ELECTROCHEMICAL REDUCTION OF THE CARBONYL GROUP

DISSERTATION

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

by

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The Ohio State University

1953

Approved by:

[Signature]
Adviser
ACKNOWLEDGEMENT

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ELECTROCHEMICAL REDUCTION OF THE CARBONYL GROUP

INTRODUCTION

The electrochemical reduction of aldehydes and ketones has been the subject of numerous experiments since this method of reduction was first described\(^1\), even before the beginning of the century.

The carbonyl group in aldehydes and ketones can be reduced to different types of products, depending on the type of compound and the experimental conditions used. In general the carbonyl group can be reduced in three ways as follows:

\[
2R-CO-R' + 2H^+ + 2e^- \rightarrow R'-C-C-R' \quad \text{(pinacol)}
\]

\[
R-CO-R' + 2H^+ + 2e^- \rightarrow R-C-R' \quad \text{(alcohol)}
\]

\[
R-CO-R' + 4H^+ + 4e^- \rightarrow R-CH_2-R' + H_2O \quad \text{(hydrocarbon)}
\]

Aldehydes and ketones are non-conductors of the electric current, and so their electrochemical reduction must be carried out in an electrolyte. This may be
acidic, basic, or neutral, the nature of the products being largely influenced by the electrolyte and the cathode.

A cadmium cathode in 30 to 50 percent sulfuric acid is generally preferred for reductions of the carbonyl group to methylene. Lead or mercury in acid solution usually gives mixtures of hydrocarbon, alcohol and pinacol, along with metal alkyls.

In alkaline solutions the products, alcohol or pinacol but never hydrocarbon, are dependent on the nature of the aldehyde or ketone. Aromatic aldehydes and mixed aromatic-aliphatic ketones are usually reduced to the pinacol in good yield. Substituted benzophenones are more frequently reduced to the corresponding benzhydrol. In contrast to these reductions of compounds containing aromatic groups, the reduction of aliphatic aldehydes and ketones in alkaline solution has received relatively little study.

Aliphatic aldehydes

F. Muller\textsuperscript{1} reported the reduction of formaldehyde to

\begin{enumerate}
\end{enumerate}

methyl alcohol in alkaline solution at a copper or silver cathode.
G. Shima\(^1\) reported the reduction of crotonaldehyde


\[\text{to } \alpha\text{-butyl alcohol in 50 percent yield in sodium bicarbonate solution at a mercury cathode.}\]

H. J. Creighton\(^2\) has reported the reduction of


\[\text{glucose at an amalgamated lead cathode in sodium hydrate solution to give sorbitol and mannitol, a process which for a while was practised industrially by Atlas Powder Company.}\]

\textbf{Aliphatic ketones}

The first report of the electrolytic reduction of acetone in alkaline solution appeared in a patent issued to Merck\(^3\) in 1899. Low yields of iso-propyl alcohol and

\(\text{(3)}\) E. Merck, German Patent 113,719, (1899).

\[\text{pinacol were obtained at a lead or carbon cathode.}\]

Three years later Elbs and Brand\(^4\) verified many of


\[\text{the patent claims. These workers also reported that methyl ethyl ketone under the same conditions gave a poor yield of alcohol, and only traces of the pinacol.}\]
Tafel and Emmert\(^1\) reported the reduction of levulinic acid to \(\gamma\)-hydroxy valeric acid at a lead cathode in sodium hydroxide solution. After lactonization of the hydroxy acid, \(\gamma\)-valerolactone was recovered in 61 percent yield. These authors could find no evidence for the formation of any pinacol-type product. \(\alpha,\alpha\)-Dimethyl levulinic acid was reduced and condensed to the lactone of \(\gamma\)-hydroxy-\(\alpha,\alpha\)-dimethyl \(n\)-valeric acid under the same conditions in 42 percent yield.

Kyrides\(^2\) reported the reduction of 3-methyl-4-pentan-2-one to the diol:

\[
\begin{array}{c}
\text{CH}_3 - \text{CH} - \text{C}(\text{CH}_3) - \text{CH} - \text{CH}_3 \\
\text{H} & \text{O} & \text{H} & \text{O} & \text{H}
\end{array}
\]

at a mercury cathode in potassium bicarbonate solution in 66 percent yield.

Takagi and his co-workers\(^3\) reported the reduction of acetone by ammonium amalgam (prepared electrolytically). \(\text{Iso}\)-propyl alcohol was the main product, with pinacol and traces of amines as byproducts. Similarly methyl ethyl
ketone gave sec-butyl alcohol and traces of amine.

The first systematic investigation of the reduction of acetone in alkaline solution was reported by Wilson and Wilson\(^1\) in 1941. These authors studied the reduction in potassium hydroxide solution at a mercury cathode. The effects of current density, temperature and alkali concentration on the relative amounts of pinacol and isopropyl alcohol were studied. Variation of pinacol with current density presented a rather complex relationship which could not be fully explained. Over the temperature range from 6 to 25\(^\circ\)C., more pinacol was formed at lower temperatures. The effect of increased alkali concentration was most striking. As the concentration of electrolyte (potassium hydroxide) increased from 0.09 to 1.82 N, the reported yield of pinacol increased from 22 to 59 percent.

In 1944, Hennig and Kimball\(^2\) reported an investigation of the kinetics of the electro-reduction of acetone, and proposed a mechanism for the reduction at a mercury cathode in alkaline solution. They determined the reduction rate at various acetone concentrations, in varying

---


concentrations of sodium hydroxide, sodium chloride, sodium sulfate, barium hydroxide and potassium hydroxide.

It was found that at low acetone concentrations, the rate of formation of iso-propyl alcohol was proportional to the acetone concentration, while the rate of formation of pinacol was proportional to the square of the acetone concentration. At somewhat higher acetone concentrations, the pinacol rate became linear with acetone concentration, and near saturation the iso-propyl alcohol rate became practically independent of acetone concentration. At constant current density, increasing the concentration of sodium hydroxide decreased the yield of iso-propyl alcohol, and increased the yield of pinacol. Substitution of sodium chloride or sodium sulfate for sodium hydroxide caused an increase in alcohol, but lowered pinacol. Substitution of barium hydroxide for sodium hydroxide stopped the reduction entirely, while substitution of potassium hydroxide for sodium hydroxide increased the yields of both pinacol and alcohol. Increasing the current density was accompanied by a decrease in the fraction of the current that went into pinacol and alcohol, i.e. current efficiency.

These experimental results were explained by a mechanism involving adsorption of the acetone on the mercury surface. After picking up a hydrogen atom, the product might separate from the surface as a free radical, in
which case pinacol would be the final product, or it might first add an electron, and then dissociate and add a second proton to become \textit{iso}-propyl alcohol.

In 1945, McHenry et al\(^1\) reported that they were un-


able to obtain the maximum yields of pinacol reported by Wilson and Wilson.

In 1950, Udupa\(^2\) reported a brief study of the reduc-

(2) H. V. Udupa, Ph.D. Dissertation, Ohio State University (1950).

tion of acetone in alkaline solution at amalgamated cath-
odes. Amalgamated monel and amalgamated copper cathodes gave higher yields of pinacol than did the amalgamated lead cathode. Rotation of the cathode raised them still further, and higher current densities could be used without loss of current efficiency or yield of pinacol.

Udupa obtained only poor yields of pinacol by reduction at an amalgamated copper cathode in sulfuric acid solution. However, potassium carbonate proved to be as satisfactory as potassium hydroxide with respect to the yield of pinacol obtained. The yield of pinacol was also improved by increasing the proportion of acetone to alkali in the catholyte.
Purpose of the Investigation

The purpose of this investigation was to study the effect of the nature and concentration of alkali, concentration of the acetone, temperature, rotation of the cathode, current density, the use of aqueous methanol as solvent, and the use of salts as electrolytes, on the formation of pinacol by electrochemical reduction of acetone. It was hoped to apply the results to the study of the reduction of other aliphatic ketones.
PART I
THE REDUCTION OF ACETONE IN ALKALINE SOLUTION AT AN
AMALGAMATED COPPER CATHODE

Current Efficiency Measurement

An apparatus was devised by which the amount of hydrogen taken up during reduction could be measured. It consisted essentially of two electrolytic cells connected in series, the first, or reference cell, being used to electrolyze a sulfuric acid solution. The volume of hydrogen liberated at the cathode of this cell was a measure of the total hydrogen available for reduction of acetone. The second, or reduction cell, contained the acetone solution to be reduced. The amount of hydrogen liberated at the cathode of this cell, subtracted from the amount liberated in the reference cell, gave the amount of hydrogen utilized in reducing acetone. From the ratio of the hydrogen absorbed to the total hydrogen available, the overall current efficiency of acetone reduction could be calculated.

Pinacol Formation

By analysis of the catholyte from the reduction cell, the amount of pinacol present was determined. The hydrogen required to produce this pinacol from acetone could then be subtracted from the total hydrogen absorbed, permitting the calculation of the amount of iso-propyl
alcohol produced. From these data the value of "r", the ratio of \textit{Moles acetone converted to pinacol} could be \textit{Moles acetone converted to alcohol} calculated, as could the percentage of pinacol produced, based on the acetone converted. The percentage conversion on a molar basis was calculated from the amount of acetone converted to alcohol and pinacol, and the amount of acetone present at the beginning of the electrolysis.

\textbf{CHAPTER I}

\textbf{THE REDUCTION OF ACETONE IN SODIUM HYDROXIDE SOLUTION AT AN AMALGAMATED COPPER CATHODE}

A series of reductions were run on acetone in sodium hydroxide solution to determine the effect of various experimental conditions on the yield of pinacol obtained. The variables studied were:

(a) Concentration of electrolyte  
(b) Concentration of acetone  
(c) Temperature  
(d) Rotation of the cathode  
(e) Addition of methanol as second solvent  
(f) Current density

Acetone was also reduced under similar conditions at a mercury cathode for purposes of comparison.
(a) Concentration of Electrolyte

Several sets of experiments were run in which all variables except the concentration of sodium hydroxide in the catholyte were kept constant. The results are summarized in Tables 1 and 2.

TABLE 1
Effect of Concentration of Sodium Hydroxide on the Reduction of Acetone at a Stationary Amalgamated Copper Cathode

Catholyte: 7.5 ml. acetone, NaOH solution to 75 ml. total volume;
Current density: 50 ma./cm.²;
Temp.: 6-10°C.; Anode: Fe gauze;
Anolyte: 2 N NaOH or 1 M Na₂CO₃.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[NaOH] N</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>132-1</td>
<td>.91</td>
<td>90</td>
<td>10</td>
<td>.30</td>
<td>23</td>
</tr>
<tr>
<td>147-1</td>
<td>1.8</td>
<td>87</td>
<td>10</td>
<td>.28</td>
<td>22</td>
</tr>
</tbody>
</table>

TABLE 2
Effect of Concentration of Sodium Hydroxide on the Reduction of Acetone at a Rotating Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, NaOH solution to 75 ml. total volume;
Current density: 50 ma./cm.²; Rot’n speed: 2000 rpm.;
Temp.: 4-7°C.; Anode: Fe gauze; Anolyte: 2 N NaOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[NaOH] N</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-3</td>
<td>1.5</td>
<td>98</td>
<td>4.1</td>
<td>.53</td>
<td>35</td>
</tr>
<tr>
<td>175-1</td>
<td>1.5</td>
<td>99</td>
<td>4.4</td>
<td>.49</td>
<td>33</td>
</tr>
<tr>
<td>289-1</td>
<td>.52</td>
<td>99</td>
<td>5.8</td>
<td>.48</td>
<td>32</td>
</tr>
</tbody>
</table>
From these experiments, it appears that the concentration of sodium hydroxide in the catholyte had very little effect on the yields of pinacol obtained, whether the amalgamated copper cathode was stationary or rotating.

(b) **Concentration of Acetone**

Sets of experiments with rotating and stationary cathodes were run in which the concentration of acetone was varied. The results are given in Tables 3 and 4.

**TABLE 3**

**Effect of Concentration of Acetone on Reduction at a Stationary Amalgamated Copper Cathode**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>147-1</td>
<td>10</td>
<td>87</td>
<td>10.1</td>
<td>.28</td>
<td>22</td>
</tr>
<tr>
<td>149-1</td>
<td>30</td>
<td>97</td>
<td>4.1</td>
<td>.35</td>
<td>26</td>
</tr>
<tr>
<td>282-2</td>
<td>40</td>
<td>95</td>
<td>5.1</td>
<td>.41</td>
<td>29</td>
</tr>
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</table>

**TABLE 4**

**Effect of Concentration of Acetone on Reduction at a Rotating Amalgamated Copper Cathode**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catholyte: acetone and NaOH solution to total volume of 75 ml.; [NaOH] = 1.5-1.8 N; Current density: 50 ma./cm.²; Temp.: 3-10°C; Anode: Fe gauze; Anolyte: 2 N NaOH.
With the stationary cathode, increased acetone concentration increased the yield of pinacol. On rotating, pinacol yields rose and were not influenced appreciably by acetone concentration.

(c) Temperature

The effect of varying the temperature on the yield of pinacol was investigated for a 30 percent (by volume) acetone solution at stationary and rotating cathodes. The results are given in Tables 5 and 6.

TABLE 5

Effect of Temperature on the Reduction of Acetone at a Stationary Amalgamated Copper Cathode

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. C.</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot; Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>161-3</td>
<td>0</td>
<td>93</td>
<td>3.8</td>
<td>.31</td>
</tr>
<tr>
<td>149-1</td>
<td>5-9</td>
<td>97</td>
<td>4.1</td>
<td>.35</td>
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<td>280-1</td>
<td>16-19</td>
<td>96</td>
<td>5.6</td>
<td>.31</td>
</tr>
<tr>
<td>159-1</td>
<td>31</td>
<td>95</td>
<td>3.9</td>
<td>.27</td>
</tr>
</tbody>
</table>

Catholyte: 22.5 ml. acetone, 55 ml. 2 N NaOH, total 75 ml.;
Current density: 50 ma./cm.²;
Anode: Fe gauze; Anolyte: 2 N NaOH.
TABLE 6

Effect of Temperature on the Reduction of Acetone at a Rotating Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 2N NaOH, total 75 ml.;
Current density: 50 ma./cm.²; Rot'n speed: 2000 rpm;
Anode: Fe gauze; Anolyte: 2 N NaOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. C.</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>162-4</td>
<td>1-3</td>
<td>96</td>
<td>4.1</td>
<td>.47</td>
<td>32</td>
</tr>
<tr>
<td>175-1</td>
<td>5-7</td>
<td>99</td>
<td>4.4</td>
<td>.49</td>
<td>33</td>
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<tr>
<td>285-1</td>
<td>18-20</td>
<td>93</td>
<td>5.4</td>
<td>.41</td>
<td>29</td>
</tr>
<tr>
<td>287-2</td>
<td>29-30</td>
<td>95</td>
<td>5.5</td>
<td>.25</td>
<td>20</td>
</tr>
</tbody>
</table>

At both stationary and rotating cathodes, the yields of pinacol were reduced if the temperature of the catholyte was raised. This temperature effect was more pronounced at a rotating cathode.

(d) Rotation of the Cathode

The data previously given supported the view that rotation of the cathode increased the yield of pinacol. A selection of results showing the effect of varying the speed of rotation is given in Table 7.

TABLE 7

Effect of Speed of Rotation of an Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 2 N NaOH, total 75 ml.;
Current density: 50 ma./cm.²;
Temp.: 5-9°C.; Anode: Fe Gauze; Anolyte: 2N NaOH.
Rotating the cathode gave improved yields of pinacol. In the apparatus used, a rotation speed of 2000 - 1000 rpm could be maintained easily without excessive vibration, and seemed to give slightly better yields of pinacol than those obtained at the higher rotation speed of 3100 rpm. A rotation speed of 2000 rpm was used for most of the studies at a rotating cathode.

(e) Addition of Methanol as Second Solvent

In the case of catholytes having a high electrolyte concentration and containing more than about 40 percent acetone by volume, a separation into two layers occurred. The possibility was considered of adding methanol as a second solvent, to give a homogeneous solution. Accordingly, reductions were run on a solution which was homogeneous with or without the added methanol, to determine the effect on the yield of pinacol obtained. The results are given in Table 8.
TABLE 8

Effect of Added Methanol on the Reduction at a Rotating Amalgamated Copper Cathode

Current density: 50 ma./cm.²; Rot'n speed: 2000 rpm; Temp.: 5-7°C.; Anode: Fe gauze; Anolyte: 2 N NaOH; Curr. Eff.: 97%; Conversion: 2.6-2.7%.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Composition of Catholyte</th>
<th>&quot;r&quot;</th>
<th>% Pinacol</th>
</tr>
</thead>
<tbody>
<tr>
<td>166-3</td>
<td>35 ml. acetone, 35 ml. 2N NaOH, 14 ml. H₂O, total 79 ml.</td>
<td>.42</td>
<td>30</td>
</tr>
<tr>
<td>165-1</td>
<td>above with 14 ml. MeOH in place of H₂O, total 78 ml.</td>
<td>.28</td>
<td>22</td>
</tr>
</tbody>
</table>

From these experiments it appears that the addition of methanol as a second solvent reduced the amount of pinacol formed on reduction of acetone at a rotating amalgamated copper cathode.

(f) Current Density

The effect of varying current density while other conditions were constant was investigated at stationary and rotating cathodes. The results are given in Tables 9, 10, and 11.

TABLE 9

Effect of Current Density on the Reduction of a 10 % Acetone Solution at a Stationary Amalgamated Copper Cathode

Catholyte: 7.5 ml. acetone, 1 N NaOH to total of 75 ml.; Temperature: 6-10°C.; Anode: Fe gauze; Anolyte: 2N NaOH.
TABLE 9 (cont.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>C.D. (ma./cm.²)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>132-1</td>
<td>50</td>
<td>90</td>
<td>10.0</td>
<td>.30</td>
<td>23</td>
</tr>
<tr>
<td>134-1</td>
<td>100</td>
<td>88</td>
<td>9.1</td>
<td>.26</td>
<td>21</td>
</tr>
</tbody>
</table>

TABLE 10

Effect of Current Density on the Reduction of a 30% Acetone Solution at a Stationary Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 2N NaOH, total temperature 5-11°C.; 75 ml.;
Anode: Fe gauze; Anolyte: 2N NaOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>C.D. (ma./cm.²)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>149-1</td>
<td>50</td>
<td>97</td>
<td>4.1</td>
<td>.35</td>
<td>26</td>
</tr>
<tr>
<td>173-3</td>
<td>150</td>
<td>98</td>
<td>7.0</td>
<td>.33</td>
<td>25</td>
</tr>
</tbody>
</table>

TABLE 11

Effect of Current Density on the Reduction of a 30% Acetone Solution at a Rotating Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 2N NaOH, total 75 ml.;
Temperature: 5-8°C.; Rot'n speed: 2000 rpm;
Anode: Fe gauze; Anolyte: 2N NaOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>C.D. (ma./cm.²)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>175-1</td>
<td>50</td>
<td>99</td>
<td>4.4</td>
<td>.49</td>
<td>33</td>
</tr>
<tr>
<td>172-1</td>
<td>150</td>
<td>99</td>
<td>7.3</td>
<td>.41</td>
<td>29</td>
</tr>
</tbody>
</table>

From Tables 9 and 10, it appears that current densities of 50 to 150 ma./cm.² have little effect on the
yield of pinacol at a stationary amalgamated copper cathode. At a rotating cathode, a better yield of pinacol was obtained at the lower current density.

(g) **Comparison of Amalgamated Copper and Mercury Cathodes**

For comparison purposes, acetone was reduced at a mercury cathode under conditions approximating those for a similar reduction at a stationary amalgamated copper cathode. The results are compared in Table 12.

**TABLE 12**

**Comparison of a Stationary Amalgamated Copper Cathode with a Mercury Cathode in Sodium Hydroxide Solution**

<table>
<thead>
<tr>
<th>Catholyte: 22.5 g/l acetone, 55 ml. 2N NaOH, total temperature 0-2°C; 75 ml;</th>
<th>Anode: Fe gauze; Anolyte: 2N NaOH.</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>161-3</td>
<td>Cu/Hg</td>
<td>50</td>
<td>93</td>
<td>3.8</td>
</tr>
<tr>
<td>235-1</td>
<td>Hg*</td>
<td>56</td>
<td>99</td>
<td>3.8</td>
</tr>
</tbody>
</table>

* The mercury cathode contained some solid sodium amalgam after the reduction. This was neglected in calculating the current efficiency and pinacol yield.

From these experiments, a stationary amalgamated copper cathode was superior to a mercury cathode in the yield of pinacol obtained. Apparently this was due to the fact that the mercury layer on copper does not build up any appreciable concentration of dissolved sodium. Further
evidence for this idea comes from the observation that the amalgamated copper cathodes were always shiny at the end of a reduction, with no indication of any disintegration of the surface due to amalgam formation.

CHAPTER II
THE REDUCTION OF ACETONE IN POTASSIUM HYDROXIDE SOLUTION AT AN AMALGAMATED COPPER CATHODE

A series of reduction experiments were run on acetone in potassium hydroxide solution to determine the effect of various experimental conditions on the yield of pinacol obtained. The variables studied were:

(a) Concentration of electrolyte
(b) Concentration of acetone
(c) Temperature
(d) Rotation of the cathode
(e) Addition of methanol as second solvent
(f) Current density

For comparison purposes, acetone was reduced at a mercury cathode in potassium hydroxide solution. In another experiment, potassium hydroxide was replaced by potassium carbonate as electrolyte.

(a) Concentration of Electrolyte

Acetone was reduced at stationary and rotating amalgamated copper cathodes, with concentration of potassium
hydroxide being the only variable. The results are given in Tables 13 and 14.

**TABLE 13**

**Effect of Concentration of Potassium Hydroxide on the Reduction at a Stationary Amalgamated Copper Cathode**

Catholyte: 22.5 ml. acetone, KOH solution to total of 75 ml.;
Current density: 50 ma./cm.²;
Temp.: 4-8°C.; Anodes: Fe gauze; Anolytes: 1 N KOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[KOH] N</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>125-2*</td>
<td>.37</td>
<td>98</td>
<td>3.6</td>
<td>.57</td>
<td>36</td>
</tr>
<tr>
<td>250-3</td>
<td>.75</td>
<td>91</td>
<td>6.6</td>
<td>.54</td>
<td>35</td>
</tr>
</tbody>
</table>

* Anolytes: M/2 K₂CO₃.

**TABLE 14**

**Effect of Concentration of Potassium Hydroxide on the Reduction at a Rotating Amalgamated Copper Cathode**

Catholyte: 15 ml. acetone, KOH solution to total of 75 ml.;
Current density: 100 ma./cm.²; Rot'n speed: 2000 rpm;
Temp.: 3-6°C.; Anode: Fe gauze; Anolyte: 0.5 N KOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[KOH] N</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>195-1</td>
<td>.24</td>
<td>97</td>
<td>8.6</td>
<td>.49</td>
<td>33</td>
</tr>
<tr>
<td>199-1</td>
<td>.51</td>
<td>95</td>
<td>8.6</td>
<td>.49</td>
<td>33</td>
</tr>
<tr>
<td>201-1*</td>
<td>.78</td>
<td>94</td>
<td>8.6</td>
<td>.54</td>
<td>35</td>
</tr>
</tbody>
</table>

* Anolyte: 0.8 N KOH.

From these experiments it appears that the concentration of potassium hydroxide in the catholyte had little
effect on the yields of pinacol obtained at either stationary or rotating amalgamated copper cathodes.

(b) **Concentration of Acetone**

Acetone in varying concentrations was reduced at stationary and rotating amalgamated copper cathodes. The results are given in Tables 15 and 16.

<table>
<thead>
<tr>
<th>TABLE 15</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Effect of Concentration of Acetone on Reduction at a Stationary Amalgamated Copper Cathode</strong></td>
</tr>
<tr>
<td>Catholyte: acetone in KOH solution, total volume 75 ml., [KOH] = 0.47-0.54 N;</td>
</tr>
<tr>
<td>Current density: 100 ma./cm.²; Temp. 3-8°C.; Anode: Fe gauze; Anolytes 0.5-1 N KOH.</td>
</tr>
<tr>
<td><strong>Run No.</strong></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>127-1*</td>
</tr>
<tr>
<td>197-1</td>
</tr>
<tr>
<td>291-1</td>
</tr>
<tr>
<td>* Anolyte: M/2 K₂CO₃.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE 16</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Effect of Concentration of Acetone on Reduction at a Rotating Amalgamated Copper Cathode</strong></td>
</tr>
<tr>
<td>Catholyte: acetone in KOH solution, total volume 75 ml., [KOH] = 0.33-0.37 N;</td>
</tr>
<tr>
<td>Current density: 150 ma./cm.²; Rot'n speed: 2000 rpm; Temp.: 10-14°C.; Anode: Fe gauze; Anolytes: 0.5-1N KOH.</td>
</tr>
</tbody>
</table>
At both stationary and rotating cathodes, the yield of pinacol increased with increasing concentration of acetone. The slight drop in pinacol yield as acetone concentration increased from 50-60 percent by volume may have been due to the fact that at the higher acetone concentration the catholyte was not homogeneous, but had separated into two layers.

(c) **Temperature**

The effect of catholyte temperature on the yield of pinacol was investigated for a 30 percent (by volume) acetone solution at stationary and rotating amalgamated copper cathodes. The results are shown in Tables 17 and 18.

### TABLE 17

**Effect of Temperature on the Reduction at a Stationary Amalgamated Copper Cathode**

- **Catholyte:** 22.5 ml. acetone, 39 ml. 1 N KOH, H₂O to total of 75 ml.;
- **Current density:** 100 ma./cm²;
- **Anode:** Fe gauze;
- **Anolyte:** 1 N KOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>293-1</td>
<td>10</td>
<td>98</td>
<td>12.4</td>
<td>.31</td>
<td>24</td>
</tr>
<tr>
<td>193-1</td>
<td>30</td>
<td>96</td>
<td>5.9</td>
<td>.56</td>
<td>37</td>
</tr>
<tr>
<td>202-3</td>
<td>50</td>
<td>99</td>
<td>4.8</td>
<td>.78</td>
<td>44</td>
</tr>
<tr>
<td>206-4</td>
<td>60</td>
<td>95</td>
<td>4.5</td>
<td>.70</td>
<td>41</td>
</tr>
</tbody>
</table>
TABLE 17 (cont.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>291-1</td>
<td>4-6</td>
<td>94</td>
<td>5.6</td>
<td>.52</td>
<td>34</td>
</tr>
<tr>
<td>303-1</td>
<td>20-23</td>
<td>89</td>
<td>6.1</td>
<td>.45</td>
<td>31</td>
</tr>
</tbody>
</table>

TABLE 18

Effect of Temperature on the Reduction at a Rotating Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 39 ml. 1 N KOH, H2O to total of 75 ml.;
Current density: 100 ma./cm.²; Rot'n speed: 2000 rpm;
Anode: Fe gauze; Anolyte: 1 N KOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>295-1</td>
<td>4-6</td>
<td>99</td>
<td>6.3</td>
<td>.78</td>
<td>44</td>
</tr>
<tr>
<td>301-1</td>
<td>24-26</td>
<td>99</td>
<td>6.1</td>
<td>.51</td>
<td>34</td>
</tr>
</tbody>
</table>

From these experiments, it is evident that higher pinacol yields were obtained at lower temperatures, in the reduction of acetone at stationary or rotating amalgamated copper cathodes. The temperature effect was more pronounced at a rotating cathode.

(d) Rotation of the Cathode

Previous data indicate that under otherwise similar conditions, rotation of the cathode increased the yield of pinacol. Several groups of experiments were run in which rotation of the cathode was the only variable. These experiments are summarized in Tables 19, 20 and 21.
TABLE 19

**Effect of Rotation of the Cathode on the Reduction of a 10% Acetone Solution at an Amalgamated Copper Cathode**

Catholyte: 7.5 ml. acetone, KOH solution to total of 75 ml.; [KOH]: 0.46 N;
Current density: 50 ma./cm.²;
Temp.: 4-10°C.; Anode: Fe gauze; Anolyte: 30% K₂CO₃.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Speed (rpm)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>121-4</td>
<td>0</td>
<td>94</td>
<td>10.0</td>
<td>.36</td>
<td>26</td>
</tr>
<tr>
<td>120-3</td>
<td>2500</td>
<td>94</td>
<td>10.0</td>
<td>.39</td>
<td>28</td>
</tr>
<tr>
<td>123-1</td>
<td>4000</td>
<td>93</td>
<td>9.8</td>
<td>.36</td>
<td>27</td>
</tr>
</tbody>
</table>

TABLE 20

**Effect of Rotation of the Cathode on the Reduction of a 20% Acetone Solution at an Amalgamated Copper Cathode**

Catholyte: 15 ml. acetone, KOH solution to total of 75 ml.; [KOH]: 0.51 N;
Current density: 100 ma./cm.²;
Temp.: 3-7°C.; Anode: Fe gauze; Anolyte: 0.5 N KOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Speed (rpm)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>197-1</td>
<td>0</td>
<td>90</td>
<td>7.8</td>
<td>.37</td>
<td>27</td>
</tr>
<tr>
<td>199-1</td>
<td>2000</td>
<td>95</td>
<td>8.5</td>
<td>.49</td>
<td>33</td>
</tr>
</tbody>
</table>

TABLE 21

**Effect of Rotation of the Cathode on the Reduction of a 30% Acetone Solution at an Amalgamated Copper Cathode**

Catholyte: 22.5 ml. acetone, 39 ml. 1 N KOH, H₂O to total of 75 ml.;
Current density: 100 ma./cm.²;
Temp.: 4-6°C.; Anode: Fe gauze; Anolyte: 1 N KOH.
In all these experiments, the yield of pinacol was better at a rotating cathode than at a stationary cathode. This effect was much greater at higher acetone concentrations.

(e) Addition of Methanol as Second Solvent

Experiments were run on the reduction of acetone in potassium hydroxide with and without the addition of methanol. The results are indicated in Table 22.

TABLE 22

Effect of Added Methanol on the Reduction at a Rotating Amalgamated Copper Cathode

Current density: 150 ma./cm.²; Rot'n speed: 2000 rpm; Temp.: 10-14°C.; Anode: Fe gauze; Anolyte: 0.5-0.8 N KOH; Conversion: 4.8-4.4%. 

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>202-3</td>
<td>37.5 ml. acetone, 22 ml. 1 N KOH, H₂O to 75 ml.</td>
<td>99</td>
<td>.78</td>
<td>44</td>
</tr>
<tr>
<td>205-1</td>
<td>37.5 ml. acetone, 22 ml. 1 N KOH, 10 ml. MeOH, H₂O to 75 ml.</td>
<td>94</td>
<td>.61</td>
<td>38</td>
</tr>
</tbody>
</table>
From these results, it appears that addition of methanol to the catholyte lowered the yield of pinacol formed on reduction of acetone.

(f) Current Density

The effect of varying current density while other conditions were constant was investigated at both stationary and rotating amalgamated copper cathodes in potassium hydroxide solution. The results are indicated in Tables 23, 24 and 25.

**TABLE 23**

**Effect of Current Density on the Reduction of a 10% Acetone Solution at a Stationary Amalgamated Copper Cathode**

Catholyte: 7.5 ml. acetone, 0.5 N KOH solution to total of 75 ml.;
Temp. 5-9°C.; Anode: Fe gauze; Anolyte: 30% K₂CO₃.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>C.D. (ma/cm²)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>121-4</td>
<td>50</td>
<td>94</td>
<td>10</td>
<td>.36</td>
<td>26</td>
</tr>
<tr>
<td>127-1</td>
<td>100</td>
<td>95</td>
<td>10</td>
<td>.36</td>
<td>27</td>
</tr>
</tbody>
</table>

**TABLE 24**

**Effect of Current Density on the Reduction of a 30% Acetone Solution at a Stationary Amalgamated Copper Cathode**

Catholyte: 22.5 ml. acetone, KOH solution to 75 ml.;
KOH: 0.38-0.54 N.;
Temp.: 4-8°C.; Anode: Fe gauze; Anolyte: 1 N KOH.
TABLE 24 (cont.)

| Run No. | C.D. (ma./cm.
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>125-2*</td>
<td>50</td>
</tr>
<tr>
<td>291-1</td>
<td>100</td>
</tr>
</tbody>
</table>

* Anolyte: 30 % K₂CO₃.

TABLE 25

Effect of Current Density on the Reduction of a 30% Acetone Solution at a Rotating Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 38 ml. 1 N K\text{OH}, H₂O to total of 75 ml.;
Rot'n speed: 2000 rpm;
Temp.: 3-7°C.; Anode: Fe gauze; Anolyte: 1 N K\text{OH}.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>337-1</td>
<td>50</td>
<td>97</td>
<td>7.6</td>
<td>.65</td>
<td>39</td>
</tr>
<tr>
<td>295-1</td>
<td>100</td>
<td>99</td>
<td>6.3</td>
<td>.78</td>
<td>44</td>
</tr>
</tbody>
</table>

At a stationary cathode in 10 or 30 percent acetone solution, the current density of 50 or 100 ma./cm.² seemed to make very little difference in the yield of pinacol obtained. At a rotating cathode, the higher current density seemed to give a slightly better yield.

Comparison of Amalgamated Copper and Mercury as Cathodes

In order to compare the effectiveness of amalgamated copper with mercury as cathodes in the reduction of acetone to pinacol, acetone was reduced at a cathode consisting
of a pool of mercury in a bakelite cup. The solution used, the porous pot, and the cell arrangement were similar to those used in reduction at an amalgamated copper cathode. After the reduction, the mercury cathode contained some solid potassium amalgam. The amount of amalgam present was estimated, and a suitable correction made for the hydrogen utilized in acetone reduction. The result of this experiment is compared with several reductions at an amalgamated copper cathode in Table 26.

**TABLE 26**

Comparison of a Stationary Amalgamated Copper Cathode with a Mercury Cathode in Potassium Hydroxide Solution.

Catholyte: 22.5 ml. acetone, KOH solution to total of 75 ml.;
Temp. 4-8°C.; Anode: Fe gauze; Anolyte: 1 N KOH;
Curr. Eff.: 91-94%; Conversion: 5.6-6.6%.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[KOH] N</th>
<th>Cathode</th>
<th>C.D. (ma./cm.²)</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>250-3</td>
<td>.75</td>
<td>Cu/Hg</td>
<td>50</td>
<td>.54</td>
<td>35</td>
</tr>
<tr>
<td>291-1</td>
<td>.54</td>
<td>Cu/Hg</td>
<td>100</td>
<td>.52</td>
<td>34</td>
</tr>
<tr>
<td>252-1</td>
<td>.71</td>
<td>Hg</td>
<td>112</td>
<td>.47</td>
<td>32</td>
</tr>
</tbody>
</table>

It appears that, after making a correction for the potassium amalgam formed at the mercury cathode, there was little difference between mercury and amalgamated copper cathodes in the yield of pinacol in potassium hydroxide solution under otherwise comparable conditions.
Comparison of Potassium Carbonate with Potassium Hydroxide as Electrolytes in the Reduction of Acetone at an Amalgamated Copper Cathode

To determine the influence of the electrolyte anion on the reduction of acetone to pinacol, potassium hydroxide was replaced by potassium carbonate as electrolyte. The result is compared with a similar reduction using potassium hydroxide as electrolyte in Table 27.

**TABLE 27**

**Effect of using Potassium Carbonate as Electrolyte in the Reduction of Acetone at a Stationary Amalgamated Copper Cathode**

| Catholyte: 7.5 ml. acetone, electrolyte to total of 75 ml.; Current density: 50 ma./cm.²; Temp.: 4-11°C; Anode: Fe gauze; Anolyte: 30% K₂CO₃. |
|---------|-------------|------------|------------|-----|---------|
| 121-4   | KOH         | 94         | 10.0       | .36 | 26      |
| 130-1   | K₂CO₃       | 94         | 10.4       | .29 | 23      |

From these results, potassium hydroxide gave about the same yield of pinacol as did potassium carbonate when used as electrolyte.
CHAPTER III
THE REDUCTION OF ACETONE IN TETRAMETHYLAMMONIUM HYDROXIDE SOLUTION AT AN AMALGAMATED COPPER CATHODE

A series of reductions were run on acetone in tetramethylammonium hydroxide solution at an amalgamated copper cathode to determine the effect of various experimental conditions on the yield of pinacol obtained. The variables studied were:

(a) Concentration of electrolyte
(b) Concentration of acetone
(c) Temperature
(d) Rotation of the cathode
(e) Current density

Acetone was also reduced at a mercury cathode in tetramethylammonium hydroxide solution to compare pure mercury and amalgamated copper as cathodes. To determine the effect of the anion on the reduction of acetone, tetramethylammonium methyl sulfate was used in place of the hydroxide as electrolyte.

(a) Concentration of Electrolyte
Acetone was reduced at stationary and rotating cathodes in various concentrations of tetramethylammonium hydroxide. The results are given in Tables 28, 29, and 30.
### TABLE 28

Effect of Tetramethylammonium Hydroxide Concentration on the Reduction at a Stationary Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, Me₄NOH solution to total of 75 ml.; Current density: 50 ma./cm.²; Temp.: 7-15°C; Anode: Pb; Anolyte: 0.5 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[Me₄NOH] N</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>189-4</td>
<td>.17</td>
<td>99</td>
<td>5.5</td>
<td>.51</td>
<td>34</td>
</tr>
<tr>
<td>140-1</td>
<td>.41</td>
<td>98</td>
<td>6.1</td>
<td>.62</td>
<td>38</td>
</tr>
</tbody>
</table>

### TABLE 29

Effect of Tetramethylammonium Hydroxide Concentration on the Reduction at a Stationary Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, Me₄NOH solution to total of 75 ml.; Current density: 50 ma./cm.²; Temp.: 3-8°C; Anode: Pb; Anolyte: 1 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[Me₄NOH] N</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>219-3</td>
<td>.63</td>
<td>85</td>
<td>5.5</td>
<td>.82</td>
<td>45</td>
</tr>
<tr>
<td>224-3</td>
<td>.65</td>
<td>97</td>
<td>6.3</td>
<td>.84</td>
<td>46</td>
</tr>
<tr>
<td>307-5</td>
<td>.92</td>
<td>89</td>
<td>6.7</td>
<td>.57</td>
<td>36</td>
</tr>
<tr>
<td>248-2</td>
<td>1.21</td>
<td>91</td>
<td>6.4</td>
<td>.56</td>
<td>36</td>
</tr>
</tbody>
</table>

### TABLE 30

Effect of Tetramethylammonium Hydroxide Concentration on the Reduction at a Rotating Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, Me₄NOH solution to total of 75 ml.; Current density: 50 ma./cm.²; Rot'n speed: 2000 rpm; Temp.: 6-11°C; Anode: Pb; Anolyte: 1 M Me₄NMeSO₄.
With the exception of Run Numbers 219-3 and 224-3, the yield of pinacol at a stationary cathode seemed to be independent of changes in alkali concentration, within the limits of experimental reproducibility. These two runs were made using two different cathodes, so that the result seems to be reproducible. At a rotating cathode the pinacol yield was much higher at the higher alkali concentration.

(b) Concentration of Acetone

Several sets of experiments were run in which different concentrations of acetone were reduced at stationary and rotating amalgamated copper cathodes. The results of these experiments are shown in Tables 31, 32 and 33.

TABLE 31

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Me₄NOH N</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>155-3</td>
<td>.15</td>
<td>97</td>
<td>4.3</td>
<td>.37</td>
<td>27</td>
</tr>
<tr>
<td>345-2</td>
<td>.61</td>
<td>96</td>
<td>8.6</td>
<td>1.03</td>
<td>53</td>
</tr>
</tbody>
</table>

Effect of Acetone Concentration on Reduction at a Stationary Amalgamated Copper Cathode

Catholyte: acetone and Me₄NOH to total of 75 ml.; [Me₄NOH]₂ \(=\) 0.15-0.18 N; Current density: 50 ma./cm.²; Temp. 8-15°C.; Anodes: Pb; Anolyte: 0.5 M Me₄NMeSO₄.
### TABLE 31 (cont.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>136-1*</td>
<td>10</td>
<td>92</td>
<td>9.9</td>
<td>.18</td>
<td>15</td>
</tr>
<tr>
<td>189-4</td>
<td>30</td>
<td>99</td>
<td>5.5</td>
<td>.51</td>
<td>34</td>
</tr>
</tbody>
</table>

* Anode: Fe gauze.

### TABLE 32

Effect of Acetone Concentration on Reduction at a Stationary Amalgamated Copper Cathode

Catholyte: acetone and Me₄NOH to total volume of 75 ml. \([\text{Me}_4\text{NOH}]: 0.55-0.65 \text{ N}\);
Current density: 50 ma./cm.²;
Temp. 4-8 °C.; Anode; Pb; Anolyte: 0.5 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>219-3</td>
<td>30</td>
<td>85</td>
<td>5.5</td>
<td>.82</td>
<td>45</td>
</tr>
<tr>
<td>224-3</td>
<td>30</td>
<td>97</td>
<td>6.3</td>
<td>.84</td>
<td>46</td>
</tr>
<tr>
<td>222-2*</td>
<td>40</td>
<td>88</td>
<td>3.5</td>
<td>1.14</td>
<td>53</td>
</tr>
</tbody>
</table>

* Anolyte: 0.5 M Me₄NOH.

### TABLE 33

Effect of Acetone Concentration on Reduction at a Rotating Amalgamated Copper Cathode

Catholyte: acetone and Me₄NOH to total volume of 75 ml.; \([\text{Me}_4\text{NOH}]: .53-.65 \text{ N}\);
Current density: 50 ma./cm.²; Rot'n speed: 2000 rpm;
Temp.: 5-11 °C.; Anode: Pb; Anolyte: 1 M Me₄NMeSO₄.
TABLE 33 (cont.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>340-1</td>
<td>30</td>
<td>97</td>
<td>8.4</td>
<td>1.09</td>
<td>52</td>
</tr>
<tr>
<td>342-1</td>
<td>40</td>
<td>96</td>
<td>5.2</td>
<td>0.90</td>
<td>47</td>
</tr>
</tbody>
</table>

At a stationary cathode, the yield of pinacol increased with increasing concentration of acetone. In the case of a rotating cathode, a slightly lower yield of pinacol was obtained at the highest acetone concentrations.

(c) Temperature

The effect of catholyte temperature on the yield of pinacol was investigated for a 30 percent (by volume) acetone solution at both stationary and rotating amalgamated copper cathodes. The results are shown in Tables 34 and 35.

TABLE 34

Effect of Temperature on the Reduction at a Stationary Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 0.87 N Me₂NOH, total 75 ml.; Anode: Pb; Anolyte: 0.5 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>219-3</td>
<td>4-6</td>
<td>85</td>
<td>5.5</td>
<td>.82</td>
<td>45</td>
</tr>
<tr>
<td>245-4*</td>
<td>26-32</td>
<td>88</td>
<td>5.3</td>
<td>.63</td>
<td>39</td>
</tr>
</tbody>
</table>

* Anode: Fe gauze.
TABLE 35

Effect of Temperature on Reduction at a Rotating Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 0.84 N Me₄NOH, total 75 ml.;
Current density: 50 ma./cm.²; Rot'n speed: 2000 rpm;
Anode: Pb; Anolyte: 1 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>345-2</td>
<td>6-11</td>
<td>96</td>
<td>8.6</td>
<td>1.03</td>
<td>53</td>
</tr>
<tr>
<td>347-1</td>
<td>26-30</td>
<td>89</td>
<td>5.6</td>
<td>.61</td>
<td>38</td>
</tr>
</tbody>
</table>

In these experiments, higher pinacol yields were obtained at lower temperatures, under otherwise similar conditions.

(d) Rotation of the Cathode

The effect of rotating the amalgamated copper cathode was investigated under a number of different conditions, and the results were recorded in Tables 36 to 40.

TABLE 36

Effect of Rotating the Cathode on the Yield of Pinacol at an Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 0.23 N Me₄NOH, total 75 ml.;
Current density: 50 ma./cm.²;
Temp.: 9-15°C.; Anode: Pb; Anolyte: 0.5 M Me₄NMeSO₄.
TABLE 36 (cont.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Speed (rpm)</th>
<th>Curr. Eff. (%)</th>
<th>Conversion (%)</th>
<th>&quot;r&quot;</th>
<th>Pinacol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>189-4</td>
<td>0</td>
<td>99</td>
<td>5.5</td>
<td>.51</td>
<td>34</td>
</tr>
<tr>
<td>155-3</td>
<td>2000</td>
<td>97</td>
<td>4.3</td>
<td>.37</td>
<td>27</td>
</tr>
</tbody>
</table>

TABLE 37

Effect of Rotating the Cathode

Catholyte: as in Table 36; Current density: 150 ma./cm.\(^2\); Temp.: 12-19°C; Anode: Pb; Anolyte: 0.5 M Me\(_4\)NMeSO\(_4\).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Speed (rpm)</th>
<th>Curr. Eff. (%)</th>
<th>Conversion (%)</th>
<th>&quot;r&quot;</th>
<th>Pinacol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>217-1</td>
<td>0</td>
<td>86</td>
<td>4.8</td>
<td>.26</td>
<td>21</td>
</tr>
<tr>
<td>188-2</td>
<td>2000</td>
<td>97</td>
<td>5.2</td>
<td>.29</td>
<td>23</td>
</tr>
</tbody>
</table>

TABLE 38

Effect of Rotating the Cathode

Catholyte: 22.5 ml. acetone, 0.85 N Me\(_4\)NOH to 75 ml., 2 Me\(_4\)NOH; 0.65 N; Current density: 50 ma./cm.\(^2\); Temp. 4-11°C; Anode: Pb; Anolyte: 0.5 M Me\(_4\)NMeSO\(_4\).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Speed (rpm)</th>
<th>Curr. Eff. (%)</th>
<th>Conversion (%)</th>
<th>&quot;r&quot;</th>
<th>Pinacol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>224-3</td>
<td>0</td>
<td>97</td>
<td>6.3</td>
<td>.84</td>
<td>46</td>
</tr>
<tr>
<td>340-1*</td>
<td>2000</td>
<td>97</td>
<td>8.4</td>
<td>1.09</td>
<td>52</td>
</tr>
</tbody>
</table>

* Anolyte: 1 M Me\(_4\)NMeSO\(_4\).*

TABLE 39

Effect of Rotating the Cathode

Catholyte: as in Table 38; Current density: 50 ma./cm.\(^2\);
Temp.: 26-32°C.; Anode: Pb; Anolyte: Me₄NMeSO₄.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Speed (rpm)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>245-4</td>
<td>0</td>
<td>88</td>
<td>5.3</td>
<td>.63</td>
<td>39</td>
</tr>
<tr>
<td>347-1</td>
<td>2000</td>
<td>89</td>
<td>5.6</td>
<td>.61</td>
<td>38</td>
</tr>
</tbody>
</table>

TABLE 40

Effect of Rotating the Cathode

Catholyte: 30 ml. acetone, 49 ml. 0.85 N Me₄NOH, total 75 ml.;
Current density: 50 ma./cm.²;
Temp.: 3-9°C.; Anode: Pb; Anolyte: 0.5 M Me₄NOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Speed (rpm)</th>
<th>Curr. Eff. %</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>222-2</td>
<td>0</td>
<td>88</td>
<td>3.5</td>
<td>1.14</td>
<td>53</td>
</tr>
<tr>
<td>342-1*</td>
<td>2000</td>
<td>96</td>
<td>5.2</td>
<td>.90</td>
<td>47</td>
</tr>
</tbody>
</table>

* Anolyte: 1 M Me₄NMeSO₄.

At higher temperatures and higher current densities, rotation of the cathode did not seem to affect pinacol yields (Tables 37 and 39). In Tables 36 and 40, the yield of pinacol was lower at a rotating cathode, while in Table 38 it was higher.

(e) Current Density

The effect of varying the current density was investigated at a stationary and a rotating cathode. The results are shown in Tables 41 and 42.
TABLE 41

Effect of Current Density on the Reduction at a Stationary Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 0.23 N Me₄NOH, total 75 ml.;
Temp.: 9-15°C.; Anode: Pb; Anolyte: 0.5 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>189-4</td>
<td>50</td>
<td>99</td>
<td>5.5</td>
<td>0.51</td>
</tr>
<tr>
<td>217-1</td>
<td>150</td>
<td>86</td>
<td>4.8</td>
<td>0.26</td>
</tr>
</tbody>
</table>

TABLE 42

Effect of Current Density on the Reduction at a Rotating Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, 55 ml. 0.23 N Me₄NOH, total 75 ml.;
Rot'n speed: 2000 rpm; Temp.: 10-19°C.; Anode: Pb; Anolyte: 0.5 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>155-3</td>
<td>50</td>
<td>97</td>
<td>4.3</td>
<td>0.37</td>
</tr>
<tr>
<td>188-2</td>
<td>150</td>
<td>97</td>
<td>5.2</td>
<td>0.29</td>
</tr>
</tbody>
</table>

For both stationary and rotating cathodes in tetra-methylammonium hydroxide solution, the yield of pinacol was reduced at the higher current density.

Comparison of Amalgamated Copper and Mercury as Cathodes

In order to compare amalgamated copper and pure mercury as cathodes in the reduction of acetone to pinacol, acetone was reduced at a cathode consisting of a pool of
mercury contained in a bakelite cup. The solution used, the porous pot, and the cell arrangement were the same as those used for reduction at an amalgamated copper cathode. No solid tetramethylammonium amalgam appeared to be present in the mercury cathode after the reduction. The result at mercury is compared with that at amalgamated copper in Table 43.

**TABLE 43**
Comparison of a Stationary Amalgamated Copper Cathode with a Mercury Cathode for Reduction in Tetramethylammonium Hydroxide

| Catholyte: 22.5 ml. acetone, 55 ml. 0.8 N Me₄NOH, Curr. Eff.: 97-99%; total 75 ml.; Temp.: 2-8°C.; Anode: Pb; Anolyte: 0.5 M Me₄NMeS₄.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Cathode</th>
<th>C.D. (ma./cm.²)</th>
<th>Conversion %</th>
<th>&quot;r&quot;</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>224-3</td>
<td>Cu/Hg</td>
<td>50</td>
<td>6.3</td>
<td>.84</td>
<td>46</td>
</tr>
<tr>
<td>231-2</td>
<td>Hg</td>
<td>56</td>
<td>5.1</td>
<td>1.12</td>
<td>53</td>
</tr>
</tbody>
</table>

From these results, it appears that a mercury cathode gave better yields of pinacol than did an amalgamated copper cathode in tetramethylammonium hydroxide solution.

Comparison of Tetramethylammonium Methyl Sulfate and Tetramethylammonium Hydroxide as Electrolytes in the Reduction of Acetone at an Amalgamated Copper Cathode

To determine the influence of the electrolyte anion on the reduction of acetone to pinacol, tetramethyl-
ammonium methyl sulfate was used as catholyte, and the results compared with a similar reduction in tetramethylammonium hydroxide, as in Table 44.

**TABLE 44**

**Effect of using Tetramethylammonium Methyl Sulfate as Electrolyte in the Reduction at a Stationary Amalgamated Copper Cathode**

<table>
<thead>
<tr>
<th>Catholytes</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.5 ml. acetone, electrolyte to total of 75 ml;</td>
<td>20.5</td>
</tr>
<tr>
<td>Current density: 50 ma/cm²;</td>
<td>50</td>
</tr>
<tr>
<td>Temp.: 7-14°C; Anode: Pb; Anolyte: 0.5 M Me₄NMeSO₄;</td>
<td>7-14°C</td>
</tr>
<tr>
<td>Curr. Eff.: 98%;</td>
<td>98%</td>
</tr>
</tbody>
</table>

The use of tetramethylammonium methyl sulfate in place of the hydroxide resulted in a considerable decrease in the amount of pinacol formed.

**CHAPTER IV**

**DISCUSSION**

**Reproducibility of Data**

The reproducibility of the results obtained for the reduction of acetone in alkaline solution at an amalgamated copper cathode was very good. A selection of these results is included in Tables 45 to 50, which follow.
TABLE 45
Reproducibility of Pinacol Formation at a Rotating Amalgamated Copper Cathode in Sodium Hydroxide Solution

Catholytes: 22.5 ml. acetone, 2 N NaOH to total of 75 ml.;
Current density: 50 ma./cm.²; Rot'n speed: 2000 rpm;
Anode: Fe gauze; Anolytes: 2 N NaOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C.</th>
<th>Curr. Eff. %</th>
<th>% Pinacol</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-3</td>
<td>5-7</td>
<td>98</td>
<td>35</td>
</tr>
<tr>
<td>162-4</td>
<td>1-3</td>
<td>96</td>
<td>32</td>
</tr>
<tr>
<td>175-1</td>
<td>5-7</td>
<td>99</td>
<td>33</td>
</tr>
</tbody>
</table>

TABLE 46
Reproducibility of Pinacol Formation at a Stationary Amalgamated Copper Cathode in Sodium Hydroxide Solution

Catholytes: 22.5 ml. acetone, 2 N NaOH to total of 75 ml.;
Anode: Fe gauze; Anolytes: 2 N NaOH.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp. °C.</th>
<th>C.D. (ma./cm.²)</th>
<th>Curr. Eff. %</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>149-1</td>
<td>5-9</td>
<td>50</td>
<td>97</td>
<td>26</td>
</tr>
<tr>
<td>161-3</td>
<td>-1-1</td>
<td>50</td>
<td>93</td>
<td>23</td>
</tr>
<tr>
<td>173-3</td>
<td>7-11</td>
<td>150</td>
<td>98</td>
<td>25</td>
</tr>
</tbody>
</table>

The data of Table 45 represent the best yields of pinacol obtained in a sodium hydroxide solution.

TABLE 47
Reproducibility of Pinacol Formation at a Rotating Amalgamated Copper Cathode in Potassium Hydroxide Solution

Catholytes: acetone and KOH as indicated, total 75 ml.; Rot'n speed: 2000 rpm;
TABLE 47 (cont.)

Anode: Fe gauze; Anolyte: 0.5 - 1.0 N KOH; Curr. Eff. 95-99%.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>[KOH] N</th>
<th>Temp. C.</th>
<th>C.D. (ma./cm.²)</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>202-3</td>
<td>50</td>
<td>.35</td>
<td>10-13</td>
<td>150</td>
<td>44</td>
</tr>
<tr>
<td>206-4</td>
<td>60</td>
<td>.33</td>
<td>13-14</td>
<td>150</td>
<td>41</td>
</tr>
<tr>
<td>295-1</td>
<td>30</td>
<td>.53</td>
<td>4-6</td>
<td>100</td>
<td>44</td>
</tr>
<tr>
<td>337-1</td>
<td>30</td>
<td>.59</td>
<td>3-7</td>
<td>50</td>
<td>39</td>
</tr>
</tbody>
</table>

TABLE 48

Reproducibility of Pinacol Formation at a Stationary Amalgamated Copper Cathode in Potassium Hydroxide Solution

Catholyte: 22.5 ml. acetone, KOH solution to 75 ml.; Anode: Fe gauze; Anolyte: 1 M KOH or K₂CO₃.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>[KOH] N</th>
<th>Temp. C.</th>
<th>C.D. (ma./cm.²)</th>
<th>Curr. Eff. %</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>125-2</td>
<td>.37</td>
<td>4-8</td>
<td>50</td>
<td>98</td>
<td>36</td>
</tr>
<tr>
<td>250-3</td>
<td>.75</td>
<td>4-8</td>
<td>50</td>
<td>91</td>
<td>35</td>
</tr>
<tr>
<td>291-1</td>
<td>.54</td>
<td>4-6</td>
<td>100</td>
<td>94</td>
<td>34</td>
</tr>
</tbody>
</table>

The data of Tables 47 and 48 represent the best yields of pinacol at rotating and stationary cathodes, respectively, in potassium hydroxide solution.

TABLE 49

Reproducibility of Pinacol Formation at a Rotating Amalgamated Copper Cathode in Tetramethylammonium Hydroxide Solution

Catholyte: acetone and Me₄NOH to total of 75 ml.; Current density: 50 ma./cm.²; Rot'n speed: 2000 rpm; Anode: Pb; Anolyte: 1 M Me₄NMeSO₄; Curr. Eff.: 96 %.
TABLE 49 (cont.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>Me₄NOH</th>
<th>Temp. °C.</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>340-1</td>
<td>30</td>
<td>.65</td>
<td>5-11</td>
<td>52</td>
</tr>
<tr>
<td>342-1</td>
<td>40</td>
<td>.53</td>
<td>3-9</td>
<td>47</td>
</tr>
<tr>
<td>345-2</td>
<td>30</td>
<td>.61</td>
<td>6-11</td>
<td>53</td>
</tr>
</tbody>
</table>

In Run Numbers 340-1 and 342-1, the 0.8 N Me₄NOH used was prepared using an ion exchange resin. In Run Number 345-2, the Me₄NOH used was prepared by an electrolytic method.

TABLE 50

Reproducibility of Pinacol Formation at a Stationary Amalgamated Copper Cathode in Tetramethylammonium Hydroxide Solution

Catholyte: acetone and Me₄NOH in total of 75 ml.; Current density: 50 ma./cm.²; Temp. 4-8°C.; Anode: Pb; Anolyte: Me₄NOH and Me₄NMe₃SO₄.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acetone (volume %)</th>
<th>Me₄NOH</th>
<th>Curr. Eff. %</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>219-3</td>
<td>30</td>
<td>.63</td>
<td>85</td>
<td>45</td>
</tr>
<tr>
<td>222-2</td>
<td>40</td>
<td>.55</td>
<td>88</td>
<td>53</td>
</tr>
<tr>
<td>224-3</td>
<td>30</td>
<td>.65</td>
<td>97</td>
<td>46</td>
</tr>
</tbody>
</table>

In Run Numbers 219-3 and 222-2, the cathode used had a surface area of 9.5 cm.², while in Run Number 224-3 the cathode had a surface area of 17.0 cm.². The data in Tables 49 and 50 represent the highest yields of pinacol obtained at rotating and stationary cathodes, respectively.
in tetramethylammonium hydroxide solution.

Effect of the Nature of the Electrolyte

(a) Nature of the Cation

The nature of the electrolyte has a considerable influence on the amount of pinacol obtained at an amalgamated copper cathode. The maximum yields of pinacol obtained at rotating and stationary cathodes in sodium, potassium, and tetramethylammonium hydroxide solutions are compared in Tables 51 and 52.

Table 51

Effect of Nature of Electrolyte Cation on the Yield of Pinacol at a Rotating Amalgamated Copper Cathode

<table>
<thead>
<tr>
<th>Run No</th>
<th>Electrolyte</th>
<th>Temp. °C.</th>
<th>C.D. (ma./cm.²)</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>150-3</td>
<td>1.5 N NaOH</td>
<td>5-7</td>
<td>50</td>
<td>35</td>
</tr>
<tr>
<td>295-1</td>
<td>.53 N KOH</td>
<td>4-6</td>
<td>100</td>
<td>44</td>
</tr>
<tr>
<td>345-2</td>
<td>.61 N Me₄NOH</td>
<td>6-11</td>
<td>50</td>
<td>53</td>
</tr>
</tbody>
</table>

Table 52

Effect of Nature of Electrolyte Cation on the Yield of Pinacol at a Stationary Amalgamated Copper Cathode

Catholyte: 22.5 ml. acetone, electrolyte to 75 ml.
TABLE 52 (cont.)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Electrolyte</th>
<th>Temp. °C.</th>
<th>C.D. (ma./cm.²)</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>149-1</td>
<td>1.5 N NaOH</td>
<td>5-9</td>
<td>50</td>
<td>26</td>
</tr>
<tr>
<td>125-2</td>
<td>.37 N KOH</td>
<td>4-8</td>
<td>50</td>
<td>36</td>
</tr>
<tr>
<td>224-3</td>
<td>.65 N Me₄NOH</td>
<td>4-8</td>
<td>50</td>
<td>46</td>
</tr>
</tbody>
</table>

These results support the suggestion by Hennig and Kimball\(^1\), that the reduction of acetone is seen to be furthered by using a more difficultly reducible cation\(^\)\(^{-}\). This concept is also supported by data obtained from the field of polarography. The reduction potentials of the alkali metal cations have the following values, relative to the saturated calomel electrode:

\[
\begin{align*}
\text{NH}_4^+ & \quad -2.05 \text{ v.} \\
\text{Na}^+ & \quad -2.07 \text{ v.} \\
\text{K}^+ & \quad -2.10 \text{ v.} \\
\text{Li}^+ & \quad -2.31 \text{ v.} \\
\text{R}_4\text{N}^+ & \quad -2.2 \text{ to } -2.4 \text{ v.}
\end{align*}
\]


graphic determination of acetone and methyl ethyl ketone, and assigned values for the reduction potentials as -2.20 and -2.25 v. respectively. These values were determined in a 0.025 N solution of tetramethylammonium iodide. In hydrochloric acid, lithium chloride, or sodium hydroxide, no positive results were obtained.

At a dropping mercury cathode, it must therefore be concluded that with sodium or potassium salts as supporting electrolytes, the alkali metal cation is reduced in preference to acetone. The same type of conclusion may be drawn from the present work, in which acetone was reduced at a mercury cathode. The results are recorded in Table 53.

**TABLE 53**

Effect of Nature of Electrolyte Cation on the Yield of Pinacol at a Mercury Cathode

Catholyte: 22.5 ml. acetone, electrolyte to 75 ml.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Electrolyte</th>
<th>Temp. C.</th>
<th>C.D. (ma./cm.²)</th>
<th>Pinacol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>235-1</td>
<td>1.4 N NaOH</td>
<td>1-2</td>
<td>56</td>
<td>6</td>
</tr>
<tr>
<td>252-1</td>
<td>.71 N KOH</td>
<td>4-5</td>
<td>112</td>
<td>30</td>
</tr>
<tr>
<td>231-2</td>
<td>.64 N Me₄NOH</td>
<td>2-4</td>
<td>56</td>
<td>53</td>
</tr>
</tbody>
</table>

In Run Number 235-1, the alkali concentration in the catholyte decreased from 1.55 to 1.29 N during the electrolysis, and solid sodium amalgam was found in the mercury cathode. In Run Number 252-1, the alkali concen-
tration in the catholyte decreased from 0.75 to 0.65 N, and a smaller amount of solid potassium amalgam was found.

In Run Number 231-2, the alkali concentration was constant (0.640 to 0.645 N) throughout the reduction, and no evidence of amalgam formation was observed. The instability of tetramethylammonium amalgam in the presence of water has been noted by McCoy and Moore\(^1\).


These data all support the idea that the reduction potential of the electrolyte cation in relation to that of acetone has an important effect on the yield of pinacol obtained at a mercury cathode. At an amalgamated copper cathode, the problem of reduction of the electrolyte is much less serious, as evidenced by the much higher yields of pinacol in sodium hydroxide solution, and the slightly higher yields in potassium hydroxide solution. In tetramethylammonium hydroxide solution, where amalgam formation is not a problem, mercury and amalgamated copper are equally effective as cathodes.

(b) **Nature of the Anion**

Replacement of hydroxide by some other anion in the electrolyte has some effect on the yields of pinacol obtained.
For example, Hennig and Kimball\(^1\) obtained a lower yield of pinacol when either sodium chloride or sodium sulfate replaced sodium hydroxide in the reduction at a mercury cathode. Udupa\(^2\) found that replacement of potassium hydroxide by potassium carbonate had very little effect on the yield of pinacol at an amalgamated copper cathode.

In the present work, it was found that the yield of pinacol was about the same in potassium hydroxide as in potassium carbonate. (See Table 27). In the case of tetramethylammonium hydroxide and the methyl sulfate, the hydroxide gave a much better yield. (See Table 44). It was observed that a neutral solution of tetramethylammonium methyl sulfate became acidic on standing, probably due to hydrolysis of the methyl sulfate anion.

Hennig and Kimball\(^3\) have suggested that at a mercury cathode, the formation of pinacol is favored by the presence of hydroxide ions because of its effect on an acid-base equilibrium among the reaction intermediates in the reduction of acetone. The fact that Wilson and Wilson\(^4\)
could detect no pinacol formation in the reduction of acetone in sulfuric acid solution at a mercury cathode is also consistent with this idea.

A potassium carbonate solution is alkaline because of hydrolysis of the carbonate anion to form a buffer solution. Sodium chloride and sodium sulfate would not undergo hydrolysis. However, the methyl sulfate anion probably reacts with water according to the equation:

\[ \text{MeSO}_4^- + \text{H}_2\text{O} \rightarrow \text{MeOH} + \text{H}^+ + \text{SO}_4^{2-} \]

The acidity of the resulting solution may be the reason for the decreased yield of pinacol.

**Effect of Alkali Concentration**

In contrast to the results reported by Wilson and Wilson (above), and by Hennig and Kimball, at a mercury cathode, a variation of alkali concentration seems to have little effect on the yields of pinacol obtained in potassium and sodium hydroxide solutions at an amalgamated copper cathode. (See Tables 1, 2, 13, and 14.) In tetramethylammonium hydroxide, a concentration of about 0.6 N seemed to give the best yields, at either stationary or rotating cathodes. (See Tables 28, 29, and 30.) This
apparent effect of alkali concentration was not noticed in other solutions of tetramethylammonium hydroxide, from 0.15 to 1.21 N., in which the yield of pinacol at a stationary cathode ranged only from 34 to 39 percent.

In the work of Wilson and Wilson\(^1\), which indicated

(1) Reference (1), page 5.

a large increase in pinacol yield with higher potassium hydroxide concentrations, the reason may be that these workers isolated the high-boiling residue from the reduction, and weighed it as pinacol. At higher acetone and alkali concentrations, it is probable that appreciable amounts of acetone condensation products were formed\(^2\).

(2) cf. Elbs and Brand, Reference (4), page 3.

In the present work, non-pinacolic condensation products would not affect the analysis of pinacol.

Further evidence in support of this explanation is to be found in the analysis of a sample of distilled pinacol, (b.p. 175-185\(^{\circ}\)C.; Literature b.p. 177\(^{\circ}\)C.), prepared by electrolysis of acetone in potassium hydroxide solution at an amalgamated copper cathode by Robert Lieberman\(^3\). This


distilled sample of "pinacol" gave an analysis of only
82 percent purity by periodate titration. The infra-red spectrum of the sample indicated the presence of impurities containing ethylenic double bonds and carbonyl groups, such as might be expected in mesityl oxide and other acetone condensation products.

In the work of Hennig and Kimball\(^1\), the effect of

(1) Reference (2), page 5.

alkali concentration on pinacol yield was investigated for sodium hydroxide concentrations of 0.13 to 1.0 N. "Increasing sodium hydroxide concentration decreased the yield of \textit{iso}-propyl alcohol, and increased the yield of pinacol (except at high concentrations of acetone and sodium hydroxide)". It should be noted that these authors found that the problem of amalgam formation was much more serious in the dilute solutions, and also that the overall current efficiency was lower at the higher alkali concentrations. Thus it is possible that the apparent effect of alkali concentration on pinacol yield was due to variations in the amount of amalgam being formed simultaneously.

\textbf{Effect of Acetone Concentration}

The effects of acetone concentration on the yield of pinacol at rotating and stationary cathodes, in sodium, potassium, and tetramethylammonium hydroxide solutions, are represented graphically in Figure I. At a station-
Figure 1
Effect of Acetone Concentration on the Yield of Pinacol at an Amalgamated Copper Cathode
ary amalgamated copper cathode, increasing the acetone concentration lead to an increase in pinacol yield in all three electrolytes. At a rotating cathode in sodium hydroxide solution, acetone concentration had little effect on the pinacol yield, except for a slight drop at the highest acetone concentration. With potassium hydroxide as electrolyte at a rotating cathode, increased acetone concentration lead to higher pinacol yields, except at the highest acetone concentration used (60 percent). In tetramethylammonium hydroxide, the maximum pinacol yield was obtained when the acetone concentration was 30 percent. The drop in pinacol yields at the highest acetone concentrations may be only apparent, since the magnitude of the decrease is close to the limit of reproducibility of the experimental data. It is also possible that other factors such as overvoltage and reduction potential might be different in solutions of high acetone concentration. The tendency to separate into two layers, the upper rich in acetone, was noticed with the solutions having high acetone concentrations. This might reduce pinacol yield by decreasing the amount of acetone present in the aqueous layer, in which reduction actually would take place.

These conclusions are in general agreement with the results of Hennig and Kimball¹, who found that at higher

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¹ Reference (2), page 5.
acetone concentrations, the rate of pinacol formation was proportional to the first power of the acetone concentration, while at low acetone concentrations the rate was proportional to the second power of the acetone concentration. This was ascribed to "saturation" of the diffusion layer on the cathode surface with acetone molecules at the higher acetone concentrations. If the catholyte is well stirred (i.e. by rotating the cathode), the thickness of the diffusion layer is decreased, and the "saturated" condition at the cathode surface is attained at a lower "bulk" acetone concentration.

**Effect of Temperature**

At stationary or rotating cathodes, in sodium, potassium or tetramethylammonium hydroxide solutions, the yield of pinacol was decreased at higher temperatures. This effect was most noticeable at rotating cathodes, where the pinacol yield was decreased by 10 to 15 percent for a temperature increase of 20°C. (cf. Tables 5 and 6, 17 and 18. 34 and 35.) In the temperature range from 20 to 30°C., rotating the cathode ceased to have any influence on the yield of pinacol. This suggests that a higher temperature and rotation of the cathode have opposite effects on the reduction process to form pinacol. At about 25°C the two effects balance each other, and the same yields are obtained at either stationary or rotating cathodes.
Such a balance between agitation and temperature effects has recently been reported, where ultrasonic energy was used to agitate the catholyte in the plating out of nickel.\(^1\) At 50\(^\circ\)C., application of ultrasonic energy ceased to have any beneficial effect on the plating out process as compared with mechanical agitation, while at 20\(^\circ\)C. ultrasonics were superior.

**Effect of Rotation of the Cathode**

Provided that the temperature was kept below 20\(^\circ\)C., rotation of the cathode improved the yields of pinacol obtained in sodium and potassium hydroxides. In sodium hydroxide solution with 30 percent acetone, 2000 rpm appeared to give a better yield of pinacol than 3100 rpm as rotation speed. (Table 7). Using potassium hydroxide as electrolyte in a 10 percent acetone solution, rotation of the cathode at up to 4000 rpm had little effect. (Table 19) However, as acetone concentration increased, rotation of the cathode lead to considerable improvement in the pinacol yield (Tables 20 and 21). In tetramethylammonium hydroxide, the results were less definite. At higher temperatures or current densities, rotation had little effect. (Tables 39 and 37). With 30 percent acetone in 0.15 N tetramethylammonium hydroxide, rotation seemed to lower

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the pinacol yield (Table 36). This was also the case with 40 percent acetone in 0.54 N tetramethylammonium hydroxide (Table 40). However, with 30 percent acetone in 0.65 N tetramethylammonium hydroxide, rotation of the cathode improved the pinacol yield (Table 38).

**Effect of Addition of Methanol**

The addition of methanol to the catholyte resulted in a decrease in the pinacol yield in both sodium and potassium hydroxide solutions (Tables 8 and 22). This may be due to the adsorption of the methanol on the cathode surface, so that the amount of acetone present on the surface was reduced.

**Effect of Current Density**

At a stationary cathode in sodium or potassium hydroxide solutions, current densities from 50 to 150 ma./cm.\(^2\) seemed to have no effect on the yield of pinacol. (Tables 9, 10, 23, and 24.) At a rotating cathode in sodium hydroxide, and at either stationary or rotating cathodes in tetramethylammonium hydroxide, a current density of 150 ma./cm.\(^2\) gave an appreciably lower yield of pinacol than a current density of 50 ma./cm.\(^2\) (Tables 11, 41 and 42). At a rotating cathode in potassium hydroxide solution, the pinacol yield seemed to improve as the current density increased from 50 to 100 ma./cm.\(^2\) (Table 25).

This last result appears to be in agreement with the
results of Udupa\textsuperscript{1}, and also with the general change of pinacol yield with current density as reported by Wilson and Wilson\textsuperscript{2}, and by Hennig and Kimball\textsuperscript{3}.

(1) Reference (2), page 7.
(2) Reference (1), page 5.
(3) Reference (2), page 5.

Current Efficiency

In the reduction of acetone in alkaline solution, the current efficiency with respect to other reduction products than hydrogen is good, usually above 90\%. At an amalgamated copper cathode, the amount of amalgam formed is also small, so that the current efficiency of acetone reduction is good.

CHAPTER V
PINACOL ANALYSIS

Pinacol in solution can be analyzed by oxidative cleavage with periodate or with lead tetra-acetate. The former reagent is generally recommended for aqueous solutions\textsuperscript{4}. Price and Kroll\textsuperscript{5} showed that the oxidation proceeds more rapidly in an acid solution.

Slotterbeck\(^1\) stated that the presence of acetone and iso-propyl alcohol did not interfere with the oxidation of pinacol, though Hennig and Kimball\(^2\) claimed that a small amount of the acetone (0.030 % of acetone concentration) was oxidized by periodic acid.

Several methods are available for the determination of the amount of periodate reduced to iodate by pinacol according to the reaction:

\[(CH_3)_2-C-C-(CH_3)_2 + IO_4^- \rightarrow 2 CH_3COCH_3 + H_2O + IO_3^-\]

Slotterbeck\(^1\) determined the amount of periodate consumed by adding excess potassium iodide. The periodate and iodate differ in the amount of iodine they will liberate from an acidified iodide solution. Thus, titration of the liberated iodine with a standard thiosulfate solution, using starch as indicator, permitted determination of the amount of pinacol originally present.

Duke\(^3\) has developed another method of analysis, in which the mixture of periodate and iodate from the oxidation is completely reduced to iodide with sodium arsenite solution. The excess arsenite is then titrated with a
standard iodine solution, to the starch end point. Staker

(1) D. Staker, Ph. D. Dissertation, Ohio State University, (1952).

has developed a convenient procedure based on this method. This will be referred to as the "Standard Procedure".

Pinacol by Standard Procedure

A sample containing 0.005 mole of pinacol was weighed out, dissolved in water, diluted to 100 ml., and 10 ml. aliquots taken for analysis. Four ml. of 0.25 M periodic acid was added, and after oxidation of the pinacol was complete, 25 ml. of 0.1 N sodium arsenite was added. The excess arsenite was titrated with a 0.1 N standard iodine solution to the starch end point. A blank of 10 ml. distilled water was treated in the same way. The difference in volume of iodine solution required for the sample and for the blank was determined. The amount of pinacol in the original sample was then calculated from the equation:

\[
\text{Percent Pinacol} = \frac{100(V_s - V_b)(N_i/2)(M)}{1000(w)(a.f.)}
\]

where:

- \(V_s\) = volume of \(I_2\) solution required for sample
- \(V_b\) = volume of \(I_2\) solution required for blank
- \(N_i\) = normality of \(I_2\) solution
- \(M\) = molecular weight of pinacol
- \(w\) = weight of sample taken
- \(a.f.\) = aliquot fraction taken
In the present application of this latter method, modification of the Standard Procedure was desirable. For example, it was desirable to titrate directly the pinacol present in the strongly alkaline catholytes obtained after reduction of acetone, without isolation of the pinacol. This presented difficulties, since direct addition of periodic acid to the catholyte resulted in the precipitation of sodium or potassium periodate. These precipitates dissolved very slowly, so that the time required for complete oxidation of the pinacol present became too long for convenience. In order to avoid this, and to utilize the more rapid reaction in acid solution, dilute sulfuric acid was used to adjust the catholyte to a pH of about 2 before the periodic acid was added.

It was also found that a blank containing only distilled water was not satisfactory. The total volume of iodine solution required to titrate the sample was found to change with time. The end point in the sample, which contained acetone, also faded rapidly, presumably due to iodination of acetone. However, by using a blank which contained the same amount of acetone and alkali as the aliquot of the diluted catholyte, reproducible pinacol results were obtained.

**Pinacol by Modified Procedure**

The procedure finally adopted was as follows:-

The catholyte from a reduction (ca. 75 ml.) was
diluted to 100 ml. with distilled water. Aliquots were taken of such volume (10, 20 or 25 ml.) that about 0.0005 moles of pinacol was present. These were acidified by dropwise addition of sulfuric acid, to a pH of 2. Four ml. of 0.25 M periodic acid was added, and after oxidation of the pinacol was complete, 25 ml. of 0.1 N sodium arsenite was added. The excess arsenite was titrated with a 0.1 N standard iodine solution until a brownish-purple end point was reached, which persisted for at least 30 seconds. A blank, containing acetone and alkali in the same amounts as in the aliquot sample, was treated in the same way. From the difference in volume of iodine solution required for the sample and for the blank, the amount of pinacol could be calculated, as in the "Standard Procedure".

To test the accuracy of this method of determining the amount of pinacol in the catholyte after a reduction of acetone, a number of synthetic samples were made up with known amounts of pinacol, and the alkali and acetone which would be in a typical catholyte were added before the sample was analyzed. The sample of pinacol used was shown by the "Standard Procedure" to have a pinacol content of 82 percent.

A sample was made up from the 82 percent pure pinacol, with enough acetone and tetramethylammonium hydroxide added to simulate the catholyte from reduction of a 30
percent acetone solution in 0.65 N tetramethylammonium hydroxide. Analysis by the "Modified Procedure" indicated a purity of 78.0 and 77.6 percent in duplicate samples. Analysis of a synthetic sample representing a catholyte from reduction of 30 percent acetone in 1.5 N sodium hydroxide indicated a purity of 74 and 78 percent for the pinacol in duplicate samples. Analysis of a synthetic sample representing a catholyte from reduction of 30 percent acetone in 0.37 N potassium hydroxide gave values of 75 and 77 percent pinacol.

From these data, the modified procedure gives results which are five to ten percent low. Thus the results reported for the yield of pinacol in the reduction experiments are also presumably low. No correction has been made in the pinacol yields reported, since the correction involved is close to the limits of reproducibility of the reduction experiments themselves.

It was also shown that the salts formed by neutralization of the catholyte with sulfuric acid, or the acid itself, had no effect on the analytical results. Allowing the known pinacol samples to stand with added sodium sulfate for 18.5 hours, and with excess dilute sulfuric acid for 10.5 hours before analyzing, gave a pinacol analysis of 82 percent. Thus no pinacolone rearrangement of the pinacol takes place under these conditions. It appears that the acetone in the catholyte is the only substance
present which interferes with the pinacol analysis. This is in agreement with the conclusions of Hennig and Kimball.1

(1) Reference (2), page 5.

In some preliminary experiments, an effort was made to distill off the acetone before analyzing the catholyte for pinacol, but this did not give reproducible results.

To check the reliability of the "Standard Procedure", an attempt was made to obtain pinacol of high purity. The pinacol sample available, with a boiling point range of 175 to 185°C., gave an analysis of 82 percent by the "Standard Procedure". A sample of this crude pinacol was distilled with benzene to remove water, and then redistilled under vacuum. Two samples of pure pinacol, having boiling points of 74-75°C./10 mm., and 75-76°C./10 mm., were collected. Analysis of two portions of each of these samples gave pinacol contents of 93, 95, 93 and 93 percent. These pinacol samples were solid at room temperature. (Literature m.p. of anhydrous pinacol, 41°C.) Further purification, with suitable precautions to exclude moisture, would thus be expected to give analytical values of close to 100 percent for the pinacol content.
CHAPTER VI
THE PREPARATION OF TETRAMETHYLAMMONIUM HYDROXIDE

Introduction
The method almost universally used for making quat-ernary ammonium hydroxides involves their preparation from quaternary ammonium halides. The iodide is gener-ally used, and is made by the reaction of a tertiary am­ine with an alkyl iodide in an aqueous medium. This re-action gives nearly quantitative yields because of the insolubility of the quaternary ammonium iodide that is formed. The recommended method for converting the iodide to the hydroxide involves the addition of moist silver oxide to the iodide solution. Silver iodide precipitates and the quaternary ammonium hydroxide is formed in solution.

Using this method, the quaternary ammonium hydrox­ide solution is contaminated with sodium ions absorbed on the moist silver oxide from the sodium hydroxide used to prepare it. If excess silver oxide is used to ensure complete reaction of the halide, the solution also con-tains some silver ions because of the amphoteric nature of silver oxide. Yields of the quaternary ammonium hydroxide are poor, (about 35 percent), and the cost of the silver oxide makes the use of this classical procedure prohibitive for the preparation of the relatively large quantities of pure tetramethylammonium hydroxide needed.
for use as an electrolyte.

A satisfactory procedure for the preparation of tetramethylammonium hydroxide in large quantities and fairly high concentration has been developed by George A. Simmons. Reaction of trimethylamine with methyl bromide in iso-propanol gave tetramethylammonium bromide. An aqueous solution of this salt was passed through a column of Dowex-2, a strongly basic anion exchange resin. From two liters of a 1.2 M solution of the bromide, about one liter of solution 1 M in hydroxide ion (80% conversion) was obtained, along with a liter of a solution of lower hydroxide concentration. The solution obtained was virtually free of metallic cations, but contained some unconverted bromide. If necessary, this bromide could be removed by crystallization from iso-propanol after removal of the water under vacuum at a low temperature.

For use as an electrolyte in the reduction of acetone, the presence of bromide ions was undesirable, since the free bromine liberated on electrolysis would lead to excessive corrosion of the anode, and possible reaction with the acetone or its reduction products. Dr. C. L.
Wilson has suggested that tetramethylammonium hydroxide might be prepared through the reaction of trimethylamine with methyl sulfate to give a quaternary ammonium salt that could then be converted to the quaternary hydroxide. Dr. Wilson has also suggested that tetramethylammonium hydroxide might be prepared by electrolysis of a solution of the corresponding salt in a divided cell. The observation is frequently made that in such an electrolytic cell, the alkalinity of the catholyte increases as electrolysis proceeds. A process for the preparation of sodium hydroxide from sodium sulfate, which utilizes this phenomenon, has been described recently in a Japanese patent. According to the patent, a saturated solution of sodium sulfate is electrolyzed to obtain sodium hydroxide at the cathode compartment. Sulfuric acid in the anode compartment is removed with acid absorbing resin, and the solution is returned to the electrolytic bath with added sodium sulfate. The cation absorbing resin is regenerated with aqueous ammonium hydroxide.

(1) Dr. C. L. Wilson, private communication.

Preparation of Tetramethylammonium Methyl Sulfate

Methyl sulfate has been used quite extensively with tertiary aromatic amines to form the corresponding quaternary ammonium methyl sulfates. However the application of this method to simple aliphatic tertiary amines has received little attention in the literature. Blankart\(^1\)


reported in 1936 that reaction of PhCH\(_2\)CO\(_2\)CH\(_2\)C(Me)\(_2\)CH\(_2\)-N(Et)\(_2\) with methyl sulfate produced a crystalline water-soluble quaternary ammonium methyl sulfate.

In 1940, Kuhn\(^2\) and his co-workers reported preparation of dimethyldihexyl- and dimethyldicetyl-ammonium methyl sulfates from methyldihexylamine and methyldicetylamine respectively by treatment with methyl sulfate in dry benzene at 100\(^\circ\)C. in a sealed tube, followed by crystallization from ethyl acetate. The products were hygroscopic needles melting at 35\(^\circ\)C. and 129-30\(^\circ\)C. respectively. In the same year, a patent was issued to G. Roeder\(^3\) covering the formation of acetyl-\(\beta\)-methyl

(2) R. Kuhn, D. Jerchel and O. Westphal, Ber. 23B, 1095 (1940).

(3) G. Roeder, U.S. Patent 2,192,204 (1940).
choline methyl sulfate by reaction of $\text{CH}_3\text{CH(COAc)CH}_2\text{-N(Me)}_2$ with methyl sulfate.

Recently, J.B. Niederl and Associates, Inc.\(^1\) have

\(^{1}\) U.S. Patent 2,569,326 (1951).

taken out a patent on the reaction of tertiary alkyl amines with unsymmetrical dialkyl sulfates. The reactants in equimolar amounts were heated on a steam bath in a closed vessel, the product being washed with ether and recrystallized from ethyl acetate.

For tetramethylammonium methyl sulfate, the most convenient procedure found in the present work involved the introduction of gaseous trimethylamine into a cooled solution of methyl sulfate in methanol. The product was very soluble in methanol (about 300 g./l. at 0°C.), but by vigorous cooling in an ice-salt bath, well formed white needles could be obtained. The use of ethyl ether, benzene and iso-propyl alcohol as solvents in the reaction resulted in a product that was poorly crystallized, and hard to purify further. The best product was obtained by passing trimethylamine into the methyl sulfate solution until the latter was strongly alkaline. This ensured complete reaction of the methyl sulfate, and simplified purification, as the excess amine and methanol could be removed under vacuum. Pure tetramethylammonium methyl sulfate could thus be obtained in 80 percent yields based on
methyl sulfate, without further crystallization. A sample crystallized twice from a methanol-iso-propanol mixture melted at 235-239°C.

**Preparation of Tetramethylammonium Hydroxide**

Tetramethylammonium hydroxide was prepared from tetramethylammonium methyl sulfate by use of an ion exchange resin (Dowex-2), and also by electrolysis of the salt solution in a divided cell.

**A. Ion Exchange Resin**

A solution of tetramethylammonium methyl sulfate was passed through a column of Dowex-2, (a strongly basic anion exchange resin obtained from the Dow Chemical Company). Samples of the column effluent were taken periodically, and titrated with standard hydrochloric acid solution. Figure 2 shows plots of the alkali concentration vs. the total volume of effluent from the column.

Curve A resulted from passing two liters of 1.0 M tetramethylammonium methyl sulfate through the column as received, (resin in hydroxyl form), and then adding distilled water. One liter of tetramethylammonium hydroxide solution, $[\text{OH}^-] > 0.8 \text{ M}$, was obtained, along with another liter of solution having a lower alkali concentration. After regeneration of the ion exchange resin with 10 percent sodium hydroxide solution, a second solution of 2.75 liters of 1.0 M tetramethylammonium methyl sulfate was passed through the column before addition of distilled
Figure 2
Dependence of Concentration of Tetramethylammonium Hydroxide on Volume of 1.0 M Aqueous Tetramethylammonium Methyl Sulfate Passed Through Dowex-2
water, giving the data represented by Curve B. A further 1.1 liters of tetramethylammonium hydroxide solution was obtained, along with a considerable volume of solution which was less than 80 percent converted to the hydroxide.

In some preliminary experiments, it was shown that it was possible to obtain conversions of 94–97 percent of the salt to the hydroxide. Passing these solutions through a fresh column of the ion exchange resin resulted in no further increase in alkali concentration. Similarly a ten-fold dilution of the solution resulted in only a small increase in the percent of salt converted.

B. Electrolysis

The electrolysis of quaternary ammonium salts has received very little attention in the literature. McCoy and Moore\(^1\) have reported the electrolysis of tetramethylammonium chloride in absolute alcohol, using a platinum or silver-plated platinum anode and a mercury cathode at low temperatures. The tetramethylammonium amalgam formed reacted with water to give an intensely alkaline solution, presumably containing tetramethylammonium hydroxide. LeBlanc\(^2\) probably got the same substance by the electrolysis.


\(2\) M. LeBlanc, \textit{Z. physik. Chem.}, 5, 467 (1890).
ysis of aqueous solutions of tetramethylammonium chloride at a mercury cathode.

**Electrolysis of Tetramethylammonium Methyl Sulfate**

Tetramethylammonium hydroxide solutions were prepared by electrolyzing a solution of tetramethylammonium methyl sulfate at a copper or nickel cathode in a divided cell, with sulfuric acid solution as anolyte, and a lead anode. Under these conditions, the alkali concentration in the catholyte increased during the electrolysis until a certain value had been reached. Continuation of the electrolysis then resulted in no further change in concentration, and finally a drop in concentration.

Thus, electrolysis of 200 ml. of 0.34 M tetramethylammonium methyl sulfate at a rotating copper cathode at 13 to 26°C., using a 0.5 M sulfuric acid solution as anolyte at a sheet lead anode, gave a catholyte with an alkali concentration of 0.22 N after 14.75 ampere hours of current had been passed through the cell. After 16.4 ampere hours, the alkali concentration was unchanged, while after 25 ampere hours it had dropped to 0.19 N.

In another experiment, electrolysis of 250 ml. of 1.36 M tetramethylammonium methyl sulfate at a nickel cathode at 15 to 30°C., using a 0.5 M sulfuric acid solution as anolyte, and a lead anode, gave a catholyte with an alkali concentration of 0.37 N after 54 ampere hours had been passed. After 72 ampere hours, the alkali
concentration was 0.61 N, and remained at this value after 94.5 ampere hours.

When a solution of tetramethylammonium methyl sulfate replaced the sulfuric acid as anolyte, continued electrolysis resulted in a continual increase in the alkali content of the catholyte. Thus, electrolysis of 200 ml. of a 1.0 M solution of the salt at a stainless steel cathode, using the same solution as anolyte at a lead anode, at a temperature of 30 to 39°c., gave 208 ml. of a solution having an alkali concentration of 0.90 N after 60 ampere hours of current has passed. The final concentration of tetramethylammonium ion in the catholyte was 1.23 M, showing that some of the increase in alkali concentration was due to migration of the tetramethylammonium ion from the anolyte to the catholyte. This will account for the limiting value of hydroxide concentration reached in the catholyte when sulfuric acid was used as anolyte.

In another experiment, 250 ml. of 1.0 M tetramethylammonium methyl sulfate solution was electrolyzed at a nickel cathode at a temperature of 42 to 70°C. After 6 ampere hours, the alkali concentration in the catholyte was 0.42 N, while after a total of 17.5 ampere hours, 210 ml. of a 0.84 N solution of tetramethylammonium hydroxide was obtained. The final concentration of tetramethylammonium ion in the catholyte was 1.33 M.
CHAPTER VII
EXPERIMENTAL

Preparation of Tetramethylammonium Methyl Sulfate

Materials: Methyl sulfate, from Maynard Chemical Company
Trimethylamine, (99% pure) from Matheson Co.
Methanol, Baker and Adamson Reagent Grade.

Procedure:

A solution of 126.2 g. redistilled methyl sulfate (1.0 mole) in 100 ml. methanol, contained in a 250 ml.
three-necked round-bottomed flask fitted with gas inlet and outlet tubes and a glycerin-sealed glass stirrer, was
cooled to 0°C. in an ice bath. Trimethylamine gas from
a cylinder was condensed in a graduated tube cooled in
a dry ice-isopropanol mixture, until 75 g. (1.1 mole)
of liquid trimethylamine (100 ml. at -78°C.) had collected. The dry ice bath was then removed, and the trimethylamine was allowed to evaporate slowly. The gas
was passed first through a 250 ml. bottle which served
as a safety trap, and then into the methyl sulfate solution through a delivery tube extending below the surface
of the liquid. Absorption of the trimethylamine was very
efficient, as indicated by the absence of any concensate
in a dry ice-isopropanol trap connected to the gas outlet
tube of the reaction flask.

When all the trimethylamine had been bubbled into
the solution, a mass of white crystalline salt had collected in the solution. The flask and contents were cooled below 0°C. in an ice-salt mixture, and the tetramethylammonium methyl sulfate was obtained by rapid suction filtration. It was very hygroscopic, but was dehydrated in a vacuum dessicator. Further salt was recovered by evaporation of the mother liquors, to give a total of 145 g. of dry, well crystallized tetramethylammonium methyl sulfate (78 percent based on methyl sulfate).

The solubility of the salt in the mother liquor was determined by taking 10 ml. of a saturated solution at 0°C., and evaporating to constant weight on a hot plate. The residue weighed 3.0 g., so that the solubility of tetramethylammonium methyl sulfate in methanol is about 300 grams per liter.

In several larger scale runs, methyl sulfate was used without distillation. The reaction mixture was straw-colored, but the salt obtained was white. In these runs, more methyl sulfate and trimethylamine were added to the mother liquors from the first portions of crystallized salt. An excess of trimethylamine was necessary to obtain well crystallized salt, as tetramethylammonium methyl sulfate was found to be very soluble in an acidic mother liquor. The total yield of dry crystallized salt in these runs was 66 to 80 percent, based on methyl sulfate.

A sample of the salt, crystallized twice from a
methanol-isopropanol mixture, and dried in a vacuum drying pistol at 56°C. at 1 mm. pressure for 3.5 hours, melted at 235-8°C. (uncorrected) with some decomposition.

Analysis: *

Found: %

C, 32.39; H, 7.50; N, 8.26
Calc. for C₅H₁₅NO₄S: 32.41 7.56 8.16

* by Clark Microanalytical Laboratory.

Preparation of Tetramethylammonium Hydroxide by Ion Exchange

Materials: Dowex-2, a strongly basic anion exchange resin, (20-50 mesh) from the Dow Chemical Company.
Sodium Hydroxide Solution, 10% by weight, prepared from Mallinckrodt Analytical Reagent Grade Sodium Hydroxide pellets.
Standard Hydrochloric Acid Solution, 0.1001 and 0.5021 N, was prepared by the Control and Reagent Laboratory, The Ohio State University.

Ion Exchange Columns:

Column "A". In the preliminary studies of the conversion of tetramethylammonium methyl sulfate to the quaternary hydroxide with Dowex-2, the column used was contained in a 50 ml. burette. This was filled with distilled water, and dry Dowex-2 (22.2 g.) was dropped in until the wet resin volume was about 35 ml. The resin was converted to the hydroxide form by allowing 10 percent sodium hydroxide solution (400 ml.) to flow through the column at a rate of
one drop per second. The column was then washed with distilled water (750 ml.) at 1 to 2 drops per second, until 15 ml. of effluent, with two drops of phenolphthalein indicator added, was neutralized by one drop of 0.1001 N hydrochloric acid. The column was then ready for use.

Column "B". For the larger scale preparation of tetramethylammonium hydroxide, the column of Dowex-2 was contained in a pyrex tube, (2 1/8 inches inside diameter), fitted with a stopcock at its lower end. The resin (1600 g. dry basis) filled the column to a height of about 30 inches when thoroughly wet. The column, filled with distilled water, was inverted, and then set upright to allow the resin to pack evenly, thus avoiding channelling. The resin in this column was converted to the hydroxide form by allowing 10 percent sodium hydroxide solution (24.5 l. containing 2718 g. sodium hydroxide) to run through the column at a rate of 1 to 2 drops per second. The column was then washed with distilled water (5 to 7 l.), at a flow rate of about one drop per second, until the effluent was practically neutral (15 ml. effluent neutralized by one drop of 0.1001 N hydrochloric acid). The regenerated column was then ready for use.

Preparation of Tetramethylammonium Hydroxide using

Column "A".

(1) Tetramethylammonium methyl sulfate (9.1 g.)
was dissolved in water to make 280 ml. of a 0.175 M solution. After drawing the water to the top of the resin bed in regenerated Column "A", the above solution was allowed to percolate through the column at about 30 drops, (2 ml.), per minute. Samples of the effluent were collected at intervals, and a 4 ml. portion of each was titrated to the phenolphthalein end point with 0.1001 M hydrochloric acid to determine the alkali concentration. The results are given in Table 54.

**TABLE 54**

*Conversion of a 0.175 M solution of Tetramethylammonium Methyl Sulfate to the Hydroxide, using Column "A"*

Solution: 280 ml. of 0.175 M Me₄NMe₂SO₄.

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Volume of Fraction (ml.)</th>
<th>Total Volume (ml.)</th>
<th>Normality of Me₄NOH</th>
</tr>
</thead>
<tbody>
<tr>
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<td>40</td>
<td>.097</td>
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<td>2</td>
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<td>.170</td>
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<td>241</td>
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<td>272</td>
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</tr>
<tr>
<td>12</td>
<td>10</td>
<td>282</td>
<td>.016</td>
</tr>
</tbody>
</table>

Fractions 2-6 were combined to give 150 ml. of tetramethylammonium hydroxide (94-97 percent pure).

Fractions 1 and 6-12 were combined to be recycled.
Column "A" was regenerated according to the procedure given.

(2) Tetramethylammonium methyl sulfate (10.5 g.) was dissolved in water to make 155 ml. of 0.35 M solution. After draining the water to the top of the resin bed in regenerated Column "A", the above solution was allowed to percolate through the column at a rate of 40 drops per minute. Samples of the effluent were collected at intervals, and a portion of each was titrated to the phenolphthalein end point with 0.1001 N hydrochloric acid to determine the alkali concentration. The results are given in Table 55.

TABLE 55

Conversion of a 0.35 M Solution of Tetramethylammonium Methyl Sulfate to the Hydroxide, using Column "A"

Solution: 155 ml. of 0.35 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Volume of Fraction (ml.)</th>
<th>Total Volume (ml.)</th>
<th>Normality of Me₄NOH</th>
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</thead>
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<td>.328</td>
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<tr>
<td>4</td>
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<td>78</td>
<td>.335</td>
</tr>
<tr>
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<td>16</td>
<td>94</td>
<td>.333</td>
</tr>
<tr>
<td>7</td>
<td>18</td>
<td>112</td>
<td>.208</td>
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<td>8</td>
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</tr>
<tr>
<td>10</td>
<td>7</td>
<td>153</td>
<td>.039</td>
</tr>
</tbody>
</table>

Fractions 3-6 were combined to give 62 ml. of tetramethylammonium hydroxide (93.5-95.5 percent pure).
Fractions 1, 2, and 7-10 were combined, to be recycled. Column "A" was regenerated according to the procedure given.

(3) **Effect of Recycling the "Pure" Solutions of Tetramethylammonium Hydroxide**

Portions of the "pure" tetramethylammonium hydroxide from above were combined to give 170 ml. of a solution in which the concentration of the hydroxide was 0.216 M. This solution was passed through regenerated Column "A". Of the effluent, 142 ml. was recovered having an alkali concentration of 0.214 to 0.218 N. Thus the percent conversion of the salt to the hydroxide could not be significantly increased by recycling the best fractions of effluent. The loss was due to "hold-up" in the resin column, and due to dilution caused by adding distilled water to wash the last portions of solution through the column.

(4) **Effect of Concentration on the Conversion to Tetramethylammonium Hydroxide**

A 15 ml. portion of a 0.219 N solution of tetramethylammonium hydroxide (93-97 percent converted) was diluted with distilled water to make 150 ml. of a 0.0219 N solution. From 130 ml. of this diluted solution passed through regenerated Column "A", there was obtained 95 ml. of effluent having an alkali concentration of 0.0221 to 0.0225 N. This indicated that a ten-fold dilution of the
salt solution would increase the completeness of conversion of tetramethylammonium methyl sulfate to the hydroxide by only 1-3 percent.

(5) Recycling of Partially Converted Solutions of Tetramethylammonium Methyl Sulfate

Recycling of the partially converted salt solutions through freshly regenerated Column "A" resulted in the recovery of more tetramethylammonium hydroxide of high purity. All such solutions from Column "A" were combined to give a stock solution of tetramethylammonium hydroxide which had a concentration of 0.229 N. This stock solution was used in experiments on the reduction of acetone.

Preparation of Tetramethylammonium Hydroxide using Column "B"

Run Number 1.

After draining the water in the column to the top of the resin bed, 378 g. of tetramethylammonium methyl sulfate in two liters of solution in distilled water (1.0 M) was run through the column at one drop per second. The effluent was collected in fractions of 60-90 ml. A portion of each fraction was titrated with standard hydrochloric acid, using phenolphthalein as indicator, to determine the concentration of tetramethylammonium hydroxide. The results are summarized in Table 56, and in Figure 2, (Curve A), on page 70.
TABLE 56

Conversion of a 1.0 M Solution of Tetramethylammonium Methyl Sulfate to the Hydroxide using Column "B"

Solution: 2 liters of 1.0 M Me₄NMeSO₄.

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Volume of Fraction (ml.)</th>
<th>Total Volume (ml.)</th>
<th>Normality of Me₄NOH</th>
</tr>
</thead>
<tbody>
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<td>85</td>
<td>----</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>155</td>
<td>----</td>
</tr>
<tr>
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</tr>
<tr>
<td>26</td>
<td>39</td>
<td>2028</td>
<td>.196</td>
</tr>
</tbody>
</table>

Fractions 12-18, (574 ml.) were combined. \( N > 0.87 \)

Fractions 10,11,19,20,21 (422 ml.) were combined. \( 0.87 > N > 0.80 \)

Fractions 9,22,23,24 (283 ml.) were combined. \( 0.80 > N > 0.70 \)

Fractions 6,7,8,25,26 were combined. \( 0.70 > N \).
Column "B" was regenerated according to the indicated procedure.

Run Number 2.

After draining the water in the regenerated column to the top of the resin bed, 2.75 liters of a 1.0 M solution of tetramethylammonium methyl sulfate (containing 515 g. of dry salt) was run through the column at a rate of 3 ml. per minute. Fractions of the effluent were collected at intervals, and a portion of each was titrated with 0.5021 N hydrochloric acid, using phenolphthalein as indicator, to determine the concentration of tetramethylammonium hydroxide. The results are indicated in Table 57 and in Figure 2, (Curve B), on page 70.

**TABLE 57**

**Conversion of a 1.0 M Solution of Tetramethylammonium Methyl Sulfate to the Hydroxide using Column "B"**

Solution: 2.75 liters of 1.0 M Me₄NMMeSO₄.

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Volume of Fraction (ml.)</th>
<th>Total Volume (ml.)</th>
<th>Normality of Me₄NOH</th>
</tr>
</thead>
<tbody>
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<td>12</td>
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<td>1012</td>
<td>.824</td>
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</table>

(cont.)
**TABLE 57 (cont.)**

<table>
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<th>Total Volume (ml.)</th>
<th>Normality of Me₄NOH</th>
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<tr>
<td>28</td>
<td>188</td>
<td>2783</td>
<td>.461</td>
</tr>
<tr>
<td>29*</td>
<td>240</td>
<td>3023</td>
<td>.232</td>
</tr>
<tr>
<td>30</td>
<td>116</td>
<td>3139</td>
<td>.095</td>
</tr>
</tbody>
</table>

* After the solution level had reached the top of the resin bed, distilled water was added to carry the rest of the solution through the column.

Fractions 15-20, (718 ml.) were combined. N > 0.866

Fractions 11-14, (417 ml.) were combined.

0.866 > N > 0.80

Fractions 9,10,21 (258 ml.) were combined.

0.80 > N > 0.70

The best fractions of tetramethylammonium hydroxide from Run s 1 and 2 on Column "B" were used in experiments on the reduction of acetone.

**Concentration of Tetramethylammonium Hydroxide Solution**

Tetramethylammonium hydroxide solution (594 ml. of the best fractions from Column "B", N > 0.86) was evaporated at below room temperature for several days in a
stream of dry air to a volume of 242 ml. This concentrated solution had an alkali concentration of 1.65 N. About one fourth of the total amount of tetramethylammonium hydroxide was decomposed by this method of concentration. The concentrated solution was used in experiments on the reduction of acetone.

**Preparation of Tetramethylammonium Hydroxide by Electrolysis**

**Materials:**
- Tetramethylammonium methyl sulfate solutions: prepared from the dry salt.
- Sulfuric Acid, 0.5 M: prepared from the concentrated acid (du Pont Co.)
- Standard Hydrochloric Acid solutions, 0.1001 and 0.5021 N: from Control and Reagent Laboratory, The Ohio State University.

**Electrolysis of Tetramethylammonium Methyl Sulfate at a Copper Cathode, using Sulfuric Acid as Anolyte**

- **Cathode:** solid copper cylinder, height 7.4 cm., diameter 1.8 cm., (surface area: 50 cm.²), rotating at 1500 rpm;
- **Catholyte:** 200 ml. of 0.34 M Me₄NMeSO₄ (prepared from 12.6 g. of dry salt) in a porous clay pot, diameter 5.7 cm., height 14.8 cm., (Coors Porcelain Co.);
- **Anode:** sheet lead, 21 x 10 cm., surrounding porous pot;
- **Anolyte:** 250 ml. of 0.5 M H₂SO₄ contained in a 600
ml. electrolytic beaker;

Current: 3 amps;

Temperature: 13-26°C., (Cell cooled in ice water).

The current was passed through the cell for 5.5 hours, (16.4 amp. hours), by which time the catholyte was strongly basic. Final volume of catholyte was 211 ml. A sample of the catholyte was titrated with standard hydrochloric acid solution to the phenolphthalein end point, indicating a hydroxide concentration of 0.22 N.

This procedure was repeated, using fresh catholyte and anolyte, the temperature being maintained at 17-22°C. After 5.4 hours (16.1 amp. hrs.), the catholyte had a total volume of 228 ml., and a hydroxide concentration of 0.218 N. After an additional 3 hours (total 25.1 amp. hrs.), the volume was 233 ml., and the alkali concentration was 0.192 N.

In a third run, the temperature was 14-25°C. After the current had passed through the cell for 4.9 hours (14.8 amp. hrs.), the hydroxide concentration was 0.22 N.

Electrolysis of Tetramethylammonium Methyl Sulfate at a Nickel Cathode, using Sulfuric Acid as Anolyte

Cathode: Nickel sheet, 12.5 x 7.5 cm., bent into an open cylinder;

Catholyte: 250 ml. of 1.36 M Me₄NMeSO₄ (prepared from 63 g. of dry salt) in a porous clay pot,
diameter 7.7 cm., height 12.7 cm., (Coors Porcelain Co.);

Anode: sheet lead, 21 x 10 cm., surrounding porous pot;

Anolyte: 0.5 M H$_2$SO$_4$ contained in a 600 ml. beaker;
Current: 9.0-9.3 amps.;
Temperature: 15-30°C., (cell cooled in ice water).
At various times, samples of the catholyte were taken, and the tetramethylammonium hydroxide concentration was determined by titration with standard hydrochloric acid solution. The alkali concentrations, after various total amounts of current passed, are recorded graphically in Figure 3, (Curve a). The final volume of the catholyte was 290 ml.

Electrolysis of Tetramethylammonium Methyl Sulfate at a Stainless Steel Gauze Cathode. (Anolyte same as Catholyte)

Cathode: stainless steel gauze, 100 mesh, 3.5 x 18 cm.;
Catholyte: 200 ml. of 1.0 M Me$_4$NMgSO$_4$ (slightly acid, pH 3, due to hydrolysis of the salt) in a porous clay pot, diameter 7.7 cm., height 12.7 cm., (Coors Porcelain Co.);
Anode: sheet lead, 21 x 10 cm., surrounding porous pot;
Anolyte: same as catholyte, in a 600 ml. beaker;
Figure 3
Variation of Hydroxide Ion Concentration in Catholyte with Total Current Passed
Current: 6 amps.;
Temperature: 30-40°C.

Current was passed through the cell for a total of 10 hours (60 amp. hrs.). Samples of the catholyte were taken periodically, and titrated with standard hydrochloric acid. The tetramethylammonium hydroxide concentrations in the catholyte after various amounts of current had been passed are recorded graphically in Figure 3 (Curve "D"). The final volume of the catholyte was 208 ml., and the final concentration of tetramethylammonium ion was 1.23 M, with a hydroxide concentration of 0.90 N.

**Electrolysis of Tetramethylammonium Methyl Sulfate at a Copper or Nickel Cathode (Anolyte same as Catholyte)**

Cathode: sheet copper or nickel, 12.5 x 7.5 cm.;
Catholyte: 250 ml. of 1.0 M Me₄NMe₅SO₄, (neutral, pH 7, prepared by dissolving 92.5 g. of dry salt and diluting to 500 ml. with distilled water) in a porous clay pot, diameter 7.7 cm., height 12.7 cm., (Coors Porcelain Co.);
Anode: sheet lead, 21 x 10 cm., surrounding porous pot;
Anolyte: 125 ml. of 1.0 M Me₄NMe₅SO₄ in a 600 ml. beaker;
Current: 6 amps.;
Temperature: 42-70°C.
Current was passed through the cell for 1.25 hours using the nickel cathode, and 1.67 hours using the copper cathode, (total 17.5 amp. hrs.). The voltage drop across the cell, and the temperature, increased during the electrolysis, due to deposition of lead from the anode in the pores of the clay pot. At intervals, a sample of the catholyte was analyzed by titration with standard hydrochloric acid solution, to determine the tetramethylammonium hydroxide concentration. The hydroxide concentrations after various amounts of current passed are recorded graphically in Figure 3 (Curve "C"). The final volume of the catholyte was 218 ml., and the final tetramethylammonium ion concentration was 218 ml., and the final tetramethylammonium ion concentration was 1.33 M, with a hydroxide ion concentration of 0.84 N.

This solution was used as catholyte in experiments on the reduction of acetone.

Determination of Tetramethylammonium Ion Concentration

The method used was essentially that of Bikerman¹,

(1) J.J. Bikerman, Z. anal. Chem. 90, 335 (1932).

in which a sample containing tetramethylammonium ion is decomposed by heating in strong sodium hydroxide solution, to give trimethylamine. This is steam distilled into a standard acid solution, and the un-neutralized acid is
back-titrated with standard alkali, to determine the amount (and concentration) of tetramethylammonium ion in the sample.

Apparatus:

A 50 ml. distilling flask with a long neck was connected to a condenser through a spray-trap. The condenser was provided with an adapter extending to the bottom of a 50 ml. round-bottomed flask containing an acid solution, which served as a trap for the trimethylamine.

Procedure:

The sample (1 ml., containing about 1 m.eq. Me₄N⁺) was added to 4 ml. of 30 percent sodium hydroxide solution in the distilling flask. The acid trap contained 25.00 ml. of 0.1001 N hydrochloric acid. After making all connections gas-tight, the distilling flask was heated, gently at first, until most of the water had distilled over, and the residue stopped bubbling. The distilling flask was allowed to cool, (taking precautions to avoid sucking back of the hydrochloric acid solution through the condenser), and 4 ml. of distilled water was added to the distilling flask. The distillation to dryness was repeated. After allowing the apparatus to cool, the distilling flask was disconnected, and the condenser, adapter, and trap contents were washed into a 200 ml. erlenmeyer flask with distilled water. The acid solution was then titrated with 0.1035 N sodium hydroxide, to the phenol-
phthalein end point. A blank of 1 ml. of distilled water was treated in the same way as the sample. From the difference in amount of standard base solution required to neutralize the acid solutions from sample and blank, the amount (and concentration) of tetramethylammonium ion in the sample was determined.

Results and Calculations:

Analysis of a 1.0 M $\text{Me}_4\text{NMeSO}_4$ solution prepared by dissolving 185.2 g. (1 mole) of the salt in distilled water, and diluting to 1 liter, gave the following data:

Sample: 1 ml. of 1.0 M $\text{Me}_4\text{NMeSO}_4$.

<table>
<thead>
<tr>
<th>NaOH concentration</th>
<th>0.1035 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of NaOH required for blank</td>
<td>24.17 ml.</td>
</tr>
<tr>
<td>Volume of NaOH required for sample</td>
<td>15.12 ml.</td>
</tr>
<tr>
<td>Volume difference</td>
<td>9.05 ml.</td>
</tr>
</tbody>
</table>

$$\left[\text{Me}_4\text{N}^+\right] \text{ in sample} = \frac{9.05 \times 0.1035}{1.00} = 0.936 \text{ M}$$

A duplicate analysis gave——— 0.940 M.

This procedure was used to determine the tetramethylammonium ion concentration in the catholytes obtained from electrolysis of tetramethylammonium methyl sulfate.

Accuracy of Pinacol Analysis by the "Modified Procedure"

To test the accuracy of the "Modified Procedure" for analysis of pinacol in alkaline catholytes after the reduction of acetone, a series of solutions were made up
containing the same amount of pinacol. To some of these were added sufficient acetone and alkali to represent the diluted catholyte after a reduction experiment. These samples were then analyzed by the "Modified Procedure", (page 60), and the results were compared with those obtained by the "Standard Procedure", (page 59), in the absence of acetone and alkali.

Procedure:

The pinacol sample used had a boiling point range of 175-185°C. A portion of this pinacol, containing about 0.005 mole, was weighed out, dissolved in water, and diluted to 100 ml. Aliquots (10 ml.) of this solution were pipetted into 200 ml. erlenmeyer flasks, while 10 ml. samples of distilled water served as blanks.

To each of Samples 1 and 2, and Blanks 1 and 2, were added 2.25 ml. of acetone and 5.5 ml. of 0.87 N Me₄NOH. These solutions then represented samples of a catholyte containing 30 percent acetone and 0.65 N Me₄NOH.

To each of Samples 3 and 4, and Blanks 3 and 4, were added 2.25 ml. of acetone and 5.5 ml. of 2 N NaOH. These solutions then represented samples of a catholyte containing 30 percent acetone and 1.5 N NaOH.

To each of Samples 5 and 6, and Blanks 5 and 6, were added 2.25 ml. of acetone and 2.75 ml. of 1 N KOH. These solutions then represented samples of a catholyte containing 30 percent acetone and 0.37 N KOH.
Nothing was added to Samples and Blanks 7, 8, 9 and 10 before analysis.

The analytical results are indicated in Table 58.

**TABLE 58**

Comparison of "Modified" and "Standard" Procedures of Pinacol Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Representing Catholyte</th>
<th>Procedure</th>
<th>% Pinacol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30% acetone in .65 N Me₄NOH</td>
<td>Mod.</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>ditto</td>
<td>Mod.</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>30% acetone in 1.5 N NaOH</td>
<td>Mod.</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>ditto</td>
<td>Mod.</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>30% acetone in .37 N KOH</td>
<td>Mod.</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>ditto</td>
<td>Mod.</td>
<td>77</td>
</tr>
<tr>
<td>7</td>
<td>-----</td>
<td>Std.</td>
<td>82</td>
</tr>
<tr>
<td>8</td>
<td>-----</td>
<td>Std.</td>
<td>84</td>
</tr>
<tr>
<td>9</td>
<td>-----</td>
<td>Std.</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>-----</td>
<td>Std.</td>
<td>80</td>
</tr>
</tbody>
</table>

From these results, it may be seem that the "Modified" procedure gives results that are 4 to 8 percent below those for the "Standard Procedure", using the same sample of pinacol.
The Reduction of Acetone in Alkaline Solution at Amalgamated Copper Cathodes

Materials:

**Acetone**: C.P. grade

**Potassium and Sodium Hydroxide Solutions**: made up from Mallinckrodt Analytical Reagent Grade pellets with distilled water

**Potassium Carbonate**: Baker and Adamson Reagent Grade

**Tetramethylammonium Methyl Sulfate**: as on page 74

**Tetramethylammonium Hydroxide**: as on pages 76-90

**Methanol**: Baker and Adamson Reagent Grade

**Sulfuric and Nitric Acids**: C.P. reagents

**Mercury**: Cathodic grade, triple distilled

**Potassium Iodide**: Mallinckrodt Analytical Reagent

**Sodium Bicarbonate**: Mallinckrodt Analytical Reagent

**Standard solutions of periodic acid, sodium arsenite, hydrochloric acid, and iodine**: Control and Reagent Laboratory, Ohio State University.

Apparatus:

The apparatus consisted of two electrolytic cells, (a reference cell and a reduction cell), connected in series with an ammeter and a variable resistance, as in Figure 4. The direct current used was obtained from a storage battery or from an alternating current rectifying battery charger. A portable Simpson voltmeter was used
Figure 4
Apparatus for Reduction of Acetone
to determine potential drops across the cells.

**Reference Cell:**

The reference cell, in which hydrogen was liberated by the current flowing through the circuit, was contained in a 600 ml. electrolytic beaker filled with 0.5 M sulfuric acid anolyte, and with a sheet lead cylinder to serve as anode. The cathode compartment was a porous clay thimble (Coors Porcelain Co.), containing 0.5 M sulfuric acid as catholyte, and a piece of platinum wire, which served as cathode. The cathode compartment was tightly closed by a two-holed rubber stopped, one hole carrying a gas outlet tube, the other a piece of glass tubing into which the platinum wire cathode was sealed. Electrical contact between the cathode and the circuit was made by a short column of mercury in the glass tube. The gas outlet from this reference cell lead through a piece of "tygon" tubing to a gas burette, in which the hydrogen produced by electrolysis was collected over water.

**Reduction Cell:**

The reduction cell was contained in a 400 ml. beaker, with an open cylinder of sheet lead, or an iron wire gauze to serve as anode. The cathode compartment was a porous clay pot (5.1 cm. x 9.6 cm.) of 85 ml. capacity (Coors Porcelain Co.), fitted with a rubber stopper carrying a thermometer, a gas outlet tube, and a gas-tight sealed
bearing supporting a stainless steel shaft which furnished an electrical connection with the cylindrical cathode. The part of the steel shaft in contact with the catholyte was insulated by a sheath of "tygon" tubing, so that only the cylindrical cathode was in electrical contact with the solution. The gas-tight sealed bearing, which permitted rotation of the cathode at high speeds without gas leakage, has been described in detail by Thomas Camilli\(^1\).

\(^1\) Thomas Camilli, Ph.D. Dissertation, Ohio State University (1953).

The gas delivery tube from the cathode compartment of the reduction cell was connected to a gas burette, in which the hydrogen evolved on electrolysis was collected over water.

The temperature of the reduction cell was regulated by placing the containing beaker in a suitable bath of water or ice-salt mixture, depending on the temperature desired.

The same porous clay pot was used for all acetone reduction experiments with this apparatus, as both Wilson and Wilson\(^2\) and Hennig and Kimball\(^3\) found that

\(^2\) Reference (1), page 5.
\(^3\) Reference (2), page 5.

the yield of pinacol varied somewhat in different pots,
due presumably to variations in the current distribution through the pot.

**Cathodes:**

The cylindrical cathodes used were turned out from solid copper rod, and screwed or press-fitted onto the stainless steel shaft. Either of two cathodes was used in all the experiments on the reduction of acetone. These were:

- **Cathode "A":** height 0.576 in., diameter 0.580 in.,
  total surface area: 1.467 in.\(^2\) or 9.47 cm.\(^2\).

- **Cathode "B":** height 0.855 in., diameter 0.720 in.,
  total surface area: 2.638 in.\(^2\) or 17.02 cm.\(^2\).

The portion of the top of the cylinder which was covered by the "tygon" insulation on the shaft was not included in the cathode surface areas.

After some experimentation, it was found that the copper cathodes could be amalgamated most easily by dipping them into some nitric acid in which a few drops of mercury had been dissolved. Once the cathode was amalgamated, the mercury surface could be restored by scrubbing the cathode with "dutch cleanser" before each experiment, to remove a thin dark film which formed on prolonged exposure to the air. The clean cathode was rinsed with distilled water, dipped into the mercuric nitrate solution, and wiped clean with a towel just before use. By reducing an identical catholyte at either of the two cathodes under
the same conditions, it was shown that the same results could be obtained at either cathode. (See Table 29, pages 31 and 32).

When the cathode was to be rotated, electrical contact was made to the stainless steel shaft through a strip of sheet copper bent tightly around the shaft. The speed of rotation of the shaft was determined by means of a neon discharge tube stroboscope. At 2000 rpm, the actual rotation speed varied from 1800 to 2200 rpm.

**Reduction Procedure:**

A typical reduction experiment (Run No. 150-3) was as follows:

**Reduction of 30% Acetone in 1.5 N NaOH at Rotating Amalgamated Copper Cathode**

- **Cathode:** amalgamated copper cathode "A", area 9.47 cm.$^2$, rotating at 2000 rpm;
- **Catholyte:** 22.5 ml. (0.306 moles) acetone, 55 ml. 2 N NaOH, total volume 75 ml.;
- **Anolyte:** 2 N NaOH solution;
- **Anode:** Fe gauze;
- **Temperature of catholyte:** 5-7°C.;
- **Current:** 0.47 amp.; Current density: 50 ma./cm.$^2$;
- **Potential drop across cell:** 5.4 to 3.8 volts;
- **Atmospheric pressure:** 744 mm.; Temperature: 29°C.

The current was passed for 90 minutes, at which time 300 ml. of hydrogen had been evolved from the reference
cell. Meanwhile 5 ml. had been evolved from the reduction cell. The final volume of the catholyte was 75 ml., so that 295 ml. of hydrogen had been absorbed. This represented a current efficiency of 98.3 percent. The catholyte was diluted with distilled water to 100 ml., and aliquot portions were taken for analysis.

**Calculation of Amount of Hydrogen Absorbed:**

The number of equivalents of hydrogen absorbed in the reduction cell was calculated as indicated below;

295 ml. of hydrogen collected over water at 744 mm. pressure and 29°C. is equivalent to

\[
\frac{295 \times 273 \times 744-30}{302 \times 760} = 250 \text{ ml. } H_2 \text{ at S.T.P.}
\]

This is the same as 250/22400 or 0.01119 moles of hydrogen, or 0.02238 equivalents of hydrogen, absorbed in the reduction cell.

**Pinacol Analysis:**

A blank solution was made up from 22.5 ml. acetone and 55 ml. 2 N NaOH, diluted to 100 ml. with distilled water. Three aliquots (20 ml.) of the diluted catholyte and of the blank solution were pipetted into 200 ml. erlenmeyer flasks. These samples and blanks were diluted with distilled water, and acidified to pH 2 (Fisher Alk-acid Test Paper) with dilute sulfuric acid. Periodic acid (4 ml. of 0.25 M) solution was added to each set of sample and blank, and the time noted. The three sets of
sample and blank were allowed different times for oxidation of the pinacol, a constant result for the amount of pinacol present showing that oxidation was complete. Typical oxidation times were 30, 50 and 70 minutes.

At the end of the oxidation time, saturated sodium bicarbonate solution (10 ml.) was added, and then 0.1 N sodium arsenite (25 ml.), to the sample and blank. The reduction of the iodate and periodate to iodide was allowed to proceed for 30 minutes. After addition of 10 percent potassium iodide solution (1 ml.) and 1 percent starch solution (4 ml.), the sample and blank were titrated with 0.1 N iodine solution to a dark purplish-brown end point which persisted for at least 30 seconds.

Results:

The results are indicated below:

Sample 1: Oxidation time---------------------- 30 minutes  
Reduction time---------------------- 30 minutes  
Volume of 0.1032 N \( \text{I}_2 \) for sample---------------------- 16.71 ml.  
Volume of 0.1032 N \( \text{I}_2 \) for blank---------------------- 7.59 ml.  
Volume difference---------------------- 9.12 ml.  
Moles pinacol present---------------------- 0.00235*

* The number of moles of pinacol was calculated from the equation:

\[
\text{Moles Pinacol} = \frac{(N_i)(V_s-V_b)}{2000(a.f.)}
\]

where \( N_i \) = Normality of iodine solution  
\( V_s \) = Volume of iodine solution for sample
Vb = Volume of iodine solution for blank

a.f. = Aliquot fraction of catholyte taken

Sample 2:  Oxidation time ------------- 50 minutes
Reduction time ------------- 30 minutes
Volume of 0.1032 N I₂ for sample -------------- 17.52 ml.
Volume of 0.1032 N I₂ for blank -------------- 8.36 ml.
Volume difference -------------- 9.16 ml.
Moles pinacol present -------------- 0.00236

Sample 3:  Oxidation time ------------- 70 minutes
Reduction time ------------- 30 minutes
Volume of 0.1032 N I₂ for sample -------------- 17.77 ml.
Volume of 0.1032 N I₂ for blank -------------- 8.83 ml.
Volume difference -------------- 8.94 ml.
Moles pinacol present -------------- 0.00230

Mean moles pinacol -------------- 0.00234

This requires 0.00468 equivalents of hydrogen.

Equivalents of hydrogen used for reduction to alcohol
= 0.02238 - 0.00468 = 0.01770

Moles of alcohol formed = 0.00885

Moles acetone reduced to pinacol = \( \frac{0.00468}{0.00885} = 0.53 \)

Moles acetone reduced to alcohol = \( \frac{0.00468}{0.0153} \)

Total acetone converted = 0.01353 moles, which is \( \frac{0.01353}{0.306} \times 100 = 4.1 \% \) of the acetone present.

The yield of pinacol is \( \frac{0.00468}{0.0153} \times 100 = 34.6 \% \) of the total acetone reduction products.
In the pinacol analysis procedure, the aliquot of the diluted catholyte taken for each sample varied with the amount of pinacol expected. If more than 0.005 moles of pinacol was expected, the aliquot taken was 10 ml., while if the pinacol yield was very low, 25 ml. aliquots were taken. In the analysis of catholytes potassium hydroxide, it was necessary to allow much longer oxidation times with periodic acid, and also longer reduction times with sodium arsenite, because of precipitation of potassium periodate, even in the acidified solution. Oxidation times of 1, 2, and 3 hours, and a reduction time of 1 hour, were generally adequate in this case.

Analysis of Alkali Concentration in Catholyte

In experiments where an accurate value of the alkali concentration was needed, appropriate samples of the diluted blank (for initial alkali concentration) and of the diluted catholyte (for final alkali concentration) were titrated with a standard hydrochloric acid solution to the phenolphthalein end point. Calculations of the mean alkali concentration during the electrolytic reduction could thus be made. Typical data and calculations are shown below.

Analysis for [NaOH] in Catholyte

Initial catholyte volume 74 ml., final volume 72 ml.
Catholyte and blank diluted to 100 ml.

A 4 ml. sample of the diluted blank was neutralized
by 8.53 ml. of 0.5021 N HCl.

Initial \([\text{NaOH}]\) = \(\frac{8.53}{4.00} \times 0.5021 \times \frac{100}{74} = 1.45 \text{ N}\)

A 4 ml. sample of the diluted catholyte was neutralized by 8.50 ml. of 0.5021 N HCl.

Final \([\text{NaOH}]\) = \(\frac{8.50}{4.00} \times 0.5021 \times \frac{100}{72} = 1.48 \text{ N}\)

Mean \([\text{NaCl}]\) = 1.465 N.

Reduction of Acetone at a Mercury Cathode

For experiments on the reduction of acetone at a mercury cathode, a pool of mercury contained in a bakelite cup of inside diameter 1.182 inches was used. The bakelite cup was fitted into the same porous pot used for reductions at an amalgamated copper cathode. Electrical contact with the mercury cathode was provided by a piece of platinum wire sealed into a glass tube, so that the wire was completely covered by the mercury pool, and did not make direct contact with the catholyte. In calculating the current density at the mercury cathode, the area of the mercury surface was taken as the inner cross-sectional area of the bakelite cup (7.10 cm\(^2\)), neglecting the curvature of the mercury surface. All other details of the reduction procedure and the pinacol analysis were the same as those used with an amalgamated copper cathode.

When sodium hydroxide was used as electrolyte, the
mercury cathode after the reduction contained much solid sodium amalgam. The quantity present, however, was not estimated. In the case of potassium hydroxide, an estimation of the amount of potassium amalgam in the mercury cathode was made by adding dilute sulfuric acid, and measuring the amount of hydrogen evolved. An appropriate correction was made for the amount of hydrogen used in the reduction of acetone. With tetramethylammonium hydroxide, no amalgam formation was observed.
PART II
THE REDUCTION OF OTHER ALIPHATIC KETONES IN ALKALINE SOLUTION AT AN AMALGAMATED COPPER CATHODE

CHAPTER I
LEVULINIC ACID

In contrast with most simple aliphatic ketones except acetone itself, levulinic acid and its salts are readily soluble in water. Since a high concentration of the ketone apparently favors higher yields of pinacol, reduction of levulinic acid seemed to present interesting possibilities, insofar as the expected pinacol has never been described in the literature.

\[
2 \text{-OOC-CH}_2\text{-CH}_2\text{-CO-CH}_3 \ + \ 2 \text{e}^- \ + \ 2 \text{H}_2\text{O} \rightarrow \left[\text{-OOC-CH}_2\text{-CH}_2\text{-CH}_3\right]_2 \ + \ 2 \text{OH}^- \\
\]

Tafel and Emmert\(^1\) obtained \(\gamma\)-hydroxy-valeric acid by reduction of levulinic acid at a lead cathode in sodium hydroxide, but were unable to find any pinacol type product.

A solution of potassium levulinate in excess potassium hydroxide was reduced at a rotating amalgamated copper cathode. The only product obtained was \(\gamma\)-hydroxy-valeric acid, which was recovered as \(\gamma\)-valerolactone in 58.4 percent yield. Periodate titration of the residue

\(^1\) Reference (1), page 4.
from distillation of the $\gamma$-valerolactone indicated no more than traces of the pinacol product were present.

**Experimental**

**Materials:**

Levulinic acid: the dark brown material obtained from Delta Chemical Co. was redistilled under vacuum, and a fraction, b.p. 111.5 - 114°C./2mm., was used.

Potassium Hydroxide: Mallinckrodt Analytical Reagent.

**Reduction of Potassium Levulinate at an Amalgamated Copper Cathode**

Cathode: a solid copper cylinder, with amalgamated surface. (see Figure 5);

Catholyte: redistilled levulinic acid (29.1 g., 0.25 mole) dissolved in 3 M KOH (100 ml.) contained in a porous clay pot, diameter 5.7 cm., height 14.9 cm., (Coors Porcelain Co.);

Anode: Fe gauze;

Anolyte: 3 M KOH solution contained in a 600 ml. electrolytic beaker;

Current: 2 amperes; Current density: 40 ma./cm.$^2$;

Temperature: 12 to 18°C.;

Potential across cell: 4.8 to 4.2 volts.

The current was passed through the cell for 9 hours, (18 amp. hrs.). Theory for 0.25 moles of ketone going to
Figure 5

Cathode surface
Area = 50 cm$^2$

$\frac{1}{4}$" copper rod

Insulation ("tygon" tubing)

Solid copper cylinder
3" x $\frac{3}{4}$" with amalgamated surface

Amalgamated Copper Cathode
pinacol, 6.7 amp. hrs.; going to alcohol, 13.4 amp. hrs.

At the end of the reduction, the cathode was coated with a gray deposit, which rubbed off easily, leaving a shiny mercury surface.

The catholyte was acidified with sulfuric acid, cooling in ice so that the temperature was never above 25°C. Much white solid (K₂SO₄) precipitated. The acid solution was extracted continuously with ether for 25 hours. After drying of the ethereal extract with magnesium sulfate, distillation of the ether left a residue (19.1 g.). When this was distilled under vacuum, there was some decomposition. The following fractions were obtained:

(1) b.p. 64-69°/5 mm. n_D^{20} 1.4313 weight 4.58 g.
(2) b.p. 69-66°/4.5 mm. n_D^{20} 1.4322 weight 8.87 g.
(3) b.p. 61-62°/4.5 mm. n_D^{20} 1.4306 weight 1.15 g.

Literature values for γ-valerolactone:

b.p. 83-84°/13 mm., n_D^{25} 1.4306

The infra-red spectra of these fractions were identical with those of an authentic sample of γ-valerolactone. The combined fractions (total 14.6 g.) represent a 58.4 percent yield, based on the levulinic acid.

The residue from the distilling flask was dissolved in aqueous methanol, and its pinacol content determined by periodate titration. From the analytical results, 0.00019 moles (0.044 g.) of the pinacol was present.
CHAPTER II

METHYL ETHYL KETONE

Methyl ethyl ketone differs from acetone in that it is much less soluble in water. Since high ketone concentration seems to be necessary for the production of pinacol by electrolytic reduction, it may be expected that yields of the pinacol would be reduced. Further, since the reduction potential of methyl ethyl ketone is even lower than that of acetone, (cf. page 46), it might be expected that current efficiencies in sodium or potassium hydroxide would also be low, since reduction of the electrolyte or of water would be easier.

These observations are supported by the few available references to this reduction in the literature. Thus Elbs and Brand\(^1\) obtained a poor yield of the alcohol and only traces of pinacol by reduction of methyl ethyl ketone in sodium hydroxide at a lead cathode. Similarly, Takagi\(^2\)

\(^{(1)}\) Reference (4), page 3.

\(^{(2)}\) Reference (3), page 4.

reported \(\alpha\)-butyl alcohol and traces of amines, but no pinacol, as products in the reduction with ammonium amalgam.

A solution of methyl ethyl ketone in tetramethylammonium hydroxide was reduced at a rotating amalgamated
copper cathode. The current efficiency with respect to ketone reduction was 99.6 percent. However the only product obtained was s-butyl alcohol, in almost quantitative yield. Periodate titration of the high boiling organic residue indicated the presence of only traces of the pinacol.

**Experimental**

**Materials:**

- Methyl Ethyl Ketone: Eastman Kodak White Label;
- Tetramethylammonium Hydroxide: prepared as on page 87.

**Apparatus:**

The apparatus used was the same as that for the acetone reduction experiments (page 95 et seq.).

**Reduction of Methyl Ethyl Ketone at an Amalgamated Copper Cathode in Tetramethylammonium Hydroxide**

Cathode: amalgamated copper cathode "B", (page 99), rotating at 2000 rpm;

Catholyte: methyl ethyl ketone (30 ml.) and 0.85 N Me$_4$NOH (40 ml.), total 69 ml.;

Anode: Pb;

Anolyte: 1 M Me$_4$NMeSO$_4$;

Current: 0.85 amperes, or 50 ma./cm.$^2$;

Temperature: 6 to 8°C.;

Potential across cell: 4.5 to 3.8 volts.
The current was passed for 4.25 hours, during which time 1700 ml. of hydrogen was evolved by the reference cell, and 6 ml. by the reduction cell. This represented 0.134 equivalents of hydrogen absorbed, with a current efficiency of 99.6 percent. The catholyte was heterogeneous throughout the reduction, and separated into two layers on standing.

Water was added, and the catholyte was distilled until the vapor temperature was 98.5°C. The distillate was saturated with sodium bisulfite to combine with the unreacted ketone. The aqueous solution was saturated with salt, and extracted with eight portions of ether, (total 200 ml.). The ethereal solution was dried over magnesium sulfate, and the ether removed through a fractionating column. The residue was distilled, and the fraction boiling at 89 to 97°C., (4.5 g.), was collected as crude ɑ-butyl alcohol.

The aqueous residue from distillation of the catholyte was saturated with sodium chloride, and extracted continuously with ether for a week. The ethereal solution was dried over magnesium sulfate, and the ether distilled off. The residue was a viscous tan-colored liquid (ca. 0.5 g.). This was taken up in ethanol, diluted to 100 ml. with distilled water, and its pinacol content determined by periodate titration. From the analytical results, 0.00027 moles (0.039 g,) of the pinacol
were present.

The absence of more than traces of pinacol was doubtless due to the low ketone concentration in the aqueous layer of the catholyte. The high current efficiency demonstrates the usefulness of tetramethylammonium hydroxide as electrolyte in electrolytic reductions of difficultly reducible compounds.
The purpose of this investigation was to determine the effect of various experimental conditions on the yield of pinacol obtained by reduction of acetone in alkaline solution. The reductions were carried out in an apparatus which permitted determination of the total amount of hydrogen utilized in acetone reduction. A satisfactory procedure, involving periodate titration, was developed for determining the amount of pinacol formed in the catholyte. Since pinacol and \textit{iso}-propyl alcohol are the only reduction products, the alcohol yields could be determined by difference, from the total hydrogen absorbed and the amount used to form pinacol.

An amalgamated copper cathode was shown to give yields of pinacol which are reproducible, and at least as good as those at a mercury cathode. The use of tetramethylammonium hydroxide as electrolyte gave better yields of pinacol than did the use of potassium or sodium hydroxide. In the cases of potassium and sodium hydroxide, alkali concentration had little effect on pinacol yields, but with tetramethylammonium hydroxide the maximum yields were obtained when the alkali concentration was about 0.6 M.

Increased acetone concentration improved the pinacol yield until the catholyte became heterogeneous at
high acetone concentrations. This was less significant at a rotating cathode. Addition of methanol to the catholyte lowered the pinacol yield.

A lower catholyte temperature gave higher pinacol yields. At the lower temperatures, rotation of the cathode also gave improved pinacol yields, but above 25°C., rotation of the cathode had no effect.

Current densities from 50 to 150 milliamperes per square centimeter had little effect in sodium or potassium hydroxide solutions, but in tetramethylammonium hydroxide, higher pinacol yields were obtained at the lower current density.

The use of potassium carbonate in place of potassium hydroxide did not affect pinacol yields, but replacement of tetramethylammonium hydroxide by tetramethylammonium methyl sulfate as electrolyte resulted in a lower pinacol yield.

Tetramethylammonium methyl sulfate was prepared by the reaction of trimethylamine with methyl sulfate in cold methanol. Tetramethylammonium hydroxide solutions were prepared from this salt by passing an aqueous solution through a column of Dowex-2, (a strongly basic anion exchange resin), or by electrolyzing the solution in a divided cell to form the hydroxide in the cathode compartment.
Reduction of levulinic acid in potassium hydroxide solution at an amalgamated copper cathode gave only traces of the pinacol type product. \( \gamma \)-Hydroxy-valeric acid was recovered from the catholyte as \( \gamma \)-valerolactone in 58 percent yield.

Reduction of methyl ethyl ketone in tetramethylammonium hydroxide solution at an amalgamated copper cathode gave an almost quantitative yield of sec-butyralcohol.
I, Glenn William Mansell, was born in Sanford, Manitoba, Canada, November 20, 1926. I received my secondary school education in the public High School at Lac du Bonnet, Manitoba, Canada. My undergraduate training was obtained from the University of Manitoba, Winnipeg, from which I received the degree Bachelor of Science with Honors in 1948. From this same institution I received the degree Master of Science in 1950, having completed my research in 1949, while in receipt of a Bursary from the National Research Council of Canada. Upon entering the Ohio State University in 1949, I was appointed as an Assistant in the Department of General Chemistry, which position I held until July 1951. From July 1951 to July 1952, I was appointed Monsanto Chemical Corporation Fellow. I was then reappointed as Assistant, holding this position until I completed the requirements for the degree Doctor of Philosophy in the Autumn Quarter of 1953.