

RATE-RETARDING EFFECT OF PRODUCTS ON SOME PAIRS OF REACTIONS CATALYSED BY Al_2O_3 AND PdO AND DIFFERENCES IN THEIR INTERACTIONS WITH CATALYST SURFACE

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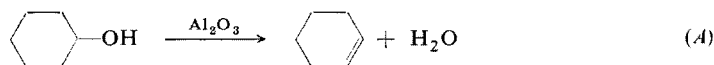
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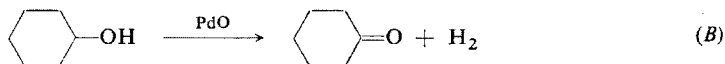
Kinetics of the dehydration of cyclohexanol on alumina and of its dehydrogenation on palladium oxide at 225°C in vapour phase was studied and the effect of reaction products was determined for both catalysts. Reaction products are adsorbed not only on the catalyst on which they are formed but also on the catalyst which does not catalyse their formation. The values of the so-called kinetic adsorption coefficients indicate both specific and nonspecific interaction with catalyst surface. Similar results were obtained also for the dehydration of 1-methyl-1-cyclohexanol on Al_2O_3 and decarbonylation of benzaldehyde on PdO at 180°C . It is suggested that catalytic reaction could take place from physically adsorbed layer by interaction with specific, active catalyst centers.

When studying parallel dehydrogenation and dehydration of 2-propanol on lanthanum(III) oxide¹ we have found that each of these reactions is retarded not only by its own reaction products but also by the products of the other, parallel reaction. As the dehydrogenation and dehydration of this compound proceed likely on active centers of different type, this could indicate that the product is adsorbed not only on the centers on which it is formed but also on other sites of catalyst surface.

In order to verify the above assumption we have studied the reaction of cyclohexanol on alumina, on which the compound is selectively dehydrated (equation (A)),

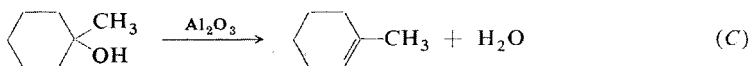


and on palladium(II) oxide that catalyses only its dehydrogenation (equation (B)).



The aim of this study was to ascertain how the products of these two reactions, *i.e.* cyclohexene, water, cyclohexanone and hydrogen, influence both the reaction which takes place on alumina and that proceeding on palladium(II) oxide, *i.e.* whether the above compounds adsorb also on the catalyst on which they cannot be formed

from cyclohexanol. To complement the results, we wished to study on these catalysts also two independent reactions of two starting compounds of different types and the effect of their products: on alumina, it was dehydration of a tertiary alcohol which cannot undergo dehydrogenation (1-methyl-1-cyclohexanol, equation (C)) and cannot therefore react on palladium(II) oxide



and on palladium oxide, it was decarbonylation of benzaldehyde to benzene and carbon oxide (equation (D)); this reaction should not be catalysed by alumina.



EXPERIMENTAL

Compounds Used

Cyclohexanol, cyclohexanone, benzaldehyde and benzene (analytical purity grade, Lachema, Brno) were distilled before use. Cyclohexene and 1-methylcyclohexene were prepared by dehydration of cyclohexanol or 2-methylcyclohexanol on alumina at 250°C, dried and rectified. 1-Methyl-1-cyclohexanol was obtained by the Grignard reaction from cyclohexanone. Nitrogen (for lamps, Technoplyn, Ostrava) was purified by passing the gas over copper impregnated on kieselguhr at 250°C, electrolytic hydrogen (Electrochemische Werke, Bitterfeld, GDR) was purified by passing over a deoxidation palladium catalyst (Chemické závody, Záluží); both gases were then dried with potassium hydroxide.

Alumina was commercial pelleted catalyst (Chemické závody, Záluží); the pellets were crushed and 0.1–0.2 mm particles were further used; its specific surface was 145 m²/g. Palladium(II) oxide was prepared by precipitation of 10% palladium chloride solution (Kovohutě, Vestec) with 10% potassium hydroxide solution; the palladium hydroxide so formed was then washed several times with distilled water, dried at 110°C and dehydrated in a tubular furnace in a stream of nitrogen, the temperature being increased at a rate of 1.5°C per min; the sample was heated at the final temperature 400°C for 6 h. After partial desintegration, the fraction 0.1–0.2 mm was further used; its specific surface equaled to 40 m²/g.

Apparatus and Procedure

A glass flow reactor with reactants in vapour phase was used similarly as in previous works, e.g.^{1,2}. In experiments in which one of the products was added to the starting reactant a solution of both components (when mutually miscible) was prepared first and then it was introduced by a constant rate with hypodermic syringe (5 ml) to an evaporator in which vapours of this mixture were mixed with a stream of nitrogen such that the desired partial pressure would be achieved (the total pressure in the apparatus was atmospheric). Immiscible product was fed by a separate hypodermic syringe, hydrogen was fed by means of a fine needle valve and differential flow meter directly into the evaporator. The catalyst (0.02–0.2 g) mixed with glass beads was placed in a vertical glass tubular reactor (9 mm i.d.) equipped with a thermocouple well (5 mm

e.d.). The reactor was heated with a vertical electric furnace, the temperature within the catalyst bed was $225 \pm 0.5^\circ\text{C}$ or $180 \pm 0.5^\circ\text{C}$. The reaction mixture from the reactor outlet was condensed in a trap cooled to -78°C . After steady state was established, three samples of the reaction mixture were successively withdrawn and analysed by gas chromatography (Chrom II instrument, Laboratorní přístroje, Prague, a flame-ionisation detector, nitrogen as a carrier gas; a $3.2\text{ m} \times 8\text{ mm}$ column). The reaction mixtures from the dehydrogenation and dehydration of cyclohexanol, inclusive added compounds, and the reaction mixtures from the dehydration of 1-methyl-1-cyclohexanol itself or with added 1-methylcyclohexene, water or benzene, were analysed with the use of 15% poly(ethylene glycol) 400 on Chromosorb at 120°C . The reaction mixture obtained in the dehydration of 1-methyl-1-cyclohexanol carried out in the presence of benzaldehyde and the reaction mixtures produced by the decarbonylation of benzaldehyde, inclusive added substances, were analysed with the use of 15% dinonyl sebacate on Celite at 150°C .

Kinetic Measurements and Treatment of Data

Before commencing kinetic measurements it was verified that under the conditions used the reaction rate is not influenced by both internal and external diffusion. Measurements of initial rates of the reactions (A)–(D) were carried out at partial pressures of the starting component varying from 0.05 to 0.9 atm. Reaction rates were calculated as the slopes in the origin of the conversion *vs.* reciprocal space velocity plots. These dependences were linear for conversion up to 5%, at which most of the measurements were carried out. Conversion in the reactions (A) and (C) was calculated from the alkene content, that in the reaction (B) from the content of cyclohexanone and in the reaction (D) from the content of benzene. Each reaction rate was determined from at least three different conversions. As the activity of the catalysts decreased to some extent with the time of their performance, each reaction rate determination was made with fresh catalyst sample. A decrease in the activity of the sample during this determination was allowed for in such a way that the first measurement of conversion was finally repeated and the conversions found for the other measurements were corrected under the assumption that the activity decrease from the first to the last measurement is linear.

Data on initial reaction rates of dehydration (A) and dehydrogenation (B) in dependence on the partial pressure of cyclohexanol were treated by two-parameter nonlinear regression on a computer, using the sums of squared deviations of the experimental from calculated reaction rates as a minimized function.

The effect of products was determined by reaction rate measurements at several partial pressures of the compound investigated (systematically changed up to 0.7 atm by adding the compound in various amounts to the starting reactant whose partial pressure was also changed). In the case of the dehydration and dehydrogenation of cyclohexanol these data and the rate equations which best described the reaction of cyclohexanol itself were used to calculate the values of adsorption coefficients of the products by one-parameter nonlinear regression. The whole set of rate data (in the absence and presence of a given product) was also treated by three-parameter nonlinear regression, giving very similar results to those obtained by successive treatment of the data (first of those obtained without the product and then of those obtained in the presence of the product.)

RESULTS

Dehydration and Dehydrogenation of Cyclohexanol at 225°C

The rate data obtained for the dehydration and dehydrogenation of cyclohexanol in the absence of products were treated with two-parameter nonlinear regression

using 9 equations of the Langmuir–Hinshelwood type; their basic forms are presented in Table I. Equations of the type *B* ($s = 2-4$), *C* ($s = 2$) and *A* ($s = 1$) described best both reactions. These equations were further used to express the effect of the products (cyclohexene, water and cyclohexanone; the effect of hydrogen on dehydrogenation had to be described by a more complex function—see later). For this purpose the denominators of rate equations of the types *A* and *B* were extended by the adsorption term of the product $K_R p_R$ or $2\sqrt{K_R p_R}$. For equations of the type *C* that describe a model in which adsorption of the starting compound *A* is taking place on two active centers without dissociation of the molecule, the denominators of the rate equations had after their extending the following forms:

$$\{1 + K_R p_R + \sqrt{[(1 + K_R p_R)^2 + 8K_A p_A]}\}^s$$

for the model involving adsorption of the product *R* without dissociation on one center or

$$\{1 + \sqrt{[1 + 8(K_A p_A + K_R p_R)^2]}\}^s$$

for the model involving adsorption of the product *R* without dissociation on two centers.

Treatment of the rate data obtained in the presence of products by one- and three-parameter nonlinear regression with the use of these extended equations has led to exclusion of equations of the type *A* and *C* as less suitable. From the inspection of the results of the treatment of data obtained in the absence and presence of products the remaining best three equations of the type *B* can be arranged in the following order (according to the exponent s in the denominator): for the dehydration $s = 3, 2, 4$ and for the dehydrogenation $s = 2, 3, 4$. The resulting equations which describe the course of the reactions in the presence of all the products (except hydrogen for the dehydrogenation) have the following forms; for the dehydration on alumina:

$$r = kK_A p_A / [1 + 2(K_A p_A)^{0.5} + K_{EN} p_{EN} + 2(K_W p_W)^{0.5} + 2(K_{ON} p_{ON})^{0.5}]^s \quad (1)$$

and for the dehydrogenation on palladium(II) oxide:

$$r = kK_A p_A / [1 + 2(K_A p_A)^{0.5} + K_{EN} p_{EN} + 2(K_W p_W)^{0.5} + K_{ON} p_{ON}]^s \quad (2)$$

The corresponding values of the constants are summarized in Table II (only for the equations with the exponent $s = 2$ or 3 which were better than those with the exponent $s = 4$).

The other dehydrogenation product, hydrogen, did not affect the dehydration on alumina. However, an interesting effect of hydrogen was observed in the dehydrogenation on palladium(II) oxide (Fig. 1). While a small addition of hydrogen (to the partial pressure 0.03 atm) strongly inhibits the dehydrogenation, further increase of the partial pressure accelerates dehydrogenation up to a certain limit value; at hydrogen partial pressures higher than 0.15 atm, the reaction rate is higher than that in the absence of hydrogen, under otherwise identical conditions (hydrogen replaced by nitrogen, Fig. 1, broken line). The effect of hydrogen can be explained in the following way. Hydrogen is held by palladium(II) oxide surface in dependence on its partial pressure, the original catalytic centers being inactivated and new centers being formed which are also catalytically active for the dehydrogenation of cyclohexanol. It seems likely that the surface of the palladium oxide is reduced to metallic

TABLE I

Basic Types of the Rate Equations Used

Type	Basic form of the Eq.	Exponent s
A	$r = kK_A p_A / (1 + K_A p_A)^s$	-4
B	$r = kK_A p_A / [1 + 2(K_A p_A)^{0.5}]^s$	2-4
C	$r = 2^s k K_A p_A / [1 + (1 + 8 K_A p_A)^{0.5}]^s$	2, 3

TABLE II

Values of Constants of Rate Eqs (1) and (2) for the Dehydration and Dehydrogenation of Cyclohexanol at 225°C Carried out in the Presence of Products

Reaction (catalyst)	s	k	K_A	K_{EN}	K_W	K_{ON}
Dehydration (Al ₂ O ₃)	2	171	4.8	1.1	0.64	2.1
Dehydrogenation (PdO)	2	91	2.1	1.7	0.83	757
Dehydration (Al ₂ O ₃)	3	748	0.65	0.43	0.09	0.25
Dehydrogenation (PdO)	3	366	0.36	0.70	0.13	276

palladium which is also active for the dehydrogenation. We are dealing here with the reaction taking place simultaneously on two different kinds of active centres; the number of the centers of one type (and therefore also the corresponding reaction rate) decreases with increasing partial pressure of hydrogen, while the number of the centers of the other type, and thus also the reaction rate, increases. We have attempted to express this superposition of the two processes in formal kinetics way. The expression for the reaction rate would consist in this case of two terms: *a*) a term which describes the rate of the dehydrogenation of cyclohexanol on the initial surface of palladium(II) oxide; the rate is strongly decreased by hydrogen which is expressed by the term $K_H p_H$ or $(K_H p_H)^{0.5}$ in the denominator; *b*) a term which describes dehydrogenation rate on new centers formed by interaction of hydrogen with palladium oxide surface. As this rate tends to achieve a limit value as partial pressure of hydrogen increases, one can assume that the surface is being occupied by hydrogen until its saturation (*i.e.* obviously to the complete reduction of the surface), which can be expressed by the Langmuir isotherm. The estimated limit value of the reaction rate obtained at

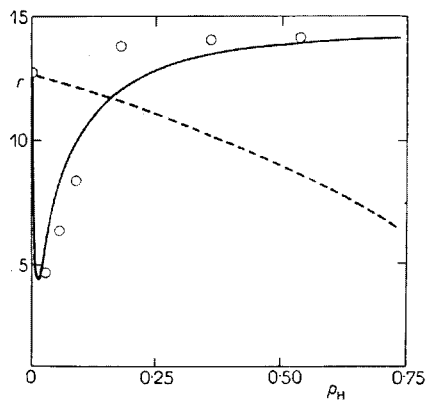


FIG. 1

Initial Reaction Rate of Dehydrogenation of Cyclohexanol, r [$\text{mol h}^{-1} \text{kg}^{-1}$], on Palladium Oxide at 225°C in Dependence on Partial Pressure of Hydrogen p_H [atm]

Points represent experimental data, the full curve was calculated by means of the equation (3) with the exponents $u = v = z = 1$ and the values $K_H = 650 \text{ atm}^{-1}$ and $K'_H = 20.6 \text{ atm}^{-1}$, the broken line was found experimentally when hydrogen was replaced by nitrogen.

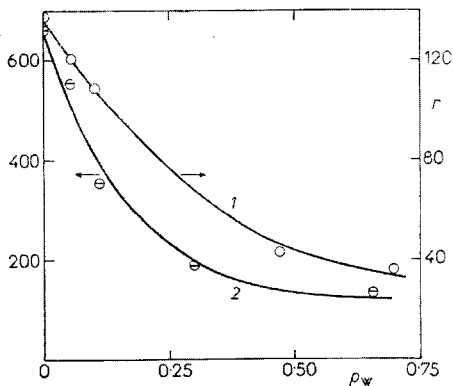


FIG. 2

Dependence of Initial Reaction Rate r [$\text{mol h}^{-1} \text{kg}^{-1}$] on Partial Pressure of Water p_w [atm] for Dehydration of 1-Methyl-1-cyclohexanol on Alumina (Curve 1) and for Decarbonylation of Benzaldehyde on Palladium Oxide (curve 2)

higher partial pressures of hydrogen ($15.2 \text{ mol h}^{-1} \text{ kg}^{-1}$) is then multiplied by this hyperbolic function.

$$r = \frac{91 \times 2.1 p_A}{[1 + 2(2.1 p_A)^{0.5} + (K_H p_H)^v]^2} + 15.2 \frac{(K'_H p_H)^u}{[1 + (K'_H p_H)^v]^{1/z}} \quad (3)$$

The above concept is expressed by equations of the type (3), assuming that hydrogen can interact with the surface of palladium oxide and form new centers either in molecular ($v = 1$) or dissociated form ($v = 0.5$). Into the first term of the right-hand side of the equation (3) which describes the reaction rate on the surface of palladium(II) oxide itself we substituted the constants $k = 91$ and $K_A = 2.1$ obtained by nonlinear regression treatment of the rate data on the dehydrogenation in the absence of hydrogen by means of equation of the type (B) with the exponent $s = 2$ (Table II). We used further the equation (3) in its three variants with different combinations of the exponents u , v and z ($u = v = z = 1$; $u = 1, v = z = 0.5$; $u = v = 0.5, z = 1$) for treating the rate data on the dehydrogenation of cyclohexanol in the presence of hydrogen by means of two-parameter nonlinear regression. The equation (3) with the exponents $u = v = z = 1$ and the constants $K'_H = 20.6 \text{ atm}^{-1}$ and $K_H = 650 \text{ atm}^{-1}$ described best the data obtained. From this equation and the above constants the full curve 1 in Fig. 1 was calculated which confirms principal agreement of the model with the experiment.

Dehydration of 1-Methyl-1-cyclohexanol and Decarbonylation of Benzaldehyde at 180°C

These reactions and the effect of the products were studied only qualitatively. The dehydration of 1-methyl-1-cyclohexanol was found to be essentially zero order in the partial pressure region $p_A = 0.1-0.9$, and from the effect of 1-methylcyclohexene on this reaction it can be concluded that this product adsorbs more strongly than the starting alcohol³.

The effect of water on the dehydration of 1-methyl-1-cyclohexanol on alumina and on the decarbonylation of benzaldehyde on palladium oxide is qualitatively represented in Fig. 2. As follows from the figure, water – the dehydration product – retards both reactions to a similar extent, the decarbonylation on palladium oxide being inhibited only somewhat less strongly than the dehydration on alumina.

The effect of 1-methylcyclohexene and 1-methyl-1-cyclohexanol on the decarbonylation of benzaldehyde was weak and the effect of benzene on this reaction was highly irregular and could not be evaluated.

On the contrary, the effect of benzene and benzaldehyde on the dehydration of 1-methyl-1-cyclohexanol on alumina which is represented in Fig. 3a, b by the dependences of the reaction rate on the partial pressure of the respective product is similar

for both compounds added. The dependences show reproducibly (for different partial pressures of the starting alcohol) a minimum for the reaction rate around the partial pressure of the product of about 0.3 atm. The reason why at the higher partial pressures of the added aromatic compound the reaction rate increases is not yet clear. From Fig. 3 it follows, however, that also a compound which does not react on alumina (benzaldehyde) or is not formed (benzene) is adsorbed on this catalyst and exerts rate-retarding effect on the reaction (when added in the amount less than or comparable to the amount of the reacting alcohol).

DISCUSSION

As follows from the results of the study of the dehydration and dehydrogenation of cyclohexanol, the reaction products retard both the reaction by which they are produced and the reaction on the other catalyst which does not lead to their formation (with the exception of hydrogen on alumina). Some of these products (cyclohexene, water) have adsorption coefficients (that express this rate-retarding effect) very similar for both catalysts (Table II). This means that these substances are adsorbed approximately to the same extent on the catalyst which is responsible for their formation as are on the catalyst on which they cannot be formed, *i.e.* this adsorption is not specific.* Also the values of the adsorption coefficient of the starting compound, cyclohexanol, on alumina and on palladium oxide do not differ significantly. On the contrary, spe-

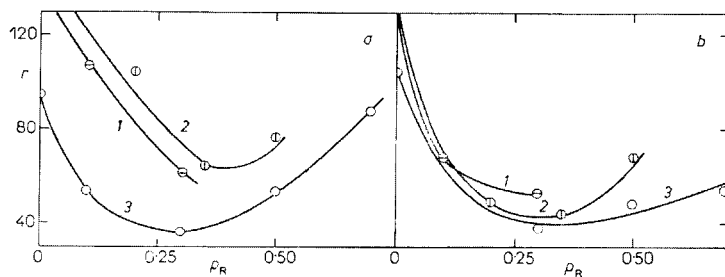


FIG. 3

Dependence of Initial Reaction Rate r [$\text{mol h}^{-1} \text{kg}^{-1}$] of Dehydration of 1-Methyl-1-cyclohexanol on Alumina at 180°C on Partial Pressure p_R [atm] of *a* Benzene and *b* Benzaldehyde; Initial Partial Pressure of 1-Methyl-1-cyclohexanol: 0.6 atm (curve 1), 0.4 atm (curve 2) and 0.2 atm (curve 3)

* Only kinetic data do not allow to speak of the type of this adsorption in more detail. If this adsorption is multilayer, the values obtained cannot be referred to, of course, as the adsorption coefficients in the strict physical meaning. In such a case these values express in a simplified way the extent of the adsorption of a given substance and the degree of its rate-retarding effect on a given reaction.

cific effect (a marked rate-retarding effect on the dehydrogenation on PdO) is shown by cyclohexanone and hydrogen; however, also cyclohexanone adsorbs on the dehydration catalyst (alumina) having the adsorption coefficient comparable to the coefficients for the other substances. Similarly as in the previous work¹ these results can be interpreted such that on the above catalysts the compounds present in the reaction system interact with the catalyst surface (this interaction being mainly of physical nature) on the sites which have not to be identical with the active centers. In agreement with this concept about mainly physical character of this interaction is, in addition to nonspecificity of the adsorption of some compounds on the two so different catalysts, also negligible adsorption of hydrogen as a light gas on alumina which does not catalyse its formation. Along with nonspecific adsorption, also adsorption of the components of a given reaction can take place on the active centers for this reaction; thus, cyclohexanone and hydrogen remain obviously bonded to the reaction centers of palladium oxide on which they were formed and retard significantly the reaction of their formation.

Also qualitative results of the study of other reactions on alumina and palladium oxide (dehydration of 1-methyl-1-cyclohexanol and decarbonylation of benzaldehyde) support the above concept. Similarly, water and benzene retard both reactions, *i.e.* not only the reaction by which they were formed, and even benzaldehyde (the starting compound in the decarbonylation) adsorbs on alumina, although it does not react on this catalyst.

It seems therefore probable that catalytic reaction proceeds from physically adsorbed layer (in which all the components are present and compete with one another) by interaction of the starting reactant with chemically specific active centers. It can be proved that on the basis of this assumption about two types of adsorption the rate equations are also obtained which are identical with equations of the Langmuir-Hinshelwood type. Adsorption coefficients of the components have in these equations either the value corresponding to nonspecific adsorption (if the components do not adsorb on reaction centers) or are higher due to the contribution of the other term which includes the coefficient corresponding to the adsorption on reaction centers (if the components adsorb also on these centers).

LIST OF SYMBOLS

k	rate constant [mol h ⁻¹ kg ⁻¹]
K_i	adsorption coefficient of compound i [atm ⁻¹]
K_H, K'_H	parameters [atm ⁻¹] in the equation (3) expressing the effect of hydrogen on the rate of dehydrogenation of cyclohexanol
p_i	partial pressure of compound i [atm]
r	reaction rate [mol h ⁻¹ kg ⁻¹]
s	general exponent in rate equations
u, v, z	exponents in equation (3)

Denotation of Substances (subscripts):

A	starting compound
EN	cyclohexene
H	hydrogen
ON	cyclohexanone
R	product in general
W	water

REFERENCES

1. Jambor J., Beránek L.: *This Journal* 40, 1374 (1975).
2. Šimoník J., Beránek L.: *This Journal* 37, 353 (1972).
3. Zieliński J., Beránek L.: Unpublished results.

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