

KINETICS OF INDIVIDUAL STEPS IN REACTION NETWORK ETHANOL-DIETHYL ETHER-ETHYLENE-WATER ON ALUMINA

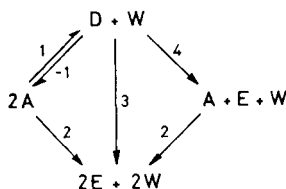
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The rates of single reactions have been measured at 250°C in the complex reaction of ethanol dehydration to ethylene and to diethyl ether involving also hydrolysis of the ether, its disproportionation to ethanol and ethylene and its dehydration to ethylene. The found dependences of the initial reaction rates on partial pressures of the reactants were correlated by semiempirical Langmuir-Hinshelwood type rate equations.

The dehydration of primary alcohols is described by a complex reaction scheme: beside the parallel dehydrations of the alcohol to alkene and dialkyl ether, the system includes also the disproportionation of the formed ether to the alcohol and alkene and the decomposition of the ether to two molecules of the alkene and one molecule of water. In the presence of water, the hydrolysis of the ether (reverse reaction to its formation from the alcohol) may be significant. Thus, the complete reaction scheme of alcohol dehydration is, according to Knözinger and Röss¹, composed of several path-ways (Scheme 1).



SCHEME 1

The kinetics of steps 1 and 2 in Scheme 1 have been studied by a number of authors (the literature has been reviewed recently²). For ethylene formation from ethanol (step 2), the most frequently used rate equations were of the type

$$r_2 = k_2 K_A p_A / (1 + K_A p_A + K_W p_W)^n \quad (1)$$

with $n = 1$ or 2. The kinetic description of diethyl ether formation from ethanol (step 1) has got less attention. Eq. (1) with $n = 1$ was applied, as well as Eqs (2) and (3)

$$r_1 = k_1 [K_A p_A / (1 + K_A p_A)]^2 \quad (2)$$

$$r_1 = k_1(K_A p_A)^{0.5} / [1 + (K_A p_A)^{0.5} + K_W p_W]. \quad (3)$$

Of the other steps in Scheme 1, Butt, Bliss and Walker³ described the decomposition of ether (steps 3 and 4) by Eq. (4) ($j = 3$ or 4)

$$r_j = k K_D p_D / (1 + K_D p_D + K_A p_A + K_W p_W). \quad (4)$$

Eqs (1) to (4) correspond to simple Langmuir-Hinshelwood models of surface reactions. However, the recent results (*e.g.*⁴⁻⁶) on the mechanism of alcohol and ether dehydration on alumina indicated deep interactions of the organic reactants and water with the catalyst surface, especially with alumina. The working surface of alumina consists of surface hydroxyl groups of several kinds, surface alkoxides, oxygen atoms and aluminium atoms, the relative concentrations of which depend on the composition of the gaseous phase and consequently on the conversion of the starting compounds. The active centres are formed by ensembles of these groups and atoms, containing acidic and basic components which cooperate in the elimination of water. Beside that, the working surface is partly covered by adsorbed alcohol, ether and water molecules held to the surface by hydrogen bonds. Thus, simple kinetic models assuming constancy of the number of active centres and their unchanging quality during the whole range of reactants conversion may fail. Moreover, parallel operation of two different mechanisms for a single reaction step may not be excluded.

The purpose of the present work was to obtain kinetic description of all steps in Scheme 1, based on consistent data obtained by the same experimental arrangement and, in designing the rate equations, allowing at least partly for the intricacies of the reactions on the surface of alumina.

EXPERIMENTAL

Catalyst. Pure aluminium hydroxide (Condea Pural SB) was calcined for 3 hours at 600°C, kept in a desiccator over a saturated LiCl solution and conditioned at 450°C in nitrogen stream for 5 hours before experiments. Surface area was 206 m² g⁻¹, particle size 0.16–0.25 mm.

Reactants. Ethanol (99%) was dried by the reaction with magnesium, distilled through a column and kept in sealed flasks; water content was 0.05 to 0.08 mole %. Diethyl ether p.a. was dried by sodium and distilled. Nitrogen from pressure cylinder was led through columns containing an oxygen absorbant and molecular sieve 5A; the content of oxygen and of water in the resulting stream was around 15 ppm.

Apparatus. A flow reactor, consisting of a stainless steel tube of 4 mm i.d. was used. The temperature was measured outside the tube by a thermocouple and automatically controlled. Ethanol was fed from a syringe driven by an electrical motor, diethyl ether was evaporated into the nitrogen stream in a saturator kept at constant temperature. Nitrogen flow was measured by a capillary flowmeter. The gaseous reaction products leaving the reactor were led through a sampling valve connected directly to a gas chromatograph.

Procedure. The catalyst (20–500 mg) was placed in the reactor and heated in a stream of nitrogen to 450°C. After 5 hours at this level, the temperature was lowered to 250°C for kinetic measurements. In preliminary experiments, the regions of conversions were estimated where the linear approximation for calculation of initial reaction rates as the product of conversion and reciprocal space velocity may be used (up to 3% in case of the ethanol reaction to ethylene and

diethyl ether). The rates were measured after 3 hours of running the experiment when the steady-state was safely established. Preliminary experiments also showed that the rate of dehydration is not influenced by the presence of ethylene in the feed.

Analysis. Gas chromatographic column (2 m) contained a mixture of Porapacks P and Q (1 : 4), its temperature was 90°C, the flow of hydrogen 50 ml min⁻¹, the peaks were detected by a thermal conductivity cell. The volume of the gas sampling loop was about 3 ml. The quantitative evaluation was based on previous calibration and on peak heights.

Treatment of conversion data. The conversions were calculated from partial pressures of the components determined by means of peak heights. In case of ethanol feed, the following equations were used for the conversions to diethyl ether (D) and ethylene (E), respectively

$$x_D = 2p_D(\alpha + 1)/(P - p_E) \quad (5)$$

$$x_E = p_E(\alpha + 1)/(P - p_E) \quad (6)$$

The initial reaction rates were then calculated as

$$r_j^0 = x_i/(W/F_A), \quad (7)$$

where $j = 1, 2$ (see numbering of the individual steps in Scheme 1) and $i = D, E$. In case of diethyl ether feed, rates of formation of products were calculated by

$$R_i = Fp_i/WP. \quad (8)$$

The initial reaction rates have been then $r_3^0 = R_W$ and $r_4^0 = R_A$. However, in experiments with water added to the feed from a syringe this procedure was not applicable because the change in water concentration could not be determined with sufficient accuracy. Therefore, it was assumed that step 3 in Scheme 1 is influenced by water to the same extent as step 2. The influence of water on this reaction could be measured independently and then $r_4^0 = R_E - 2r_3^0$ and $r_{-1}^0 = R_A - r_4^0$.

Treatment of rate data. The data $r_i^0 - p_j^0$ were correlated by rate equations of the power-law and Langmuir-Hinshelwood types using non-linear estimation method by Marquardt in Hančič's⁷ modification. The best fitting models were selected from about 20 different equations for individual reaction steps. The models were discriminated using a statistical criterion.

RESULTS AND DISCUSSION

Diethyl Ether Formation

At the temperature used (250°C), the predominant primary product from ethanol dehydration was diethyl ether. Initial rates of its formation r_1^0 in dependence on the partial pressure of ethanol in the feed p_A^0 yielded the best fit with Eq. (2); the values of its constants are given in Table I. The fit of the calculated curves to the experimental points is seen in Fig. 1. In terms of reaction mechanism, Eq. (2) describes the case where both ethanol molecules are adsorbed in the same way. This seems improbable (*cf.*^{4,6}) because different bonds are splitted in the reacting alcohol molecules (in one O—H, in the second C—O) requiring different activation through

adsorption. Therefore, we attempted to use Eq. (9) for correlation, however, the calculation yielded exactly the same values for K_{A1} and K'_{A1}

$$r_1^0 = k_1 K_{A1} K'_{A1} (p_A^0)^2 / (1 + K_{A1} p_A^0) (1 + K'_{A1} p_A^0). \quad (9)$$

For description of water influence upon the rate, the adsorption term $K_{W1} p_W^0$ was inserted into the denominator of Eq. (2). The fit was unsatisfactory for higher concentrations of water in the feed and various other modifications of Eq. (2) were therefore tested. The best fit was obtained by using an adjustable exponent at p_W^0

TABLE I
Values of parameters of rate equations for 250°C

Step	Equation	k_j (mol h ⁻¹ kg ⁻¹)	K_i (kPa ⁻¹)
1	(2), (10)	$k_1 = 148$	$K_{A1} = 0.465$ $K_{W1} = 1.05$
-1	(15)	$k_{-1} = 110$	$K_{D1} = 0.007$ $K'_{W1} = 0.243$
2	(13), (14)	$k_2 = 23.8$ $k'_2 = 6.14$	$K_{A2} = 0.195$ $K_{W2} = 602$ $K'_{W1} = 1.80$
3	(16)	$k_3 = 2.64$	$K_{D3} = 0.030$ $K_{W3} = 0.485$
4	(17)	$k_4 K_{D4} = 0.03^a$	$K_{W4} = 0.824$

^a In mol h⁻¹ kg⁻¹ kPa⁻¹.

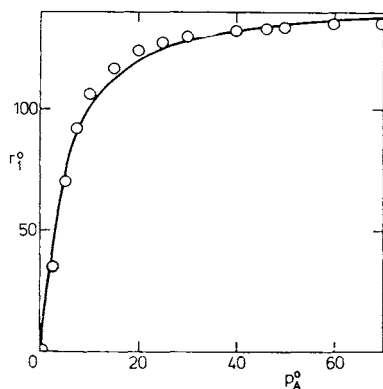


FIG. 1
Rate of ethanol dehydration to diethyl ether in dependence on partial pressure of ethanol in the feed. Points experimental, curve calculated by means of Eq. (2)

for which the value 1.2 was obtained by optimization procedure, together with $K_{W1} = 1.05 \text{ kPa}^{-1}$. Eq. (10) describes the result; it can be interpreted as blocking more than one site by a water molecule

$$r_1^0 = k_1(K_{A1}P)^2/[1 + K_{A1}p_A^0 + K_{W1}(p_W^0)^{1.2}]^2. \quad (10)$$

The confrontation of experimental data and values calculated using Eq. (10) is presented in Fig. 2a-c.

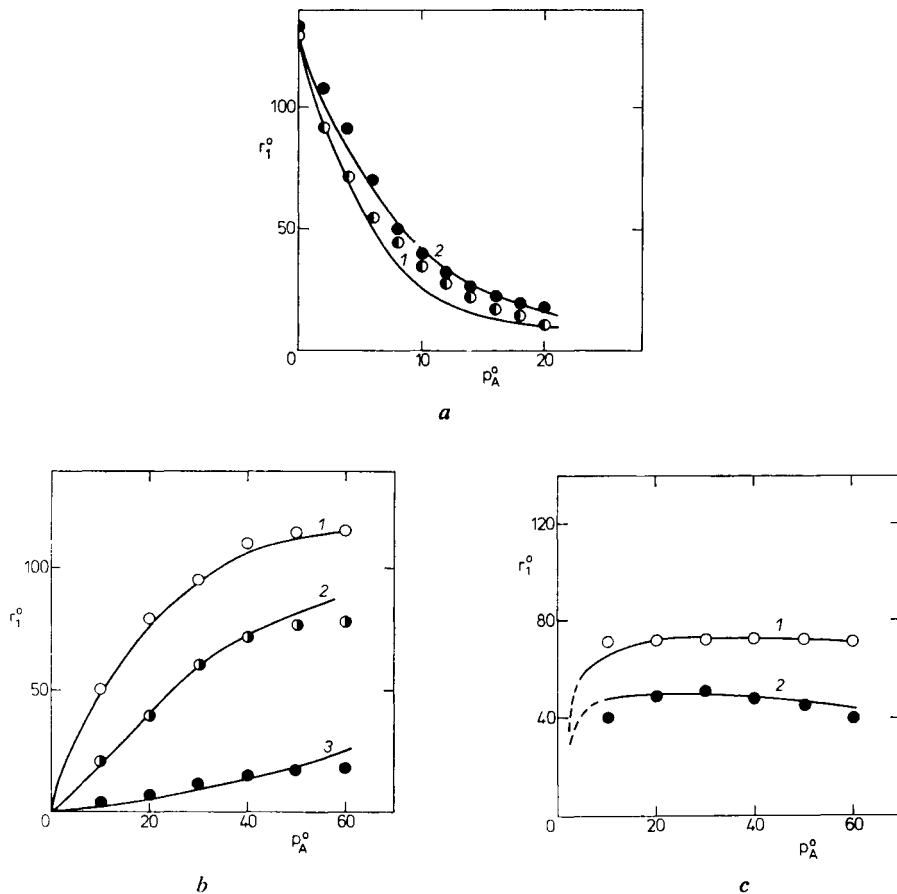


FIG. 2

Rate of ethanol dehydration to diethyl ether: a) in dependence on mean partial pressure of water at constant partial pressure of ethanol of 1 $p_A^0 = 30 \text{ kPa}$, 2 $p_A^0 = 46 \text{ kPa}$; b) in dependence on partial pressure of ethanol at constant mean partial pressure of water of 1 $p_W = 2 \text{ kPa}$, 2 $p_W = 5 \text{ kPa}$, 3 $p_W = 20 \text{ kPa}$; c) in dependence on partial pressure of ethanol at constant water/ethanol ratio 1 $p_W^0/p_A^0 = 0.12$, 2 $p_W^0/p_A^0 = 0.20$. In all cases points are experimental, curves calculated by means of Eq. (10)

Ethylene Formation from Ethanol

The initial reaction rates of ethylene formation from ethanol (step 2 in Scheme 1) in dependence on partial pressure of the alcohol in the feed are depicted as points in Fig. 3. Their course, showing a maximum and approaching the zero-order behaviour, could not be described by any standard rate equation. Similar dependencies have been reported by some authors⁸⁻¹⁰. The form of the experimental curve suggests parallel operation of two reaction mechanisms.

At first, a simple rate equation of the Langmuir-Hinshelwood type with two adsorption terms in the denominator was tested (Eq. (11)) which gave acceptable fit, as judged by sum of squared deviations, but which didn't model satisfactorily the course of the experimental dependence. The values of the found parameters were $k_2 = 11.8 \text{ mol h}^{-1} \text{ kg}^{-1}$, $K_{A2} = 0.695 \text{ kPa}^{-1}$, $K'_{A2} = 0.011 \text{ kPa}^{-1}$ and the calculated curve is numbered by 2 in Fig. 3

$$r_2^0 = \frac{k_2 K_{A2} p_A^0}{(1 + K_{A2} p_A^0)(1 + K'_{A2} p_A^0)} \quad (11)$$

Next, a combination of two rate expressions has been used (Eq. (12)). At first, the correlation was calculated for different K_{A2} in both expressions; however, approximately the same values were obtained. Thus, the calculation was repeated with a pooled parameter K_{A2} (Eq. (13)). In Fig. 3, curve 1 corresponds to the correlation by Eq. (13), curves 3 and 4 depict the separate contributions of the first and second terms of Eq. (12), respectively,

$$r_2^0 = \frac{k_2 K'_{A2} p_A^0}{1 + K'_{A2} p_A^0} + \frac{k'_2 K''_{A2} p_A^0}{(1 + K''_{A2} p_A^0)^2} \quad (12)$$

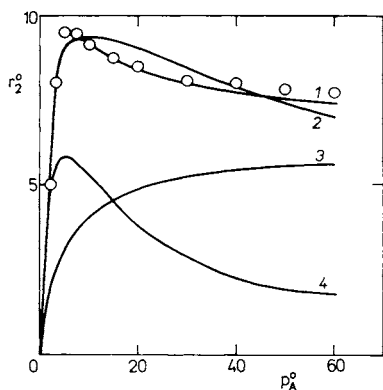


FIG. 3
Rate of ethanol dehydration to ethylene in dependence on partial pressure of ethanol in the feed. Points are experimental, curves calculated (see text)

$$r_2^0 = \left(k_2 + \frac{k'_2}{1 + K_{A_2} p_A^0} \right) \frac{K_{A_2} p_A^0}{1 + K_{A_2} p_A^0}. \quad (13)$$

The form of Eqs (12) or (13) can be explained by competition between two different reaction mechanisms. One of them, represented by the first term of Eq. (12), is an ordinary monomolecular surface reaction, observed by most authors (*cf.*²), which gives a zero-order dependence on alcohol concentration at its higher values (curve 3 in Fig. 3). We believe that surface hydroxyl groups are responsible for this mechanism, acting as Brønsted acid, yielding a proton to the hydroxyl group of the alcohol and thus starting the elimination of water. Curve 4 in Fig. 3 shows autoinhibition of alkene formation by ethanol and we assume that it reflects the mechanism involving a surface ethoxide as an intermediate of relative stability; the evidence for this mechanism was obtained in our previous work⁶ where nonstationary experiments were used. The decomposition of the surface ethoxide into ethylene can be suppressed by its preferential interaction with a second ethanol molecule under eventual formation of diethyl ether. This competitive path-way will be more pronounced with increasing ethanol partial pressure.

For the description of the influence of water on the reaction rate, two adjustable parameters have been added to Eq. (12), yielding Eq. (14) (when $K'_{A_2} = K''_{A_2}$). The reason for introducing two adsorption coefficients for water into the rate equation was the assumption on two modes of water adsorption, by hydrogen bridging (K_{W_2}) and by incorporation⁶ into the surface layer (K'_{W_2}).

$$r_2^0 = \frac{k_2 K_{A_2} p_A^0}{1 + K_{A_2} p_A^0 + K'_{W_2} p_W^0} + \frac{k'_2 K_{A_2} p_A^0}{(1 + K_{A_2} p_A^0 + K_{W_2} p_W^0)(1 + K'_{W_2} p_W^0)(1 + K_{A_2} p_A^0 + K'_{W_2} p_W^0)}. \quad (14)$$

However, Eq. (14) didn't give a satisfactory description of water influence on the reaction rate equally as any of its modifications and examples of the fit are given in Fig. 4a, b. The reason of this failure is a complex nature of the interaction of water with the surface of alumina which may change the number of active sites for various mechanisms.

Influence of Water on the Selectivity of Ethanol Dehydration

Addition of water into the feed not only diminishes the rate of ethanol transformation but also changes the ratio of ethylene to diethyl ether. The relative formation of ethylene is suppressed more strongly than that of diethyl ether. Fig. 5 demonstrates

this fact which could be expected on the basis of different reaction mechanisms for the parallel reactions (*cf.*⁶) and different kinetics.

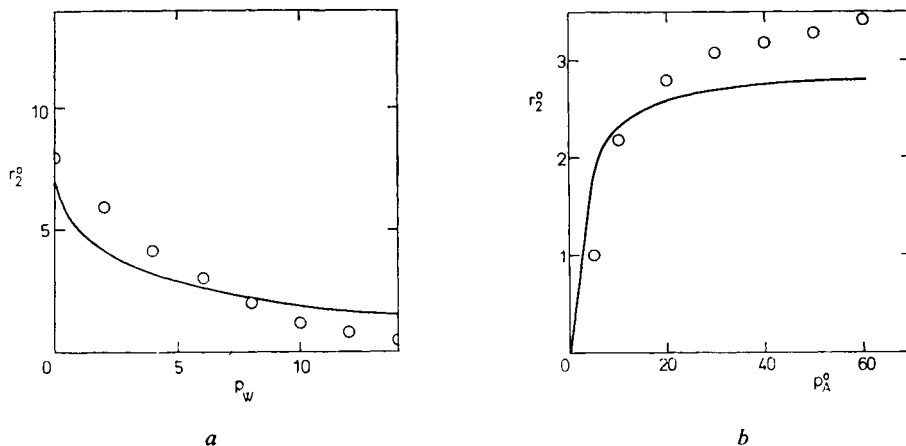


FIG. 4

Rate of ethanol dehydration to ethylene: *a*) in dependence on partial pressure of water at constant partial pressure of ethanol $p_A^0 = 46$ kPa; *b*) in dependence on partial pressure of ethanol at constant water/ethanol ratio of 0.12. Points are experimental, curves calculated by means of Eq. (14)

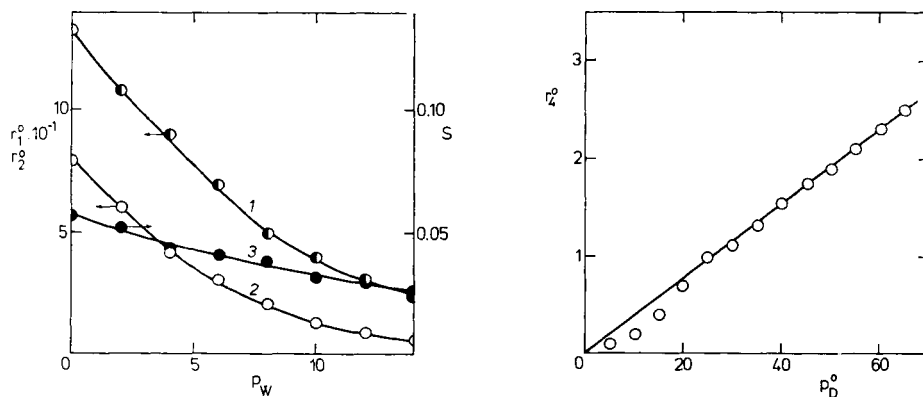


FIG. 5

The dependence of rates of ethanol dehydration 1 to diethyl ether and 2 to ethylene on mean partial pressure of water. Curve 3 is the selectivity $S = r_2/(r_1 + r_2)$

FIG. 6

Rate of diethyl ether hydrolysis in dependence on mean partial pressure of water at constant ether partial pressure of 65 kPa. Points experimental, curve calculated by means of Eq. (15)

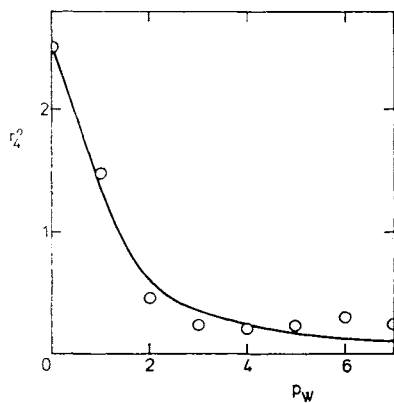


FIG. 7

Rate of diethyl ether dehydration to ethylene in dependence on partial pressure of diethyl ether. Points experimental, curve calculated by means of Eq. (16)

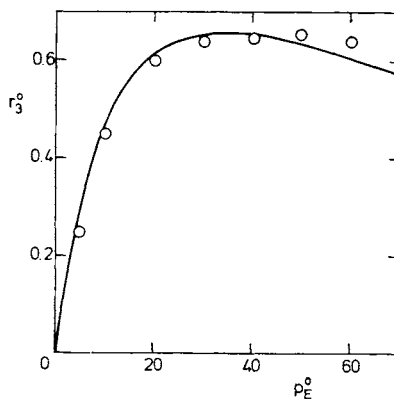


FIG. 8

Rate of diethyl ether dehydration to ethylene in dependence on mean partial pressure of water at constant ether partial pressure of 65 kPa. Points experimental, curve calculated by means of Eq. (16)

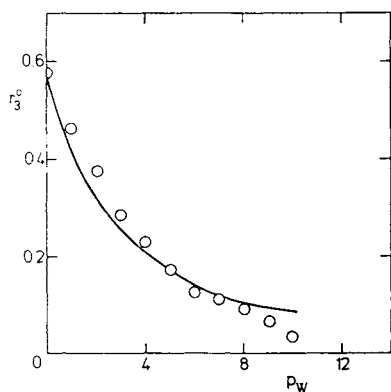


FIG. 9

Rate of diethyl ether disproportionation in dependence on partial pressure of the ether in the feed. Points experimental, curve calculated by means of Eq. (17)

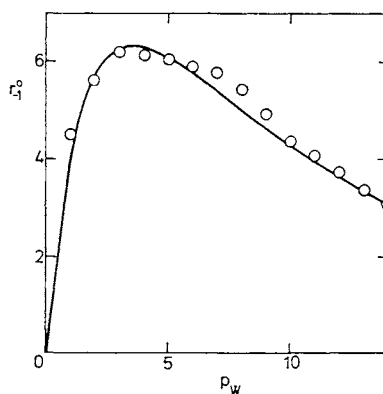


FIG. 10

Rate of diethyl ether disproportionation in dependence on partial pressure of water at constant ether partial pressure of 65 kPa. Points experimental, curve calculated by means of Eq. (17)

Diethyl Ether Hydrolysis and Decomposition

The step 3 of Scheme 1 was studied together with step 4 by reaction of diethyl ether and the individual participation of the both steps were estimated from the ratio of ethylene and ethanol in the products. The hydrolysis of diethyl ether (step -1) was studied by addition of water vapour to the feed. For treatment of data it was assumed that the influence of water on step 3 is the same as on step 2. The data were best fitted by Eqs (15)–(17) which must be regarded as empirical expressions.

$$r_{-1}^0 = k_{-1} K_{D1} K'_{W1} p_D^0 p_W^0 / [1 + K_{D1} p_D + K'_{W1} (p_W^0)^{1.2}]^2 \quad (15)$$

$$r_3^0 = k_3 K_{D3} p_E^0 / (1 + K_{D3} p_D^0 + K_{W3} p_W^0)^2 \quad (16)$$

$$r_4^0 = k_4 K_{D4} p_D^0 / [1 + K_{W4} (p_W^0)^{1.8}] \quad (17)$$

The values of the constants are summarized in Table I. The fit of the calculated curves to experimental points is demonstrated in Figs 6–10.

Consistency of Rate Equations and Their Parameters

The question of consistency of rate equations for individual steps in Scheme 1 can be examined from two points of view. The first one concerns the form of the rate equations. In our case, we have only one requirement: the denominator of equations for steps 1 and -1 should be the same. As Eqs (10) and (15) show this is fulfilled provided that terms $K_D p_D$ and $K_A p_A$, respectively, would be inserted for description of the reactions outside the initial reaction rate region. However, we have chosen Eq. (15) from several equally fitting expressions on this basis.

The second point is consistency of values of adsorption coefficients K_{ij} . We have to consider the low accuracy of determination of these parameters from experimental data (error 50 to 100%). In the range of this uncertainty, the values of K_{W1} , K'_{W1} , K'_{W2} , K_{W3} and K_{W4} are the same, with a mean value of 0.88. The value of K_{W2} is much higher because it represents another type of adsorption. Also the values of K_{Dj} are consistent, as well as K_{Aj} . The mean values decrease in the order $K_W > K_A > K_D$ as could be expected on the basis of chemical nature of water, alcohol and ether.

The obtained set of consistent rate equations will be examined for suitability to describe the integral data in a following paper¹¹.

LIST OF SYMBOLS

A	ethanol
D	diethyl ether
E	ethylene
W	water

F_i	feed rate of compound i	[mol h ⁻¹]
k_j	rate constant of step j	[kPa ⁻¹]
K_{ij}	adsorption coefficient of compound i in step j	[kPa ⁻¹]
p_2^0	partial pressure of compound i in the feed	[kPa]
P	total pressure	[kPa]
r_j	reaction rate of step j	[mol h ⁻¹ kg ⁻¹]
R_i	rate of formation of compound i	[mol h ⁻¹ kg ⁻¹]
W	weight of catalyst	[kg]
x_i	conversion of compound i	—
α	molar ratio of reactant i to inert gas in the feed	—

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