

Mechanism of Dehydrogenation of Secondary Alcohols on Chromia

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Using chromium(III) oxide as catalyst, there were measured the kinetics of dehydrogenation of 2-propanol, the kinetic isotope effects with deuterated 2-propanols, the effect of pre-treatment of the catalyst in hydrogen and in oxygen on its activity and the influence of some substances added to the feed on conversion. On the basis of these experimental data, together with some results from the following paper and quantum-chemical models of adsorption and surface reaction, a mechanism of dehydrogenation of secondary alcohols on Cr_2O_3 was proposed. It consists of adsorption and surface reaction, in which the breaking of the $\text{C}_\alpha\text{-H}_\alpha$ bond is considered the rate determining step, on active centers formed by groups of surface Cr^{3+} and O^{2-} atoms.

INTRODUCTION

A mechanism of dehydrogenation of secondary alcohols on oxidic catalysts was suggested by Eucken and Heuer (1,2) and Wicke (3) according to which the reaction proceeds on metal-oxygen pairs. Another mechanism was proposed by Hauffe (4) under the assumption that the surface of the catalyst behaves as a semiconductor. In his mechanism, the first step of the reaction is the adsorption of alcohol accompanied by a transfer of one electron from the α -hydrogen. The second step is the adsorption of a polarized OH group and a rapid surface reaction follows. Desorption of the ketone which is hindered by the increasing concentration of electrons in the boundary layer, was regarded as the rate limiting step. Krylov (5) has assumed a similar mechanism for the dehydrogenation of 2-propanol on ZnO including dissociative adsorption of the alcohol. The mechanism proposed by Wolkenstein (6) includes radical type species; he has assumed that the rate determining step is dissociative adsorption of the alcohol and that the surface of the catalyst

behaves as a *n*-type semiconductor. The testing of these mechanisms by measurement of the electrical conductivity during adsorption and desorption of alcohols and ketones on various oxides has not brought the expected evidence (7). Hauffe and Wolkenstein have regarded a catalyst as a nonstructured solid phase with semiconducting properties which govern the mechanism and the activity of the catalyst.

A different view on catalysis by oxides was proposed by Dowden and Wells (8) with their theory of coordinative chemisorption. Burwell *et al.* (9) assumed on the basis of this theory that the catalytic activity of chromium oxide depends on the presence of coordinatively unsaturated Cr^{3+} ions on the surface: two types of alcohol adsorption are possible, a nondissociative one on Cr^{3+} and a dissociative one on $\text{Cr}^{3+}\text{-O}^{2-}$ pairs.

The presence of dissociatively adsorbed water and alcohols on chromium oxide (10,11) and on other oxides (12,13) has been demonstrated using ir spectroscopy. By the same method surface species of the type $[\text{R}_2\text{-COO}]\text{Cr}$ have been detected (11)

which are probably the adsorbed form of ketones and aldehydes.

In the present paper we intend to obtain a further insight into the mechanism of alcohol dehydrogenation on chromium oxide on the basis of experimental and quantum chemical results. Our goal was a mechanism which does not require any assumptions about the existence of surface ions and radicals not in accord with contemporary ideas of organic chemistry.

EXPERIMENTAL METHODS

2-Propanol and 2-butanol were commercial chemicals, declared as pure. Other alcohols were synthesized from corresponding ketones by reduction with LiAlH_4 . Deuterated alcohols, 2-propanol-OD (99.0%) and 2-propanol-2D₁ (92.4%) were supplied by the Institut für physikalische Stofftrennung, Leipzig, GDR. Water content in the alcohols was 0.02–0.10% as determined by the Karl Fischer method. The catalyst was prepared by calcination of chromium hydroxide to 700°C; it had a specific area of 4.6 m²/g and 0.10–0.25 mm grains were used for catalytic experiments. According to spectral analysis the main impurities were calcium, sodium, potassium and magnesium (all under 0.1%).

Kinetics of dehydrogenation were measured using a flow reactor with a direct sampling of the gaseous products (0.4 ml) into a gas chromatograph (14) which included a column of 2 m length filled with 5% polyethylene glycol on a support. Nitrogen, used as diluent in the catalytic experiments, was freed of oxygen and water. The reaction rates were measured at 350°C under conditions such that external and internal diffusion did not interfere and the obtained conversion values were corrected to standard activity of the catalyst according to control experiments at fixed conditions. The partial pressure of 2-propanol in the feed was varied in the range 0.15–1.00 atm, and the conversion did not exceed 10%.

RESULTS AND DISCUSSION

Experimental dependences of initial reaction rates r_A^0 on partial pressures of 2-propanol in the feed p_A^0 were fitted by means of nonlinear regression (15) to 20 Langmuir–Hinshelwood type equations. The best rate equations were selected using the criterion of maximal likelihood; five rate equations gave very good fit. From these Eq. (1) was used for discussion in this paper; the same relation was

TABLE I
CONSTANTS OF THE RATE EQ. (1) AND CHANGES IN QUANTUM-CHEMICAL INDICES IN $\text{R} \cdot \text{CHOH} \cdot \text{CH}_3$

R	k (mol/hr kg)	K_A (atm ⁻¹)	Δq^a (10 ⁻² e)	Δw^b (%)	$\Delta(\Delta E)^c$ (kcal/mol)
CH ₃	145.6 ^d	2.08 ^d	-9.77	-4.04	0.00
C ₂ H ₅	110.9 ^d	2.34 ^d	-9.43	-3.91	-2.40
<i>i</i> -C ₃ H ₇	44.6 ^d	4.30 ^d	-9.23	-3.38	-3.07
<i>i</i> -C ₄ H ₉	39.2 ^d	3.32 ^d	-9.18	-3.74	-6.81
<i>t</i> -C ₄ H ₉	20.3 ^d	1.13 ^d	-9.00	-3.69	-4.77
2-Propanol-OD	161.9	2.54	—	—	—
2-Propanol-2D ₁	80.7	3.32	—	—	—

^a Charge change on H_α.

^b Change of Wiberg's index of the bond C_α-H_α.

^c Change in total energy in respect to 2-propanol.

^d Taken from Ref. (23).

found suitable also by García de la Banda (17) for dehydrogenation of 2-propanol on a Cr_2O_3 catalyst:

$$r^0 = kK_{\text{A}}p_{\text{A}}^0 / (1 + K_{\text{A}}p_{\text{A}}^0)^2. \quad (1)$$

The values of the rate constant k and adsorption coefficient K_{A} are given in Table 1. In terms of the Langmuir-Hinshelwood mechanism, Eq. (1) corresponds to one-center adsorption of the alcohol and to surface reaction as the rate determining step requiring an empty site. However, we regard Eq. (1) as a semiempirical relation and we do not wish to interpret its form as a proof of a particular mechanism.

The kinetic isotope effect was calculated as the ratio of rate constants of nondeuterated and deuterated species $\alpha = k_{\text{H}}/k_{\text{D}}$. Table 1 shows that the substitution of α -hydrogen by deuterium decreases the rate, whereas the presence of D in the hydroxyl group has no influence. The value of α for the dehydrogenation of 2-propanol-2D₁ is, after correction to 100% content of the isotope, 1.94.

For comparison with experimental results quantum-chemical calculations were made using the CNDO/2 method (18) and standard geometry (19) of the models. Charge and bond strength were calculated for 2-propanol and for structures I, II and III,

which served as models for the surface complexes. In their construction the staggered conformations and sp^3 hybridization on the oxygen atom were accepted. The position of the hydrogen atom of the hydroxyl group H_{OH} is seen from the Newman projection along the C_{α} -O bond. The atoms O, H_{OH} and O in structure I and the atoms C_{α} , H and H^+ in structure III are collinear. The O-H bond in the hydroxyl ion OH^- of structure I is parallel to the C_{α} -O bond. The results are given in Tables 2 and 3. Charges were obtained from electron densities by subtracting the core and bond strength corresponding to Wiberg's bond index (20).

In the series of alcohols (2-propanol, 2-butanol, 3-methyl-2-butanol, 4-methyl-2-pentanol and 3,3-dimethyl-2-butanol) the calculations were limited to the alcohol and the anion II. The results are summarized in Table 1.

Two basic experimental facts must be respected in our mechanistic considerations, namely, (a) the reactivity of 2-alkanols ($\text{R}\cdot\text{CHOH}\cdot\text{CH}_3$) decreases with increasing size of the alkyl group R (Table 1) and (b) the splitting of the α -hydrogen is a part of the rate determining step, as follows from the kinetic isotope effect. Further experiments were made with the aim of ascertaining the nature of the active

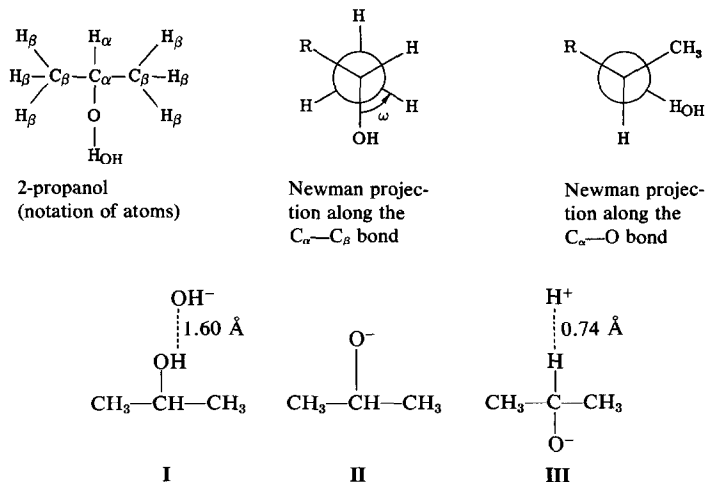


TABLE 2
CHARGE ON SOME ATOMS^a

Atom	2-Propanol	Structure			CH ₃ · CO ⁺ H ₂ · CH ₃ ^b
		I	II	III	
H _α	-3.15	-5.15	-12.92	13.48	3.59
H _β (60°)	0.32	-2.33	-4.48	1.47	4.09
H _β (180°)	0.88	-3.12	-7.19	-0.52	7.99
H _β (300°)	1.29	-0.95	-3.82	4.39	5.55
H _{OH}	13.40	25.58	—	—	30.32

^a In 10⁻² e. The definition of the dihedral angle ω (see the Newman projection along the C_α-C_β bond).

^b Model for dehydration, see Ref. (22).

centers on Cr₂O₃. The influence on the activity of pretreating the catalysts in nitrogen, hydrogen and oxygen at 350°C was studied. The oxidation of the catalyst resulted in a decrease of activity in comparison with heating in nitrogen; hydrogen did not change the activity. Further we have found that addition of water, pyridine, acetic acid and other substances which can be adsorbed on surface coordinatively unsaturated Cr³⁺ ions (9,10) hinders the reaction (Table 4). Nondek and Kraus (23) have brought evidence that the catalytic activity of chromium oxide in dehydrogenation of secondary alcohols depends on the degree of surface dehydration which influences the concentration and nature of coordinatively unsaturated Cr³⁺ ions. All these findings lead us to the conclusion that the dehydrogenation of alcohols pro-

ceeds on surface Cr³⁺. A further support for this view was obtained by studying the electronic reflectance spectra of a series of chromium oxide preparations and by correlating these spectra with catalytic activity of the samples (24).

Sedláček and Kraus (22) have concluded from quantum-chemical calculations that the adsorption of an alcohol by means of a free electron pair of its oxygen on a electron deficient center leads to dehydration (see Tables 2 and 3). Therefore, we studied in the present paper by this method models of adsorption which would cause changes in the alcohol resulting eventually in dehydrogenation. Model I representing adsorption of an alcohol by means of a hydrogen bond (21) differs from 2-propanol by strengthening the C_α-O bond, by weakening the C_α-H bond and by local-

TABLE 3
CHANGE IN BOND STRENGTH^a

Bond	Structure			CH ₃ · CO ⁺ H ₂ · CH ₃ ^b
	I	II	III	
C _α -C _β	-0.51	-3.09	-0.08	-0.02
C _α -O	3.27	2.84	32.12	-21.43
C _α -H _α	-0.69	-4.04	-64.74	0.96
C _β -H _β (60°)	-0.04	-0.46	-0.02	-0.17
C _β -H _β (180°)	-0.13	-0.97	-0.02	-1.30
C _β -H _β (300°)	-0.03	-0.36	-1.26	-0.23
O-H _{OH}	-20.28	—	—	-7.52

^a Percent, in respect to 2-propanol.

^b Model for dehydration, see Ref. (22).

TABLE 4
EFFECT OF ADDITION OF SOME COMPOUNDS TO
2-PROPANOL ON THE CONVERSION^a

Substance	Relative conversion
Pure 2-propanol	1.00
Diethyl ether (1% mol)	0.95
Dimethylamine (1% mol)	0.80
Acetic acid (1% mol)	0.05
Pyridine (1% mol)	0.65
Water (1% mol)	0.80

^a Partial pressure of 2-propanol, 0.5 atm; nitrogen, 0.5 atm; reaction temp, 350°C; 0.1 g of catalyst; feed rate, 0.1 mol/hr of 2-propanol.

ization of the negative charge on H_{α} . The same changes but stronger may be observed (Table 2 and 3) with species II which is a model of surface alcoholate.

The rate determining step includes the rupture of the C_{α} -H bond, as shown by the kinetic isotope effect. This step may be visualized as an interaction of H_{α} with surface Cr^{3+} or with a positively polarized H atom (originating from the previously split O-H group of the alcohol) bound to the active center; this is modeled by structure III. The next step will be the formation of a hydrogen molecule. In structure III, the sum of charges on both methyl groups, C_{α} and O is 0.644 e higher than the same sum in structure II. This shows that even the not fully separated H_2 molecule carries away an appreciable negative charge from the alcoholate species. For full separation the H_{α} atom must be split off with two electrons, i.e., as H^- . Models similar to II

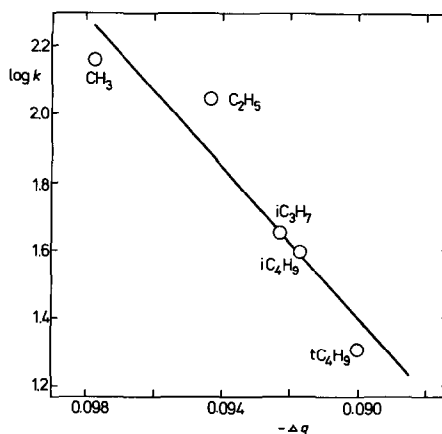
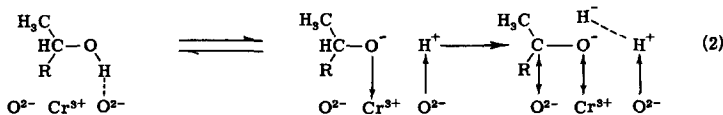
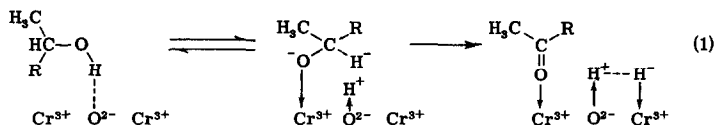


Fig. 1. Correlation of experimental values of $\log k$ and change of charge on H_{α} atom caused by deprotonation of hydroxyl group (model II) of alcohols $R\text{-CHOH}\cdot\text{CH}_3$.

but with Cr^{3+} and other metal ions interacting with the alcoholate ion are dealt with in a following paper (25). However, it can be mentioned now that the changes within the alcohol structure are of the same nature as presented here.

Concerning the dependence of the reactivity of the alcohols on their structure, Table 1 shows parallelism between the values of k and K_A and quantum-chemical indices of the corresponding alcoholate ions. With decreasing Δ (ΔE) values the adsorption coefficient K_A increases, i.e., the stability of the surface alcoholate increases. The logarithm of the rate constant and the change of the negative charge Δq on H_{α} gives a satisfactory linear relationship (see Fig. 1). This can be interpreted as a result of the decreasing facil-



ity of fission of H_α in the form of H^- with a decrease of its negative charge.

The rate determining step can probably include also an interaction of surface O^{2-} with C_α . In this way the formation of surface carboxylate structures (II) of the type $R^1R^2CO_2-Cr$ may be explained. Our findings enable us to propose the mechanisms of alcohol dehydrogenation on Cr_2O_3 in the form of schemes (1) or (2). It is very probable that both paths can operate simultaneously according to the local structure of the surface which can have several arrangements [cf. (23)]. Our mechanisms assume heterolytic splitting of all bonds. Similar schemes can be written for homolytic rearrangements; however, we regard such mechanisms on ionic surfaces of oxides to be highly improbable.

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