at partial pressure of 0.1 atm in the feed increases the conversion, and esterification, therefore, does not follow a simple kinetics. Further disadvantage of the above reaction lies in spontaneous esterification of the acid due to its own acidity. The conversion, during the period of the preparation of starting mixture of acetic acid and alcohol, kinetic

TABLE 2

DEPENDENCE OF CONVERSION ON PARTICLE SIZE OF MACRORETICULAR CATALYST (see Experimental Methods)

Temp, 120°C; molar ratio of components, 1:1; for esterification, W/F (acid) $= 1.06 \times 10^{-3}$ hr $kg_{catalyst}$ $mole^{-1}$; for reesterification, W/F (ester) $= 0.34 \times 10^{-3}$ hr $kg_{catalyst}$ $mole^{-1}$.

$CH_3COOH + C_2H_5OH$		$HCOOC_2H_5 + C_3H_7OH$	
Particle size (mm)	Conversion (%)	Particle size (mm)	Conversion (%)
0.4–0.5	16.9	0.16–0.315	14.4
0.2–0.315	13.6	0.09–0.16	15.6
0.09–0.16	13.0	0.063–0.09	14.0
Powder[a]	15.2	Powder[a]	14.7

[a] Obtained by fine powdering of <0.063-mm fraction.

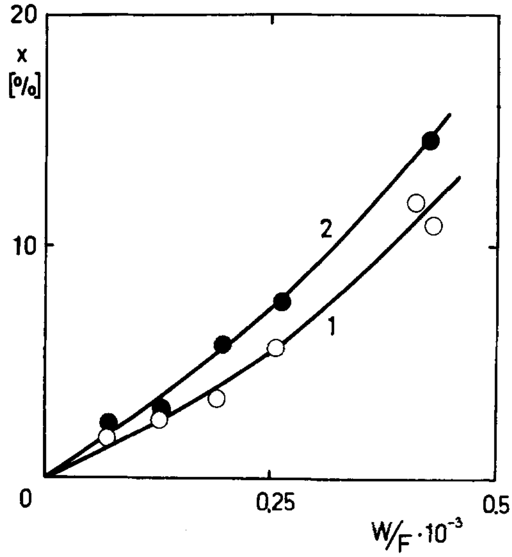


FIG. 1. Effect of water on esterification of acetic acid with ethanol; dependence of conversion on reciprocal value of space velocity. Molar ratio of reactants 1:1; temp 120°C; (1) partial pressure (atm) of: reactants, 0.8; nitrogen, 0.2; (2) partial pressure (atm) of: reactants, 0.8; water, 0.1; nitrogen, 0.1.

measurement, and analysis of reaction product, may amount to as much as 2%. Furthermore, at reaction temperature, acetic acid molecules are dimerized to a great extent, which makes it difficult to determine partial pressures and introduces further confusion to the problem of reaction mechanism (e.g., whether monomer and/or dimer adsorb and react).

All the above reasons compelled us to choose reesterification of organic acid esters with alcohols [Eq. (I)] as the model reaction, because in this case similar phenomena are not operative. In addition, reaction heat is practically negligible since formed and cleft bonds are of the same kind. We have further found that neither by standing of mixture of ester and alcohol at ambient temperature, nor by passing their vapors at 120°C through the reactor packed with glass balls the reaction takes place. On the other hand, dehydration of alcohol may be an undesired side reaction. On reacting ethyl acetate with 1-propanol (1:1 molar ratio) at 120°C to 40% conversion approx 0.4% olefines and 1% ether is formed. The amount of the above substances increases with increasing temperature, and that is why we have used temperature 120°C at which formation of these side products does not interfere with the determination of initial reaction rates.

Since the values of equilibrium constants of esterification of a certain acid with members of homologic series of alcohols do not substantially differ from one another [e.g., (*19*)], equilibrium constants of reesterification have to acquire values close to unity. Therefore, in the determination of initial reaction rates, the conversion has to be low enough to suppress the influence of reverse reaction. For instance, in the case of 1:1 molar mixture of ester and alcohol, we kept conversions below 5%.

Kinetic Analysis

In the kinetic analysis, we made use of the method of initial reaction rates. Statistical treatment of the data was the same as in previous studies of our Laboratory (*20–23*).

Kinetic data were interpreted by means of different rate equations for reesterification reaction. On deriving these equations we started from concepts accepted for mechanism of acid catalyzed esterification and hydrolysis in liquid phase (*24*); reesterification of esters with alcohols is, in fact, general case of esterification and hydrolysis. For the most frequently occurring case where these reactions proceed with the cleavage of the acyl–oxygen bond, two mechanisms were proposed by Ingold (*24*). After having been rewritten for reesterification, these have the following forms:

Monomolecular ($A_{AC}1$) mechanism:

$$\mathrm{RCOOR^1 + H^{(+)} \rightleftarrows RCOO^{(+)}HR^1}, \qquad \text{(II-1)}$$

$$\mathrm{RCOO^{(+)}HR^1 \rightleftarrows RCO^{(+)} + R^1OH}, \qquad \text{(II-2)}$$

$$\mathrm{RCO^{(+)} + R^2OH \rightleftarrows RCOO^{(+)}HR^2}, \qquad \text{(II-3)}$$

$$\mathrm{RCOO^{(+)}HR^2 \rightleftarrows RCOOR^2 + H^{(+)}}. \qquad \text{(II-4)}$$

In the bimolecular ($A_{AC}2$) mechanism, the second and third steps (II-2, II-3) take place simultaneously

$$\mathrm{RCOO^{(+)}HR_1 + R_2OH \rightleftarrows RCOO^{(+)}HR_2 + R_1OH}. \qquad \text{(III)}$$

From the viewpoint of heterogeneous catalysis, the first (II-1) and the last step (II-4) (addition and splitting-off of proton) may be regarded as chemisorption of ester on an acid site of solid catalyst or as its desorption from this site, respectively. The other steps correspond to surface reaction of chemisorbed ester with alcohol from gaseous phase (or physically adsorbed), which proceeds in either two steps (II-2, II-3: $A_{AC}1$ mechanism) or one step (III: $A_{AC}2$ mechanism).

Based on these concepts and presumption on equality of acidic sites of the catalyst, the equations for initial reaction rates listed in Table 3 [Eqs. (1)–(9)] were derived. These equations describe cases where any of the above-mentioned steps may be rate-determining. We have further presumed that, while ester is chemisorbed on acidic sites, alcohol may be adsorbed on other sites of catalyst, e.g., physically adsorbed on polymer skeleton of catalyst. As the assumed analogy between heterogeneous and homo-

TABLE 3

Survey of Kinetic Equations Derived $r = f(k_i, K_i, p_A, p_B)$

Eq. no.	Rate-determining step[a]	Way of adsorption[c] of compound		$f(k_i, K_i, p_A, p_B)$	Corresponds to mechanism in homogeneous medium
		A	B		
(1)	adsA	1	0	$k_{adsA}p_A$	$A_{AC}1$, $A_{AC}2$
(2)	sr-II-2	1	0	$k_sK_Ap_A/(1 + K_Ap_A)$	$A_{AC}1$
(3)	sr-II-3	1	0	k_sp_B	$A_{AC}1$
(4)	desR	1	0	$k_{desR}K'_3p_B/(1 + K'_3p_B)$	$A_{AC}1$
(5)	sr-III	1	0	$k_sK_Ap_Ap_B/(1 + K_Ap_A)$	$A_{AC}2$
(6)	desR	1	0	k_{desR}	$A_{AC}2$
(7)	sr-II-3[b]	1	1	$k_sK_Bp_B/(1 + K_Bp_B)$	$A_{AC}1$
(8)	desR[b]	1	1	$k_{desR}K'_3(K_B/K_D)p_B/[1 + (K_B + K'_3K_B)p_B]$	$A_{AC}1$
(9)	sr-III[b]	1	1	$k_sK_AK_Bp_Ap_B/(1 + K_Ap_A)(1 + K_Bp_B)$	$A_{AC}2$
(10)	adsA	2	1	$k_{adsA}p_A/(1 + K_Bp_B)^2$	
(11)	adsB	1	2	$k_{adsB}p_B/(1 + K_Ap_A)^2$	
(12)	sr	1	0	$k_sK_Ap_Ap_B/(1 + K_Ap_A)^2$	
(13)	sr	2	0	$k_sK_Ap_Ap_B/[1 + (K_Ap_A)^{1/2}]^2$	
(14)	sr	0	1	$k_sK_Bp_Ap_B/(1 + K_Bp_B)$	
(15)	sr	0	1	$k_sK_Bp_Ap_B/(1 + K_Bp_B)^2$	
(16)	sr	0	2	$k_sK_Bp_Ap_B/[1 + (K_Bp_B)^{1/2}]^2$	
(17)	sr	1	1	$k_sK_AK_Bp_Ap_B/(1 + K_Ap_A + K_Bp_B)^2$	
(18)	sr	1	1	$k_sK_AK_Bp_Ap_B/(1 + K_Ap_A + K_Bp_B)^3$	
(19)	sr	1	2	$k_sK_AK_Bp_Ap_B/[1 + K_Ap_A + (K_Bp_B)^{1/2}]^3$	
(20)	sr	2	1	$k_sK_AK_Bp_Ap_B/[1 + (K_Ap_A)^{1/2} + K_Bp_B]^3$	
(21)	sr	2	2	$k_sK_AK_Bp_Ap_B/[1 + (K_Ap_A)^{1/2} + (K_Bp_B)^{1/2}]^4$	
(22)	sr[b]	1	2	$k_sK_AK_Bp_Ap_B/(1 + K_Ap_A)[1 + (K_Bp_B)^{1/2}]^2$	
(23)	sr[b]	2	1	$k_sK_AK_Bp_Ap_B/[1 + (K_Ap_A)^{1/2}]^2(1 + K_Bp_B)$	
(24)	sr[b]	2	2	$k_sK_AK_Bp_Ap_B/[1 + (K_Ap_A)^{1/2}]^2[1 + (K_Bp_B)^{1/2}]^2$	
(25)	adsA	1	1	$k_{adsA}p_A/(1 + K_Bp_B)$	$A_{AL}1$
(26)	adsB	1	1	$k_{adsB}p_B/(1 + K_Ap_A)$	$A_{AL}1$
(27)	sr-IV-2a	1	1	$k_sK_Ap_A/(1 + K_Ap_A + K_Bp_B)$	$A_{AL}1$
(28)	sr-IV-2b	1	1	$k_sK_Bp_B/(1 + K_Ap_A + K_Bp_B)$	$A_{AL}1$

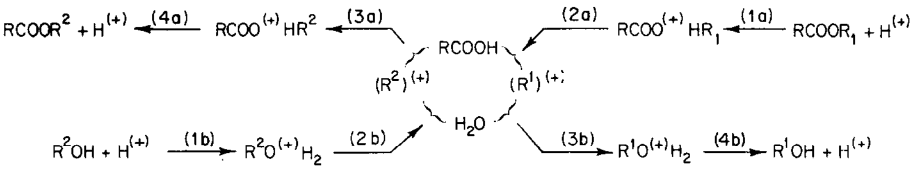
[a] Symbols denote: adsA = adsorption of ester, adsB = adsorption of alcohol; desR = desorption of ester formed, sr = surface reaction of alcohol with ester (Roman and Arabic numerals refer to Eqs. II, III, and Scheme IV).

[b] Alcohol adsorbed on different sites than ester.

[c] 0 = compound is not adsorbed and reacts directly from gaseous phase; 1 = compound is adsorbed without dissociation; 2 = compound is adsorbed with dissociation.

geneous reaction is not quite warranted, we have also used a set of other equations expressing other possible kinetic models, e.g., alcohol adsorbed and ester reacting from gaseous phase or both the components chemisorbed, one or both of them with dissociation. Equations describing these cases, derived on the basis of Langmuir-Hinshelwood conceptions, are also presented in Table 3 [Eqs. (10)–(24)].

We have further considered the $\mathrm{A_{AL}1}$ mechanism presuming the splitting of the alkyl–oxygen bond, though it is highly improbable (*24*). According to this mechanism, reesterification consists of a four-stage hydrolysis [steps (1a), (2a), (3b), (4b) in Scheme IV] and four-stage esterification [steps (1b), (2b), (3a), (4a)] proceeding as parallel reactions. However, as we have not succeeded in detecting the presence of water or acetic acid in any case, it seems unlikely that steps (3) and (4) would be rate-determining. In addition, analysis of these cases revealed that the initial reaction rate should be independent of partial pressure of the starting compounds, which is not in agreement with our observation. That is why, in mathematical treatment of rate data, these cases were disregarded. The remaining cases (i.e., steps (1a), (2a), (1b) or (2b) as rate-determining) lead, under the assumption that water and acetic acid are present in imperceptible amounts, to relations (25)–(28) (Table 3).



Scheme IV

The equations derived (Table 3) were confronted with rate data determined for all of the five reesterification reactions under study. For this purpose, the data were treated successively by linear and nonlinear regression (*23*). The linearized forms of rate equations giving poor correlation were eliminated and only equations having the square of correlation coefficient higher than 0.7 were used. All equations for the $\mathrm{A_{AC}1}$ mechanism ($\rho^2 < 0.5$) as well as all equations for the $\mathrm{A_{AL}1}$ mechanism did not fit experimental data. Of equations for the $\mathrm{A_{AC}2}$ mechanism and of other equations in Table 3, those presuming adsorption of some of the reactants or desorption of some of the products to be a rate-determining step did not comport with the data ($\rho^2 <$ 0.5). The remaining equations for the $\mathrm{A_{AC}2}$ mechanism and its modifications assuming surface reaction to be rate-determining [Eqs. (5), (9), (12)–(24)], were then treated by means of nonlinear regression, the sum of squares of deviations between the found and calculated reaction rate (Q) being taken as the suitability criterion. Equation (19) presuming a bimolecular reaction between ester and alcohol, both the compounds being adsorbed on the same kind of active sites, turned out to be the most suitable. Additional eight equations [(9), (17), (18), (20)–(24)], which expressed a similar mechanistic concept did not fit the experimental data so well. For their further appreciation we applied the critical sum of squares of deviations Q_{crit} according to (*23*) (using a significance level of $\alpha = 0.05$). To some of studied reactions these equations are applicable (the Q value was lower than the Q_{crit} value), however, each of these equations turned out to be inapplicable to at least one of the reaction studied. Equation (19) satisfied the criterion in all cases. Equations (5) and (12)–(16) seem to be quite improbable since their Q values are in all cases higher than the Q_{crit} values. These equations presume only one of the reaction components adsorbed and the other reacting directly from the gaseous phase.

From the results of kinetic analysis it thus follows that the reaction proceeds by a bimolecular mechanism which is similar to the $\mathrm{A_{AC}2}$ mechanism, in which however, both ester and alcohol are adsorbed (whether on

TABLE 4
Values of Constants of Kinetic Eq. (19)

Reaction components		Rate constant k (moles hr^{-1} $\text{kg}^{-1}_{\text{catalyst}}$)	Adsorption coefficients	
A	B		K_A (atm^{-1})	K_B (atm^{-1})
Ethyl acetate	Methanol	2625	1.3	0.3
	1-Propanol	284	1.0	2.8
	2,2-Dimethylpropanol	80.4	0.9	7.6
	1-Propanol	284	1.0	2.8
isobutyrate	1-Propanol	55.8	0.55	3.1
formate	1-Propanol	37050	0.4	1.8

the same or on different parts of surface cannot be unambiguously determined).

The present investigation makes it possible to appreciate physical meaning of adsorption coefficients (Table 4). The values for ethyl acetate (K_A) obtained by means of kinetic analysis of its reaction with methanol, 1-propanol, and 2,2-dimethylpropanol are very close to one another, while the adsorption coefficients of the alcohols (K_B) differ from one another more than 22 times and the corresponding rate constants more than 32 times. Similarly, the values of adsorption coefficient of 1-propanol (K_B) found on the basis of its reaction with ethyl acetate or ethyl isobutyrate agree well (2.8 and 3.1 atm^{-1}), while the values of rate constants as well as those of adsorption coefficients of ethyl acetate and ethyl isobutyrate differ several times. A somewhat different value of adsorption coefficient K_B (1.8 atm^{-1}) was found in the reaction of 1-propanol with ethyl formate which is apparently due to an inaccuracy of experimental measurements because of very fast reaction. Thus, it can be said that the adsorption coefficients obtained by kinetic analysis do not depend on the nature of the other reaction component, and that these so-called kinetic adsorption coefficients are, in this case, not only empirical constants valid for one certain reaction but that they characterize the compound in question more generally. Since in using sulfonated resin as catalyst Langmuir's assumption of equivalency of active sites can be considered as fulfilled, we believe that the values found are true adsorption coefficients of reaction components on catalytically active surface.

Additional verification of the physical meaning of kinetic adsorption coefficients based on kinetic study of competitive reactions of a certain compound and comparison of values thus obtained with results of direct adsorption measurements on ion exchange resins is subject of further study.

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