THE ELECTROCHEMICAL REDUCTION OF METHYL VINYL KETONE
IN AQUEOUS SOLUTIONS

APPROVED:

Graduate Committee:

[Signatures]

Major Professor

Committee Member

Committee Member

Committee Member

Chairman of the Department of Chemistry

Dean of the Graduate School
THE ELECTROCHEMICAL REDUCTION OF METHYL VINYL KETONE
IN AQUEOUS SOLUTIONS

DISSERTATION

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By

Eddie Carroll French, B.S., M.S.
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CHAPTER I

INTRODUCTION

Organic electrochemistry was started more than one hundred years ago, when Kolbe (11) observed the formation of hydrocarbon products when an electric current was passed through a solution of carboxylic acids. Since that time considerable work has been done in organic electrochemistry, a large part of which is summarized in several reviews (1, 3, 4, 5, 6, 7, 8, 16, 17, 18). Two points are apparent upon surveying this literature. First, most of the work was done by chemists seeking a quick method to synthesize compounds which were difficult to obtain otherwise. Many others were motivated by a philosophy of mere curiosity: "Let's pass some current through it and see what it makes." As a result, usually little or no effort was made to understand the chemistry involved, or to determine mechanisms which would lead to better understanding of the reactions. Secondly, a major part of this work was done prior to 1950. This is particularly important when one observes that not until the mid-1950's was the theory of organic chemistry sufficiently developed to permit mechanistic explanations of electro-organic reactions. Also, within the last few years a similar remarkable advance in analytical techniques has occurred, probably
the most important being the development of gas chromatography. Finally, new types of electronic equipment have aided the organic electrochemist tremendously in his study of electrode processes. In the light of all these recent advances, it is now possible to make an in-depth study of a system with an approach designed to determine the electrode processes and the factors or conditions which control them. This is the general goal of the overall study of which the present work is one part.

Electro-organic reactions can be classified into reductions, oxidations, cathodic (or reductive) couplings, anodic couplings, and substitutions. This study deals with the closely related reduction and reductive coupling reactions. Even more specifically, it is a study of the reduction of methyl vinyl ketone (3-buten-2-one) (MVK), which contains a carbon-carbon double bond and a carbonyl group, both of which can be reduced by electrochemical methods.

While isolated ethylenic groups are difficult to reduce electrochemically, those that are in conjugation with an electron withdrawing group, such as carbonyl and nitrile, are quite easily reduced. In a similar manner, the carbonyl group becomes easier to reduce when it is conjugated with an electron withdrawing group (12). The ease of reduction of the carbonyl group is also very dependent on the media. For example, Wilson and Wilson (20) showed that acetone is more readily reduced in concentrated sodium hydroxide than
in dilute solutions. Also, Suzuki and Elving (15) reported that the first half-wave potential of benzophenone becomes more negative with increasing pH to the extent of about 60 mV per pH unit. Sugino and Nonaka (14) give the half-wave potential for the reduction of acetone as -1.2 V in 20 percent sulfuric acid on mercury, while it shifted to -2.4 V in a quaternary ammonium salt solution on mercury.

Ethylenic groups are reduced to saturated hydrocarbon chains or undergo a reductive coupling (reduction and coupling) to form the dimer (2). The general reactions are

\[
\text{CH}_2=\text{CHR} + 2e^- + 2\text{H}^+ + \text{CH}_3\text{CH}_2\text{R} \quad \text{(reduction)}
\]

\[
2\text{CH}_2=\text{CHR} + 2e^- + 2\text{H}^+ \rightarrow \text{RCH}_2\text{CH}_2\text{CH}_2\text{R} \quad \text{(dimer)}
\]

The reduction of the carbonyl group has also been studied extensively. Carbonyl groups can be reduced electrochemically to hydrocarbons (13) (under extreme conditions), alcohols (13), and they can be dimerized to form glycols (19).

For example:

(1) \( \text{RCR} + 4e^- + 4\text{H}^+ \rightarrow \text{RCH}_2\text{R} + \text{H}_2\text{O} \quad \text{(reduction)} \)

(2) \( \text{RCR} + 2e^- + 2\text{H}^+ \rightarrow \text{R} \cdot \text{OH} \quad \text{(reduction)} \)

(3) \( 2\text{RCR} + 2e^- + 2\text{H}^+ \rightarrow \text{R} \cdot \text{OH} \quad \text{(dimerization)} \)

There are several approaches to determining the mechanisms of organic reactions, including, for example, kinetic
studies, solvent effects, radical effects, and searches for intermediates. All of these may and should be applied to electro-organic reactions, although in far too many studies these conventional approaches have been neglected. As in organic reactions, it is essential to know the course of the overall reaction under a known set of conditions and to be able to reproduce them before any mechanistic study can be meaningful.

It is frequently possible to write reduction reactions for a number of possible products. For example, several reasonable reduction products can be written for the conjugated difunctional molecule of methyl vinyl ketone. Some of these are written below:

1. \( \ce{CH3CH2OCH3} \)
2. \( \ce{CH2=CH-C-CH3} \)
3. \( \ce{CH3OCH2CH2CH2OCH3} \)
4. \( \ce{CH2=CH-OH-CH=CH2} \)
5. \( \ce{CH3CH2CH2CHOCH3} \)
6. \( \ce{CH3CCH-CHOCH3} \)
7. \( \ce{CH3CH=COCH2CH2CH3} \)
8. \( \ce{CH3CH=CO-CH=CH2} \)
9. \( \ce{CH3CH2C-OHCH3} \)
10. \( \ce{CH3CH2CH3OH} \)
In cases of reduction of compounds such as methyl vinyl ketone, where several products are possible, a certain product or a group of products would be logically explained by one mechanism while another group of products would suggest still another mechanism. Once a probable mechanism has been established in this manner it can be tested by variation of other variables to establish specific kinetic effects, and by identifying intermediates, as, for example, with electron spin resonance spectroscopy (ESR).

This is the approach that has been taken in our study of the electrolysis of MVK. The major products were first identified (separation by preparative gas chromatography and identification by nuclear magnetic resonance [NMR] and infrared [IR] spectroscopy) and their relative proportions formed during electrolysis determined as a function of cathode potential. Some unexpected trends of product distributions were observed, which, while they do not firmly establish the reaction mechanism, do give us the most probable routes, and tell us the direction to take in further confirmatory studies.

It is conceded by many responsible investigators that the cathode potential at which an electro-organic reaction takes place is probably the most important single variable. The potential of a cathode is a measure of its thermodynamic reducing power, being directly related to the Gibbs Free Energy, $\Delta G$, by the equation

$$-\Delta G = nFE$$
In this expression \( n \) is the number of electrons transferred per molecule of reactant, \( F \) is the Faraday charge, and \( E \) is the potential between the two half-cells which make up the complete reaction. If the potential in an electro-organic reduction reaction is measured relative to the standard hydrogen electrode (SHE), it can be related directly to the strength of known chemical reducing agents. For example, a potential of -0.8 V vs SHE is approximately the thermodynamic equivalent of zinc metal, while a potential of -2.7 V is equivalent to the much more strongly reducing sodium metal.

An example of the effect of the cathode potential on the course of a reaction is the reduction of nitrobenzene, first observed by Haber in 1897 (9). Harwood et al. (10) studied the reduction of nitrobenzene in acid solution at controlled potential and proposed the following reaction scheme:
Harwood observed that p-aminophenol is the major product formed at -0.4 V vs SHE, with aniline completely absent. Higher potentials of -0.6 V, -0.8 V, and -0.9 V gave aniline as a major product. By combining controlled potential with changes in temperature (to alter the kinetics of the rearrangement reactions) and pH, it was possible to choose conditions to optimize yields in azoxybenzene, in p-aminophenol, or in aniline.

When one attempts to polarize certain metals to higher cathodic potentials (more negative), a phenomenon known as overvoltage is encountered. Overvoltage, which is primarily a function of the electrode metal, is the difference between the thermodynamic potential at which the reaction is in equilibrium and the actual potential which is required to force the reaction to take place at a given finite rate. The most common and most widely studied overvoltage is that associated with the hydrogen evolution reaction (HER)

\[ 2H_2O^+ + 2e^- \rightarrow H_2(g) + 2H_2O \]

The phenomenon of hydrogen overvoltage has broad applicability to electro-organic studies since hydrogen ions as a pH factor and hydrogen gas (or adsorbed atomic hydrogen) as reducing agents are so important in reduction reactions. Mercury, lead, and zinc are high hydrogen overvoltage electrodes (0.9-1.0 V). Copper, nickel, and iron are intermediate (0.6-0.7 V), with platinum, platinum-black, palladium, and gold being low hydrogen overvoltage electrodes (0.03-0.3 V).
In aqueous solutions, once the overvoltage potential of an electrode is reached, an increase in imposed current simply increases the rate of hydrogen evolution with very little additional polarization of the electrode. For example, Curve A on Figure I is typical for a low overvoltage electrode in an aqueous solution.

When the overvoltage potential is reached (about -0.2 V), a hundred-fold increase in current increases the potential by only 0.1 V, while at potentials below the hydrogen overvoltage a very small increase in current increases the potential by almost 0.4 V. This is a serious problem on low overvoltage electrodes such as platinum, since frequently large quantities of hydrogen are evolved at potentials below which the organic molecule (depolarizer) can be reduced. By using high hydrogen overvoltage cathodes (Curve B), such as mercury and zinc, the hydrogen evolution reaction can be "delayed" until a higher potential is reached. This additional reducing power thus makes it possible to study the effect of the cathode potential over a wider range, as well as greatly increasing the number of compounds that can be reduced.

From a thermodynamic point of view there is a certain minimum driving force necessary to reduce hydrogen ions to hydrogen gas. The question then arises: Why is hydrogen gas evolved at much lower potentials on platinum than on mercury? The answer lies in kinetics, in which there are
Figure 1 — Polarization Curves for Low and High Hydrogen Overvoltage Electrodes
two possible ways of describing what may be the same type of effect. Thus it may be said that the hydrogen evolution reaction (HER) is kinetically hindered on mercury or that it is catalyzed on the platinum. In either case a certain minimum thermodynamic driving force must be furnished, after which kinetic factors take over and determine the relationship between current (the kinetic factor) and potential (the thermodynamic factor). Frequently catalytic electrodes show unusual behavior in that a low overvoltage electrode will effect a reduction that does not occur on a higher overvoltage electrode, even though biased at the same potential (13). It should be emphasized that on most electrodes the reaction will still show potential dependency, as is the case for the reduction of nitro-benzene, but the range may be displaced by catalytic factors inherent in the metal of the cathode.

In summary, cathode potential is a determining thermodynamic factor, in that it must reach a certain value for the electro-organic reduction to become possible. After reaching this value, kinetic factors must then be considered, catalytic effects being one of these, and potential above the reversible thermodynamic requirement (overvoltage) being the other.
CHAPTER BIBLIOGRAPHY


CHAPTER II

ELECTROCHEMICAL REDUCTION OF CARBON-Carbon
DOUBLE BONDS AND CARBONYL GROUPS

In electro-organic chemistry, the primary reactions of electron transfer between solution species and a metal electrode, and the associated interaction of the anions or radicals formed are of fundamental interest, but are not yet well understood. The mechanism of the electrochemical reduction of olefinic bonds is still very much in doubt. Proposed mechanisms include those involving free radical, radical anion, and dianion intermediates. Various experimental approaches have been used to study the problem; however, the most common are controlled potential macro-electrolyses (large scale electrolysis and identification of products) and polarography. Another method of study, which has been largely overlooked, is the determination of the effects of cathode potential on the distribution of products.

The literature contains only a few references of recent origin to the electrochemical reduction of olefins conjugated with electron withdrawing groups such as carbonyl and nitrile groups. The reduction of $\alpha, \beta$-unsaturated ketones and aldehydes has been studied by Wiemann and coworker (13, 19, 20, 21). The majority of their reductions have been done
by normal chemical means of employing a metal such as zinc, sodium, or magnesium as a reducing agent. They have studied the "effect of potential on the products" by reducing various \( \alpha, \beta \)-unsaturated ketones with sodium (high reduction potential) and zinc (low reduction potential), for example. More precisely stated, they have studied the effect of the strength of the reducing agent on the products. They conclude that at low reduction potentials (weaker reducing agents) glycols are favored and that at higher potentials (stronger reducing agents) diketones are favored. For example, at low potentials the reduction is

\[
2\text{RCCH}=\text{CH}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{CH}_2=\text{C}-\text{C}-\text{CH}=\text{CH}_2 (\alpha\text{-glycol})
\]

and at high potentials the reduction is

\[
2\text{RCCH}=\text{CH}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{RCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{R} (\text{diketone})
\]

Wiemann proposes a free radical mechanism which accounts for the formation of the observed products. It involves the addition of a proton, followed by an electron transfer from the metal to the carbonium ion at high potentials.

\[
\text{R-CCH}=\text{CH}_2 + \text{H}^+ \rightarrow \text{R-CCH}_2\text{CH}_2
\]

\[
\text{R-CCH}=\text{CH}_2 + e^- \rightarrow \text{R-CCH}_2\text{CH}_2
\]
Two of these radicals can couple to form the diketone.

\[ 2 \text{ROCH}_2\text{CH}_2 + \text{ROCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CCH}_3 \]

Similarly, at low potentials the mechanism is

\[ \text{ROCH} = \text{CH}_2 + \text{H}^+ + \text{R-CCH=CH}_2 \]

\[ \text{R-CCH=CH}_2 + \text{e}^- \rightarrow \text{R-CCH=CH}_2 \]

Again, two of these radicals can couple to form the \( \alpha \)-glycol.

\[ 2\text{CH}_2=\text{CHCR} + \text{CH}_2=\text{CH-C-CH}=\text{CH}_2 \]

The results of their very limited electrochemical reduction studies agree with the conclusion stated that high potentials (strong reducing agents) favor diketones (\( \beta, \beta \)-coupling), and low potentials will favor \( \alpha \)-glycols (carbonyl-carbonyl coupling). Wiemann and Paget (21) show that the amount of \( \beta, \beta \)-coupling of mesityl oxide in acid solutions does not change on mercury, lead, and tin cathodes, but the amount of carbonyl-carbonyl coupling increases in the order of mercury, lead, and tin, which is, according to Wiemann, the order of decreasing potential. More correctly, it is the order of decreasing hydrogen overvoltage.

It should be pointed out that the operating potential available with a given electrode metal is limited by the overvoltage, but is primarily a function of the current density (Figure 1, p.9). Wiemann made no mention of current
density or of having measured the potential of the cathode surface versus a reference electrode. Under these conditions the variation of carbonyl-carbonyl coupling on the various electrodes could just as well be a kinetic effect due to catalytic effects of the electrodes as previously discussed, rather than a function of the free energy of the system.

Wiemann (19, 20) bases his mechanism on the fact that it explains the observed products, it requires a one-electron transfer, as shown by polarographic studies (5, 6, 13, 16), and it enables him to explain the variation with potential based on a model proposed by J. Kossanyi (7). Kossanyi pictures acrolein as having these charge distributions:

\[
\begin{align*}
\text{CH}_2 &= \text{CH} \quad \text{CH}_3 \quad \text{O} \\
+0.174 &\quad -0.51 \quad +0.375 \quad -0.493
\end{align*}
\]

According to Wiemann and Kossanyi, formation of the radical

\[
\text{CH}_2=\text{CH} \cdot \text{CH}_3
\]

at low potentials is due to increased protonation of the oxygen atom (due to its greater negative charge) which increases the positive charge of the carbonyl carbon, thus accounting for its reduction at lower potentials. The formation of the

\[
\text{CH}_2-\text{CH}_2 \cdot \text{CH}_3
\]

radical, which leads to the diketone, by similar reasoning requires a higher potential. This mechanism is in agreement
with the work of Y. Arad et al. (1), in acid solution for the reduction of acrylonitrile (AN). Y. Arad et al. propose a dianion mechanism for the reduction of AN in neutral solution which is very similar to that proposed by Baizer (3), Wawzonek (17), Tomilov (14), and Umemoto (15).

From polarography of AN in neutral aqueous solutions, Arad concluded a two-electron transfer step at a half-wave potential of -1.95 V vs saturated calomel electrode (SCE) to form propionitrile (PN). This is in agreement with polarographic results reported by Platonova (10), Sevast'Yanova (11), and Lazarov (8). They propose the following dianionic mechanism:

\[
\begin{align*}
(1) & \quad \text{CH}_2\text{=CHCN} + 2e^- \rightarrow (\text{CH}_2\text{CHCN})^2^- + H_2O \\
& \quad \rightarrow (\text{CH}_3\text{CHCN})^- + H_2O \\
& \quad \downarrow + \text{CH}_3\text{CH}_2\text{CN} \\
(2) & \quad (\text{CH}_2\text{CHCN})^2^- + \text{CH}_2\text{=CHCN} \rightarrow \text{NCCHCH}_2\text{CH}_2\text{CHCN} + 2H_2O \\
& \quad \downarrow \quad \text{NCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}
\end{align*}
\]

for the formation of PN, and

\[
\begin{align*}
(2) & \quad (\text{CH}_2\text{CHCN})^2^- + \text{CH}_2\text{=CHCN} \rightarrow \text{NCCHCH}_2\text{CH}_2\text{CHCN} + 2H_2O \\
& \quad \downarrow \quad \text{NCCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CN}
\end{align*}
\]

to form adiponitirle (ADN). The rate determining steps are \( k_2 \) and \( k_3 \). Assuming that reaction (1) leads only to PN and reaction (2) leads only to ADN, the ratio of ADN/PN should be equal to

\[
\frac{k_3 [\text{AN}]}{k_2 [H_2O]}
\]

Using the bulk concentrations of water and AN and an average experimental value of ADN/PN, \( k_3/k_2 = 4 \), which says that AN
is more reactive than water towards the dianion species. Baizer (3) proposes that AN undergoes an overall two-electron uptake at the cathode, probably in two successive one-electron steps (17), with the second electron being thermodynamically more easily acquired (thus at a more positive voltage) than the first. This would account for the single wave observed in the polarographic reduction of these compounds. The first step is

$$\text{A}$$

CH$_2$:CHCN + e$^{-}$ + $[$•CH$_2$:CHCN$]$$^{-}$

In the presence of large quantities of water this radical anion extracts a proton from water, giving a free radical.

$$[$•CH$_2$:CHCN$]$$^{-}$ $+$ H$_2$:O $+$ •CH$_2$:CH$_2$:CN $+$ OH$^{-}$

This free radical can then acquire a second electron and a proton, to form PN.

•CH$_2$:CH$_2$:CN $+$ e$^{-}$ $+$ CH$_2$:CH$_2$:CN

CH$_2$:CH$_2$:CN $+$ H$_2$:O $+$ CH$_3$:CH$_2$:CN $+$ OH$^{-}$

In the presence of high concentrations of AN, the radical anion (A) is further reduced to a dianion.

$$[$•CH$_2$:CHCN$]$$^{-}$ $+$ e$^{-}$ $+$ [CH$_2$:CHCN]$^-$

This dianion can attack, at the 8 position, a polarized but not yet reduced, AN molecule on the surface of the electrode.

[CH$_2$:CHCN]$^-$ $+$ CH$_2$:=CHCN $+$ NCCHCH$_2$:CH$_2$:CHCN

This dianion dimer can then become protonated to form ADN.

NCCHCH$_2$:CH$_2$:CHCN $+$ 2H$_2$:O $+$ NCCH$_2$:CH$_2$:CH$_2$:CH$_2$:CN $+$ 2OH$^{-}$
In support of this mechanism Baizer points out that free radical inhibitors do not affect the hydro-dimerization of AN, there is no polymer formed, there is agreement with the polarographic data, and there is a proper variation of the ratio of PN/ADN when the concentration of AN was varied.

Umemoto (15) studied the electrolytic reduction mechanism of anthracene by the use of polarography and electron spin resonance (ESR) spectroscopy. The polarograms in anhydrous dimethylformamide (DMF) showed two well-defined waves. The first wave corresponded to the formation of a radical anion and the second wave to the reduction of the radical anion to the dianion. These results can be explained by the mechanism:

\[ \text{R} + e^- \rightarrow \text{R}^- \]  \hspace{1cm} \text{(First wave)}
\[ \text{R}^- + e^- \rightarrow \text{R}^2^- \]  \hspace{1cm} \text{(Second wave)}
\[ \text{R}^2^- + 2\text{H}^+ \rightarrow \text{RH}_2 \]

In this case, the presence of the intermediate radical anions were confirmed by ESR spectra.

When water was added to the system, the half-wave potential of the first wave remained unchanged but that of the second wave shifted to a less negative potential, and the first wave increased in height at the expense of the second wave. This result indicated that the radical anion reacts readily with water. This was confirmed by observing that the rate of decrease of the ESR signal intensity with time was faster in solutions of high water concentration.
These results were explained by the following mechanism:

\[
\begin{align*}
R + e^- & \rightarrow R^- \\
R^- + H_2O & \rightarrow RH_2 + OH^- \\
RH_2 + e^- & \rightarrow RH^- \\
RH^- + H_2O & \rightarrow RH_2 + OH^- 
\end{align*}
\]

The findings of Umemoto contradict the proposed mechanism of Baizer. In an anhydrous solution Umemoto observed a dianion species as Baizer proposed; however Umemoto showed that the rate of the decrease of the ESR signal intensity for the dianion species was fast in the presence of the high concentrations of water. This is strong evidence in favor of the protonation mechanism given above.

Tomilov and Klimov (14) studied the hydro-dimerization of AN by varying the concentration of AN and supporting electrolyte (McKee's Salt). They proposed a dianion mechanism identical to that of Baizer. Based only on data showing the influence of the AN concentration on cathode potential (constant current density), they state, "The process of hydro-dimerization of AN depends comparatively little upon the cathode potential." They also reported low yields of ADN on platinum cathodes in McKee's Salt. They assumed the ADN was formed as a result of hydrogenation of acrylonitrile by atomic hydrogen, without giving supporting data.

Polarographic studies by Michielli and Elving (9) on benzophenone in aprotic solvents on a dropping mercury electrode show two waves, the first being slightly larger than
the second. They suggest a reduction mechanism in pyridine of two successive one-electron steps. The first is the reduction to the radical anion $C$, which is then reduced to the dicarbanion $D$.

$$\begin{align*}
B & \rightarrow C \\
(C_6H_5)_2C=O + e^- & \rightarrow [(C_6H_5)_2CO^-] \\
D & \rightarrow C + e^- + [(C_6H_5)_2CO^-]
\end{align*}$$

The lower value for the limiting current of the second wave may be due to one of the following: (1) repulsion of the anion $C$ from the electrode, (2) dimerization of $C$ to a product which is nonreducible in the potential range available, (3) formation of the free radical

$$(C_6H_5)_2\cdot COH$$

from $C$ and any water which may be present in the solvent, and (4) disproportionation of $C$ to $B$ and $D$. They consider explanation (3) the most reasonable.

In the presence of protons the second one-electron benzophenone reduction step merges with the first. The addition of the first electron is followed by the addition of a proton to the radical anion $C$ before it can diffuse away from the surface of the electrode. This proton addition is probably simultaneous with the addition of the electron since the half-wave potential shifts in the positive direction (easier to reduce) with increasing proton availability (18).
The mechanism proposed by Michielli and Elvin is then:

\[ \text{B} \rightarrow \text{C} \quad (\text{C}_6\text{H}_5)_2\text{C}=\text{O} + e^- \rightarrow [(\text{C}_6\text{H}_5)_2\text{CO}]^- \]

\[ \text{E} \quad \text{C} + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)_2\text{COH} + \text{OH}^- \]

\[ \text{F} \quad \text{E} + e^- \rightarrow [(\text{C}_6\text{H}_5)_2\text{COH}]^- \]

\[ \text{G} \quad \text{F} + \text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5)_2\text{CHOH} + \text{OH}^- \]

Dimerization can occur by the attack of \( \text{F} \) on \( \text{B} \) followed by addition of a proton to form the pinacol.

Ashworth (2) proposed a ketone reduction mechanism very similar to Elving's, except that in acid solutions he suggests the formation of a carbonium ion.

(3) \( \text{RR'CO} \rightarrow \text{RR'C}^+ + \text{H}^+ + \text{OH}^- \)

(4) \( \text{RR'C}^+ \text{OH} + e^- \rightarrow \text{RR'COH} \)

Elving negates the possibility of carbonium ion formation because of (1) the insensitivity of the half-wave potential to ionic strength, (2) the strong pH dependency, which indicates electron transfer and proton pickup to be simultaneous, (3) the large wave height which, if a carbonium ion were the reducible species should be small since the equilibrium of reaction (3) would be far to the left (carbonium ions being short-lived) and (4) if the reducible species were formed by a reaction in solution, the wave could be kinetically rather than diffusion controlled.
Sugino and Nonaka (12) have studied the cathodic crossed hydrocoupling of acetone and acrylonitrile in acid solutions on mercury. Controlled potential macro-electrolyses of mixtures of acetone and AN on mercury at the reduction potential of acetone (half-wave potential equal -1.2 V), which is well below the reduction potential of AN, gave γ-hydroxy-γ-methylvaleronitrile. They postulate the formation of an anionic species.

\[
(\text{CH}_3)_2\text{CO} + e^- \rightarrow (\text{CH}_3)_2\text{CO}^- + \text{H}^+ + (\text{CH}_3)_2\text{COH} + e^- + (\text{CH}_3)_2\text{COH}
\]

This anion then attacks an AN molecule, which is also on the electrode surface, to form γ-hydroxy-γ-methylvaleronitrile (H).

\[
(\text{CH}_3)_2\text{COH} + \text{CH}_2=\text{CHCN} + \text{H}^+ \rightarrow (\text{CH}_3)_2\overset{\text{OH}}{\text{COH}}_2\text{CH}_2\text{CN}
\]

The existence of the \((\text{CH}_3)_2\text{COH}\) anion is supported by polarographic work of Yamura et al. (22), which showed a two-electron uptake in solutions using tetramethylammonium p-toluene sulphonate as supporting electrolyte.

It should be mentioned that the reduction potential of acetone in tetramethylammonium p-toluene sulphonate is -2.4 V vs SCE, some 1.2 V higher than it is in sulfuric acid. It is certainly possible that two entirely different mechanisms are operative at potentials as widely separated as these.

Sugino and Nonaka also discuss the possibility of a free radical process occurring which involves the adsorbed hydrogen atom, but discount it on the negative evidence that no polymerization of AN occurs. The free radical mechanism
would be:

$$\ce{(CH_3)_2CO + e^- \rightarrow (CH_3)_2\ddot{\ce{CO}} + H^+ + (CH_3)_2\ddot{\ce{COH}}}$$

$$\ce{(CH_3)_2\ddot{\ce{COH}} + \ce{CH_2=CHCN} \rightarrow (CH_3)_2\ddot{\ce{COH}_2CHCN}}$$

$$\ce{(CH_3)_2\ddot{\ce{COH}} + \ce{CH_2=CHCN} \rightarrow (CH_3)_2\ddot{\ce{COH}} + \ce{CH_2=CHCN}}$$

The hydrogen atom is produced by the reduction of water.

$$\ce{2\ce{H_2O} + 2e^- \rightarrow 2\ce{H_2} + 2\ce{OH^-}}$$

Brown and Lister (4) also report the same high yields of \(\gamma\)-hydroxy-\(\gamma\)-methylvaleronitrile from the cross coupling of acetone and AN in sulfuric acid on mercury. However, they postulate a radical mechanism:

$$\ce{(CH_3)_2CO + e^- \rightarrow (CH_3)_2\ddot{\ce{CO}} + H^+ + (CH_3)_2\ddot{\ce{COH}}_{ad}}$$

$$\ce{(CH_3)_2\ddot{\ce{COH}}_{ad} + \ce{CH_2=CHCN} \rightarrow (CH_3)_2\ddot{\ce{COH}}_{ad}}$$

$$\ce{(CH_3)_2\ddot{\ce{COH}}_{ad} + \ce{CH_2=CHCN}_{ad}}$$

$$\ce{(CH_3)_2\ddot{\ce{COH}}_{ad} + \ce{CH_2=CHCN}_{ad} \rightarrow (CH_3)_2\ddot{\ce{COH}}_{ad} + \ce{CH_2=CHCN}_{ad}}$$

In defense of this mechanism they state (1) that the carbanion mechanism proposed by Sugino and Nonaka seems unlikely under the strong acid conditions, (2) the isolation of organo-mercury products indicates the presence of an intermediate which possesses a radical nature, and (3) the slope of the steady-state polarization curves (57 mV per decade of current) indicates that the rate-determining step is a chemical process following a one-electron transfer. They further state that the absence of copious amounts of polymer,
plus the possibility of re-oxidizing all of the intermediates (as established by cyclic voltammetry), indicates that the radical is confined to the electrode surface.

In summary, mechanisms proposed have been based primarily on polarization data and chemical effects in large scale electrolyses, usually at the half-wave potential or slightly higher. The mechanisms proposed involve resonance stabilized radical and anion radical species, rarely carbonium ions, and occasionally the adsorbed hydrogen atom. Finally, there is considerable disagreement as to the mechanisms, and none can be said to be firmly established.
CHAPTER BIBLIOGRAPHY


CHAPTER III

EXPERIMENTAL

Electrolysis Cell

The electrolysis cell (Figure 2) was a one-liter resin flask with three ground glass joints in the top of the cell, that served as entrances for the anode, cathode, and reference electrode probe. A fourth served as a gas vent or as a thermometer well. All the glass joints were lubricated with stopcock grease in order to seal any gas leaks and allow measurement of gas evolution rates during electrolyses.

The anode was separated from the cathode by the use of a large medium-porosity alundum extraction cup. The alundum cup was very effective in preventing the mixing of anolyte (saturated solution of KHCO₃) and catholyte, with only a small amount of diffusion occurring between the two solutions.

The alundum cup was sealed to a glass joint with paraffin wax, which was inert to the electrolysis mixture. The glass joint was connected to a small-diameter tube and sealed in an opening in the top of the cell. The portion of the alundum cup that was above the electrolysis solution was coated with paraffin wax to prevent leakage of the anode gases into the cathode compartment, and vice-versa. The cell was tested for leaks by electrolysis of a dilute solution of sodium hydroxide and measuring the volume of
Figure 2 — Electrolysis Cell
hydrogen liberated from the cathode and the volume of oxygen liberated from the anode. Each volume checked very closely with the theoretical volume by Faraday's Law after correction was made for temperature, pressure, and water vapor.

Placement of the reference electrode probe (Figure 3) relative to the cathode was very critical. In electrolyses using high current densities through dioxane-water systems, the IR drop through the solution can be a significant part of the total applied potential, and also, if one is not very careful, a significant part of the potential difference between the working cathode and the reference. In this study the data on product distributions were much more reproducible when low potentials were used, probably a result of a more accurate measurement of the cathode potential when the current densities are low. At higher (more negative) potentials, with increasing current densities, variations in placement of the reference probe introduce larger errors between the set (control) potential and the actual operating potential. To obtain the minimum IR drop (corresponding to minimum error) between probe tip and working cathode surface, the tip was moved via the ground joint relative to the cathode surface until a maximum was observed in the current associated with a given set potential.

It is appropriate to comment at this point on the almost routine approach to electro-organic studies taken by the majority of investigators in this field. A polarogram
Figure 3 -- Reference Probe
will be done to determine the potential range of reduction, followed then by a single macro-electrolysis using a mercury pool electrode set at the half-wave potential. Product analyses will then be reported from this single electrolysis. It is exactly this potential region near the half-wave potential (as will be shown in Chapter IV) in which the product distribution is most variable. While operating at lower potentials, where errors in potential measurements are smaller, results are quite reproducible (though potential dependent), and at higher potentials results are quite reproducible because the potential dependence disappears. The accurate measurement of potentials, in which electrode geometry and placement play an important role, is an essential ingredient to reproducible, meaningful studies of electro-organic reactions.

Electrodes

Platinum and zinc cathodes were used during this study. The platinum cathode (50 cm.$^2$ surface area) was cleaned in aqua regia until a bright surface appeared and then rinsed in distilled water. When the platinum electrode was treated in this manner good reproducibility of open circuit potentials and current-potential curves was obtained.

A new piece of zinc (Fisher: 99.5 per cent purity) with a surface area of 50 cm.$^2$ was used in each electrolysis, since the surface became rough and pitted during the electrolysis. Each electrode was sanded to a bright metallic luster before use to remove oxides present on the surface.
The auxiliary anode was a platinum gauze (50 cm.² surface area), and the reference a commercial saturated calomel electrode (SCE).

**Electrical Equipment**

A diagram of the electrical circuit is shown in Figure 4. An Anotrol Model 4700 Potentiostat was used to control the cathode potential versus the reference electrode. A distinction needs to be made between the working or cathode potential and the applied potential. The working potential is the potential measured between the working electrode (cathode in this study) and the reference electrode (labeled C and R respectively in Figure 4). The applied potential is the driving force of the electrolysis current and is applied between electrodes C and A by an electronically controlled d.c. power supply in the potentiostat.

The circuit is a three electrode system (anode, cathode, and reference) comprising two circuits, with the cathode (in this case) common to both circuits. The variable power supply of the electrolysis circuit composed of the anode and cathode (A and C in Figure 4) is regulated by the reference circuit composed of the cathode and reference (C and R in Figure 4), so that only sufficient voltage is applied to provide an electrolysis current which will polarize the cathode to a preset fixed potential versus the reference electrode. The voltmeter is used to measure the working cathode potential accurately.
Figure 4 -- Electrical Circuit
Reagents

Methyl vinyl ketone (3-buten-2-one) (MVK) was purchased from Aldrich Chemical Company. When purchased it contained approximately 5 area per cent impurities by gas chromatography (GC) analysis. The impurities were identified as acetone and 6-acetyl-5,6-dihydro-2-methyl pyran.

\[
\begin{array}{c}
\text{CH}_3\text{C}-
\end{array}
\]

\[
\begin{array}{c}
\text{C}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3
\end{array}
\]

Distillation of the MVK immediately before use and collection of the middle cut (35°C and 20 mm) gave MVK with a purity of 99.0 per cent, which was used in the electrolyses. The co-solvent, p-dioxane, was also distilled to remove the peroxides, which are frequently found in ethers. Water was prepared by distilling de-ionized water. Reagent grade potassium bicarbonate purchased from Fisher Chemical company was used as received.

Electrolysis Procedure

Exactly 200 grams of distilled water, 100 grams of p-dioxane, and 50 grams of potassium bicarbonate were added to the electrolysis cell and placed in the constant temperature bath and allowed to cool to 10°C. This temperature was chosen to optimize the balance between hydrogen evolution and organic reduction. Hydrogen evolution was so vigorous at temperatures near 25°C that current efficiencies
for the organic reduction were unacceptably low. Temperatures lower than 10°C resulted in excessively high electrolytic resistance.

The potassium bicarbonate was used as a supporting electrolyte to buffer the solution at a pH of about 8.3. If the pH of the catholyte was allowed to increase to more than about 9.5 to 10, due to the formation of hydroxide ions from the electrolysis of water, large amounts of polymerization occurred. When the pH was maintained near 8.3 with an excess of bicarbonate (more equivalents of bicarbonate present than equivalents of current passed), no polymerization of MVK occurred.

One hundred and forty grams of MVK (10°C) were added slowly to the cell. The slow addition and cold MVK helped eliminate the formation of 6-acetyl-5,6-dihydro-2-methyl pyran, which formed and discolored the solution if the solution became warm from the rapid addition of MVK. The top of the cell, which held the anode compartment, cathode, and reference probe was secured in place and nitrogen was bubbled through the reaction mixture for 30 minutes to remove any dissolved oxygen. The potentiostat was set to the desired potential and the electrolysis was started.

Hydrogen gas evolution rates were determined by a bubble type gas flow meter. Hydrogen evolution rates were calculated in ml of hydrogen per 100 coulombs.
The amount of current that passed through the cell (number of coulombs) was recorded on a Brown recorder. A standard ammeter was used to calibrate the recorder.

The initial qualitative work in separation and identification of products required extensive effort in selection and preparation of GC columns to obtain the right adsorbents and conditions for the preparative GC. Details of this work will not be described.

For the subsequent quantitative work, samples were taken periodically from the cell during the electrolysis and analyzed on a P and M Model 700 dual column gas chromatograph. After the conclusion of the run (approximately 30,000 to 40,000 coulombs) the catholyte solution was removed from the cell and excess sodium carbonate added to it. This caused a separation of the organics (excess MVK and products) from the aqueous phase. The last traces of water were removed from the organic layer by anhydrous magnesium sulfate. The organic portion was weighed and its volume measured. A small sample of this organic portion was injected into the GC. The GC column was a 20 per cent PFAP on Chromosorb W (AWDMCS), 60-80 mesh, 20 feet long. A standard set of GC conditions (isothermal at 100°C for 18 minutes, then linearly programmed at 5°C per minute to 230°C) was used for all analyses. The flow rate of the helium carrier gas was 60 ml per minute.
Areas of each product peak were converted to total grams of product produced by an appropriate factor determined from calibration curves made for each product from pure samples of each product and an aliquot factor.
CHAPTER IV

RESULTS AND DISCUSSION

The reduction of methyl vinyl ketone can result in the formation of several different products, the most important of which are listed below:

a. \( \text{CH}_3\text{CH}_2\text{CCH}_3 \) 2-butaneone

b. \( \text{CH}_2=\text{CH}\text{CCH}_3 \) 3-buten-2-ol

c. \( \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CCH}_3 \) 2,7-octanedione

d. \( \text{CH}_2=\text{CH}\text{CCH=CH}_2 \) 3,4-dimethyl-3,4-dihydroxy-1,5-hexadiene

e. \( \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CCH}_3 \) 3-methyl-2,6-heptanedione

f. \( \text{CH}_3\text{CCHCH}_3 \) 3,4-dimethyl-2,5-hexanedione

g. \( \text{CH}_2=\text{CH}\text{C}-\text{CH}_2\text{CH}_2\text{CCH}_3 \) 5-hydroxy-5-methyl-6-hepten-2-one

There exist numerous possibilities of other products from multiple couplings; however, these will normally be present in only very small amounts, and the discussion will
be limited to the first generation products. It should be noted that when electrolyses were carried beyond 75 to 80 per cent of the theoretical Faradays required for complete reduction, these multiple coupling products showed up in increasing quantities as small peaks on the gas chromatograph. Because there are so many possible electrolysis products, before any meaningful study of the reaction can proceed it is necessary to determine the course of the reaction by identifying the major products and as many of the minor products as possible. It is also necessary to obtain a charge balance in which one can account for the total number of coulombs which have been passed, and a mass balance to account for the MVK.

The general procedure for identification of the electrolysis products was to collect a pure sample of each product by preparative gas chromatography (GC) and combine infrared (IR), nuclear magnetic resonance (NMR), and mass spectroscopy (MS) analyses to determine the structural formula of each product. Whenever quantities of each product could be purchased or prepared independently, IR and NMR spectra of the authentic samples were compared directly with the spectra of the electrolysis products. The matching of GC retention times of authentic samples with electrolysis products at various conditions and on two or three different GC columns was also used to help identify some products...
Electrolysis Products

The electrolysis of MVK formed three products on a platinum electrode and two products on a zinc electrode in sufficient quantities that the effect of the cathode potential on their relative proportions could be determined. Two other electrolysis products that were formed in small yields were identified, and a third formed in small yields was not identified.

2-Butanone (methyl ethyl ketone)

Methyl vinyl ketone (I) was reduced electrochemically on both platinum and zinc to 2-butanone (methyl ethyl ketone) (MEK) (II) according to the equation:

\[
\text{I} \quad \text{II} \\
\text{CH}_2=\text{C}-\text{CH}_3 + 2e^- + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{C}-\text{CH}_3 + 2\text{OH}^-
\]

The IR spectrum shows strong absorption bands at about 2950 cm\(^{-1}\) due to aliphatic C-H stretching. Absorption due to the C-H bending vibration was observed in the 1350 to 1450 cm\(^{-1}\) region. Strong absorption bands, due to the C=O stretch, were observed at 1700 cm\(^{-1}\), 1000 cm\(^{-1}\), 940 cm\(^{-1}\), and 760 cm\(^{-1}\). These absorptions were identical to those shown in the standard IR spectrum of MEK by Sadtler (7).

The NMR spectrum confirmed the identification of MEK as

\[
\text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_3
\]

c b a
TABLE I
NMR DATA FOR 2-BUTANONE

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>δ</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartet</td>
<td>2.25 - 2.62</td>
<td>2</td>
<td>b</td>
</tr>
<tr>
<td>singlet</td>
<td>2.07</td>
<td>3</td>
<td>a</td>
</tr>
<tr>
<td>triplet</td>
<td>0.86 - 1.11</td>
<td>3</td>
<td>c</td>
</tr>
</tbody>
</table>

The quartet (due to coupling with the adjacent methyl protons) at 2.25 to 2.62 δ assigned to protons labeled b and the singlet at 2.07 δ assigned to the protons labeled a are shifted downfield due to the deshielding effect of the oxygen atom on the adjacent carbon atom. The triplet (due to coupling with the adjacent methylene protons) at 0.86 - 1.11 δ is assigned to the methyl protons c, and has the expected δ value for aliphatic methyl protons. Comparison of these data with the NMR spectrum of an authentic sample of MEK showed them to be identical.

The GC retention time was identical with the retention time of an authentic sample of MEK on the FFAP column at the conditions described previously and on a 20 per cent carbowax 20 M column on chromosorb G (AWDMCS), 8 feet long, programmed from 120°C to 220°C at 5°C per minute.
2,7-Octanedione

MVK underwent a reductive coupling to form 2,7-octanedione (III) on both platinum and zinc electrodes.

\[
2\text{CH}_2=\text{CHOCH}_3 + 2e^- + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + 2\text{H}^+
\]

The coupling occurred through the \( \beta \) carbon atom of two molecules of MVK to form the straight chain eight carbon dione.

The MS spectrum of a sample believed to be 2,7-octanedione showed a small parent peak of mass 142 with a base peak of mass 43. Other large peaks occurred at mass to charge (m/e) ratios of 55, 57, 71, 85, and 99.

The IR spectrum showed absorption bands at about 2950 cm\(^{-1}\) due to aliphatic C-H stretching, a band at 1700 cm\(^{-1}\) due to C=O stretching and bands in the 1325 to 1450 cm\(^{-1}\) region attributed to C-H bending vibrations. The spectrum was very similar to that given for 2,5-hexanedione by Sadtler (8).

The NMR spectrum confirmed the identification of 2,7-octanedione as

\[
\begin{align*}
\text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{a b c c b a}
\end{align*}
\]

by the following data:
TABLE II
NMR DATA FOR 2,7-OCTANEDIONE

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>δ</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
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<tr>
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<td>2.29 - 2.61</td>
<td>4</td>
<td>b</td>
</tr>
<tr>
<td>singlet</td>
<td>2.12</td>
<td>6</td>
<td>a</td>
</tr>
<tr>
<td>multiplet</td>
<td>1.40 - 1.70</td>
<td>4</td>
<td>c</td>
</tr>
</tbody>
</table>

These NMR data are consistent with the proposed structure. Protons a and b are shifted down field due to the deshielding effect of the oxygen atom on the adjacent carbon atom. The protons labeled c are coupled to the four adjacent protons to form the observed multiplet at the expected δ value for aliphatic methylene protons. The multiplets are due to virtual coupling of the methylene protons.

The electrolysis product believed to be 2,7-octanedione had identical GC retention times on the carbowax 20 M and the FFAP columns previously mentioned as a sample of 2,7-octanedione prepared from the anodic coupling (Kolbe Coupling) of levulinic acid. Also, the melting point (43°C) is in agreement with the literature value and the melting point of the 2,7-octanedione prepared from levulinic acid.

3-Methyl-2,6-Heptanedione

On a platinum electrode MVK underwent a reductive coupling in which the coupling occurred between the β carbon atom on one molecule and an α carbon atom on a second
molecule of MVK. This resulted in the formation of the branched chain 3-methyl-2,6-heptanedione (IV).

\[
2\text{CH}_2=\text{CHCCH}_3 + 2e^- + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CCHCH}_2\text{CH}_2\text{CCCH}_3 + 20\text{K}^-
\]

The reaction is therefore analogous to that observed by Jones and Ledford (4), who found that the electrolytic hydro-dimerizations of crotononitrile and methacrylonitrile involve the participation of the \(\alpha\)-carbon as well as the \(\beta\)-carbon. Although the dimerization of methacrylonitrile occurs largely through the \(\beta\)-carbon atoms of two molecules, about two per cent under their electrolysis conditions involved coupling through the \(\alpha\)-carbon.

\[
\text{CH}_3\text{C}=:\text{CHCN} + 2e^- + 2\text{H}^+ \rightarrow \text{NCCHCHCH}_2\text{CN}\text{CH}_3
\]

Their coupling products were identified by nuclear magnetic resonance, mass, and infrared spectra.

This reaction was also observed on a zinc cathode but in such small quantities that no definite trend with cathode potential could be established. It should be emphasized that the above equations are intended to represent only the stoichiometry of the reactions, and do not represent mechanisms.

Mass spectrometry showed a parent peak of mass 142 and a base peak of 43. Other large peaks were observed at m/e ratios of 58, 72, 85, and 99.
The IR spectrum was very similar to that for 2,7-octanedione. The band at about 2950 cm\(^{-1}\) due to stretching of the aliphatic C-H bond and the band at 1700 cm\(^{-1}\) due to C=O stretching were identical. The bands in the 1325 cm\(^{-1}\) to 1450 cm\(^{-1}\) region due to C-H bending were more intense and a new absorption band appeared at 1350 cm\(^{-1}\). This is attributed to the additional methyl group in the 3-methyl-2,6-heptanediione. The standard IR spectrum for the similar compound 3,4-dimethyl-2,5-hexanediione, also shows additional absorption bands in this region when compared with the IR spectrum of 2,5-hexanediione (8).

The NMR spectrum was very useful in confirming the presence of 3-methyl-2,6-heptanediione.

\[
\text{CH}_3\text{C-CH-CH}_2\text{CH}_2\text{C-CH}_3
\]

\[
\begin{array}{cccc}
\text{f} & \text{c} & \text{b} & \text{a} \\
\text{d} & \\
\end{array}
\]

**TABLE III**

**NMR DATA FOR 3-METHYL-2,6-HEPTANEDIONE**

<table>
<thead>
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<th>Multiplicity</th>
<th>(\delta)</th>
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<th>Assignment</th>
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<tr>
<td>doublet</td>
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<td>3</td>
<td>d</td>
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<tr>
<td>quartet</td>
<td>1.43 - 1.95</td>
<td>2</td>
<td>c</td>
</tr>
<tr>
<td>singlet</td>
<td>2.06</td>
<td>3</td>
<td>f</td>
</tr>
<tr>
<td>singlet</td>
<td>2.07</td>
<td>3</td>
<td>a</td>
</tr>
<tr>
<td>multiplet</td>
<td>2.23 - 2.62</td>
<td>3</td>
<td>b &amp; e</td>
</tr>
</tbody>
</table>
The sharp doublet at 0.99 - 1.11 δ is assigned to the methyl protons d adjacent to the single proton e. This δ value is normal for methyl protons in this environment. The quartet at 1.43 - 1.95 δ, assigned to the methylene protons labeled c, is shifted farther down field than the corresponding protons in 2,7-octanedione, also labeled c. This is expected, however, since these protons are one carbon atom closer to an additional oxygen atom.

The two singlets at 2.06 and 2.07 δ appear as one singlet except when this portion of the spectrum is expanded. These two singlets are assigned to protons f and a, which are not magnetically equivalent due to the asymmetry of the molecule.

The δ values of the broad multiplet at 2.23 - 2.62 δ, assigned to protons b and e, are almost identical to the δ values (2.29 - 2.61) of the corresponding protons (labeled b) in 2,7-octanedione. This is also expected, since these protons are all in a similar environment adjacent to carbonyl groups which shift them far down field.

3-Buten-2-ol and 2-Butanol

Two additional electrolysis products were formed in small quantities. They were 3-buten-2-ol (V) and 2-butanol (VI). Their formation can be represented by the equations:

\[ \text{CH}_2=\text{CHCH}_3 + 2e^- + 2\text{H}_2\text{O} \rightarrow \text{CH}_2=\text{CHOCHCH}_3 + 2\text{OH}^- \]
and

\[ \text{I} \quad \frac{\text{CH}_2=\text{CHCH}_3 + 4e^- + 4\text{H}_2\text{O}}{} \quad \text{VI} \quad \frac{\text{CH}_3\text{CH}_2\text{CHCH}_3 + 4\text{OH}^-}{\text{CH}_3\text{CH}_2\text{CHCH}_3 + 4\text{OH}^-} \]

The yields of these products were usually less than one per cent, and although GC analysis showed them to be present, any variation in yields was within the range of experimental error. Thus it was impossible to determine any change in yields with variation of cathode potential or to collect sufficient quantity of sample of either of them for IR, NMR, and MS analysis.

Since 3-buten-2-ol was an expected electrolysis product, identification was made by matching the retention times of peaks in the electrolysis sample with the retention times of an authentic sample of 3-buten-2-ol. The matching technique was first to inject a sample of the electrolysis solution into the GC and observe the number of peaks and their sizes. Secondly, an identical sample plus either 0.1 microliters of 3-buten-2-ol or 0.1 microliters of 2-butanol (in the same syringe) was injected at the same GC conditions, and again the number of peaks and their sizes were observed. The one that increased in size was assumed to be the one corresponding to 3-buten-2-ol or 2-butanol. This procedure was carried out on FFAP, Carbowax 20M, and Porapak Q columns under at least two sets of conditions for each column.

Since it is necessary to reduce both the vinyl and the carbonyl groups to form 2-butanol, there are two possible reduction paths that may lead to its formation. These are
the reduction of MVK to 3-buten-2-ol, which is then re-
duced to 2-butanol, or the reduction of MVK to methyl ethyl
ketone, which is then reduced to 2-butanol. Since both
3-buten-2-ol and 2-butanol were produced in such low yields,
the pathway is not of major importance; however, one exper-
iment was done to try to resolve the question. The usual
electrolysis conditions were used except methyl ethyl ketone
was substituted in place of MVK. After approximately 20,000
coulombs were passed through the solution the analysis showed
2-butanol to be absent. Thus it is assumed that the 2-butanol
is formed by the reduction of 3-buten-2-ol. The obvious ex-
periment of replacing MVK with 3-buten-2-ol was not done
because of the unavailability of 3-buten-2-ol in the neces-
sary quantities.

Absence of 3,4-Dimethyl-3,4-
Dihydroxy-1,5-Hexadiene

A sixth electrolysis product was observed in small
quantities, but could not be identified, since due to its
similarity in physical properties to 2,7-octanedione it was
impossible to separate it by preparative GC or other phys-
ical methods. Although this product was present in only
small quantities (less than 1.0 per cent), it was neverthe-
less present in significantly greater amounts than were the
other trace products previously mentioned (less than 0.1 per
cent). Since 3,4-dimethyl-3,4-dihydroxy-1,5-hexadiene (DVG)
was an expected product of this reaction, and had been
reported as an electrolysis product by others (6, 13), it was strongly suspected that this unidentified product might be the DVG. In fact, one of the original objectives of this investigation was to determine whether or not electrolysis potentials could be adjusted so as to favor coupling through the olefin or through the carbonyl group as desired. Since, coupling through the carbonyl carbon would yield DVG, considerable effort was devoted to searching for this compound among the minor products.

A sample of DVG was prepared chemically by reduction of MVK with zinc amalgam in aqueous acetic acid solution, and separated by preparative GC. The DVG thus prepared was identified by IR and NMR spectra. The IR spectrum showed a broad absorption band at 3125 cm.\(^{-1}\) (C-H stretch due to olefinic hydrogens), a weak band at 1650 cm.\(^{-1}\), and two strong absorption bands at 930 and 1020 cm.\(^{-1}\). All are indicative of vinyl groups. The absorptions due to C-H stretching (3000 cm.\(^{-1}\)), and C-H bending (1375-1475 cm.\(^{-1}\)), were also present. Comparison with the IR spectrum for 3,4-dihydroxy-1,5-hexadiene (10) showed the absorption bands indicative of the vinyl groups and the hydroxide groups to be almost identical.

The NMR spectrum confirmed the identification of 3,4-dimethyl-3,4-dihydroxy-1,5-hexadiene.
Two broad multiplets 5.0-5.5 δ and 5.75-6.35 δ show the characteristic splitting of vinyl protons and were assigned to protons a and b. A broad singlet at 3.5 δ was assigned to the protons labeled d bonded to the oxygen atoms and the singlet at 1.25 δ to the methyl protons labeled c. The singlet at 1.25 δ showed splitting of about one cycle per second, which is due to the methyl groups being attached to the asymmetric carbon atoms.

A sample of DVG was then injected into the GC simultaneously with electrolysis samples by the technique described previously. The GC retention time of DVG did not correspond to the retention time of the unidentified peak or to any of the peaks observed in the electrolysis mixture. The absence of 3,4-dimethyl-3,4-dihydroxy-1,5-hexadiene (DVG) and the extremely low yield of 3-buten-2-ol show that there was very little reduction occurring at the carbonyl carbon under the electrolysis conditions. Kossanyi (5) and Wiemann (12, 13) reported the formation of the DVG in acidic solutions (buffered acetic acid solutions). Baizer (1) reduced MVK in an acetonitrile-water solution (pH = 8) but did not report the formation of any DVG. Sugino and Nonaka (11) reported the reduction of acetone and the coupling of acetone and acrylonitrile in 20 per cent sulfuric at a potential below that at which acrylonitrile is reduced. They also report that the half-wave potential of acetone on mercury is -1.2 V vs SCE, in 20 per cent sulfuric, but is
-2.4 V vs SCE in a quaternary ammonium salt solution of pH near neutral. Wilson and Wilson (14) showed that when acetone was reduced on a mercury cathode the yield of pinacol increases sharply with increasing concentration of base. From these studies it is evident that the carbonyl group is not readily attacked in neutral or slightly basic media but becomes susceptible to reduction in strongly acidic or strongly basic solutions. In retrospect, therefore, the absence of DVG under our electrolysis conditions (pH = 8.3) is consistent with previously reported work.

Non-electrochemical Products

Two other products were formed during the electrolyses that were not a result of electrochemical reduction, but were formed by a simultaneous chemical reaction. They were identified as 4-hydroxy-2-butanone (VII) and 3-oxobutyl ether (VIII).

4-Hydroxy-2-Butanone

The 4-hydroxy-2-butanone resulted from the 1,4 addition of water to MVK by the Michael Addition.

\[
\begin{align*}
&\text{I} \quad \text{II} \\
&\text{CH}_2=\text{CHCCH}_3 + \text{H}_2\text{O} + \text{HOCH}_2\text{CH}_2\text{CCH}_3 \\
&\quad \text{OH}^- \\
&\quad \text{VII}
\end{align*}
\]

The hydroxide ions were produced as a result of the electrochemical reduction and were therefore available to catalyze this reaction.
MS showed a parent peak at mass 88, the base peak at mass 43, and other large peaks at m/e ratios of 73, 70, 58, and 55.

The IR spectrum showed a large broad absorption band between 3200-3700 cm.\(^{-1}\) indicative of an alcohol. The strong band at 1060 cm.\(^{-1}\) due to the C-O stretch indicated it is a primary alcohol. A strong band at 1700 cm.\(^{-1}\) showed the presence of the carbonyl group. Bands at about 2950 cm.\(^{-1}\) (aliphatic C-H stretch) and 1325 to 1450 cm.\(^{-1}\) (C-H bending vibrations) were also present.

The NMR spectrum confirmed the structure of the 4-hydroxy-2-butanone as

\[
\text{HOCH}_2\text{CH}_2\text{CCH}_3
\]

\[
d\quad c\quad b\quad a
\]

**TABLE IV**

**NMR DATA FOR 4-HYDROXY-2-BUTANONE**

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>(\delta)</th>
<th>Integration</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>singlet</td>
<td>2.9</td>
<td>3</td>
<td>a</td>
</tr>
<tr>
<td>triplet</td>
<td>2.58 - 2.81</td>
<td>2</td>
<td>b</td>
</tr>
<tr>
<td>triplet</td>
<td>3.80 - 3.95</td>
<td>2</td>
<td>c</td>
</tr>
<tr>
<td>singlet</td>
<td>2.9 (CDCl(_3))</td>
<td>1</td>
<td>d</td>
</tr>
<tr>
<td></td>
<td>4.25 (CC(_1)(_4))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The methyl protons (a) and the methylene protons (b) are shifted down field due to the deshielding effect of the
carbonyl oxygen atom. Protons labeled a and b are on carbon atoms adjacent to a carbon atom bonded to an oxygen atom and are not shifted down field as far as the methylene protons (c) that are bonded to a carbon atom that is also bonded to an oxygen atom. The δ position of proton (d), which is bonded to oxygen, changes in different solvents which is expected for alcohols.

3-Oxobutyl Ether

The 3-oxobutyl ether resulted from the 1,4 addition of 4-hydroxy-2-butanone to MVK, also by the Michael Addition.

\[
\text{CH}_2=\text{CHCCH}_3 + \text{HOCH}_2\text{CH}_2\text{CCH}_3 \rightarrow \text{CH}_3\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCCH}_3
\]

The fact that this compound was not formed as a result of an electrochemical reaction was demonstrated qualitatively by passing 10 ma of current through an electrolysis mixture for two hours (72 coulombs). GC analysis (using area percent as weight percent) showed more than two grams of the ether was present in the mixture. The theoretical amount that could be formed by electrolysis from 72 coulombs of charge is about 0.03 grams.

MS did not show a parent peak at mass 158; however, the cracking pattern strongly indicated 3-oxobutyl ether. Large peaks were observed at m/e ratios of 43, 55, 57, 70, 71, 72, 87, 101, 115, and 140, which are all expected fragments for this compound.
The NMR spectrum confirmed the structure as

\[
\begin{array}{c}
\text{CH}_3\text{CCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CCH}_3 \\
a \quad b \quad c \quad c \quad b \quad a
\end{array}
\]

A large singlet at 2.12 δ is due to the methyl protons labeled a. A triplet at 2.50 to 2.75 δ is assigned to the methylene protons labeled b. A triplet at 3.55 to 3.80 δ is due to the methylene protons labeled c.

The formation of 4-hydroxy-2-butanone (VII) as a function of coulombs of current passed is represented by Curve II of Figure 5. It was formed at a faster rate than was theoretically possible electrochemically (the number of molecules of VII present was greater than the number of electrons that had been passed through the solution). It is not known for sure why its rate of formation changed so abruptly and its concentration decreased slightly. The formation of the ether (VIII) cannot account for the sudden change since only small amounts of the ether were formed. It was also observed that the 4-hydroxy-2-butanone was not stable. When the electrolysis solution (pH = 8.5) was allowed to stand overnight the concentration of 4-hydroxy-2-butanone decreased by as much as a factor of 10. This suggests a slowly established equilibrium of

\[
\begin{align*}
\text{HOCH}_2\text{CH}_2\text{OCH}_3 & \rightleftharpoons \text{CH}_2=\text{CHCH}_3 + \text{H}_2\text{O} \\
\end{align*}
\]

which lies far to the right. Another explanation for the disappearance of the 4-hydroxy-2-butanone would be its electrochemical reduction to 1,3-butanediol. A careful check
failed to reveal any 1,3-butanediol, and further reductions are very unlikely, since it is known to be extremely difficult to electrochemically reduce alcohols to hydrocarbons.

A small amount of 4-hydroxy-2-butanone was detected by GC analyses in blank runs in which the electrolysis conditions were reproduced but no current was passed through the solution. This quantity was insignificant compared with the amount of 4-hydroxy-2-butanone formed during electrolyses. These same analyses also showed that the electrolysis products (MEK, 2,7-octanediol, and 3-methyl-2,5-heptanediol) were not formed under these blank conditions.

A plot of coulombs passed versus grams of products formed (Figure 5) shows that the rate of product formation is not linear (Curves III, IV, V), but decreases near the end of the experiment. This is probably due to the decrease in the concentration of MVK and the subsequent formation of more hydrogen. The decrease in MVK concentration is due to two factors. One is simply that it is consumed during electrolysis in the formation of products. Secondly, and probably more important, is a solubility phenomenon. During the electrolysis hydroxide ions are formed either as a by-product of the reduction of MVK or in the reduction of water to evolve hydrogen gas. These hydroxide ions react with the bicarbonate ions (present to buffer the solution at pH 8.3) to form carbonate ions. The carbonate ions are more soluble in water than the bicarbonate and cause salting out of the
Figure 5 -- Grams of Products Formed and Grams of Methyl Vinyl Ketone Consumed as a Function of Coulombs Passed
organics and separation of the catholyte into two layers. Thus the concentration of MVK in the aqueous layer (most of the current passes through the aqueous layer) is much lower near the end of the run than early in the run, causing the decrease in efficiency of the reduction of MVK, and the increase in hydrogen evolution.

The percentage of current which went to produce organic products decreased with an increase in cathode potential (Table V). The corresponding increase in hydrogen evolution with increased cathode potential was also observed, but was variable (Figure 6), and made the measurement of the hydrogen evolution rates very inaccurate. Without the availability of hydrogen evolution rates the quantities of hydrogen produced could not be calculated, thus making it impossible to determine a complete and accurate charge balance. Only in the cases where little or no hydrogen gas was evolved (-0.80 and -1.0 V in Table V) could a charge balance be obtained. These charge balances are shown in Table VI.

A mass balance between the reactant (MVK) and the products was obtained (Table VII). The missing two per cent of MVK could be due to evaporation through the gas vent or may be due to analytical error.

The charge balance for the low potential runs and the mass balance at higher potentials on both platinum and zinc cathode show conclusively that no other organic products were formed in any significant quantities during the
**TABLE V**

EFFECT OF CATHODE POTENTIAL ON THE AMOUNT OF CURRENT PRODUCING ORGANIC PRODUCTS

<table>
<thead>
<tr>
<th>Cathode Potential Volts vs SCE</th>
<th>Per Cent Current to Organic Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.80</td>
<td>107</td>
</tr>
<tr>
<td>-1.00</td>
<td>102</td>
</tr>
<tr>
<td>-1.25</td>
<td>89.4</td>
</tr>
<tr>
<td>-1.50</td>
<td>89.5</td>
</tr>
<tr>
<td>-1.80</td>
<td>75.3</td>
</tr>
<tr>
<td>-2.00</td>
<td>67.4</td>
</tr>
<tr>
<td>-2.20</td>
<td>76.7</td>
</tr>
<tr>
<td>-2.50</td>
<td>83.5</td>
</tr>
<tr>
<td>-3.00</td>
<td>79.0</td>
</tr>
</tbody>
</table>
Figure 6 -- Typical Hydrogen Evolution Rates as a Function of Coulombs Passed on Zinc Cathodes
<table>
<thead>
<tr>
<th>Cathode Potential</th>
<th>Total Coulombs Passed</th>
<th>MEK</th>
<th>2,7-Octanedione</th>
<th>3-Methyl-2,6-Hep-tanedione</th>
<th>Other Products</th>
<th>Total Coulombs to Products</th>
<th>Per Cent Current to Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.80</td>
<td>44,000</td>
<td>41,300</td>
<td>640</td>
<td>5,260</td>
<td>700</td>
<td>47,000</td>
<td>107</td>
</tr>
<tr>
<td>-1.00</td>
<td>29,200</td>
<td>29,200</td>
<td>3,000</td>
<td>3,900</td>
<td>2,250</td>
<td>38,350</td>
<td>102</td>
</tr>
</tbody>
</table>
### TABLE VII
MASS BALANCE OF MVK AND PRODUCTS

<table>
<thead>
<tr>
<th>Electrode Metal</th>
<th>Potential vs SCE</th>
<th>Grams MVK Start</th>
<th>Grams MVK End</th>
<th>Grams MEK</th>
<th>Grams 2,7-dione</th>
<th>Grams *4-hydroxy 2-butanone</th>
<th>Grams MVK in Anode</th>
<th>Grams other Products</th>
<th>Total Products and MVK</th>
<th>Per Cent Products and MVK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>-1.60</td>
<td>140</td>
<td>113.0</td>
<td>2.65</td>
<td>7.3</td>
<td>7.25</td>
<td>6.1</td>
<td>1.0</td>
<td>137.3</td>
<td>98.0</td>
</tr>
<tr>
<td>Zn</td>
<td>-1.70</td>
<td>140</td>
<td>119.4</td>
<td>4.3</td>
<td>6.4</td>
<td>1.5</td>
<td>5.2</td>
<td>0.5</td>
<td>137.2</td>
<td>98.0</td>
</tr>
</tbody>
</table>

* Corrected for grams of MVK consumed in its formation
electrolysis. These data also confirm the assumption that the deficit of current, which was not used in the production of organic products (Table V), was consumed in producing hydrogen gas.

In summary, there are four major products formed by the electrolysis of MVK in a basic aqueous solution. They are methyl ethyl ketone, 2,7-octanedione, 3-methyl-2-6-heptanedione and hydrogen. It has already been shown that the amount of hydrogen produced increases with an increase in cathode potential. The effect of cathode potential on the relative proportions of the three organic products will be discussed later.

Steady state polarization curves (potential vs log current density) have frequently been used to formulate mechanisms. For simple systems, particularly inorganic systems where the course of the overall reaction is well established and unique, polarization data are very valuable. However, for systems involving multiple possible sequential steps and simultaneous reactions, interpretation of these curves should be carefully qualified. Data obtained as a function of MVK concentration during this investigation are shown for platinum in Figure 7 and for zinc in Figure 8. The two curves in the absence of MVK are hydrogen evolution curves, and are about as expected in terms of potential region (high overvoltage on zinc, low overvoltage on platinum). The Tafel slopes in both cases are similar, but higher than
Figure 7 — The Effect of the Methyl Vinyl Ketone Concentration on the Cathodic Polarization Curve on Platinum
Figure 8 — The Effect of the Methyl Vinyl Ketone Concentration on the Cathodic Polarization Curve on Zinc
expected, running 260-290 mV/decade of current, while the usual hydrogen Tafel slope in strictly aqueous systems is 120 mV/decade (2). In the presence of the dioxane, however, as with any adsorbable organic, Tafel slopes of this value are not surprising; in fact, very low concentrations ($10^{-5}$ M) of certain strongly adsorbed substances can cause the Tafel slopes to move abruptly from the normal 120 mV/decade to values near 300 mV/decade in the potential region where the adsorption occurs (the adsorption itself is potential sensitive), and then back to 120 mV/decade when further potential changes cause desorption (3). The high slopes observed thus indicate only that the dioxane solvent molecules are adsorbed within the double layer, and remain so over the entire potential range studied.

There are two additional aspects of these polarization curves which give some insight into the physical processes occurring during the reaction, although not too much can be inferred mechanistically. The first is the persistence of the high Tafel slopes on platinum electrodes with increasing concentration of MVK, while on zinc the Tafel slope falls off with increasing MVK concentration until it reaches a "normal" value of 110 mV/decade at the higher concentrations. Now the shifts in the polarization curves to higher currents on both electrodes are clearly due to reduction of the MVK, since the hydrogen currents are actually suppressed by addition of MVK (Figure 9). This persistence of slope in the
Figure 9 -- The Effect of the Methyl Vinyl Ketone Concentration on the Hydrogen Evolution Rates
case of platinum clearly indicates that the MVK is only weakly adsorbed, and is not really competitive with the di-

oxane, in the potential region -0.80 V to -1.60 V vs SCE. However, on zinc the MVK must be strongly enough adsorbed in the -1.6 V region to essentially displace the dioxane and exhibit a Tafel slope consistent with a simple one-electron discharge as an initial slow step. While the data cannot be used too strongly in establishing a mechanism, primarily because of the complexity associated with the potential dependent ad-
sorption, this behavior is nevertheless consistent with the mechanism to be formulated from our electrolysis results.

A second point to be noted in these curves is the change in current, at a given constant potential in the Tafel region, with unit change of concentration of MVK. This is called the electrochemical reaction order, and is usually expressed as

\[
\frac{d \log i}{d \log [\text{MVK}]}
\]

where \( i \) is current density and [MVK] is in moles/liter. In a "normal" electrochemical reduction, one in which the ad-
sorption is described by the linear portion of the adsorption isotherm and which involves a direct uptake of electrons by the reactant, the order will be unity. Conversely, the "reacting" concentration (that within the double layer) is often related to the bulk concentration in moles per liter in a non-linear fashion, and reaction orders may deviate con-
siderably from unity. For MVK on platinum the order is near
0.3, while on zinc at -1.6 V vs SCE, it is very nearly 1.0. If the surface concentration of the MVK (or fraction \( \theta \) of the electrode surface covered by adsorbed MVK, which is essentially the same thing), is controlling the current, then the orders say that it takes more MVK to induce a given increase in \( \theta \) on platinum than it does on zinc. Since most isotherms have a characteristic sigmoid shape, (Figure 10) then it appears that with platinum one is operating in the upper part of the curve (the large bulk of the \( \theta \) is provided by dioxane, which MVK will not displace on platinum), while with zinc one is operating over the middle linear region of the curve. The order observations are therefore consistent with the previous conclusion from the Tafel slopes that the MVK is not specifically or strongly adsorbed on platinum, but is so on zinc. Of course it should be borne in mind that the potential ranges on the two metals are different, and this, as well as the nature of the metal, can affect the adsorption not only of MVK, but also of dioxane with which it competes.

The hydrogen evolution reactions, which is suppressed initially by the dioxane adsorption to a Tafel slope of 260-290 mV/decade, is suppressed even further by the addition of MVK, and the additional suppression is more or less independent of the electrode metal. While polarization data for the hydrogen reaction cannot be obtained due to the overwhelming percentage of the total current which goes to MVK reduction,
Figure 10 -- Typical Adsorption Isotherm for Organic Molecules on a Metal
it is still possible to measure actual hydrogen evolution rates over intervals of time, and these are shown as a function of MVK concentration in Figure 9. The similarity of the two concentration dependencies shows merely that the water species which is reduced to hydrogen is a poor competitor for the electrode surface, and loses out to both the dioxane and the MVK.

The effect of cathode potential on the ratio,

\[
\frac{\text{grams of 2,7-octanedione}}{\text{grams of methyl ethyl ketone}}
\]

on a platinum electrode (Figure 11), and for a zinc electrode (Figure 12), shows an increase in the ratio at lower potentials and then a leveling off trend at higher potentials. Plots of ratio of this type greatly magnify any irregularities which occur; hence the two erratic points in Figure 11 could be caused by only minor analytical errors. However, the general regular nature of these curves is convincing evidence that the ratio of the 2,7-octanedione to methyl ethyl ketone is a function of the cathode potential. The ratio,

\[
\frac{\text{grams of 2,7-octanedione}}{\text{grams of 3-methyl-2,6-heptanediophone}}
\]

is also a function of the cathode potential (Figure 13). The curve is very smooth at lower potentials, where larger amounts of 3-methyl-2,6-heptanediophone are formed; however, at higher potentials where the amount of 3-methyl-2,6-heptanediophone formed is very small, the data became somewhat
Figure 11: The Effect of the Cathode Potential on the Ratio of
Grams of 2,7-Octanedione on a Platinum Electrode
Grams of Methyl Ethyl Ketone
Figure 12 -- The Effect of the Cathode Potential on the Ratio
Grams of 2,7-Octanediol on a Zinc Electrode
Grams of Methyl Ethyl Ketone
Figure 13 -- The Effect of the Cathode Potential on the Ratio
Grans of 2,7-Octanedione  on a Platinum Electrode
Grans of 3-Methyl-2,6-Heptanedione
erratic, again due to small errors in the determination of 3-methyl-2,6-heptanedione.

The effect of cathode potential on the per cent current producing methyl ethyl ketone, 2,7-octanedione and 3-methyl-2,6-heptanedione (Figure 14) on a platinum cathode shows that the yields of MEK and 3-methyl-2,6-heptanedione are at a maximum at low potentials and decrease steadily with increasing potentials until a potential of about -2.20 V vs SCE is reached. The ratios of the products do not vary at higher cathode potentials, probably due to diffusion control of the rate of reduction of MVK, which will be discussed later.

The effect of cathode potential on the per cent current producing methyl ethyl ketone and 2,7-octanedione on a zinc cathode (Figure 15) shows three important differences from the platinum data. First, only small amounts of 3-methyl-2,6-heptanedione were formed and the errors in analysis were such that no trend in yield versus cathode potential could be established; hence data for this compound are not plotted in Figure 15. Secondly, on zinc the percentage of current which went toward the formation of 2,7-octanedione remained less than the amount which went to produce MEK over the entire range of potentials. Thirdly, on zinc the potential range in which the product ratio was a function of potential was much narrower (only about 0.2 V) than on platinum (about 1.4 V). The potential dependent region on zinc is compressed
Figure 14 -- The Effect of the Cathode Potential on the Per Cent of Current to Organic Products on a Platinum Electrode
Figure 15 -- The Effect of the Cathode Potential on the Per Cent of the Current to Organic Products on a Zinc Electrode
from both directions when compared to platinum. The shift at low potentials is probably due to the kinetic effect discussed earlier. The potentials of -0.80 V on platinum and -1.45 V on zinc vs SCE were the lowest potentials at which reduction of MVK occurred. This indicates that there was either a catalytic effect on platinum or a hindering kinetic effect on zinc. The reason for the shift at higher potentials is not so clear-cut. A reasonable explanation, which would also explain the lower percentage of current producing 2,7-octanenedione on zinc than on platinum, is based on a difference in the rates of diffusion of MVK to the electrode surface. On the platinum electrode the electrode surface remained clean and bright, with no visible attack on the metal surface. However, when a zinc electrode was used it quickly became coated with a soft, white material believed to be zinc carbonate (it was not zinc oxide since the solution was deaerated with nitrogen before the electrolysis). This zinc carbonate coating could greatly limit the rate of diffusion of MVK to the electrode surface. This would cause the surface concentration of the intermediate species which dimerizes to 2,7-octanenedione to be lower (thus less 2,7-octanenedione), and also account for the flat regions of the curves occurring at lower potentials on zinc than on platinum.

In summary, it was found that MVK was adsorbed on the electrode surface and was reduced to MEK, 2,7-octanenedione and 3-methyl-2,6-heptanenedione. A fourth product was hydrogen gas.
The relative ratios of the yields of these organic products were shown to be a function of the cathode potential at lower potentials and independent of the cathode potential at higher potentials.

The reason for the potential dependency of this reaction and a proposed reaction mechanism will be discussed in the following chapter.
CHAPTER BIBLIOGRAPHY


CHAPTER V

DISCUSSION OF MECHANISM

The data presented in Figures 14 and 15 do not lend themselves readily to either a free-radical or an ionic-mechanistic interpretation. A free-radical mechanism postulating the formation of the radical species

\[ \text{CH}_2\text{CH}_2\text{CCH}_3 \]

(1)

can be used to explain the relative proportion of 2-butanone and 2,7-octanedione with variation of potential. The basis for the explanation is that at higher potentials (higher current densities) the concentration of the free radical is higher, which favors dimerization. This mechanism cannot explain the formation of the \( \alpha, \beta \)-coupling product, 3-methyl-2,6-heptanedione. An ionic mechanism can explain the formation of the observed products, but no single ionic mechanism explains the effect of cathode potential on the relative proportion of products.

Others who have done similar electrochemical reductions were not aware of the effect of cathode potential on the relative proportions of the products. They based their interpretations primarily on polarization and polarographic data in conjunction with the effects of pH, concentration of depolarizer, and solvent effects. These are certainly valid
methods of approaching the problem; however, the neces-
sity of explaining the effect of cathode potential on the
ratio of products places new restrictions on the mechanism
which have never been imposed previously.

Based on the data presented, the mechanism in Figure 16
is proposed.

By direct electron transfer from the cathode metal an
adsorbed MVK molecule is reduced to the radical anion $A$,
which can react in three ways.

One, the radical anion $A$ can react with water (with rate
constant $k_2$) to form the adsorbed radical $B$, which can be
easily reduced by a second electron from the cathode to
form the $\beta$ anion $C$ (radicals are reduced at the same po-
tential or lower potentials than neutral molecules or anions)
(3, 4). This anion $C$ can then extract a proton from a water
molecule to form 2-butanone (MEK). An alternate reaction
would be the nucleophilic attack of the anion $C$ at the $\beta$
position of MVK, which, after protonation, would lead to 2,7-
octanedione. Apparently, this does not occur to any extent
since almost no 2,7-octanedione is formed at low cathode po-
tentials where the yield of MEK is at a maximum.

Two, it can dimerize to form the $\alpha, \alpha'$dianion $D$ ($k_3$),
which in turn reacts with two molecules of water to form 2,7-
octanedione. The dimerization of radical anions is well
known and has been demonstrated by Dadley (2) and Chaudhuri
(1) among others. The dicarbanion $D$ should be readily formed
Initial Step Toward all Products:

\[ \text{CH}_2=\text{CHCCH}_3 + e^- k_1 \rightarrow \text{CH}_2=\text{CHCCH}_3 \]  \[ \text{A} \]

Pathway to Methyl Ethyl Ketone:

\[ [\text{A}] + \text{H}_2\text{O} k_2 \rightarrow \dot{\text{CH}}_2\text{-CH}_2\text{CCH}_3 + e^- \rightarrow \text{CH}_2\text{CH}_2\text{CCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{CCH}_3 \]

\[ [\text{B}] \quad [\text{C}] \quad \text{MEK} \]

Pathway to 2,7-Octanedione:

\[ 2[\text{A}] k_3 \rightarrow \text{CH}_3\text{CCHCH}_2\text{CH}_2\text{CCH}_3 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CCH}_3 \]

\[ \text{CH}_3\text{C=CHCH}_2\text{CH=CH}_3 \quad 2,7\text{-Octanedione} \]

Pathway to 3-Methyl-2,6-Heptanedione:

\[ [\text{A}] + \text{CH}_2=\text{CHCCH}_3 k_4 \rightarrow \dot{\text{CH}}_2\text{CHCCH}_3 + \text{H}_2\text{O} \rightarrow \dot{\text{CH}}_2\text{CHCCH}_3 \]

\[ \text{CH}_2\text{CH}_2\text{CCH}_3 \quad \text{CH}_2\text{CH}_2\text{CCH}_3 \]

\[ [\text{F}] + e^- \rightarrow \text{CH}_3\text{CCHCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CCHCH}_3 \]

\[ \quad \text{3-Methyl-2,6-Heptanedione} \]

Figure 16 -- Reaction Mechanism for the Formation of Methyl Ethyl Ketone, 2,7-Octanadione, and 3-Methyl-2,6-Heptanadione from Methyl Vinyl Ketone
since it is a conjugated system and is stabilized by the resonance forms

\[
\text{CH}_3\text{C} = \text{CHCH}_2\text{CH}_2\text{CH} = \text{CH}_3 \rightarrow \text{CH}_3\text{C} = \text{CHCH}_2\text{CH}_2\text{CH} = \text{CH}_3 \quad \text{etc.}
\]

Three, it can react with a neutral molecule of MVK to form the radical anion dimer E, which then reacts with water to form the adsorbed radical F, which is reduced by a second electron to the anion G. The anion G can react with water to form 3-methyl-2,6-heptanedione, which is a result of coupling between the α carbon atom of one MVK molecule with the β carbon atom of another MVK molecule.

Since the radical anion A is a common intermediate leading to the formation of the three products, the relative rates of the reaction of A in the three proposed pathways \( k_2, k_3, k_4 \) will determine the relative ratios of the products. The relative rates of these three reaction pathways are a function of the rate of formation of the radical anion A, which is a function of the cathode potential. For example, at high potentials, which correspond to high rates of formation of A and therefore high concentrations of A on the electrode surface, the dimerization reaction, which leads to 2,7-octanedione, is favored. This is analogous to any homogeneous second order reaction. Electrolysis at lower potentials decreases the rate of formation of A, which results in lower concentrations of the radical anion A on the surface, which leads to MEK and 3-methyl-2,6-heptanedione, since the dimerization reaction is no longer favored, thus allowing the
reactions with water \( (k_2) \) and MVK \( (k_4) \) to predominate. Thus the proposed mechanism explains the shifts in the relative yields of MEK and 2,7-octanедione as shown in Figures 14 and 15.

The determination of the fraction \( 0 \) of the electrode surface covered by adsorbed MVK molecules as a function of the potential would be a valuable aid in substantiating the proposed mechanism. Data of this type can be obtained from electrochemical stripping and pulse methods. From these data surface concentrations of the reacting species as a function of potential could be determined and correlated with the relative proportions of the products. Such a correlation would lend strong support to the kinetically controlled mechanism which is proposed.

According to this mechanism the ratio of MEK to 3-methyl-2,6-heptanедione should be constant over the potential range studied (Figure 17) except for a possible effect of a decrease in MVK concentration near the electrode at higher potentials. While operating at high potentials (fast rates of reduction), the availability of MVK may become diffusion limited. This would cause a decrease in the reaction rate of \( A \) with MVK and a consequent increase in the MEK to 3-methyl-2,6-heptanедione ratio. An increase in this ratio was observed.

Even though the ratio of the products is determined by the relative rates of the three reaction pathways of \( A \), these three rates are determined by the rate of formation of \( A \),
which is dependent on the cathode potential. In this manner the cathode potential controls the ratios of the products by controlling the rate of the rate-determining step, $k_1$.

The effect of the cathode potential (Figures 14 and 15) can be readily explained by this mechanism. Low potentials (slow rates of formation of A and low concentrations of A) favor reactions $k_2$ and $k_4$, which lead to MEK and 3-methyl-2,6-heptanedione. The maximum yields of these two products were observed at low potentials (Figure 14, Curves I and III; Figure 15, Curve I). When the potential is increased to higher values, the rate of formation of A increases along with an increase in the concentration of A on the electrode surface, resulting in an increase in the rate $k_3$ and a decrease in rates $k_2$ and $k_4$. This decrease in MEK and 3-methyl-2,6-heptanedione yield is observed along with an increase in the yields of 2,7-octanediol. These trends continue with increasing potential until the rate of formation of radical $A$ becomes diffusion controlled (limited by the rate at which MVK can be transported to the electrode surface).

Once the rate of formation of A becomes diffusion controlled, any additional increase in potential has no effect on the rate of its formation, which results in the potential region in which the ratios of the products are constant as observed in Figures 14 and 15.

In summary, the mechanism is both an ionic and free radical mechanism which depends on the rate of formation of
a single radical anion intermediate to determine the relative ratio of products. This single intermediate is formed in a rate-controlling step, whose rate is controlled by the cathode potential. Thus the cathode potential controls the relative ratios of the products formed through its kinetic influence, rather than through any thermodynamic factors.
CHAPTER BIBLIOGRAPHY

CHAPTER VI

CONCLUSIONS

Methyl vinyl ketone is reduced primarily to methyl ethyl ketone and 2,7-octanedione on zinc, but only small amounts of 3-methyl-2,6-heptanedione are formed. On platinum the products are methyl ethyl ketone and 2,7-octanedione, but significantly larger amounts of 3-methyl-2,6-heptanedione. On both electrodes these products account for 98 per cent of the methyl vinyl ketone consumed.

Methyl vinyl ketone is reduced on platinum at some 0.7 V less negative (less reducing) than it is on zinc. This difference is due to catalytic effects, the reaction being hindered to a much smaller extent on platinum than it is on zinc.

The polymerization of methyl vinyl ketone can be eliminated during the electrolysis in aqueous solutions by buffering to pH of 8.3 with potassium bicarbonate.

In this solvent system the vinyl group readily undergoes reduction and reductive coupling; the carbonyl group, however, is attacked only slightly if at all even under the extremely strong reducing conditions of 3.0 V vs SCE.

The polarization data and the reaction orders show that MVK is not specifically adsorbed on platinum and will not
displace adsorbed p-dioxane; however, on zinc MVK is specifically adsorbed. The steady state reaction kinetics are in agreement with the mechanism established from the macro-electrolysis data.

The relative ratios of the reduction products are a function of the cathode potential at low potentials but become independent of the potential at higher potentials, where the rate of reduction of the methyl vinyl ketone becomes diffusion limited. This establishes that the effect of potential on the reaction is kinetic, rather than thermodynamic.

The mechanism of the reaction involves the initial formation of a radical anion.

\[ \text{CH}_2\text{CHCCH}_3 \]^0

The rate of formation and surface concentration of the radical anion are potential dependent. The electrolysis products are formed from this radical anion by it reacting with water, methyl vinyl ketone, or dimerizing with itself. While the rates of these reactions are themselves potential independent, they are a function of the surface concentration of the intermediate, which, as stated above, is potential dependent.
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