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A STUDY OF THE KOLBE ELECTROLYSIS
USING MIXED MONO-ETHYL GLUTARATE
AND MONO-ETHYL MALONATE

BY

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THIS THESIS

SUBMITTED BY

Richard Gilbert

TO THE

DEPARTMENT OF CHEMISTRY
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OF THE DEGREE OF

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William B. Martin, Jr.

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INTRODUCTION

THE STUDY OF ELECTROLYTIC REACTIONS OF ORGANIC COMPOUNDS WAS FIRST ATTEMPTED SOON AFTER THE DISCOVERY OF THE ELECTROLYSIS OF WATER IN 1800. THESE REACTIONS WERE NOT USED IN SYNTHESIS UNTIL AFTER 1847 WHEN KOLBE DISCOVERED THAT ALIPHATIC HYDROCARBONS COULD BE MADE BY THE ELECTROLYSIS OF THE SALTS OF ALIPHATIC ACIDS. THE FIELD HAS GREATLY INCREASED SINCE THEN, AND IT IS NOW POSSIBLE TO CARRY OUT SYNTHESIS BY ELECTROLYTIC REDUCTION, OXIDATION, CATHODIC COUPLING, ANODIC COUPLING, AND SUBSTITUTION.

IT WAS THE PURPOSE OF THIS WORK TO ATTEMPT ONE MIXED KOLBE REACTION AND ANALYZE ITS PRODUCTS QUALITATIVELY NOT QUANTITATIVELY. IF TIME PERMITTED, QUANTITATIVE ANALYSES WOULD BE ATTEMPTED.

HISTORY

THE KOLBE ELECTROLYSIS, AS HAS BEEN PREVIOUSLY MENTIONED, IS NOT A NEW PROCESS; BUT MORE INTENSE INQUIRIES INTO THE NATURE OF THE SYNTHESIS HAVE BEEN MADE QUITE RECENTLY. AS A BASIS FOR THE UNDERSTANDING OF THE KOLBE REACTIONS, G. W. THIESSEN (10) HAS WRITTEN AN EXCELLENT PAPER, THE BASIC FACTS OF WHICH WILL BE INCORPORATED IN THIS PAPER. THIESSEN SETS DOWN IN HIS PAPER THREE BASIC THEORIES WHICH ARE SAID TO ACCOUNT FOR THE REACTIONS.

THE FIRST OF THESE THEORIES STATES THE HYDROGEN PEROXIDE, FORMED BY THE ELECTROLYSIS OF WATER, REACTS WITH THE RCOOH OR (RCOO^-) , ITS ION, TO PRODUCE THE DESIRED PRODUCTS. ANOTHER THEORY IS THAT OXYGEN TRANSFERRED FROM THE ANODE TO THE ACID PRODUCES THE DESIRED PRODUCTS. THE FINAL THEORY, WHICH SEEMS TO BE THE MOST LIKELY, IS THAT THE FREE RADICAL $\text{RCOO}\cdot$, FORMED BY ELECTRON REMOVAL FROM THE ACID ION RCOO^- , COMES FIRST. $\text{R}\cdot$ IS FORMED NEXT BY LOSS OF CO_2 AND FURTHER REACTS TO FORM THE PRODUCTS.

THE OPTIMUM CONDITIONS FOR OPERATION AS SUGGESTED BY THIESSEN ARE AS FOLLOWS:

- A) THE ANODE SHOULD BE OF SMOOTH PLATINUM.
- B) THE TEMPERATURE SHOULD BE LOW.
- C) THE CONCENTRATIONS OF THE REACTANTS SHOULD BE HIGH.
- D) THE FREE ACID SHOULD BE IN EXCESS.
- E) THE SALT CONCENTRATION SHOULD BE HIGH.
- F) THE SUGGESTED VOLTAGE SHOULD BE ABOUT 1.7 TO 2 VOLTS.

EVEN USING THESE CONDITIONS, REACTIONS ARE USUALLY OF LOW EFFICIENCY, AND THE PRODUCTS FORMED MAY BE HARD TO PURIFY.

IN LIEU OF THESE CONDITIONS THERE ARE STILL THREE MAJOR INHIBITIONS THAT PREVENT THE KOLBE ACTION:

- A) THE ETHENOID TYPE
- B) THE BENZENOID TYPE
- C) THE CYCLOHEXANOID TYPE.

THE RELATIVE ORDER OF STRENGTH OF THESE INHIBITIONS IS BENZENOID > CYCLOHEXANOID > ETHENOID.

THESE THREE INHIBITIONS HAVE BEEN STUDIED IN GREAT DETAIL BY MANY MEN DURING THESE PAST YEARS. B. E. CONWAY AND M. DZIECIUCH (2) HAVE MADE CAREFUL STUDIES OF THE ETHENOID INHIBITIONS. THEY HAVE ALSO STUDIED THE EFFECT OF DIFFERENT MEDIA IN WHICH THE KOLBE ELECTROLYSIS IS RUN. AN EXAMPLE OF ONE OF THEIR EXPERIMENTS IS THE REACTION OF THE TRIFLUOROACETATE ION IN 100% TRIFLUOROACETIC ACID; A DECARBOXYLATION AND COUPLING REACTION, YIELDING HEXAFLUROETHANE. FROM THEIR DATA IT HAS BEEN SHOWN THAT DECARBOXYLATIONS IN AQUEOUS MEDIA ARE MORE COMPLEX REACTIONS THAN WHEN RUN IN ORGANIC SOLVENTS.

THIS RESULT HAS BEEN VERIFIED BY FLOYD RAWLINGS, GARRETT THEISSEN AND DEAN PETERSON IN THEIR RECENT PAPER ON THE CYCLOHEXANOID INHIBITION (9). POTASSIUM CYCLOHEXANE CARBOXYLATE AND UNINHIBITED POTASSIUM ACETATE WERE COMBINED IN WATER AT VARIOUS CONCENTRATIONS. AFTER ELECTROLYSIS HAD BEEN COMPLETED, A LIGHT YELLOW VISCOUS OIL WAS FORMED. IDENTIFICATION OF THE COMPONENTS OF THE OIL BY VAPOR-PHASE CHROMATOGRAPHY AND INFRA-RED SPECTROSCOPY, AND BY PHYSICAL PROPERTIES (BOILING POINT, INDEX OF REFRACTION, ETC.) WAS MADE, AND CONSTITUENTS WERE FOUND TO BE:

- | | |
|-----------------------|-------------------------|
| A) CYCLOHEXANE | (R-H) |
| B) METHYLCYCLOHEXENE | (R-R') |
| C) CYCLOHEXANOL | (R-OH) |
| D) CYCLOHEXYL ACETATE | (CH ₃ COOR') |
| E) DICYCLOHEXYL | (R-R) |
| F) CYCLOHEXANONE | (ROH - 2H) |

IT IS SUPPOSED THAT THESE PRODUCTS WERE FORMED BY THE MECHANISM PROPOSED IN THE THIRD THEORY THAT WAS MENTIONED PREVIOUSLY, (I.E., BY FREE RADICALS COMBINING OR ABSTRACTING HYDROGEN OR OXYGEN). AS A SIDE NOTE, THE GASES THAT WERE COLLECTED AT THE ANODE WERE FOUND TO BE CARBON DIOXIDE, OXYGEN, METHANE, AND ETHANE. AS CAN BE SEEN FROM THE ABOVE RESULTS, AQUEOUS SOLUTIONS CAN BECOME QUITE A PROBLEM WHEN IDENTIFICATION OR ISOLATION OF PRODUCTS IS NEEDED.

A METHOD OF GETTING AROUND THIS DIFFICULTY HAS BEEN SUGGESTED BY F. FICHTER (4); BY CHANGING THE SOLVENT FROM WATER TO METHANOL-WATER, TO METHANOL-WATER-PYRIDINE, TO PYRIDINE ALONE, HE HAS ELIMINATED THE BENZENOID AND CYCLOHEXANOID INHIBITIONS, AND HAS IN ALL CASES RECORDED, SHOWN R-R SYNTHESIS WITH CARBON DIOXIDE EVOLUTION.

ELECTROCHEMICAL EXPERIMENTAL WORK HAS BEEN DONE IN MANY FIELDS BESIDES THAT PART OF ORGANIC INVOLVING CARBOXYLIC ACIDS OR THEIR ESTERS. FOR EXAMPLES, THE BOOK BY LOUIS MEITES (7) ON THE USE OF POLAROGRAPHY DEALS WITH ANALYTICAL ELECTROLYTIC WORK WITH OXIDATION AND REDUCTION OF MANY ORGANIC AND FUNCTIONAL COMPOUNDS BESIDES CARBOXYLIC ACIDS. J. A. BUTLER (1) IN HIS BOOK DISCUSSES VARIOUS REACTION MECHANISMS THAT TAKE PLACE AT THE SURFACE OF BOTH THE ELECTRODES AND IN THE SOLVENT. FRANK D. POPP AND

HARRY P. SCHULTZ (8) RECENTLY DELVED INTO THE ELECTROLYTIC REDUCTION OF ORGANIC COMPOUNDS. IN ALL THESE INSTANCES, THE REACTIONS AND THEORIES CAN BE RELATED IN SOME MANNER TO THIS WORK, BUT THEIR SPECIFIC EXPERIMENTS ARE QUITE DIFFERENT. IN THIS WAY THEY HAVE SOME INTEREST TO READERS CONCERNED WITH THE BACKGROUND FOR THIS THESIS.

EXPERIMENTAL

THE EXPERIMENTAL DATA OF THIS PAPER HAS BEEN DIVIDED INTO THREE PARTS. THE FIRST TWO PARTS DEALING WITH THE PREPARATION OF THE TWO REACTANTS, AND THE THIRD PART DEALING WITH THE ELECTROLYSIS ITSELF.

PART I PREPARATION OF MONO-ETHYL GLUTARATE ($C_2H_5OOC-(CH_2)_3-COOH$)

TO 114 GMS. (1 MOLE) OF GLUTARIC ANHYDRIDE, 150 ML. OF ABSOLUTE ETHANOL WAS ADDED, AND THE SOLUTION AFTER THOROUGH MIXING WAS ALLOWED TO STAND FOR A WEEK. IN THIS WAY THE CHANCES OF ANY ANHYDRIDE REMAINING OUT OF SOLUTION WERE MINUMIZED. THE RESULTANT MIXTURE WAS THEN ADDED TO 100 ML. OF ETHER AND PUT IN A SEPARATORY FUNNEL. APPROXIMATELY 5% SODIUM HYDROXIDE WAS THEN ADDED IN SIX 25 ML. ALIQUOTS IN ORDER TO TAKE UP THE HALF-ESTERS AND THE DI-ACID THAT SHOULD HAVE BEEN FORMED IN THE INITIAL REACTION. THE AQUEOUS LAYER WAS DRAWN OFF EACH TIME AND FOUND TO BE ACIDIC INDICATING THE PRESENCE OF THE DESIRED HALF ACID. NO TRACE OF EXCESS BASE WAS AS YET FOUND. A 30 ML. ALIQUOT OF NaOH WAS THEN ADDED. THE SOLUTION DIVIDED UP INTO TWO DISTINCT LAYERS. THE TOP ONE CONTAINING ETHER AND DISSOLVED ANHYDRIDE WAS PALE YELLOW, THE BOTTOM ONE WAS COLORLESS. AS A SAMPLE TEST 30 ML. MORE OF SODIUM HYDROXIDE WAS PLACED IN THE FUNNEL AND ONCE AGAIN THE RESOLVING INTO TWO LAYERS TOOK PLACE BUT NOT AS DISTINCTLY AS BEFORE. IN THIS EXTRACTION THE SOLUTION DRAINED OFF WAS ACIDIC. AFTER SIX OR SEVEN OF THESE EXTRACTIONS THE ETHER LAYER SLOWLY BECAME CLEAR AND THE EXTRACTION SOLUTION BECAME BASIC.

THE AQUEOUS EXTRACT BEING BASIC, WAS NOW ACIDIFIED WITH DILUTE HCl TO A PH OF 1-2. THIS SOLUTION CONTAINING THE MONO-ESTER AND DI-ACID WAS EXTRACTED SIX TIMES WITH 30 ML. ALIQUOTS OF ETHER IN ORDER TO ETHER-EXTRACT

THE MONO-ESTER. THE ETHER SOLUTION WAS THEN FILTERED THROUGH ANHYDROUS Na_2SO_4 AND THEN DISTILLED. AT $157^\circ - 160^\circ\text{C}$ A PALE YELLOW LIQUID CAME OVER AND WAS COLLECTED. THE TOTAL AMOUNT COLLECTED WEIGHED 60.06 GMS. A NEUTRALIZATION EQUIVALENT WAS RUN ON THIS SUBSTANCE. A 1.0218 GM. SAMPLE OF THIS MATERIAL WAS TITRATED WITH .219 N SODIUM HYDROXIDE, USING PHENOLPHTHALEIN AS AN INDICATOR. THE SAMPLE REQUIRED 29.39 ML. OF SODIUM HYDROXIDE. AS A CHECK ANOTHER SAMPLE WEIGHING 1.0469 GMS. WAS TITRATED WITH THE SAME BASE AND INDICATOR AND REQUIRED 30.18 ML. OF NaOH . BELOW ARE CALCULATIONS:

A. FOR 1.0218 GMS. OF MONO-ETHYL GLUTARATE ($\text{MW}=160$)

$$(\text{VOLUME}) \times (\text{NORMALITY}) = \text{MILLIEQUIVALENTS}$$

$$(29.39 \text{ ML}) \times (.219 \text{ N}) = 6.43 \text{ MEQ.}$$

$$\text{MOLECULAR WT.} = \frac{1.0218}{6.43} \times 1000 = 158.8$$

B. FOR 1.0469 GM. OF MONO-ETHYL GLUTARATE ($\text{MW}=160$)

$$(\text{VOLUME}) \times (\text{NORMALITY}) = \text{MILLIEQUIVALENTS}$$

$$(30.18 \text{ ML}) \times (.219 \text{ N}) = \text{MILLIEQUIVALENTS } (6.60)$$

$$\text{MOLECULAR WT.} = \frac{1.0469}{6.60} \times 1000 = 158.2$$

$$\text{AVERAGE MW} = 158.5$$

$$\% \text{ PURITY} = \frac{158.5}{160.0} \times 100 = 99.0\% \text{ "PURE"}$$

THE BOILING POINT AS REPORTED BY A HANDBOOK (5) IS $160^\circ - 165^\circ\text{C}$.

TO ATTEMPT TO VERIFY THE FACT FURTHER SEVERAL $5\mu\text{l}$ SAMPLE RUNS WERE MADE ON THE VAPOR-PHASE CHROMATOGRAPH. THE HELIUM FLOW RATE WAS ADJUSTED TWO UNITS ON THE PERKINS AND ELMER COMPANY FLOW METER AND THE PRESSURE IN THE INSTRUMENT WAS 10 POUNDS OVER 1 ATMOSPHERE. THE RECORDING VOLTAGE WAS 7.95 VOLTS. THE TEMPERATURE WAS SET AT 165°C USING A (PERKINS AND ELMER

COMPANY) "R" COLUMN. AT THE END OF ONE MINUTE A SMALL AIR PEAK WAS EVIDENT. AT 3 MINUTES A PEAK OF 46 x 2 CAME OFF. AT 5 MINUTES A STRONGER PEAK OF 60 x 2 CAME OFF. THEN AT 6 MINUTES A WIDE SPREAD PEAK BECAME EVIDENT, RISING TO 30 x 1 BUT EXTENDING OVER A CONSIDERABLE AREA. FROM SUCCESSIVE RUNS ON SAMPLES VARYING THE WATER AND ETHANOL CONCENTRATIONS, TWO OF THE PEAKS WERE IDENTIFIED AS WATER AND ETHANOL. THE 3 MINUTE PEAK WAS TAKEN TO BE ACETONE BECAUSE THE SYRINGE WAS RINSED OUT WITH IT EACH TIME. THE 5 MINUTE PEAK WAS ETHANOL, AND THE 6 MINUTE PEAK, WATER. REPRODUCIBILITY OF THE CHROMATOGRAMS WAS VARIABLE. THE PRODUCT WAS ASSUMED TO BE THE DESIRED MONO-ETHYL GLUTARATE, ON THE BASIS OF BOILING POINT AND NEUTRALIZATION EQUIVALENT ALONE.

PART II PREPARATION OF MONO-ETHYL MALONATE ($C_2H_5OOC-CH_2-COOH$)

TO 132 GMS. (1 MOLE) OF DI-ETHYL MALONATE, 40 GMS. OF SODIUM HYDROXIDE, 60 ML. OF 95% ETHANOL AND 100 ML. OF WATER WERE ADDED, AND THE MIXTURE WAS REFLUXED FOR TWO TO THREE HOURS. THE MIXTURE THEN SEPARATED INTO TWO LAYERS, ONE AQUEOUS AND ONE ALCOHOLIC. THE AQUEOUS LAYER WAS DRAINED OFF AND PUT ASIDE. THE ALCOHOLIC LAYER WAS DISTILLED AT $80^{\circ}-90^{\circ}C$, AND THEN RESIDUE LEFT AFTER DISTILLATION WAS EXTRACTED WITH 100 ML. OF ETHER AND 25 ML. OF 10% SODIUM BICARBONATE SOLUTION. THE ETHER WAS ONCE AGAIN RE-EXTRACTED WITH 25 ML. OF THE BICARBONATE. THEN THE AQUEOUS LAYER, WHICH HAD BEEN PUT ASIDE, WAS ADDED TO THIS BICARBONATE SOLUTION. THIS NEW SOLUTION WAS CAREFULLY ACIDIFIED TO A PH OF 1-2 WITH DILUTE HCl. THEN IT WAS EXTRACTED WITH 30 ML. ALIQUOTS OF ETHER SEVERAL TIMES TO MAKE SURE THAT ALL THE MONO-ESTER WOULD BE TAKEN UP. ANY MALONIC ACID ITSELF IS FAR MORE SOLUABLE IN WATER THAN IN ETHER. FINALLY, THE ETHER SOLUTION WAS PLACED IN A HOOD AND THE

ETHER ALLOWED TO EVAPORATE. AFTER THE ETHER WAS DRIVEN OFF, 24.14 GMS. OF SUBSTANCE REMAINED. THE REFRACTIVE INDEX OF THIS MATERIAL WAS TAKEN AND ALSO THE BOILING POINT. THEY WERE COMPARED WITH THE VALUES FOUND IN A HANDBOOK (5). THE OBSERVED VALUE OF THE REFRACTIVE INDEX TAKEN AT 25°C WAS 1.4251. THE OBSERVED BOILING POINT WAS 143°-144°C. THE VALUES OBTAINED FROM THE HANDBOOK AND CORRECTED TO THE LABORATORY CONDITIONS WERE 1.4250 FOR THE REFRACTIVE INDEX, AND 145°C FOR THE BOILING POINT. A NEUTRALIZATION EQUIVALENT OF THIS SUBSTANCE WAS ALSO RUN. A 1.0245 GM. SAMPLE OF THIS MATERIAL WAS TITRATED WITH .170N SODIUM HYDROXIDE USING PHENOLPHTHALEIN AS AN INDICATOR. IT REQUIRED 49.25 ML. OF BASE. ONCE AGAIN A CHECK SAMPLE WAS RUN USING THE SAME INDICATOR AND BASE.

THE 1.0223 GM. SAMPLE REQUIRED 49.10 ML. OF BASE. BELOW ARE THE RESULTS.

- A. FOR 1.0245 GM. OF MONO-ETHYL MALONATE (MW=132)

$$(\text{VOLUME}) \times (\text{NORMALITY}) = \text{MILLIEQUIVALENTS}$$

$$(49.25 \text{ ML.}) \times (.170\text{N}) = 8.372 \text{ MEQ.}$$

$$\text{MOLECULAR WT.} = \frac{1.0245}{8.372} \times 1000 = 122.2$$

- B. FOR 1.0223 GM. OF MONO-ETHYL MALONATE (MW=132)

$$(\text{VOLUME}) \times (\text{NORMALITY}) = \text{MILLIEQUIVALENTS}$$

$$(49.10 \text{ ML.}) \times .170\text{N} = 8.347 \text{ MEQ.}$$

$$\text{MOLECULAR WEIGHT} = \frac{1.0223}{8.347} \times 1000 = 122.4$$

$$\text{AVERAGE MOLECULAR WEIGHT} = 122.35$$

$$\% \text{ PURITY} = \frac{122.35}{132.00} \times 100 = 92.4\% \text{ "PURE"}$$

A VAPOR-PHASE CHROMATOGRAPH WAS RUN ALSO ON THIS SUBSTANCE. THE SETTINGS ON THE INSTRUMENT WERE THE SAME AS WHEN THE OTHER RUN WAS MADE EXCEPT THAT

THE TEMPERATURE IN THIS RUN WAS SET AT 145°C . AT THE END OF 1 MINUTE A PEAK OF 98×16 WAS ENCOUNTERED. AT 4 MINUTES A PEAK OF 78×8 SHOWED UP. AT 19 MINUTES A WIDE PEAK OF 31×1 SHOWED UP, SIMILAR TO THAT FOUND IN THE GLUTARATE. FINALLY, AT 56 MINUTES, ANOTHER WIDE PEAK OF 26×1 WAS OUTLINED. THESE PEAKS WERE REPRODUCIBLE IN THREE RUNS, BUT OWING TO THE IMPURITIES IN THE UNKNOWN THEY WERE UNABLE TO BE POSITIVELY IDENTIFIED. THE PEAK AT 4 MINUTES WAS TAKEN TO BE ETHYL ACETATE BY RUNNING PURE ETHYL ACETATE AND WATCHING FOR ITS PEAKS. THE ETHYL ACETATE IS BELIEVED TO OCCUR DUE TO DECARBOXYLATION IN THE INJECTION PORT OF THE VAPOR-PHASE FRACTOMETER COLUMN, WHERE TEMPERATURES ARE PROBABLY 10°C HIGHER THAN THE COLUMN PROPER; MONO-ETHYL MALONATE IS REPORTED TO DECARBOXYLATE AT 155°C , A LITTLE ABOVE ITS BOILING POINT. THE PEAKS AT 19 MINUTES AND 56 MINUTES COULD HAVE BEEN THE MONO-ESTER AND DI-ACID RESPECTIVELY, BUT THERE WAS NO DEFINITE WAY TO VERIFY THAT AT THAT TIME.

ON THE BASIS OF THE SYNTHETIC METHOD, THE BOILING POINT AND REFRACTIVE INDEX, AND THE NEUTRALIZATION EQUIVALENT, THE SUBSTANCE COLLECTED WAS ASSUMED TO BE MONO-ETHYL MALONATE.

PART III

THE ELECTROLYSIS

THE APPARATUS USED IN THE KOLBE ELECTROLYSIS IS QUITE SIMPLE. THE DIAGRAMS ON THE FOLLOWING PAGES WILL BEAR THIS OUT. IT SHOULD BE NOTED THAT TWO ELECTROLYSES WERE CARRIED OUT. THE FIRST RUN INVOLVED AN AQUEOUS MEDIA, AND THE SECOND INVOLVED AN ORGANIC SOLVENT. FIGURE A IS THE APPARATUS FOR THE AQUEOUS ELECTROLYSIS, AND FIGURE B IS THAT FOR THE ORGANIC SOLVENT RUN. FIGURE C IS A SCHEMATIC DIAGRAM SHOWING THE ELECTRICAL CIRCUITRY OF THE SYSTEM.

IN THE AQUEOUS RUN, 14.3 GMS. (.089 MOLES) OF THE MONO-ETHYL GLUTARATE WERE ADDED TO 11.7 GMS. (.089 MOLES) OF THE MONO-ETHYL MALONATE SO THAT THE SOLUTION CONTAINED .178 MOLES OF REACTIVE SUBSTANCES. THEN .107 MOLES OF POTASSIUM HYDROXIDE AND 250 ML. OF WATER WERE ADDED TO MAKE .107 MOLES OF THE POTASSIUM SALT OF THE MONO-ESTERS AND .071 MOLES OF EXCESS MONO-ACIDS. THE ELECTRODES USED WERE OF SHINY PLATINUM. THE ANODE BEING A THIN SHEET OF PLATINUM FOIL AND THE CATHODE A #22 PLATINUM WIRE, BOTH BEING SEPARATED BY A SHEET OF MYLAR INSULATION. THE VOLTAGE FOR THE REACTION WAS 3.7 VOLTS. THE REASON THAT 1.7 VOLTS WAS NOT USED WAS THAT THE RESISTANCE OF THE SOLUTION WAS NEARLY 3.0×10^4 OHMS. FOR THIS REASON THE CURRENT GOING THROUGH THE SYSTEM WAS NOT HIGH ENOUGH TO MAKE THE RUN IN A REASONABLE AMOUNT OF TIME. THE VOLTAGE WAS BY AN ORDINARY SEARS-ROEBUCK 6-VOLT CAR BATTERY. THE REACTION MIXTURE WAS SURROUNDED BY A COLD WATER JACKET AND WAS ELECTROLYZED FOR $43\frac{1}{4}$ HOURS. AT THE END OF THIS TIME, A LIGHT YELLOW OIL HAD FORMED ON THE TOP OF THE REACTING SOLUTION. THE OIL WAS COLLECTED AND ANALYZED BY VAPOR-PHASE CHROMATOGRAPHY. THE COLUMN USED WAS AN "R" COLUMN UNDER THE SAME CONDITIONS AS THE MONO-ESTERS HAD BEEN RUN. A PATTERN SIMILAR TO THE MALONATE

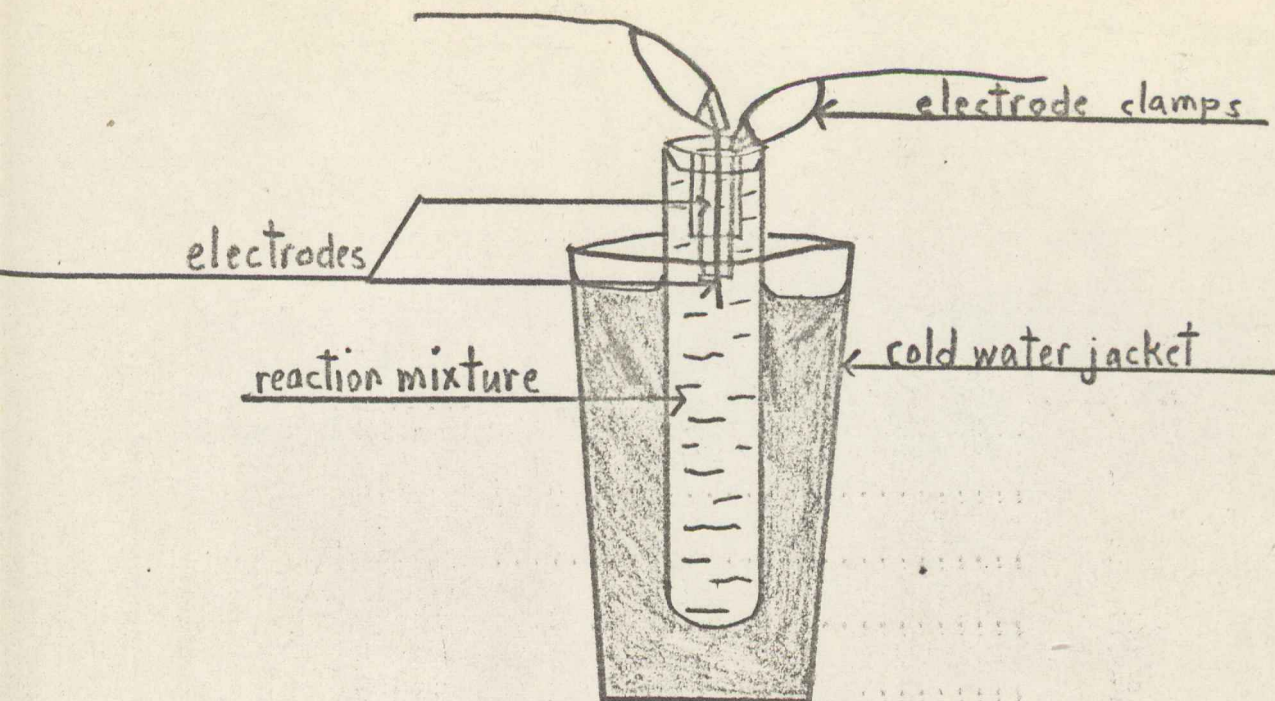


Fig. A

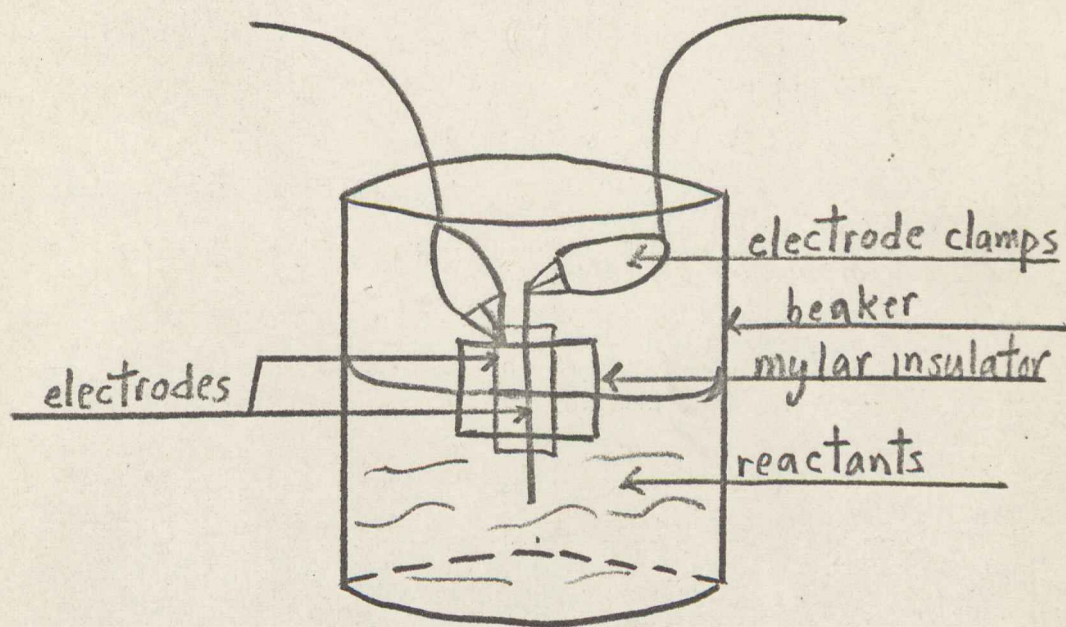


Fig. B

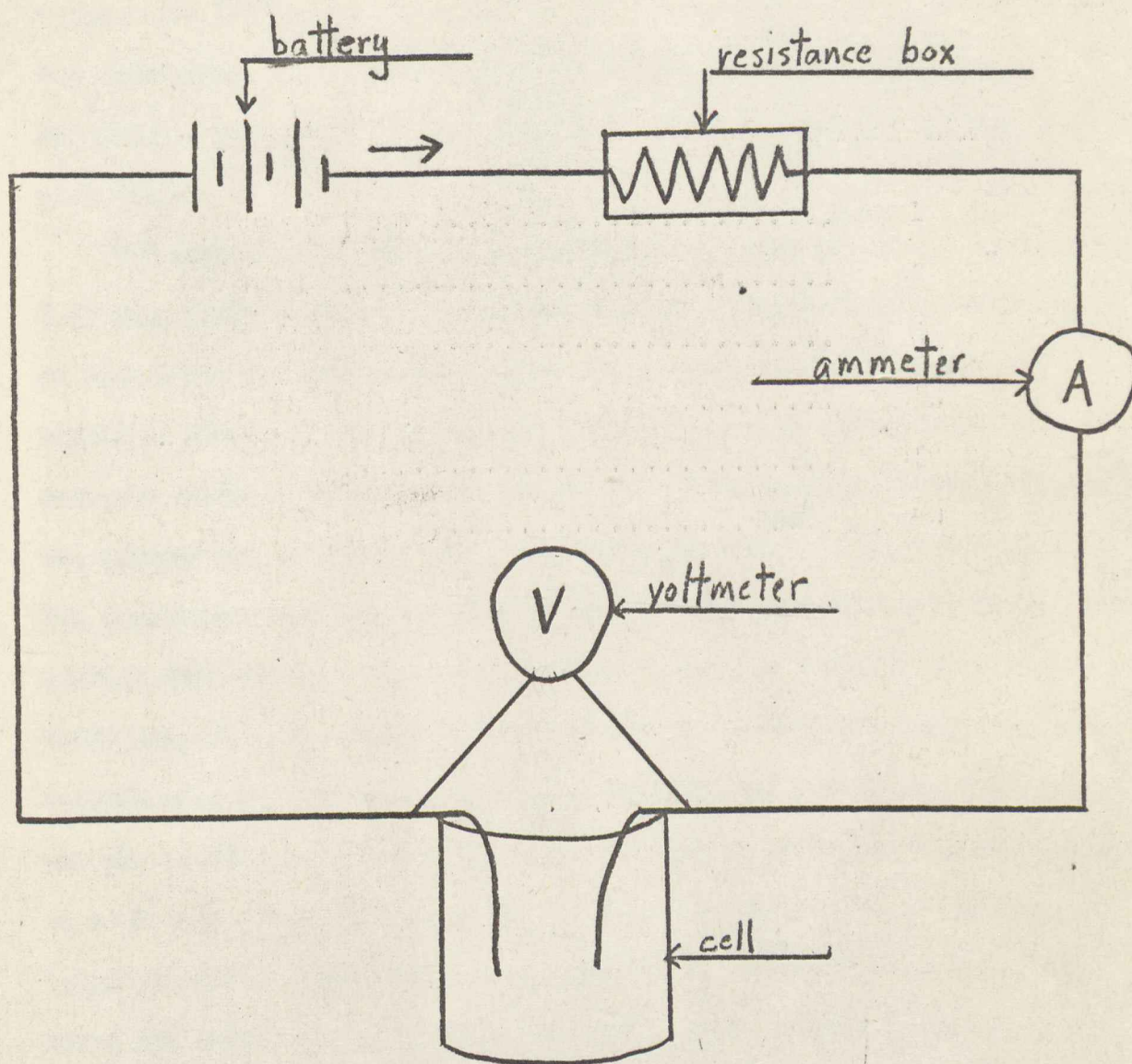


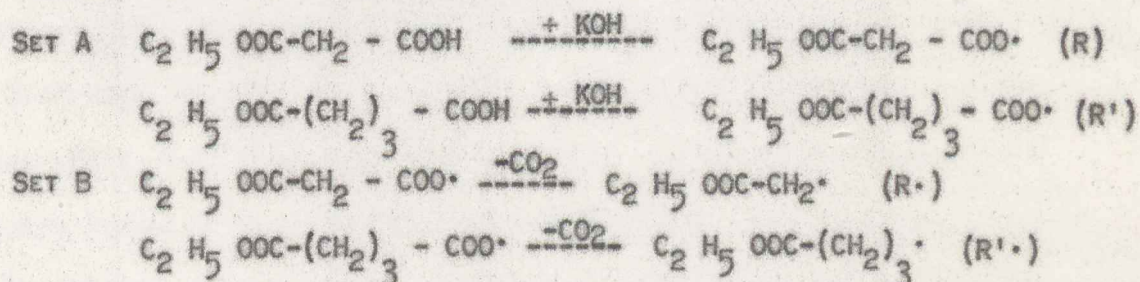
Fig. C

HALF-ESTER WAS GIVEN OFF, BUT SINCE THE COLUMN COULD NOT BE USED AT TEMPERATURES ABOVE 180°C , THE SUBSTANCE HAD TO BE ANALYZED IN A COLUMN OWNED BY THE SCHENECTADY CHEMICAL COMPANY. THE ANALYZATIONS WERE MADE BY MR. BEVERLY ADAMS, AND HIS RESULTS WILL FOLLOW IN THE NEXT SECTION OF THIS THESIS.

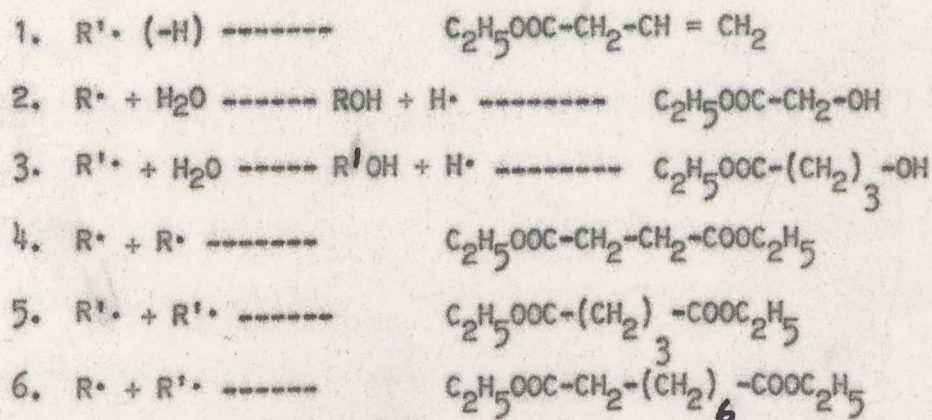
THE ORGANIC SOLVENT USED IN THE SECOND RUN WAS PYRIDINE. IN THIS RUN, 7.15 GMS. (.045 MOLES) OF MONO-ETHYL GLUTARATE AND 5.85 GMS. (.045 MOLES) OF MONO-ETHYL MALONATE WERE COMBINED WITH 2.30 GMS. (.044 MOLES) OF POTASSIUM HYDROXIDE TO MAKE UP THE REACTION MIXTURE. THEN 20 ML. OF PYRIDINE SOLVENT WAS ADDED AND THE MIXTURE STIRRED BEFORE ELECTROLYZING. THE MIXTURE WAS HETEROGENEOUS. THE APPARATUS USED IS SHOWN IN FIGURE B. THE ELECTRODES USED IN THIS PART OF THE RUN WERE THE SAME AS BEFORE. THE VOLTAGE ONCE AGAIN WAS SET AT 3.7 VOLTS BECAUSE OF RESISTANCE PROBLEMS. THERE WAS, HOWEVER, NO WATER BATH TO COOL THE REACTANTS AS BEFORE. THE ELECTROLYSIS RAN 100 HRS. AT THE END OF THAT TIME THE ENTIRE SOLUTION WAS PUT IN 200 ML. OF WATER AND SLOWLY ACIDIFIED WITH 42.5 ML. OF 4M HCl TO A PH OF 2. THIS WAS TO ALLOW THE PYRIDINE CHLORIDE TO SETTLE OUT. THEN THE SOLUTION WAS WASHED WITH THREE 30 ML. ALIQUOTS OF ETHER. THE ETHER WAS WASHED WITH COLD (0°C) WATER AND THEN EVAPORATED UNDER THE HOOD. AFTER EVAPORATION WAS COMPLETE, A DARK YELLOW OIL REMAINED IN THE DISH. THIS SUBSTANCE WAS COLLECTED IN A SMALL VIAL AND SUBJECTED TO VAPOR-PHASE CHROMATOGRAPHIC ANALYSIS.

DISCUSSION AND CONCLUSIONS

THE PRODUCTS FORMED FROM THIS ELECTROLYSIS ARE, IN A MANNER OF SPEAKING, PREDICTABLE. TO BE SURE, THE PRODUCTS THAT ARE USUALLY FORMED ARE OF A WIDE VARIETY. TAKING THE FOLLOWING REACTIONS AS THE MOST PROBABLE, THE READER CAN SEE EXACTLY WHAT SHOULD FORM:



IN SET A, THE POTASSIUM SALT IS FORMED LEAVING THE RADICAL R AND R' RESPECTIVELY. IN SET B, THE DECARBOXYLATION OF THESE RADICALS LEAVES R· AND R'·. NOW THE TWO PRODUCTS FORMED FROM DECARBOXYLATION REACT TO FORM THE POSSIBLE PRODUCTS BELOW.



OF THE PRODUCTS FORMED, NUMBERS 2 AND 3 CAN ONLY BE FORMED FROM THE AQUEOUS MEDIA. THE REACTION R (-H) DOES NOT OCCUR SINCE THERE IS NO ADJACENT -CH₂- GROUP AVAILABLE FOR DEHYDRATION ON THE MALONATE ION. THE PRODUCTS OF THESE REACTIONS ARE LISTED BELOW WITH THEIR BOILING POINTS.

1. BUT-3-ENEOATE	BP. 114°C
2. ETHYL GLYCOLATE	BP. 160°C

3. ETHYL-3-HYDROXY BUTYRATE	BP. $116^{\circ}\text{--}117^{\circ}\text{C}/8\text{MM.}$
4. DI-ETHYL SUCCINATE	BP. 217°C
5. DI-ETHYL SUBERATE	BP. 282°C
6. DI-ETHYL ADIPATE	BP. $239^{\circ}\text{--}240^{\circ}\text{C}$

AS MENTIONED PREVIOUSLY THE TWO UNKNOWN WERE RUN ON A VAPOR-PHASE CHROMATOGRAPH. THE INSTRUMENT USED WAS AN F AND M SCIENTIFIC COMPANY MODEL 720 WITH DUAL COLUMNS AND AN THERMAL CONDUCTIVITY DETECTOR. THE COLUMN ITSELF WAS A FOUR FOOT, LOW-LOADED COLUMN. IT WAS PACKED WITH 0.5% CELANESE ESTER #9 ON A 60 - 80 MESH CHOMASORB W. THE CARRIER GAS WAS HELIUM FLOWING AT THE RATE OF 40 CC./MIN. THE COLUMN TEMPERATURE WAS ISOTHERMALLY HELD AT 100°C . THE DETECTOR TEMPERATURE WAS 280°C AND THE INJECTION PORT WAS 290°C . THE BRIDGE POWER WAS SET AT 150 MILLIAMPERES. THE SAMPLE SIZES FOR THE UNKNOWN SUBSTANCES WERE $1\mu\text{l}$. THE SAMPLE SIZES FOR THE COMPARISON ESTERS WERE $.2\mu\text{l}$.

THE SAMPLES OF THE KNOWN ESTERS WERE RUN FIRST. AT 2 MINUTES DI-ETHYL SUCCINATE CAME OFF WITH 73×1 ATTENUATION. AT $5\frac{1}{2}$ MINUTES DI-ETHYL ADIPATE CAME OFF WITH 23×1 ATTENUATION. SAMPLE #1, THE AQUEOUS UNKNOWN, SHOWED GOOD SIGNS OF THE DI-ETHYL SUCCINATE AT 2 MINUTES, HOWEVER, THE DI-ETHYL ADIPATE DID NOT SHOW UP. INSTEAD A PEAK AT $4\frac{1}{2}$ -5 MINUTES APPEARED CONSISTENTLY IN ALL THE OTHER RUNS. AN UNIDENTIFIABLE PEAK AT $8\frac{1}{2}$ MINUTES WAS PRESENT AT THE FIRST RUN BUT WAS NOT REPRODUCIBLE. SAMPLE #2, THE PYRIDINE UNKNOWN, SHOWED REPRODUCIBLE DI-ETHYL SUCCINATE RESULTS, AND ONCE AGAIN THE PEAK AT $4\frac{1}{2}$ -5 MINUTES WAS EVIDENT. IN BOTH SAMPLES, INITIAL PEAKS OCCURRED ALMOST AS SOON AS THE SAMPLES WERE INJECTED. THESE WERE PROBABLY DUE TO SMALL AMOUNTS OF AIR AND WATER.

NOW THE PROBLEM WAS TO INTERPRET THIS DATA. IT WAS VERY APPARENT THAT VERY LITTLE, IF ANY, OF THE DI-ETHYL SUBERATE WAS PRODUCED. THE DI-ETHYL ADIPATE MAY HAVE BEEN FORMED TO A GREATER EXTENT, BUT EVEN THIS SUBSTANCE WAS NOT APPARENT. BY FAR, THE GREATEST PRODUCT FORMED WAS THE DI-ETHYL SUCCINATE. THERE SEEMED TO BE GOOD EVIDENCE THAT THIS SHOULD BE SO. THE MALONATE ION IS BY FAR THE SMALLER OF THE TWO SALT IONS. THEREFORE, IT SHOULD MOVE THROUGH THE SOLUTION MUCH MORE QUICKLY THAN THE GLUTARATE ION. THIS MEANS THAT MORE DECARBOXYLATE MALONATE RADICALS ARE FORMED AND HAVE A BETTER CHANCE TO DIMERIZE. ONE CAN SEE THAT THE $R - R$ TYPE OF COMBINATION WOULD BE THE MOST PREVALENT, THE $R-R'$ LESS PREVALENT, AND THE $R'-R'$ TYPE THE LEAST PREVALENT OF ALL. THE PEAKS THAT HAD COME OFF AT $4\frac{1}{2}$ -5 MINUTES WERE SUPPOSED TO BE EITHER UNREACTED MONO-ETHYL MALONATE OR MONO-ETHYL GLUTARATE, OR SOME OF THE $R'-H$, $R-OH$, AND $R'-OH$. UPON COMPARING VALUES FOR THE BOILING POINTS OF THE MONO-ETHYL ESTERS, THEY WERE FOUND TO BE:

- | | |
|-------------------------|---------------------------|
| 1. MONO-ETHYL MALONATE | BP. 145°C |
| 2. MONO-ETHYL GLUTARATE | BP. 165°C |

THIS EVIDENCE SUGGESTS THAT THE $4\frac{1}{2}$ MINUTE PEAK COULD BE THE GLUTARATE ACID HALF-ESTER. SINCE THE MALONATE HALF-ESTER IS MORE SOLUABLE IN WATER THAN THE GLUTARATE HALF-ESTER, THE OIL FORMED BY THE ELECTROLYSIS WOULD BE MOST LIKELY TO TAKE UP THE MONO-ETHYL GLUTARATE BECAUSE OF ITS MORE ALIPHATIC NATURE. THIS WOULD ALSO SUPPORT THE PREVIOUS SUPPOSITION THAT THE $R'-R'$ FORMATION WOULD BE UNLIKELY. ONE CAN EASILY SEE THAT THE MORE UNREACTED GLUTARIC ACID HALF-ESTER TAKEN UP WOULD LEAVE THAT MUCH LESS IN THE REACTING MIXTURE, WHICH WOULD LESSEN THE FORMATION OF $R'-R'$ EVEN FURTHER.

THE REASON THAT THERE IS AN "INVERSION" IN ORDER OF ELECTRONS VERSUS ORDER OF BOILING POINTS IN THIS VAPOR FRACTIONATION IS SUPPOSEDLY BECAUSE OF HYDROGEN BONDING IN THE MONO-ETHYL GLUTARATE, WHEREAS IN DI-ETHYL SUCCINATES THERE ISN'T ANY OPPORTUNITY FOR THIS TO OCCUR.

SUMMARY

GATHERING ALL THE INFORMATION TOGETHER THAT HAS BEEN COLLECTED, IT WOULD BE SAFE TO SAY THAT THE ELECTROLYSIS PRODUCED THE EXPECTED DI-ETHYL SUCCINATE, BUT NO EVIDENCE OF THE DI-ETHYL SUBERATE WAS SEEN. THE DI-ETHYL ADIPATE WAS NOT POSITIVELY IDENTIFIED, BUT THERE WAS SOME EVIDENCE OF ANOTHER PRODUCT BESIDES THE DI-ETHYL SUCCINATE. IT WAS SUPPOSED THAT THIS PRODUCT WAS SOME UNREACTED MONO-ETHYL GLUTARATE.

THIS THESIS HAS BEEN JUST ONE OF A GREATER NUMBER OF EXPERIMENTS HAVING TO DO WITH THE KOLBE ELECTROLYSIS. IT IS THE AUTHOR'S HOPE THAT THE PAPER WILL THROW SOME MORE LIGHT ON ELECTROLYSES OF THIS NATURE.

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