ELECTROLYTIC REDUCTION OF ACETYLENIC BONDS

A. P. Tomilov

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1. INTRODUCTION

The hydrogenation of acetylenic bonds in organic compounds takes place stepwise and can in general be represented as follows:

$$-C\equiv C- \xrightarrow{2H} -CH=CH- \xrightarrow{2H} -CH_2-CH_2-$$

By choosing certain conditions, the hydrogenation can be stopped at the stage at which the ethylenic compound is produced. Reduction of acetylenic to ethylenic compounds is important in preparative organic chemistry and much research [1] has been devoted to a study of this reaction. However, the problem of the selective hydrogenation of acetylenic to ethylenic bonds has not yet been solved satisfactorily.

One of the possible ways of both partial and complete hydrogenation of acetylenic bonds is their electrochemical reduction. Since a considerable amount of work has been devoted to this electrochemical reduction, it is useful to discuss the prospects of employing electrolysis for carrying out reactions of this type.

2. MECHANISM OF THE ELECTROLYTIC REDUCTION OF ACETYLENIC BONDS

The mechanism of the electrolytic reduction of acetylenic compounds depends, to a considerable degree, on their general structure. Isolated acetylenic bonds (not conjugated with ethylenic bonds or with electron-accepting functional groups) are easily reduced by catalytically activated hydrogen. In such cases the electrolytic reduction process does not differ in principle from catalytic hydrogenation [2]. Study of the reaction mechanism for catalytic and electrolytic reduction of acetylenic alcohols by the charging-curve method showed that their electrolytic reduction takes place at more negative potentials than the discharge of hydrogen ions and cannot therefore be brought about by protons [3,4].

With the mechanism discussed, the electrolytic reduction takes place at cathodes of platinum, palladium, nickel, cobalt, and other metals which possess a low hydrogen overpotential.

The mechanism of electrolytic reduction at copper and silver cathodes did not receive a careful examination, but it has been suggested that intermediate organometallic complexes play an active part in this process [5-8]. One piece of evidence for this hypothesis is, for example, the formation of an organo-copper compound in the electrolytic reduction of dimethylethynylmethanol at a copper cathode. This compound decomposes and separates out as a precipitate of composition C_5H_7OCu when the solution obtained on reduction is saturated with carbon dioxide [6]. In the light of these ideas, the decreased tendency of phenylethynylmethanol to electrolytic reduction at a copper cathode is explained by the instability of the copper complexes it yields.

Acetylenic compounds containing double bonds or electron-accepting functional groups conjugated with the acetylenic bonds are reduced on metals with a high hydrogen overpotential (lead, mercury) by an electronic mechanism. Such compounds (which we shall designate as having "activated acetylenic bonds") are reduced at a dropping mercury cathode; this permits a detailed study of the mechanism of their electrolytic reduction [10-17]. For example, in the reduction of phenylacetylene and diphenylacetylene in aqueous dioxane at a dropping mercury cathode one four-electron wave, independent of the pH, is observed; this indicates that under these conditions the reduction takes place in one step with complete saturation of the acetylenic bond. The mechanism can be expressed thus:

$$R + e \rightleftharpoons R^- \text{ (potential-determining stage)},$$

$$R^- + e \longrightarrow R^{2-},$$

$$R^{2-} + 2H_2O \longrightarrow RH_2 + 2OH^- \text{ (fast)}.$$

The ethylenic compound formed requires for its reduction a less negative potential and is immediately reduced, by a similar scheme, to the saturated compound.

The reduction mechanism changes somewhat when some non-aqueous solvents, *e.g.* dimethylformamide, are used [10,11,18]. In this solvent reduction takes place with the formation of intermediate radical-anions as shown by the presence of two one-electron waves in the polarogram.

For example, the reduction of diphenylacetylene can be expressed as follows:

$$\text{first wave } C_6H_5C\equiv CC_6H_5 + e \rightarrow [C_6H_5\dot{C}=\dot{C}C_6H_5]^- \text{ (slow)},$$

$$\text{second wave } [C_6H_5\dot{C}=\dot{C}C_6H_5]^- + e \rightarrow [C_6H_5\dot{C}=\dot{C}C_6H_5]^{2-} \text{ (slow)},$$

$$[C_6H_5\dot{C}=\dot{C}C_6H_5]^{2-} + 2H^+ \rightarrow C_6H_5CH=CHC_6H_5.$$

The stability of the free radical-anion is confirmed by the fact that electrolytic reduction of diphenylacetylene in the presence of carbon dioxide is accompanied by the formation of diphenylmaleic anhydride and diphenylfumaric acid. The formation of the latter can be described by the following scheme [10]:

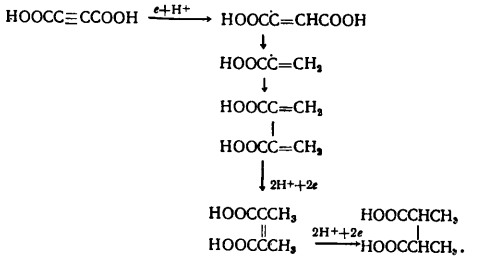
$$[C_6H_5\dot{C}-\dot{C}C_6H_5]^- + CO_2 \rightarrow C_6H_5C(COO^-)=\dot{C}C_6H_5,$$

$$C_6H_5C(COO^-)=\dot{C}C_6H_5 + e \rightarrow C_6H_5C(COO^-)=\dot{C}C_6H_5,$$

$$C_6H_5C(COO^-)=\dot{C}C_6H_5 + CO_2 \rightarrow C_6H_5C(COO^-)=CC_6H_5(COO^-).$$

The reduction of acetylenedicarboxylic acid takes place by a similar scheme, but the corresponding free radical-anion is unstable and becomes decarboxylated [15]; the

radicals formed dimerise and the dimeric product is reduced at the same potential:



3. EFFECT OF ELECTROLYSIS CONDITIONS

a. Electrode material. The nature of the reduction products is determined to a considerable extent by the cathode material used. At platinum, platinised platinum, palladium, nickel, and cobalt cathodes reduction usually takes place without stopping at the ethylenic compound stage, a mixture of both ethylenic and saturated compounds being formed[6,9,19-25]. However, since the ethylenic and acetylenic bonds are electrolytically hydrogenated at different rates and at somewhat different potentials on platinum-group metals[8,20], it is possible to achieve selective hydrogenation of the acetylenic bond on these metals using electrolysis at a controlled potential.

The most generally useful electrode materials for selective hydrogenation of acetylenic to ethylenic compounds are copper, silver, and copper–silver alloys[6,7,9,20-22,24,26-43].

Preparation of the cathode surface plays a big part in successful electrolytic reduction. Preliminary oxidation by heating in a burner flame is recommended for creating an active surface on a copper cathode. During the work the activity of the copper electrode is quickly lost and it must be renewed by oxidation before each operation. Silver and copper–silver electrodes possess considerably greater stability. The latter are most conveniently prepared by immersing a purified copper cathode in dilute aqueous silver nitrate for some minutes. Such a cathode can be used in several successive operations without any additional treatment. However, even with copper–silver cathodes it is apparently impossible to secure prolonged working of the electrode without activation.

As previously noted, compounds having "activated" acetylenic bonds are reduced at a mercury cathode[12-15,18], complete saturation of the acetylenic bond taking place. These compounds are also reduced by alkali metal amalgams[26]. In work with a mercury cathode the formation of heavy organomercury compounds as well as reduction products is observed[6,9,21,22].

In addition to a mercury cathode, it is possible to use other metals with a high hydrogen overpotential, for example zinc, for the electrolytic reduction of compounds with "activated" acetylenic bonds. A zinc cathode also loses its activity quickly, and for stable working addition to the solution of a zinc salt and the periodic removal of the zinc sponge precipitated on the cathode are recommended.

b. Current density. At a platinum cathode an increase in current density favours formation of a saturated compound[46]. In the hydrogenation of vinylacetylene at a copper amalgam cathode, raising the current density from 1 to 2 A dm^{-2} considerably increases the formation of tarry products which settle on the cathode surface and lead to a reduction in the yield of hydrogenation products from 45 to 36% (based on the reagent). When the current density is doubled, the product yield in the reduction of dec-5-yne at a rotating nickel cathode falls from 75 to 50%.[47]

A reduced yield of reduction products with increasing current density was observed in the electrolytic reduction of butynediol at a copper–silver cathode[43]. The authors explain this by a rise in the cathode potential and give the following dependence of the yield of butenediol on that potential:

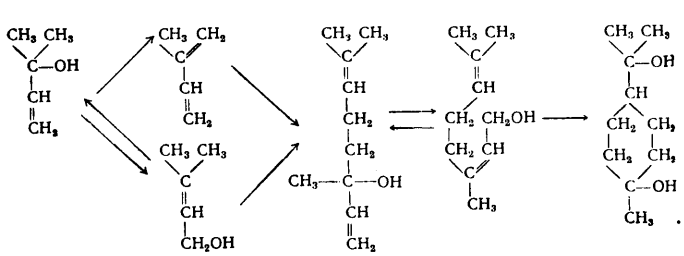
Cathode potential, V	Current yield of butenediol, %
1.50	55.0
1.40	57.5
1.30	65.8
1.20	73.7

In connection with what has been written the selective hydrogenation of acetylenic compounds is usually carried out at current densities not exceeding 1–2 A dm^{-2} (100–200 A m^{-2}), namely:

	A dm^{-2}
Dimethylethynylmethanol	0.5–1.0[28]
	0.77[31]
Dimethyl(vinylethynyl)methanol	0.5–2.0[38]
Methylcyclopropylethynylmethanol	0.5–1.0[39]
Diacetylene glycols	0.8[41]
1-Ethynylcyclohexanol	0.5–0.6[42]
Butynediol	0.05–1.5[33]
Vinylacetylene	1–1.5[34]

c. Choice of electrolyte and solvent. There is no essential difference in the use of an alkaline or acidic electrolyte for hydrogenation of a triple bond[47,48]. For example, acetylene is hydrogenated to ethylene to the same extent both in 10% sulphuric acid and in 10% sodium hydroxide solution[47].

However many ethylenic compounds are unstable in acidic solutions and undergo further changes. For example, in the electrolytic reduction of acetylene in 65% sulphuric acid the ethylene formed is absorbed by sulphuric acid with the formation of ethyl hydrogen sulphate, which hydrolyses to ethyl ether[46]. Even more complex changes are observed in the electrolytic reduction of acetylenic alcohols in acidic solutions[49,50]. Thus, in the electrolytic reduction of dimethylethynylmethanol, apart from an ethylenic alcohol, there is partial formation of geraniol, linaloöl, and terpene hydrate, the formation of which can be represented by the equations



Therefore to avoid possible secondary processes, the electrolytic reduction is usually carried out in a weakly alkaline medium, using as electrolyte dilute aqueous sodium hydroxide[6,7,24-26,30,32,35,36,40,41], potassium hydroxide[20,33,43], or sodium bicarbonate[19,28,37-39,42].

Aqueous sodium chloride can also be used as electrolyte and the anodic process can then be employed for the simultaneous production of elementary chlorine[51].

Since most acetylenic compounds are weakly soluble in water, addition of a solvent, usually ethanol, to the electrolyte is recommended[7,26,30,32,35,39,41]. For polarographic measurements, aqueous ethanol[13], aqueous dioxane[11,12,14], and anhydrous dimethylformamide[10,18] have been used.

d. Concentration of substance being electrolysed. Although, for the maximum rate of reduction and for avoiding concentration phenomena, it is desirable to work with the highest possible concentrations of organic substances, secondary processes leading to a fall in the yield of reduced compounds are observed at high concentrations. Thus, in the electrolytic reduction of dimethylethynylmethanol the following dependence of yield of dimethylvinylmethanol on the reactant concentration is found[9,3]:

Dimethylethynylmethanol concentration, g litre^{-1}	Yield of dimethylvinylmethanol, %
50	78.3
100	72.6
150	73.0
200	69.5

Although the highest rate of hydrogenation is observed with a concentration of 150 g litre^{-1}, a reduction in the concentration of the substance being reduced favours formation of dimethylvinylmethanol.

An increase in the concentration of butynediol in solution reduces the yield of butenediol[43].

In most researches the effect of reactant concentration on the reduction process was not studied, and dilute solutions, not exceeding 5–10%, were used[1,7,26,28,30,32,33,41,42]. Stirring of the solution is said to favour the reduction process[3].

e. Temperature. In most cases a change in temperature has almost no effect on the course of the reduction process. Thus, the composition of the products in the reduction of dimethylethynylmethanol does not vary significantly on changing the temperature from 15° to 50°,[28] in the reduction of butynediol on passing from 0° to 80°,[33] and in the reduction of acetylenic hydrocarbons at a spongy nickel cathode on passing from 20° to 80°.[47] However, at higher temperatures evaporation losses of the substance being hydrogenated increase significantly and formation of tarry products is observed[9]. Therefore to obtain pure substances it is desirable to use low temperatures.

4. EFFECT OF THE STRUCTURE OF THE ORGANIC SUBSTANCE ON THE ELECTROLYTIC REDUCTION PROCESS

Results for the electrolytic reduction of various acetylenic hydrocarbons are given in Table 1. The compounds studied were mainly those with "activated" acetylenic bonds, *i.e.* hydrocarbons in which the acetylenic bond adjoins a benzene ring or is conjugated with an unsaturated carbon–carbon bond. In the latter case reduction starts at the acetylenic bond and is evidently not very selective because a complex mixture of products is formed in the electrolytic reduction of divinylacetylene on various electrode materials[26].

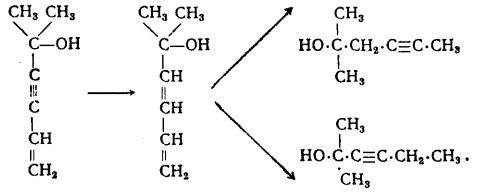
A more complicated carbon skeleton in the acetylenic compound and especially branching of the carbon chain leads to some increase in the reduction potential of the acetylenic bond, which is apparently due to steric hindrance[14].

The electrolytic reduction of acetylenic alcohols and their ethers has been studied in most detail (see Table 2). All the compounds studied can be reduced to ethylenic alcohols sufficiently selectively and, apart from the necessity of choosing a suitable solvent for substances not readily soluble in water, the structure of the compounds being reduced does not affect substantially the course of the electrochemical process.

The experiments on the electrolytic reduction of butynediol at a copper–silver cathode with a controlled potential, in which an exceptionally pure hydrogenation product was obtained[20,43], deserve special attention.

When the alcohol molecule being reduced contains two conjugated acetylenic bonds or an ethylenic bond conjugated to an acetylenic bond, the composition of the reduction products is substantially more complicated. The intermediate products are diene compounds which undergo intramolecular rearrangements; dehydration processes are also possible. All things considered, these secondary processes lead to the formation of a complex mixture of products.

Thus, for example, in the hydrogenation of vinylethynyldimethylmethanol the corresponding diene alcohol is formed and, on account of its instability, is partially isomerised, a mixture of at least three isomeric products being formed[5]:



Similar transformations, complicated by dehydration, are observed in the electrolytic reduction of 2,7-dimethyl-2,7-dihydroxyocta-3,5-diyne[41].

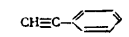
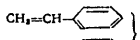
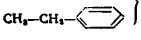
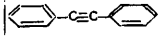
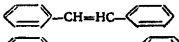
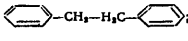
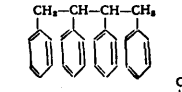
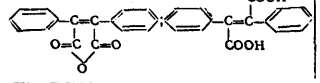
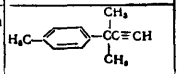
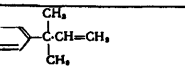
The reduction of other acetylenic compounds has been little studied (see Table 3). Acetylenic bonds activated by polar groups (COOH, > CO, CH_2Br) are reduced at a dropping mercury cathode at considerably more positive potentials than enyne hydrocarbons.

Interesting hydrodimerisation processes are observed in the electrolytic reduction of acetylenedicarboxylic acid and its monoethyl ester[15]. The mechanism of this reaction has been discussed previously.

5. INDIRECT USE OF ELECTROLYSIS IN THE REDUCTION OF ACETYLENIC COMPOUNDS

A number of processes have been described in which the indirect use of electrochemical processes was proposed for the selective reduction of acetylenic to ethylenic compounds. For example, it is proposed to use electrolysis to

TABLE 1. Electrolytic reduction of acetylenic hydrocarbons.

	Acetylenic compound	Reduction product	Cathode material	Electrolyte	Solvent	Current density, A dm^{-2}	Reduction potential, $E_{1/2}$	Yield, % acc. to substance	Yield, % acc. to current	References
1	2	3	4	5	6	7	8	9	10	11
C_3	$HC\equiv CH$	$CH_2=CH_2$; $CH_3\cdot CH_3$	Pt	acid; alkali						48,60,61
		$C_6H_4OSO_3$	Pt	65% sulphuric acid						46
		$CH_3=CH_2$	Co,Ni	alkali						25
		$CH_3=CH_2$	Zn							45
C_4	$CH_2=CH-C\equiv CH$	$CH_2=CH-CH=CH_2$	Cu(Pt)	Na_2CO_3		1 : 1.5		95.8		34
		$CH_3=CH-CH=CH_2$	Cu(Pt)					100.0		27
		$CH_3-CH_2\cdot CH=CH_2$	Hg	$(C_2H_5)_4NBr$			—2.23			12
		$CH_3-CH_2\cdot CH=CH_2$	Hg	$(C_4H_9)_4NI$	75% dioxane		—2.4			14
	$CH\equiv C-C\equiv CH$	$CH_3-CH_2-C\equiv CH$	Hg	$(C_2H_5)_4NBr$			—2.27			12
C_5	$CH_2C\equiv C-CH=CH_2$	$CH_3\cdot CH_2\cdot CH_2\cdot CH=CH_2$	Hg	$(C_4H_9)_4NI$	ditto		—2.63			14
	$CH\equiv C-C(CH_3)=CH_2$	$CH_3-CH_2-C(CH_3)=CH_2$	Hg	$(C_4H_9)_4NI$	»		—2.51			14
	$CH\equiv C-CH=CH-CH_3$	$CH_3\cdot CH_2\cdot CH=CH\cdot CH_3$	Hg	$(C_4H_9)_4NI$	»		—2.61—2.62			14
C_8	$CH_2=CH\cdot C\equiv C\cdot CH=CH_2$	$CH_2=CH-CH=CH-CH=CH_2$	Cu	5% NaOH	alcohol	2			20	26
		$CH_2=CH-C=CH-CH=CH_2$	CuHg	ditto	»	2			42	26
		$CH_2=CH-C\equiv C-CH_2-CH_3$	Ni	»	»				20—22	26
		$CH_2-CH=C=C=CH-CH_3$	Hg	»	»					
			Hg	$(C_4H_9)_4NI$	dioxane		E_1=—2.07 E_2=—2.55		42	26 12
			Hg	$(C_4H_9)_4NI$	dimethyl-formamide		E_1=—1.74 E_2=—2.23			18
	$CH_3\cdot CH_2\cdot C\equiv C\cdot CH=CH_2$	$CH_3\cdot CH_2\cdot CH_2CH_2\cdot CH=CH_2$	Hg	$(C_4H_9)_4NI$	75% dioxane		—2.60—2.61			14
	$CH_3\cdot C\equiv C\cdot C(CH_3)=CH_2$	$CH_3\cdot CH_2\cdot CH_2\cdot C(CH_3)=CH_2$	Hg	$(C_4H_9)_4NI$	ditto		—2.80			14
	$CH\equiv C\cdot C(CH_3)=CH-CH_3$	$CH_3\cdot CH_2\cdot C(CH_3)=CH-CH_3$	Hg	$(C_4H_9)_4NI$	»		—2.56—2.55			14
C_7	$CH\equiv C\cdot C_4H_{11}$	$CH_2=CH\cdot C_4H_{11}$	Ni	H_2SO_4; KOH	96% alcohol				65	47
C_8	$C_4H_9C\equiv C\cdot CH=CH_2$	$C_4H_9\cdot CH_2\cdot CH_2\cdot CH=CH_2$	Hg	$(C_4H_9)_4NI$	75% dioxane		2.56			14
	$CH\equiv C-C(CH_3)=CH_2$	$CH_3\cdot CH_2\cdot C(CH_3)=CH_2$	Hg	$(C_4H_9)_4NI$	ditto		—2.58—2.59			14
			Ni	H_2SO_4; KOH	95% alcohol					47
			Hg	$(C_4H_9)_4NI$	70% dioxane		—2.376			11,12
	$C_4H_7C\equiv C\cdot C_4H_7$	$C_4H_7\cdot CH=CH\cdot C_4H_7$	Ni	H_2SO_4; KOH	95% alcohol				80	47
C_9	$CH_3-C\equiv C-C(CH_3)=CH_2$	$CH_3\cdot CH_2\cdot CH_2\cdot C(CH_3)=CH_2$	Hg	$(C_4H_9)_4NI$	75% dioxane		—2.83—2.84			14
C_{10}	$C_6H_{13}-C\equiv C-CH=CH_2$	$C_6H_{13}CH_2\cdot CH_2\cdot CH=CH_2$	Hg	$(C_4H_9)_4NI$	ditto		—2.55—2.54			14
	$C_5H_9C\equiv C-C(CH_3)=CH_2$	$C_5H_9\cdot CH_2\cdot CH_2\cdot C(CH_3)=CH_2$	Hg	$(C_4H_9)_4NI$	»		—2.82			14
	$C_4H_9C\equiv C\cdot C_4H_9$	$C_4H_9CH=CHC_4H_9$ (*cis*)	Ni	H_2SO_4; KOH	95% alcohol				75	47
			Ni	H_2SO_4; KOH	ditto				80	47
			Hg	$(C_4H_9)_4NI$	80% alcohol		—2.195			11,12
			Hg	$(C_4H_9)_4NI$	75% dioxane					10
	$+CO_2$		Hg	$(C_4H_9)_4NI$	ditto					10
C_{11}			CuAg	NaOH	alcohol			80		7

obtain highly active zinc sponge, which is employed as a reducing agent for a number of acetylenic compounds[52]. It is thought possible to use sodium amalgam, which is easily obtained electrolytically, for reducing vinylacetylene to butadiene[26]. However the most effective selective reducing agent for acetylenic bonds is chromium(II) chloride[1]. The reduction of acetylene, for example, with this reagent can be represented by

$$2CrCl_2+2HCl+C_2H_2 \rightarrow 2CrCl_3+C_2H_4.$$

The chromium(II) chloride is converted into the corresponding compound of tervalent chromium from which a bivalent compound is easily regenerated electrochemically. Construction of an electrolysis cell, in which the cathodic process results in the regeneration of the bivalent chromium,

$$2CrCl_3+2H \rightarrow CrCl_2+2HCl,$$

and the anodic process in the production of chlorine gas, has been proposed. The electrodes are graphite rods. At

TABLE 2. Electrolytic reduction of acetylenic alcohols and their ethers.

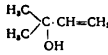
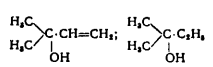
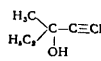
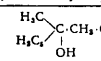
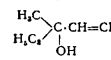
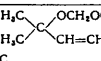
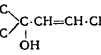
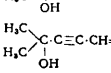
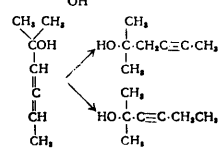
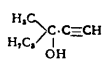
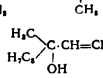
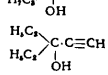
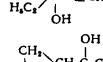
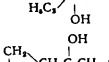
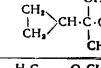
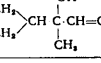
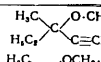
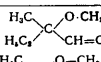
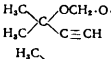
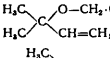
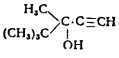
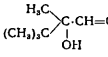
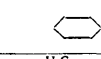
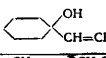
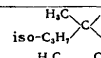
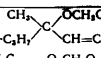
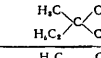
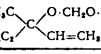
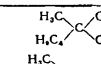
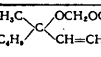
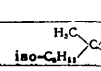
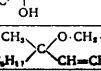
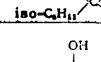
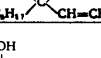
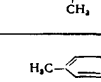
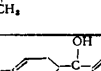
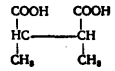
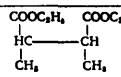
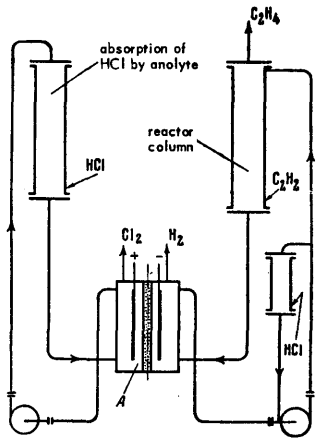
	Acetylenic compound	Reduction product	Cathode material	Electrolyte	Solvent	Current density, A dm^{-2}	Reduction potential	Yield, % acc. to substance	Yield, % acc. to current	References
1	2	3	4	5	6	7	8	9	10	11
C_4	$HOCH_2C{\equiv}C{\cdot}CH_2OH$	$HOCH_2CH{=}CH{\cdot}CH_2OH$	Ag CuAg	NaOH 2% KOH		1.0	1.2		90	33 20,43
C_5			Cu CuAg any metal covered with silver Ni sponge PtPt	Na_2CO_3		0.5—1.0		95 87		6,9,21, 22,28 31 24,39 3,6
		 geraniol, linaloöl, terpene hydrate	Cu	H_2SO_4						49,50
C_6			PtPt					46		6
			CuAg	Na_2CO_3				59.6— —63.4		9
C_7			CuAg Cu	NaOH	alcohol					40
			Cu CuAg	Na_2CO_3	»			80—90		35 5
			Cu	Na_2CO_3	0.5—2.0			57—60		19,38
			CuAg	NaOH				75—80		37
			CuAg	NaOH	alcohol			80—82		32
			Cu	NaOH	»			60—65		32
			Cu	$NaHCO_3$		0.1—0.05		60—70		39
C_8			Cu AgCu	1% NaOH	»					40
			Cu AgCu	1% NaOH	»					40
			CuAg	1% NaOH	»			52		30
			Cu	1% $NaHCO_3$	»			88—83		36,42
C_9			CuAg	1% $NaHCO_3$	»					40
			CuAg	1% $NaHCO_3$	»					40
C_{10}			CuAg	1% $NaHCO_3$	»					40
			CuAg							
			Cu	NaOH	»					34,41
C_{11}			CuAg	1% $NaHCO_3$						40
C_{12}			CuAg							5 7
C_{16}			Cu AgCu	NaOH						

TABLE 3. Electrolytic reduction of other acetylenic compounds.

	Acetylenic compound	Reduction product	Cathode material	Electrolyte	Solvent	Current density, A dm^{-2}	Solution pH	Reduction potential	Current yield, %	References
C_3	$CH_2BrC{\equiv}CH$		Hg	buffer solutions	50% alcohol		5.45 9.10	—0.84 —0.91		13
C_4	$HOOCC{\equiv}CCOOH$		Hg							15
C_8	$C_2H_5OOC{\cdot}C{\equiv}C{\cdot}COOH$		Hg							15
C_9	$C_2H_5OOC{\cdot}C{\equiv}C{\cdot}COOC_2H_5$	$C_2H_5OOC{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5$	Hg							15
C_9	$C_6H_5C{\equiv}C{\cdot}CHO$		Hg	buffer solutions	50% alcohol		1.3 4.9 7.2 8.6	—0.64 —0.84:—1.30 —0.95:1.25 —1.25		13
C_{15}	$C_6H_5C{\equiv}C{\cdot}CO{\cdot}C_6H_5$		Hg	ditto	ditto		1.3 4.9 7.2 8.6	—0.53: 0.96 —0.74: 1.06 —0.89: 1.08 —1.08: 1.57		13
C_{17}	$C_6H_5C{\equiv}CCOC{\equiv}CC_6H_5$		Hg	»	»		1.3 7.2 8.6 11.3	—0.39 —0.73 —0.85 —0.93		13



a cathodic current density of 7.8–9.3 A dm^{-2} and a temperature of 20°–25° the chromium salt is reduced with a current yield up to 90%.[53-56]

A scheme for the technical reduction of acetylene to ethylene is shown in the Figure. The electrolytic cell *A* is a sealed chamber divided by a porous diaphragm. The anolyte is circulated, by a pump, through an absorption column where the loss of chloride owing to liberation of chlorine gas is made up by absorption of HCl. The catholyte similarly passes through another absorption column where sufficient HCl is absorbed to compensate for its loss by migration to the anolyte through the diaphragm. The catholyte is supplied by the pump to the reactor where acetylene is continuously reduced by chromium(II) chloride, and then, with a lowered chromium(II) chloride content, is returned to the electrolytic cell. This method has been used to reduce acetylene to ethylene[53,57], and to reduce diacetylene[58] and vinylacetylene[59] to butadiene. However, the low rate of reaction of the chromium(II) chloride with acetylenic compounds does not allow a sufficiently effective apparatus to be set up, and hence the method has not found any appreciable industrial application.

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This review shows that many acetylenic compounds can be reduced electrochemically, both to ethylenic and to saturated derivatives.

From the preparative viewpoint the possibility of accomplishing partial hydrogenation of an acetylenic to an ethylenic bond electrochemically at a silver or copper–silver cathode at a controlled potential deserves special attention.

Electrolysis can be applied successfully to the regeneration of chromium(II) compounds, which are effective in the selective reduction of acetylenic bonds.

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THE METHOD OF MOLECULAR ORBITALS AND SPIN DENSITY IN PARAMAGNETIC RESONANCE

I.D. Morozova

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INTRODUCTION

The development of the technique of electron paramagnetic resonance and of nuclear magnetic resonance has made it possible to investigate the behaviour of a large number of molecules and free radicals in a magnetic field. Quantum chemistry and one of its techniques, the molecular orbital method, play an important part in the theoretical interpretation of paramagnetic resonance spectra. Application of this method to the study of organic free radicals, molecules in which an unpaired electron is linked with the whole system, *i.e.* is regarded as located in a molecular and not an atomic orbital, can give valuable information about the structure of these compounds.