THE ELECTROLYTIC REDUCTION OF ACETYLENIC GLYCOLS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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Approved by:

[Signature]

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to the behavior of cathodes in class 2, which produce only the \( \Delta^e \)
and \( \Delta^r \) hexenoic acids, active platinum and nickel cathodes give rise,
in addition, to considerable amounts of \( \Delta^s \) hexenoic and fully saturated
hexoic acids.

Compounds containing isolated ethylenic and acetylenic linkages
are not generally reduced at class 2 cathodes. For example, purified
allyl alcohol and heptyne-1 are not reduced at the dropping mercury
electrode.\(^1\) However, hydrocarbons in which the double or triple bond

\(\text{(1) Kolthoff, I. M. and Lingane, J. J., "Polarography", Volume 2,}

is conjugated with an aromatic ring, polynuclear aromatic hydrocarbons
and aliphatic hydrocarbons such as allene and those containing conjugated
double bonds are reducible at the dropping mercury electrode.

Phenyl substituted olefins and acetylenes (styrene and stilbene,
phenylacetylene and diphenylacetylene) give well-defined waves in a
medium of 50 to 75 per cent dioxane with tetrabutylammonium iodide as
the supporting electrolyte.\(^2\)

\(\text{(2) Cf. Kolthoff and Lingane, loc. cit.}\)

Diamond and Soffer\(^3\) have reduced naphthyl methyl ethers to the

\(\text{(3) Diamond, G. B. and Soffer, M. D., J. Am. Chem. Soc. 74, 4126 (1952).}\)

corresponding dihydronaphthalenes at a mercury cathode using tetrabutyl
ammonium iodide as electrolyte. They claimed that 2,7,8-trimethoxy
naphthalene gave 2,7,8-trimethoxy-1,4-dihydronaphthalene. If
this is true then the reduction probably proceeded by a 1-4 addition of
Ultraviolet Adsorption Spectrum of Product from Electrolytic Reduction of 2,4 Hexadiyne-1,6-Diol Using Copper Cathode
FIGURE 30
I was born in Hoosick Falls, New York, May 20, 1923. I attended the oldest public school in the village of Hoosick Falls. My undergraduate training was obtained at Rensselaer Polytechnic Institute, from which I received the degree Bachelor of Science in 1947. From this same institution I received the degree Master of Science in 1948. Between the years 1943 and 1946 I served in the Army of the United States. In 1948 I received an appointment as Assistant in the Department of Chemistry of The Ohio State University. I held this position until April 1951 at which time I received a General Aniline and Film Research Fellowship. I completed the requirements for the Degree Doctor of Philosophy in the Winter Quarter of 1953.
The electrolytic reduction of acetylenic hydrocarbons.

The electrolytic reduction of acetylenic hydrocarbons at class 1 cathodes has been investigated by Campbell and Young (loc. cit). They have reduced substituted acetylenic hydrocarbons at a spongy nickel cathode to the corresponding olefins. With the exception of phenylacetylene which yielded ethylbenzene and styrene, the product in every case was pure olefin. These authors were unable to obtain any reduction of the aliphatic acetylenic hydrocarbons when cadmium, lead and amalgamated lead were used as cathodes (class 2 cathodes).

Campbell and Young attempted to reduce 5-decyne at a spongy copper cathode but obtained only a small amount of material, which they claimed to be cis-5-decene.

The olefins they obtained from the reduction of the acetylenic hydrocarbons at a spongy nickel cathode were predominately of the cis configuration. 5-Decyne and 4-octyne give cis 5-decene and cis 4-octene respectively, while diphenylacetylene gave cis stilbene.

The electrolytic reduction of ethynyl carbinols.

Recently studies have been made on the electrolytic reduction of ethynyl carbinols by A. I. Lebedeva. She found that dimethyl ethynyl carbinol could be reduced at cathodes of smooth Cu, Ag and spongy copper and also spongy nickel and platinized platinum in a sodium hydroxide

(2) Idem. ibid. 19, 69 (1949), C.A. 44:461.
solution. The latter two reduced the ethynyl carbinol to 2-methylbutanol-2 with no stop at the vinyl carbinol. Smooth nickel, platinum, mercury, iron, aluminum and zinc were found to be ineffective in the reduction of the ethynyl carbinol. Lebedeva also investigated the effect of various cathodes on the electrolytic reduction of dimethyl vinyl carbinol. Cathodes such as smooth Cu, Ag, Au, Cd, Zn, Al, Sn, Sb, Bi, Fe, Ni, Pd, Pt and Hg all turned out to be very inefficient, while spongy nickel on copper and platinized platinum were very effective in reducing the vinyl carbinol to 2-methylbutanol-2.

Lebedeva concluded that the reduction of ethynyl carbinols on copper and silver proceeded by a different mechanism from that which took place on a spongy nickel or platinized platinum cathode. She envisaged the formation of a copper or silver acetylide, which was reduced to the olefin. Since the olefin cannot form an analogous metal derivative it is stable toward further reduction. The reduction of ethynyl and vinyl carbinol to the butanol-2 probably proceeded by a mechanism analogous to the usual catalytic hydrogenation with a metal and hydrogen gas.

I. A. Shikeev,¹ has reduced methyl propyl ethynyl carbinol at a smooth copper cathode, in a sodium carbonate solution, to methyl propyl vinyl carbinol and a small amount of 2-ethyl pentanol-2. The formation of 2-ethyl pentanol-2 would apparently indicate that Lebedeva's mechanism, acetylide formation, was not the only path by which reduction can take place at a smooth copper cathode. It would follow from the "acetylide

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mechanism" that disubstituted acetylenes would not be reduced at copper and silver cathodes.

The advantages of studying the electrolytic reduction of 2-butyne-1,4-diol.

The vinyl carbinols obtained from the reduction of ethynyl carbinols, unfortunately, have only one isomeric form. Therefore, the present work was initiated with 2-butyne-1,4-diol since two isomeric butenediols are possible, if, indeed, reaction can be realized. The occurrence of reduction would, too, rule out Lebedeva's theory involving acetylide formation.

2-Butyne-1,4-diol, also had a great practical attraction in that it was very soluble in a solution of aqueous electrolyte.

The reduction of 2-butyne-1,4-diol to 2-butene-1,4-diol.

The partial reduction of 2-butyne-1,4-diol to cis 2-butene-1,4-diol is known to be effected either by zinc and aqueous sodium hydroxide\(^1\) or

\[\text{(1) Reppe, W. and Schnabel, R., U. S. Pat. 2,267,749.}\]

by hydrogenation over partly poisoned catalysts.\(^2\) The cis-diol has

\[\text{(2) Farbend, I. G., F. Pat. 853,148; General Aniline Film Corp., U. S. Pat. 2,300,598.}\]

now been prepared in excellent yield by hydrogenation at atmospheric pressure over 0.5% palladium calcium carbonate\(^3\) or Raney nickel\(^4\) by

\[\text{(3) Johnson, A. W., J. Chem. Soc. 1946, 1014.}\]

taking advantage of the distinct change in the rate of hydrogenation after absorption of one equivalent of hydrogen.

Complete hydrogenation of 2-butyne-1,4-diol can be effected by a variety of catalysts, e.g. nickel on pumice,\(^1\) copper,\(^2\) platinum,\(^3\) nickel, cobalt or silver.\(^4\)

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(2) General Aniline Film Corp., U. S. Pat. 2,335,795.
(3) Lespieu, Compt. rend. 150, 1761 (1910).
(4) Farbenind, I. G., B. Pat. 508,944; U. S. Pat. 2,319,707; F. Pat. 844,533.

The reduction of 2-butyne-1,4-diol, exclusively to trans 2-butene-1,4-diols has as yet not been accomplished. A mixture of cis and trans-diols has been claimed, when 2-butyne-1,4-diol was treated with metallic zinc and alkali.\(^5\) Pure trans 2-butene-1,4-diol has been prepared by the bromination of 1,3-butadiene to the trans 1,4-dibromo-2-butene. The 1,4-dibromo-2-butene was converted to the diacetoxy compound with sodium acetate in acetic acid. The diacetoxy compound was either hydrolyzed or subjected to alcoholysis to obtain the trans 2-butene-1,4-diol.\(^6\)

(5) Farbenind, I. G., F. Pat. 834,111; Brit. Pat. 508,543.

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Valette (loc. cit.) obtained the trans 2-butene-1,4-diol by another route. He brominated cis 2-butene-1,4-diol with PBr\(_3\) and isolated the
cis 1,4-dibromo-2-butene. The cis dibromobutene was heated to 120° for 2 hours and the trans 1,4-dibromo-2-butene was obtained. The trans dibromobutene was converted to the diacetoxybutene and then hydrolyzed to yield the trans 2-butene-1,4-diol.

Establishment of the configuration of the butenediols.

The geometrical isomer obtained from hydrogenation of 2-butyne-1,4-diol has been fairly well established (cf. Valette loc. cit.). Valette has shown by Raman spectra that the product from the hydrogenation of 2-butyne-1,4-diol with Raney nickel contains no trans ethylenic lines and no acetylenic lines. This product when reacted with KMnO₄ in the presence of MgSO₄ yields the inactive erythritol. Lozac'h¹


(see also Copenhaver and Bigelow) has indicated that with H₂O₂ the product obtained is the racemic erythritol. If the hydroxylation using KMnO₄ proceeded by cis- addition² and the hydroxylation using H₂O₂ went in the trans direction³ then the formation of inactive and


racemic erythritols would, indeed, indicate that the original 2-butene-1,4-diol had the cis configuration.
Valette (loc. cit.) has shown that the dibromide, obtained by heating cis 1,4-dibromo-2-butene, when brominated with Br₂ yields the inactive tetrabromide. Since, addition of bromine to a carbon-carbon double bond has been shown to take place by trans addition, it is reasonable to assume, therefore, that the cis 1,4-dibromo-2-butene when heated to 120° was converted to the trans 1,4-dibromo-2-butene.

The 2-butene-1,4-diol obtained from this trans 1,4-dibromo-2-butene via the diacetoxy compound and hydrolysis, when heated with benzoyl chloride gave a dibenzoate (m. 101°) that had the same melting point as the dibenzoate obtained by Prevost. The dibenzoate which Prevost obtained was prepared by treating the dibromide from the reaction of 1,3-butadiene and bromine at -20°, with silver benzoate. Prevost claimed that only the trans 1,4-dibromo-2-butene and not the cis was formed when 1,3-butadiene was brominated in this manner.

Further evidence that the addition of halogens to 1,3-butadiene should yield the trans 1,4-dihalogen-2-butene comes from the work of Mislow and Hellman. They have shown that chlorination of 1,3-butadiene at -77° and in the dark produced a 1,4-dichloro-2-butene which yielded only trans 2-butene when reacted with lithium aluminum hydride.
Correspondingly the reduction of 2-butyne-1,4-diol with Raney nickel produced a 2-butene-1,4-diol that gave a 1,4-dichloro-2-butene with PCl₃, which in turn formed only \textit{cis} 2-butene when reacted with lithium aluminum hydride.

There is, conceivably, another method whereby the \textit{cis} and \textit{trans} butenediols could be prepared and that is by the reduction of maleic and fumaric acids or their dimethyl esters with lithium aluminum hydride. The reduction of fumaric acid has already been accomplished\(^1\)


and the product claimed was \textit{trans} 2-butene-1,4-diol.

However, any attempt to reduce either the fumaric acid or the dimethyl esters of fumaric and maleic acid ended in failure (cf. Experimental).

\textbf{Experimental}

The reduction of 2-butyne-1,4-diol using Raney nickel as a catalyst.

A 1625 ml. water solution containing 569 g. of 2-butyne-1,4-diol was hydrogenated in the presence of 5 g. of Raney nickel for 72 hours. The hydrogenation of butynediol to butenediol required 6.8 moles of hydrogen, corresponding to a drop in pressure of 1240 pounds. After the reduction was completed the Raney nickel was filtered off, and the water removed by distillation under diminished pressure. The product obtained was 566 g. of a yellow colored liquid, b.p. 112-114° at 3-4 mm.
The reduction of 2-butyne-1,4-diol using Raney nickel as a catalyst and absolute alcohol as solvent.

A solution of 70 g. (0.81 moles) of 2-butyne-1,4-diol in 130 g. of absolute alcohol was hydrogenated in the presence of Raney nickel. The hydrogenation was stopped at the end of one hour at which time 0.81 moles of hydrogen had been absorbed, corresponding to a drop in pressure of 68 pounds. After the reduction was completed the Raney nickel was filtered off, and the alcohol removed under diminished pressure. The product obtained was 57 g. of a light, yellow, colored liquid, b.p. 113-115° at 3-4 mm.

Preparation of trans-1,4-dibromo-2-butene.

A 500 ml. three neck flask, fitted with a gas inlet, addition funnel, and mechanical stirrer was immersed in a dewar flask containing dry ice and acetone. A cardboard cover with holes in the proper places to accommodate the necks of the flask was used to prevent light from striking the reaction mixture. The necks of the flask as well as the gas inlet tube and the addition funnel from the ground glass joint to the stopcock were painted black.

A solution of 75 ml. of carbon tetrachloride and 75 ml. of chloroform was added to the flask. Then 100 ml. of 1,3-butadiene (1.2 moles) was condensed in a dry ice trap. This trap was connected to a KOH drying tower and then to the gas inlet tube of the reaction flask. A solution of 27 ml. of bromine (0.5 moles) in 25 ml. of carbon tetrachloride and 25 ml. of chloroform was added to the addition funnel.

The stirrer was started and the trap containing the butadiene was allowed to warm so that butadiene passed into the reaction flask. The bromine was added to the reaction flask at a rate such that the butadiene
was always in excess. This was necessary in order to keep the formation
of 1,2,3,4-tetrabromobutane to a minimum. The reaction mixture was
stirred for an hour after all the butadiene and bromine had been added.
The carbon tetrachloride and chloroform were then removed under
diminished pressure. A crystalline solid remained. The solid was
recrystallized from petroleum ether (b.p. 60-165\degree) m.p. 53\degree (lit. 54\degree
for trans-1,4-dibromobutene). The weight of the solid was 75 g.
(A theoretical yield of 70\% based on bromine.)

Preparation of trans-1,4-diacetoxy-2-butene.

A solution of 75 g. of 1,4-dibromo-2-butene and 150 ml. of glacial
acetic acid containing 61 g. of potassium acetate and 40 ml. of acetic
anhydride was refluxed for 8 hours. Then the potassium bromide was
filtered off and the acetic acid removed by distillation under reduced
pressure. Some potassium bromide and potassium acetate precipitated
during the distillation. This precipitate was filtered and the solids
washed with benzene. The filter cake was dissolved in water extracted
twice with 40 ml. portions of benzene and twice with 40 ml. portions of
ether. All the extracts plus the washings from the filter cake were
combined, the solvent was removed and the residue distilled. The
product was 58 g. of a colorless liquid, b.p. 80\degree at 1 mm., n_D^25 1.4415
(yield 95\%).

Preparation of trans-2-butene-1,4-diol from trans-1,4-diacetoxy-
2-butene.

A mixture of 55 g. of the diacetoxy compound and 205 g. of absolute
ethyl alcohol containing 4\% sodium ethoxide was refluxed overnight.
Most of the ethyl alcohol and ethyl acetate were removed by distillation
under vacuum. Approximately 50 ml. of water was added and the mixture
ACKNOWLEDGEMENT

It is customary at this time to thank those who have assisted during the course of this work. I, therefore, perform this task not as a duty, but as a pleasure to express my humble gratitude to Professor C. L. Wilson, whose advice and inspiration has enabled me to complete this investigation.

I, also, wish to thank the General Aniline and Film Company for a grant-in-aid, from April 1951 to December 1952.
neutralized with concentrated hydrochloric acid. The remaining ethyl alcohol and water were removed under diminished pressure and the product distilled. The product obtained was 22 g. of a colorless liquid b.p. 108° at 3 mm. $n_D^{25}$ 1.4707 (yield 78%).

The chlorination of 1,3-butadiene.

The chlorination apparatus consisted of a 500 ml. 3 necked flask immersed in a Dewar containing dry ice and acetone, and was equipped with a stirrer and two gas inlets. A cardboard cover with three holes to accommodate the necks of the flask was placed over the Dewar to keep light from striking the reaction mixture. Then 150 ml. (1.8 moles) of butadiene passed over potassium hydroxide and 50 ml. (1.1 moles) of chlorine dried by passing through sulfuric acid were passed simultaneously into 150 g. of carbon tetrachloride and 150 g. of chloroform. The butadiene was passed in at such a rate so as to maintain it in excess. Both the chlorine and butadiene were measured first by condensing them in a calibrated dry ice trap. The traps were then allowed to warm up and the gases passed into the reaction flask. After all the butadiene and chlorine had been passed into the flask, stirring was continued for another hour. The flask was then removed from the dry ice acetone and allowed to warm to room temperature. The chloroform and carbon tetrachloride were removed and the product distilled. A liquid weighing 44 g. b.p. 37° at 5 mm., $n_D^{23}$ 1.4870 was obtained. (A yield of 51 per cent based on chlorine).

The hydrolysis of trans 1,4-dichloro-2-butene with sodium carbonate solution

A solution of 30 g. of trans 1,4-dichloro-2-butene, 200 ml. of water and 35 g. of sodium carbonate were heated together at 90-95° for
six hours. Water was removed under vacuum. The salts that precipitated were filtered and washed with alcohol. The alcohol was removed and the product distilled. A colorless liquid weighing 10 g., b.p. 105-111° at 35 mm., which amounted to a 45% yield was obtained.

**The reduction of 2-butyne-1,4-diol with zinc dust and sodium hydroxide.**

A solution weighing 61 g. of 35% sodium hydroxide was allowed to drop in the course of 2 hours while stirring at 20° into a mixture of 57 g. of 2-butyne-1,4-diol, 30 g. of water and 59 g. of zinc dust, care being taken by cooling with ice water that the temperature did not rise appreciably above 20°C. After the mixture had been stirred for 20 hours at 20°C, the zinc oxide formed was filtered off and the filtered residue washed with water to a weakly alkaline reaction. The filtrates were combined and hydrochloric acid added until acid to litmus. The water was then evaporated under reduced pressure and the oily residue, thus obtained, was filtered by suction from the salts that precipitated. The filtered residue was washed several times with alcohol, the alcohol filtrates were combined with the oily fraction and the alcohol removed by distillation under reduced pressure. The residue was distilled, and 41 g. of a mixture of cis 2-butene-1,4-diol and unreduced 2-butyne-1,4-diol, b.p. 104-107° at 2 mm. were recovered.

**An attempt to use a differential apparatus for the determination of the efficiency of various cathodes.**

Exploratory experiments were carried out in what can be called a differential apparatus.¹ Two similar electrolysis cells, embodying

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¹ Pomilio, U., Z. Elektrochem. 21, 444 (1915).
porous pots formed the cathode compartments. One cell served as a hydrogen coulometer, the other as a reduction cell. The hydrogen evolution was measured in two similar 50 cc. gas burettes each connected to a leveling bulb filled with water. The reducing efficiency of any cathode in a given medium could be determined in this way, with a small amount of material (0.08 g.). The current was 0.10 amp.

One additional feature was added to this differential apparatus. The cathode in the reduction cell was made in the form of a small cylinder (1.9 diameter x 1.4 cm. height) that could be attached to a stainless steel shaft, thereby permitting the cathode to be rotated. Thus, the efficiency of a stationary vs. a rotating cathode could be studied.

The results obtained from this differential apparatus were unreliable. With most of the cathodes, Pb, Ag, Zn, etc., studied (except spongy copper and nickel), this method indicated that reduction did not take place at these cathodes. This was not true. The uncertainty was caused by the low efficiency of the electrolytic reduction of 2-butyne-1,4-diol. The method was not sensitive enough to detect reduction, when it occurred.

The preparation and use of the plating solutions.

The plating solutions were prepared as follows:

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<tr>
<th>Metal</th>
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<td>Cu</td>
<td>15 g. CuSO(_4); 950 ml. water; 10 g. H(_2)SO(_4)</td>
</tr>
<tr>
<td>Ni</td>
<td>15 g. NiSO(_4)(\cdot)(NH(_4))(_2)SO(_4)(\cdot)6H(_2)O; 30 ml. NH(_4)OH; 600 ml. water</td>
</tr>
<tr>
<td>Ag</td>
<td>10 g. Ag(_2)SO(_4); 30 ml. NH(_4)OH; 250 ml. water</td>
</tr>
<tr>
<td>Zn</td>
<td>10 g. ZnSO(_4); 250 ml. water; 10 g. H(_2)SO(_4)</td>
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A metal gauze or sheet, preferably of the same metal that was to be plated, was then made the cathode in an electrolysis cell. It was necessary, in order to obtain a spongy surface, to carry out the electrolysis at a high current density, 10-16 amps/sq.dm. The electrolysis was carried out for about 25 to 30 minutes or until the desired spongy character was obtained.

The technique used in electrolytic reduction.

The reductions were carried out in most cases in a Coors porous pot that served as the cathode compartment. The anode compartment was usually a beaker large enough to accommodate the porous pot. In most all reductions, except where noted, the porous pot was placed in the beaker and surrounded by the anolyte. The temperature of the reaction was maintained between 25-30°, by surrounding the beaker with ice, and placing glass cooling coils in both the anode and cathode compartments through which ice water could be circulated. See Fig. 1.

When basic or neutral electrolyte was used it was necessary to add electrolyte, from time to time, to the anode compartment to counteract the loss caused by migration of solution to the cathode compartment. In acid solution the reverse was necessary, electrolyte had to be added to the cathode compartment.
FIGURE 1
ELECTROCHEMICAL REDUCTION CELL
The electrolytic reduction of 2-butyne-1,4-diol at spongy lead cathode in basic solution

Cathode: Lead sheet plated with spongy lead 6 x 10.5 cm.

Anode: Iron wire gauze

Catholyte: 90 g. of 2-butyne-1,4-diol, 30 ml. 1 N NaOH,
120 ml. water

Anolyte: 600 ml. 4 N NaOH

Cathode compartment: Porous pot inside diameter 7 cm.,
height 12.5 cm.

Anode compartment: 1 liter beaker

Current: 4 amps.

Time: 29 hours (116 amp hours)

The catholyte was neutralized with sulfuric acid and the water removed under diminished pressure. The precipitated salt was filtered and washed with ethanol. The remaining water and ethanol were removed. The product obtained was a liquid weighing 57 g. and b.p. 110-111° at 1-1.5 mm.

A second reduction using 86 g. of 2-butyne-1,4-diol was performed. The current was 4 amps and it was passed through the cell for 28 hours. The catholyte was neutralized with hydrochloric acid and extracted with ether for 5 days. The product obtained was a liquid weighing 46 g., b.p. 105° at 0.5 mm.
The electrolytic reduction of 2-butyne-1,4-diol at an amalgamated copper cathode

Cathode: Copper sheet 7 x 11 cm. amalgamated with mercury
Anode: Iron wire gauze
Catholyte: 86 g. (1 mole) 2-butyne-1,4-diol, 30 ml. 1 N NaOH,
120 ml. water
Anolyte: 600 ml. 4 N NaOH
Cathode compartment: Porous pot inside diameter 7 cm.,
height 12.5 cm.
Anode compartment: 1 liter beaker
Current: 3 amps
Time: 44 hours (132 amp hours)

The catholyte was neutralized with sulfuric acid and the water removed under diminished pressure. The precipitated salt was filtered and washed with ethanol. The remaining water and ethanol were removed. The product obtained was a liquid weighing 46 g., b.p. 104° at 0.5 mm.
The liquid solidified on standing, which indicated that a large amount of unreduced 2-butyne-1,4-diol was present in the product.
The electrolytic reduction of 2-butyne-1,4-diol using a spongy copper cathode.

Cathode: A copper wire gauze 8 x 12.8 cm. plated with spongy copper.
Anode: Iron wire gauze.
Catholyte: 350 g. of 35% solution of 2-butyne-1,4-diol (G.A.F.)
100 ml. of 1 N NaOH
Anolyte: 1200 ml. of 4 N NaOH
Cathode compartment: A porous pot 10.3 cm. inside diameter,
height 28 cm.
Anode compartment: a four liter beaker
Current: 4 amps.
Time: 19 hours (76 amp hours)
The reduction was interrupted at the end of three hours, nine hours and sixteen hours and each time the cathode was removed, cleaned and replated with spongy copper.

When 76 amp hours of current had been passed, the catholyte was neutralized with concentrated sulfuric acid. The water was removed under diminished pressure and the precipitated sodium sulfate was filtered off. The salt was washed several times with ethyl alcohol. The filtrate and washings were combined and the remaining water and alcohol were removed. The liquid residue was distilled and 48 g. b.p. 109° at 2.5 mm., \( \eta^2_{D} \) 1.4750, was obtained. The recovery was 39% of the original 2-butyne-1,4-diol.
The electrolytic reduction of 2-butyne-1,4-diol at a spongy zinc cathode.

Cathode: A zinc foil 7 x 10 cm. plated with spongy zinc.

Anode: Iron wire gauze.

Catholyte: 86 g. (1 mole) 2-butyne-1,4-diol, 50 ml. 1 N NaOH, 200 ml. water

Anolyte: 500 ml. 4 N NaOH

Cathode compartment: A porous pot inside diameter 7 cm., height 12.5 cm.

Anode compartment: One liter beaker

Current: 4 amps.

Time: 20 hours (80 amp hours)

The catholyte was neutralized with concentrated hydrochloric acid, saturated with sodium chloride and extracted continuously for 5 days with ether. The ether was removed and the liquid residue distilled. The weight of the distilled material was 37 g., b.p. 102° at 0.5 mm. This was a recovery of 43% based on the original butyndiol. A second run was also made starting with 53 g. of 2-butyne-1,4-diol and passing 33 amp hours of current. A liquid weighing 21 g. b.p. 105° at 1.5 mm. was obtained. (A recovery of 38% based on butyndiol).

A second reduction of 2-butyne-1,4-diol using a spongy copper cathode.

Cathode: A copper wire gauze 15 x 22.5 cm. plated with spongy copper.

Anode: Iron bar.

Catholyte: 86 g. (1 mole) 2-butyne-1,4-diol, 400 ml. water, 3.2 g. NaOH
Anolyte: 200 ml. 4 N NaOH
Cathode compartment: 600 ml. beaker
Anode compartment: Porous pot 4.5 cm. inside diameter, 14.5 cm. height
Current: 5 amps.
Time: 11 hours (55 amp. hours)
The catholyte was neutralized with concentrated hydrochloric acid, saturated with sodium chloride and extracted continuously for 14 days with ether. The ether was removed and liquid residue distilled. The weight of material was 62 g., b.p. 97° at 0.5 mm. This was a recovery of about 72% based on the original butyndiol.

The attempted electrolytic reduction of 2-butyne-1,4-diol at a smooth lead cathode.
Cathode: Lead sheet 6 x 10.5 cm.
Anode: Lead
Catholyte: 500 g. of 35% 2-butyne-1,4-diol solutions, 120 ml. water, 25 ml. concentrated H₂SO₄
Anolyte: 15 ml. concentrated H₂SO₄, 125 ml. water
Cathode compartment: One liter beaker
Anode compartment: A porous pot, 4.5 cm. inside diameter, 14.5 cm. height
Current: 3 amps.
Time: 36 hours (108 amp. hours)
The catholyte was neutralized with 16% NaOH solution and the water removed under diminished pressure. The sodium sulfate that precipitated was filtered and washed, several times with ethanol. The filtrate and
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alcohol washings were combined and the alcohol removed under vacuum. The residue remaining solidified on cooling. The residue turned out to be unreacted starting material, 2-butyne-1,4-diol, weight 125 g.

The electrolytic reduction of 2-butyne-1,4-diol at a spongy silver cathode.
Cathode: A silver gauze 6 x 9 cm. plated with spongy silver.
Anode: Iron wire gauze, 15 x 24 cm.
Catholyte: 86 g. (1 mole) 2-butyne-1,4-diol, 120 ml. of water, 30 ml. of 1 N NaOH
Anolyte: 500 ml. of 4 N NaOH
Cathode compartment: A porous pot 7.6 cm. inside diameter, 12.5 cm. in height.
Anode compartment: One liter beaker
Current: 5 amps.
Time: 19 hours (95 amp hours).
The catholyte was neutralized with sulfuric acid. The water was removed under vacuum and sodium sulfate filtered, washed with absolute ethyl alcohol and washings combined with the filtrate. The ethyl alcohol was removed under vacuum and residue distilled. The material recovered had a b.p. 115-117° at 1.5 mm. and weighed 58 g. This was a 67% recovery based on original butynediol.

Electrolytic reduction of 2-butyne-1,4-diol at a spongy cobalt cathode.
Cathode: Slomin platinum electrode plated with cobalt. Platinum 30.5 mm. in height by 150 mm. circumference.
Anode: Lead
Catholyte: 50 g. of 2-butyne-1,4-diol, 80 ml. of water, 20 ml. of 1 N NaOH
Anolyte: 600 ml. 4 N NaOH
Cathode compartment: Porous pot inside diameter 7 cm., height 12.5 cm.
Anode compartment: 1 liter beaker
Current: 4 amps.
Time: 12 hours (48 amp hours).

At the end of 12 hours the current was turned off and the cathode removed and rinsed with water into the catholyte. The catholyte was neutralized with concentrated hydrochloric acid and then saturated with sodium chloride. This solution was extracted continuously with ether for 6 days. The ether was removed and the residue distilled. The product obtained, weighed 26 g., b.p. 105° at 0.5 mm., and solidified on standing. The solid was unreacted 2-butyne-1,4-diol (a 54% recovery).

**Electrolytic reduction of 2-butyne-1,4-diol at spongy cadmium cathode.**

Cathode: Same as described in experiment with cobalt, except the platinum electrode was plated with cadmium.

Anode: Lead
Catholyte: 50 g. 2-butyne-1,4-diol, 80 ml. of water, 20 ml. of 1 N NaOH
Anolyte: 600 ml. 4 N NaOH
Cathode compartment: Porous pot inside diameter 7 cm., height 12.5 cm.
Anode compartment: 1 liter beaker
Current: 4 amps.

Time: 12.5 hours (50 amp hours)

The catholyte at end of the reaction was neutralized with concentrated hydrochloric acid, saturated with sodium chloride and extracted with ether for 6 days. The residue was distilled, 26.5 g. b.p. 105° at 0.5-1 mm. was obtained while 3 g. of solid 2-butyne-1,4-diol remained. (A 58% recovery).

The electrolytic reduction of 2-butyne-1,4-diol at spongy tin cathode.

Cathode: Tin sheet 40.5 mm. x 40.5 mm. plated with tin.
Anode: Lead
Catholyte: 50 g. of 2-butyne-1,4-diol, 80 ml. of water, 20 ml. 1 N NaOH
Anolyte: 600 ml. 4 N NaOH
Cathode compartment: Porous pot inside diameter 7 cm., height 12.5 cm.

Current: 3 amps.

Time: 15 hours (45 amp hours)

The reaction products were recovered in the same manner previously described for reduction at a cadmium cathode. A product weighing 25 g., b.p. 105° at 0.5 mm. was recovered, plus 11 g. of 2-butyne-1,4-diol which solidified in the condenser.

The attempted electrolytic reduction of 2-butyne-1,4-diol at spongy lead cathode in acid solution.

Cathode: Lead sheet 6 x 10.5 cm. plated with spongy lead
Anode: Lead
Catholyte: 90 g. (1.04 mole) 2-butyne-1,4-diol, 50 ml. 20% H₂SO₄, 100 ml. H₂O
Anolyte: 250 ml. 20% H₂SO₄
Cathode compartment: Porous pot 12.7 x 7 cm. inside diameter
Anode compartment: 1 liter beaker
Current: 4 amperes.
Time: 28 hours (112 amp hours).

The catholyte was neutralized with sodium carbonate, saturated with sodium chloride and extracted continuously for 5 days with ether; the ether was removed and the liquid residue distilled under diminished pressure. When the forerun, water, was removed the residue solidified. The residue was distilled, b.p. 105° at 0.5 mm., weight 58 g., which was a recovery of 62% based on the original butynediol.

The electrolytic reduction of 2-butyne-1,4-diol at a spongy copper cathode in neutral solution.

Cathode: Copper wire gauze plated with spongy copper, 7 x 11 cm.
Anode: Iron wire gauze
Catholyte: 43 g. (0.5 mole) 2-butyne-1,4-diol, 120 ml. 10% KH₂PO₄
Anolyte: 500 ml. 10% KH₂PO₄
Cathode compartment: Porous pot inside diameter 7 cm., height 12.5 cm.
Anode compartment: 1 liter beaker
Current: 6 amperes.
Time: 10 hours (60 amp hours).

The catholyte was tested from time to time with Fisher alka acid test paper and when it was found to be going alkaline a small amount of
concentrated $\text{H}_3\text{PO}_4$ was added.

At the end of 10 hours the catholyte was extracted four times with 150 ml. portions of ether. The ether extract was dried over $\text{Na}_2\text{SO}_4$.

The water layer was distilled under vacuum to remove the water, the salts were filtered off and washed several times with ethanol. The ethanol was removed and the liquid residue distilled. A liquid weighing 16 g., b.p. 92-95° at 1.0 mm. was obtained.

The ether was removed and residue distilled. A colorless liquid weighing 48 g., b.p. 110-112° was obtained. A small sample gave a positive test for unsaturation. This in all probability was a mixture of butyl and crotyl alcohol.

The electrolytic reduction of 2-butyne-1,4-diol at spongy copper cathode in acid solution.

Cathode: Copper wire gauze 7 x 11 cm. plated with spongy copper

Anode: Lead

Catholyte: 86 g. (1 mole) 2-butyne-1,4-diol, 150 ml. 10% $\text{H}_2\text{SO}_4$

Anolyte: 500 ml. 10% $\text{H}_2\text{SO}_4$

Cathode compartment: A porous pot 7 cm. inside diameter, 12.5 cm. height

Anode compartment: 1 liter beaker

Current: 4 amps.

Time: 33 hours (132 amp hours)

The catholyte was neutralized with solid $\text{Na}_2\text{CO}_3$ and distilled till 50 ml. of solution b.p. 92-100° had been collected. The remaining water was removed under diminished pressure and the salt that precipitated out was filtered and washed several times with ethanol. The ethanol was removed and residue distilled. Twenty-five grams b.p. 105° at 1 mm. was
obtained. This was a 29% recovery based on original starting material.

The fraction that distilled 92-100° was saturated with Na₂CO₃, two layers formed. The top layer was removed and dried over anhydrous sodium sulfate and distilled. A clear liquid weighing 3 g., b.p. 116° was obtained which gave a positive test for unsaturation. This was likely to be crotyl and some n-butyl alcohol.

The electrolytic reduction of 2-butyne-1,4-diol at a spongy nickel cathode in basic solution.
Cathode: A solid nickel sheet 6.5 x 16.5 cm. plated with spongy nickel
Anode: Iron wire gauze
Catholyte: 86 g. (1 mole) 2-butyne-1,4-diol, 30 ml. 1 N NaOH, 120 ml. water
Anolyte: 600 ml. 4 N NaOH
Current: 5 amps.
Time: 15.5 hours (77.5 amp hours)
The catholyte was neutralized using concentrated sulfuric acid.
The water was removed under diminished pressure and the salts that precipitated were filtered and washed with ethanol. The ethanol was removed and the residue distilled. A liquid weighing 40 g., b.p. 110° at 2 mm. was obtained. (A recovery of 46.5%).

The electrolytic reduction of 2-butyne-1,4-diol at a spongy nickel cathode in acid solution.
Cathode: A nickel wire gauze 6.5 x 16.5 cm. plated with spongy nickel
Anode: Lead
Catholyte: 43 g. (0.5 mole) 2-butyne-1,4-diol, 150 ml. 10% H₂SO₄
Anolyte: 500 ml. 10% H₂SO₄
Current: 4 amps.
Time: 18 hours (72 amp.hours)

The catholyte was neutralized with solid Na₂SO₃ and extracted four times with 50 ml. portions of ether. The ether extracts were combined and dried over anhydrous Na₂SO₄.

The water was removed under diminished pressure and the precipitated salts were filtered and washed several times with ethanol. The ethanol was removed and the liquid remaining was distilled. A liquid weighing 13 g., b.p. 104-105° at 1 mm. was collected. This was a recovery of 30% based on butynediol.

The ether from the extraction was removed and 1 g. of material was obtained. This gave a positive test for unsaturation.

**An attempt to reduce 2-butyne-1,4-diol using sodium and liquid ammonia.**

A solution containing 10 g. of 2-butyne-1,4-diol dissolved in 200 ml. of liquid ammonia was prepared in a 500 ml. Erlenmeyer flask. Then 10 g. of sodium metal was added until the solution was a deep blue color. Then 25 g. of NH₄Cl was added, followed by the addition of 100 ml. of ethanol. The NH₃ was allowed to evaporate and the inorganic salts filtered and washed with ethanol. The washings and filtrate were combined and the alcohol removed under vacuum. The remaining residue was distilled and 4.4 g. of material, b.p. 123° at 3.5 mm., m.p. 39° were obtained. A dibenzoate was prepared, m.p. 65-66° (2-butyne-1,4-dibenzoate, m.p. 76-77°).
This was apparently a mixture of \textit{trans} 2-butene-1,4-diol and 2-butyne-1,4-diol.

\textbf{An attempt to prepare \textit{trans} 2-butene-1,4-diol from dimethylfumarate.}

In a one liter three necked flask fitted with a reflux condenser and drying tube, addition funnel, and stirrer 20 g. (0.14 moles) of dimethyl fumarate was dissolved in 100 ml. of anhydrous tetrahydrofuran. The solution was cooled in an ice salt bath and 6.8 g. (0.18 moles) of lithium aluminum hydride dissolved in 200 ml. of dry tetrahydrofuran was added slowly with stirring to the solution of dimethyl fumarate. The time required for addition was one hour, after which the mixture was stirred for an additional hour. The excess lithium aluminum hydride was destroyed with ethyl acetate. Ten grams of water was added to the mixture, followed by 250 ml. of 10 per cent sulfuric acid solution. This mixture was then stirred for 12 hours. The tetrahydrofuran was removed under diminished pressure and the aqueous residue extracted continuously for four days with diethyl ether. The ether was removed and an amber colored viscous liquid remained. This residue would not distill at 0.5 mm. and at a bath temperature of 210°. The weight of the liquid was 7 grams.

\textbf{A second attempt to prepare \textit{trans} 2-butene-1,4-diol from dimethylfumarate.}

In this attempt the reaction was carried out using the same procedure as above with the addition of dimethyl fumarate solution to the lithium aluminum hydride solution as the only difference. The final product was 7 g. of an amber colored viscous liquid that would not distill at 0.5 mm. and 210°.
An attempt to prepare trans 2-butene-1,4-diol from fumaric acid.

Anhydrous ether (200 ml.) was placed in a one liter three necked flask fitted with a mechanical stirrer, dropping funnel and condenser equipped with drying tube. Then 19.5 g. (0.5 mole) of lithium aluminum hydride was dissolved in the ether by stirring for two hours. A slurry of 22.8 g. (0.2 mole) of fumaric acid and 250 ml. of dry ether was added slowly and the resultant mixture stirred at room temperature for 24 hours. The excess hydride was then cautiously destroyed with water and the lithium aluminum organo intermediate decomposed with twenty per cent sulfuric acid. The two layers were separated and the aqueous layer was continuously extracted with ether for three days. When the ether was removed no residue remained. The aqueous layer was made strongly acid with concentrated sulfuric acid and a white precipitate was obtained, which after filtering, washing, and drying proved to be fumaric acid. The weight of the recovered fumaric acid was 15 g.

An attempt to prepare cis 2-butene-1,4-diol from dimethyl maleate.

In a one liter 3 necked flask fitted with condenser and drying tube, addition funnel and mechanical stirrer 20 g. (0.14 mole) of dimethyl maleate was dissolved in 100 ml. of anhydrous ether. The solution was cooled in an ice salt bath and 6.8 g. (0.18 mole) of lithium aluminum hydride dissolved in 200 ml. of anhydrous ether was added slowly with stirring to the dimethyl maleate solution. After the hydride was added the mixture was stirred for an additional hour. Then the excess hydride was destroyed with ethyl acetate. Water (10 g.) was added to destroy the complex and then 250 ml. of 10% sulfuric acid solution and
the mixture was allowed to stand overnight. The ether layer was removed and the water layer extracted continuously with ether for 4 days. The ether layer and extract were combined and the ether and alcohols present were removed. A viscous amber colored residue remained. This residue could not be distilled even at 0.5 mm. pressure. The weight of this residue was 7 grams.

Attempted Electrolytic reduction of cis 2-butene-1,4-diol to butane-1,4-diol.

Cathode: A copper wire gauze 7 x 11 cm. plated with spongy copper from a copper sulfate solution.

Anode: An iron wire gauze

Catholyte: 4.4 g. (0.5 mole) of cis 2-butene-1,4-diol, 30 ml. of 1 N NaOH, 120 ml. of water

Anolyte: 500 ml. of 4 N NaOH

Cathode compartment: A porous pot inside diameter 7 cm., height 12.5 cm.

Anode compartment: one liter beaker

Current: 4 amps.

Time: 14 hours (56 amp hours).

The catholyte was extracted three times with 50 ml. portions of ether. After which it was neutralized with concentrated sulfuric acid and then extracted continuously for six days. The combined extracts from first extraction were dried over anhydrous sodium sulfate and the ether was then removed. The remaining liquid was distilled and 12 g., b.p. 110-116°C, nD23 1.4030 and one gram of higher boiling material was obtained. A 3,5-dinitrobenzoate of the 12 g. fraction was prepared m.p. 60-61°C.
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<td>The Attempted Electrolytic Reduction of 2-butyne-1,4-diol at a Spongy Lead Cathode in Acid Solution</td>
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<td>The Electrolytic Reduction of 2-butyne-1,4-diol at a Spongy Copper Cathode in Neutral Solution</td>
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<td>The Electrolytic Reduction of 2-butyne-1,4-diol at a Spongy Nickel Cathode in Basic Solution</td>
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(3,5-Dinitrobenzoate of n-butyl alcohol, m.p. 66°).

The ether from the continuous ether extraction was removed and the remaining liquid distilled, and 4 g. of material b.p. 95° at 1 mm. was obtained. A positive test for unsaturation was observed when a portion of this material was tested with bromine. The water was then removed from the catholyte under diminished pressure the salt filtered and washed with ethanol and the ethanol removed. There was no residue remaining.

The anolyte was also neutralized using concentrated hydrochloric acid. It was then saturated with sodium chloride and extracted continuously for 8 days with ether. When the ether and water from the extraction were removed, there was no residue remaining. The water from the anolyte layer was removed under vacuum and the salt precipitating out was filtered and washed with ethanol. Upon removal of the water there was no residue remaining.

Preparation of pure cis 2-butene-1,4-diol, trans 2-butene-1,4-diol, 2-butyne-1,4-diol and butane-1,4-diol for spectral purposes.

Pure cis 2-butene-1,4-diol was obtained from the hydrogenation of 2-butyne-1,4-diol using Raney nickel in ethanol (see page 11). The cis 2-butene-1,4-diol was fractionated under vacuum until no acetylenic lines appeared in the Raman Spectra. A small sample (.001 mole) was hydrogenated in a microhydrogenator and the sample analyzed 99-100% butenediol. [Dibenzoate m.p. 67°].

The pure trans 2-butene-1,4-diol was obtained from the preparation already outlined (see pages 11-12).
Pure butynediol was obtained by extracting it continuously with ether from a 35% water solution (obtained from General Aniline and Film Corp.) and then redistilling.

Pure butane-1,4-diol was obtained by redistilling the material obtained from General Aniline and Film Corp.

The analytical procedure using Raman spectrograph.

I. Qualitative identification of Isomers.

Before the products from the reduction reactions could be analyzed spectroscopically, it was necessary that all impurities that could cause fluorescence be removed. This was accomplished by heating 20-25 ml. of the material with Darco G-60 about 5 to 10 minutes then filtering distilling the material directly into the Raman sample tube, using a special distillation flask and receiver (see Figure 30). It was also necessary that all joints on the distillation apparatus be grease-free otherwise the sample would be contaminated with fluorescent material. Sometimes it was necessary to add 4 or 5 drops of nitrobenzene which helped quench fluorescence by collisions of the second order. The spectrograph used was a Lane Wells Model 40-A6 spectrograph and 60-A2 excitation equipment. The exciting line was the 4358 Å Hg line. The arcs used are water jacketed low pressure Hg arcs, operated at a current of 25 amps. The power consumption at maximum current is about 4 kilowatts per arc. The low pressure arcs have the advantage of:


(1) low intensity of continuous background, (2) relatively weak satellites of the 4358 Å Hg line, and (3) decreased pressure broadening of the 4358 Å line. A filter jacket of saturated sodium nitrite solution was used to isolate
the 4358 Å Hg line. An exposure of 30 minutes was generally sufficient to record the ethylenic and acetylenic lines. The spectra were photographed on Eastman Kodak F-103 film strip and developed for 5 minutes in E.K. - D19 washed, fixed for 10 minutes then washed and allowed to dry.

The shifts of the Raman lines from the exciting lines were obtained by exposing the film strip to an argon arc spectra before exposing the sample. After the film had been developed it was placed on the stage of a traveling microscope and the distance \( Y \) between the two argon lines 4132 Å and 4965 Å was determined. The distance \( X \) between the argon line 4132 Å and Raman lines was obtained. Then \( X/Y = x \), and in order to find the frequency shift from the 4358 Å Hg line for each Raman line, a table was consulted and for each value of \( x \) there was a corresponding frequency shift in cm\(^{-1}\).

II. Quantitative Procedure.\(^1\)


Solutions containing known amounts of cis 2-butene-1,4-diol and 2-butyne-1,4-diol and butane-1,4-diol were made up as follows:

<table>
<thead>
<tr>
<th>Std. No.</th>
<th>g. 2-butene-1,4-diol</th>
<th>g. 2-butyne-1,4-diol</th>
<th>g. butane-1,4-diol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.67 g.</td>
<td>14.33 g.</td>
<td>0.00 g.</td>
</tr>
<tr>
<td>2</td>
<td>17.50 g.</td>
<td>3.75 g.</td>
<td>3.75 g.</td>
</tr>
<tr>
<td>3</td>
<td>21.25 g.</td>
<td>2.50 g.</td>
<td>1.25 g.</td>
</tr>
<tr>
<td>4</td>
<td>21.25 g.</td>
<td>1.25 g.</td>
<td>2.50 g.</td>
</tr>
<tr>
<td>5</td>
<td>23.75 g.</td>
<td>1.25 g.</td>
<td>0.00 g.</td>
</tr>
</tbody>
</table>
The spectrum of the above standards was obtained in the same manner as outlined in the qualitative procedure. The time of exposure being exactly thirty minutes and the lamp current 25 amps per lamp. The film was developed for exactly five minutes in D-19 solution and fixed for ten minutes in the acid fixing solution. The temperature for developing and fixing was 26.0°.

The line pair chosen was the 1660 cm\(^{-1}\) line for the cis 2-butene-1,4-diol and the 2280 cm\(^{-1}\) line for 2-butyne-1,4-diol. The densities of each of the lines was obtained on a Leeds and Northrup microphotometer equipped with a Speedomax pen recorder, which gives densities directly. The paper moves at a speed of 2 inches per minute and the plate was scanned at one mm. per minute. The densities obtained in this manner were converted to relative intensities by the following plate calibration procedure.\(^1\) The spectra of pure chloroform was recorded at various times of exposure 10, 20, 30, 40 minutes, and developed the same as for the above standard samples. The density of the 459 cm\(^{-1}\) line was obtained for each time of exposure on the Leeds and Northrup microphotometer. A plot of density vs. time of exposure (relative intensity) was prepared. The densities obtained from the microphotometer tracings of the standard samples were converted to relative intensities from this plot. The intensity of the background was subtracted from the peak intensity of the line to get the corrected intensity.

The ratio of intensity of the 1660 cm\(^{-1}\) line of cis 2-butene-1,4-diol and the 2280 cm\(^{-1}\) line for 2-butyne-1,4-diol was obtained for each

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standard and this ratio was plotted against the ratio grams of cis 2-butene-1,4-diol vs. grams of 2-butyne-1,4-diol, and a working curve obtained.

The ratio of intensities for this line pair in the samples analyzed was obtained in the same manner as described for the standard samples. The gram ratio was obtained from the working curve and knowing the weight of sample in the Raman tube, the weight of cis 2-butene-1,4-diol and 2-butyne-1,4-diol was then determined.

The presence and amount of butane-1,4-diol in the product was determined by hydrogenating one thousandth of a mole of the sample using platinum oxide catalyst and hydrogen. The hydrogenation was performed in a microhydrogenator and the value for the amount of hydrogen absorbed was a measure of the total unsaturation, due to butene and butyndiols. To determine the amount of butanediol the following calculation was necessary.

\[ g_x = \text{grams cis 2-butene-1,4-diol} \]
\[ g_y = \text{grams 2-butyne-1,4-diol} \]
\[ X = \text{moles cis 2-butene-1,4-diol} \]
\[ Y = \text{moles of butyne-1,4-diol} \]
\[ \frac{g_x}{g_y} = A \text{ (from the working curve)} \]
\[ \frac{g_x}{38} = X \]
\[ \frac{g_y}{86} = Y \]
\[ \frac{X}{Y} = A \frac{86}{38} \]

---

\[ X = \frac{86A}{88} ; \quad Y = \frac{88X}{86A} \]

\[ H = \text{moles hydrogen absorbed by the sample} \]

\[ X + 2Y = H \]

\[ \frac{86A}{88} + 2Y = H \]

\[ Y = \frac{H}{86A} + 2 \]

\[ X = H - 2 \frac{88}{86A} + 2 \]

then grams of sample taken for hydrogenation minus \( \frac{86Y + 88X}{86A} \) equals grams of butanediol.

**Formation of volatile material during reduction of 2-butyne-1,4-diol.**

Cathode: Copper wire gauze plated with spongy copper 6 x 9 cm.

Anode: Iron wire gauze

Catholyte: 22 g. (0.26 mole) 2-butyne-1,4-diol, 20 ml. 1 N NaOH solution, 80 ml. water

Anolyte: 600 ml. 4 N NaOH

Cathode compartment: A porous pot inside diameter 7 cm., height 12.5 cm. Fitted with a rubber stopper through which a glass tube with the cathode sealed into it was inserted.

Anode compartment: 1 liter beaker

Current: 4 amps

Time: 15 hours (60 amp hours)

The cathode compartment was connected to a dry ice trap to prevent the escape of any volatile material. The catholyte was neutralized with HCl, saturated with sodium chloride and extracted continuously for 10 days with ether. The ether was removed and residue distilled. Two fractions one amounted to 10 g., b.p. 116-117°C, \( n^D_{25} = 1.4105 \) and the second
fraction weighing 11.3 g., b.p. 90-92° at 1 mm. were obtained. The infrared spectrum of the first fraction was recorded.

The only material that condensed in the dry ice trap was water vapor.

Attempt to determine possible decomposition products from electrolytic reduction of 2-butyne-1,4-diol.

Cathode: Copper wire gauze plated with spongy copper from copper sulfate solution, 6 x 9 cm.

Anode: Iron wire gauze

Catholyte: 86 g. (1 mole) 2-butyne-1,4-diol, 30 ml. of 1 N NaOH, 120 ml. water

Anolyte: 600 ml. 4 N NaOH

Cathode compartment: A porous pot inside diameter 7 cm.; height 12.5 cm. Fitted with a rubber stopper through which a glass tube with cathode sealed into it was inserted.

Anode compartment: 1 liter beaker

Current: 4 amps

Time: Total 25.5 hours (102 amp hours)

The cathode compartment was connected in series to a dry ice acetone trap, a 2,4-dinitrophenylhydrazine hydrochloride bubbler and a ammoniacal cuprous chloride bubbler which in turn was connected to a water aspirator. The purpose of the water aspirator was to draw air through the system in order to sweep any volatile material out of the cathode compartment and into the various traps.

After the reaction had been running for 5 hours a portion of the anolyte was neutralized with hydrochloric acid and tested for unsaturation,
with bromine water and also with neutral potassium permanganate. The test was positive in both cases. The reaction was interrupted at the end of fourteen hours at which time the anolyte was again tested for unsaturation and again gave a positive test.

Before the reaction was continued the cathode was removed, washed with distilled water, cleaned with dilute hydrochloric acid and replated with spongy copper. The anolyte was also removed and fresh 4 N NaOH was added. The 2,4-dinitrophenylhydrazine and the ammoniacal cuprous chloride bubblers were removed and a bromine water bubbler was added in their place. The reaction was again resumed and allowed to proceed for 11.5 hours. At the end of which time the catholyte was neutralized with concentrated hydrochloric acid saturated with sodium chloride and extracted ten days, with ether. The anolyte was treated in a similar manner. The ether from the catholyte extraction was dried over anhydrous sodium sulfate and then removed, and the remaining residue distilled. Four grams of material b.p. 116-117° were obtained from the first fraction and 52.5 grams b.p. 87-88°/5 mm. was obtained from the second fraction, which amounted to a 57% recovery of glycol.

About 5 ml. of material had collected in the dry ice trap, which proved to be water. The 2,4-dinitrophenylhydrazine bubbler failed to detect any aldehyde and the ammoniacal cuprous chloride bubbler failed to detect any acetylene. The bromine water bubbler used in the second case gave no indication that any olefin was formed.

An experiment to determine where the loss of material occurred during the electrolytic reduction of 2-butylene-1,4-diol.

Cathode and Anode: Slomin platinum electrodes
Catholyte: 10 g. of 2-butyne-1,4-diol, 10 ml. of 1 N NaOH, 40 ml. of water
Anolyte: 100 ml. of 4 N NaOH
Cathode compartment: A porous pot inside diameter 4.5 cm., height 9.7 cm.
Anode compartment: A 250 ml. beaker
Time: 12 hours
Before the start of the reaction a sample was removed from the anode compartment, neutralized with sulfuric acid and tested for unsaturation using bromine water and also with neutral permanganate solution. The test was negative. After the reaction was started samples were taken from the anode compartment at regular intervals and tested as before for unsaturation. In every case there was a positive test for unsaturation.
A similar reaction was carried out using 2-butene-1,4-diol with identical results.
An experiment to determine the migration of 2-butyne-1,4-diol through the porous pot when no current was passing and the efficiency of isolation of material from the catholyte.
Cathode: none
Anode: none
Catholyte: 46 g. (0.53 mole) of 2-butyne-1,4-diol, 30 ml. 1 N NaOH, 120 ml. of water
Anolyte: 300 ml. 4 N NaOH
Cathode compartment: A porous pot inside diameter 7 cm., height 12.5 cm.
Anode compartment: 1 liter beaker
The porous pot was placed inside the one liter beaker and allowed to stand for 72 hours. At the end of which time the catholyte was neutralized with conc. sulfuric acid. The water was removed under diminished pressure, the salt that precipitated out was filtered and washed with alcohol. The remaining water and alcohol were removed under vacuum and residue remaining was distilled. Thirty-seven grams of material m.p. 64° and 4 grams of tar remaining in flask were recovered. The anolyte was worked up in an identical manner and 5 grams of 2-butyne-1,4-diol were recovered.

An experiment to determine the migration of cis 2-butene-1,4-diol through the porous pot when no current was passing and the efficiency of isolation of the material from the catholyte.

Cathode: Copper wire gauze plated with spongy copper from copper sulfate plating both.

Anode: Iron wire gauze

Catholyte: 44 g. (0.5 mole) of cis 2-butene-1,4-diol, 30 ml. 1 N NaOH, 120 ml. of water

Anolyte: 600 ml. 4 N NaOH

Cathode compartment: a porous pot inside diameter 7 cm., height 12.5 cm.

Anode compartment: 1 liter beaker

Amp: 0.0

Time: 21 hours

A sample from the anode compartment was tested at the start of the experiment with bromine water and with neutral potassium permanganate for unsaturation, the test was negative. At the end of the 21 hours a
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<td>28</td>
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<tr>
<td>An Attempt to Prepare trans 2-butene-1,4-diol from Fumaric Acid</td>
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A sample from the anode compartment was tested again for unsaturation and a very faint positive test was observed. Approximately 95% of the starting material was recovered from the catholyte, when the catholyte was worked up in the same manner as for the experiment using 2-butyne-1,4-diol.

**The electrolytic reduction of 2-butyne-1,4-diol at a mercury cathode using tetraethyl ammonium hydroxide as electrolyte.**

Cathode: Mercury covering the bottom of the cathode compartment
Anode: Lead sheet
Catholyte: 50 g. 2-butyne-1,4-diol, 100 ml. H₂O, 150 ml. 10% tetraethyl ammonium hydroxide
Anolyte: 50 ml. H₂SO₄, 200 ml. H₂O
Cathode compartment: Borous pot inside diameter 9 cm., height 20 cm.
Anode compartment: 3 liter beaker
Current: 3 amps
Time: 15 hours (75 amp hours)

It was necessary to use sulfuric acid as anolyte to prevent the rapid migration of water from the anolyte to the catholyte when the quaternary ammonium hydroxide was used in the anolyte. A large amount of a grayish solid appeared during the reduction, this apparently was an amalgam.

The catholyte was extracted continuously with ether for 6 days. The ether was removed and the product remaining distilled. A substance weighing 14 g., b.p. 110° at 2 mm. was obtained. This material solidified on standing which indicated that the majority of the product was unreduced 2-butyne-1,4-diol.
The Raman spectrum of this product was obtained. The spectrum indicated that very little reduction of the 2-butene-1,4-diol had occurred. The microphotometer tracing of the spectrum showed that a mixture of cis and trans 2-butene-1,4-diol was formed.

**Electrolytic reduction of 2,4-hexadiyne-1,6-diol at spongy copper cathode.**

Cathode: A 6 x 9.5 cm. copper wire gauze plated with spongy copper

Anode: Iron wire gauze

Catholyte: 55 g. (0.5 mole) of 2,4-hexadiyne-1,6-diol, 100 ml. of ethyl alcohol, 70 ml. of water, 30 ml. of 1 N NaOH

Anolyte: 600 ml. 4 N NaOH

Cathode compartment: A porous pot inside diameter 7 cm., height 12.5 cm. Fitted with a rubber stopper through which a copper wire sealed in a glass tube was connected to the cathode, and also a glass tube that was connected to a trap immersed in dry ice and acetone.

Anode compartment: 1 liter beaker

Current: 4 amps.

Time: 21.2 hours (84.8 amp hours)

At the end of the reaction the catholyte was extracted with two 100 ml. portions of hot benzene and then with two 100 ml. portions of ether, both extracts dried over anhydrous sodium sulfate. The aqueous layer was neutralized with concentrated hydrochloric acid, saturated with sodium chloride and continuously extracted for 5 days with ether. The first ether extract was combined with continuous ether extract and the 10 ml. of material that had condensed in the dry ice trap. This mixture was
dried over anhydrous sodium sulfate and the ether removed. This residue and benzene extract were combined and the benzene plus the ethyl alcohol that was used in the reduction were removed. The residue was distilled and 8.6 g. b.p. 84-86°/30 mm., n\textsubscript{D}^2 1.4741, was obtained. Analysis: Calculated for C\textsubscript{6}H\textsubscript{10}O: C, 73.46; H, 10.30.

Found: C, 69.03; H, 10.32.

When 0.00104 moles (0.102 g.) of this material was hydrogenated in a micro hydrogenator, 0.002 moles of hydrogen were absorbed.

(1) Siggia, S., "Quantitative Organic Analysis via Functional Groups"

The hydroxyl value was determined by the method outlined by Siggia.\textsuperscript{2}

(2) Ibid, page 3.

A weighed sample containing about 0.002 mole of hydroxyl was introduced into a glass stoppered iodine flask together with 5.00 ml. of the acetylating reagent. The reagent was accurately measured, a pipet being used. The glass stopper was well moistened with pyridine and loosely sealed. The flask was put on a steam bath for 45 minutes. Then 10 ml. of water was added by way of the well on the top of the flask, and the flask was swirled to bring the water in contact with all the reagent. After 2 minutes the flask was cooled in ice or under running water, with the stopper partly opened to prevent a partial vacuum from forming inside the flask. The sides of the flask and stopper were rinsed with 10 ml. of n-butanol, a few drops of indicator
added, and the contents titrated with 0.5 N sodium hydroxide.
Calculated for $\text{C}_9\text{H}_{10}\text{O}: \text{OH}, 17.3\%$. Found: OH, 17.2\%.

A one gram sample of this material and one gram of maleic
anhydride were mixed together in 5 ml. of benzene and the mixture was
allowed to stand for 5 days, during which time a waxy solid formed.
The benzene was removed and several attempts were made to recrystallize
the solid. The following solvents, toluene, acetic acid, ethanol,
cyclohexanone, and pyridine were tried, but the material could not be
recrystallized.

An attempt was made to prepare both the 3,5-dinitrobenzoate and
the $\alpha$-naphthyl urethane, but in each case an oil that would not
solidify was obtained.

The ultraviolet absorption spectrum was obtained on an ethanolic
solution of the compound, see Figure 29. The wavelength at the maximum
absorption $\mu = 225$ and $\varepsilon = 13,132$.

The electrolytic reduction of 2,4-hexadiyn-1,4-diol at spongy
nickel cathode.
Cathode: Nickel gauze plated with spongy nickel from the nickel
plating solution. Size 7 x 8 cm.
Anode: Lead
Catholyte: 27.5 g. (0.25 mole) 2,4-hexadiyn-1,6-diol, 60 ml. of
ethanol, 40 ml. of water, 30 ml. of 4\% KOH
Cathode compartment: Porous pot inside diameter 7 cm., height
12.5 cm.
Anode compartment: 1 liter beaker
Current: 4 amps.
Time: 10 hours (40 amp hours)

The catholyte was neutralized with concentrated hydrochloric acid, saturated with sodium chloride and continuously extracted with ether for ten days. The ether extract was dried over drierite and the ether and alcohol removed. The residue was a solid weighing 16 grams. This solid was recrystallized from a 5 to 1 mixture of benzene and ethyl acetate m.p. 110-112°. Mixed with pure 2,4-hexadiyne-1,6-diol this solid did not depress the melting point of the pure hexadiynediol. The 16 grams amounted to a recovery of 59% of the initial starting material.

**Electrolytic reduction of 2,4-hexadiyne-1,6-diol at an oxidized copper cathode.**

Cathode: Copper wire gauze 14 x 15 cm. oxidized in a gas oxygen flame
Anode: Lead
Catholyte: 88 g. (0.89 mole) 2,4-hexadiyne-1,6-diol, 200 ml. of tetrahydrofuran, 30 ml. of water, 20 ml. of 1 N NaOH
Anolyte: 200 ml. of 4 N NaOH
Cathode compartment: 1 liter beaker
Anode compartment: a porous pot inside diameter 7 cm., length 13 cm.
Current: 5 amps.
Time: 17.1 hours (85.5 amp hours)

When the reaction was completed the catholyte was neutralized with concentrated hydrochloric acid, saturated with sodium chloride and extracted five times with ether. The ether extracts were combined and dried over anhydrous sodium sulfate. The ether was removed and remaining liquid distilled. Two fractions were obtained one weighing 11 g., b.p.
94° at 70 mm., $n_D^{22} 1.4583$ and the other weighing 2 g. b.p. 50° at 1 mm., $n_D^{22} 1.4869$. When 0.098 grams of the first fraction was hydrogenated using a platinum oxide catalyst in a microhydrogenator (cf. Siggia loc. cit.), the material absorbed 0.016 moles of hydrogen. Several attempts were made to prepare a 3,5-dinitrobenzoate and an $\alpha$-naphthyl urethane but they were unsuccessful. In each case, an oil was obtained which would not crystallize.

The reduction of methyl sorbate to sorbyl alcohol (2,4-hexadiene-1-ol).

Methyl sorbate, 22 g. (0.17 mole) was dissolved in 100 ml. of anhydrous ether in a one liter three necked flask fitted with a dropping funnel, condenser fitted with drying tube, and mechanical stirrer. The flask was cooled in an ice bath and $\frac{1}{2}$ g. (0.11 mole) of lithium aluminum hydride dissolved in 200 ml. of anhydrous ether and added dropwise to the ether solution of ether and methyl sorbate. The total time for additions was one hour. The reaction was allowed to stir for an additional hour and a half. The excess lithium aluminum hydride was destroyed with ethyl acetate followed by the addition of 10 ml. of water. Then 200 ml. of 10% sulfuric acid was added and mixture allowed to stir for twenty-four hours. The ether layer was removed and water layer extracted five times with 100 ml. portions of ether. The ether layer and extract were combined and the ether removed. The liquid remaining was distilled, and 10 g., b.p. 89-90° at 45 mm. which solidified on cooling, m.p. 31°, $n_D^{22} 1.4964$, was obtained. This was a yield of 59°. A 3,5-dinitrobenzoate m.p. 86-87° was prepared (literature value m.p. 85°). The infrared and Raman spectrum were also obtained (see Figure 26 and Table 12).
Reduction of propargyl alcohol at oxidized copper cathode

Cathode: Copper wire gauze 14 x 15 cm. oxidized in a gas flame

Anode: Lead

Catholyte: 56 g. (1 mole) of propargyl alcohol, 400 ml. of water, 100 ml. of 1 N NaOH

Anolyte: 50 ml. 4 N NaOH

Cathode compartment: 1 liter beaker

Anode compartment: Porous pot inside diameter 4.5 cm., height 14.8 cm.

Current: 5 amps.

Time: 15 hours (65 amp hours)

When the reaction was completed the catholyte was neutralized with concentrated hydrochloric acid, saturated with sodium chloride and extracted six times with 75 ml. portions of ether. The ether was removed and the residue dried over anhydrous calcium sulfate. A liquid weighing 16 g., b.p. 91-96°, n_D^20 1.4016, was recovered. (Literature for allyl-alcohol b.p. 96-97°; propylalcohol 96-97°; propargyl alcohol 114-116°). The 16 g. was a recovery of 29% based on the original propargyl alcohol.

An α-naphthyl urethane was prepared and the melting point after five recrystallizations from skellysolve F and two from chloroform remained at 100-101°. (Literature for allylalcohol m.p. 108°; propyl alcohol m.p. 80°). The material also gave a faint test for propargyl alcohol with alcoholic silver nitrate.

The percent unsaturation calculated as allyl alcohol was obtained by adding bromine in acetic acid to a weighed sample of the material. The excess bromine was determined by liberating iodine from potassium iodide and titrating the iodine with sodium thiosulfate using starch
as an indicator. The percent unsaturation calculated as allyl alcohol was 62.6%.

Results

The Raman spectra of 2-butyne-1,4-diol, cis 2-butene-1,4-diol, trans 2-butene-1,4-diol, trans 1,4-diacetoxy-2-butene.

The Raman spectra of the above compounds were determined, on the neat liquid (except 2-butyne-1,4-diol) in a 15 ml. sample tube, following the procedure that has already been outlined.

Table 1

cis 2-butene-1,4-diol (from reduction of 2-butyne-1,4-diol with hydrogen and Raney nickel)

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency cm⁻¹</th>
<th>Observed</th>
<th>Literature¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>939</td>
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</tr>
<tr>
<td>3</td>
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<td>4</td>
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<td>5</td>
<td>1260</td>
<td></td>
<td>1256 (2)</td>
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<tr>
<td>6</td>
<td>1350</td>
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<td>7</td>
<td>1467</td>
<td>1472 (1/2)</td>
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<td>8</td>
<td>1592</td>
<td></td>
<td></td>
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<tr>
<td>9</td>
<td>1661 (v.s.)</td>
<td>1660 (4)</td>
<td></td>
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</tbody>
</table>

### Table 2

cis 2-butene-1,4-diol (from reduction of 2-butyne-1,4-diol and spongy copper)

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency cm(^{-1})</th>
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<tr>
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</tr>
<tr>
<td>9</td>
<td>1658</td>
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### Table 3

cis 2-butene-1,4-diol (zinc dust and alkali, reduction of 2-butyne-1,4-diol)

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<th>Band</th>
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<td>10</td>
<td>2215</td>
</tr>
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<td>2280</td>
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Table 4

**trans 1,4-diacetoxy-2-butene**

<table>
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<tr>
<th>Band</th>
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<tr>
<td></td>
<td>Observed</td>
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<td>12</td>
<td>1682 (v.s.)</td>
</tr>
<tr>
<td>13</td>
<td>1739</td>
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</table>

(1) Valette, A., loc. cit.
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<tr>
<th>Band</th>
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</thead>
<tbody>
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<td>2</td>
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<tr>
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<tr>
<td>13</td>
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### Table 6
**2-butyne-1,4-diol (13.12 g. in 11.87 g. water)**

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<th>Frequency cm(^{-1})</th>
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</tr>
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<td>3</td>
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</tr>
<tr>
<td>4</td>
<td>2217</td>
</tr>
<tr>
<td>5</td>
<td>2278</td>
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Table 7

Butane-1,4-diol (G.A.F.)

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<th>Frequency cm⁻¹</th>
</tr>
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</tr>
<tr>
<td>10</td>
<td>1478</td>
</tr>
</tbody>
</table>

Table 8

Mixture 88.5% cis 2-butene-1,4-diol and 11.5% butane-1,4-diol

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>936</td>
</tr>
<tr>
<td>2</td>
<td>980</td>
</tr>
<tr>
<td>3</td>
<td>1028</td>
</tr>
<tr>
<td>4</td>
<td>1257</td>
</tr>
<tr>
<td>5</td>
<td>1463</td>
</tr>
<tr>
<td>6</td>
<td>1659</td>
</tr>
</tbody>
</table>
Table 9

Raman spectra of the product from 2-butylene-1,4-diol
reduced at a spongy zinc cathode

<table>
<thead>
<tr>
<th>Band</th>
<th>1st Run</th>
<th>2nd Run</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1002</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1027</td>
<td>1025</td>
</tr>
<tr>
<td>3</td>
<td>1299</td>
<td>1294</td>
</tr>
<tr>
<td>4</td>
<td>1348</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1457</td>
<td>1455</td>
</tr>
<tr>
<td>6</td>
<td>1589</td>
<td>1589</td>
</tr>
<tr>
<td>7</td>
<td>1664(s)</td>
<td>1661(s)</td>
</tr>
<tr>
<td>8</td>
<td>1674(s)</td>
<td>1675(s)</td>
</tr>
<tr>
<td>9</td>
<td>2221</td>
<td>2211</td>
</tr>
<tr>
<td>10</td>
<td>2286</td>
<td>2276</td>
</tr>
</tbody>
</table>
Table 10

Summary of the Raman spectra from the products obtained at the various cathodes

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Experimental Page No.</th>
<th>C=C Frequency cm(^{-1})</th>
<th>C=CH Frequency cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>18 and 19</td>
<td>1660</td>
<td>2219; 2280</td>
</tr>
<tr>
<td>Ag</td>
<td>21</td>
<td>1661</td>
<td>2220; 2285</td>
</tr>
<tr>
<td>Ni (basic)</td>
<td>26</td>
<td>1660</td>
<td>2222; 2282</td>
</tr>
<tr>
<td>Ni (acid)</td>
<td>26</td>
<td>1659</td>
<td>2217; 2281</td>
</tr>
<tr>
<td>Co</td>
<td>21</td>
<td>1659</td>
<td>2220; 2283</td>
</tr>
<tr>
<td>Zn</td>
<td>19</td>
<td>1661, 1675</td>
<td>2211; 2276</td>
</tr>
<tr>
<td>Pb</td>
<td>17</td>
<td>1675</td>
<td>2219; 2283</td>
</tr>
<tr>
<td>Pb</td>
<td>17</td>
<td>1676</td>
<td>2219; 2280</td>
</tr>
<tr>
<td>Cd</td>
<td>22</td>
<td>1675</td>
<td>2216; 2282</td>
</tr>
<tr>
<td>Sn</td>
<td>23</td>
<td>1676</td>
<td>2220; 2280</td>
</tr>
<tr>
<td>Hg (amalgamated Cu)</td>
<td>17a</td>
<td>1676</td>
<td>2217; 2283</td>
</tr>
<tr>
<td>Cu (neutral)</td>
<td>24</td>
<td>1659</td>
<td>none</td>
</tr>
<tr>
<td>Cu (acid)</td>
<td>25</td>
<td>1661</td>
<td>none</td>
</tr>
<tr>
<td>Pb (acid)</td>
<td>23</td>
<td>none</td>
<td>2218; 2284</td>
</tr>
</tbody>
</table>
Table 11

Unsaturation values, based on hydrogen absorbed, for the products obtained in the electrolytic reductions

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Experimental Page No.</th>
<th>Electrolyte</th>
<th>Weight of Sample</th>
<th>Moles H₂ Absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>18</td>
<td>NaOH</td>
<td>0.089</td>
<td>0.000935</td>
</tr>
<tr>
<td>Cu</td>
<td>19</td>
<td>NaOH</td>
<td>0.086</td>
<td>0.00116</td>
</tr>
<tr>
<td>Ni</td>
<td>26</td>
<td>NaOH</td>
<td>0.086</td>
<td>0.00078</td>
</tr>
<tr>
<td>Ag</td>
<td>21</td>
<td>NaOH</td>
<td>0.086</td>
<td>0.00138</td>
</tr>
<tr>
<td>Co</td>
<td>21</td>
<td>NaOH</td>
<td>0.083</td>
<td>0.0017</td>
</tr>
<tr>
<td>Cu</td>
<td>25</td>
<td>H₂SO₄</td>
<td>0.089</td>
<td>0.0010</td>
</tr>
<tr>
<td>Cu</td>
<td>24</td>
<td>KH₂PO₄-H₃PO₄</td>
<td>0.085</td>
<td>0.00076</td>
</tr>
</tbody>
</table>

Table 12

Raman spectra of reduction product of 2,4-hexadiyne-1,6-diol and for methyl sorbate and sorbyl alcohol (2,4-hexadiene-1-ol).

<table>
<thead>
<tr>
<th>Reduction product Frequency cm⁻¹</th>
<th>Methyl Sorbate Frequency cm⁻¹</th>
<th>Sorbyl Alcohol Frequency cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1379</td>
<td>1142</td>
<td>1160</td>
</tr>
<tr>
<td>1416</td>
<td>--</td>
<td>1295</td>
</tr>
<tr>
<td>1445</td>
<td>--</td>
<td>1379</td>
</tr>
<tr>
<td>1554</td>
<td>1591</td>
<td>1450</td>
</tr>
<tr>
<td>1602</td>
<td>1616</td>
<td>1563</td>
</tr>
<tr>
<td>1653(s)</td>
<td>1648(s)</td>
<td>1606</td>
</tr>
<tr>
<td></td>
<td>1720</td>
<td>1663(s)</td>
</tr>
</tbody>
</table>
Table 13

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Catholyte</th>
<th>Moles butynediol</th>
<th>Number amp hours</th>
<th>Total recovered</th>
<th>Butenediol in total</th>
<th>Unchanged butynediol %</th>
<th>Butane-diol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>NaOH</td>
<td>1.0</td>
<td>55</td>
<td>72.4</td>
<td>91.2 cis</td>
<td>8.8</td>
<td>0</td>
</tr>
<tr>
<td>Cu</td>
<td>NaOH</td>
<td>1.4</td>
<td>76</td>
<td>39.2</td>
<td>92.5 cis</td>
<td>0</td>
<td>7.5</td>
</tr>
<tr>
<td>Cu</td>
<td>H₂SO₄</td>
<td>1.0</td>
<td>132</td>
<td>29.1</td>
<td>100 cis</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cu</td>
<td>neutral KH₂PO₄−H₃PO₄</td>
<td>0.5</td>
<td>54</td>
<td>38.0</td>
<td>78.5 cis</td>
<td>0</td>
<td>21.5</td>
</tr>
<tr>
<td>Ag</td>
<td>NaOH</td>
<td>1.0</td>
<td>95</td>
<td>67.5</td>
<td>72.2 cis</td>
<td>27.8</td>
<td>0</td>
</tr>
<tr>
<td>Zn</td>
<td>NaOH</td>
<td>1.0</td>
<td>81</td>
<td>43.0</td>
<td>cis and trans present</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>NaOH</td>
<td>1.0</td>
<td>77.5</td>
<td>46.5</td>
<td>69.0 cis</td>
<td>5.3</td>
<td>25.5</td>
</tr>
<tr>
<td>Ni⁶</td>
<td>H₂SO₄</td>
<td>0.5</td>
<td>72</td>
<td>30.2</td>
<td>- cis</td>
<td>present</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>NaOH</td>
<td>0.58</td>
<td>48</td>
<td>53.5</td>
<td>26.4 cis</td>
<td>73.5</td>
<td>0</td>
</tr>
<tr>
<td>Cd</td>
<td>NaOH</td>
<td>0.58</td>
<td>50</td>
<td>53.0</td>
<td>trans</td>
<td>present</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>NaOH</td>
<td>1.0</td>
<td>112</td>
<td>53.6</td>
<td>trans</td>
<td>present</td>
<td>-</td>
</tr>
<tr>
<td>Sn</td>
<td>NaOH</td>
<td>0.58</td>
<td>45</td>
<td>62.0</td>
<td>trans</td>
<td>present</td>
<td>-</td>
</tr>
<tr>
<td>Hg</td>
<td>(C₂H₅)₄NOH</td>
<td>0.58</td>
<td>75</td>
<td>28.0</td>
<td>cis and trans major product</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(Amalgamated Cu)</td>
<td>NaOH</td>
<td>1.0</td>
<td>132</td>
<td>53.5</td>
<td>trans</td>
<td>present</td>
<td>-</td>
</tr>
<tr>
<td>Pb</td>
<td>H₂SO₄</td>
<td>1.04</td>
<td>112</td>
<td>62.0</td>
<td>none</td>
<td>present</td>
<td>-</td>
</tr>
</tbody>
</table>

*Insufficient material to analyze by Raman spectrum*
Discussion

The results of the electrochemical experiments are collected in Table 1. It was surprising that so many cathodes reduced 2-butyne-1,4-diol, especially those of high overvoltage metals. The efficiency of Cu and Ag discounts any possibility that copper and silver acetylides (cf. introduction) were intermediates in the reduction.

Considering the group of catalytic metals (Cu, Ni, Ag, Co) it is, perhaps, not surprising that these metals as cathodes gave uniformly cis-reduction, since catalytic reduction of acetylenic glycols using hydrogen and iron, copper, silver, nickel and cobalt\(^1\) is claimed to produce cis ethylenic glycols. In fact the addition of hydrogen catalytically to acetylenes is predominately a cis addition.\(^2\)

(1) Johnston, A. W., "The Chemistry of the Acetylenic Compounds".

Volume 1. The Acetylenic Alcohols", Edward Arnold and Co.,


Dissolving zinc in sodium hydroxide\(^3\) has also been used to reduce acetylenic glycols and in particular 2-butyne-1,4-diol. The product in this case was claimed to be mainly cis 2-butene-1,4-diol. This result has been confirmed in this work. It is surprising that when zinc is used as a cathode (Table 1) it produced a mixture of cis and trans 2-butene-1,4-diol. From the stereochemical point of view zinc therefore
assumes an intermediate position between the so-called catalytic metals (Cu, Ag, Ni, Co) which give cis and the non-catalytic metals (Pb, Cd, Sn, amalgamated Cu) which give only trans butenediol.

It is remarkable that at amalgamated copper, lead, zinc, tin, and cadmium all metals of recognized high overvoltage trans-diol is the sole product. In fact it is altogether remarkable that reduction takes place at all since polarographic studies (cf. introduction) have indicated that acetylenic compounds are not reducible at a dropping mercury electrode unless they are conjugated with a phenyl, carboxyl, nitro, and etc. groups. Another interesting point is the failure of spongy lead in acid solution to reduce 2-butyne-1,4-diol. It is necessary that the potential required to reduce 2-butyne-1,4-diol be less than the potential required to liberate H₂ at the electrode, and, in the case where the electrolyte is sodium hydroxide, this appears to be true since butynediol can be reduced at spongy lead in sodium hydroxide. While in acid solution hydrogen evolution appears to be the only reaction taking place at spongy lead.

The electrochemical reduction of 2-butyne-1,4-diol to trans 2-butene-1,4-diol using Pb, Cd, Sn and amalgamated copper must proceed by a mechanism different from that taking place at spongy Cu, Ni, Co, and Ag since a different stereoisomer results from the second group of cathodes. As to what this mechanism may be it is not quite clear. Those cathodes that favor trans reduction are of the class 2 type, analogous to dissolving metals (cf. introduction), since the reduction of disubstituted acetylenic compounds by sodium and liquid ammonia gives the trans-olefin exclusively. The mechanism is, perhaps similar to the
electron transfer mechanism of Conant,\textsuperscript{1} a mechanism by which he has shown the reduction of certain organic compounds by vanadous salts takes place. This electron transfer mechanism was later extended by Wilson\textsuperscript{2} to electrochemical reductions.

\textsuperscript{1} Conant, J. B., Chem. Rev. \textbf{2}, 1 (1927).

\textsuperscript{2} Wilson, C. L., Record of Chemical Progress, Winter Issue, 1948.

If at high o.v. cathodes CEC is reduced by an electron transfer mechanism then trans reduction might be expected since sodium in liquid ammonia also reduces trans. During reduction the intermediate anion can be considered free of the surface and able to take on a second proton to give the stable isomer rather like the trans addition of Br\textsubscript{2} in homogeneous solution. For cis reduction adsorption on the metallic surface is most likely the true explanation.

**Low recovery of olefinic glycol**

The electrolytic reduction of butynediol had one limitation and that was the low recovery of glycol products. There could be several causes for this. Butynediol might be expected to decompose into formaldehyde and acetylene in the presence of sodium hydroxide solution. This hardly seems likely since this decomposition proceeds only at temperatures higher than those (above 30°) of our experiments. A second possibility is that the electrochemical process results in fission of the molecule into low boiling products. Attempts were made to detect low boiling material by means of a dry ice trap and suitable detectors, through which the gases from the cathode had to pass. The detectors
were first a vessel containing 2,4-dinitrophenylhydrazine hydrochloride solution for aldehyde and second, one containing ammoniacal cuprous chloride solution for acetylene.

The only material condensing in the dry ice trap was water vapor and no reaction was observed in the other two traps. On this evidence the low recovery could not be due to such decomposition of butynediol.

It was possible that low yields were due to poor recovery. To check this an experiment was conducted using butynediol in the catholyte, subjecting it to treatment identical with that in an electrochemical experiment, except that the current was not turned on. The recovery from the catholyte was 96% of the initial amount. Another experiment showed that cis butenediolic could also be recovered in high yield. It was concluded, therefore, that the trouble was not one of isolation.

One clue for this low recovery was the demonstration that in the products from an electrochemical reduction carried out for an extended period of time volatile materials were, indeed, formed. These, however, proved not to be aldehydeic or acetylenic but were primary alcohols, crotyl and butyl, formed by fission of one OH group from butyne or butenediolic. The butyl alcohol coming from complete reduction of the double or triple bond. Thus a loss of material by this method would be easy. Experiment showed that cis butenediolic was split to form crotyl and some butyl alcohols but the recovery was only 32%. It was never possible in an experiment to account for more than 75% of the material.

To test the migration of material through the porous pot under the influence of the electrical current an experiment using smooth platinum electrodes was performed. The choice of a smooth platinum cathode was
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made because reduction at it is almost negligible. Both butyne and cis
butene diols were examined and in both cases after about 30 minutes
with the current on the anolyte gave a positive test for unsaturation.
However, it was never possible to isolate anything from the anolyte.
Perhaps, any material that migrated was completely oxidized at the
anode to CO$_2$ and water. Therefore, it might be concluded that a
major portion of material could be lost in this fashion.

Analytical Methods

After preliminary experiments had been shown that 2-butyne-1,4-diol
could be reduced electrolytically, it was necessary to devise a scheme
for analyzing the resultant product. The following compounds were
possible components of the reduction product: unreduced 2-butyne-1,4-
diol, cis 2-butene-1,4-diol, trans 2-butene-1,4-diol and butane-1,4-diol.
It was essential therefore to devise a method that would indicate
which of these were present and to what extent.

Several methods were considered. First the methods for analyzing
for unreacted 2-butyne-1,4-diol. General Aniline and Film Company$^1$ have

(1) Private communication, General Aniline Film Company to Prof. C. L.
Wilson, 1951.


a scheme whereby 2-butyne-1,4-diol can be determined in the presence of
butene and butanediol. The sample containing the butanediol in methanol
was treated with ethyl ether boron trifluoride complex and mercuric
oxide followed by the addition of water and then hydroxylamine hydrochloride.
The hydrochloric acid liberated was then titrated with standard sodium
hydroxide solution. However, the results cannot be trusted too implicitly.
The average variation is 5%, and for amounts below 10% 2-butyne-1,4-diol the results are not conclusive.

A second possibility was the addition of sodium bisulfite to the triple bond and then determining the excess sodium bisulfate.


Unfortunately, sodium bisulfate could not be made to add to butynediol under the conditions of the determination.

The third method considered, was the addition of mercuric chloride to butynediol. The mercury salt thus formed, would precipitate and could be filtered and weighed. However, when a mixture of butynediol and cis butenediol was treated with mercuric chloride, the mercuric complex failed to precipitate.

The determination of cis and trans butenediols also had its difficulties. The application of dipole moments or refractive indices was ruled out when very little difference was noted between the values recorded for cis and trans butenediols.

The cyclization of cis 2-butyne-1,4-diol to 2,5-dihydrofuran was thought to be a promising method for determining cis butenediol. However, it was shown by Valette (loc.cit) that cis butenediol when
heated with hydrochloric acid yielded only 35% dihydrofuran and 65% crotonaldehyde, while trans butenediol under the same conditions produced 100% crotonaldehyde. Therefore, it would be rather difficult to devise a satisfactory quantitative method using this procedure.

Next, the absorption spectra of each of the possible products from the reduction was examined. First, infrared absorption curves were obtained on each of the pure materials: cis and trans butenediols, butanediol and butynediol. The spectra indicated that infrared analysis would be unsatisfactory since the absorption peaks were broad and the differences in the spectrum of each compound were too small to be used in any analytical method. (See Figures 13, 14, 15 and 16).

Finally, the Raman spectra of each of the pure materials was examined (in the case of 2-butyne-1,4-diol the spectra was taken on a 50% water solution). It was apparent that this method was satisfactory at least for determining qualitatively the composition of the reduction products. Although this method proved useful in the quantitative determination of the products, it had some disadvantages, which lessened its desirability as a routine procedure.

The value of 1660 cm\(^{-1}\) obtained for the double bond vibration of cis 2-butene-1,4-diol verified the value that Valette (loc.cit) obtained. The value for the double bond vibration of trans 2-butene-1,4-diol, 1675 cm\(^{-1}\), was in keeping with the theory that the trans double bond vibration should be some 15 cm\(^{-1}\) greater than the cis double bond vibration.\(^1\) For 2-butyne-1,4-diol, the frequency 2280 cm\(^{-1}\).

was assigned to the carbon-carbon triple bond which was the value to be expected for a disubstituted acetylenic compound (cf. Hibben loc. cit.). However, the Raman spectra of butane-1,4-diols had no characteristic group frequency that could be used to identify it, unequivocally, in a mixture containing butene and butynediols. It was necessary to determine the butanediol, by first obtaining the amounts of butenediols and any unreacted butynediol from the Raman spectra and then obtaining the total amount of unsaturation by the microhydrogenation method. The value for total unsaturation obtained by hydrogenation was compared with the value obtained by calculating it from the amounts of butene and butynediol, which were obtained from the Raman analysis. The difference, if any, was attributed to butanediol.

For obtaining total unsaturation, the microhydrogenation method was preferred over the bromine number method, since complete addition of bromine to butynediol was uncertain even when catalyzed with mercury salt.

(1) Cf. Siggia, S., loc. cit. page 33.

The quantitative analysis has as already been mentioned certain disadvantages, which limit its usefulness as a routine method. The following are some of the major disadvantages encountered. Any material that was to be analyzed by Raman spectra must be free from all substances that would fluoresce when radiated with the light from the mercury arc. In order to prevent fluorescence, it was necessary, first to treat the sample with Darco G-60, filter off the charcoal and then wash it with methanol to remove the absorbed glycols. After which the methanol was removed and the material distilled into the Raman
sample tube. Here, it can be seen are two possible sources of error. The composition of the material being analyzed can change during treatment with G-60, since all the material may not be completely removed from the charcoal by washing with methanol. Also, in the distillation, it is essential that all the material be transferred from the distillation flask into the sample tube otherwise the composition in the Raman tube would not be correct. In order to insure complete transfer during the distillation the temperature had to be higher than 120°. However, with a high temperature, decomposition may occur and the products from this decomposition can contaminate the sample and cause fluorescence.

There was still another difficulty and this stems from the fact that the materials analyzed were glycols. It is known that hydroxylic compounds are strongly associated in the liquid state. Thus, the Raman scattering of these compounds may not be directly proportional to the number of molecules in solution. This difficulty can be lessened by using the method, of "standard samples", as outlined in the experimental part. This method, however, required a number of standard samples; these samples had to be known mixtures of the compounds that would appear in the unknown samples.

 cis-2-Butene-1,4-diol was one of the reduction products that could be obtained pure and in a large quantity. This was in part the reason why the quantitative analysis was performed only in those cases where the reduction gave cis 2-butene-1,4-diol. Another reason was the difficulty encountered in obtaining a satisfactory Raman spectrum of the product from the trans-reduction of 2-butyne-1,4-diol. This difficulty arose from the presence of a large amount of unreduced 2-butyne-1,4-diol
in the product. When there was an appreciable quantity of 2-butyne-1,4-diol in a sample the Raman spectrum contained considerable background, which was difficult to overcome, even though the precautions outlined were followed. This background was probably caused by oxidation products from 2-butyne-1,4-diol, that fluoresce when irradiated with the mercury arcs. It should be mentioned, that products from the trans-reduction alone were not the only ones that caused this difficulty. In the cases where the cis-reduction was inefficient at silver and cobalt cathodes this difficulty was also encountered. This objection did not, however, impair the qualitative analysis of the samples which was of primary interest since it was the more important in this work to know the configuration of the butenediols that were produced. Then, if possible determine the relative amounts produced.

The electrolytic reduction of propargyl alcohol

The reduction of propargyl alcohol was performed for two reasons, one was to test the effectiveness of an oxidized copper cathode and second to determine whether or not the recovery of product after electrolysis was as poor as in the case of the 2-butyne-1,4-diol reduction. The propargyl alcohol was rather good in this respect, since its reduction products allyl and propyl alcohol were very soluble in ether and could be extracted easily from a water solution, saturated with sodium chloride.

The oxidized copper cathode proved to be very effective in reducing a carbon-carbon triple bond. The propargyl alcohol was reduced not only to allyl alcohol but probably n-propyl alcohol was also formed since the value of unsaturation based on allyl alcohol for the reduction
product was only 62.6 per cent. The lack of propargyl alcohol in the product, considering that only 11 amp hours more than the theoretical amount of current was passed, was still another indication that this reduction was one of high efficiency.

The recovery of product was very low in comparison with the recovery of the product from the 2-butyne-1,4-diol reduction. This could not be accounted for by poor recovery, since the reduction products of propargyl alcohol, allyl and propyl alcohol, can be extracted from water very easily with ether.

Another surprising fact was the probable formation of propyl alcohol. The presence of propyl alcohol would rule out the theory that a copper acetylide was formed and then disrupted by one mole of hydrogen to give only allyl alcohol (cf. introduction).

The electrolytic reduction of 2,4-hexadiyne-1,6-diol

The electrolytic reduction of a conjugated triple-bond diol has been reported by Lebedeva. She has reduced 2,7-dimethyl-3,5-octadiyne-


2,7-diol at an oxidized copper cathode in a sodium hydroxide solution to (I) a mixture of 2,7-dimethyl-3,5-octadiene-2,7-diol and 2,7-dimethyl-4-octyne-2,7-diol; and a liquid fraction which was 2,7-dimethyl-2,4-octadiene-7-ol; and (II) which had the formula C_{10}H_{18}O_2 but was not identified. When the experiment was carried out on 10 g. of the diynediol for 20 amp hours no initial glycol remained and 38% I, 8% II along with a 39% liquid fraction was formed.
The reduction in this case of a conjugated triple bond system electrolytically at a spongy copper and oxidized copper cathodes produced rather surprising results. The electrolytic reduction of 2-hexadiyne-1,6-diol did not yield any of the expected 2,4-hexadiene-1,6-diol but, instead the only product turned out to be a hexadieneol. The absorption in the ultraviolet was at a wavelength \( \lambda = 225 \) and \( \epsilon = 13,132 \) which, indicated a conjugated double bonded system.\(^1\) Two moles of hydrogen were absorbed per mole of compound and the hydroxyl value was correct for one hydroxyl group per molecule. However, any attempt to prepare a crystalline maleic anhydride adduct, a 3,5-dinitrobenzoate or an \( \alpha \)-naphthyl urethane derivative failed. A sample of pure sorbyl alcohol (2,4-hexadiene-1-ol) was prepared, by the reduction of methyl sorbate with lithium aluminum hydride. This alcohol formed a 3,5-dinitrobenzoate that agreed with the value given in the literature.

The infrared spectrum of the 2,4-hexadiene-1-ol from methyl sorbate did not compare with the product from the electrolytic reduction of 2,4-hexadiyne-1,6-diol (cf. Figs. 26-27). The Raman spectrum, also, were not in agreement, the double bond frequency in the product from electrolytic reduction was 1653 cm\(^{-1}\) while the frequency for 2,4-hexadiene-1-ol was 1663 cm\(^{-1}\). The product from the electrolytic reduction of 2,4-hexadiyne-1,6-diol in all probability was 2,4-hexadiene-1-ol but of the cis-cis configuration. The configurations of sorbic acid, methyl sorbate and hence sorbyl alcohol that was obtained by the lithium aluminum hydride reduction of methyl sorbate should all be the same.

\(^1\) Braude, E. A., Chemical Society Annual Reports 62, 120 (1945).
However, as far as can be ascertained the geometrical configuration of sorbic acid has not been determined. Therefore, the only justification for postulating the \textit{cis-cis} configuration for the electrolytic reduction product of 2,4-hexadiyne-1,6-diol is the fact that copper cathodes reduce disubstituted acetylenes to the \textit{cis} olefins, and also the Raman frequency for the double bond in trans-olefins should be 10 to 15 wave numbers higher than the frequency for cis-olefins, which is true in this case (cf. Hibben \textit{loc.cit}).

It is difficult to realize why hexadieneol should be the only product obtained from the hexadiynediol. The amount of C-OH fission in the reduction of butynediol is rather small in comparison to the amount with hexadiynediol. The fact that hydrogenolysis or OH fission takes place readily when an alcohol, for example, has the structure \(-\text{C}=\text{C}-\text{CH}_2\text{OH}\), where the double bond is resistant to hydrogenation as in benzyl alcohol\(^1\) may be a reason for this behavior. The double bonds in the hexadiynediol that is formed in the reduction may be more resistant to further hydrogenation but the compound may be easily susceptible to hydrogenolysis and thus undergoes fission, to form the hexadieneol. This in fact, may very well be the case since the structure of hexadieneol

\[
\text{HO} \text{CH}_3 \\
\text{H} \text{C}=\text{C}=\text{C} \text{CH}_2\text{OH}
\]

is not too unrelated to benzyl alcohol.

Another interesting fact was the poor recovery of material. The only product obtained was the hexadieneol which amounted to between 13 and 16 per cent recovery based on the original starting material.
In one reduction the cathode compartment was connected to a dry ice trap to prevent the escape of any volatile material; the material that was collected in the trap was not sufficient to account for the amount lost.

The one experiment using a nickel cathode was a disappointment, since the only product recovered was unreduced hexadiynediol. The answer probably resides in the fact that the spongy nickel cathode was not active enough to effect reduction.

Summary

The electrochemical reduction of 2-butyne-1,4-diol has been investigated at a number of cathodes. It was found that 2-butyne-1,4-diol could be reduced to cis 2-butene-1,4-diol at cathodes such as spongy copper, nickel, silver and cobalt. At a spongy zinc cathode a mixture of cis and trans butenediol was obtained. The cathodes of spongy lead, tin, cadmium and amalgamated copper reduced butynediol to the trans butenediol. The reduction was best carried out using an alkaline electrolyte such as sodium hydroxide.

One of the major difficulties encountered in the reduction was the low recovery of product, which could not be accounted for by the decomposition of the butynediol or of its reduction product butenediol. It was noted, however, that a mixture of crotyl and butyl alcohol was obtained when butynediol was electrolyzed for an extended period of time at a spongy copper or nickel cathode. These same products were also obtained when an attempt was made to reduce butenediol to butanediol. The fission of one OH group from butenediol was the probable explanation for their formation.
ELECTROLYTIC REDUCTION OF ACETYLENIC GLYCOLS

Introduction

The stereochemical course of electrolytic reduction of organic molecules has in the past received very little attention. Mettler\(^1\)

\(^{1}\) Mettler, C., Ber. 89, 2941 (1906).

in 1906 claimed that the reduction of phthalic acid at a lead cathode gave trans 1,2-dihydrophthalic acid. Campbell and Young\(^2\) reduced various acetylenic hydrocarbons at a spongy nickel cathode and obtained the cis-ethylenic hydrocarbons.


Thus, the purpose of this investigation was to determine what effect, if any, the cathode and the physical nature of its surface had on the stereochemical course of electrolytic reduction.

The physical nature of the cathode and its effect on reduction.

At the outset it is convenient to divide electrolytic reductions into two classes depending on the physical nature of the cathode:\(^3\)


they are:

1. Spongy nickel, platinum, copper, etc. at which it will be seen the reduction is essentially of a catalytic nature.

2. Most other metallic cathodes (smooth) which simulate the reducing properties commonly attributed to dissolving metals, such as zinc in acid or metallic couples such as sodium amalgam.
A method, based upon Raman spectra, for analyzing the products from the reduction of 2-butyne-1,4-diol both qualitatively and quantitatively, is described.

The reduction of a conjugated diyne 2,4-hexadiyne-1,6-diol, at a copper cathode was attempted, and the only product isolated was apparently 2,4-hexadiene-1-ol. This product probably resulted from the fission of one OH group from 2,4-hexadiene-1,6-diol.

Propargyl alcohol was reduced at an oxidized copper cathode to give mainly allyl alcohol and propyl alcohol.
APPENDIX - I

Microphotometer tracings of the Raman spectra.

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<td><em>trans</em>-2-butene-1,4-diol</td>
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<td>butane-1,4-diol</td>
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<td>Reduction product at spongy copper cathode (basic solution)</td>
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<td>Reduction product at spongy nickel cathode (basic solution)</td>
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<td>10</td>
<td>50:50 mixture by volume of <em>cis</em> 2-butene-1,4-diol and <em>trans</em> 2-butene-1,4-diol</td>
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<td>11</td>
<td>Reduction product at spongy zinc cathode</td>
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<td>12</td>
<td>Reduction product at spongy cobalt cathode</td>
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<td>31</td>
<td>Reduction product at mercury cathode using (C₂H₅)₄NOH as catholyte, showing the tracing of the ethylenic frequencies only</td>
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FIGURE 6

1660 cm\(^{-1}\)

2222 cm\(^{-1}\)

2282 cm\(^{-1}\)
1675 cm$^{-1}$

2219 cm$^{-1}$

2283 cm$^{-1}$
When cathodes such as spongy nickel or platinized platinum are employed in reduction, the process contrasts sharply with that occurring at smooth cathodes. The ethylenic bonds, in positions other than α, β to a carbonyl, carboxyl, nitro, or phenyl group which are usually resistant to attack by the cathodes and reagents of class 2 are easily reduced. Oleic acid, for example, may be reduced to stearic acid at a cathode of prepared nickel, whereas it is unaffected at cathodes of mercury, smooth lead and copper and other metals. Phenol has been reduced to cyclohexanol at platinized platinum, although it remains unchanged at mercury and smooth lead. Even phenanthrene can be partly hydrogenated at a cathode of palladized platinum. It is clear in these instances that reduction is proceeding in a manner usually considered typical of catalytic hydrogenation.

The special properties of prepared cathodes are again evident in the reduction of sorbic acid and vinyl acrylic acid. In contrast

(1 and 2) Pomilio, U., Z. Elektrochem. 21, 444 (1915).
(3) Forkin, S., ibid, 12, 749 (1906).
(7) Idem, ibid., 1936, 574
FIGURE II

1661 cm$^{-1}$

1675 cm$^{-1}$

2211 cm$^{-1}$

2276 cm$^{-1}$
1659 cm\(^{-1}\)

2220 cm\(^{-1}\)

2283 cm\(^{-1}\)
Figure 31

1660 cm\(^{-1}\)

1675 cm\(^{-1}\)
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<td>19</td>
<td>trans-1,4-dichloro-2-butene in sandwich cell, NaCl reference cell</td>
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<td>trans-1,4-diacetoxo-2-butene in sandwich cell, NaCl reference cell</td>
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<td>21</td>
<td>upper, trans-1,4-dibromo-2-butne 2% in CCl₄, 0.1 mm cell, lower, 5% in CCl₄, 0.1 mm cell</td>
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<td>22</td>
<td>lower, product from reduction of cis 2-butene-1,4-diol page 30 upper, pure n-butyl alcohol in sandwich cell, NaCl reference cell</td>
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<td>27</td>
<td>Product from reduction of 2,4-hexadiyne-1,6-diol at spoogy copper cathode. upper 1:10 in benzene 0.1 mm. cell used; lower sandwich cell NaCl reference cell</td>
</tr>
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<td>Product from reduction of 2,4-hexadiyne-1,6-diol at oxidized copper cathode b.p. 94°/70 mm. in sandwich cell NaCl reference cell</td>
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