THE KINETICS OF THE ISOMERIZATION OF ALLYL ALCOHOL TO PROPIONALDEHYDE ON PALLADIUM

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Employing the method of the initial reaction rates, the kinetics of isomerization of gaseous allyl alcohol to propionaldehyde at 120°C has been studied; the catalyst was palladium (0·1%) on active carbon. The reaction proceeded only in the presence of hydrogen. The experimental data best fitted the rate equations derived under the assumption that hydrogen activated the surface of the catalyst and increased the concentration of the active centres.

In a previous study[1] we have ascertained that isomerization of crotyl alcohol to butyraldehyde, catalysed by platinum and iron on silicagel, proceeds by the mono-molecular and the bimolecular mechanisms simultaneously, the latter mechanism requiring the presence of hydrogen. In studying the isomerization of unsaturated alcohols on platinum group metals, especially palladium, we observed[2,3] that the reaction failed to occur in the absence of hydrogen. The present paper deals with the role of hydrogen in more detail; the model reaction was isomerization of allyl alcohol catalyzed by palladium on active carbon.

EXPERIMENTAL

Chemicals. Allyl alcohol, *puriss.* (Berlin-Chemie), was distilled before use and its purity was checked by gas chromatography. Electrolytic hydrogen (Východočeské chemické závody, Pardu-bice-Rybitvi) and bulb nitrogen (Technoplyn, Ostrava) were freed from traces of oxygen by passing over heated copper and dried in a column of sodium hydroxide. The catalyst (0·1% Pd on active carbon Supersorbon, particle size 0·16—0·315 mm) was prepared as previously described[3].

Procedure. The isomerization of gaseous substrates at 120°C in a flow apparatus[3,4] was follow-ed by a standard method of kinetic measurements[4]. The weights of the catalyst were 0·02 to 0·04 g, the reciprocal space velocity was $0.29 . 10^{-3} — 1.08 . 10^{-3}$ h kg mol^{-1}. For the sake of comparability of the activity of the individual portions of the catalyst, always freshly reduced directly in the catalytic bed, first a test experiment under standard conditions was performed on each portion and according to the results the measured conversions were then corrected. It has been verified that with the given particle size of the catalyst and the given space velocity the reaction rate was not influenced by either external or internal diffusion. The reaction products were analysed by gas chromatography in an apparatus Chrom 3 (Laboratorní přístroje, Prague) with a flame-ionization detection with diglycerol (15% on Cellite) as the stationary phase and nitrogen as the carrier gas. The length of the column was 3 m, temperature 83°C.

RESULTS AND DISCUSSION

The kinetic analysis of the isomerization of allyl alcohol to propionaldehyde on palladium were performed by the method of the initial reaction rates; the conversion did not exceed 10%. The isomerization was an irreversible reaction, failing to occur without the presence of at least a small quantity of hydrogen (Fig. 1). In the presence of hydrogen it was accompanied, to a small extent, by hydrogenation of allyl alcohol to 1-propanol. As a parallel reaction, in the region of the initial reaction rates, the hydrogenation did not interfere with the kinetic analysis of the isomeriza-tion. There were measured 19 values of the initial reaction rate, r, of the isomerization in the ranges of partial pressures of allyl alcohol 0·05—0·9 atm and hydrogen 0·1—0·95 atm. The total pressure of the reactants never exceeded 1 atm and was reduced by their dilution with nitrogen. An example of the dependence of ten values of r on the composition of the starting mixture, determined at the total pressure of 1 atm, is shown in Fig. 1. To evaluate the data 19 rate equations have been derived (their general forms are given in Table I) under the assumptions of uniform activity of the catalytic centres and assuming the surface reaction was the rate-determining step. The possibility that this step would be adsorption of the reactants or desorption of the product could be ruled out from the very shape of the curve expressing the dependence of the reaction rate on the partial pressure of the reactants (Fig. 1).

In speculation about the role of hydrogen in the surface reaction two principal ideas were considered: a) hydrogen, in some form or other, participates in the rate-controlling step of the isomerization, b) the presence of hydrogen has merely an in-fluence on the concentration of the active centres. The former possibility led to the normal Langmuir–Hinshelwood equations for a bimolecular reaction (equation type (1) in Table I) or to the equations for the adsorption of allyl alcohol on two centres without dissociation of the molecule[5] (equation type (2)). It has also been considered that the rate-determining step might be the formation of a semihydrogenated inter-mediate from an adsorbed molecule of allyl alcohol and an adsorbed atom of hydro-
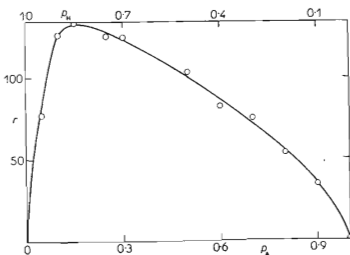

FIG. 1

Initial Isomerization Rate, r[mol h^{-1} kg^{-1}], as a Function of the Initial Partial Pressures [atm] of Allyl Alcohol, p_A and Hydrogen, p_H, at a Total Pressure $p_A + p_H = 1$ atm

gen (Eq. (3)). Eq. (4) describes the case in which adsorption of allyl alcohol (A) accompanied by splitting-off of a hydrogen atom gives rise to an intermediate of the π-allylic type (M), which recombines with the hydrogen atom in the rate-determining step with the formation of propionaldehyde (P):

$$A(g) \rightleftharpoons M(ads) + H(ads)$$

$$M(ads) + H(ads) \longrightarrow P(ads) \rightleftharpoons P(g).$$

(A)
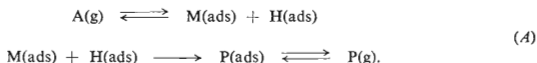
The possibility b) led to equation types (5) to (8). Equations of the types (5) and (6) have been derived from Scheme B, according to which the rate-determining step of the isomerization is a monomolecular surface reaction of allyl alcohol (step 1), accompanied by parallel formation of a non-desorbable product N, which poisons the active centres (step 2).
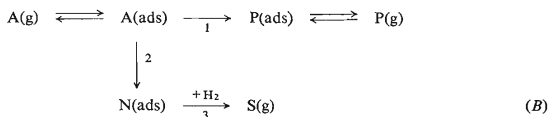
TABLE I

Types of the Rate Equations Employed

The values of a and b equal 0·5 or 1, depending on whether the adsorption of the given substance is assumed to occur with or without dissociation. The postulated rate-controlling steps: sr A + H_2 surface reaction of allyl alcohol with a molecule of hydrogen adsorbed with or without dissociation, sr A + H surface reaction of allyl alcohol with an adsorbed atom of hydrogen, sr A monomolecular surface reaction of allyl alcohol. The symbols: A designates allyl alcohol, r the initial reaction rate, k_s the rate constant of the surface reaction of allyl alcohol, K_A and K_H the adsorption coefficients of allyl alcohol and hydrogen respectively, p_A and p_H the initial partial pressures of allyl alcohol and hydrogen, k_2 and k_3 the rate constants of steps 2 and 3 in Scheme B.

Equation type	Right-hand side of the rate equation $r = f(p_A, p_H)$	Effect of hydrogen	Rate-controlling step	s
(1)	$k_s K_A K_H p_A p_H / [1 + (K_A p_A)^a + (k_H p_H)^b]^s$	kin.	sr A + H_2	$2-4$
(2)^a	$k_s K_H p_H (\{[1 + (K_H p_H)^b]^2 + 8 K_A p_A\}^{1/2} - [1 + (K_H p_H)^b]\}^s / 4 (K_A p_A)^{s-1}$	kin.	sr A + H_2	$3,4$
(3)	$k_s K_A p_A (K_H p_H)^{1/2} / [1 + K_A p_A + (K_H p_H)^{1/2}]^2$	kin.	sr A + H	--
(4)	$k_s K_A p_A / [1 + (K_H p_H)^{1/2} + K_A p_A / (K_H p_H)^{1/2}]^2$	kin.	Scheme (A)	--
(5)^b	$k_s K_A p_A / [1 + K_A p_A + (k_2 K_A / k_3) (p_A / p_H)]^s$	akt.	sr A Scheme (B)	$1,2$
(6)^c	$k_s K_A p_A / [1 + K_A p_A + K_H p_H + (k_2 K_A^2 / k_3 K_H) \cdot (p_A^2 / p_H)]^s$	akt.	sr A Scheme (B)	$1,2$
(7)^d	$k_s K_A p_A L(p_H) / [1 + (K_A p_A)^a]^{1/a}$	akt.	sr A	--
(8)^e	$k_s K_A p_A L(p_H) / [1 + (K_A p_A)^a]^{1/a}$	akt.	sr A	--

^{a} Adsorption of A on two centres without dissociation[5]. ^{b} Hydrogen is not adsorbed. ^{c} Hydrogen is adsorbed. $^d L(p_H) = K_H p_H / [1 + (K_H p_H)^b]^{1/b}$. $^e L(p_H) = (K_H p_H)^{1/2} / [1 + (K_H p_H)^{1/2}]$.

$$A(g) \rightleftharpoons A(ads) \xrightarrow{\ 1\ } P(ads) \rightleftharpoons P(g)$$

$$\downarrow 2$$

$$N(ads) \xrightarrow{\ +H_2\ \ 3\ } S(g) \qquad (B)$$

The action of hydrogen consists in the removal of this intermediate N in the third step, in which it participates either from the gaseous phase (equation type (5), the second step is monomolecular) or adsorbed (equation type (6), the second step is bimolecular). To determine the surface concentration of the intermediate N we employed the approximation of a steady state $(r_2 = r_3)$.

A different effect of hydrogen on the concentration of the active centres is expressed by equations of the type (7) and (8). According to these, the rate-controlling step of the isomerization is a monomolecular surface reaction of allyl alcohol adsorbed on one or two centres. Hydrogen is assumed to keep the surface of the catalyst in the state necessary for the catalytic reaction, so that only the centres covered by hydrogen are catalytically active in the isomerization of allyl alcohol. The concentration of these activated centres, L, is then a function of the partial pressure of hydrogen, expressed by a Langmuir isotherm.

All the 19 derived equations have been employed to evaluate the experimental data by the non-linear regression[6]. On the basis of the values of Q, i.e. the sum of the squared differences between the experimentally determined reaction rate and that calculated from a given equation with the use of the optimum values of its constants,

TABLE II
Equations Consistent with the Critical Value of the Sum of the Squared Deviations[6], Q

Order	Eq. type	Values of exponents	Q
1	(7)	$a = 1, \quad b = 0.5$	1 954
2	(5)	$s = 1$	1 999
3	(1)	$a = 0.5, \ b = 0.5, \ s = 4$	2 040
4	(7)	$a = 1, \quad b = 1$	2 053
5	(7)	$a = 0.5, \ b = 0.5$	2 210
6	(7)	$a = 0.5, \ b = 1$	2 303
7	(3)	—	2 332
8	(1)	$a = 0.5, \ b = 1, \quad s = 3$	2 387
9	(8)	$a = 1$	2 404
10	(8)	$a = 0.5$	2 735
11	(2)	$b = 0.5, \ s = 4$	2 752
12	(2)	$b = 1, \quad s = 3$	2 910

an order of suitability of the equations was made. The equations that were inconsistent with the critical value[6] of Q were excluded. The remaining equations are ordered according to the increasing values of Q in Table II. The most appropriate equations have proved to be the kinetic equations based on the idea of an activating effect of hydrogen (hypothesis b)).

Out of these, the best one was Eq. (7a)

$$r = k_s K_A p_A K_H p_H / (1 + K_A p_A)(1 + \sqrt{K_H p_H})^2 \qquad (7a)$$

with constants k_s 620 mol h^{-1} kg^{-1}, K_A 31·3 atm^{-1}, K_H 1·02 atm^{-1}. The equations postulating the kinetic effect of hydrogen, *i.e.* its participation in the rate-controlling step, were less satisfactory.

As, however, the difference in Q between these equations and those based on the assumption of an activating effect of hydrogen was not marked we tried to elucidate the role of hydrogen in the reaction by the use of deuterium. The formed propionaldehyde was isolated by gas chromatography and analysed by infrared spectroscopy. The spectrum contained no band corresponding to the stretching vibrations of the bonds C—D or O—D. The absence of deuterium in the product proves that it does not participate in any of the individual steps of the isomerization, including the rate-determining step. This finding vindicates the idea that the favourable effect of hydrogen on the isomerization rate of allyl alcohol consists in its activating the surface of the palladium catalyst.

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