2584 © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***56***, *2584—2588 (1983)* [Vol. 56, No. 9

Stereochemical Studies of the Electrolytic Reactions of Organic Compounds. Part 18. Comparative Study of Hydrogenation on Metal-black Cathodes and Catalysts

Tsutomu Nonaka,* Masahiko Takahashi, and Toshio Fuchigami
Department of Electronic Chemistry, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama, 227

(Received March 10, 1983)

Stereoselective hydrogenation on metal-black cathodes and catalysts, which were prepared by electrodeposition under the same conditions, was comparatively investigated. Stereoisomeric ratios of alcohols formed from the ketones on the Pd- and Pt-black cathodes seemed to be almost equal to those on the corresponding metal-black catalysts, while the yields were quite different between the cathodic and catalytic hydrogenations. On the other hand, results of the hydrogenation of the acetylenes on the cathodes were also different, in not only the yield but also the isomeric ratio, from those on the catalysts. In addition to stereoselectivity, relative hydrogenation rates between *cis*- and *trans*-olefins were compared in both the cathodic and catalytic hydrogenations. It was also found that a mercury pool cathode gave quite different stereochemical results in the hydrogenation of the unsaturated compounds from those obtained with either the metal-black cathodes or the catalysts.

A variety of studies on stereoselective and stereospecific hydrogenations of unsaturated compounds on metal catalysts has been extensively reported, while such studies using catalytically-active metal cathodes have been more rarely reported. Campbell[1)] and Sakuma[2)] reported that some acetylenic compounds could be hydrogenated on spongy nickel and Pd-black cathodes, respectively, to give the corresponding *cis*-olefins as major products. Kita *et al.*[3)] have recently indicated the ratio of *cis*-2-butene to *trans*-2-butene formed as minor products in the cathodic hydrogenation of 1,3-butadiene on a Pt-black cathode. However, these results were not compared with the hydrogenation on catalysts consisting of the same metal components and/or might be incomplete in isomeric analysis of the products. In this work, the hydrogenation of unsaturated compounds to the corresponding stereoisomeric product mixtures on metal-black cathodes and catalysts was comparatively investigated. In addition to this, results obtained were compared with those of the reductive hydrogenation on a mercury cathode which induces a typical cathodic reaction by direct electron-transfer between the cathode and substrates.

In an earlier work,[4)] we supposed that the hydrogenation of nitriles on a Pd-black cathode may resemble that on Pd-black catalysts in view of substituent effect. Moreover, it may be consentient that the cathodic hydrogenation on the active metal cathodes resembles the catalytic hydrogenation in gross natures, since the general course of the cathodic hydrogenation is seemed to be very similar to that of the catalytic hydrogenation, as illustrated in Fig. 1. However, it should be difficult to exclude completely that there may be some differences between the both hydrogenations, because of few comparative studies reported. In this viewpoint, it is interesting to compare the cathodic hydrogenation with the catalytic hydrogenation on the same metal: If the both hydrogenations give the same result, the cathodic hydrogenation may be able to be an excellent method, instead of catalytic one in some cases, without any gaseous hydrogen sources, air-tight reactors and efficient stirring equipments, while it can be used as a characteristic method in a case where the both give otherwise results. In addition, comparative studies of the both hydrogenations may result in some new informations available for a mechanistic discussion on the hydrogenations.

A metal catalyst surface is electrically neutral or slightly positive.[5)] On the catalyst surface, hydrogen molecules dissociate and the resulting atomic hydrogen adsorbs. An unsaturated compound molecule contacts with the catalyst surface and its π-electron is donated to the unoccupied d-band of the catalyst to form a π-adsorption state. This is an oxidized state rather than reduced one. An active adsorbing species, which is a π-complex-adsorption or σ-adsorption state, is formed by the back-donation of an electron from the catalyst, and the hydrogenation is completed *via* a partially hydrogenated state resulted by the attack of the adsorbing atomic hydrogen and the consequent fission of a bond between the catalyst and the substrate. In Fig. 1, the general course of the hydrogenation on metal catalysts and also cathodes is illustrated.[5)]

In the case of hydrogenation on catalytic cathodes, hydrogen is formed by the discharge of protons on the cathode surface. Since the cathode surface should be more negative than the catalyst surface, some differences between the cathodic and catalytic hydrogenations on the same kind of metal may be found.

In a previous work,[6)] it was found that the stereoisomeric ratio cis/trans of 4-*t*-butylcyclohexanol formed in the cathodic and catalytic hydrogenation of 4-*t*-butylcyclohexanone on Pt-black in a strongly acidic solution was greatly affected by the preparative method of Pt-black: The ratio cis/trans varied in the ranges of 0.9—4.3 and 0.9—2.7 in the cathodic and catalytic hydrogenation, respectively.

In this work, similar stereochemical comparison was made under a variety of reaction conditions, extending the substrate compounds to an open-chain ketone and also acetylenic and olefinic compounds. For a successful investigation, following situations should be required: (a) The cathode and the catalyst prepared

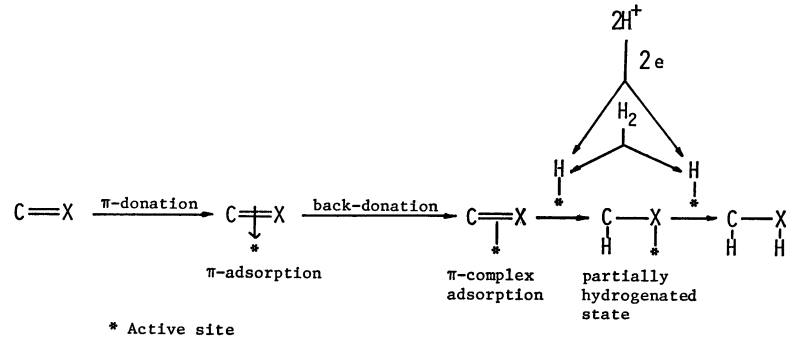

Fig. 1. General course of hydrogenation of unsaturated bond on active metal cathode and catalyst.

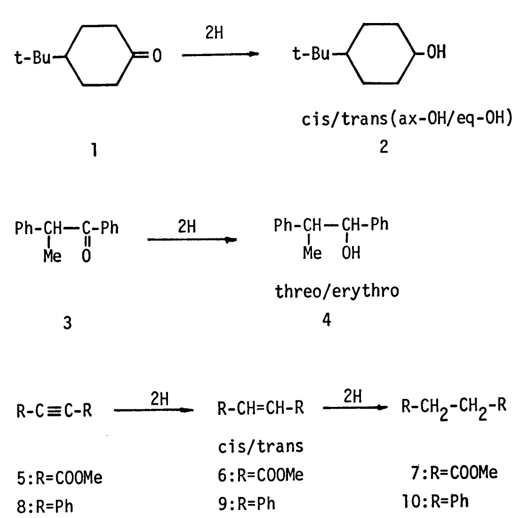

Fig. 2. Hydrogenation of unsaturated compounds.

Table 1. Hydrogenation of 4-*t*-butylcyclohexanone (**1**) on Pt- and Pd-black cathodes and catalysts

Cathode or catalyst	Solution	4-*t*-Butylcyclohexanol (**2**)			
		Cathodic		Catalytic	
		Yield/%	cis/trans	Yield/%	cis/trans
Pt-black	A[a]	46 63[d]	0.9 1.1	48	0.9
Pt-black	WA[b]	3	0.2	16	0.2
Pt-black	B[c]	5	1.0	100	1.0
Pd-black	A[a]	30	0.1	0	—
Pd-black	B[c]	0	—	0	—
Hg-pool	A[a]	30	0.2	—	—
Hg-pool	B[c]	16	0.4	—	—

a) Strongly acidic. b) Weakly acidic. c) Strongly basic. d) Electrolyzed at 2.0 A dm^{-2} (at 0.5 A dm^{-2} unless stated otherwise).

from the same kind of metal by the same method can be used. (b) The same type of reaction of the same substrate compound can occur on the cathode and the catalyst prepared thus. (c) The cathodic and catalytic reactions can proceed under the same conditions to give detectable stereochemical results. Items (a) and (b) could be almost completely satisfied, while it seemed to be difficult to give the strictly same reaction conditions(Item (c)) for the cathodic and catalytic hydrogenation because of no catalytic reaction factors corresponding to current density and amount of charge passed in the electrolytic reaction.

Results and Discussion

In this work, the hydrogenation of ketones(*t*-butylcyclohexanone (**1**) and 1,2-diphenyl-1-propanone (**3**)), acetylenes (dimethyl acetylenedicarboxylate (**5**) and diphenylacetylene (**8**)) and olefins (dimethyl maleate (cis-**6**), dimethyl fumarate (*trans*-**6**), *cis*-stilbene (*cis*-**9**), and *trans*-stilbene (*trans*-**9**)) on metal (Pt and/or Pd)-black cathodes and catalysts were comparatively investigated under the same reaction conditions. Results on a mercury cathode were also given for comparison with the above hydrogenation.

Metal-black Cathodes and Catalysts. Generally, hydrogenation is greatly affected by the preparative procedure of catalysts. Therefore, in comparative studies of cathodic and catalytic hydrogenation on metal-blacks, the preparative procedure should be strictly controlled. Pt-black electrodeposited on Pt-plates from a chloroplatinic acid solution containing a small amount of lead(II) acetate was used in this work, because Pt-black prepared thus gave more reproducible results in both the cathodic and catalytic hydrogenations than others.[6] Pd-black was also electrodeposited on Pd-plates from a palladium chloride solution without lead(II) acetate.

One of the metal-black plates prepared at the same time, under the same conditions and by the same procedure was used as a cathode in an electrolytic cell, and another one was placed in a margen-flask for catalytic hydrogenation.

Stereoselective Hydrogenation of Ketones. As shown in Table 1, 4-*t*-butylcyclohexanone (**1**) was hydrogenated on both Pt-black cathode and catalyst in a wide pH range to give 4-*t*-butylcyclohexanol (**2**). Although the isomeric ratio of **2** formed in the cathodic hydrogenation was slightly influenced by current density, the ratio seemed almost equal to that in the catalytic hydrogenation.

On the other hand, **1** could not be hydrogenated on the Pd-black catalyst in both strongly acidic(A-solution) and basic(B-solution) media. In contrast, **1** could be hydrogenated on the Pd-black cathode in the A-solution to give **2** in 30% yield. This result may suggest that an oxygen-Pd bonding(Fig. 1) on the cathode in a partially hydrogenated state is weakened by its negative polarization and consequently that the hydrogenation can proceed more easily.

The hydrogenation of methylcyclohexanones on the Pd-black cathode in the A-solution hardly proceeded to result in only 1—2% yields. Comparison of this fact with the result obtained in the hydrogenation of **1** suggests that steric hindrance between the cathode surface and the *t*-butyl group weakens the oxygen-Pd bonding in the partially hydrogenated state and promotes the progress of the hydrogenation to the final state.

In the B- and weakly acidic (WA) solutions, the isomeric ratios of **2** formed on the Pt-black cathode were equal to those on the Pt-black catalyst, as described above, but the yields were extremely lower. The cathode should be more negetively polarized in the B- and WA-solutions than the A-solution. Therefore, the lower yields may be due to such a more negative polarization of the Pt-black cathode.

As a conclusion, the yield of **2** is influenced by the polarization of cathode and catalyst, while the isomeric ratio is not. More exactly describing, the negative polarization of the Pt-black suppresses the adsorption of substrate on it and decreases the yield, while on the Pd-black the polarization assists to cleave the oxygen-Pd bonding in the partially hydrogenated state and increases the yield. Such a difference between the Pt- and Pd-blacks may be caused by the stronger adsorption[7] and bonding[8] in the latter.

A mercury-pool cathode, which is a typical high hydrogen overvoltage one, resulted in the isomeric ratio smaller than the thermodynamic equilibrium value(0.25[9]) in the A-solution, while larger in the B-solution. Different stereochemical results between the metal-black and mercury-pool cathodes should be due to different reaction mechanism between the both cathodes.

At the next stage of the investigation, the stereoselective hydrogenation of open-chain ketones was attempted: Among 1,2-diphenyl-1-propanone (**3**), 3-phenyl-2-butanone, and 4-phenyl-2-pentanone, only **3** could be hydrogenated on either the Pd-black cathode or catalyst, and others could not.

Table 2. Hydrogenation of 1,2-diphenyl-1-propanone (**3**) on Pt- and Pd-black cathodes and catalysts

Cathode or catalyst	Solution	1,2-Diphenyl-1-propanol (**4**) Cathodic Yield/%	threo/erythro	Catalytic Yield/%	threo/erythro
Pt-black	A[a]	72	0.0	27	0.0
Pt-black	WA[b]	100	0.1	30	0.0
Pt-black	B[c]	11	0.0	14	0.0
Pd-black	A[a]	72 19[d]	0.5 0.45	23	0.5
Pd-black	WA[b]	78	1.0	100	0.6
Pd-black	B[c]	0	—	0	—
Hg-pool	A[a]	11	0.5	—	—
Hg-pool	WA[b]	94	0.4	—	—
Hg-pool	B[c]	98	0.3	—	—

a) Strongly acidic. b) Weakly acidic. c) Strongly basic. d) Electrolyzed at 2.0 A dm^{-2} (at 0.5 A dm^{-2} unless stated otherwise).

As shown in Table 2, **3** could be hydrogenated on Pt- and Pd-black cathodes and catalysts to give 1,2-diphenyl-1-propanol (**4**) in good yields. The isomeric ratio threo/erythro of **4** formed in the cathodic hydrogenation seemed almost equal to that in the catalytic hydrogenation, except for the result obtained on the Pd-black in the WA-solution. It seems difficult to rationalize this exceptional result. An Hg-cathode gave some different isomeric ratios from those on the metal-black cathodes.

Stereoselective Hydrogenation of Acetylenes. Dimethyl acetylenedicarboxylate (**5**) was hydrogenated on the Pd-black cathode and catalyst to give the corresponding olefin(dimethyl maleate; *cis*-**6** and fumarate; *trans*-**6**), as shown in Table 3. In this hydrogenation, a part of **6** formed seemed to be hydrogeanated further to dimethyl succinate (**7**). Therefore, in order to discuss strictly stereochemical results obtained, some correction should be made for the estimation of isomeric ratio cis/trans of **6**. For the correction, the relative hydrogenation rate ratio k_c/k_t of *cis*-**6** to *trans*-**6** was used. The detailed description of k_c/k_t is given in the following item.

Both the uncorrected and corrected isomeric ratios of **6** obtained in the cathodic hydrogenation were smaller than those in the catalytic hydrogenation in

Table 3. Hydrogenation of dimethyl acetylenedicarboxylate (**5**) on Pd-black cathode[a] and catalyst

Cathode or catalyst	Solution	Dimethyl 2-butenedioate (**6**) Cathodic Yield/%	cis/trans[b]	Catalytic Yield/%	cis/trans[b]	Dimethyl succinate (**7**) Catalytic yield/%	Catalytic yield/%
Pd-black	A[c]	13	12(1.4)	40	32(3.9)	35	21
Pd-black	WA[d]	10	12(1.2)	12	19(1.7)	40	29
Pd-black	B[e]	Trace	–(0.9)	3	∞(1.1)	13	9
Hg-pool	A[c]	32	0.0	—	—	30	—
Hg-pool	B[e]	27	0.0	—	—	Trace	—

a) Electrolyzed at 0.5 A dm^{-2}. b) Figures in parentheses show the corrected values. c) Strongly acidic. d) Weakly acidic. e) Strongly basic.

Table 4. HYDROGENATION OF 1,2-DIPHENYLACETYLENE (**8**) ON Pd- AND Pt-BLACK CATHODS[a] AND CATALYSTS

Cathod or catalyst	Solution	Stilbene (**9**) Cathodic Yield/%	Stilbene (**9**) Cathodic cis/trans[b]	Stilbene (**9**) Catalytic Yield/%	Stilbene (**9**) Catalytic cis/trans[b]	1,2-Diphenylethane (**10**) Cathodic yield/%	1,2-Diphenylethane (**10**) Catalytic yield/%
Pd-black	A[c]	68	46(6.1)	77	24(6.4)	20	10
Pd-black	B[d]	60	7(4.8)	82	7(5.8)	9	7
Pt-black	A[c]	27	9	36	7	32	30
Pt-black	B[d]	82	16	20	4	2	Trace
Hg-pool	A[c]	1	0.6	—	—	Trace	—
Hg-pool	B[d]	8	0.2	—	—	Trace	—

a) Electrolyzed at 0.5 A dm^{-2}. b) Figures in parentheses show the corrected values. c) Strongly acidic. d) Strongly basic.

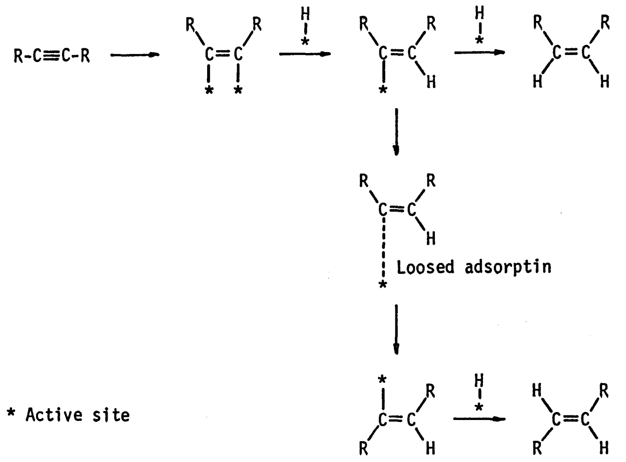

Fig. 3. Stereochemical course of hydrogenation of acetylenes.

the same solution. The cathodic hydrogenation of diphenylacetylene (**8**) on the Pd-black also gave smaller cis/trans ratios of stilbene (**9**) than the catalytic hydrogenation, as shown in Table 4.

Generally, disubstituted acetylenes are hydrogenated on metal catalysts to give the *cis*-olefins, which are thermodynamically less stable than the corresponding *trans*-olefins, in excess.[10] As illustrated in Fig. 3, an acetylene molecule adsorbs in the *cis*-olefin form(sp^2) on the catalyst[11] and hydrogenated *via* the partially hydrogenated state.[12] If the adsorption is loosed by steric hindrance between the adsorbing species and the catalyst, so-called the catalyst hindrance, the formation of the *cis*-olefin is suppressed in some extent.[13] The stronger adsorption reasonably causes the higher catalyst hindrance. Therefore, the more negative polarization of the Pd-black also causes the weaker adsorption and the lower hindrance, and cosequently the supression of the *cis*-olefin formation. This is a rationalization for the smaller cis/trans ratio in the cathodic hydrogenation than the catalytic hydrogenation.

The cis/trans ratio decreased in the B-solution in both the cathodic and catalytic hydrogenations. This may be rationalized as due to weak adsorption in basic solution[14,15] or the isomerization of olefin formed,[16] though the hydrogenation was not carried out under so drastic that the isomerization occurs easily.

It is noticeable that the hydrogenation of **8** on the Pt-black resulted in a reversed situation, comparing with that on the Pd-black, though any corrected isomeric ratios of **9** could not be given. It may be also interesting to note that the Hg-pool cathode afforded the completely reversed isomeric ratios of **9** to the metal-blacks.

Table 5. HYDROGENATION RATE RATIO(k_c/k_t) OF *cis*-OLEFINS TO THE *trans*-OLEFINS ON Pd-BLACK CATHODE[a] AND CATALYST

Olefin	Solution	k_c/k_t[b] Cathodic	k_c/k_t[b] Catalytic
Dimethyl 2-butene-dioate (**6**)	A[c]	0.81	0.87
	WA[d]	0.86	1.01
	B[e]	0.96	1.11
Stilbene (**9**)	A[c]	0.84	0.28
	WA[d]	0.84	0.82
	B[e]	0.99	1.39

a) Electrolyzed at 0.5 A dm^{-2}. b) Equimolar mixtures of *cis*- and *trans*-olefins were incompletely hydrogenated and the ratio k_c/k_t was calculated from amounts of unreacted olefins. c) Strongly acidic. d) Weakly acidic. e) Strongly basic.

Hydrogenation Rate Ratio of cis-*Olefins to the* trans-*Olefins.* Mixtures of *cis*- and *trans*-olefins (**6** and **9**) were hydrogenated with insufficient amounts of electricity and hydrogen on the Pd-black cathode and catalyst, respectively. The hydrogenation rate ratio (k_c/k_t) of the *cis*-olefin to the *trans*-olefin was calculated from amounts of the unreacted olefin isomers, considering their average concentrations during the hydrogenation:

$$k_c/k_t = \frac{(c_1-c_2)}{(t_1-t_2)}\cdot\frac{(t_1+t_2)/2}{(c_1+c_2)/2} = \frac{(c_1-c_2)(t_1+t_2)}{(t_1-t_2)(c_1+c_2)},$$

where c_1 and c_2 are the initial and final concentrations of the *cis*-olefin, and t_1 and t_2 are those of the *trans*-olefin. Table 5 shows k_c/k_t values obtained in the hydrogenation of the equimolar mixtures of the isomers ($c_1=t_1$).

Results for each olefin are apparently clear and interesting, as shown in Table 5. However, it seems difficult to rationalize comprehensively these kinetic data, because (a) the hydrogenation course involves several activation steps,[17] and (b) the rate-determining step can not be specified.[18]

Experimental

Materials. *Ketones*: Cyclic ketones (**1** and three methylcyclohexanones) were commercially supplied from Tokyo Kasei Co., while open-chain ketones (**3**, 3-phenyl-2-butanone and 4-phenyl-2-pentanone) were prepared by methods of our earlier works.[19,20]

Acetylenes and Olefins: All the compounds (**5**, **6**, **8**, and **9**) were commercially supplied.

Standard Samples of Products: The compounds **2**, **6**, **7**, and **10** were commercially supplied, while *threo-* and *erythro-***4** were prepared by the method of earlier work.[19]

Metal-blacks: Pt-black was electrodeposited on a Pt plate (Area, 7.7 cm^2) from 33 ml of an aqueous solution containing chloroplatinic acid (1.0 g as $H_2[PtCl_6]\cdot 6H_2O$) and lead(II) acetate (7 mg) by passing electricity at 2 A$\cdot$dm^{-2} of current density for 10 min. Pd-black was also deposited on a Pd plate (area, 7.7 cm^2) from 33 ml of 1 M (1 M= 1 mol dm^{-3}) HCl containing palladium chloride (0.2 g) by the same procedure as the above. The Pt- and Pd-blacks prepared thus were repeatedly washed with cold water, and then cathodically treated at 2 A dm^{-2} in 1 M H_2SO_4 for 30 min and sulfuric acid was rinsed out with warm water.

Usually, two pieces of the metal-blacks were prepared for the cathodic and catalytic hydrogenations at same time.

Reaction Solutions: Three kinds of solutions were used: A-solution, 1 M H_2SO_4-CH_3OH (1:1, v/v); WA-solution, 3 M AcONa-3 M AcOH-CH_3OH (1:1:2, v/v); B-solution, 2 M NaOH-CH_3OH (1:1, v/v). 100 ml of the solution containing the substrate in 10—50 mM was used for each experiment.

Hydrogenation. *Cathodic Hydrogenation*: 2 F/mol was passed for each electrolysis at 0.5 A dm^{-2} and room temperature, except for the case of **3** where 20 F/mol was passed.

Catalytic Hydrogenation: The hydrogenation was carried out in a margen-flask, in which the metal-black plate was placed, at atmospheric pressure and room temperature. The concentration of substrate was same as that in the corresponding cathodic hydrogenation. The margen-flask was continuously shaken till 1 mol H_2/1 mol substrate was taken up.

Product Analysis. After the hydrogenation, the reaction solution was neutralized with aqueous sulfuric acid or sodium hydroxide and then extracted repeatedly with ether. The combined ethereal extract was dried over anhydrous sodium sulfate. The solution concentrated by evaporation was subjected to gas-chromatographic analysis under following conditions: A 2.25 m PEG 20 M column at 90 °C for **1**, **2**, and **5**—**7**; a 4 m PEG 20 M column at 200 °C for **8**—**10**; a 4 m Apiezon Grease L column at 200 °C for **3** and **4**.

In the hydrogenation of **1** and **3**, the corresponding alkanes and hydrodimers were also formed as by-products, but these were not analyzed quatitatively.

The authors wish to thank professor Taro Sekine for his helpful suggestions and discussions. This work was partly supported by a Grant-in-Aid for Scientific Research No. 0055320 from the Ministry of Education, Science and Culture.

References

1) K. N. Campbell, *J. Am. Chem. Soc.*, **65**, 965 (1943).

2) M. Sakuma, *J. Electrochem. Soc. Jpn.*, **28**, 164 (1960).

3) H. Kita and N. Kubota, *Electrochim. Acta*, **27**, 861 (1982).

4) Y. Hatta, N. Yui, T. Nonaka, and K. Odo, *Nippon Kagaku Kaishi*, **1974**, 2277.

5) S. Mitsui and M. Imaizumi, *Nippon Kagaku Zasshi*, **77**, 1516 (1956).

6) T. Nonaka, M. Takahashi, and T. Fuchigami, *J. Electrochem. Soc. Jpn.*, **51**, 129 (1983).

7) Since Pd-catalysts are more sensitive to "catalyst hindrance" than Pt-catalysts, the absorption on the Pd-catalysts may be stronger.

8) E. Breitner, E. Roginski, and P. N. Rylander, *J. Org. Chem.*, **24**, 1855 (1959).

9) S. Mitsui, H. Saito, and K. Hebiguchi, The 24th National Meeting of the Chem. Soc. of Jpn., 1967, Abstract III, p. 88.

10) W. Orshnik, G. Karmas, and A. D. Mebane, *J. Am. Chem. Soc.*, **74**, 295 (1952).

11) F. J. McQuillin, W. O. Ord, and P. L. Simpson, *J. Chem. Soc.*, **1963**, 5995.

12) J. Sheridan, *J. Chem. Soc.*, **1945**, 133.

13) W. Surber, *Helv. Chim. Acta*, **39**, 1299 (1956).

14) S. Pietra and C. B. Riolo, *Gazz. Chim. Ital.*, **86**, 1129 (1956); *Chem. Abstr.*, **52**, 269d (1958).

15) F. J. McQuillin and W. O. Ord, *J. Chem. Soc.*, **1959**, 2902.

16) R. Romanet, *Compt. Rend.*, **236**, 1044, 1176, 1677 (1953).

17) S. Siegel, *Adv. Catal.* **16**, 123 (1966).

18) S. Mitsui, "Organic Reaction Mechanism (Yuki Han-no Kiko," ed by M. Imoto, Tokyo Kagaku Dojin, Tokyo (1970), Vol. 13, Part 1, p. 11.

19) T. Nonaka, Y. Kusayanagi, and T. Fuchigami, *Electrochim. Acta*, **25**, 1679 (1980).

20) T. Nonaka and Y. Kusayanagi, *Electrochim. Acta*, **26**, 893 (1981).