Electrocatalytic Reduction Using Raney Nickel

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The Raney nickel catalyst was employed as a catalytic electrode in the electrohydrogenation of various unsaturated compounds, including ketones, aromatic aldehydes, Schiff's bases, oximes, nitriles, aromatic nitro compounds, olefins, and acetylenes. The hydrogen generated electrochemically was adsorbed and activated at the surface of the catalyst; it effectively hydrogenated these compounds, affording products which are very similar to those obtained in a normal catalytic hydrogenation with Raney nickel.

Although the Raney nickel (Ra/Ni) catalyst has been widely used as a catalyst in catalytic hydrogenation in the laboratory and on an industrial scale,[1] its application as a catalyst for electrochemical hydrogenation seems to have attracted very little attention.[2,3] Because of a large surface area and a high hydrogen-adsorption activity, Ra/Ni was expected to be applicable as a catalytic electrode. If the electrolytically generated hydrogen is directly used as a reducing agent at the surface of the catalyst, in the hydrogenation with Ra/Ni, it may be possible to avoid the use of an autoclave and comperessed hydrogen gas. Thus, we have attempted electrohydrogenation using a cathode made of nickel plate covered with Ra/Ni powder, and examined its reduction ability.

Results and Discussion

Preparative electrolyses were carried out in the cell depicted in Fig. 2. Almost all of the substrates were electrolyzed in methanol containing sodium methoxide under a constant current and at room temperature. The amount of the catalyst used was 2 g per 0.1 mol of the substrate.

At first, in preliminary experiments using benzophenone, the following facts were confirmed: a) when the Ra/Ni catalyst is omitted and the nickel plate alone is used as the cathode, the reduction of benzophenone to benzhydrol is extremely slow (the current efficiency is less than 10%); instead hydrogen is evolved; b) when the surface of the nickel plate is covered with the catalyst, the reduction proceeds essentially quantitatively, and c) if no current is passed through and hydrogen gas is bubbled through the catholyte in the presence of the catalyst, only about a 20% yield of benzhydrol is formed by the reaction over a period of 10 h. Apparently, Ra/Ni exerted an excellent electrode-catalytic effect.

Table 1 shows the results of the electrohydrogenation of various compounds.

All the ketones employed were effectively reduced predominantly to give the corresponding secondary alcohols. In these cases, hardly no glycols were detectable.[3] Analogous results were obtained with aromatic aldehydes;[4] however, aliphatic aldehydes could not be used since they formed aldol adducts in this medium.

Carbon-nitrogen unsaturated compounds, such as Schiff's bases,[5] nitriles,[6] and oximes,[7] were reduced equally well to the respective amines. The nonaque-

ous system of methanolic sodium methoxide appeared to be particularly favorable for the reduction of these compounds, which tend to involve C–N bond cleavage in an aqueous solution.[8] Either nitriles or oximes were electrolyzed in the presence of excess amounts of ammonia in order to suppress the formation of undesirable secondary amines.[9]

Under the same conditions, nitrobenzenes afforded anilines as the main products, along with a small amount of hydrodimers,[3,10] whereas aliphatic nitro compounds were not reducible. Probably, this was due to the formation of the anion of the aci-form in the basic solution, which prevented the reduction.[8]

According to this method, not only carbon-carbon conjugated double bonds with a carbonyl group, *etc.*,[11] but also isolated double bonds which are very resistant to conventional electrolytic reduction[12] could readily be hydrogenated. The selective reduction of acetylenes to olefins was not successful, however, since it always was attended by a subsequent reduction to alkanes.

Next, in order to examine the cathodic behavior of Ra/Ni, current-potential relationships were measured in a 0.1 mol dm^{-3} sodium methoxide–methanol solution.
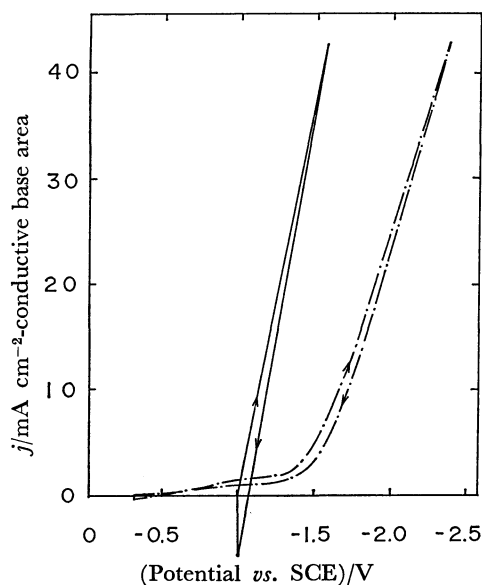

Fig. 1. Current-potential curves for 0.1 M NaOMe–MeOH. ———: at Ra/Ni cathode, ————: at Ni-plate cathode. Sweep rate of 0.1 V/s was used.
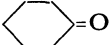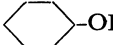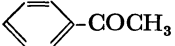
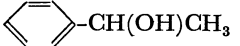TABLE 1. ELECTROHYDROGENATION USING RANEY NICKEL CATALYST[a)]
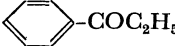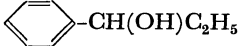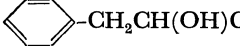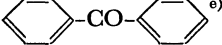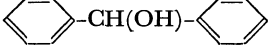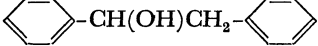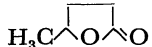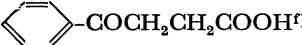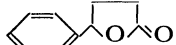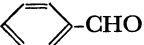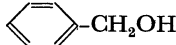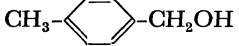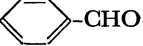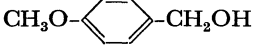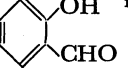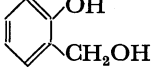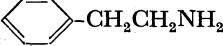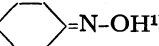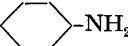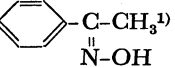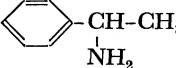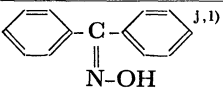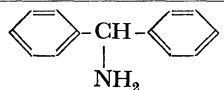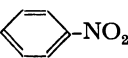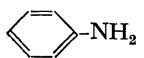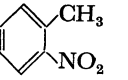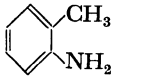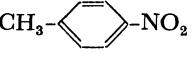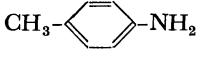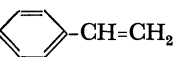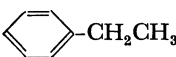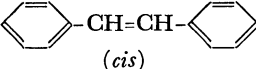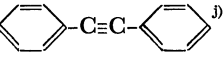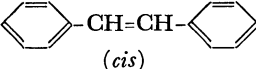
Starting material	Product[b)]	Consumed current F/mol	Isolated yield[c)] %	Isolation method	Bp θ_b/°C(mmHg) or Mp θ_m/°C Obsd[d)]	Ref.
[Ketones: $\rangle C{=}O + 2H^+ + 2e^- \longrightarrow \rangle CH{-}OH$]						
$n\text{-}C_3H_7COC_3H_7$	$n\text{-}C_3H_7CH(OH)C_3H_7$	3.4	71	A	153—154	154[17)]
$n\text{-}C_5H_{11}COCH_3$	$n\text{-}C_5H_{11}CH(OH)CH_3$	3.4	73	A	156—158	158—160[17)]
$i\text{-}C_4H_9COCH_3$	$i\text{-}C_4H_9CH(OH)CH_3$	2.8	75 (80)	A	129—131	130—131 (763)[17)]
⟨ring⟩=O	⟨ring⟩-OH	3.7	70 (97)	A	157—160	161[17)]
⟨ring⟩-COCH₃	⟨ring⟩-CH(OH)CH₃	3.4	82 (97)	A	93—94 (13)	98—99 (20)[17)]
⟨ring⟩-COC₂H₅	⟨ring⟩-CH(OH)C₂H₅	3.7	73	B	97—99 (12)	106—108 (18)[17)]
⟨ring⟩-CH₂COCH₃	⟨ring⟩-CH₂CH(OH)CH₃	3.4	70	B	95—98 (12)	219—221,[17)] 107 (15)[18)]
⟨ring⟩-CO-⟨ring⟩[e)]	⟨ring⟩-CH(OH)-⟨ring⟩	3.6	82 (90)	B	66—68 [MeOH]	69[17)]
⟨ring⟩-COCH₂-⟨ring⟩	⟨ring⟩-CH(OH)CH₂-⟨ring⟩	2.9	71	B	66—68 [Hexane]	67[17)]
[r-Keto acids]						
$CH_3COCH_2CH_2COOH^{f)}$	H₃C⟨O O structure⟩	2.8	73	B[g)]	85—86 (15)	83—84 (13)[17)]
⟨ring⟩-COCH₂CH₂COOH[f)]	⟨O O structure⟩	2.8	80	B	38 [MeOH]	38[17)]
[Aldehydes: $-CHO + 2H^+ + 2e^- \longrightarrow -CH_2OH$]						
⟨ring⟩-CHO	⟨ring⟩-CH₂OH	2.2	70	B[h)]	91—92 (11)	93 (10)[17)]
CH₃-⟨ring⟩-CHO	CH₃-⟨ring⟩-CH₂OH	2.2	76	B[h)]	59—61 [Hexane]	61—62[17)]
CH₃O-⟨ring⟩-CHO	CH₃O-⟨ring⟩-CH₂OH	2.2	71	B[h)]	136—139 (12)	128—130 (8)[17)]
⟨ring-OH⟩ CHO[f)]	⟨ring-OH⟩ CH₂OH	2.2	83	B	80—83 [Benzene]	87[17)], 84[19)]
[Schiff's Bases: $-N{=}CH- + 2H^+ + 2e^- \longrightarrow -NHCH_2-$]						
$n\text{-}C_4H_9N{=}CHC_3H_7$	$n\text{-}C_4H_9NHC_4H_9$	2.8	79	C	156—160	159[17)]
$n\text{-}C_4H_9N{=}CH\text{-}⟨ring⟩$	$n\text{-}C_4H_9NHCH_2\text{-}⟨ring⟩$	2.8	75	C	107—109 (12)	226—230[20)]
⟨ring⟩-N=CH-⟨ring⟩	⟨ring⟩-NHCH₂-⟨ring⟩	2.8	74	C[i)]	213—215 [H₂O]	214—216[17)]
⟨ring⟩-CH₂N=CH-⟨ring⟩	⟨ring⟩-CH₂NHCH₂-⟨ring⟩	2.8	80	C[i)]	257—258 [H₂O]	256[17)]
[Nitriles: $-C{\equiv}N + 4H^+ + 4e^- \longrightarrow -CH_2NH_2$]						
$n\text{-}C_4H_9CN^{1)}$	$n\text{-}C_5H_{11}NH_2$	5.4	72	C	103	104[17)]
$n\text{-}C_6H_{13}CN^{1)}$	$n\text{-}C_7H_{15}NH_2$	5.1	76	C	154	155 (760)[17)]
$NC(CH_2)_4CN^{j,1)}$	$H_2N(CH_2)_6NH_2$	10.0	70 (87)	k)	85 (15)	100 (20)[17)]
⟨ring⟩-CN[1)]	⟨ring⟩-CH₂NH₂	6.3	75	C	69—70 (12)	185[17)], 74/15[21)]
⟨ring⟩-CH₂CN[1)]	⟨ring⟩-CH₂CH₂NH₂	5.6	71	C	82—83 (12)	197—198[17)], 92—93 (19)[s)]
[Oximes: $={}N{-}OH + 4H^+ + 4e^- \longrightarrow -NH_2$]						
⟨ring⟩=N-OH[1)]	⟨ring⟩-NH₂	6.7	65 (77)	C	131—134	134[17)]
⟨ring⟩-C-CH₃[1)] (N-OH)	⟨ring⟩-CH-CH₃ (NH₂)	6.7	62	C	71—72 (12)	87 (24)[17)], 80—81 (18)[22)]

Table 1. Continued.

Starting material	Product[b]	Consumed current F/mol	Isolated yield[c] %	Isolation method	Bp θ_b/°C(mmHg) or Mp θ_m/°C Obsd[d]	Ref.
⬡-C(=N-OH)-⬡ [j,1]	⬡-CH(-NH₂)-⬡	6.7	62	C	163—167(12)	175—176(23)[17]

[Nitro compounds: $-NO_2 + 6H^+ + 6e^- \longrightarrow -NH_2$]

⬡-NO₂	⬡-NH₂	6.2	63(72)	C	75(12)	92(33)[17]
⬡(CH₃)(NO₂)	⬡(CH₃)(NH₂)	5.6	58(66)	C	83(12)	92(18)[17]
CH₃-⬡-NO₂	CH₃-⬡-NH₂	6.7	60(71)	C	40—43	42[17]

[Unsaturated hydrocarbons: $\text{C=C} + 2H^+ + 2e^- \longrightarrow \text{CH-CH}$]

n-C₆H₁₃CH=CH₂	n-C₈H₁₈	3.2	66(76)	D	124—126	125.7[17]
n-C₅H₁₁CH=CHCH₂	n-C₈H₁₈	3.2	(70)			
⬡-CH=CH₂	⬡-CH₂CH₃	2.6	75(85)	D	133—135	136[17]
n-C₆H₁₃C≡CH	n-C₆H₁₃CH=CH₂	2.0	(11)	m, n)		
	n-C₈H₁₈		(39)			
⬡-C≡C-⬡ [j]	⬡-CH=CH-⬡ (cis)	5.6	(22)	m)		
	⬡-CH₂CH₂-⬡		(60)			

[α,β-Unsaturated carboxylic acids]

CH₃CH=CHCOOH[f]	n-C₃H₇COOH	2.8	60	B	156—160	162[17]
⬡-CH=CHCOOH[f]	⬡-CH₂CH₂COOH	2.5	75	B	50—51 [Hexane]	48.5[11],[17]

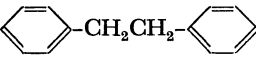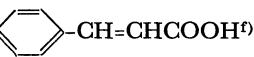a) Anolyte: starting material (0.10 mol) in 150 ml of MeOH containing 0.15 mol of NaOMe. Raney nickel catalyst: 2 g. Constant current: 0.75 A. Temperature: ca. 15 °C. b) The products obtained were identified by a comparison of their phisical and IR-spectral data with those of authentic samples or with the literature data. c) Value in brackets refers to yield estimated by GLC. d) Boiling points and melting points are uncorrected. (1 mmHg ≈ 133.322 Pa). e) 180 ml of methanol was used. f) Electrolyzed in 150 ml of a 1.67 mol dm⁻³ NaOH aq solution. g) Continuously extracted with diethyl ether for 12 h. h) The crude products were treated with a saturated sodium hydrogensulfite solution before distillation. i) Isolated as HCl-salt. j) 0.05 mol was used. k) After the removal of the methanol, the residue was diluted with 30 ml of water, refluxed for 10 h, and then continuously extracted with diethyl ether for 12 h. l) An excess amount of ammonia was added to the catholyte. m) Analytical samples were obtained by preparative GLC and were identified with authentic samples by NMR and mass spectroscopy. n) Unreacted acetylene was recovered in a yield of 44%.

As is shown in Fig. 1, the sodium methoxide–methanol electrolyte system was discharged at the potential of −1.0 V vs. SCE at a nickel-plate cathode covered with Ra/Ni, in contrast to the potential of −1.5 V at a nickel-plate cathode. Interestingly, in spite of an appreciable increase in the electrolytic current (10 A/dm²-coductive base area), no evolution of hydrogen was observed, presumably because of a strong adsorption of hydrogen to the Ra/Ni electrode. In this system, the substrates employed, such as ketones and nitriles, showed no reduction waves below the potential of −1.0 V. Consequently, it was reasonable to assume that the reduction takes place by adsorbed hydrogen atoms which are electrolytically generated and activated under the catalytic influence. rather

than by direct electron-transfer between the substrate and the electrode.

In conclusion, the Ra/Ni electrode brought about the hydrogenation of various compounds, and the course of the reaction resembled that taken by a normal catalytic hydrogenation with Ra/Ni and elemental hydrogen. It seemed to be especially attractive in that the reduction using Ra/Ni, which usually requires an increased temperature and pressure except for the use of Ra/Ni W-6, is possible at room temperature and atmospheric pressure,[14] while the hydrogenation of aromatic nuclei[15] or the hydrogenolysis of carbonyl groups of acid amides or esters was impossible. Application to compounds with two different functional groups is currently being undertaken, including the
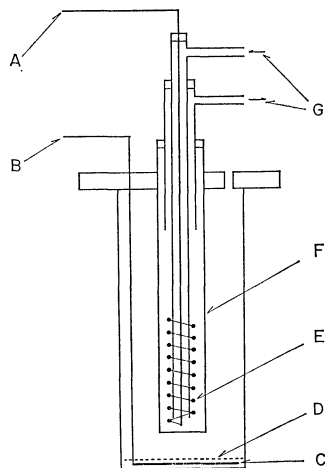
Fig. 2. Preparative scale electrolysis cell.
A: Lead to anode, B: lead to cathode, C: nickel plate, D: Raney nickel catalyst, E: platinum coil anode, F: ceramic cup, G: inlet and outlet of anolyte (to pump).

use of other Raney catalysts, *e.g.*, Ra/Co, Ra/Cu, and Ra/Fe.

Experimental

Apparatus.   The preparative electrolyses were carried out in the two-compartment cell depicted in Fig. 2. On the bottom of the cathode compartment (200 ml), a conductive base of nickel plate ($\phi=5.0$ cm) is placed. As the anode compartment, a ceramic cup (2 mm wall thickness, 17 cm high, and 1.8 cm in diameter) is used; it is provided with a platinum coil anode and an inlet and outlet for the circulation of the anolyte. The cell is externally cooled with water.

Preparation of Raney Nickel Catalyst.   In a 300-ml round-bottom flask, 4.0 g of Raney nickel alloy powder (Ni content, *ca.* 50%) is suspended in 40 ml of distilled water. Then, 6.5 g of sodium hydroxide pellets are added all at once. An exothermic reaction occurs with a vigorous evolution of hydrogen. After the evolution of hydrogen slows, the suspension is digested at 60 °C on a steam bath for 30 min with occasional shaking and then allowed to attain room temperature. The alkaline solution is decanted, and the nickel is washed three times with 50-ml portions of distilled water, followed by three washings with 25-ml portions of methanol. The Raney nickel catalyst obtained in this manner weighs about 2 g, and its activity is comparable to that of W-2.[16]

General Procedure.   The cathode compartment is charged with 0.10 mol of a substrate dissolved in 150 ml of methanol containing 0.15 mol of sodium methoxide (unsaturated carboxylic acids, keto acids, and salicylaldehyde are electrolyzed in 150 ml of 1.67 mol dm^{-3} aqueous sodium hydroxide). Then, about 2 g of freshly prepared Raney nickel catalyst is added to the catholyte and allowed to settle on the nickel plate. The anolyte of the same concentration of methanolic sodium methoxide is circulated by pumping, and the current is turned on. During the electrolysis, the catholyte is occasionally stirred with a glass rod.

All electrolyses were conducted under a constant current of 0.75 A until almost all of the substrate has been consumed (1.1—1.8 of the theoretical current is passed through). After the reduction, the catholyte is filtered from the catalyst and

treated as follows.

Work-up Procedure.   *A)*: The resulting catholyte is diluted to 2 volumes with methanol, and carbon dioxide is bubbled into the solution. The precipitated sodium carbonate is filtered off and washed with methanol (20 ml × 2). The filtrate and washings are combined and distilled.

B): After the removal of the solvent, the residue is acidified with 18% hydrochloric acid. The separated oily layer is extracted with diethyl ether (30 ml × 4), dried with magnesium sulfate, and distilled or recrystallized.

C): The reaction mixture is concentrated to 1/2 volume, acidified with 18% hydrochloric acid, and evaporated to dryness. The remaining solid is dissolved in water, washed thoroughly with diethyl ether, and made strongly alkaline with sodium hydroxide. The separated oily layer is extracted with diethyl ether (30 ml × 4), dried with sodium hydroxide, and distilled over a few pellets of sodium hydroxide.

D): The catholyte is poured into 2 volumes of water. The separated oily layer is extracted with hexane (30 ml × 4), washed with water, dried with anhydrous potassium carbonate, and distilled.

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