

Electro-catalytic Reduction of Ketones Using Nickel-Aluminum Alloys

By Toshio ARAI

Department of Chemistry, Faculty of Liberal Arts and Science, Shinshu University

(Received Sept. 30, 1957)

Electro-catalytic reduction is an indirect electrochemical reaction and it is a method of reductions by electrolysis, that is, electrolysis was generally conducted by using a cathode covered with metals which are generally used as hydrogenation catalyst or by using an electrolyte suspended with catalytic metals. These methods are called an electro-catalytic reduction.

In these cases, it was supposed that electrolysis was used only for the evolution of hydrogen, that is, hydrogen ions which are discharged at a cathode appear as hydrogen gas and this hydrogen gas is used as hydrogenation by the action of catalytic metals.

These methods are peculiarly effective in some cases. These examples are as follows; the reduction of pyrroline to pyrrolidine,⁽¹⁾ acetonitrile to ethylamine,⁽²⁾ aminoacetonitrile to ethylenediamine,⁽³⁾ and the preparation of sorbite from glucose⁽⁴⁾.

In the previous communication⁽⁵⁾, it has been reported that the reduction of acetophenone by an electrolytic catalytic reduction using Raney nickel in alkaline solution was thought to be favorable. Moreover, in this experiment, the author tried to prepare corresponding alcohols from various ketones by an electrolytic method with nickel-aluminum alloy and found a way to produce them with a satisfactory result in weak alkaline electrolyte with nickel-aluminum alloy suspended.

In general, Raney nickel is prepared from the decomposition of nickel-aluminum alloy in sodium hydroxide solution and it is stocked as alcoholic solution.

In this experiment, it was thought that nickel-aluminum alloy was decomposed by an electrolyte, 5% sodium hydroxide solution, to Raney nickel and aluminum hydroxide and the former acted as a catalyst and the latter was dissolved in a electrolyte, thus electro-catalytic reduction of ketones proceeded smoothly to corresponding alcohols.

Experimental

(I) *Reduction of liquid ketones*

The electrolysis was conducted under following conditions;

Cathode: lead, nickel and copper plate 100 cm².

Cathodic solution: 5% sodium hydroxide solution.

Anode: carbon plate.

Anodic solution: 5% sodium hydroxide solution.

Current density: 2-3 amp./sq. dm.

Liquid ketone (10-20g.) was mixed with 5% sodium hydroxide solution and the mixture was placed in a porous pot, nickel-aluminum alloy which corresponded from about 5-10% by weight of the ketone was added to catholyte gradually and after the evolution of hydrogen gas was ceased the electrolysis was carried out by vigorously stirring the cathodic solution and the electrolytic bath was cooled by running water.

The current density was 2-3 amp./sq. dm. The completion of electrolysis was recognized when a small quantity of cathodic solution gave a negative ketone test with 2,4-dinitrophenylhydrazine reagent after acidifying. The amount of electric current which passed was about four times as much as theoretical amount.

After finishing the electrolysis, the cathodic solution was filtered and had the nickel therein filtered off and the filtrate was made slightly acidic by the addition of sulfuric acid.

Then it was extracted with ether and the combined ether extracts were dried over anhydrous potassium carbonate. The ether was removed and the residue distilled under reduced or normal pressure. The yield was 75-85%.

The reduction product gave a negative ketone test with 2,4-dinitrophenylhydrazine reagent and it was mixed with phenylisocyanate or 3,5-dinitrobenzoylchloride and the derivatives of alcohol were obtained. This sec.-alcohol obtained was oxidized with potassium chromate and sulfuric acid and the corresponding original ketone was prepared.

(II) *Reduction of solid ketones*

Five g. of ketone (benzophenone, benzoin, and benzil) was dissolved in a mixture of alcohol 50 ml. and 5% sodium sodium hydroxide solution 70 ml. with heating, and this solution was placed in a cathode chamber. Other conditions were the same with liquid ketones but these solid ketones were not dissolved easily at a low temperature then the electrolytic chamber was kept at from 40° to 50°C.

After finishing the electrolysis nickel of the catholyte was filtered off and the filtrate was made slightly acidic, to which water was added in order to decrease the solubility of reduction product, then the crystals were

Table 1 Rational formulae of the ketones and boiling points or melting points of the reduction products

No.	Ketones		Reduction products		b. p. or m. p. °C
(1)	Acetophenone	$C_6H_5COCH_3$	Phenylmethylcarbinol	$C_6H_5CHOHCH_3$	b. p. 98-102°/18mm
(2)	Propiophenone	$C_6H_5COCH_2CH_3$	Phenylethylcarbinol	$C_6H_5CHOHCH_2CH_3$	b. p. 168-112°/20mm
(3)	p-Methylacetophenone	$CH_3-C_6H_4COCH_3$	p-Tolylmethylcarbinol	$CH_3-C_6H_4CHOHCH_3$	b. p. 109-113°/20mm
(4)	p-Methoxyacetophenone	$CH_3O-C_6H_4CHOHCH_3$	p-Methoxyphenylmethylcarbinol	$CH_3O-C_6H_4CHOHCH_3$	b. p. 135-139°/20mm
(5)	Phenylacetone	$C_6H_5CH_2COCH_3$	Benzylmethylcarbinol	$C_6H_5CH_2CHOHCH_3$	b. p. 110-114°/21mm
(6)	Benzalacetone	$C_6H_5CH=CHCOCH_3$	4-Phenylbutanol Diphenyldiacetylbutane	$C_6H_5CH_2CH_2CHOHCH_3$ $[CH_3COCH_2CH(C_6H_5)-]_2$	b. p. 120-124°/20mm m. p. 158-160°
(7)	Cyclopentanone	C_4H_8-CO	Cyclopentanol	C_4H_9CHOH	b. p. 140-142°
(8)	Cyclohexanone	$C_5H_{10}-CO$	Cyclohexanol	$C_5H_{11}CHOH$	b. p. 160-162°
(9)	Methylcyclohexanone*	$CH_3C_5H_9CO$	Methylcyclohexanol	$CH_3-C_5H_9CHOH$	b. p. 170-175°
(10)	Benzophenone	$C_6H_5COC_6H_5$	Benzhydrol	$C_6H_5CHOHC_6H_5$	m. p. 66-67°
(11)	Benzoin	$C_6H_5CHOHCOC_6H_5$	Hydrobenzoin	$C_6H_5CHOHCHOHC_6H_5$	m. p. 135-137°
(12)	Benzil	$C_6H_5COCOC_6H_5$	Hydrobenzoin	$C_6H_5CHOHCHOHC_6H_5$	m. p. 135-137°
(13)	1-Acetylnaphthalene	$CH_3COC_{10}H_7$	Not reduced		
(14)	d-Camphor	$C_9H_{16}CO$	Not reduced		

*Methylcyclohexanone used in this experiment was prepared from hydrogenation of a mixture of o-, m-, and p-cresol, therefore the mixture of 1-, 2-, and 3-methylcyclohexanol was obtained.

deposited, the deposit was filtered off and the filtrate was extracted with ether. The ether was removed and the residue was combined with the deposit which was obtained previously. Almost quantitative yield was obtained.

The amount of electric current which passed was about two and half times as much as theoretical.

Benzhydrol was recrystallized from ligroin and needle crystal were obtained and the acetylated benzhydrol was recrystallized from acetic acid, m. p. 40-41°C. Hydrobenzoin was recrystallized from 50% alcohol and plate crystals were obtained and diacetyl hydrobenzoin was prepared, m. p. 132°C.

Results and discussion

The electrolytic reduction of the aliphatic and aromatic ketones using a lead cathode in a alkaline solution are reduced to the corresponding alcohol⁽⁶⁾. Benzophenone, for example, are easily reduced to benzhydrol in a alkaline solution at a high temperature, but the mixed ketone like acetophenone are reduced to pinacol in acid or alkaline solution⁽⁷⁾.

In this method the corresponding alcohol was obtained easily from the mixed ketone but the pure electrolytic reduction was better than this method in case of the preparation of alcohol from aromatic ketones.

In a reduction of the mixed ketone at a high temperature tar like materials were produced in a some quantity and the yield was decreased. In case of aromatic ketones the reduction at a high temperature was favorable.

The current density had an effect on the current efficiency, that is, the higher the current density, the lower the current efficiency, therefore it was thought to be favorable that the current density was decreased and the electrolysis was conducted for a long time.

The yield of 2-hydroxybutylbenzene from benzalacetone was decreased to 65%. The distilling residue was diphenyldiacetylbutane (m. p. 158-160°C) which was prepared from the condensation of two molecular benzalacetone, this yield was reached about 15%.

1-Acetylnaphthalene and d-camphor were reduced in the same way but reduction products were not obtained and original ketones were recovered.

Summary

Electro-catalytic reduction of various ketones (aromatic, mixed, and cyclic ketones) was studied. Electrolysis was carried out in a weak sodium hydroxide solution, in which nickel-aluminum alloy was suspended. Nickel-aluminum alloy was decomposed to Raney nickel in a alkaline electrolyte. Various ketones were reduced to corresponding alcohols with a good yield at a low

temperature or a high temperature.

Acknowledgment. The author expresses his sincere thanks to Professor B. Sakurai for his kind guidance and encouragement throughout this work.

References

- (1) SAKURAI, B. (1936) *Bull. Chem. Soc. Japan* 11, 374.
- (2) OTA, M. (1942) *J. Chem. Soc. Japan* 63, 1762.
- (3) SUGII, Y. and MORI, T. (1952) *J. Agric. Soc. Japan* 25, 294.
- (4) BELENSKAYA, N. and BELOZERSKII, N. (1950) *Chem. Abst.* 44, 956.
- (5) SAKURAI, B. and ARAI, T. (1955) *Bull. Chem. Soc. Japan* 28, 93.
- (6) ELBS, K. and BRAND, K. (1902) *Z. Elektrochem.* 8, 783.
- (7) SWANN, S. and HERSON, C. (1935) *Electrochem. Soc., Reprint* 67, 49.
- (8) MULLER, E. (1910) *Z. Elektrochem.* 16, 236.