[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Kolbe Electrolyses of *cis* and *trans* Methyl Hydrogen Hexahydrophthalate

C. G. OVERBERGER AND PETER KABASAKALIAN[1]

Received April 30, 1956

The Kolbe electrolysis of *cis* and *trans* methyl hydrogen hexahydrophthalate in anhydrous methanol has been carried out. Identical mixtures of uncoupled products were obtained from both isomers, indicative of the formation of radicals which are free. Thus, the methyl ester of 1-cyclohexene-1-carboxylic acid, the ester of 2-cyclohexene-1-carboxylic acid, and the methyl ester of cyclohexanecarboxylic acid were obtained as monomeric products. Dimeric materials (coupled products) were obtained for the first time from methyl hydrogen hexahydrophthalates. Saponification of the mixture of dimeric esters for experimental convenience gave two perhydrodiphenic acids, *trans-anti-trans* and *trans-syn-trans*. These were separated and identified quantitatively by adsorption chromatography and infrared analysis. Since epimerization occurred on all centers *alpha* to the carboxyl group, no conclusion about the stereochemistry of the radicals can be deduced from the ratios of coupled products.

It had previously been reported[2] that the Kolbe electrolysis of methyl hydrogen *trans*-hexahydrophthalate gave only monomeric materials and no coupled products. This was in contrast to the isomeric methyl hydrogen *trans*-hexahydroterephthalate which had been reported[3a] to give an appreciable yield (32%) of the Kolbe coupled product under different reaction conditions. From this result it might be concluded that an ester group *ortho* to the carbon on which the odd electron is situated favored the disproportionation process.

After some preliminary work on the electrolysis procedure, it was apparent that coupled products could be obtained from either methyl hydrogen *trans*-hexahydrophthalate or the *cis*-isomer indicating that the above conclusion was in error. The electrolysis of methyl hydrogen *cis* and *trans*-hexahydrophthalate offered an approach to the problem of the stereochemistry of the radicals obtained in the Kolbe process. This paper describes an initial phase of the work and is primarily designed to obtain model procedures for continued research. Previous work[3b] has indicated that the radicals became planar, thus Wallis and Adams have demonstrated that the electrolyses of *d*- and *l*-methylethylacetic acid both gave inactive 3,4-dimethylhexane. In the course of the work, some useful operating procedures and information on the Kolbe electrolysis for practicing organic chemists were developed and although much of the experimental detail has been omitted from this manuscript, some of the more interesting results are briefly mentioned in the discussion section. Data obtained from the electrolysis of sodium methoxide solutions are also included.

EXPERIMENTAL[4]

Absorption spectra. The ultraviolet absorption spectra were measured in 1-cm. quartz cells in methanol solutions using a Cary model 11 recording spectrophotometer. Infrared absorption spectra were obtained with a Perkin-Elmer model 21 double beam recording spectrophotometer with a sodium chloride prism using a Nujol mull between sodium chloride plates.

Polarograms. The polarograms were taken with a Sargent recording polarograph, model XXI. The characteristics of the capillary were m = 1.925 mg. sec.$^{-1}$ and t = 3.75 sec. at open circuit in 50% methanol solutions. The height of the mercury column was 40 cm. All potentials were measured against the normal calomel electrode (N.C.E.).

Electrolyses. (A) Electrolysis equipment. The electrolysis cell was made up of a cylindrical glass vessel of 100-ml. capacity with a ground glass lip and a jacket for cooling water. A ground glass cover with holes for a thermometer, electrodes, vent, and sample opening enclosed the cell. The cell was placed on a magnetic stirrer which provided continuous agitation. The electrodes were made up of 6 one-inch squares of smooth platinum sheets, 0.002 inches thick, which were spaced 2 mm. apart and parallel to each other. Alternate sheets were connected together electrically. Direct current was obtained from a filtered full-wave selenium rectifier.

(*B*) *Control of electrolyses.* The course of the electrolyses was followed by three methods. (1) *p*H. A small Beckman glass and calomel electrode were inserted into the solution. The *p*H was read directly on a Leeds and Northrup AC-operated *p*H indicator when the electrolysis current was turned off. The electrolysis was terminated when the apparent *p*H reached a value of about 9. (2) *Ultraviolet absorption.* A sample was taken with a hypodermic syringe using a No. 22 needle during the course of the electrolysis. One drop was diluted to 10 ml. with methanol and its ultraviolet absorption at 220 mμ was determined. The electrolysis was terminated when the ultraviolet absorption of the solution stopped increasing. (3) *Free acid.* A 0.10-ml. sample, obtained with the aid of a hypodermic syringe, was titrated with 0.1 *N* sodium hydroxide using a 2-ml. microburette, phenolphthalein being used as an indicator. The electrolysis was stopped when the amount of free acid in the solution reached zero.

(*C*) *Electrode preparation.* The electrodes were prepared prior to electrolysis and whenever the current efficiency dropped to zero. It was found convenient to use a modification of Shaw and Remick's[5] method for reactivating the electrodes. The electrodes were inserted into an alkaline

---

(1) This paper comprises a portion of a thesis presented by Mr. Peter Kabasakalian in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(2) Fichter and Simon, *Helv. Chim. Acta*, **17**, 1218 (1934).

(3a) Fichter and Holbro, *Helv. Chim. Acta*, **21**, 141 (1938).

(3b) Wallis and Adams, *J. Am. Chem. Soc.*, **55**, 3838 (1933).

(4) All melting points are corrected.

(5) Shaw and Remick, *J. Electrochem. Soc.*, **97**, 324 (1950).

cyanide solution having the composition: NaOH, 50 g./l.; KCN, 10 g./l.; Na_2CO_3, 50 g./l. A continuous polarity reversing switch was inserted between the D.C. voltage supply and the cell. While the polarity of the electrodes was reversed every 2.5 seconds, the cell was subjected for 10 to 20 minutes to as high a current density as possible (about 35 ma. cm.$^{-2}$) so that a vigorous evolution of gas resulted. The electrodes then were suitably washed.

(*D*) *Conductivity measurements.* The conductance of the electrolyte solutions were measured at 1000 cycles with an Industrial Instrument Conductivity Bridge, Model RC 16.

(*E*) *Operating conditions.* The Kolbe electrolyses of methanolic solutions of the free acid, containing 2% sodium salt as an electrolyte, were carried out according to the general procedure of Greaves, Linstead, Shephard, Thomas, and Weedon.[6] The temperature of the electrolyte was maintained at 50–60° by circulating ice-water through the cell jacket. The current was kept at 2.00 amperes during the electrolysis (30–40 volts applied to the cell). The free acid titer was used to control the electrolyses.

(*F*) *Electrochemical reduction.* (1) *Basic Conditions.* After completion of the normal electrolysis, when all the free acid was depleted, the electrolysis was continued for an equal number of ampere-hours. The ultraviolet absorption of the solution was determined as described above. (2) *Acidic Conditions.* After completion of the normal electrolysis, 6.0 g. (0.10 mole) of glacial acetic acid was added and the electrolysis was continued until the free acid fell to zero again. The ultraviolet absorption of the solution was determined as usual.

(*G*) *Electrolysis of sodium methoxide.* A solution containing 20 ml. of 0.2 *N* sodium methoxide in methanol and 60 ml. of methanol was electrolyzed for 6 hours. The temperature of the solution was kept at 11° by circulating ice-water while 1.00 ampere was passed through the cell (8 volts applied). At regular intervals samples of 0.10 ml. of the electrolyzed solution were diluted to 10 ml. with 0.025 *M* tetrabutylammonium hydroxide solution. The formaldehyde content of the samples then was determined by measuring the polarographic reduction current according to the intersection point method. Nothing was present which polarographically reduced before the formaldehyde. The formaldehyde content was also determined by bisulfite titration according to the method of Siggia and Maxcy.[7]

(*H*) *Solvent products.* During the Kolbe electrolyses of methyl hydrogen hexahydrophthalate, formaldehyde production was determined as outlined above. Nothing was polarographically reducible before the formaldehyde. The final electrolyzed solution was quantitatively analyzed for the presence of ethylene glycol according to the procedure of Pohle, Mehlenbacher, and Cook.[8]

Preparation of methyl hydrogen cis-hexahydrophthalate (IA). A solution of 154 g. (1.00 mole) of *cis*-hexahydrophthalic anhydride in 300 ml. of anhydrous methanol was refluxed overnight according to the general procedure of Fichter and Simon[2] who prepared the *trans* isomer. The isolation procedure was modified as follows. After transfer of the reaction mixture to an evaporating dish, it was concentrated on a steam-bath. The resulting viscous oil was allowed to stand at room temperature and after two days, it solidified to give 186 g. (100%) of solid, m.p. 64–65°. Recrystallization from a benzene-petroleum ether (b.p. 30–75°) solution gave 167 g. (90%) of product, m.p. 68–69° (m.p. 68.5–69°, by catalytic reduction of methyl hydrogen phthalate, no yield given).[9]

Attempted isomerization of methyl hydrogen cis-hexahydrophthalate (IA) *under electrolysis condition.* A solution of 18.6 g. (0.100 mole) of methyl hydrogen *cis*-hexahydrophthalate in 60 ml. of anhydrous methanol and 10 ml. of 0.20 *N* sodium methoxide was refluxed for two hours. The solution then was distilled at atmospheric pressure until all the methanol was removed. The residue, 18.0 g. (97%), solidified on standing, m.p. 63–67°. Its infrared spectrum did not indicate the presence of any *trans* isomer. The residue was extracted with 1.0 l. of petroleum ether (b.p. 30–75°) leaving behind 0.5 g. (2.5%) of solid whose infrared spectrum did not indicate the presence of any methyl hydrogen *trans*-hexahydrophthalate. The petroleum ether extract was concentrated to a low volume permitting the crystallization of 15.3 g. (82%) of solids, m.p. 68–69°. A mixture melting point with an authentic sample of methyl hydrogen *cis*-hexahydrophthalate melted at 68–69°. On concentrating the petroleum ether solution to dryness, 1.6 g. (8.6%) of solid, m.p. 64–65°, was recovered whose infrared spectrum did not indicate the presence of any methyl hydrogen *trans*-hexahydrophthalate.

Preparation of methyl hydrogen trans-hexahydrophthalate (IB). (*A*) *trans-Hexahydrophthalic acid* (VI) *and trans-hexahydrophthalic anhydride.* This acid and anhydride were prepared according to the general procedure of Davis and Linstead[10] from dimethyl *cis*-hexahydrophthalate (VA). The acid melted at 227–229° (m.p. 227–229°)[10] and the anhydride (69.5%) from hexane melted at 142–144° (m.p. 142.5–144°, no yield given).[10]

(*B*) *Methyl hydrogen trans-hexahydrophthalate* (IB). A solution of 154 g. (1.00 mole) of *trans*-hexahydrophthalic anhydride in 300 ml. of anhydrous methanol was refluxed overnight according to the general procedure of Fichter and Simon.[2] After transferring to an evaporating dish, the reaction mixture was concentrated on a steam-bath and the resulting viscous oil partially crystallized. The solid was removed by filtration and washed with water, (80%), m.p. 96–97° (m.p. 96–97°, no yield given).[2]

Preparation of the methyl ester of 1-cyclohexene-1-carboxylic acid (IIa). A solution of 313 g. (1.98 moles) of the methyl ester of 1-hydroxycyclohexane-1-carboxylic acid in 500 ml. of benzene was cautiously added over a two-hour period to a stirred mixture of 439 g. (2.11 moles) of finely ground phosphorus pentachloride in 500 ml. of benzene according to the general procedure of Helfer[11] who prepared the ethyl ester and did not report specific directions. After refluxing overnight, the reaction mixture was poured into 4.0 l. of ice water, and the solution cautiously was neutralized with potassium carbonate. The solution was extracted three times with 1.0-l. portions of ethyl ether, the ether extracts were dried, and the residue was fractionated. A fraction boiling at 95–96°/27 mm., amounted to 160 g. (57.6%); n_D^{25} 1.4730, λ_{max}^{MeOH}, 219 mμ, $E_{1\ cm.}^{1\%}$, 732, $\epsilon_{max.}$, 10,260 (b.p. 85°/15 mm., n_D^{25} 1.4719, prepared by the direct esterification of 1-cyclohexene-1-carboxylic acid obtained from the hydrolysis of the reaction product of 1-cyano-1,2-dibromocyclohexane and the sodium salt of diethyl malonate, no yield given).[12]

The product was polarographically reduced at 25° in 50% methanol solution containing 0.1 *M* tetrabutylammonium chloride. $E_{1/2}$, −2.076 v., $E'_{1/2}$, −2.308 v., $(I_d + I'_d)/C$, 34.6 μa./mg./ml.

Preparation of the methyl ester of cyclohexanecarboxylic acid (IIc). A solution of 134 g. (0.96 mole) of the methyl ester of 1-cyclohexene-1-carboxylic acid (IIa) in 500 ml. of methanol was reduced catalytically with 28 g. of Raney nickel at 1500 p.s.i. and 140°. The totally reduced material was isolated and fractionated to give 81 g. (59.6%), b.p. 78°/24 mm., n_D^{25} 1.4410, no appreciable ultraviolet absorption (b.p. 183°, n_D^{15} 1.45372, prepared from cyclohexane-

---

(6) Greaves, Linstead, Shephard, Thomas, and Weedon, *J. Chem. Soc.*, 3326 (1950).

(7) Siggia and Maxcy, *Anal. Chem.*, **19**, 1023 (1947).

(8) Pohle, Mehlenbacher, and Cook, *Oil and Soap*, **22**, 115 (1945)

(9) Vavon and Peignier, *Bull. soc. chim.*, [4] **45**, 293 (1929).

(10) Davis and Linstead, *J. Chem. Soc.*, 1425 (1950).

(11) Helfer, *Helv. Chim. Acta*, **9**, 814 (1926).

(12) Mousseron and Winternitz, *Bull. soc. chim. France*, **13**, 604 (1946).

carboxylic acid obtained by the catalytic reduction of anisic acid, no yield given).[13]

Anal. Calc'd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.48; H, 9.84.

Kolbe electrolysis of methyl hydrogen cis-hexahydrophthalate (IA). A solution of 18.6 g. (0.100 mole) of methyl hydrogen *cis*-hexahydrophthalate in 60 ml. of anhydrous methanol and 10 ml. of 0.20 *N* sodium methoxide was electrolyzed. The electrolysis usually required about two hours and the water-white starting solution turned pale yellow. The electrolyzed solution was distilled at atmospheric pressure until the distillation temperature started to rise over 70° and most of the methanol was removed. The reaction mixture then was subjected to steam-distillation. The first 150 ml. of distillate (fraction A) was collected and a second phase (II), very slightly heavier than water, readily separated. The steam-distillation was continued until the distillate no longer turned cloudy on cooling. About 2.5–3.0 l. of distillate were usually collected at this point. The distillation was continued until the distillate amounted to 5.5 l. (fraction B). The residue composed fraction C.

Fraction A gave 6.50 g. (46.1%) of oil (II) which was identified as a mixture of the methyl ester of 1-cyclohexene-1-carboxylic acid (IIa), the methyl ester of 2-cyclohexene-1-carboxylic acid (IIb), and the methyl ester of cyclohexanecarboxylic acid (IIc). A Karl-Fischer titration of 1.00 g. (0.0071 mole) of II revealed the presence of 14 mg. (1.4%) of water. The ultraviolet absorption spectrum of II was determined in methanol, $\lambda_{max.}$, 219 mμ, $E^{1\%}_{1\,cm.}$, 148 (20.2% of IIa).

The isomerization of 1.00 g. (0.0071 mole) of II according to the general procedure of Kon and Linstead[14] in 50 ml. of 0.2 *N* sodium methoxide in methanol was carried out at 25° for 150 hours. After acidification with acetic acid, the ultraviolet absorption of the mixture was determined in methanol, $\lambda_{max.}$, 219 mμ, $E^{1\%}_{1\,cm.}$, 280 (38.3% of IIa).

A solution of II in 50% methanol-water containing 0.1 *M* tetrabutylammonium chloride as an electrolyte was reduced by means of a polarograph at 25°, $E_{1/2}$, −2.062 v., $E'_{1/2}$, −2.284 v.; $(I_d + I'_d)/C$, 6.50 μa./mg./ml. (18.8% of IIa).

Using 0.500 g. of Adams' catalyst, 3.00 g. (0.0213 mole) of II in 100 ml. of methanol was reduced at room temperature under one atmosphere of hydrogen. The hydrogen uptake amounted to 242 ml. or 50.7% of the theoretical amount based on one double bond. After the reduction, 2.73 g. (90%) of the methyl ester of cyclohexanecarboxylic acid was isolated, b.p. 77°/24 mm., n^{25}_{D} 1.4420, and proved to be identical to the authentic sample prepared above by comparison of their infrared spectra.

The acid amide was prepared in 38.5% yield, m.p. 185–186° (m.p. 185–186°, no yield given).[15] A mixture melting point with an authentic sample of cyclohexanecarboxamide, m.p. 185–186°, melted at 185–186°.

Anal. Calc'd for $C_7H_{13}NO$: C, 66.10; H, 10.30. Found: C, 65.95; H, 10.37.

Fraction B was extracted three times with 1.0-l. portions of ethyl ether. The ether extract was dried and concentrated to give 4.52 g. (32.0%) of a viscous oil (III). The molecular weight was determined cryoscopically with benzene as a solvent.

Anal. Calc'd for $C_{16}H_{26}O_4$: Mol. wt., 282.4. Found: Mol. wt., 280.5.

A solution of 4.52 g. (0.0160 mole) of III in 250 ml. of methanol and 40 g. of 85% potassium hydroxide pellets was refluxed for 4 days according to the procedure of Linstead and Doering.[16] The solution then was transferred to an evaporating dish and 250 ml. of water which was first used to rinse the saponification flask was added to it. The mixture was concentrated on a steam-bath in a hood overnight, and the residue was taken up in 250 ml. of water and cautiously acidified with conc'd hydrochloric acid. After cooling, the solution was extracted three times with 250-ml. portions of ethyl ether, and the ether extracts were dried and concentrated to give a white solid product (IV), 3.706 g. (91.1%), m.p. 170–190°.

A large sample of material corresponding to IV was recrystallized in order to isolate samples of the pure perhydrodiphenic acids. A 22.20-g. (0.087 mole) sample was taken up in the minimum of benzene and crystallized to give 14.70 g. (66.2%), m.p. 210–214°. This material was subsequently recrystallized from dilute acetic acid. The fractions obtained were further recrystallized until the majority of the material fell into two fractions.

Fractions melting at 236–239° (IVB) amounted to 5.632 g. (25.4%). Repeated recrystallizations from dilute acetic acid gave material melting at 245–246°. $\lambda^{Nujol}_{max.}$, 5.78 μ, 6.04 μ, (doublet for carboxylic acid) (m.p. 246–248° for *trans-anti-trans* perhydrodiphenic acid).[16]

Anal. Calc'd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72; Neut. equiv., 127.2. Found: C, 66.33; H, 8.99; Neut. equiv., 126.

The anhydride was prepared with acetyl chloride in 60% yield, m.p. 240–242° (m.p. 242°, no yield given).[17]

Fractions melting between 214° and 222° (IVA) amounted to 5.526 g. (24.9%). Repeated recrystallization from dilute acetic acid yielded material melting at 222–223°, $\lambda^{Nujol}_{max.}$ 5.84 μ, 5.92 μ (doublet for carboxylic acid). A mixture melting point with an authentic sample of *trans-syn-trans* perhydrodiphenic acid,[16] m.p. 222–223°, melted at 222–223°. Its infrared spectrum was found to be identical with that of the authentic material.

Anal. Calc'd for $C_{14}H_{22}O_4$: Neut. equiv., 127.2. Found: Neut. equiv., 128.

Fraction C was concentrated to dryness on a steam-bath. A plastic solid was obtained weighing 0.87 g. of which 0.42 g. can be attributed to the charged sodium salt. The remainder 0.45 g. (2.4%), was a non-steam distillable product.

Kolbe electrolysis of methyl hydrogen trans-hexahydrophthalate (IB). A solution of 18.6 g. (0.100 mole) of methyl hydrogen *trans*-hexahydrophthalate in 60 ml. of anhydrous methanol and 10 ml. of 0.20 *N* sodium methoxide was electrolyzed in the same manner as its *cis* isomer. The procedure for the distillation of the *cis* isomer was repeated obtaining identical fractions.

Fraction A gave 6.67 g. (47.3%) of oil (II). A Karl-Fischer titration of 1.00 g. (0.0071 mole) of II revealed the presence of 14 mg. (1.4%) of water.

The ultraviolet absorption spectrum of II was determined in methanol: $\lambda_{max.}$ 219 mμ, $E^{1\%}_{1\,cm.}$, 147 (20.1% of IIa).

A solution of II in 50% methanol-water containing 0.1 *M* tetrabutylammonium chloride as an electrolyte was reduced by a polarograph at 25°. $E_{1/2}$, −2.064 v., $E'_{1/2}$, −2.298 v., $(I_d + I'_d)/C$, 6.50 μa./mg./ml. (18.8% of IIa).

Using 0.500 g. of Adams' catalyst, 3.00 g. (0.0213 mole) of II in 100 ml. of methanol was reduced at room temperature under one atmosphere of hydrogen. The hydrogen uptake amounted to 235 ml. or 49.2% of the theoretical amount based on one double bond.

Fraction B on extraction yielded 4.45 g. (31.5%) of a viscous oil (III).

A solution of 4.45 g. (0.0158 mole) of III was saponified in the same manner as previously described to give 3.50 g. (87.3%), m.p. 160–180° (IV).

Fraction C gave a plastic solid weighing 0.70 g. of which 0.42 g. can be attributed to the charged sodium salt. The remainder, 0.28 g. (1.5%) was a non-steam distillable product.

---

(13) Lumsden, *J. Chem. Soc.*, **87**, 90 (1905).

(14) Kon and Linstead, *J. Chem. Soc.*, 1269 (1929).

(15) Markownikoff, *Ber.*, **25**, 3355 (1892).

(16) Linstead and Doering, *J. Am. Chem. Soc.*, **64**, 1991 (1942).

(17) Linstead and Walpole, *J. Chem. Soc.*, 850 (1939).

Silicic acid adsorption chromatography of the saponification product IV. The procedure used for the silicic acid adsorption chromatography was a modification of the procedures of Marvel and Rands,[18] Marvel and Light,[19] and Baldwin, Loeblich and Lawrence.[20]

A large column similar to that used by Marvel and Light[19] for their water-insoluble acid fraction was developed with a mixture of *n*-butanol and chloroform according to the general procedure of Baldwin, Loeblich, and Lawrence.[20]

(*A*) *Perhydrodiphenic acids from cis-methyl hydrogen hexahydrophthalate.* The finely ground crude IV, 3.402 g. (0.01338 mole) was chromatographed. A plot of the weight of the fraction *versus* the fraction number yielded a chromatogram with two bands, a large broad one and a small one. The infrared spectrum of each fraction was obtained. Infrared analyses demonstrated that the large broad band was composed of only two products, *trans-syn-trans* perhydrodiphenic acid (IVA) and *trans-anti-trans* perhydrodiphenic acid (IVB); the former being initially removed from the column. Infrared analyses also showed that there was a sharp demarcation between the two isomers.

trans-syn-trans-Perhydrodiphenic acid (IVA). The total amount of those fractions whose infrared spectrum corresponded to that of authentic *trans-syn-trans* perhydrodiphenic acid, amounted to 1.466 g. (43.1%).

trans-anti-trans-Perhydrodiphenic acid (IVB). The total of all those fractions whose infrared spectrum corresponded to that of *trans-anti-trans*-perhydrodiphenic acid previously characterized, amounted to 1.410 g. (41.4%).

The small second band found in the weight chromatogram plot which followed the large broad band was found to have an infrared spectrum identical with that of authentic *trans*-hexahydrophthalic acid (VI). This fraction amounted to 0.217 g. (6.4%), m.p. 220–228°. Recrystallization gave a material melting at 227–229°. A mixture melting point with an authentic sample, m.p. 227–229°, melted at 227–229°.

(*B*) *Perhydrodiphenic acids from trans-methyl hydrogen hexahydrophthalate.* The finely ground crude IV, 3.268 g. (0.01285 mole) was chromatographed in the manner described above. The total of all the fractions whose infrared spectrum corresponded to that of *trans-syn-trans* perhydrodiphenic acid (IVA), amounted to 1.436 g. (44.0%). The total of all the fractions whose infrared spectrum was identical with that of *trans-anti-trans* perhydrodiphenic acid (IVB), amounted to 1.399 g. (42.8%).

The total of all the fractions whose infrared spectrum was identical with that of *trans*-hexahydrophthalic acid (VI) amounted to 0.111 g. (3.4%).

RESULTS

The increase in optical density at 220 mμ. during the electrolysis of the half ester of hexahydrophthalic acid is shown in Figure 1. The free acid titer variation during the electrolysis is shown in Figure 2. The optical density and free acid variation for another electrolysis, which started normally, became abnormal (current efficiency dropped to zero), and returned to normalcy after reactivation of the electrodes, is shown in Figure 3 and Figure 4 respectively. The polarographic reduction current for the formaldehyde produced during the electrolysis of sodium methoxide is shown in Figure 5.

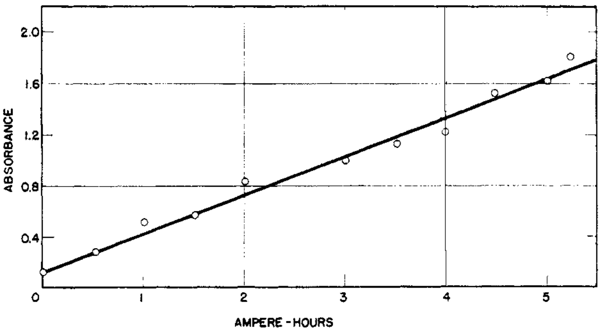


FIG. 1.—THE VARIATION OF ABSORBANCE OF AN ELECTROLYZED SOLUTION AT 220 mμ DURING A NORMAL ELECTROLYSIS.

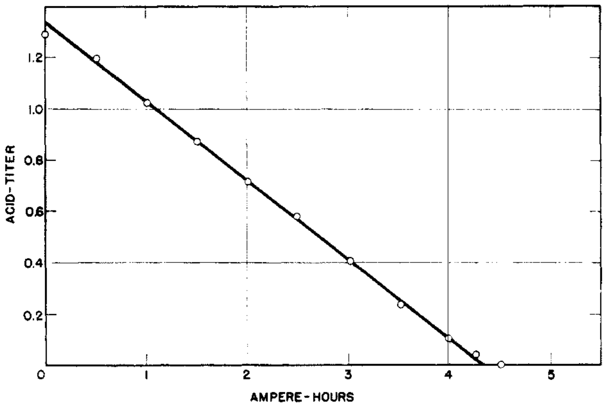


FIG. 2.—THE VARIATION OF ACID TITER OF AN ELECTROLYZED SOLUTION DURING A NORMAL ELECTROLYSIS.

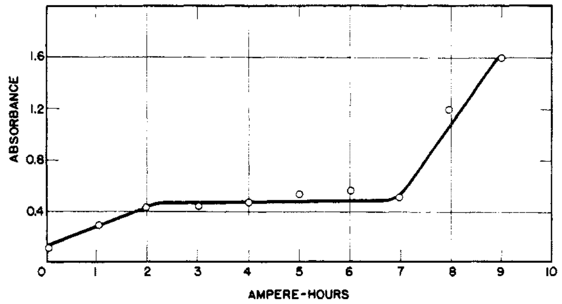


FIG. 3.—THE VARIATION OF ABSORBANCE OF AN ELECTROLYZED SOLUTION AT 220 mμ DURING AN ABNORMAL ELECTROLYSIS. THE ANODE WAS REACTIVATED BEFORE ELECTROLYSIS RETURNED TO NORMAL.

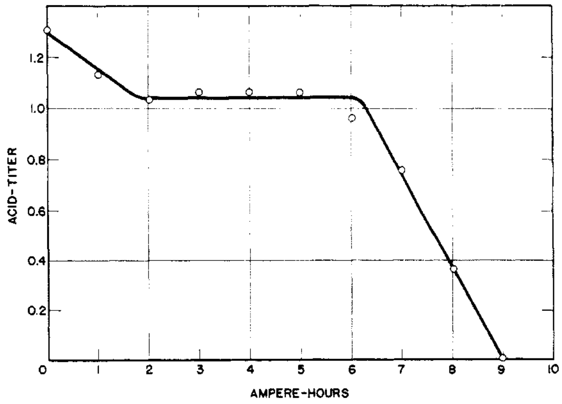


FIG. 4.—THE VARIATION OF ACID TITER OF AN ELECTROLYZED SOLUTION DURING AN ABNORMAL ELECTROLYSIS. THE ANODE WAS REACTIVATED BEFORE ELECTROLYSIS RETURNED TO NORMAL.

---

(18) Marvel and Rands, Jr., *J. Am. Chem. Soc.*, **72**, 2642 (1950).

(19) Marvel and Light, Jr., *J. Am. Chem. Soc.*, **72**, 3887 (1950).

(20) Baldwin, Loeblich and Lawrence, *Anal. Chem.*, **26**, 760 (1954).

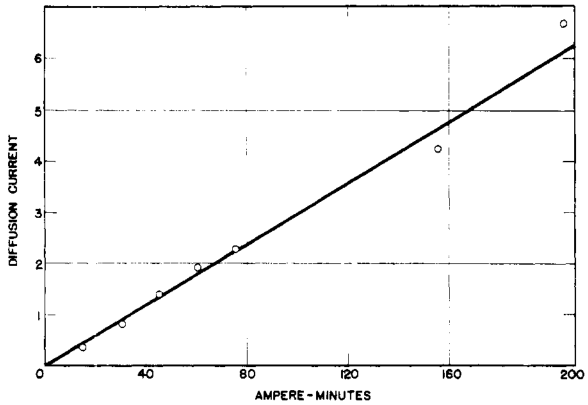


FIG. 5.—THE VARIATION OF POLAROGRAPHIC DIFFUSION CURRENT DUE TO FORMALDEHYDE DURING THE ELECTROLYSIS OF A SODIUM METHOXIDE SOLUTION.

From conductivity measurements, it was found that: (1) The conductivity of alcohols with the same salt concentration varies as follows: water > methanol > ethanol > propanol-2 > > 2-methylpropanol-2. (2) The conductivity of salts of carboxylic acids in methanol varies according to the nature of the cations as follows: potassium > sodium > lithium >> hydrogen. (3) The conductivity in methanol increases linearly with increasing temperature. (4) The conductivities of sodium salts of fatty acids in methanol are very similar, being only slightly greater for the first few members of the series. Sodium methoxide in methanol has only a slightly better conductivity than the acid salts. (5) The presence of free acid decreases the conductivity of its sodium salt solution.

No evidence for the occurrence of isomerization of the methyl hydrogen *cis*-hexahydrophthalate to the *trans*-isomer was found under the conditions of the electrolysis.

Table I lists the yield of monomeric and dimeric products from the Kolbe electrolyses and Table II records the yields of monomeric products.

TABLE I

ELECTROLYSES PRODUCT YIELD

Starting Isomer	Yield, % *cis*	Yield, % *trans*
Uncoupled	46.1	47.3
Coupled	32.0	31.5

TABLE II

COMPOSITION OF UNCOUPLED PRODUCTS (II)

Starting Isomer		Yield, % *cis*	Yield, % *trans*
Unsaturated	α, β	20.5	20.4
	β, γ	30.9	29.5
	Total	51.4	49.9
Saturated		48.6	50.1
		Ratios	
Ratio	$\beta, \gamma/\alpha, \beta$	1.51	1.45
	Sat./Unsat.	0.95	1.00

DISCUSSION

Of the three methods, *p*H, ultraviolet absorption, and free acid titer, the last was found to be the best suited for control work. The need for constant control to follow Kolbe electrolyses is very necessary since occasionally, for no apparent reason, the current efficiency would drop to zero. This was indicated by the fact that there was no further consumption of acid (Fig. 4) and the ultraviolet absorption of the solution remained constant (Fig. 3).

From the conductance data, it was decided to use methanol as a solvent and a sodium salt as the electrolyte. Water was eliminated as a solvent since there was good evidence that it contributed to the previous failure[2] of this Kolbe coupling reaction.

No evidence for the electrochemical reduction of α,β-unsaturated esters was found during the electrolysis in the diaphragmless cell using smooth platinum electrodes. The ultraviolet absorption of the solution during excessive electrolysis under both acidic and basic conditions did not change. The fact that the ultraviolet absorption increased linearly with increase in ampere-hours (Fig. 2) instead of falling off gradually at the higher optical densities also substantiates these results.

The Kolbe reaction takes place at the anode where the anions with the lowest oxidation potentials are discharged. There are two possible anions present in methanol, the carboxylate ($RCOO^-$) and the methoxide (CH_3O^-). The auto-ionization constant for methanol[21] is 10^{-16} as compared with 10^{-14} for water at 25°.

Since the current efficiency, the equivalents of acid consumed per faraday, was found to be about 50%, side reactions must be taking place which involve either: (a) The discharge of another anion, the methoxide in this case or (b) the regeneration of the carboxylate ion.

The first would yield the methoxide radical which then could undergo the usual radical reactions:[22]

1. Hydrogen Abstraction

$$CH_3O\cdot + RH \longrightarrow CH_3OH + R\cdot$$

2. Disproportionation

$$CH_3O\cdot + CH_3O\cdot \longrightarrow CH_2O + CH_3OH$$

3. Coupling

$$CH_3O\cdot + CH_3O\cdot \longrightarrow CH_3OOCH_3$$

Previous workers[23,24] have not reported any of these products. Electrolysis of a methanolic solution of sodium methoxide (Fig. 5) was found to yield formaldehyde in amounts which could account

---

[21] McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).

[22] Rieche, *Ber.*, **61**, 951 (1928).

[23] Szilard, *Z. Electrochem.*, 12, 393 (1906).

[24] Giacomello and Lentini, *Gazz. chim. ital.*, **66**, 350 (1936).

for about 90% of the current. No dimethyl peroxide, which polarographically reduces before formaldehyde, was found.

An alternate explanation for the low current efficiency during the Kolbe electrolyses, the regeneration of carboxylate ion, involves only hydrogen abstraction.

$$R'COO^- \xrightarrow{-e} R'COO\cdot$$

$$R'COO\cdot + RH \longrightarrow R'COOH + R\cdot$$

$$R'COOH \xrightarrow{-H^+} R'COO^-$$

Here RH as before would predominantly represent the solvent methanol, which would yield the hydroxymethyl radical, which then could undergo the usual radical reactions:

1. Hydrogen abstraction

$$\cdot CH_2OH + RH \longrightarrow CH_3OH + R\cdot$$

2. Disproportionation

$$\cdot CH_2OH + \cdot CH_2OH \longrightarrow CH_2O + CH_3OH$$

3. Coupling

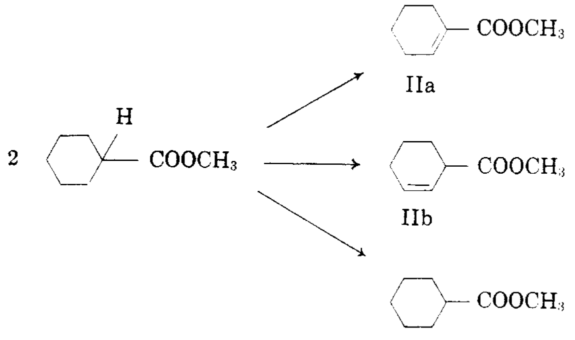
$$\cdot CH_2OH + \cdot CH_2OH \longrightarrow HOCH_2CH_2OH$$

Since both alternatives for the low current efficiency of the Kolbe electrolyses yield the same reaction product, formaldehyde, there is no way of deciding which plays a predominant part from the reaction products alone.

It is interesting to note that although no dimethyl peroxide or ethylene glycol was found in any of the Kolbe electrolyses mixtures, the amount of formaldehyde found could only account for 5–10% of the faradays consumed, thus this is not a reasonable explanation for the low current efficiency. Urry[25] recently reported the formation of acetaldehyde in Kolbe electrolyses carried out in anhydrous ethanol and could only account for 50% of the current.

A careful examination of Fichter and Simon's[2] paper revealed that the conditions under which they had carried out their Kolbe electrolysis of methyl hydrogen *trans*-hexahydrophthalate were unfavorable for a Kolbe coupling reaction, but favorable for a Hofer-Moest[26] reaction; thus, water and potassium bicarbonate were present during the electrolysis. Fichter and Holbro[3] used anhydrous methanol and the sodium salt of the acid in their Kolbe electrolysis of the isomeric methyl hydrogen *trans*-hexahydroterephthalate and obtained some coupled products. As noted, the electrolyses of the methyl hydrogen hexahydrophthalates reported here were carried out with anhydrous methanol and the sodium salt of the acid.

The electrolyses of the half esters of both the *cis*- and *trans*-hexahydrophthalic acids yielded predominantly monomeric products. The ratio of saturated to unsaturated monomeric products was found to be about 1:1. This is in contrast to Kolbe electrolyses carried out in aqueous systems where saturated monomeric products have never been found. This 1:1 ratio from methanolic systems has been obtained by Linstead, Lunt, and Weedon[27] and Ställberg-Stenhagen.[28] The latter author assumed that the high amount of saturated monomeric product was due to reduction in the electrolysis cell without a diaphragm. It has been found here that no electrochemical reduction of α,β-unsaturated esters takes place under the conditions of the experiments. The 1:1 saturated to unsaturated monomeric product ratio would indicate that the disproportionation of the secondary radical from the electrolysis is the source of the monomeric material.



IIa

IIb

IIc

Kolbe electrolyses are characterized by high yields of coupled product when α-substituted carboxylic acids, RCH_2COOH, are used. When the acid is disubstituted on the α-carbon, RR'—CHCOOH, as in the present case, disproportionation seems to play a more important role.

The total amount of unsaturation was determined by quantitative hydrogenation. Since the methyl ester of cyclohexanecarboxylic acid was isolated in 90% yield, it is clear that only the methyl ester of cyclohexanecarboxylic acid and the isomeric methyl esters of 1-cyclohexene-1-carboxylic acid could make up the monomeric product. The refractive index of the isolated methyl ester of cyclohexanecarboxylic acid did not agree with the value reported in the literature and consequently, this ester was characterized and prepared independently by reducing the methyl ester of 1-cyclohexene-1-carboxylic acid. Since our saturated ester has a lower refractive index, it is possible that the material reported in the literature which was obtained by the reduction of an aromatic ring, was contaminated with unsaturates.

Disproportionation gives two unsaturated products, an α, β, and a β, γ unsaturated ester. The

---

[25] Urry, paper presented before the *108th Meeting of the Electrochemical Society*, Pittsburgh, Pennsylvania, October, 1955.

[26] Hofer and Moest, *Ann.*, **323**, 284 (1902).

[27] Linstead, Lunt, and Weedon, *J. Chem. Soc.*, 1130 (1951).

[28] Ställberg-Stenhagen, *Arkiv Kemi*, **2**, 95 (1950).

former being conjugated, has appreciable ultraviolet absorption and is polarographically reducible. The amount of α, β isomer was determined by ultraviolet absorption and polarographic data which indicated that only about 20% of the monomeric product was the α, β unsaturated ester. This would indicate that the predominant unsaturated product (30%) is the β, γ unsaturated ester.

Isomerization of the monomeric material in methanol with sodium methoxide doubled the α, β unsaturated ester content. Considering the possibility of side reactions such as methyl ether formation[14] and hydrolysis and the equilibrium of α, β and β, γ isomers in basic solution,[29] the increase in the α, β unsaturated ester content probably accounts for most of the β, γ isomer present.

The β, γ to α, β unsaturated ester ratio was rather unexpected since the displacement on the tertiary hydrogen on the carbon α to the ester group might be favored by either a consideration of the increased driving force for obtaining the α, β isomer in the transition state as the hydrogen is removed, or by the difference in bond strengths between a tertiary and secondary hydrogen. The results indicate that a steric factor which has the opposite effect operates in this radical displacement reaction. Although the α, β, and γ carbon atoms should nearly be in the same plane, molecular models indicate that the equatorial hydrogen on the γ-carbon should be the easiest to remove.

The total amount and the ratio of the saturated and unsaturated monomeric products were found to be independent of the isomer of the methyl hydrogen hexahydrophthalate. The probability that this may be due to a possible isomerization of the *cis* half ester to the *trans* isomer under the conditions of the experiment has been eliminated. *Thus no evidence of stereospecificity was found in this reaction.*

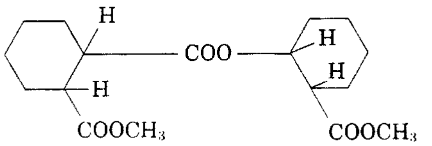
The coupling reaction can give the following isomeric products. If the radical would maintain its stereoidentity,[30] then the *cis-syn-cis* and *cis-anti-cis* perhydrodiphenic esters would result from the *cis* compound and *trans-syn-trans* and *trans-anti-trans* from the *trans* isomer. If the radical loses its tetrahedral configuration then all six diastereomeric perhydrodiphenic esters will result. For the convenience of isolation, the dimeric products were saponified following the directions of Linstead and Doering[16] to yield perhydrodiphenic acids. During the saponification, inversion takes place at the α carbons to form the stable *trans* configurations wherever possible and thus no conclusions as to the stereochemistry of the original radical can be deduced. Further work with optically active forms of the *cis* and *trans* isomers is in progress.

If these inversions take place quantitatively, the ester isomers will be reduced to two acid isomers, *trans-anti-trans* and *trans-syn-trans*.

Both isomers have been isolated by fractional crystallization from dilute acetic acid solution and have been found to agree with the properties reported by Linstead, *et al.*[16] The ratio has been found to be approximately 1:1 but the amount recovered only accounted for about 50% of the Koble coupled product fraction. Other methods were investigated for the separation of these acids. Marvel and Rands[18] developed a satisfactory method for separating organic acid mixtures by means of partition chromatography. Marvel and Light[19] and Baldwin, Loeblich, and Lawrence[20] modified the method of Marvel and Rands. The former[19] eliminated water from their chromatographic columns when they were used for the separation of water-insoluble acids. The latter[20] increased the polarity of the developing solvent in increments of 1% butanol instead of 5% butanol. Both these modifications were useful in separating the two perhydrodiphenic acids.

The saponified Kolbe coupled product (IV) from both the *cis* and the *trans* isomers of methyl hydrogen hexahydrophthalate were separated on a silicic acid column. The relative amounts of the *trans-syn-trans* and the *trans-anti-trans* isomers represented 85% of the crude saponified mixture.

Another product that was isolated as a distinct band from the chromatographic column was *trans*-hexahydrophthalic acid. This could result from two sources; further esterification of the starting half-ester followed by inversion or disproportionation or radical combination of the alkoxy radicals. In this latter case, the intermediate (VII) would yield *trans*-hexahydrosalicyclic acid as well as



VII

trans-hexahydrophthalic acid. Since none of the hexahydrosalicyclic acid was isolated, it is assumed that the further esterification of the half esters was the predominant source for the *trans*-hexahydrophthalic acid.

BROOKLYN 1, N. Y.

---

(29) Boorman and Linstead, *J. Chem. Soc.*, 258 (1935).

(30) We are indebted to one of the referees for a correction of the stereochemical interpretation.