

SELECTIVITY IN THE CATALYTIC HYDROGENATION OF 2-HYDROXYCYCLOHEXANONE*

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The catalytic hydrogenation of 2-hydroxycyclohexanone has been investigated on ruthenium, nickel, rhodium, platinum and palladium. The reaction was completed usually within several hours under an atmospheric pressure of hydrogen at room temperature. It was found that ruthenium and nickel catalysts produce more *cis*-cyclohexane-1,2-diol than *trans*-diol; while platinum and palladium catalysts give rise to more *trans*-diol than *cis*-form.

Two adsorbed models, weak and strong, for the substrate were presented to account for the observed hydrogenation selectivity.

In the previous papers,^{1,2)} the catalytic hydrogenation of 5-keto-D-gluconate, has been investigated over transition metal catalysts of group VIII. These metal catalysts usually gave a mixture of D-gluconate and L-idonate as the hydrogenation product. However, the isomer ratio of the products was dependent on the catalyst species. Nickel and ruthenium gave rise to more L-idonate than platinum and palladium. Two adsorbed models (Fig. 1) for the substrate were proposed to account for the observed hydrogenation selectivity. One is that the interaction of the substrate with the catalyst surface is so strong, such as ruthenium and nickel, that the intramolecularly steric hindrance of the adsorbed state could cause the hydrogenation selectivity. The other is that the substrate is weakly adsorbed on the surface of catalyst, such as platinum and palladium, so that the adsorbed substrate is intramolecularly flexible, and hence the thermodynamic stability of the product may control the hydrogenation selectivity.

Numerous investigations have been reported so far on the catalytic hydrogenation of organic compounds with particular interest on the stereoselectivities. For example, Mitsui *et al.*³⁾ reported that the stereochemical results of the hydrogenation of cyclopentanones over Raney nickel was quite different from those over palladium or platinum catalyst. According to these authors, the hydrogenation selectivity is governed by the catalyst hindrance of the substituent especially over nickel catalyst while it is considered to be product stability controlled in the case of platinum catalyst (Table 1).

Shono and Mitani⁴⁾ investigated the stereochemistry of electroreduction of cyclic ketones.

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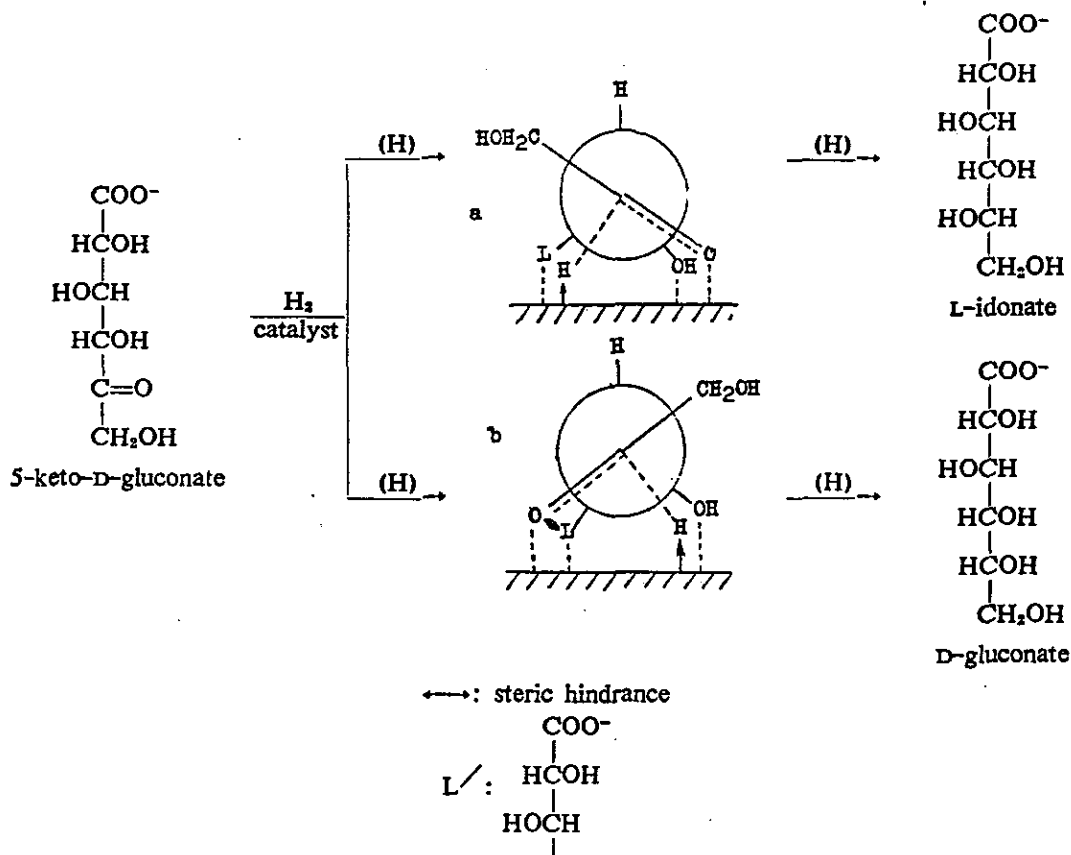

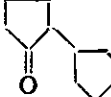


Fig. 1. Adsorption Models for 5-Keto-D-gluconate on the Surface of Catalysts.

Table 1. Hydrogenation of Substituted Cyclopentanones

Catalyst	Substrate		Nature of stereochemistry or mechanism
			
	Product (<i>cis/trans</i>)		
Raney Ni	4.26	4.26	governed by the catalyst hindrance
Pt Black	0.37	0.69	product control
5% Rh-C	1.17	0.69	
5% Pd-C	0.37	—	

It was found that the anionic species abstracts a proton at the vicinity of the surface of a bulky electrode prior to its diffusion into solution, such as electroreduction in the solution of sulfonic acid-water-methanol, thus steric factors preferentially control the stereochemistry of the products. On the other hand, the proton abstraction takes place after the active species has diffused into the solution, such as the electroreduction in isopropanol, the thermodynamic stability of the products may predominantly control the stereochemistry of reduction (Table 2).

Table 2. Electroreduction of Cyclic Ketones

Ketone	Epimer ratio (<i>cis/trans</i>)		Relative thermodynamic stability ratio
	Isopropanol	H ₂ SO ₄ -H ₂ O-MeOH	
3-Methylcyclohexanone	3.35	0.92	3.55
4-Methylcyclohexanone	0.28	1.63	0.43
4- <i>t</i> -Butylcyclohexanone	0.18	1.08	0.27
3, 3, 5-Trimethylcyclohexanone	2.85	1.50	15.66
Norcamphor	5.25	0.02	4.00
Camphor	0.32	—	0.41
Nature of stereochemistry or mechanism	product stability control	steric factors control	

It is considered that cyclic ketone is a good substrate model to investigate the nature of hydrogenation selectivity of 5-keto-D-gluconate. Because, the quantitative analysis of the two isomers produced is simple, and moreover the substrate possesses a proper bulkiness to see the insight of its adsorbed state. Thus, the use of 2-hydroxycyclohexanone as the substrate was thought to be advantageous to elucidate the mechanism of the selective hydrogenation. In the present paper the results of the selective hydrogenation of 2-hydroxycyclohexanone on various transition metal catalyst are reported.

EXPERIMENTAL

Materials: 2-Hydroxycyclohexanone of guarantee grade, supplied by K & K Laboratoris Inc., was employed as the substrate. Commercial hydrogen was used without special purification. Commercially available metal catalysts were investigated. These were Raney nickel (Kawaken Fin Chemical Co.), and 5% ruthenium, rhodium, platinum, palladium supported on an activated carbon (Japan Engelhard).

Reaction Procedure: The following general procedure was used⁵⁾. A 500 mg of 2-hydroxycyclohexanone and catalyst 100–500 mg in water 25 ml was stirred with an atmospheric pressure of hydrogen at an ordinary temperature. After the reaction was over the catalyst was filtered off and the mixture was analysed by gas chromatography.

Analytical Procedure: Shimadzu GC-5A gas chromatograph equipped with flame ionization detector was used. The products were analysed on a 2 m long glass column with 10% polyethylene glycol adipate on Chromsorb P column at 140° through nitrogen carrier gas. Identified by authentic samples⁶⁾, the retention time for *cis* and *trans*-cyclohexane-1,2-diol are 22 and 25 min. respectively.

RESULTS AND DISCUSSION

In the catalytic hydrogenation of 2-hydroxycyclohexanone, most of the products were *cis*- and *trans*-cyclohexane-1,2-diol. However, trace amount of decomposed product was present

in the products especially when platinum or ruthenium was used as the catalyst. The concentration ratio of the two diols was constant on a given catalyst and independent of contact time. Thus, it is assumed that no isomerization takes place during the hydrogenation reaction of 2-hydroxycyclohexanone.

The *cis*- product was about two times more abundant than the *trans*- product when ruthenium or Raney nickel catalyst was used as the catalyst. The *cis*- product was a little more than a half of the *trans*-product when hydrogenated on platinum, or palladium catalyst or reduced with sodium borohydride. And, using rhodium catalyst, nearly equal amounts of these two products were obtained (Table 3).

Table 3. Hydrogenation Selectivities Catalysed by Transition Metals of Group VIII.

Catalyst or reducing agents	<i>cis/trans</i>	
5% Ru-C	2.6	strongly adsorbed substrate
Raney Ni	2.0	
5% Rh-C	1.2	
5% Pd-C	0.70	weakly adsorbed substrate
NaBH ₄	0.68	
5% Pt-C	0.65	

2-Hydroxycyclohexanone in an aqueous solution may be considered to exist as the monomeric keto structure by inspection of IR, UV and NMR spectra⁹. On the other hand, Sheehan, O'Neill and White¹⁰, assuming a dimeric nature of the ketone, undertook hydrogenation study of 2-hydroxycyclohexanone on metals. However, they failed to substantiate this assumption. Further more, the monomeric 2-hydroxycyclohexanone may exist as a tautomeric mixture of keto and enol forms. Takagi, Teratani and Tanaka¹¹ studied the deuteration of cyclohexanone over transition metal catalysts, and favored therefrom the ketonic rather than the enolic type as the reactive state at the surface. The hydroxyl group of ketonic 2-hydroxycyclohexanone can either be equatorial or axial. The evidence from IR spectra of Joris and Schleiter¹² indicates that the optimum geometry for hydrogen bonding in α -hydroxy ketones is OH and C=O groups lying in the same plane. Hence it appears that the catalytic hydrogenation may occur predominantly from the monomeric ketone having an equatorial OH group (Fig. 2).

The plausible reaction course of the hydrogenation is shown in the scheme 1 on the basis of the Horiuti-Polanyi mechanism¹³. In this scheme, the substrate is adsorbed on the catalyst in such ways that the *cis*- and the *trans*- adsorbed species may respectively be present. The first hydrogen atom transfer from the catalyst to the adsorbed substrate takes place to form half-hydrogenated species, and the second hydrogen atom transfer to the half-hydrogenated states may yield epimeric products.

When 2-hydroxycyclohexanone is strongly adsorbed *via* oxygen atom interactions with the

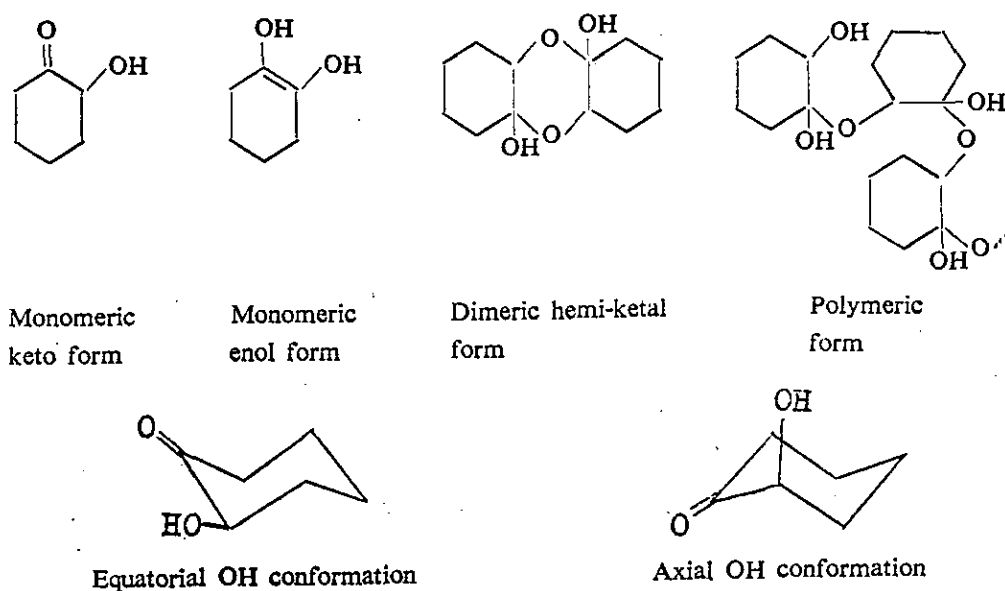
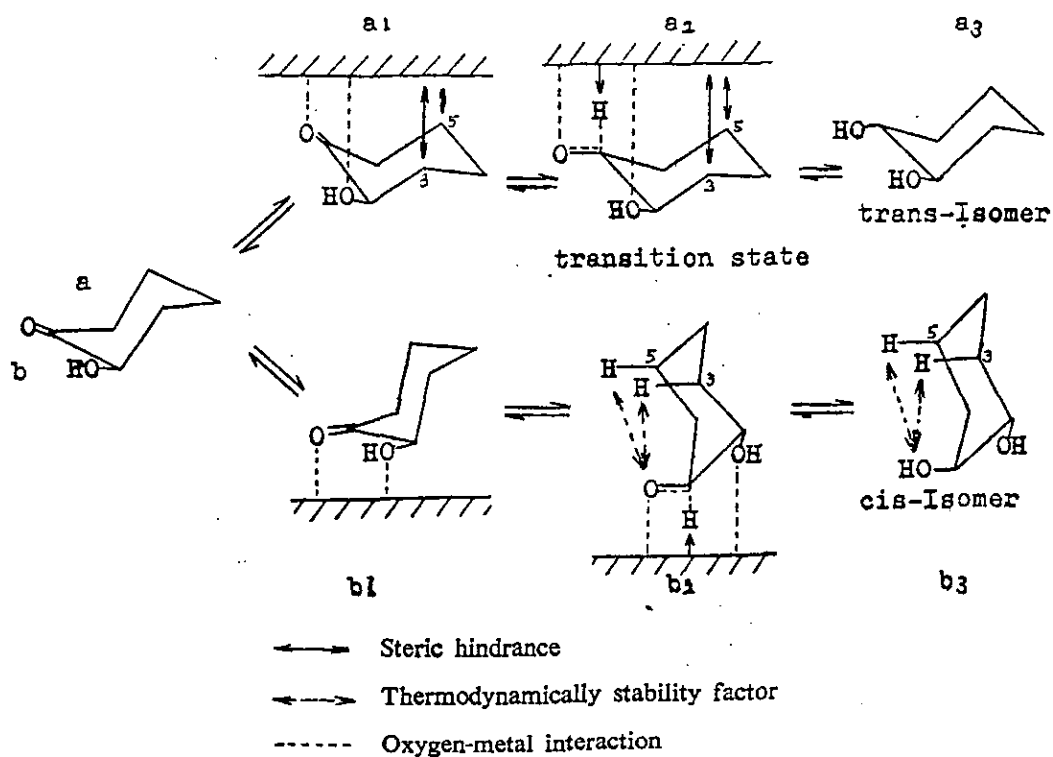


Fig. 2. Structures and Conformational Isomers of 2-Hydroxycyclohexanone

catalyst surface, such as in the case of ruthenium or nickel catalysts, it is expected that the hindrance between the catalyst surface and the axial-hydrogen atoms on C₃ and C₅ of reactant (Shown in a₁ and a₂) may play an important role in determining the stereochemistry of the reaction. Since two types of adsorptions, weak and strong, were assumed, the thermodynamically unstable *cis*- isomer may be formed predominantly for the strongly adsorbed substrate.

Scheme 1. The Course of the Hydrogenation of 2-Hydroxycyclohexanone



Having di-equatorial-OH *trans*-cyclohexane-1,2-diol is thermodynamically more stable than the *cis*-isomer with one equatorial and one axis-OH¹²). Because there are repulsive forces between the axial-OH and the hydrogen atoms on C₃ and C₆ (shown in b₁ and b₂) which are not present when the -OH is equatorial. Therefore, in the hydrogenation of weakly adsorbed substrate such as in the case of palladium or platinum catalyst, the transfer of the first hydrogen to the substrate is considered to control the product composition. The *trans*-isomer may be the major product because the reactant molecular geometry in the transition state of this reaction step is assumed to reflect the stability of reaction product. The reduction of 2-hydroxycyclohexanone by sodium borohydride, the thermodynamically stable *trans*-isomers were selectively formed in accordance with the above consideration.

In the case of rhodium catalyst, the strength of oxygen affinity with catalyst is considered between nickel and platinum. Since, the selectivity of the products was controlled by both adsorption hindrance and product stability, *cis*- and *trans*- isomers were produced nearly in the same proportion.

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