CHEMISTRY LETTERS, pp. 47-50, 1977. Published by the Chemical Society of Japan

STEREOCHEMICAL STUDIES OF THE ELECTROLYTIC REACTIONS OF ORGANIC COMPOUNDS III.[1]
ELECTROLYTIC REDUCTION OF 2-METHYLCYCLOHEXANONE TO 2-METHYLCYCLOHEXANOL

Tsutomu NONAKA, Sadayuki WACHI, and Toshio FUCHIGAMI
Department of Electrochemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

2-Methylcyclohexanone was electrolytically reduced to 2-methylcyclohexanol under a variety of conditions. The trans/cis ratio of 2-methylcyclohexanol strongly depended on cathode material, current density and organic co-solvent in aqueous sodium hydroxide, while in aqueous sulfuric acid such a strong dependence was not observed.

Kita proposed general and comprehensive rules that the most important factor in electrolytic reaction is the inherent character of an electrode metal and that *d*- and *sp*-metal cathodes give predominantly *cis* and *trans* isomers, respectively, as products in electrolysis of organic compounds.[2] The latter rule is very interesting in a stereochemical aspect but there are some doubts at the point of universal validity because of a small number of literatures, which are concerned with steric selectivity of olefins and cyclohexanols formed in electrolytic reduction of acetylenes[3-5] and cyclohexanones[6,7] respectively, cited as illustrations. Moreover, refs. (6) and (7) gave no description of electrolytic conditions such as current density and composition of catholyte.

This work dealt with electrolytic reduction of 2-methylcyclohexanone under a variety of conditions and produced a number of exact and reliable data of the formation ratio of *trans*- to *cis*-2-methylcyclohexanol.

Experimental An electrolytic cell was similar to one described in a previous paper.[8] A cathode was polished with an emery paper No.3000 before electrolysis. The catholyte and anolyte were, respectively, 70 cm^3 of an equal volume mixture of an organic solvent and 2 N sulfuric acid or 2 N sodium hydroxide.

A constant current was supplied at 25°C and 7700 C of electricity was passed through the catholyte containing 4.6 g (0.02 mol) of 2-methylcyclohexanone. Hydrogen evolution was observed during electrolysis. The catholyte was extracted with ether, after neutralized with sodium hydroxide or sulfuric acid. The ethereal extract was subjected to gas chromatographic analysis (Column length, 2.25 m; Packing, Celite 545 coated with glycerin; Temperature, 82°C) for trans- and cis-2-methylcyclohexanols.

Results and Discussion Electrolytic conditions and results are summarized in Table 1.

Percentage formation ratios of the trans isomer of 2-methylcyclohexanol in all electrolyses were considerably lower than a thermodynamical equilibrium value.[9] Catalytic hydrogenation of 2-methylcyclohexanone to 2-methylcyclohexanol with platinum and nickel catalysts afforded the trans isomer in a formation ratio close to the thermodynamical equilibrium value,[11] while the cis isomer was predominant in sodium reduction in liquid ammonia.[12]

The formation ratio of the trans isomer in an acidic medium varied much less from 60 to 70 % with electrolytic conditions. d-Metal cathodes (copper and nickel) resulted in relatively smaller ratios of the trans isomer than those in cases of sp-metal (mercury, aluminum, zinc, lead, tin and cadmium), though no isomeric ratio was reversed.[13] This fact may indicate that tentatively named "Kita's rule" is imperfectly realized.

On the other hand, in an alkaline medium the isomeric formation ratio strongly depended on electrolytic conditions. It is noticeable that a copper (d-metal) cathode resulted in a high ratio (74 %) of the trans isomer at 8.3 A/dm^2 of current density in methanol, while sp-metals such as cadmium and lead resulted in low ratios (22 and 27 %, respectively). Also, some solvent effect was observed in cases of tin and mercury cathodes. Dependence of the isomeric ratio on current density was obviously recognized in the case of tin and was not in the case of mercury. These facts point out a failure in "Kita's rule", at least, in the case of the reduction of 2-methylcyclohexanone to 2-methylcyclohexanol.

No simple correlation between the isomeric ratio or the yield of 2-methylcyclohexanol and either hydrogen overvoltages or standard electrode potentials[15] of metals used as cathodes was observed.

Only observations are represented in this paper. Further investigation from

Table 1. Electrolytic Conditions and Results

Cathode metal	Electrolyte	Organic co-solvent	Current density (A/dm^2)	2-Methylcyclohexanol Yield (%)	2-Methylcyclohexanol Trans:cis (%)
Hg	H_2SO_4	Methanol	8.3	46	69:31
Hg	H_2SO_4	Methanol	2.2	22	70:30
Hg	H_2SO_4	DMF	8.3	3	68:32
Hg	H_2SO_4	DMF	2.2	8	72:28
Hg	NaOH	Methanol	8.3	30	62:38
Hg	NaOH	Methanol	2.2	47	62:38
Hg	NaOH	DMF	8.3	4	65:35
Hg	NaOH	DMF	2.2	trace	-
Al	H_2SO_4	Methanol	8.3	2	70:30
Al	NaOH	Methanol	8.3	2	37:63
Zn	H_2SO_4	Methanol	8.3	12	68:32
Zn	NaOH	Methanol	8.3	65	75:25
Pb	H_2SO_4	Methanol	8.3	39	64:36
Pb	NaOH	Methanol	8.3	2	27:73
Sn	H_2SO_4	Methanol	8.3	18	65:35
Sn	H_2SO_4	Methanol	4.2	trace	-
Sn	H_2SO_4	DMF	8.3	9	58:42
Sn	H_2SO_4	DMF	4.2	12	60:40
Sn	H_2SO_4	Dioxane	8.3	2	58:42
Sn	NaOH	Methanol	8.3	38	37:63
Sn	NaOH	Methanol	4.2	4	63:37
Sn	NaOH	DMF	8.3	6	31:69
Sn	NaOH	DMF	4.2	11	16:84
Sn	NaOH	Dioxane	8.3	1	39:61
Cd	H_2SO_4	Methanol	8.3	29	65:35
Cd	NaOH	Methanol	8.3	3	22:78
Cu	H_2SO_4	Methanol	8.3	4	62:38
Cu	NaOH	Methanol	8.3	37	74:26
Ni	H_2SO_4	Methanol	8.3	1	61:39
Ni	NaOH	Methanol	8.3	1	17:83

a mechanistic aspect is in progress.

The authors wish to thank Professor Keijiro Odo for his valuable advice and for helpful discussions throughout this investigation.

References and Notes

1) Part II: T. Nonaka, T. Ota, and K. Odo, Bull. Chem. Soc. Jpn., in press.

2) H. Kita and M. Honda, J. Electrochem. Soc. Jpn. (DENKI KAGAKU), 38, 17 (1970); H. Kita, Extended Abstracts for the 29th Annual Meeting of Chem. Soc. Jpn., Vol. II, p937 (1973); H. Kita, J. Jpn. Petr. Inst., 19, 833 (1976).

3) K. N. Campbell and E. E. Young, J. Amer. Chem. Soc., 65, 965 (1943).

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

5) R. A. Benkeser and C. A. Tincher, J. Org. Chem., 33, 2727 (1968).

6) P. Anziani, A. Aubry, and R. Cornubert', Compt. Rend., 225, 878 (1947).

7) J. Mizuguchi and T. Sato, J. Electrochem. Soc. Jpn., 38, 148 (1970).

8) K. Sugino, K. Shirai, and T. Nonaka, Bull. Chem. Soc. Jpn., 37, 1895 (1964).

9) The thermodynamical equilibrium value at 25°C is estimated to be over 98 % from data appeared in a literature.(10)

10) E. L. Eliel and R. S. Ro, J. Amer. Chem. Soc., 79, 5992 (1957).

11) R. J. Wicker, J. Chem. Soc., 1956, 2165 (1956).

12) J. W. Huffman and J. T. Charles, J. Amer. Chem. Soc., 90, 6886 (1968).

13) Shono and Mitani had reported that almost equal amounts of the trans and cis isomers were formed in electrolysis using a carbon cathode in an aqueous sulfuric acid solution.(14)

14) T. Shono and M. Mitani, Tetrahedron, 28, 4747 (1972).

15) Yamura and Sekine had found a simple correlation between current efficiency for 2-propanol and standard electrode potentials of cathode metals in reduction of acetone in an acidic medium.(16)

16) A. Yamura and T. Sekine, J. Electrochem. Soc. Jpn., 34, 115 (1966).

(Received October 13, 1976)