KINETICS OF INDIVIDUAL REACTIONS IN REACTION NETWORK 1-BUTANOL–DI-(1-BUTYL) ETHER–BUTENES–WATER ON ALUMINA

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The complex system of six reactions occurring when 1-butanol is dehydrated on alumina at 260°C was investigated. Initial kinetics of 1-butanol, di-(1-butyl) ether and 1-butene transformationt were analyzed and best fitting rate equations for all reactions were selected. The inhibiting effecs of water on initial rates was quantitatively expressed. Very low conversion data provided additional evidence for the validity of the parallel-consecutive reaction network of alcohol dehydration. In all the alkene-forming reactions, 1-butene was the primary product which was then isomerized into a mixture of *cis*- and *trans*-2-butenes.

Dehydration of alcohols catalyzed by oxides or other catalysts of acid–base character is a well known reaction and have been reviewed several times[1-8]. However, the formation of two products, an ether and an alkene, the convertibility of the ether to the alkene and alcohol, and the formation of isomeric alkenes from alcohols higher than propanol gave rise to numerous speculations concerning the reaction network. During the two past decades, many authors used the parallel-consecutive scheme (*e.g.*[9-13]) formulated intuitively by Knözinger and Köhne from results based mainly on ethanol dehydration[11]. There remained, however, some uncertainty concerning the path-ways of ether decomposition and the lack of direct kinetic evidence of the applicability of this scheme to the dehydration of higher primary alcohols.

In the literature concerning the kinetics of individual reactions involved in alcohol dehydration, the papers prevail that analyze the kinetics of only one of the reactions, *i.e.* under conditions when the other reactions can be neglected. There are only few papers reporting serious kinetic analysis of parallel ether and alkene formation (see *e.g.*[14-17]). Gupta and Ravindram[18] attempted to describe by first order kinetics the parallel-consecutive system of three reactions (*i.e.* including ether decomposition into water and two molecules of the alkene). The most thorough kinetic analyses were performed by Butt and coworkers[9] and by Morávek and Kraus[19,20] who formulated and experimentally verified a system of Langmuir–Hinshelwood type rate equations describing satisfactorily all the four reactions involved: parallel formation of alkene and ether from alcohol, and parallel ether decompositions both with water and alcohol elimination. In all the papers mentioned (with the exception of[17] where 1-propanol was used), ethanol dehydration was investigated. In an earlier paper[21], a simplified formal kinetic analysis of the four-reaction system in 1-hexanol dehydration was performed, based on integral data only.

The aim of the present paper was *1*) to analyse the reaction network in the case of 1-butanol dehydration on alumina and the path-ways of di-(1-butyl) ether decomposition, *2*) to investigate the kinetics of individual reactions of the network and to describe them by initial rate equations, and *3*) to evaluate the effect of water as inhibiting reaction product on the kinetics of individual reactions. The results of this introductory study will be used in the following papers concerning the effect of sodium poisoning on kinetics and selectivity in 1-butanol dehydration[22] and the applicability of initial kinetics to the description of integral data in high conversion region of alcohol dehydration on alumina[23].

EXPERIMENTAL

Chemicals. 1-Butanol, analytical grade (Lachema, Brno), was rectified, dried with anhydrous magnesium sulphate and molecular sieve. Di-(1-butyl) ether, *purum* (Cambrian Chemicals, Great Britain), was rectified in the presence of calcium hydride. 1-Butene, *purum* (Fluka, Buchs, Switzerland), was used directly from pressure bottle. The purity of the chemicals was checked by gas chromatography. Nitrogen (Technoplyn, Praha) was freed from traces of oxygen by passing through a column containing a reduced Mn–Cr contact and dried with molecular sieve Calsit 5A.

Catalyst. Pure aluminium hydroxide (Pural SB, Condea Chemie GmbH, FRG) was kneaded for 1 h with destilled water to form a paste which was than extruded at 3·5 MPa. The extrudates (diameter 2 mm) were dried at 120°C and calcined at 600°C in a flow of dry nitrogen. The calcined extrudates were crushed, sieved and the fraction 0·16—0·25 mm was used. Specific surface area was 198 m^2 g^{-1}, most frequent pore radius 4 nm. Acidic properties of the surface were characterized elsewhere[22].

Apparatus and procedure. An all-glass flow apparatus consisting of a feeding device for liquids, gas lines, evaporator, preheater and a tubular reactor (cross section 0·4 cm^2) with thermocouple well was used. The reactor was directly connected to an on-line gas chromatograph with a flame ionization detector. The catalyst (0·01—0·6 g) was mixed (1 : 1) with glass balls of the same size, placed in the reactor and kept for 2 h at 300°C in a stream of dry nitrogen. The reaction was carried out at 260°C and at feed rates of the respective reactant 0·2—0·3 mol h^{-1}. The total pressure was atmospheric, the partial pressure of the reactant was varied from 2 to 63 kPa (78 kPa for 1-butene) by diluting the reactant vapours with nitrogen. After a steady catalyst activity was achieved, several analysis (5—10) of the reaction product were made at each reactant partial pressure and from the mean values the conversion was evaluated (ref.[20]).

Analysis. In order to separate the isomeric butenes and the higher boiling 1-butanol and di-(1-butyl) ether, two columns (diameter 4 mm) had to be used. In one of them (1·4 m, 15% dinonyl sebacate on Chromosorb W, 125°C) alcohol, ether, and the butene fraction were separated, the other (8 m, dimethyl sulfolane on Chromosorb W, room temperature) served for analysis of butene isomers.

Initial reaction rates. Two or three conversion values, measured at different space times W/F_i^0, were used for determination of the initial reaction rate at a given reactant partial pressure. The rates were evaluated from conversions measured in the linear part of the reaction isotherm (conversion *vs* space time). The maximum total conversions were: 2·0% for 1-butanol, 2·5% for di-(1-butyl) ether and 6% for 1-butene. At the conditions used (catalyst particle size 0·16—0·25 mm, reactant flow rate $\geqq 0{\cdot}2$ mol h^{-1}) the effects of internal as well as external diffusion were found to be negligible. The stabilization of the activity of a fresh catalyst sample was a rather slow process: 8—10 h in reactant flow at the reaction temperature were necessary in the reaction of 1-butanol and about 4 h in the reactions of di-(1-butyl) ether or 1-butene to achieve the steady activity.

After the change of reactant partial pressure or flow rate on a stabilized catalyst, the attainement of the steady state was much faster: usually 30 min were enough to achieve the new steady state.

RESULTS AND DISCUSSION

Reaction Network

It is generally accepted for ethanol dehydration that, at the very beginning of the reaction, ethylene and ethyl ether are formed by two parallel reactions (*A*) and (*B*).

$$2\,C_2H_5OH \rightleftarrows (C_2H_5)_2O + H_2O \tag{A}$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{B}$$

The same seems to be true also for the case of higher primary alcohols. We have detected, even at very low (0·8%) degree of 1-butanol transformation, the formation of 1-butene. The conversion to the butene was, at our reaction conditions (260°C, $p_A^0 = 36$ kPa) equal to 0·2% and the conversion to di-(1-butyl) ether equal to 0·6%. The ratio olefin/ether (= 0·33) remained constant up to the total butanol conversion 2% and only then it was increasing due to the consecutive transformation of the ether to the olefin.

The reaction paths of the ether to alkene transformation are still a matter of discussion. Knözinger and Köhne[11] considered ethylene formation from diethyl ether with ethanol elimination (so-called disproportionation) as the more probable reaction

$$(C_2H_5)_2O \rightarrow C_2H_4 + C_2H_5OH \tag{C}$$

since less bonds are directly concerned during the rate determining step than in the formation of two ethylene molecules with water elimination

$$(C_2H_5)_2O \rightarrow 2\,C_2H_4 + H_2O \tag{D}$$

though the latter reaction cannot be completely excluded at higher temperature.

We have investigated the transformation of di-(1-butyl) ether at very low conversions and have found that, at 260°C, reactions of the type (*C*) and (*D*) take place in parallel. As it can be seen from Fig. 1, more di-(1-butyl) ether is transformed into 1-butene than into 1-butanol in an almost constant ratio of 2·5 : 1 from the very beginning. If only the reaction of type (*C*) occured, this ratio should be stoichiometric (1 : 1), at least at very low conversions, and the increase of the ratio above unity at higher conversions, due to further transformation of alcohol to olefin, should manifest itself in a non-linearity of the alcohol curve which has not been observed up to a total conversion of 6% (see Fig. 1).

Since the reaction of the type (D) is unlikely to be a single-step reaction (four bonds would have to be broken and four new ones formed), it cannot be excluded that in its detailed mechanism some elementary steps are involved that are in common with the reaction (C). Such steps can lead to the formation of a common intermediate, which could be *e.g.* a surface alkoxide group[24]; this intermediate might then be transformed by two parallel reaction paths either to alcohol and alkene (reaction type (C)) or to water and alkene (reaction type (D)).

TABLE I

Conversions to 1- and 2-butenes at different total conversions of 1-butanol

Total conversion (%)	Conversion (%) to		*cis*/*trans* ratio of 2-butenes
	1-butene	2-butenes	
65·9	22·5	0·0	—
70·2	25·2	0·38	3·2
77·6	29·9	0·48	3·4
79·6	34·8	0·78	4·2
82·4	43·1	1·06	4·5
87·2	52·3	1·7	4·4
89·0	56·5	2·4	4·3
90·3	66·0	3·0	4·45
91·4	71·2	3·75	4·4

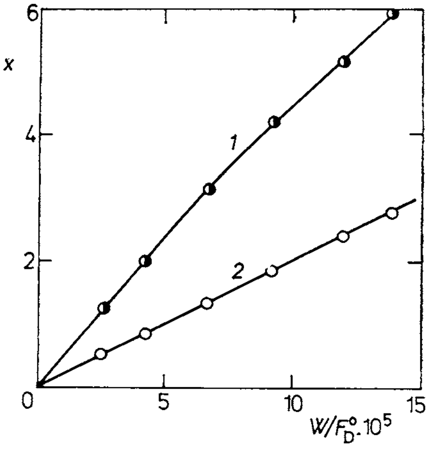


FIG. 1

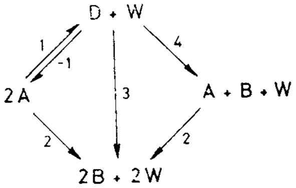
Dependence of the total conversion x (%) of di-(1-butyl) ether into 1-butene (curve *1*) and of the conversion (%) of ether to alcohol (curve *2*) on space time W/F_D^0 (h kg mol^{-1}). Initial partial pressure of ether $p_D^0 = 20{\cdot}9$ kPa

Thus, our results based on investigation of the x_i *vs* W/F_i^0 dependencies in very low conversion regions of 1-butanol and di-(1-butyl) ether transformations provided additional evidence for the correctness of the parallel-consecutive scheme and demonstrated clearly that Scheme 1 is valid also for 1-butanol dehydration on alumina.

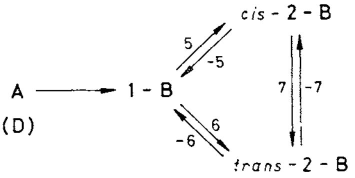
When C_4 and higher alcohols are dehydrated, several olefin isomers may be formed. However, we have observed that the primary olefinic product (both from 1-butanol and di-(1-butyl) ether) was always 1-butene. At higher conversions, a subsequent isomerization of this product to 2-butenes (with preference for the *cis* isomer) occurred. In 1-butanol dehydration, the double bond isomerization started only after about 70% of the alcohol had reacted (Table I). In di-(1-butyl) ether transformation, 2-butenes appeared already at total conversions higher than 10%. Because of these isomerization reactions, Scheme 1 has to be supplemented by a sub-scheme 2 in order to obtain the complete reaction network for 1-butanol dehydration on alumina.

Initial Kinetics

The use of the method of initial reaction rates, with 1-butanol, di-(1-butyl) ether and 1-butene, resp., as starting reactants, allowed us to separate the complex reaction network (Schemes 1 and 2) into three sub-systems of parallel reactions: *1*) ether and alkene forming dehydration of 1-butanol (reactions 1 and 2), *2*) direct alkene forming transformation (reaction 3) and disproportioantion (reaction 4) of di-(1-butyl) ether, and *3*) 1-butene isomerization to *cis*- and *trans*-2-butenes (reactions 5 and 6). Isomerizations of 2-butenes (reactions −5, −6, 7 and −7) were not investigated.

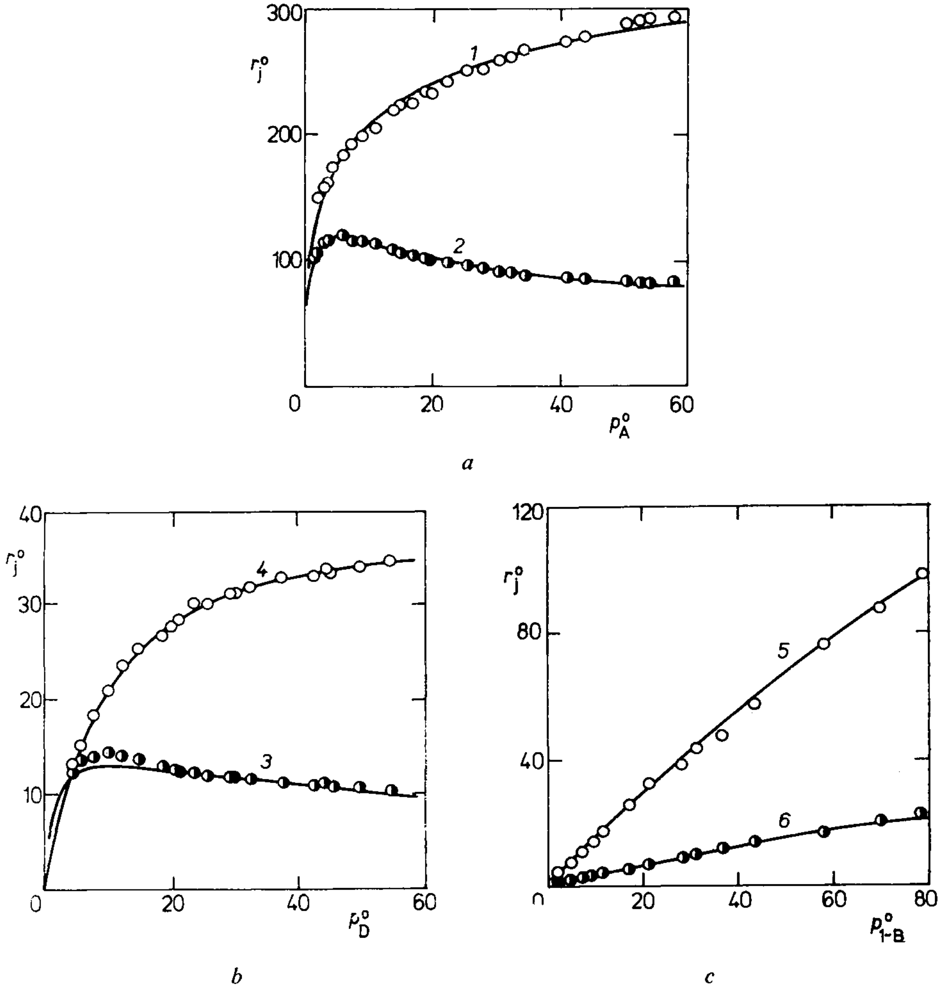


SCHEME 1



SCHEME 2

With each reactant, *15–26* initial rate values were measured in dependence on the initial partial pressure. The results are presented on Figs 2*a*–*c*. The data r_j^0 – p_i^0 were treated by means of the Marquardt nonlinear regression method in Hančil's modification[25] with the use of a large set of Langmuir–Hinshelwood type and power-law type equations. The objective function Q was the sum of squared deviations between the calculated and observed reaction rates.



a

b *c*

FIG. 2

Dependence of initial reaction rates r_j^0 (mol kg^{-1} h^{-1}) on initial partial pressure of starting reactant p_i^0 (kPa). *a* Reaction of 1-butanol, *b* of di-(1-butyl) ether, *c* of 1-butene. Numbering of curves corresponds to the reactions in the Schemes 1 and 2. Points are experimental values, curves are calculated with the use of the best fitting equation for each reaction (see Table II)

The best equations for each reaction together with their parameter values are tabulated in Table II. The minimum of the Q value was the criterion for the choice of the best equations. The fit of the best equations to the experimental r_j^0 *vs* p_i^0 dependencies is seen in Figs 2*a*–*c*.

The fit is quite good but we do not intend to draw conclusions concerning detailed reaction mechanism from the form of the best fitting equations. It is worth noting, nevertheless, that a similarity exists between reactions 1 and 4 on one side and reactions 2 and 3 on the other side (see Figs 2*a*, *b*). The $r_j^0 - p_i^0$ curves of reactions 1 and 4 have a very similar asymptotic form, whereas the curves for reactions 2 and 3 are characterized by maxima in low pressure region. This is in accordance with the forms of the corresponding rate equations in Table II from which those for reactions 2 and 3 with the exponent in the denominator higher than unity are able to express maximum while those for reactions 1 and 4 are not.

This observation might be interpreted as an indication that the mechanism of the two olefin-forming reactions 2 and 3 is similar or at least involves an analogous rate-determining step, perhaps E2 mechanism. This mechanism should be different from that operating in reactions 1 and 4; for reaction 1, *e.g.* a step having character of a nucleophilic substitution has been assumed[26].

Effect of Water

The effect of water on initial rates of each of the six reactions was investigated on stabilized catalyst. The effect was reversible (see also[27]) and with all the reactions, the addition of water lowered the rate but to a different extent. In Fig. 3 an example is given of the influence of water partial pressure on the initial rates of ether and alkene forming dehydration of 1-butanol (curves *1* and *2*). The effects were evaluated by introducing a term $K_{W,j}p_W^0$ into the denominator of the corresponding initial rate equation from Table II and treating the experimental $r_j^0 - p_W^0$ data by nonlinear regression. The estimated $K_{W,j}$ values in the modified rate equations (*1*), (*2a*), (*3a*), (*4a*), (*5*), and (*6*) are summarized in Table III. The fit of the effect of water calculated with the use of the found $K_{W,j}$ values to the experimental points is seen in Fig. 3 for the reactions 1 and 2. In the case of the other reactions, the fit was equally well.

In evaluating the effect of water on the reactions of di-(1-butyl) ether, the reverse reaction −1 (hydrolysis of the ether) had to be taken into account. Thus, we have in the system three reactions −1, 3, and 4 but only two key components. If we consider as the key components alcohol and alkene, we can write for the measured rates of their formation

$$R_A^0 = r_4^0 + 2r_{-1}^0 \qquad (7)$$

and

$$R_B^0 = r_4^0 + 2r_3^0\,. \qquad (8)$$

TABLE II
Best fitting rate equations

Reaction j (see Schemes 1 and 2)	Notation of equation	Right hand side of the rate equation $r_j^0 = f_j(p_i^0)$	Parameters of the equation[a] k_j	K_i	K'_i	Q_{min}
1	(*1*)	$k_1(K_A p_A^0)^{0.5}/[1 + (K_A p_A^0)^{0.5}]$	390	0·13	–	1·104 . 10^3
2	(*2a*)	$k_2 K_A p_A^0/[1 + 2(K_A p_A^0)^{0.5}]^3$	3 160	0·18	–	1·296 . 10^2
	(*2b*)	$8k_2 K_A p_A^0/[1 + (1 + 8K_A p_A^0)^{0.5}]^3$	953	0·17	–	2·353 . 10^2
3	(*3a*)	$k_3 K_D p_D^0/[1 + 2(K_D p_D^0)^{0.5}]^3$	387	0·13	–	1·340 . 10^0
	(*3b*)	$8k_3 K_D p_D^0/[1 + (1 + 8K_D p_D^0)^{0.5}]^3$	113	0·12	–	1·655 . 10^0
4	(*4a*)	$4k_4 K_D K'_D (p_D^0)^2/\{1 + [1 + 8K_D p_D^0(1 + K_D p_D^0)]^{0.5}\}^2$	80·3	1·51	0·15	2·361 . 10^0
	(*4b*)	$k_4(K_D p_D^0)^2/(1 + K_D p_D^0)^2$	39·2	0·29	–	3·594 . 10^0
5, 6	(*5*), (*6*)	$k_j K_{1-B} p_{1-B}^0/(1 + K_{1-B} p_{1-B}^0)$ $(j = 5, 6)$	444[b]	0·0035[b]	–	9·050 . 10^0
			184[c]	0·0017[c]	–	8·133 . 10^{-1}

[a] Dimensions: k_j (mol h^{-1} kg^{-1}); K_i, K'_i (kPa^{-1}); Q_{min} (mol^2 h^{-2} kg^{-2}); [b] for the isomerization to *cis*-2-butene ($j = 5$); [c] to *trans*-2-butene ($j = 6$).

We substituted for r_3^0 and r_4^0 the modified (with $K_{W,j}$ in the denominator) Eqs. (*3a*) and (*4a*) with the parameters given in Table II and by minimizing the objective function Q'

$$Q' = [(R_A^0 + R_B^0)_{calc} - (R_A^0 + R_B^0)_{obs}]^2 \tag{9}$$

we could find the best fitting equation for r^0_{-1} and estimate its parameters together with the parameters $K_{W,3}$ and $K_{W,4}$ (see Table III) in the modified equations (*3a*) and (*4a*). The expression for r^0_{-1} which best fitted the experimental R_A^0, R_B^0 data had the form

$$r^0_{-1} = k_{-1}K_D K_{W,-1} p_D^0 p_W^0/(1 + K_D p_D^0 + K_{W,-1} p_W^0) \tag{10}$$

with the parameter values $k_{-1} = 1{\cdot}37 \text{ mol h}^{-1} \text{ kg}^{-1}$; $K_D = 0{\cdot}39 \text{ kPa}^{-1}$; $K_{W,-1} = 3{\cdot}4 \text{ kPa}^{-1}$.

The numerical values of $K_{W,j}$ in Table III do not represent, however, any direct measure of the intensity of the inhibiting effect of water on the individual reactions

TABLE III

Values of the adsorption parameters $K_{W,j}$ of water in reactions *j*

Rate equation (see Table II)	(*1*)	(*2a*)	(*3a*)	(*4a*)	(*5*)	(*6*)
$K_{W,j}$ (kPa^{-1})	0·41	0·28	1·8	1·4	0·49	0·32

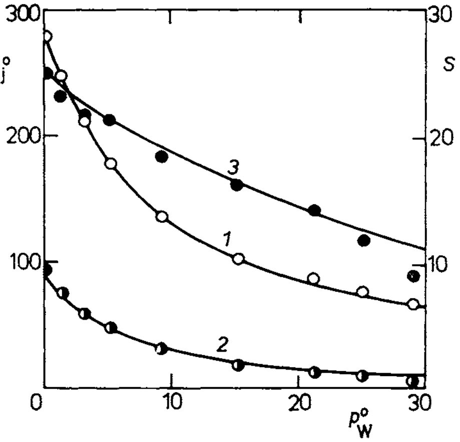


FIG. 3

Effect of initial partial pressure of water p_W^0 (kPa) on the initial rates r_j^0 (mol kg^{-1} . h^{-1}) and selectivity S (%) in 1-butanol dehydration. Points are experimental values, curves are calculated with the use of Eqs (*1*) and (*2a*) (see Table II) extended by the term $K_{W,j}p_W^0$ in the denominator; the $K_{W,j}$ values see Table III. *1* Initial rate r_1^0, *2* r_2^0, *3* selectivity S

since the kinetics of the reactions is described by rate equations of different mathematical form. A given value of $K_{W,j}$, *e.g.* in equations with third power in the denominator, such as Eqs (*2a*) or (*3a*), would lower the rate much strongly than the same numerical $K_{W,j}$ value in equations of asymptotic form such as Eqs (*1*) or (*4a*). The experimental results of the type presented in Fig. 3 revealed, however, that water exhibits stronger inhibiting effect on the isomerization of 1-butene than on the dehydration of 1-butanol; in the latter transformation, the olefin-forming reaction is supressed more than the ether-forming one (see also the selectivity curve in Fig. 3). This is also apparent from Table IV where the effects of water are expressed as relative reaction rates of individual reactions at a given water partial pressure, related to the reaction rates in the absence of water (taken as 100%). The relative rate values of ether transformation (reactions 3 and 4) are loaded with considerable error because they could not be measured directly in the presence of water for the above mentioned reasons. Nevertheless, it seems that the effect of water on the direct olefin formation is here again stronger that that on the parallel reaction (disproportionation of ether).

It may be concluded, therefore, that the addition of water to the reaction system of 1-butanol dehydration is an efficient tool for influencing selectivity: we can diminish the content of 2-butenes in the olefinic product and we are also able to vary the alkene to ether ratio.

In attempts to explain possible ways of action of water on the reaction system of 1-butanol dehydration on alumina, one has to distinguish two effects:

a) The reversible one, observed on stabilized catalysts, which has just been discussed. Because of its reversibility, it may be regarded as chemisorption of water on active catalytic sites. This effect is, with respect to the sensitivity order of individual reactions, very similar to that observed in the poisoning of alumina with sodium ions in the same reaction system[22] and it can be assumed, therefore, that the adsorption of water might be associated with acidic sites of alumina.

TABLE IV

Relative initial rates of reactions (1) to (6) in the presence of water

12x8

Partial pressure of water p_W^0 (kPa)	Relative rates[a] (%) of reactions					
	1	2	3	4	5	6
5	63·4	58·1	9·9[b]	79·1[b]	32·6	40·1
15	36·8	24·6	1·1[b]	53·0[b]	13·9	18·6

[a] Rate of each reaction in the absence of water taken as 100%; [b] values less reliable because of their indirect determination (see text).

+/18

b) Water may also have another effect on alumina consisting probably in modification of the active surface of the catalyst. This modification is probably a slow process and might be the reason for the rather long stabilization period of the activity of a fresh catalyst when contacted with the reaction mixture (see Experimental). During the stabilization period, the addition of water to the feed caused a decrease of catalytic activity which could not be fully restored after the addition of water had been stopped[27]. On the stabilized catalyst, however, the effect of water on the activity was reversible.

The fact that the reversible effect of water expressed by the parameters $K_{W,j}$ is not sufficient to extend the validity of initial rate equations to the high conversion region of 1-butanol dehydration could also be interpreted as evidence of a more complex action of water on the reaction system under study; this problem will be discussed more in detail in a following paper[23].

LIST OF SYMBOLS

F_i^0	feed rate of reactant *i* (mol h^{-1})
k_j	rate constant of the reaction *j* (mol kg^{-1} h^{-1})
K_i, K_i'	adsorption parameter of reactant *i* (kPa^{-1})
$K_{W,j}$	adsorption parameter of water in *j*-th reaction (kPa^{-1})
p_i^0	initial partial pressure of reaction component *i* (kPa)
Q	sum of squared deviations between calculated and observed reaction rates (mol^2 . . kg^{-2} h^{-2})
Q'	objective function defined by Eq. (*9*) (mol^2 kg^{-2} h^{-2})
r_j^0	initial reaction rate of *j*-th reaction (mol kg^{-1} h^{-1})
R_i	rate of formation of product i (mol kg^{-1} h^{-1})
S	$= 100r_2^0/(r_1^0 + r_2^0)$ selectivity of butenes formation from 1-butanol (%)
W	mass of catalyst (kg)
W/F_i^0	space time (reciprocal space velocity of reactant *i*) (h kg mol^{-1})
x	degree of conversion (%)

Substances:

A	1-butanol
B	butenes in general
1-B	1-butene
cis-2-B	*cis*-2-butene
trans-2-B	*trans*-2-butene
D	di-(1-butyl) ether
W	water

Indices (subscripts):

calc	calculated
obs	observed
i	reaction component
j	reactions in Schemes 1 and 2

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