JOURNAL OF CATALYSIS 27, 79-88 (1972)

Catalytic Deuteration of Cyclohexanone and Allied Reactions over Platinum Metals

YUZURU TAKAGI, SHOUSUKE TERATANI,
AND KAZUNORI TANAKA

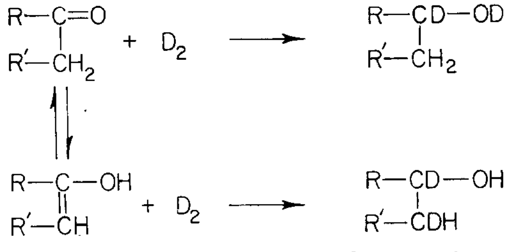
The Institute of Physical and Chemical Research, Wako-shi, Saitama Pref., Japan

Received February 10, 1972

In order to gain some insight into the mechanism of ketone hydrogenation to alcohol, cyclohexanone was deuterated over platinum metal catalysts under elevated pressure at 80°C. The straightforward addition of two deuterium atoms to the carbonyl linkage was predominant over the heavy triad (Os, Ir, Pt). In contrast, the deuteration over the light triad (Ru, Rh, Pd) was accompanied by considerable isotopic exchange at the C-2 or C-6 position, leading to substantial proportions of the polydeuterated alcohols. A mechanism for cyclohexanone hydrogenation is presented which consists of three interlinked hydrogenation paths each having a different half-hydrogenated intermediate. The deuterium incorporation into the C-2 or C-6 position is attributable to alternation between the 1-monoadsorbed and 1,2-diadsorbed intermediates.

INTRODUCTION

A ketone exists as a tautometric mixture of keto and enol forms. Consequently, there are two simplest conceivable mechanisms for ketone hydrogenation to alcohol: the straightforward addition of two hydrogen atoms to the ketonic linkage or to the enolic linkage. These two mechanisms may be distinguished by deuterating a ketone and examining the positions of the incorporated deuterium atoms:



Apparently, the ketonic mechanism forms one CD and one OD bond while the enolic mechanism yields two CD bonds. One can therefore evaluate the contribution of the enolic mechanism by comparing the number of OD or CD bonds with the conversion to alcohol.

Most of the simple monoketones contain so little of the enol form that they can be regarded as having the keto structure only. Acetone, for example, has been estimated to contain only about $2.5 \times 10^{-4}\%$ of the enol in the pure liquid (*1*). Despite such an extremely low content of enol, one might suspect that the enolic mechanism plays a significant role in ketone hydrogenation since olefinic linkages are in general much more easily reduced than carbonyl linkages (*2*). This possibility was investigated for the first time by Anderson and MacNaughton (*3*) using the above-mentioned tracer method with acetone, *n*-butyraldehyde, and several other aliphatic carbonyl compounds over platinum, nickel, and copper chromite catalysts. The results showed that at temperatures of 150 to 250°C the enolic mechanism occurred to a considerable extent, while at room temperature only the ketonic mechanism predominated; however, their analytical method was later critically reviewed (*4*). Friedman and Turkevich (*5*) deuterated acetone at room temperature over a platinum-on-charcoal catalyst, and the results favored the ketonic rather than the enolic mechanism. More recently, Kemball and Stoddart (*6*) studied the reactions

Copyright © 1972 by Academic Press, Inc.
All rights of reproduction in any form reserved.

between acetone vapor and deuterium over a number of evaporated metal films. The reaction temperatures used ranged from −35.5°C for Pt to 230.8°C for Ag, and the results also supported the ketonic mechanism.

In his extensive studies employing a variety of monoketones, Gero (*7*) revealed that cyclic ketones are generally more enolic than comparable open-chain ketones. For example, at room temperature (approx 25–28°C),* cyclohexanone contained 1.18% enol in comparison with 0.11% for 2-hexanone and 0.05% for 3-hexanone. From these results, it would appear that the role of the enolic mechanism, if any, is much more significant for cyclic ketones than for chain ketones. Although Cornet and Gault (*8*) deuterated 2-methylcyclopentanone over several metal catalysts, their purpose was not the evaluation of the importance of the enolic mechanism. Besides, the isotopic distributions of the resulting alcohol seem unlikely to allow such evaluation owing to the simultaneous occurrence of the extensive isotopic exchange. The occurrence of considerable cyclopentanone/deuterium exchange was also reported by Kemball and Stoddart (*9*) over some metal films. Since these two tracer studies were conducted in the gas phase, we initiated this research on cyclohexanone deuteration in the liquid phase in the expectation that the accompanying exchange would be quite negligible, and the role of the enolic mechanism could quantitatively be evaluated. However, even in this liquid-phase deuteration, there was substantial isotopic exchange over some catalysts. In order to explain this unexpectedly extensive exchange, additional experiments were conducted. These included exchange reaction between deuterium and cyclohexanol, and that between ordinary and deuterated cyclohexanones.

EXPERIMENTAL METHODS

Materials. The cyclohexanone used was a Guaranteed Reagent Grade material purchased from Junsei Pure Chemical Co., Tokyo. The procedure for removing the cyclohexanol contained (2 mol %) was similar to that reported by Garland and Reid (*10*). The cyclohexanone was first shaken with sodium bisulfite. The addition product formed, a white precipitate, was filtered, washed well with ethanol and ether, dried under reduced pressure, and finally treated with concentrated sodium carbonate. The resulting organic phase was separated and distilled under reduced pressure. The fraction of bp 59.5–61.0°C/33 mm Hg was collected as cyclohexanone in a purity of 99.9 mol % as judged by gas chromatography.

The Os catalyst used was prepared by reducing an osmium tetroxide suspension in isopropyl alcohol under a pressure of 80 kg/cm^2 of hydrogen for 20 min at temperatures up to 60°C. The metal thus obtained was washed repeatedly with deionized water until the filtrate was neutral, dried under reduced pressure at room temperature, and stored in a desiccator. For the preparation of the other catalysts, aqueous sodium hydroxide was added to an aqueous solution of the appropriate metal chloride, and the resulting precipitate was reduced with hydrogen. The reduction procedure was the same as that for Os except that the precipitate was suspended in water in place of the alcohol and the reduction temperature was raised to 80°C. The metals obtained were washed, dried and stored in the same fashion as in Os. Before use, the catalysts thus prepared were separately refluxed with D_2O (99.75 D-atomic %) for 2 hr, filtered off, and finally dried under reduced pressure. This D_2O pretreatment was given to eliminate the adsorbed light water, which, if it remained during the cyclohexanone deuteration, may have exchanged with the gas-phase deuterium causing complications in the isotopic distribution of cyclohexanol.

The cyclohexanol was Nippon Rikagaku guaranteed reagent grade, and used without further purification.

Cyclohexanone-2,2,6,6-d_4 was supplied by Merck Sharp and Dohme of Canada Ltd. The stated isotopic purity was 98%.

---

* The temperature of the measurements has been confirmed by private communication.

Cyclohexanol-1-d_1 was prepared by lithium aluminum deuteride reduction of cyclohexanone, and subsequent substitution of hydroxyl hydrogen for the hydroxyl deuterium. The substitution was effected by repeatedly shaking the dideuterated cyclohexanol with fresh water. NMR spectra of the cyclohexanol thus treated confirmed specific D-labeling at the C_1 position alone.

Cyclohexanol-1,2,2,3,3,4,4,5,5,6,6-d_{11} was prepared by shaking perdeuterated cyclohexanol with fresh water. The perdeuterated alcohol was supplied by Merck Sharp and Dohme of Canada Ltd., and stated to be 98% in isotopic purity.

Deuterium, 99.9% in isotopic purity, was obtained from Showa Denko Co., Tokyo, and used without further purification.

Cyclohexanone deuteration. For this reaction 4.9 g (0.05 mol) of cyclohexanone and 20 mg of a catalyst were placed in a 100-ml stirred autoclave, and subsequently deuterium at a pressure of 17–20 kg/cm^2 was admitted after several flushings. The autoclave was then transferred to a water bath thermostated at 80°C. Because of the temperature rise, the pressure increased by 1–2 kg/cm^2. Stirring was started about 5 min after thermal equilibrium was established, and continued until the pressure ceased to fall. The reaction time for each catalyst during which time the mixture was continually stirred is given in Table 1. The initial and final pressures of the reaction mixture are also included. The reaction was stopped by discontinuing the stirring and by cooling the autoclave under running water. The residual deuterium was analyzed in a mass spectrometer for isotopic dilution. The liquid phase was separated from the catalyst by decantation or filtration, and subjected to mass spectrometric analysis for isotopic distribution, NMR spectroscopy for hydrogen content at the C_1 position, and to gas chromatography for possible side reaction products and unreacted cyclohexanone.

Cyclohexanol–deuterium exchange. The procedure was analogous to that described above for cyclohexanone deuteration. Just 5.0 g (0.05 mol) of cyclohexanol and 20 mg of a catalyst were stirred in the autoclave at 80°C and a pressure of 18 to 22 kg/cm^2 of deuterium. The reaction time for each catalyst was set equal to that of cyclohexanone deuteration over that catalyst. The exchange products, i.e., the deuterated cyclohexanol and isotopically diluted deuterium, were subjected to mass spectrometry.

Cyclohexanone–deuterocyclohexanone exchange. Two different procedures (a) and (b) were employed. In (a), a mixture of 1 g of cyclohexanone-2,2,6,6-d_4 and 4 g of ordinary cyclohexanone was stirred with 20 mg of a catalyst sample in the autoclave at 80°C and approximately 22 kg/cm^2 of helium. The reaction time for each catalyst was again taken as the same as that for cyclohexanone deuteration for that catalyst. The reaction mixture was examined in a mass spectrometer. In procedure (b), the catalyst was re-reduced just before use. For the re-reduction, 20 mg of the catalyst sample was placed in the autoclave with 2 g of cyclohexanol, subsequently hydrogen was admitted, and stirring continued for 30 min at temperatures up to 80°C and at a pressure of 20 kg/cm^2. After this reduction, the hydrogen was purged, the head was taken off, and a mixture of 1 g of cyclohexanone-2,2,6,6-d_4 and 4 g of ordinary cyclohexanone was added to the catalyst–cyclohexanol suspension very carefully so as to avoid any agitation which might lead to reoxidation of the re-reduced catalyst. The exchange reaction was conducted under helium as in procedure (a).

Analyses. NMR spectra were obtained on a 60 MHz Japan Electron Optics Laboratory C-60 NMR spectrometer in a carbon tetrachloride solution containing tetramethylsilane and chloroform as internal references. The hydrogen content at C-1 was evaluated by comparing the integrated area of C-1 proton resonance at $\tau 6.5$ with that of chloroform proton resonance at $\tau 2.75$. Control experiments showed that hydrogen atoms of chloroform and hydroxyl deuterium atoms of cyclohexanol do not exchange appreciably unless the carbon tetrachloride solution is allowed to stand for a prolonged period.

The gas chromatograph used was a

TABLE 1
ISOTOPIC ANALYSES OF REACTION PRODUCTS IN CYCLOHEXANONE DEUTERATION

					Cyclohexanol[d] (%)									
Expt	Cat.	t^a (min)	P^b (kg/cm^2)	Ion[c]	d_0	d_1	d_2	d_3	d_4	d_5	d_{6-8}	D_m[e]	$H_{C\text{-}1}$[f] (%)	D_g[g] (%)
1	Ru	30	21.0–10	m	7.25	84.72	5.05	1.87	0.67	0.30	0.14	1.05	9	93.7
				f	8.06	83.04	5.47	2.02	0.94	0.34	0.13			
2	Rh	30	21.4–10	m	24.10	42.98	15.31	8.88	4.86	2.22	1.65	1.41	28	76.4
				f	24.49	42.60	15.82	8.95	4.69	2.16	1.30			
3	Pd	50	21.5–10.6	m	12.72	66.62	15.26	3.72	1.14	0.43	0.11	1.16	14	90.9
				f	11.87	68.58	15.29	2.85	1.15	0.25	—			
4	Os	15	21.6–10.2	m	3.23	95.81	0.67	0.28	—	—	—	0.98	0	97.9
				f	3.16	95.41	0.74	0.23	0.46	—	—			
5	Ir	50	18.4–7.0	m	4.91	92.27	1.76	0.68	0.25	0.13	—	0.99	3	94.4
				f	4.82	91.88	1.93	0.71	0.57	0.09	—			
6	Pt	70	20.4–8.7	m	4.57	91.50	3.00	0.61	0.20	0.11	—	1.01	4	95.4
				f	5.25	89.90	3.36	0.79	0.57	0.13	—			
7	Rh	34	21.8–10.5	m	25.86	42.69	15.17	8.27	4.22	2.19	1.59	1.36		74.9
8	Os	18	18.0–6.6	m	5.88	93.43	0.57	0.12	—	—	—	0.95		95.8
9[h]	Rh added with $(C_2H_5)_3N$			m	22.50	58.26	10.74	4.71	1.95	0.85	0.63	1.14		76.7
		55	18.9–7.8	f	22.25	56.97	11.49	5.17	2.36	0.90	0.20			

[a] Reaction time.

[b] Initial and final pressures exerted by reaction mixture.

[c] Symbols m and f represent the molecular ion M^+ and fragment ion $(M\text{–water})^+$, respectively.

[d] Hydroxyl deuterium was replaced by ordinary hydrogen before mass spectrometric analysis.

[e] Mean number of deuterium atoms incorporated into a cyclohexanol molecule, $\Sigma\, id_i/100$.

[f] Content of ordinary hydrogen at the C-1 position.

[g] D-atomic % for the residual gas-phase deuterium.

[h] The amine added was 0.28 ml (0.002 mol).

Shimadzu Model 1B instrument equipped with a flame ionization detector in place of the thermocouple detector used in the standard type. Analyses were performed at 80°C on a 10 wt% diglycerol-on-fire brick (60–80 mesh) column with nitrogen as the carrier gas.

All mass spectra were obtained on a Hitachi RMS-4 mass spectrometer equipped with an electron multiplier. Analyzing deuterated cyclohexanol samples directly in a mass spectrometer is difficult owing to the instantaneous exchange of the hydroxyl deuterium with the water adsorbed on the instrument walls. In order to avoid this difficulty, we substituted hydroxyl hydrogen for the hydroxyl deuterium prior to analysis, and the mechanism of deuteration is discussed on the basis of the number of CD bonds, i.e., the number of deuterium atoms incorporated into the cyclohexyl ring. The substitution was made by repeatedly shaking a deuterated cyclohexanol sample with fresh water. That this pretreatment does not eliminate any deuterium atom directly attached to a carbon atom was confirmed by preliminary experiments in which perdeuterated cyclohexanol was exchanged with water resulting exclusively in $C_6D_{11}OH$. Spectra for the water-treated cyclohexanol samples were taken at an ionizing voltage of 8 V, at which voltage the relative intensities of the most objectionable fragment ions, $(M + 1)^+$, $(M - 1)^+$, and $(M - 2)^+$, were minimized. Distributions of isotopic cyclohexanols were calculated based upon the molecular ion M^+ or the fragment ion $(M\text{–water})^+$ formed by loss of H_2O, HDO, or D_2O. Corrections were made for the presence of the naturally occurring heavy isotopes of hydrogen, carbon, and oxygen. The calculations based on the $(M\text{–water})^+$ fragment were made by assuming complete retention of the ring deuterium atoms in the fragmentation process.

Mass spectra for cyclohexanone samples were also obtained at the same low voltage (8 V), and the isotopic distributions were calculated based upon the molecular ion.

Mass spectra for residual-deuterium samples were taken at 80 V. The compositions of H_2, HD, and D_2 were taken as parallel to the peak heights of m/e at 2, 3, and 4 after subtraction of the contribution to m/e 2 by the atomic D^+ ion. The D^+ contribution was determined to be 0.6% by comparing the intensities of D^+ and D_2^+ peaks for a sample of pure gas-phase deuterium. The contribution to m/e 3 by H_3^+ was shown to be negligible from the mass spectra for ordinary hydrogen.

In all calculations of isotopic distributions, the conventional assumption of equal molar intensity was made for detection of isotopic molecular ions and of isotopic fragment ions $(M\text{–water})^+$. The deviations from this assumed rule were examined using cyclohexanol-d_0, -1-d_1, and -1,2,2,3,3,4,4,-5,5,6,6-d_{11}. The observed ratio of molecular peaks d_1/d_0 was 1.00 and that of d_{11}/d_0 was 1.40, and the corresponding values for the fragment ion $(M\text{–water})^+$ were 1.06 and 0.80, respectively. These results indicate that the distributions derived based on the above assumptions are not seriously erratic unless cyclohexanol samples are extensively deuterated.

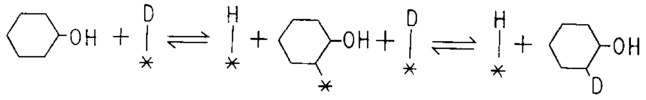
RESULTS AND DISCUSSION

The deuteration of cyclohexanone to isotopic cyclohexanols was quantitative with every catalyst used. Gas chromatography disclosed no peaks for starting ketone or any deuterogenolysis product.

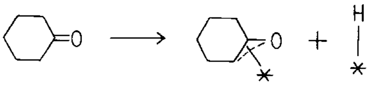
Distribution of isotopic cyclohexanols. The observed distributions of isotopic cyclohexanols are given in Table 1. Isotopic compositions are accurate to ±0.1% for the minor components, and probably a little worse for the major components. In viewing these data, it should be remembered that all of the cyclohexanol samples were water-treated before the mass spectrometric analysis so that if there was no deuterium exchange, the relative importance of the simple ketonic and enolic mechanisms could be evaluated from the proportions of the d_1 and d_2 species. However, there was more or less isotopic exchange on all catalysts, forming d_0 as well as d_3 and even more highly deuterated species. Over the heavy triadic metals (Expts 4, 5, and 6) the extent of exchange was rather small, and d_1 predominated. This suggests that ketone hydrogenation over these metals proceeds predominantly through the ketonic mechanism. In contrast, the exchange on the light triadic metals (Expts 1, 2, and 3) was quite extensive resulting in a much broader distribution pattern over the d_0 to d_5 species, and there were even traces of more highly deuterated species up to d_8. Obviously, neither the simple ketonic nor the enolic mechanism accounts for these extensive isotopic exchange. Experiments 7 and 8 show the reproducibility of the distribution of isotopic cyclohexanols for Rh and Os. The effect of amine addition upon the isotopic distribution was examined with Rh in Expt 9 which showed that amine addition reduces deuterium exchange to some extent.

Isotopic distribution within cyclohexanol molecule. Before presenting a detailed mechanism for cyclohexanone hydrogenation, it is useful to consider the distribution of deuterium within the cyclohexanol molecule. In approaching this subject, the work of Ward and Williams (*11*) is instructive. They took mass spectra of specifically deuterated cyclohexanols and showed that at ionizing voltages of 12 and 70 V, most of the (M–water)$^+$ fragments are formed by directly eliminating the hydroxyl group and one hydrogen atom at C-4. There was also a significant elimination of the C-3 and C-5 hydrogens, but very little loss of the C-2 and C-6 hydrogens, and negligible loss of the C-1 hydrogen. Table 1, on the other hand, shows that the isotopic cyclohexanol compositions worked out from the molecular ion M$^+$ are in excellent agreement with those obtained from (M–water)$^+$. This agreement, in light of the results obtained by Ward and Williams, suggests that most of the deuterium atoms entering the cyclohexyl ring are located in the C-2 and C-6 positions as well as the C-1 position. These locations are consistent with the lack of significant formation of d_6- and more highly deuterated species since only five deuterium atoms can be accommodated in the three positions, C-1, C-2, and C-6. With the exception of Os, the hydrogen content at C-1, H_{C-1}, is nearly equal to or slightly higher than the d_0 composition. The slight excess of H_{C-1} seems very reasonable since a small fraction of deuterated species may have hydrogen at C-1 as a result of isotopic exchange. The unreasonable excess of d_0 composition on Os may possibly be attributed to errors in the NMR measurement of H_{C-1}.

Mechanism for isotopic exchange. In order to establish the mechanism for cyclohexanone hydrogenation, we must decide whether or not the process responsible for the isotopic exchange during deuteration, i.e., the process causing the exchange at the C-2 or C-6 position, is involved in the sequence of steps of the hydrogenation. As such exchange processes outside the sequence, the following four mechanisms are conceivable: (i) exchange of cyclohexanol with gas-phase deuterium through a dissociatively adsorbed intermediate



where * representing the adsorption site, (ii) dissociative adsorption of cyclohexanone to form an oxoallylic species,



followed by deuteration, (iii) ordinary noncatalytic tautomerization, and (iv) surface catalyzed tautomerization such as

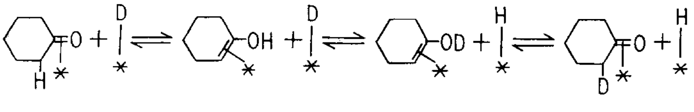


TABLE 2

Isotopic Analyses of Reaction Products in Exchange of Cyclohexanol with Gas-Phase Deuterium

Cat.	Cyclohexanol[a] (%) d_0	Cyclohexanol[a] (%) d_1	D_g[b] (%)
Ru	97.55	2.45	74.9
Rh	99.71	0.29	73.5
Pd	99.71	0.29	74.1
Os	99.35	0.65	78.6
Ir	99.60	0.40	71.1
Pt	99.82	0.18	68.9

[a] Hydroxyl deuterium was replaced by ordinary hydrogen before mass spectrometric analysis.

[b] D-atomic % for the gas-phase deuterium.

Table 2 shows the results of the exchange reactions between cyclohexanol and gas-phase deuterium attempted to examine the possibility of (i). It is seen that only a trace of cyclohexanol-d_1 was formed with every catalyst used while the gas-phase deuterium underwent considerable isotopic dilution. There were no d_2 peaks or any polydeuterated species. As previously noted, the mass spectrometric analysis of isotopic cyclohexanol was preceded by an operation for replacing the hydroxyl deuterium, so these results suggest that little deuterium entered into the cyclohexyl ring, thereby ruling out process (i). The isotopic dilution in the gas phase is almost entirely attributable to the exchange with the hydroxyl hydrogen. If process (ii), (iii), or (iv) is involved, the catalysts used would catalyze the deuterium exchange between ordinary and 2,2,6,6-tetradeuterated cyclohexanones, even in the absence of gas-phase hydrogen. Two catalysts, Rh and Pd, were chosen to check this possibility in view of their most extensive isotopic exchange during cyclohexanone deuteration. The results of these exchange experiments are shown in Table 3. Apparently, neither of these two metals catalyzed the exchange to any appreciable extent. This excludes process (ii), and suggests that tautomerizations (iii) and (iv) are so slow as to be responsible for the observed isotopic exchange. Therefore, the process of isotopic exchange during deuteration must be involved in the steps of the deuteration or hydrogenation.

Mechanism for hydrogenation. A possible reaction scheme for cyclohexanone deuteration is shown in Fig. 1. A characteristic feature of this mechanism is that the 1,2- or 1,6-diadsorbed intermediate, II_b, is not derived by direct adsorption of the enolic form of cyclohexanone. If such an adsorption process was involved, it would be followed by steps $III_{\gamma 1}$ and III_β or steps $III_{\gamma 2}$ and $III_{\gamma 3}$, thus resulting in the enolic mechanism. However, the enolic mechanism seems unlikely to be operative under our reaction conditions, in view of the lack of tautomerization in the absence of hydrogen, coupled with the very low enol content of cyclohexanone. The argument of Anderson and MacNaughton (*3*) for the enolic mechanism may be vitiated by neglect of isotopic exchange during ketone deuteration.

Although in recent years evidence has grown for π-adsorbed and π-coordinated carbonyl compounds (*12–15*), we have not

TABLE 3

Deuterium Exchange Between Ordinary and 2,2,6,6-Tetradeuterated Cyclohexanones

Isotopic species	Procedure (a)				Procedure (b); compostion (%) over Rh	
	Composition (%) over Rh		Composition (%) over Pd			
	Initial	Final	Initial	Final	Initial	Final
d_0	78.0	79.8	79.4	80.9	79.7	79.7
d_1	0.6	0.6	0.3	0.2	0.3	0.3
d_2	0.1	0.1	0.1	0.2	0.1	0.3
d_3	1.5	1.1	1.5	1.3	1.4	2.3
d_4	17.8	18.4	18.7	17.4	18.5	17.4

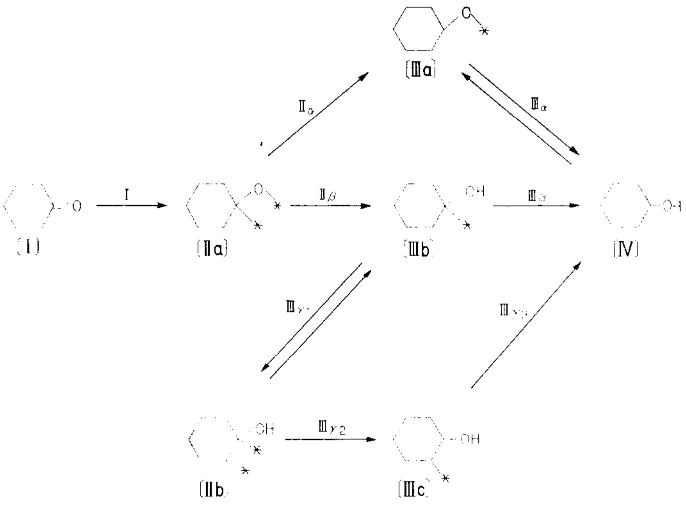


FIG. 1. Reaction scheme for cyclohexanone hydrogenation.

assumed a π-adsorbed intermediate because our experiments do not indicate either its existence or its absence.

The data of Table 2 are used in considering the nature of the last three steps, III_α, III_β, and $III_{\gamma 3}$. Since there was negligible formation of deuterated species, and hence little deuterium entering the cyclohexyl ring, steps III_β and $III_{\gamma 3}$ do not reverse. On the other hand, calculations show that the observed isotopic dilution of the gas-phase deuterium agrees closely with the value required for an isotopic exchange equilibrium with the hydroxyl hydrogens of cyclohexanol. Therefore, step III_α is reversible.

Details of hydrogenation and exchange processes. The proposed reaction scheme for cyclohexanone hydrogenation (Fig. 1) consists of three interlinked hydrogenation paths: path 1: sequence I, II_α, III_α; path 2: sequence I, II_β, III_β; path 3: sequence I, II_β, $III_{\gamma 1}$, $III_{\gamma 2}$, $III_{\gamma 3}$. Let us consider what isotopic alcohol is formed through each reaction path when cyclohexanone is deuterated. In ignorance of hydroxyl deuterium, both paths 1 and 2 should lead to the exclusive formation of the d_1-cyclohexanol deuterated at the C-1 position. Path 3, on the other hand, yields the d_2-species with one deuterium atom in C-1 and the other in C-2 or C-6. The appearance of the polydeuterated d_3–d_5 species must be attributed to the alternation between intermediate II_b and III_b, followed by the reduction through step III_β or sequence $III_{\gamma 2}$, $III_{\gamma 3}$. If the C-1 to metal bond of III_b is axial, one hydrogen at C-2 and one at C-6 are placed toward the catalyst surface, and the other two are directed away from it. Therefore, the two hydrogens close to the catalyst could be substituted by deuterium through the II_b–III_b alternation, while the remote two are left intact. Thus, the isotopic cyclohexanols formed by the subsequent deuterium addition to C-1 should be limited up to d_3. If the C-1 to metal bond is equatorial instead, the four hydrogens at C-2 and C-6 are all placed toward the catalyst at exactly the same distance from the surface plane, and they can be replaced by deuterium with the same probability. Accordingly, the isotopic cyclohexanols up to d_5 would be formed in this situation. The results of Table 1 favor the III_b intermediate with its adsorption bond in the equatorial position over that with the axial adsorption bond although the latter species may also be involved in the reaction. Table 1 also suggests that over the heavy triadic metals, the straight-through path 1 or 2, or both predominate, while over the light triadic metals, the path 2 or 3 each intervened by the II_b–III_b alternation plays an important part.

The extent of isotopic exchange, i.e., the number of deuterium atoms incorporated into the cyclohexyl ring, would be affected by (i) the importance of step II_β relative to II_α, or (ii) the importance of step $III_{\gamma 1}$ relative to III_β. While it is impossible to determine from our experiments which is the primary factor in the observed metal-to-metal variation in the extent of the exchange, it is possible to explain the effect of amine addition with Rh in terms of factor (i) by assuming the participation of positively charged hydrogen. There is some evidence that chemisorbed hydrogen is positively charged on some transition metals (*16–18*). The hydroxyl group of the produced cyclohexanol may also be a source of the charged hydrogen. When intermediate II_a is attacked by a charged hydrogen, interaction is likely with the negatively polarized hydroxyl oxygen. This interaction will probably favor the formation of intermediate III_b over III_a. Adding amine should reduce the concentration of charged hydrogens because of its strong affinity for positively charged species. This would explain the observed decrease due to amine addition in the extent of the isotopic exchange.

Correlation with olefin isomerization. In addition to the detailed mechanism of ketone hydrogenation, it is interesting to consider the relationship between the observed isotopic exchange and the isomerization of the olefinic double bond. Experiments 1–6 in Table 1 show that D_m, the mean number of deuterium atoms incorporated into a cyclohexanol molecule, falls in the sequence,

$$Rh > Pd > Ru > Pt \simeq Ir \simeq Os,$$

which is the reverse of the order of increasing D_g, as shown in Table 1. This is to be expected since the greater the number of deuterium atoms entering cyclohexanol, the greater the dilution of the gas-phase deuterium by hydrogen. Interestingly enough, the above sequence for D_m is similar to that pointed out by Bond and Wells (*19*) for the relative activity of metals in olefin isomerization or exchange at 100°C,

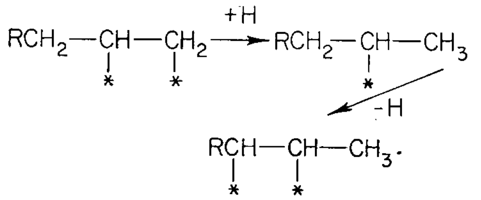
$$Rh > Pd > Ru > Os > Pt \simeq Ir.$$

More recently, Wells and Wilson (*20*) measured the activity for butene isomerization using group VIII metal catalysts, and the observed sequence was

$$Rh \simeq Pd \simeq Ru \simeq Pt \gg Ir > Os.$$

This sequence is also similar to ours for D_m, especially in that the light triad is more active than the heavy triad.

Olefin isomerization is believed to occur by either an addition-abstraction mechanism or an abstraction-addition mechanism (*21*). The addition-abstraction mechanism is characterized by the pre-formation of a metal–hydrogen bond followed by its interaction with the olefin to form a σ-bonded alkyl intermediate. The subsequent abstraction of a hydrogen atom from a different carbon atom results in the isomerization. The central part of this mechanism is shown as



Comparison of this scheme with Fig. 1 shows that the reverse and forward process of step $III_{\gamma 1}$ corresponds to this central part of olefin isomerization. This correspondence explains the close parallel between deuterium–ketone exchange and olefin isomerization.

Additional remarks. The formation of traces of cyclohexanol-d_6 to -d_8 over the light triad calls for additional explanation. In these highly deuterated species, deuterium atoms must be incorporated into the C-3 and C-5 positions in addition to the C-1, C-2, and C-6 positions. The deuterium incorporation into the C-3 and C-5 positions may be effected by the formation of 2,3- or 5,6-diadsorbed species which is led from 1,2- or 1,6-diadsorbed intermediate II_b.

The extent of deuterium incorporation into the produced alcohol was much greater in the work of Cornet and Gault (*8*) with 2-methylcyclopentanone than in this work with cyclohexanone. Especially, in their runs with Rh, there was even considerable formation of the perdeuterated alcohol. This striking difference in the extent of isotopic exchange may possibly be attributed to the difference in reaction conditions, particularly in reaction phase; the gas-phase deuteration in their study vs the liquid-phase deuteration in ours.

ACKNOWLEDGMENTS

The authors express their appreciation to Professor Emeritus K. Hirota (Osaka Univ.) for his valuable discussion. Thanks are also extended to Mrs. N. C. Knight (National Center for Atmospheric Research, Colorado) for her linguistic comments on the original manuscript. The Hitachi RMS-4 mass spectrometer used was purchased from Tokutei Kadai Sokushinhi (Selected Project Promotion Grant) from The Institute of Physical and Chemical Research.

REFERENCES

1. Schwarzenbach, G., and Wittwer, C., *Helv. Chim. Acta* **30**, 669 (1947).
2. Rylander, P. N., *in* "Catalytic Hydrogenation over Platinum Metals," p. 271. Academic Press, New York, 1967.
3. Anderson, L. C., and MacNaughton, N. W., *J. Amer. Chem. Soc.* **64**, 1456 (1942).
4. Taylor, T. I., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 5, p. 396. Reinhold, New York, 1957.
5. Friedman, L., and Turkevich, J., *J. Amer. Chem. Soc.* **74**, 1669 (1952).
6. Kemball, C., and Stoddart, C. T. H., *Proc. Roy. Soc., Ser. A* **241**, 208 (1957).
7. Gero, A., *J. Org. Chem.* **26**, 3156 (1961).
8. Cornet, D., and Gault, F. G., *J. Catal.* **7**, 140 (1967).
9. Kemball, C., and Stoddart, C. T. H., *Proc. Roy. Soc., Ser. A* **246**, 521 (1958).
10. Garland, C. E., and Reid, E. E., *J. Amer. Chem. Soc.* **47**, 2333 (1925).
11. Ward, R. S., and Williams, D. H., *J. Org. Chem.* **34**, 3373 (1969).
12. Stark, K., Lancaster, J. E., Murdoch, H. D., and Weiss, E., *Z. Naturforsch. B* **19**, 284 (1964).
13. Tate, D. P., Buss, A. A., Augl, J. M., Grasselli, J. G., Ritchey, W. M., and Knoll, F. J., *Inorg. Chem.* **4**, 1323 (1965).
14. King, R. B., and Fronzaglia, A., *Inorg. Chem.* **5**, 1837 (1966).
15. Young, R. P., and Sheppard, N., *J. Catal.* **20**, 333 (1971).
16. Eley, D. D., *Quart. Rev.* **3**, 209 (1949).
17. Hayward, D. O., and Trapnell, B. M. W., *in* "Chemisorption," 2nd ed., p. 207. Butterworths, London, 1964.
18. Nishimura, S., Katagiri, M., Watanabe, T., and Uramoto, M., *Bull. Chem. Soc. Jap.* **44**, 166 (1971).
19. Bond, G. C., and Wells, P. B., *in* "Advances in Catalysis" (W. G. Frankenburg, V. T. Komarewsky, E. K. Rideal, eds.), Vol. 15, p. 206. Academic Press, New York, 1964.
20. Wells, P. B., and Wilson, G. R., *J. Catal.* **9**, 70 (1967).
21. Meller, S. D., and Wells, P. B., *Trans. Faraday Soc.* **65**, 1873 (1969).