ELECTROLYSIS of AQUEOUS ∂-CYCLOHEXYLBUTYRATE

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In the Kolbe electrolysis, an organic anion dissolved in a polar solvent (usually water) yields an electron to an anode to become a free radical. The free radical decomposes, finally forming stable compounds. If the acid is RCOOH, the ion is RCOO, and the prime free radical is RCOO. The prime free radical usually largely decomposes, to CO_2 and the secondary free radical R. The dimer RR and the unsaturated compound (R minus H) are usually prominent products.

Certain structures within R inhibit the Kolbe action in water, so that hydroxide discharges instead of the organic anion. When this happens, oxygen replaces carbon dioxide in the anode gases. Thiessen (1950) recognized ethylenic and benzenoid inhibitions. Fichter and Holbro (1937) found that separation of the inhibiting ethenoid structure from the carboxylate end of the ion by two methylene groups cancelled the ethenoid inhibition. Fichter and Siegrist (1932) electrolyzed the cyclohexylcarboxylate ion in aqueous solution; their small yields showed the reality of a cyclohexanoid inhibition.

∂-cyclohexylbutyric acid has recently become commercially available. In it, three methylenes separate the inhibiting cyclohexyl group from the carboxylate unit. This separation might be expected to mitigate the inhibition. We, therefore, electrolyzed concentrated aqueous solutions of the potassium salt of this acid to find if it would yield more Kolbe products than its first homologue.

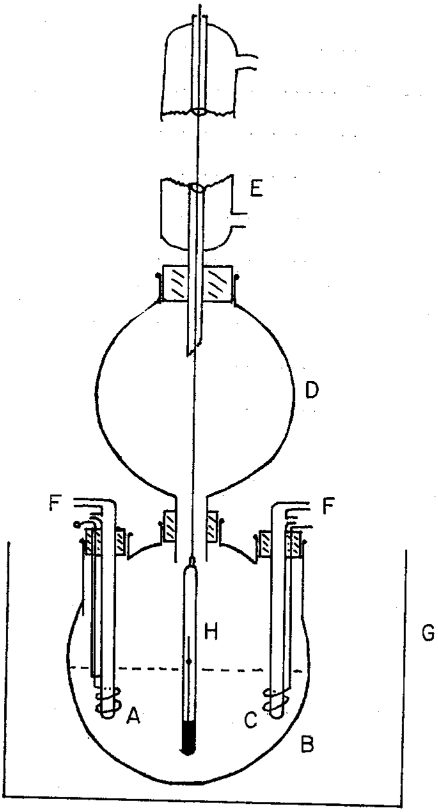

FIG. 1.—Electrolysis cell with accessories: *A*, anode (Pt wire with glass sheath); *B*, three-neck flask, 250 ml.; *C*, cathode (Pt wire); *D*, foam chamber; *E*, reflux condenser; *F*, cold-finger condensers; and *G*, tank for external cooling.

TABLE 1.—Conditions and Results

Run	1	2	3	4	5
conc. salt	1.40 M.	1.40 M.	1.77 M.	1.77 M.	1.77 M.
vol. used	100 ml.	200 ml.	100 ml.	100 ml.	100 ml.
anode current density (*amp* cm^2)	1.33	1.33	4.17	4.17	4.17
time (hrs.)	37	27.5	16.6	18.4	25.5
faradays	2.21	1.64	3.10	3.43	4.75
temp. cell, °C	63-68	63-68	63-68	60	46
external temp., °C	20	20	20	0	0
CO_2 evolved	yes	none[1]	yes	yes	not measurable
yield, R-H, gms	app. 4	none	app. 4	app. 5	none
yield, of RR	none	none	trace	trace	none
gas stirring	no	no	no	no	yes[2] with N_2 and air

[1] No CO_2 was evolved, and two phases did not appear within 27.5 hours; therefore, the run was discontinued. Runs (3, 4 and 5) were made under different conditions.

[2] Lippincott (1954) reported that Kolbe electrolysis favored production of saturated hydrocarbons below 50° C. Stirring was used to lower temperature to 43° C. However, Kolbe reaction did not take place and most of original acid was recovered.

EXPERIMENTAL

The apparatus is shown in Figure 1. The large intermediate chamber *D* was used to eliminate difficulties due to foaming. Electrodes were of platinum. Internal and external cooling was employed. A motor generator furnished direct current. Experimental conditions and results are summarized in Table 1.

The Eastman acid was used without further purification and converted to the salt solution by treatment with a concentrated solution of potassium hydroxide and water. After electrolysis, yields were recovered from the reaction mixtures by ether extraction and dried with magnesium sulfate. The dicyclohexane was collected by vacuum distillation and purified by washing with cold, concentrated sulfuric acid. Material passing over at lower temperature was collected separately and is supposed by us to be (R minus H).

Even in the most favorable runs, the amount of RR isolated was so small that the refractive index was the only numerical identifying constant which could be taken. Our value (n_D^{23} = 1.480) was in good agreement with the values (n_D^{20} = 1.4765) of Schlenk (1951 and (n_D^{21} = 1.4758) of Fieser and Leffler (1948).

The presumed (R minus H) came also in small amounts, though it was more abundant than the RR. It dissolved completely in 80% aqueous sulfuric acid solution, which indicates it is either unsaturated or oxygenated. It decolorized dilute permanganate solution, which actions indicate unsaturation. Its density was 0.855 gm./cc. at 25° C.; n_D^{25} was 1.468, and its boiling point approximated 110° at 14 mm. pressure. These constants agree fairly well with the Beilstein values of (a) 3-cyclohexyl propene-1 ($d_4^{19} = 0.813$, $n_D^{19} = 1.449$, b.p. = 152° at 760 mm.), (b) 1-propylcyclohexene ($d_4^{19} = 0.8216$, $n_D^{19} = 1.455$, b.p. = 158° at 760 mm.), and 3-propylcyclohexene ($d_4^{19} = 0.8181$, $n_D^{19} = 1.454$, b.p. = 155° at 760 mm.). The agreement is, however, not good enough to distinguish the location of the double bond.

R. Best and G. W. Thiessen of Monmouth College found, in unpublished research, that an improved yield of RR resulted from the electrolysis of the potassium salt of δ-cyclohexylbutyric acid in a pyridine-methanol solution, under the conditions of Fichter and Petrovitch (1940).

CONCLUSION

The low yields of typical Kolbe products in the electrolysis of aqueous δ-cyclohexylbutyrate ion, comparable to those of Fichter and Siegrist (1932), show that cyclohexanoid inhibition of the Kolbe electrolysis cannot be cancelled by even three methylenes intervening between the carboxylate and inhibiting groups. This contrasts with ethenoid inhibition, which can be relieved by two methylenes thus intervening.

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