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Stereoselectivity in the Hydrogenation of 4-*t*-Butylcyclohexanone with Catalytically-Active Powder Electrodes

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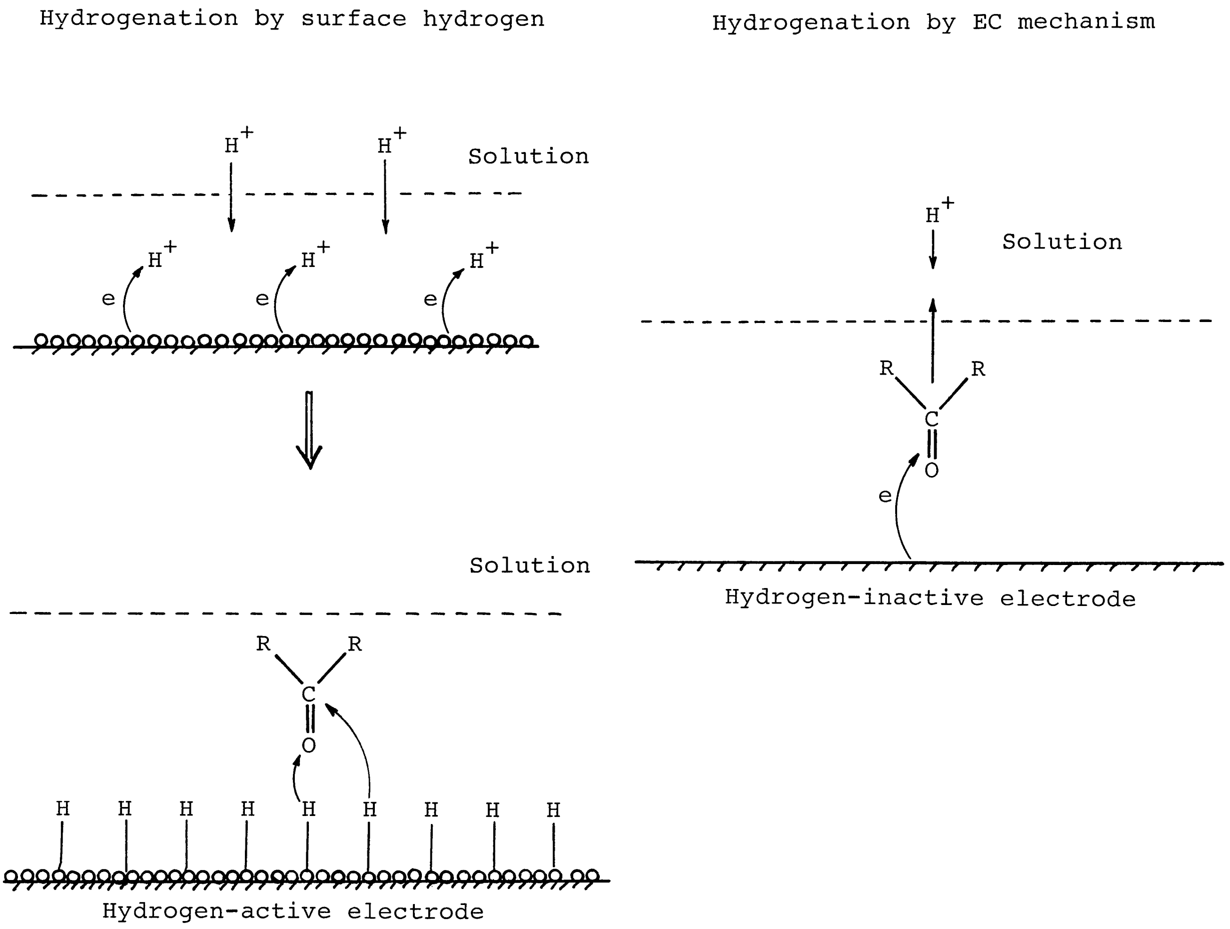
The electrocatalytic hydrogenation of the title compound was examined over Raney Ni, Raney Co, Pt-carbon and Pd-carbon as hydrogen-active powder electrodes. A high conversion of ketone to alcohol was observed on the Raney catalysts when the pK_a values of the proton sources employed were around 5. The metal-on-carbon catalysts showed a relatively low conversion of ketone regardless of the proton sources. The stereochemistry of the reaction was examined.

Since Raney Ni has been known as a useful hydrogenation catalyst, its electronic properties have also allowed its use as cathodic material.[1,2] Osa et al.[3] pointed out that hydrogenation with catalytically-active powder electrodes of group VIII transition metal had several intrinsic advantage over direct, uncatalyzed electroreductions. This reaction involved the chemisorption of atomic hydrogen from the solvent on the electrodes in the first step (Fig. 1a). The potential of this step was usually much less positive than that required to reduce a functional group via an EC mechanism (Fig. 1b). Also, the electrochemical catalysis produced hydrogen in situ and avoided the need to introduce hydrogen from an external source. The reaction could be controlled by changing the electric potential and the current. In other words, the electrocatalytic hydro-



(a) (b)

Fig. 1. Schematic representation of hydrogenation of carbonyl compounds.

Table 1. Electrocatalytic Hydrogenation of 4-*t*-Butylcyclohexanone

Catalyst proton source	pK_a	Raney Ni Yield %	Raney Ni Isomer ratio (cis%)	Raney Co Yield %	Raney Co Isomer ratio (cis%)	Pt-carbon Yield %	Pt-carbon Isomer ratio (cis%)	Pd-carbon Yield %	Pd-carbon Isomer ratio (cis%)
CCl_3COOH	0.64	5	16	5	23	—	—	—	—
$Cl_2CHCOOH$	1.26	5	22	5	19	—	—	—	—
$ClCH_2COOH$	2.86	5	22	5	19	27	21	19	23
CH_3COOH	4.76	25	45	15	19	27	23	20	22
$(CH_3)_2CHCOOH$	4.85	68	72	78	69	25	19	18	26
CH_3CH_2COOH	4.87	42	68	66	67	23	26	21	24
$(CH_3)_3CCOOH$	5.03	59	76	59	76	—	—	—	—
C_6H_5OH	9.99	20	52	24	72	35	22	21	23
H_2O	14.0	22	35	5	35	25	22	18	23
$(CH_3)_3COH$		8	35	5	37	14	22	15	16
$(CH_3)_2CHOH$		10	40	7	33	16	22	21	22
C_2H_5OH		6	32	6	16	—	—	—	—
CH_3OH		8	30	6	18	—	—	—	—

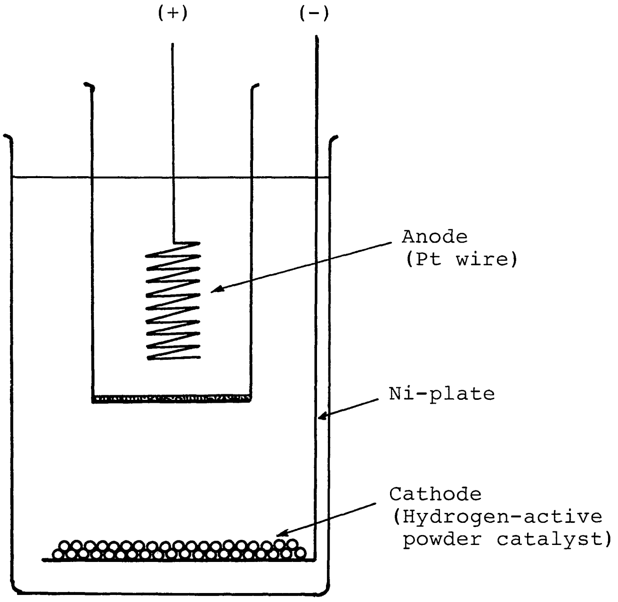


Fig. 2. Electrolysis cell.

genation on hydrogen-active powder electrodes is situated in boundaries between uncatalyzed electroreduction via an EC mechanism and ordinary catalytic hydrogenation. A number of mechanistic studies over group VIII transition metal catalysts are also found in the literature.[4)]

To the best of our knowledge, there has been no study on the stereoselective hydrogenation with active powder electrodes. 4-*t*-Butylcyclohexanone (**1**) was selected as the substrate and the stereochemistry of hydrogenation with an electrocatalytic electrode which consisted of Raney Ni, Raney Co, Pt-carbon or Pd-carbon was examined. The hydrogen adsorbed on the Raney catalyst surface was removed by treating with pentene. The electrolysis was carried out in a divided cell with the catalyst cathode and a Pt wire or graphite rod anode (Fig. 2). Table 1 tabulates the results of the electrocatalytic hydrogenation with various types of proton sources after the passage of 5×96500 C mol^{-1} of electrical charge.

Table 2. Effect of the Amount of the Catalyst on the Electrocatalytic Hydrogenation of 4-*t*-Butylcyclohexanone

Catalyst	Weight g	Yield %	Isomer ratio (cis%)
Raney Ni	1.0	68	72
	1.5	73	74
	2.0	78	70
Pt-carbon	0.02	15	19
	0.04	24	24
	0.06	23	22

The conversion of **1** to 4-*t*-butylcyclohexanol over Raney catalysts depended on the pK_a values of the proton sources. The highest conversion was 78% in a proton source with a pK_a value at around 5 under the reaction conditions employed. Decreasing or increasing the pK_a values of the proton sources reduced the conversion. The conversion was only 5% and 20%, respectively, over the Raney Ni catalyst, when chloroacetic acid and phenol were used as a proton source. When metal-on-carbon catalysts were used, the conversion of ketone to alcohol was relatively low, but no appreciable change in the conversion was observed depending on the pK_a values of the proton sources. Increasing the amount of catalyst resulted in an increase in the conversion (Table 2). In the absence of a metal catalyst, the cathodic reduction with pivalic acid as a proton source proceeded very slowly. The conversion was only 4% and the amount of *cis* alcohol was 44%.

In the ordinary catalytic hydrogenation in which sufficient hydrogen is supplied, 77 and 69% *cis* alcohol was obtained over the Raney Ni and Co catalysts, respectively, while 80% and 85% *trans* alcohol was obtained over the Pt-carbon and Pd-carbon catalysts (Table 3). In the electrocatalytic hydrogenation, the *cis*

Table 3. Comparison of the Isomeric Product Ratio between Ordinary Catalytic and Electrocatalytic Hydrogenation of 4-*t*-Butylcyclohexanone

Catalyst	Product ratio (cis%)		
	Catalytic	Electrocatalytic proton source	
		$(CH_3)_2CHCOOH$	$(CH_3)_3COH$
Raney Ni	77	72	35
Raney Co	69	69	37
Pt-carbon	20	19	22
Pd-carbon	15	26	16

alcohol was predominantly obtained at a high conversion rate over Raney catalysts (similar to ordinary catalytic hydrogenation), but the *trans* alcohol became predominant at a low conversion rate (Table 1). On the other hand, the *trans* alcohol was predominantly obtained (similar to the case of ordinary catalytic hydrogenation), and the isomeric product distribution was independent of the pK_a values of the proton sources when the carbon-supported catalysts were employed. Cathodic reduction without the electrocatalyst gave more of the *trans* alcohol than the *cis*.

The stereochemistry of the ordinary catalytic hydrogenation was interpreted in terms of the Horiuti–Polanyi mechanism which is one of the most satisfactory theories.5) The change in the product-controlling step, depending on the catalysts, coincides with a change in the ratio of the products. The Horiuti–Polanyi formulation of the mechanism of hydrogenation of unsaturated bonds may be represented by four elementary reactions; dissociation of hydrogen, adsorption of the substrate on the catalyst, first hydrogen transfer to the adsorbed species and second hydrogen transfer to the half-hydrogenated intermediate. The proportion of the stereoisomeric products will depend upon which of the elementary reactions is a product-controlling step, because the geometry and/or composition of the several possible transition states differ from one another. When the product-controlling step is the adsorption of the substrate on the catalyst or the first hydrogen transfer from the catalyst to the adsorbed species, the stereochemistry of the reaction is controlled by the interaction between the substrate and the catalyst. On the other hand, when the product-controlling step is the second hydrogen transfer from the catalyst to the half-hydrogenated species, the stereochemistry of hydrogenation is controlled by the relative stabilities of the two epimeric half-hydrogenated species.

When the pK_a value of the proton source employed in a system was more than 5, the conversion of ketone to alcohol decreased over the Raney catalyst. Since the electron transfer to protons on the cathode is more difficult in a proton source with a higher pK_a value, an insufficient supply of active hydrogen results in a decrease in the amount of hydrogen available on the catalyst surface. This permits equilibration between the *cis* and the *trans* half-hydrogenated intermediates, thus resulting in a decrease of *cis* stereoselectivity of the reaction and the *trans* alcohol becomes predominant.

When the pK_a value of the proton source was less than 5, the conversion of ketone was also small the *trans* alcohol was preferably obtained over a Raney catalyst. The surface of the Raney catalyst is damaged in acidic conditions so that metal ions are gradually eluted from the surface and the catalyst surface poisoned by those ions. This results in a low conversion and the predominant formation of the *trans* alcohol. The optimum pK_a value of the electrocatalytic hydrogenation over a Raney catalyst is around 5. On the other hand, no poisoning under acidic conditions was observed over the metal carbon catalysts and the conversion and the isomer ratio were relatively constant under all reaction conditions employed here.

The effect of current density on the conversion of ketone to alcohol and the stereochemistry was also examined (Table 4). A change in current density had no appreciable effect on the conversion and the isomeric product distribution in the hydrogenation over Raney Ni catalyst when isobutyric acid was used as the proton source. On the other hand, the conversion was improved at a lower current density when *t*-butyl alcohol was used as the proton source. In the hydrogenation over Pt-carbon, a decrease in the current density increased the conversion of ketone to alcohol. These results indicated that a part of the produced active hydrogen by electrochemical reductrion was not used in hydrogenation but was lost as molecular hydrogen to the

Table 4. Effect of the Current Density on the Electrocatalytic Hydrogenation of 4-*t*-Butylcyclohexanone

Catalyst	Proton source	Current density	Yield	Isomer ratio
		mA cm^{-2}	%	(cis%)
Raney Ni	$(CH_3)_2CHCOOH$	26.8	62	59
		13.4	68	72
		0.67	85	60
		0.40	73	58
	$(CH_3)_3COH$	13.4	8	35
		0.67	30	31
Pt-carbon	$(CH_3)_2CHCOOH$	13.4	15	19
		0.67	33	26
		0.40	36	26

Table 5. Comparison of Pt-Wire and Graphite-Rod Anodes in the Electrocatalytic Hydrogenation of 4-*t*-Butylcyclohexanone

Anode	Pt-wire				Graphite-rod			
Catalyst	Raney Ni		Raney Co		Raney Ni		Raney Co	
Proton source	Yield %	Isomer ratio (cis%)	Yield %	Isomer ratio (cis%)	Yield %	Isomer ratio (cis%)	Yield %	Isomer ratio (cis%)
CH_3COOH	15	45	15	19	32	37	41	35
$(CH_3)_2CHCOOH$	68	72	78	69	61	60	86	60
C_6H_5OH	20	52	24	72	46	47	32	44
$(CH_3)_2CHOH$	10	40	7	33	31	36	18	22

outside of the system at a relatively high current density, while the generation of active hydrogen is moderate and is efficiently used for the hydrogenation at a low current density.

When a graphite electrode was used as the anode, no appreciable change in the results of hydrogenation was observed (Table 5).

Experimental

Electrocatalytic Hydrogenation. Metal-on-carbon catalysts were commercially available. Raney catalysts which were prepared from metal-alloy were treated with pentene to remove the hydrogen adsorbed on the catalyst surface. The electrochemical cell was a conventional divided cell with a metal catalyst cathode and a platinum coil (surface area 7.48 cm^2) or graphite rod (surface area 9.86 cm^2) anode. For making contact with the metal catalyst powder, a nickel plate electrode (surface area 12.56 cm^2) was first placed on the bottom of the flask on which a known amount of metal catalyst powder was then stacked in the presence of an electrolyte solution. The electrolyte solution consisted of 50 cm^3 of a 10% tetrahydrofuran:H_2O (9:1 volume ratio) solution containing 163 mmol of $NaClO_4$, 3.1 mmol of 4-*t*-butylcyclohexanone (**1**), and 25.0 mmol of a proton source. The electrolysis was carried out at room temperature. After the passage of 5×96500 C mol^{-1} of electrical charge, the catholyte was filtered off from the catalyst and extracted three times with ether, washed with saturated NaCl solution and analyzed by gas chromatography.

Gas Chromatographic Analysis. Analyses were performed with a Simadzu GC-8A with a glass capillary column CPB20 (0.2 mm×25 m) at 120 °C. The products were compared with the authentic sample which was prepared by the LAH reduction of **1**.

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