CONCLUSIONS

1. Calculations of the atomization energies of $Cr(CO)_6$, $Fe(CO)_5$, $Mo(CO)_6$, $Ni(CO)_4$, $MnH(CO)_5$, $FeH_2(CO)_4$, and $CoH(CO)_4$ molecules have been carried out by the virial-statistical method.

2. The results of these calculations suggest that the stabilities decrease in the order

$$MnH(CO)_5 > FeH_2(CO)_4 > CoH\,(CO)_4,$$

a conclusion consistent with experimental data.

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MECHANISM OF THE VAPOR-PHASE DEHYDRATION OF CYCLOHEXANOL TO CYCLOHEXANONE ON A COPPER-MAGNESIUM CATALYST

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593.211:541.128

The results of our earlier study on the kinetics of vapor-phase dehydration of cyclohexanol to cyclohexanone on a copper–magnesium catalyst have been reported in [1]

$$C_6H_{12}O = C_6H_{10}O + H_2 \tag{1}$$

There we proposed a kinetic reaction scheme based on our kinetic data and the assumption that hydrogen detachment proceeds slowly on the catalyst surface. We have continued this work with a view to fixing the mechanism of reaction (1) more exactly, studying the isotopic hydrogen–deuterium exchange in cyclohexanol and cyclohexanone, and measuring the kinetic isotope effects in both forward and reverse directions.

EXPERIMENTAL

Experiments were carried out in a thermostated circulating-flow system [1], working with mixtures diluted with nitrogen, hydrogen, or deuterium at atmospheric pressure. The cyclohexanol and cyclohexanone used here had been redistilled through a vacuum reflux column; each substance was chromatographically pure,

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TABLE 1. Isotopic Hydrogen–Deuterium Exchange in Cyclohexanol, at Various Temperatures and under Dehydrogenation Conditions

T., °C	Degree of hydrogenation	Isotopic cyclohexanol composition, from mass spectrometric data*, %							Overall degree of exchange, %	M_D†	Degree of exchange, %	
		d_0	d_1	d_2	d_3	d_4	d_5	d_6			α-hydrogen, from PMR spectra	In hydroxyl, group, from IR spectra
170	3,0	65,5	25,8	6,7	1,6	0,4	0,1	–	34,5	1,3	16,1	15,0
210	9,2	58,9	16,1	10,4	8,4	4,2	1,5	0,2	41,1	1,8	25,0	–
240	15,7	57,2	17,7	11,0	8,1	4,3	1,4	0,2	42,8	1,7	30,0	17,6
270	24,3	62,1	14,7	9,0	7,4	4,4	1,8	0,4	37,9	1,9	33,0	28,4
300	37,0	54,8	22,1	10,0	6,4	3,9	1,8	0,6	45,2	1,8	–	–

*Calculations were carried out for the $(M-18)^+$ fragment ions, i.e., for one ring position and with no allowance for hydroxyl exchange.

†Values of M_D were obtained from the Kimball formula [5]; each value represents the mean number of deuterium atoms entering the cyclohexanol molecule in each elementary exchange step.

its constant agreeing with those reported in the literature: cyclohexanol, mp 24°C, bp 160.5°C (757 mm), n_D^{25} 1.4650; cyclohexanone, bp 156°C (757 mm), n_D^{20} 1.4509; d_4^{20} 0.9475.

Deuterated cyclohexanol, $C_6H_{11}OD$, was prepared by exchange between cyclohexanol and heavy water, following the methods of [2]. Deuterated alcohol comprised about 80% of the reaction products. The deuterated cyclohexanol was stored under purified nitrogen. Prior to use, the nitrogen, hydrogen, and deuterium were passed through a purifying train [3]. The catalyst, prepared by depositing copper on MgO, contained 40.5% copper [1]. Determined by chemisorption of oxygen, the specific surface area of the copper proved to be 42.4 m^2/g. The catalyst was reduced with either hydrogen or deuterium prior to the experiment. The degree of dehydrogenation was determined by chromatographing on a Chromosorb W–polymethylphenylsiloxane column. The PMR and mass spectra of the individual reaction products were obtained after separation on a preparative Khrom-31 chromatograph, using a column packed with polyethylene glycol on Chromosorb.

An MI-1305 mass spectrometer was used for determining the degree of exchange and isotopic distribution in cyclohexanol and cyclohexanone, working at an ionization potential of 16 V in the one case, and 18 V in the other. Hydrogen elimination gave rise to a great number of $(M-1)^+$ fragments in the course of mass spectrometry of cyclohexanol, thereby making difficult any attempted exact, molecular ion analysis. For this reason, calculations were carried out on the ion fragment resulting from elimination of water. Values of the degree of exchange given below apply to a ring with protected hydroxyl group, and are possibly low for this reason. Exact, isotopic molecular ion analysis was possible with the mass spectra of cyclohexanone. Since the deuterium of the cyclohexanol hydroxyl group might readily exchange with hydrogen during preparative separation of the reaction products [4], the degree of exchange in this group was determined by direct IR spectroscopy of the reacting mixture. Analysis was carried out with a UR-20 spectrophotometer. Deuterium in the α position of cyclohexanol was determined from the PMR spectra, the latter being obtained with a DA-60-IL Varian spectrometer working with CCl_4 solutions containing TMS and using nitrobenzene as an internal standard.

DISCUSSION OF RESULTS

Isotopic exchange in cyclohexanol was studied under the conditions of reaction (1), using deuterium as the carrier gas and working at temperatures in the 170–305°C interval with the initial partial pressures of alcohol and deuterium, P^0_{alc} and $P^0_{D_2}$, fixed at 90 and 660 mm Hg, respectively. The exchange rate was $2.6 \cdot 10^4$ h^{-1} in each experiment. The degree of exchange at equilibrium varied from 0.29 to 0.48.

Data on the degree of exchange and the isotopic distribution in cyclohexanol are given in Table 1. It is seen that there was intensive exchange, with the formation of deuterated products ranging from d_1 to d_6, at all temperatures. The deuterium concentration diminished gradually, but continuously, as the number of deuterium atoms in the cyclohexanol molecule increased. From this it was concluded than at least six of the cyclohexanol hydrogens participated, and to an equal degree, in the exchange process. The product cyclohexanone also contained various deutero compounds (ranging from d_1 to d_4), with the same isotopic distribution as the alcohols, from which it followed that the exchange mechanism was the same in alcohol and ketone.

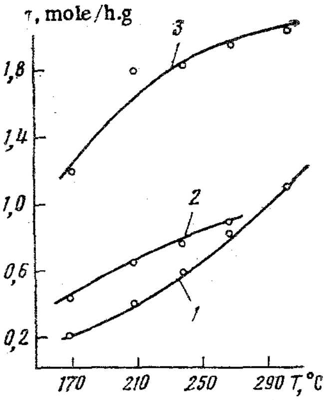


Fig. 1. Temperature variation of the rate of cyclohexanol dehydrogenation and isotopic exchange: 1) rate of cyclohexanol dehydrogenation; 2) rate of α-hydrogen exchange; 3) overall rate of ring exchange.

TABLE 2. Isotopic Distribution in the Products from Cyclohexanol Exchange under Dehydrogenation Conditions, and in the Products from Cyclohexanone Exchange under Reverse Reaction Conditions (240°C, $P^0_{C_6H_{12}O} = P^0_{C_6H_{10}O} = 90$, $P^0_{D_2} = 660$ mm)

Initial product	Isotopic distribution, %							Degree of exchange, %	Mean No. of D atoms per molecule
	d_0	d_1	d_2	d_3	d_4	d_5	d_6		
Cyclohexanol*	57,2	17,7	11,0	8,1	4,3	1,4	0,6	42,8	2,1
Cyclohexanone	79,4	14,3	4,7	1,3	0,2	–	–	20,6	1,4

*From calculations on the $(M-18)^+$ fragment ions.

The rates of isotopic exchanges and dehydrogenation both increased with rising temperature, the latter being the higher over the entire temperature interval (Fig. 1).

From this it could be concluded that the catalyst surface carried various forms of adsorbed alcohol, only certain of which actually participate in the dehydrogenation reaction. The ease of hydrogen elimination from any particular position in the cyclohexanol molecule is measured by the rate of exchange at this position. Judging from the PMR spectra, we noted that most of the alcohol molecules undergo exchange at the α position, the exchange rate being higher than the rate of dehydrogenation (cf. Fig. 1). From this it would follow that α hydrogen elimination cannot be the slow step in reaction (1). It can be seen from Table 1 that the IR spectra can be interpreted as indicating appreciable hydrogen exchange in the alcohol hydroxyl group. It should be pointed out that the results of this analysis could well be low, the product containing the deuterated hydroxyl group readily undergoing exchange with traces of water [4, 6].

Table 2 gives a comparison of the rate of cyclohexanol exchange under reaction (1) conditions and the rate of cyclohexanone exchange under reverse reaction conditions

$$C_6H_{10}O + H_2 = C_6H_{12}O \tag{2}$$

in a deuterium atmosphere. It can be seen that the overall exchange was much higher in the alcohol than in the ketone. Clearly this reflects the fact that the α-hydrogen exchanges more readily than the other hydrogen atoms in the ring.

The kinetic isotope effects were evaluated from the ratio of the reaction rates with the light and heavy isotopes at fixed degree of advancement. Kinetic isotope effects were measured for the forward reaction, replacing the cyclohexanol-OH by cyclohexanol-OD (carrier gas, nitrogen), and for the forward reaction, working in an atmosphere of hydrogen or deuterium. The isotope effect was also measured for the reverse reaction (2), replacing the hydrogen by deuterium. The results of these measurements are summarized in Table 3.

TABLE 3. Kinetic Isotopic Effect (β) in the Dehydrogenation of Cyclohexanol and the Hydrogenation of Cyclohexanone, Protium Being Replaced by Deuterium

Initial compound	T., °C	$\beta=\left(\frac{r_H}{r_D}\right)_{x=\text{const}}$
$C_6H_{11}OH$ $C_6H_{11}OD$	240	0.99
$C_6H_{11}OH$ $C_6H_{11}OD$	270	1.02
$C_6H_{11}OH$ in excess $C_6H_{11}OH$ in excess	240	1.01
$C_6H_{10}O+H_2$ $C_6H_{10}O+D_2$	240	1.30

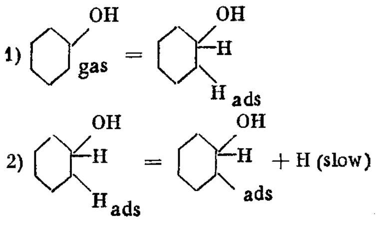
The fact that replacement of cyclohexanol-OH by cyclohexanol-OD had no effect on the isotopic distribution was taken as an indication that the hydroxyl hydrogen was not involved in the slow step of the dehydrogenation reaction. Since the rate of reaction (1) was the same in excess of either H_2 or D_2, it could be concluded that the surface hydrogen had no effect on the slow reaction steps. In view of the ease of cyclohexanol isotopic exchange, it could be assumed that it was alcohol containing up to 30% α-position deuterium which was involved in dehydrogenation in an excess deuterium. The lack of an isotopic effect in this last case was taken to indicate that α-hydrogen elimination was not the slow step in reaction (1). On this same basis, molecular adsorption of the alcohol could not have been the slow step.

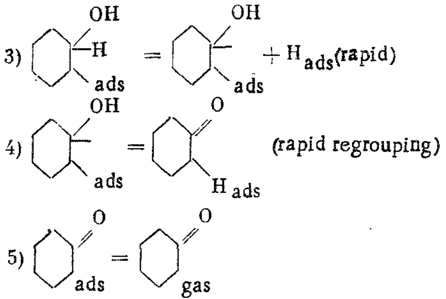
It is seen from Table 3 that a kinetic isotope effect arose on replacing the molecular hydrogen of reaction (2) by molecular deuterium. This could indicate either that the rate of the reverse reaction was determined by surface reactant interaction or by hydrogen adsorption. If, on the other hand, hydrogen adsorption was the slow step in the process, then the principle of microscopic reversibility would require that hydrogen desorption be the slow step in reaction (1). This would, however, be inconsistent with the data obtained through the kinetic and isotopic measurements, [1], to say nothing of the data applying to the adsorption of hydrogen on copper [7, 8]. Thus, all but the first of the assumptions concerning the nature of the slow step in the reaction process were eliminated from further consideration.

Mass spectrometric analysis showed that dehydrogenation of cyclohexanol-OD in an atmosphere of nitrogen yields a product containing approximately 43% deuterocyclohexanone. This result cannot be the consequence of exchange between the product cyclohexanone and the deuterium liberated in reaction (1), equilibrium exchange of only four of the cyclohexanol hydrogens being some 20%, and this only if one neglects cyclohexanol exchange, which, if taken into account, would reduce this figure still further. The effect in question here could, however, be explained as the result of rapid deuterium atom transition between the hydroxyl group and ring positions.

Thus the indication is that the hydrogen eliminated in the dehydrogenation reaction is not hydrogen from the hydroxyl group. Arguing in the same manner, we can conclude that hydrogenation does not lead to the addition of an atom of hydrogen (or deuterium) to the oxygen atom of the cyclohexanone molecule. These facts would be consistent with a so-called enol cyclohexanol dehydrogenation mechanism [6].

The data obtained here suggest the following reaction scheme for the dehydrogenation process:





6) $2H_{ads} = H_{2\,gas}$

This scheme includes rapid formation of surface alcohol compounds, slow β-hydrogen elimination with subsequent rapid α-hydrogen elimination, surface isomerization of ketone through an enol-type regrouping, and hydrogen and ketone desorption. The fact that this scheme leads to the same form of kinetic equation as was obtained in [1] is an indication of its validity. Comparison shows that this mechanism is essentially different from that proposed [9] for the dehydrogenation of isopropanol on nickel. This last is an indication that alcohol dehydrogenation cannot be described in terms of a single kinetic model.

CONCLUSIONS

1. Study has been made of the hydrogen–deuterium exchange, in cyclohexanol under dehydrogenation conditions and in cyclohexanone under hydrogenation conditions, on a copper–magnesium catalyst. The overall rate of exchange in the alcohol and the rates of exchange in the hydroxyl group and in the α positions are higher than the rate of dehydrogenation.

2. Kinetic isotope effects have been measured for the replacement of the cyclohexanol hydroxyl-group hydrogen by deuterium, for replacement of the excess hydrogen by excess deuterium in the dehydrogenation reaction, and for replacement of the molecular hydrogen by molecular deuterium in the hydrogenation reaction.

3. The results of this study have been used as a basis for a proposed reaction scheme involving slow β-hydrogen elimination followed by rapid α-hydrogen elimination and enol regrouping.

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