

KINETICS OF COMPLEX HETEROGENEOUS CATALYTIC REACTIONS. V.* PARALLEL-CONSECUTIVE HYDROGENATION OF CROTONALDEHYDE

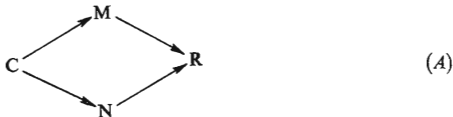
J. ŠIMONÍK** and L. BERÁNEK

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague-Suchdol*

Received December 17th, 1970

Kinetics of parallel-consecutive hydrogenation of crotonaldehyde, leading *via* butyraldehyde or *via* crotyl alcohol to butanol, has been studied. The kinetic measurements were carried out in a flow reactor with reactants in gaseous phase (total pressure less than or equal to 1 atm.) at 160°C, using platinum with added iron on the silica gel modified by sodium hydroxide as the catalyst. It was found that hydrogenation reactions are accompanied by isomerization of crotyl alcohol to butyraldehyde. Kinetic behaviour of this parallel-consecutive system consisting of five reactions was described on the basis of the results of separate study of single reactions. Equations of Langmuir-Hinshelwood type proved to be the best ones for this purpose. Their form and the values of their constants did not change on going from single reactions to the system in which all these reactions proceed simultaneously on the surface of the catalyst. Three of the hydrogenation reactions could be described by kinetic equations of identical form with unique value of adsorption coefficient for each of the present compounds in all the three reactions. Differences between the kinetic behaviour of crotyl alcohol and the behaviour of crotonaldehyde and butyraldehyde are stressed.

In previous works of this series we dealt with kinetics of some consecutive^{1,2} and parallel^{3,4} heterogeneous catalytic reactions. The aim of these studies was to verify, whether the course of such complex catalytic reactions can be described on the basis of separate examination of kinetics of single reactions and, further, whether kinetic relations and the values of their constants obtained for isolated reactions could be valid also for a coupled reaction system. In the present work we wish to report the results of analysis of a reaction network consisting of parallel and consecutive heterogeneous catalytic reactions

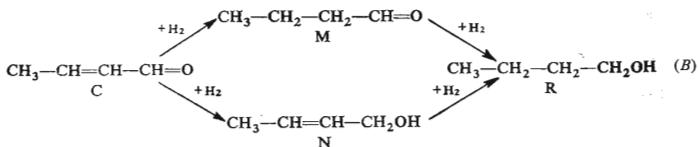


* Part IV: This Journal 35, 2367 (1970).

** Present address: Research Institute for Rubber and Plastics Technology, Gottwaldov.

The two-step parallel reactions of this type, having common product, are frequently encountered in practice, *e.g.* reactions of compounds having two different groups, or the same groups in non-equivalent positions, such as various hydrogenations, eliminations or oxidations of bi-functional compounds belong to this class. In homogeneous catalysis, kinetics of parallel-consecutive alkaline hydrolysis of diethyl ester of malic acid was studied by Svírbely and Kundell⁵. Owing to simplicity of the kinetics of single reactions (second order) the authors were able to determine the corresponding rate constants by treating simultaneously integral data for all the four reactions.

As a model reaction for a study of heterogeneously catalyzed system of the above type we chose hydrogenation of crotonaldehyde in gaseous phase at 160°C on a platinum catalyst on which hydrogenation of both the C=C and C=O bonds takes place.



Hydrogenation of crotonaldehyde has received much attention. However, most of the hitherto studies have dealt only with the description of reaction conditions and of selectivity of a catalyst, with respect to formation of butanol, butyraldehyde or crotyl alcohol. Of single reactions taking place during hydrogenation of crotonaldehyde, only hydrogenation of butyraldehyde has been studied kinetically. The kinetic data were interpreted either by means of power-type equations⁶ or with the aid of simple equations of Langmuir-Hinshelwood type^{7,8}. A quantitative kinetic study of this system of parallel-consecutive reactions as the whole or of other similar heterogeneous catalytic case, have not so far been made.

EXPERIMENTAL

Compounds Used

Crotonaldehyde (Carlo Erba, Milano), butyraldehyde and n-butanol (both Lachema, Brno) were dried over magnesium sulphate and then fractionated on a 35 TP column. The chromatographically pure compounds were stored in sealed ampules (crotonaldehyde was stabilized by hydroquinone). Crotyl alcohol was prepared by reduction of crotonaldehyde with lithium aluminium hydride; after drying and fractionation, it was also stored in sealed ampules.

Electrolytic hydrogen and nitrogen (for electric lamps), from pressure cylinders (Technoplyn, Ostrava), were freed from traces of oxygen by passing over a palladium catalyst and dried by the layer of sodium hydroxide.

The platinum catalyst was prepared by impregnation of silica gel (BDH, for chromatographic adsorption, 0.2 mm particles size) successively with aqueous solution of chloroplatinic acid (analytical purity grade, Kovohutě, Vestec) and aqueous sodium hydroxide. After evaporation of the solvent on a rotatory evaporator, the silica gel was further impregnated by aqueous solution of ferrous sulphate (chemical purity grade, Lachema, Brno) and then dried. The preparation contained 1% Pt, 0.7% Fe and 2% NaOH (w. %), its specific surface, determined by BET method,

amounted to $370 \text{ m}^2/\text{g}$. Each determination of initial reaction rate was carried out with fresh sample taken from this stock preparation. The sample was reduced directly in the reactor in a stream of hydrogen at 200°C for 2 hours.

Apparatus and Procedure

The procedure and flow equipment were similar to those described in our previous studies^{1,9-11}. Liquid reactants were fed to evaporator where their vapours were mixed with hydrogen or with a mixture of hydrogen and nitrogen of the appropriate composition. The liquid reactant to gases feeding rate ratio controlled the partial pressure of the reactant. The mixture was led from the evaporator to the U-reactor made of glass tube (9 mm inside diameter) which was placed in a silicone oil bath of constant temperature. The reactor was charged with the catalyst (0.5 g for measurements of initial reaction rates and c. 6 g for integral measurements) mixed with glass balls. The thermocouple well (the tube of 5 mm o. d.) was placed in the catalyst bed. The temperature inside the bed was maintained at $160 \pm 0.5^\circ\text{C}$. After steady state in the reactor was attained, liquid reaction products were separated from stream of gases in a trap cooled to -78°C .

Liquid reaction products were analyzed on a Shandon gas chromatograph provided with flame-ionization detector, using hydrogen as carrier gas. The separation of a mixture of crotonaldehyde, butyraldehyde, crotyl alcohol, and butanol was achieved on 20 w. % diglycerol on Cellite (30 to 80 mesh), using 2 m column and temperature 80°C . Chromatograms were evaluated by measuring the area of chromatographic peaks which were converted to weight amounts with the aid of appropriate calibration graphs.

Kinetic Measurements

Initial reaction rates were determined graphically as the slopes of experimental dependences of conversions upon reciprocal space velocities W/F in the point $x = 0$; up to $x = 0.1$ these dependences were linear. In all the measurements the pressure in the equipment was atmospheric; the pressure of reactants was reduced by diluting the reactants with nitrogen. Integral measurements (dependences of x upon W/F up to $x = 0.86$) were carried out on the same apparatus, using gradually increasing amount of the catalyst. All the measurements were carried out at condition which ensured that none of the reaction was affected by internal or external diffusion, as checked by preliminary experiments (particles size 0.2 mm, mass feed rate $G > 25 \text{ kg/m}^2 \text{ h}$).

RESULTS AND DISCUSSION

Choice of Catalyst

We were first looking for a catalyst suitable for kinetic study of the reaction network (B). Such catalyst should catalyze hydrogenation of both multiple bonds at not much different rates and its activity should be stable enough; furthermore, no undesired side reactions should proceed in its presence (Table I). Catalysts 1-4 containing copper were found to be ineffective in hydrogenation of the carbonyl group. Neither addition of barium to copper(II) chromate(III) after Adkins¹² (catalyst 5), nor the use of cadmium (catalysts 6 and 7) or nickel (catalyst 8) resulted in success. Similarly, platinum catalyst 9, used in other works^{1,13} for hydrogenation of phenol and cyclohexanone, did not catalyze hydrogenation of the carbonyl group of croton-

aldehyde. We found, that this reaction can be effected by catalyst 10, prepared after Rylander¹⁴, *i.e.* by platinum with admixtures of iron and zinc; however, side reactions were taking place to a great extent. A similar change of selectivity of platinum catalyst was also achieved by adding iron to catalyst 9; no side reactions has been observed in this case. The catalyst so prepared (11) was then used in hydrogenation of crotonaldehyde. For all the reactions studied and over the whole region of conversions its activity was found to be constant after the period of 60–90 minutes (after which steady state in the reactor was attained).

Kinetic Analysis of Isolated Reactions

Kinetic analysis of single reactions was made by the method of initial reaction rates, using conditions at which the reactions are practically irreversible (160°C). As hydrogenation of crotonaldehyde was found to be accompanied by its isomerization to butyraldehyde, the reaction network took finally the form (C).



TABLE I
Survey of Catalysts Tested

Catalyst	Active component	Carrier	Preparation	Activity for hydrogenation	
				C=C bond	C=O bond
1	Cu	kieselguhr	precipitation	active	inactive
2	Cu + 3% Cd	kieselguhr	co-precipitation	little active	inactive
3	Cu + 3% Cd	kieselguhr	precipitation and impregnation	little active	inactive
4	Cu + Cr	—	co-precipitation	active	inactive
5	Cu + Cr + Ba	—	co-precipitation	active	inactive
6	Cd	—	precipitation	inactive	inactive
7	Cd	charcoal	impregnation	inactive	inactive
8	Ni	—	precipitation	active	inactive
9	1% Pt	silica gel +2% NaOH	impregnation	active	inactive
10	1%Pt, 0.4%Fe 0.06% Zn	charcoal	impregnation	active	active
11	1% Pt 0.7% Fe	silica gel +2% NaOH	impregnation	active	active

Using the method of initial reaction rates we studied, therefore, the reaction of crotonaldehyde, measuring the rates of formation of butyraldehyde (M) and crotyl alcohol (N), the reaction of butyraldehyde (M) leading to butanol (R), and finally the reaction of crotyl alcohol (N) giving butanol (R) and, by isomerization, also butyraldehyde (M). For each of these five reactions we determined 30 values of initial reaction rates r^0 . The partial pressure of hydrogen was changed within the range of 0.05–0.97 atm, that of organic substance varied within 0.03–0.80 atm. The reaction of crotyl alcohol was also measured in the absence of hydrogen; in this case the alcohol is also isomerized¹⁵. Seven values of r^0 at partial pressures of crotyl alcohol varying from 0.08 to 0.90 atm were determined.

Experimental rate data were statistically treated by a combined method of linear and non-linear regression¹³. In interpreting data on hydrogenation reactions ($A + B \rightarrow$ products), we used 32 rate equations of the types given in Table II. These equations were derived on the basis of Langmuir–Hinshelwood concepts on assuming

TABLE II
Types of Rate Equations Used to Express r^0 Data for Reactions $A + B \rightarrow$ Products

Type of equation	Right-hand side of rate equation $r^0 = f(p_A^0, p_B^0)^a$	Rate-controlling step ^b	s	Note
(1)	$k_{ads} p_A^0 / [1 + (K_B p_B^0)^b]^s$	ads A	1, 2	
(2)	$k_{ads} p_B^0 / [1 + (K_A p_A^0)^a]^s$	ads B	1, 2	
(3)	$k_{ads} p_B^0 [(1 + 8K_A p_A^0)^{1/2} - 1]^s / (4K_A p_A^0)^s$	ads B	1, 2	adsorption of A on two centers without dissociation ¹⁷
(4)	$kK_A p_A^0 p_B^0 / [1 + (K_A p_A^0)^a]^s$	sr	1–4	B is not adsorbed
(5)	$kK_A K_B p_A^0 p_B^0 / [1 + (K_A p_A^0)^a + (K_B p_B^0)^b]^s$	sr	2–4	
(6)	$kK_A K_B p_A^0 p_B^0 / [1 + (K_A p_A^0)^a]^s \cdot [1 + (K_B p_B^0)^b]^s$	sr	1, 2	B is adsorbed on other centers than is A
(7)	$k p_B^0 [(1 + 8K_A p_A^0)^{1/2} - 1]^s / 4(K_A p_A^0)^{s-1}$	sr	2, 3	adsorption of A on two centers without dissociation ¹⁷ , B is not adsorbed
(8)	$kK_B p_B^0 \{ [1 + (K_B p_B^0)^b]^2 + 8K_A p_A^0 \}^{1/2} - [1 + (K_B p_B^0)^b]^s / 4(K_A p_A^0)^{s-1}$	sr	3, 4	adsorption of A on two centers without dissociation ¹⁷
(9)	$k(p_A^0)^a (p_B^0)^b$	—	—	empirical power-type equation

^a Values a and b equal to 1 or 0.5, depending upon whether a given substance is presumed to be adsorbed on one center without dissociation or on two centers with dissociation. ^b ads A, ads B — adsorption of compound A or B is presumed to be rate-controlling step; sr — surface reaction is presumed to be rate-controlling step.

that the rate-controlling step of the reaction is adsorption of some of the starting compounds, or surface reaction of adsorbed substances. The models at which desorption is considered as rate-controlling step were excluded on the basis of confrontation of the course of experimental integral dependences $x = f(W/F)$ (Fig. 1) with conclusions drawn from analysis of the effect of slow desorption on the composition of products of consecutive and parallel reaction^{16,17}. When deriving the equations, we made alternative assumption that the reactants may be adsorbed on one active center without dissociation or on two centers with dissociation, or that one of reactants is not adsorbed but reacts directly from gaseous phase. We considered also the cases where organic molecule adsorbs on two centers without dissociation¹⁷ or where adsorption of hydrogen occurs on other centers than that of organic substance. For purposes of comparison the data were also treated by power-type rate equation. The rate equations used to interpret kinetic data relating to isomerization of crotyl alcohol to butyraldehyde, along with discussion of somewhat unusual kinetics of this reaction, will be reported separately¹⁵.

We have found that the reactions of crotonaldehyde leading to butyraldehyde (reaction (1)) and to crotyl alcohol (reaction (2)) as well as the reaction of butyraldehyde leading to butanol (reaction (4)) can be best described by equations of the type (5) (Table II) with $a = 0.5$

$$r^0 = kK_A K_B p_A^0 p_B^0 / [1 + (K_A p_A^0)^{0.5} + (K_B p_B^0)^{0.5}]^4, \quad (10)$$

$$r^0 = kK_A K_B p_A^0 p_B^0 / [1 + (K_A p_A^0)^{0.5} + K_B p_B^0]^4, \quad (11)$$

$$r^0 = kK_A K_B p_A^0 p_B^0 / [1 + (K_A p_A^0)^{0.5} + K_B p_B^0]^3, \quad (12)$$

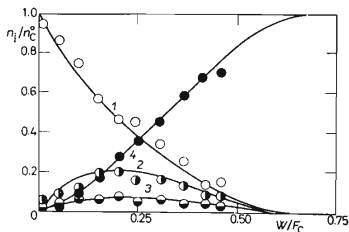


FIG. 1

Dependences of Relative Molar Concentrations of Organic Components n_i/n_C^0 on Reciprocal Space Velocity W/F_C (kg h mol^{-1}) for Hydrogenation of Crotonaldehyde by Hydrogen at Initial Ratio $M = 10$

The curves are calculated (1 crotonaldehyde, 2 butyraldehyde, 3 crotyl alcohol, 4 butanol), points represent experimental values.

which can be distinguished statistically only with difficulty; the values of the sums of squared deviations of the experimental from the calculated reaction rate Q are given in Table III. From the Table it is evident that the hydrogenation of crotyl alcohol to butanol (reaction (5)) is best described by different models, compared to those used in previous reactions (equations of the type (4) and (5) with $a = 1$), namely

$$r^0 = kK_A K_B p_A^0 p_B^0 / [1 + K_A p_A^0 + K_B p_B^0]^2, \quad (13)$$

$$r^0 = kK_A p_A^0 p_B^0 / [1 + K_A p_A^0]^2, \quad (14)$$

$$r^0 = kK_A K_B p_A^0 p_B^0 / [1 + K_A p_A^0 + (K_B p_B^0)^{0.5}]^3. \quad (15)$$

However, equations (10)–(15) all fulfil presumption that surface reaction is rate-controlling. In the case of hydrogenation of crotonaldehyde and of butyraldehyde the models considering adsorption of these substances on two centers are more probable ($a = 0.5$), and the hydrogenation of crotyl alcohol is best described by models presuming one-center adsorption of this substance ($a = 1$). Further differentiation of the mechanisms within these groups, *i.e.* the mode of hydrogen adsorption or the number of active centers taking part in the reaction, cannot be made on the basis of the sums of squared deviations only.

In Table IV are summarized the values of the constants obtained for relations (10) and (13) by non-linear regression treatment. The adsorption coefficients of crotonaldehyde determined by independent treatment of rate data for formation of butyraldehyde and for formation of crotyl alcohol are similar in value (17 atm^{-1} and 19 atm^{-1}). This indicates that the adsorbed complex is probably the same for both reactions; it might be a complex formed by 1,4-addition of the conjugated system of crotonaldehyde to two centers (in fact, treatment of the relevant kinetic data showed the adsorption of crotonaldehyde on two centers is more probable). This

TABLE III
Best Equations for Hydrogenation Reactions $A + B \rightarrow$ Products

Equation No	Value of Q for reactions			
	1	2	4	5
(10)	17.1	0.785	2.84	11.84
(11)	17.0	0.869	3.33	12.65
(12)	17.4	0.858	3.11	20.68
(13)	19.2	1.192	6.58	7.01
(14)	19.5	1.382	7.66	7.81
(15)	21.4	1.401	9.21	10.20

TABLE IV
Values of Kinetic Constants Determined From Initial Reaction Rates of Isolated Reactions

Hydrogenation of compound A	According to Eq. (10)			According to Eq. (13)		
	k_i^+	K_A	K_B	k_i^+	K_A	K_B
Crotonaldehyde to butyraldehyde	4 329	17	0.55	248	8	0.23
Crotonaldehyde to crotyl alcohol	1 758	19	0.9	108	9.5	0.68
Butyraldehyde	8 877	35	0.8	526	16	0.76
Crotyl alcohol	6 578	20	0.07	1 060	14	0.38

TABLE V
Values of Adsorption Coefficient of Butanol

From rate-retarding effect on hydrogenation	Relation	K_R
Crotonaldehyde to butyraldehyde	(10a)	1.0
to crotyl alcohol	(10a)	0.8
Butyraldehyde	(10a)	0.85
Crotyl alcohol	(13a)	7.8

complex might then react with adsorbed hydrogen, yielding either butyraldehyde or crotyl alcohol. It seems likely that the selectivity of the transformation of crotonaldehyde is dependent rather on the values of rate constants of these surface reactions than on the mode of adsorption of crotonaldehyde.

Adsorption coefficients of hydrogen should be approximately the same for all the reactions studied if these proceed on the same active centers. This seems likely for both reactions of crotonaldehyde and for the reaction of butyraldehyde. In these cases the adsorption coefficients vary between 0.55 and 0.9 atm⁻¹ (calculated from Eq. (10)). Contrarily, the value of adsorption coefficient of hydrogen determined for the hydrogenation of crotyl alcohol differs from those, found in the preceding case.

It is worthy of note that different kinetic behaviour of compounds having isolated C=C bond, when compared with those containing the C=C bond conjugated with an unsaturated carbon to heteroatom bond, has already been observed by Endrýsová and Kraus for hydrogenation on a palladium-silica gel catalyst¹⁸.

The results of kinetic analysis of isomerization of crotyl alcohol to butyraldehyde are reported separately¹⁵. It was established that the rate of this reaction in the presence of hydrogen follows Eq. (16), which combines a mono- and bimolecular mechanism.

$$r^0 = k_{3,2}K_{N,2}K_{B,2}p_N^0p_B^0/(1 + K_{N,2}p_N^0 + K_{B,2}p_B^0)^2 + k_{3,1}K_{N,1}p_N^0/(1 + K_{N,1}p_N^0 + K_{B,1}p_B^0) \quad (16)$$

with $k_{3,2} = 647$, $k_{3,1} = 3.1 \text{ mol h}^{-1} \text{ kg}^{-1}$, $K_{N,2} = 29.5$, $K_{N,1} = 4.2$, $K_{B,2} = 0.042$ and $k_{B,1} = 3.7 \text{ atm}^{-1}$.

Kinetic Description of the Coupled System

The relations for reaction rates in the system containing all the compounds specified in the reaction network (C) *i.e.* when the hydrogenation of crotonaldehyde is allowed to proceed to high conversions, are obtained by expansion of the relations for initial reaction rates (10), (13), and (16) by terms corresponding to other compounds concerned. On deriving these relations we made assumption that all the substances adsorb and thus compete with reactants for free surface, and thus decelerate the corresponding reaction. The individual reactions occurring in the system under study can be then described by the following rate equations:

$$r_1 = dx_1/d(W/F_C) = k_1^+ p_C p_B / (1 + \sqrt{(K_C p_C)} + \sqrt{(K_B p_B)} + \sqrt{(K_M p_M)} + K_N p_N + K_R p_R)^4 \quad (17a)$$

$$r_2 = dx_2/d(W/F_C) = k_2^+ p_C p_B / (1 + \sqrt{(K_C p_C)} + \sqrt{(K_B p_B)} + \sqrt{(K_M p_M)} + K_N p_N + K_R p_R)^4 \quad (17b)$$

$$r_3 = dx_3/d(W/F_C) = k_{3,2}^+ p_N p_B / (1 + \sqrt{(K_C p_C)} + K_{B,2} p_B + \sqrt{(K_M p_M)} + K_{N,2} p_N + K_R p_R)^4 + k_{3,1}^+ p_N / (1 + K_{N,1} p_N + K_{B,1} p_B) \quad (17c)$$

$$r_4 = dx_4/d(W/F_C) = k_4^+ p_M p_B / (1 + \sqrt{(K_C p_C)} + \sqrt{(K_B p_B)} + \sqrt{(K_M p_M)} + K_N p_N + K_R p_R)^4 \quad (17d)$$

$$r_5 = dx_5/d(W/F_C) = k_5^+ p_N p_B / (1 + \sqrt{(K_C p_C)} + K_B p_B + \sqrt{(K_M p_M)} + K_N p_N + K_R p_R)^2 \quad (17e)$$

The values of the constants of these equations are already known from a study of isolated reactions (Table IV and Eq. (16)), except for values of the adsorption coefficients of the final product, butanol, K_R . Its values were determined experimentally from rate-retarding effect of butanol on single reactions in the following way: To mixture of starting compounds crotonaldehyde-hydrogen, butyraldehyde-hydrogen, or crotyl alcohol-hydrogen, of different composition (p_A^0 from 0.05 to 0.25 atm,

p_B^0 from 0.25 to 0.8 atm) was added butanol (its partial pressure p_R^0 was changed from 0.1 to 0.65 atm, 6 values for each reaction), and then initial reaction rate was measured. The adsorption coefficient K_R was calculated by means of simple non-linear regression from the relations

$$r_i = k_i^+ p_A p_B / [1 + \sqrt{(K_A p_A)} + \sqrt{(K_B p_B)} + (K_R p_R)^m]^4 \quad (10a)$$

for hydrogenation of crotonaldehyde to butyraldehyde and to crotyl alcohol and for the hydrogenation of butyraldehyde, and from the relation

$$r_5 = k_5^+ p_N p_B / [1 + K_N p_N + K_B p_B + (K_R p_R)^m]^2 \quad (13a)$$

for the hydrogenation of crotyl alcohol. The obtained values of K_R are given in Table V. The better agreement with experimental data was achieved under assumption that butanol adsorbs without dissociation ($m = 1$) then when its adsorption was presumed to proceed with dissociation ($m = 0.5$).

By numerical integration of the set of equations (17a)–(17e) on a digital computer, we calculated the dependences of relative concentrations of organic substances on reciprocal space velocity. Prior to the integration, the partial pressures in Eqs (17a)–(17e) were transformed into conversions $x_1 - x_5$ by using the following relations

$$p_C = (1 - x_1 - x_2) P/Z, \quad (18a)$$

$$p_B = (M - x_1 - x_2 - x_4 - x_5) P/Z, \quad (18b)$$

$$p_M = (x_1 + x_3 - x_4) P/Z, \quad (18c)$$

$$p_N = (x_2 - x_3 - x_5) P/Z, \quad (18d)$$

$$p_R = (x_4 + x_5) P/Z, \quad (18e)$$

TABLE VI

Values of Constants k_i^+ and of Adsorption Coefficients K_j Used in Integration

Reaction in (C)	Kinetic Eq.	k_i^+	K_C	K_B	K_M	K_N	K_R
1	(17a)	4 329	18	0.55	25	14	0.9
2	(17b)	1 758	18	0.55	25	14	0.9
4	(17d)	8 877	18	0.55	25	14	0.9
5	(17e)	1 060	8.7	0.38	16	14	7.8
3	(17c)	802 ^a	18	0.042 ^a	25	29.5 ^a	0.9
		13 ^b	—	3.7 ^b	—	4.2 ^b	—

^a For bimolecular isomerization; ^b for monomolecular isomerization.

where

$$Z = 1 + M - x_1 - x_2 - x_4 - x_5. \quad (18f)$$

The integration within the limits $W/F_C = 0$ to $W/F_C = 0.7 \text{ kg h/mol}$ for $M = 10$ yielded the values of conversions $x_1 - x_5$ as a function of W/F_C , which enabled us to construct the integral curves, which are graphically represented in Fig. 1. The values of constants k_i^+ were taken from Table IV. The number of experimental adsorption coefficients for individual reactions was however reduced by their unification (Table VI). We started from the assumption that in the reactions which follow the same kinetic equation (hydrogenation of crotonaldehyde to butyraldehyde and to crotyl alcohol, and hydrogenation of butyraldehyde to butanol, Eq. (10)), the adsorption of each reaction component should be expressed by one value of the adsorption coefficient (first three lines in Table VI). As the adsorption coefficient of hydrogen we took the value obtained by kinetic analysis of hydrogenation of crotonaldehyde to butyraldehyde, since this reaction is the most important one of the reaction system studied. Similarly, as the adsorption coefficient of butyraldehyde, K_M , we took the value found by following the effect of butyraldehyde upon this reaction. The adsorption coefficient of crotonaldehyde, K_C , was expressed by the mean value of the coefficients obtained by kinetic analysis of its reaction leading to butyraldehyde and to crotyl alcohol, and the adsorption coefficient of butanol, K_R , was taken as the mean value of the coefficients determined from the rate-retarding effect of butanol on the above three reactions which follow Eq. (10) (Table V). The adsorption effect of crotyl alcohol on these three reactions was expressed by the value of K_N obtained by treatment of initial rate data for its hydrogenation.

For description of adsorption effect of the present substances on hydrogenation of crotyl alcohol we used for hydrogen and crotyl alcohol the values of adsorption coefficients obtained by kinetic analysis of initial rate data for hydrogenation of crotyl alcohol by means of Eq. (13); Similarly, for crotonaldehyde and butyraldehyde we took the adsorption coefficients found by treatment of the rate data for reactions of these compounds by means of Eq. (13) (as the adsorption coefficient of crotonaldehyde, K_C , we took again the mean value obtained by treatment of both parallel pathways of its transformation). The adsorption coefficient of butanol was expressed by the value determined from its rate-retarding effect on the hydrogenation of crotyl alcohol by means of Eq. (13a) (Table V).

For description of the effect of adsorption on isomerization of crotyl alcohol, we used for crotyl alcohol and hydrogen the values obtained by treatment of initial rate data for mono- and bimolecular isomerization (Eq. (16)). In description of the effect of other substances (crotonaldehyde, butyraldehyde, and butanol) whose rate-retarding effect on isomerization of crotyl alcohol was not studied, we used the same values as in the estimation of their effect on hydrogenation of crotonaldehyde and of butyraldehyde.

Using the same conditions for which the integral curves represented in Fig. 1 were calculated, we also determined experimentally the dependences of relative concentrations of organic reaction components (crotonaldehyde, butyraldehyde, crotyl alcohol, and butanol) on reciprocal space velocity. The obtained data are also plotted in Fig. 1. It is seen that the agreement between calculation and experiment is very good and that the kinetic description of the studied system of five reactions can be obtained by the separate study of the kinetics of single reactions. Furthermore, the isolation of reactions makes it possible to discover some reaction paths which otherwise (by studying the system as the whole) could not be established (*e.g.* isomerization of crotyl alcohol). The fact that each of the reaction components is characterized by one value of adsorption coefficient in more reactions indicates a more general meaning of these quantities.

The authors thank Mrs J. Kubešová and Mrs J. Wolfová for careful carrying out chromatographic analyses.

LIST OF SYMBOLS

a, b, m	exponent at adsorption terms in the denominator of rate equations, equaling to 1 or 0.5 in dependence on whether the given substance is presumed to be adsorbed without or with dissociation
F	feed rate (mol h^{-1})
F/W	space velocity ($\text{mol h}^{-1} \text{kg}^{-1}$)
G	mass feed rate ($\text{kg m}^{-2} \text{h}^{-1}$)
k_{ads}	rate constant of adsorption ($\text{mol h}^{-1} \text{kg}^{-1} \text{atm}^{-1}$)
k_i	rate constant of i -th surface reaction ($\text{mol h}^{-1} \text{kg}^{-1}$)
$k_{3,1}, k_{3,2}$	rate constant of monomolecular or bimolecular isomerization of crotyl alcohol ($\text{mol h}^{-1} \text{kg}^{-1}$)
k_i^+	complex constant in the numerator of rate equation of i -th reaction which equals to the product of rate constant and adsorption coefficients of reactants ($=k_i K_A K_B$)
K_j	adsorption coefficient of substance j (atm^{-1})
$K_{j,1}, K_{j,2}$	adsorption coefficient of substance j in monomolecular or bimolecular isomerization of crotyl alcohol (atm^{-1})
$M = p_B^0/p_C^0$	initial molar ratio of hydrogen to crotonaldehyde
n_j	number of mol of substance j
n_j^0	initial number of mol of substance j
p_j	partial pressure of substance j (atm)
p_j^0	initial partial pressure of substance j (atm)
P	total pressure (atm)
Q	sum of the squared deviations of the experimental from the calculated reaction rate
r_i	reaction rate of i -th reaction ($\text{mol h}^{-1} \text{kg}^{-1}$)
r_i^0	initial reaction rate of i -th reaction ($\text{mol h}^{-1} \text{kg}^{-1}$)
s	exponent in rate equations, corresponding to the number of active centers taking part in the rate-controlling step
W	weight of catalyst (kg)
x	degree of conversion
Z	polynomial defined by Eq. (18f)

α, β exponents at partial pressures of organic component and hydrogen in power-type equation (9)

Indices

Reactions (*i*):

- 1 hydrogenation of crotonaldehyde to butyraldehyde
- 2 hydrogenation of crotonaldehyde to crotyl alcohol
- 3 isomerization of crotyl alcohol to butyraldehyde
- 4 hydrogenation of butyraldehyde to butanol
- 5 hydrogenation of crotyl alcohol to butanol

Reaction components (*j*):

- A organic substance generally
- B hydrogen
- C crotonaldehyde
- M butyraldehyde
- N crotyl alcohol
- R butanol

REFERENCES

1. Hančil V., Beránek L.: Fourth International Congress on Catalysis, Moscow 1968, Symposium on Mechanism and Kinetics of Complex Catalytic Reactions, Paper No 10; Chem. Eng. Sci. 25, 1121 (1970).
2. Setínek L., Beránek L., Bažant V.: This Journal 35, 2158 (1970).
3. Rybáček L., Setínek K.: This Journal 33, 3528 (1968).
4. Zanderighi L., Setínek K., Beránek L.: This Journal 35, 2367 (1970).
5. Svirbely W. J., Kundell F. A.: J. Am. Chem. Soc. 89, 5354 (1967).
6. Sporka K., Růžička V.: This Journal 33, 1247 (1968).
7. Oldenburg C. C.: *Thesis*. University of Texas, 1957; Dissertation Abstr. 17, 1520 (1957).
8. Oldenburg C. C., Rase H. F.: A.I.C.H.E.J. 3, 462 (1957).
9. Beránek L., Kraus M., Kochloeff K., Bažant V.: This Journal 25, 2513 (1960).
10. Schneider P., Kraus M., Bažant V.: This Journal 26, 1636 (1961).
11. Setínek K., Beránek L.: J. Catal. 17, 306 (1970).
12. Adkins H., Burgoyne E. E., Schneider H. J.: J. Am. Chem. Soc. 72, 2626 (1952).
13. Hančil V., Mitschka P., Beránek L.: J. Catal. 13, 435 (1969).
14. Rylander P. N., Himelstein N., Kilrby M.: Engelhard Ind. Tech. Bull. 4, 49 (1963).
15. Šimonik J., Beránek L.: J. Catal., in press.
16. Beránek L.: This Journal 33, 3541 (1968).
17. Davidova N., Penčev V., Beránek L.: This Journal 33, 1229 (1968).
18. Endrýsová J., Kraus M.: This Journal 35, 62 (1970).

Translated by J. Hettflejš.