The Kinetics of the Electroreduction of Acetone

Gerhart R. Hennig and George E. Kimball

The Kinetics of the Electroreduction of Acetone*

GERHART R. HENNIG AND GEORGE E. KIMBALL

Department of Chemistry, Columbia University, New York, New York

(Received July 18, 1944)

The electrolytic reduction of acetone in alkaline aqueous solutions at a mercury surface has been studied with the object of determining the kinetics of the formation of isopropyl alcohol and pinacol. The reduction rate has been studied at various acetone concentrations, in varying concentrations of sodium hydroxide, in solutions of sodium sulfate, sodium chloride, barium hydroxide, and potassium hydroxide. During electrolysis the rates of formation of isopropyl alcohol and pinacol were followed continuously. It is found that at low acetone concentrations the rate of formation of isopropyl alcohol is proportional to the acetone concentration, while the rate of formation of pinacol is proportional to the square of the acetone concentration. At somewhat higher acetone concentrations the pinacol rate becomes linear in acetone concentration, and near saturation the isopropyl alcohol rate becomes practically independent of acetone concentration. At constant current density, increasing the sodium hydroxide concentration decreases the yield of isopropyl alcohol and increases the yield of pinacol (except at high concentrations of acetone and sodium hydroxide). Substitution of chloride or sulfate for hydroxide causes an increase in the alcohol rate but lowers the pinacol rate. Substitution of barium for sodium stops the reduction completely. Substitution of potassium for sodium increases both yields. Increasing the current density is accompanied by a decrease in the fraction of the current which goes into isopropyl alcohol formation and pinacol formation. It is shown that these experimental results can be explained by a modification of the mechanism proposed by Müller. The acetone is first adsorbed on the mercury with the formation of a covalent bond. The product of the adsorption may dissociate from the surface as a free radical, in which case pinacol is the final product, or it may first add on a proton and then dissociate from the surface as an ion which adds a second proton to become isopropyl alcohol.

INTRODUCTION

THE reduction of acetone by an electric current presents a number of problems of which the most important are the effect of conditions on the current efficiency of the reduction, and the effect of conditions on the stage at which the reduction stops. Acetone, like all uncharged molecules, can be reduced only in the presence of an electrolyte. Under nearly all conditions this electrolyte is also reduced at the cathode.

The reduction in acid solutions has been studied by Tafel,[1] by Schall,[2] and by Müller.[3] In these solutions hydrogen is formed by the reduction of hydrogen ions, and it has been proposed by Leslie and Butler[4] that the reduction of acetone is caused by a secondary reaction of hydrogen atoms produced at the cathode. In these solutions the reduction products are isopropyl alcohol, propane, and mercury di-isopropyl if a mercury cathode is used.

The reduction in alkaline solutions has been studied by Wilson and Wilson.[5] In these solutions, with mercury cathodes, hydrogen is not formed. If sodium or potassium hydroxide is used as the electrolyte, alkali ions are reduced, forming sodium or potassium amalgam. Under these conditions atomic hydrogen would not be expected to be the reducing agent, and it seems more plausible that the acetone is directly reduced at the mercury surface. In these solutions the acetone is reduced only to isopropyl alcohol and pinacol.

Müller[3] has proposed the following mechanism: The base step in the reduction is the formation of a covalent bond between the central carbon atom of the acetone molecule and the cathode surface. The resulting surface compound has the structure

$$\text{CH}_3-\overset{\displaystyle \text{OH}}{\underset{\displaystyle [M]}{\text{C}}}-\text{CH}_3,$$
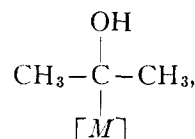
the [M] being a metal atom in the cathode surface. Müller postulates that this is formed by the hydration of acetone, followed by a displacement of one of the two resulting hydroxyls by the

* Publication assisted by the Ernest Kempton Adams Fund for Physical Research of Columbia University.
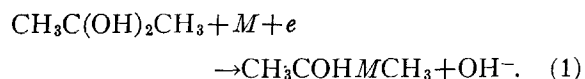[1] J. Tafel, Zeits. f. Elektrochemie 17, 972 (1911).
[2] C. Schall, Zeits. f. Elektrochemie 29, 537 (1923).
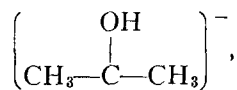[3] E. Müller, Zeits. f. Elektrochemie 33, 253 (1927).
[4] W. M. Leslie and J. A. V. Butler, Trans. Faraday Soc. 32, 989 (1936).

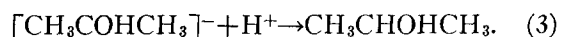[5] C. L. Wilson and K. B. Wilson, Trans. Electrochem. Soc. 80, 151 (1941).

metal atom:

$$CH_3C(OH)_2CH_3 + M + e$$
$$\rightarrow CH_3COHMCH_3 + OH^-. \quad (1)$$

If this surface compound now ionizes, the result is an ion

$$\left[\begin{array}{c} OH \\ | \\ CH_3-\underset{\cdot\cdot}{C}-CH_3 \end{array} \right]^-,$$

the reaction involving a second reduction:

$$CH_3COHMCH_3 + e$$
$$\rightarrow [CH_3COHCH_3]^- + [M]. \quad (2)$$

This ion may now pick up a proton to form isopropyl alcohol

$$[CH_3COHCH_3]^- + H^+ \rightarrow CH_3CHOHCH_3. \quad (3)$$

Alternatively the ion may react with an acetone molecule to form a pinacolate ion

$$\left[\begin{array}{c} OH \\ | \\ CH_3-\underset{\cdot\cdot}{C}-CH_3 \end{array} \right]^- + CH_3COCH_3$$

$$\rightarrow \left(\begin{array}{c} OH \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ O \end{array} \right)^-, \quad (4)$$
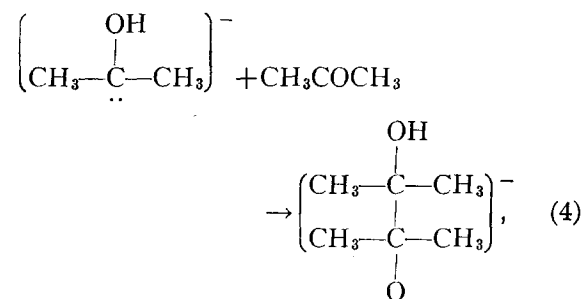
which picks up a proton to give pinacol. Müller also extends this mechanism to explain the formation of propane.

This work was undertaken to examine the kinetics of this reduction more closely, and to determine the effect of changing electrolyte and current density on the yields of the various products. As it will presently appear, the results do not agree entirely with Müller's mechanism, but a few slight changes in the mechanism produce agreement.

EXPERIMENTAL METHODS

Two different electrolytic cells were used. For concentrated solutions the cell was of approximately 200 milliliters capacity. The anode was a platinum wire bent around a cooling tube. The anode compartment was separated from the cathode compartment by a porous porcelain cup. A stirrer agitated both the catholyte and the
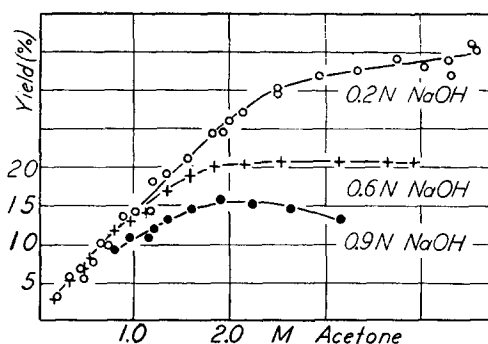

FIG. 1. Yield of alcohol plotted against molarity of acetone. Current density 0.0637 amp./cm².
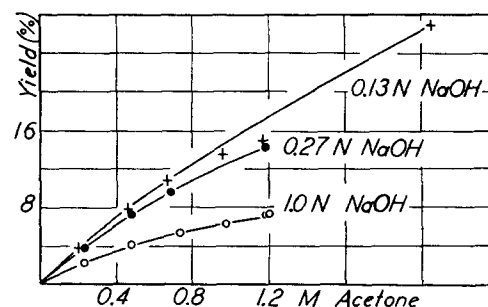

FIG. 1a. Yield of alcohol plotted against molarity of acetone. Current density 0.0360 amp./cm².

mercury cathode. For further stirring to remove sodium amalgam from the mercury surface, the mercury was forced by a siphon and suction arrangement to rise and fall in a side tube which contained strong acid. About one-fifth of the mercury was forced into the side tube every ten seconds. A side arm was provided for withdrawing samples and passing gases through the solution. The cell was closed by rubber stoppers which had been previously boiled in vacuum with paraffin.

For dilute solutions a smaller cell of approximately 65-ml capacity was used. This was of generally similar construction to the larger, but it was not provided with a side arm for passing in gases. The dilute solutions also required more violent agitation of the mercury in order to keep the amalgam concentration low enough to obtain reproducible results. The siphon which regulated the suction in the deamalgamation side tube was therefore modified so that half of the mercury in the cell was drawn into the side arm every ten seconds.

Runs were made in series in the following way.

The cathode compartment was first filled with a solution of the desired composition, and the anode compartment with 10 N sodium hydroxide. The electrolysis was then begun, adjusting the potential to keep a constant current density (usually 0.0637 amp./cm²—a total current of 0.800 amp.). The run was always stopped before there was a large change in the composition of the solution. At this point a sample of the cathode was withdrawn for analysis, but the current was kept flowing in order to prevent any sodium amalgam present from reacting with the solution. Fresh solution was added immediately in such amounts as would produce approximately the desired composition for the next run, and the next run was begun immediately. The exact composition for the new run was calculated later from the analysis of the solution at the end of the previous run and the amounts of material added. For each run the average of the compositions of the catholyte at the beginning and end was used in plotting the results.

It was found that diffusion of the reaction products (isopropyl alcohol and pinacol) through the porous cup was negligible. Nevertheless the
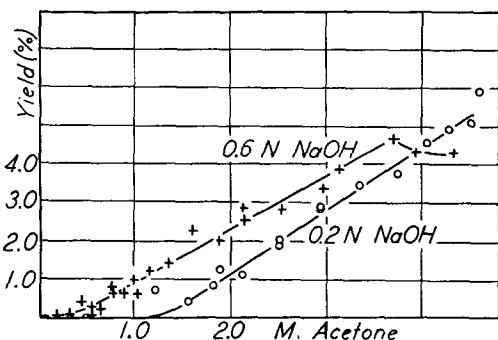

FIG. 2. Yield of pinacol plotted against molarity of acetone. Current density 0.0637 amp./cm².

FIG. 2a. Yield of pinacol plotted against molarity of acetone. Current density 0.0360 amp./cm².

variation in results noted by Wilson and Wilson[5] on changing porous cups was confirmed. The effect, although small, was outside the limits of experimental error, and no other explanation can be offered than that suggested by them on the basis of irregularities in the distribution of the current over the cathode surface caused by irregularities in the porous cup. Most of the results reported here were obtained with two cups which gave consistent results.

In a number of blank electrolyses it was found that neither isopropyl alcohol nor pinacol was reduced under the conditions used in these experiments.

The samples taken were diluted to 50 ml, if necessary, with dilute sulfuric acid so that the alkali concentration did not exceed 0.2 normal. They were analyzed by the following procedures.

Acetone was analyzed by converting it to iodoform and titrating the excess iodine. The precautions necessary in this procedure have been summarized by Goodwin.[6] We had ample opportunity to confirm the justification of all the precautions listed by Goodwin. Isopropyl alcohol and pinacol were never concentrated enough to interfere in this analysis.

Total alcohol and pinacol were determined by oxidation with standard dichromate.[7] A 10-ml sample approximately 0.01 M in alcohol in a dry flask was mixed with an equal volume of ice-cooled 0.1 N acidified standard dichromate, containing 18 N sulfuric acid. The mixture was kept in a thermostat at 25° for one hour, and was then diluted with 200 ml of ice-cold water, mixed with a potassium iodide solution, and titrated with sodium thiosulfate. It was found essential to precool the standard dichromate to prevent overheating during mixing, and also to perform the titration in an ice-cold solution to slow down the reaction between acetone and iodine which otherwise leads to fading end points. The results were reproducible to better than one percent, but a correction factor had to be introduced since the oxidation was not complete in one hour. This factor was determined by oxidations on known solutions to be 1.057.

Acetone was slightly oxidized by this procedure so that further corrections had to be
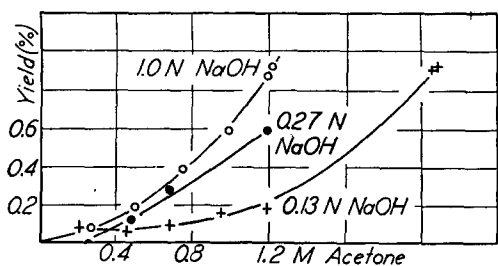
[6] L. F. Goodwin, J. Am. Chem. Soc. 42, 39 (1920).
[7] H. A. Cassar, Ind. Eng. Chem. 19, 1061 (1927).

made. The oxidation of acetone was apparently owing to the presence of diacetone alcohol formed in alkaline acetone solutions. This oxidation correction for acetone was determined for a series of solutions varying in acetone, alkali, and salt concentration. The correction factor increased linearly with the acetone concentration. In a 0.1 M acetone solution, 4.85×10^{-4} mole per liter of acetone, or 0.5 percent, was oxidized. For a given acetone concentration the oxidation factors remained independent of the alkali concentration up to at least 0.2 N, but the factor increased if the alkali concentration exceeded this value considerably. However, even a strongly alkaline solution of excessively large oxidation factor was found to return to a normal oxidation factor within a few hours after the excess alkali had been neutralized. The salt concentration did not affect the oxidation. For these reasons analyses on solutions which had at some time contained large concentrations of alkali were performed at least 24 hours after the sample had been diluted or neutralized. Acid solutions did not give a constant correction factor and were avoided.

Pinacol was determined by oxidation with periodic acid.[8] Isopropyl alcohol did not interfere. A very small amount of acetone was oxidized by periodic acid, amounting to 0.030 percent of the acetone concentration. It was confirmed that this correction does not depend on alkali or salt concentration.

Sulfate ion was determined by adding an excess of standard barium chloride after neutralization, and titrating with standard sodium carbonate solution using phenolphthalein.

Chloride ion was determined by the method of Mohr.[9] *Materials* acetone was redistilled twice, the first time from alkaline permanganate. It boiled at 56°.

Distilled water was freshly boiled to remove dissolved air.

Sodium hydroxide was rendered carbonate free by preparing a saturated solution.

Standard solutions of isopropyl alcohol were prepared from alcohol which had been dried over

[8] N. Allen, H. Y. Charbonnier, and R. M. Coleman, Ind. Eng. Chem. Anal. Ed. 12, 384 (1940).
[9] H. H. Willard and N. H. Furman, *Elementary Quantitative Analysis* (D. Van Nostrand Company, Inc., New York, 1939).

calcium oxide, redistilled over magnesium and a trace of iodine, and boiled at 60°.

The pinacol for standard solutions was recrystallized twice from water, dried first on a porous plate, then on filter paper, and weighed out immediately.

RESULTS

In order to put all of the experimental results on the same basis, the yield of isopropyl alcohol in moles for each run has been multiplied by 200 and divided by the number of faradays of current passed, and the yield of pinacol has been treated in the same way. Since the formation of a mole of either isopropyl alcohol or pinacol requires the use of two faradays, the numbers so obtained represent the percent of the current passed, which was used in the production of isopropyl alcohol or pinacol. Because of transport of metallic ions through the porous cup, it was not possible to measure exactly the amount of metallic ions reduced, but approximate measurements showed that the reduction of metallic ions was of the right order of magnitude to account for the balance of the current. Since there was no evidence of any other reduction process, the amount of reduction of metallic ions has been obtained by difference.

All measurements were made at $25° \pm 0.03°$.

The first series of measurements were made to show the effect of acetone concentration on the yields of isopropyl alcohol and pinacol. These runs were made at a current density of 0.0637 amp./cm², and in 0.2 N, 0.6 N, and 0.9 N NaOH. The results are shown in Figs. 1 and 2. A second similar series of runs was made at a lower current density of 0.0360 amp./cm² for the more dilute acetone solutions, using 0.13 N, 0.27 N, and 1.0 N NaOH as the electrolyte. These results are shown in Figs. 1a and 2a.

These figures show immediately that the yield of isopropyl alcohol in dilute acetone solutions is proportional to the acetone concentration. The yield of pinacol, on the other hand, at the lowest concentrations is proportional to the square of the acetone concentration. At moderate concentrations the pinacol yield is linear in the acetone concentration. Finally, at the highest concentrations of acetone, approaching saturation, the isopropyl alcohol yield reaches a limiting value

which depends strongly on the alkali concentration.

The same figures show that increasing the alkali concentration lowers the yield of isopropyl alcohol and increases the yield of pinacol, but in such a way that there is a net decrease in the amount of the acetone reduced. To study this effect further, a series of runs was made, again at a current density of 0.0637 amp./cm^2, but this time varying the NaOH concentration while the acetone concentration was held constant at 3.7 M, 3.0 M, 1.7 M, and 1.4 M. The results are shown in Fig. 3. It should be noted that in this figure the reciprocal of the isopropyl alcohol yield is plotted against the NaOH concentration. Theoretical considerations to be given later suggest that this plot should give a straight line. It
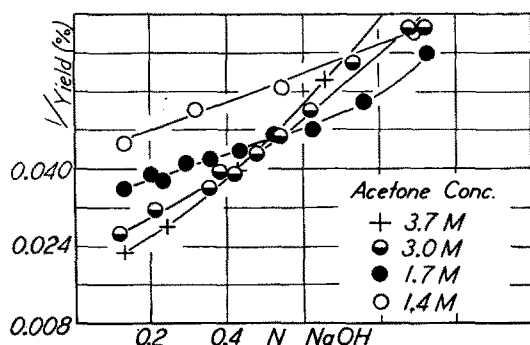

FIG. 3. Reciprocal of alcohol yield plotted against normality of sodium hydroxide. Current density 0.0637 amp./cm^2.

will be seen that this is approximately true, particularly at the lower concentrations of acetone and NaOH.

Next a series of runs was made to determine the specific effects of the nature of the electrolyte. Some typical results are shown in Fig. 4 which represents runs made in acetone concentrations of 3.0 M (in the NaOH and KOH curves) and 3.5 M (in the NaCl curve) for various concentrations of these electrolytes. The curves show that the nature of both the anion and the cation affect the yields of both isopropyl alcohol and pinacol. In order to show the cation effect experiments were tried on Ba(OH)$_2$, NaOH, and KOH. In the Ba(OH)$_2$ no reduction of acetone took place, while in KOH the yields of both products were always higher than in the same

concentration of NaOH. Thus the reduction of acetone is seen to be furthered by using a more difficultly reducible cation. Replacing the original hydroxyl ion by either sulfate or chloride increased the yield of isopropyl alcohol and lowered the yield of pinacol.

A series of runs was also made to determine the effect of amalgamating the mercury with sodium. In these the deamalgamation process was turned off and the sodium allowed to accumulate in the mercury. As the concentration of the amalgam rose the current yield of both isopropyl alcohol and pinacol rose until at an amalgam which was 0.1 molal in sodium the yield of acetone reduction products was three times what it was on pure mercury. The ratio of pinacol to isopropyl alcohol, however, showed only a very small rise as the amalgam concentration increased.

A number of runs were made in which the concentrations of acetone and electrolyte were held constant and the current density was varied. The results are shown in Figs. 5a–d. The peculiar wavy nature of some of these curves is similar to the effect found by Wilson and Wilson,[5] but it is less pronounced. There seems to be reason to suspect that the waviness could be removed completely by devising better methods of removing the sodium from the mercury. The only general observation which can be made is that decreasing the current density favors the reduction of acetone over that of sodium, the reduction to pinacol being increased more than the reduction to isopropyl alcohol.

Experiments were also tried in which the stirring rate was varied, and others in which air and hydrogen were bubbled through the solution. None of these had any effect on the rate of reduction.

DISCUSSION

Two mechanisms have been advanced to account for the production of isopropyl alcohol and pinacol from acetone. The older theory is that originated by Tafel[1] and most recently advanced by Leslie and Butler.[4] These authors state only that hydrogen atoms are the actual reducing agent. However, the only plausible possibilities based on this assumption are those in which the hydrogen atoms add directly to acetone
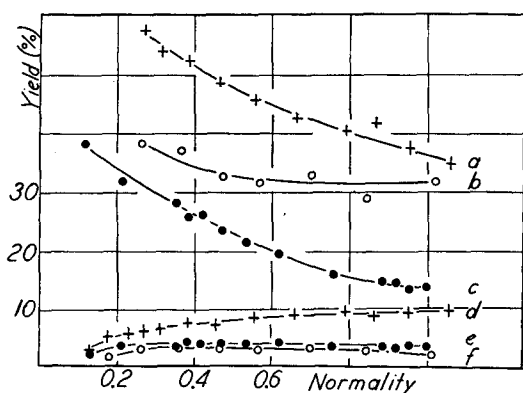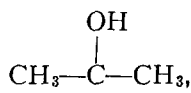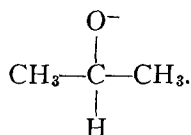
FIG. 4. Yield of alcohol and pinacol plotted against the normality of electrolyte. Current density 0.0637 amp./cm². a, alcohol yield in potassium hydroxide, 3.0 M acetone. b, alcohol yield in sodium chloride, 3.5 M acetone. c, alcohol yield in sodium hydroxide, 3.0 M acetone. d, pinacol yield in potassium hydroxide, 3.0 M acetone. e, pinacol yield in sodium hydroxide, 3.0 M acetone. f, pinacol yield in sodium chloride, 3.5 M acetone.
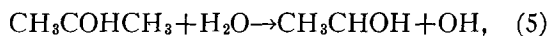
to form

$$CH_3—\underset{\cdot}{\overset{\overset{\displaystyle OH}{|}}{C}}—CH_3,$$

or

$$CH_3—\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}—CH_3.$$

The first of these could dimerize to form pinacol, or produce isopropyl alcohol by reaction with water, e.g., by

$$CH_3COHCH_3 + H_2O \rightarrow CH_3CHOH + OH, \quad (5)$$

or by reaction with a second hydrogen atom. However, none of these possibilities gives kinetics which are similar to those observed.

The direct reduction theory of Müller[3] comes closer to the observed facts. However, his mechanism predicts that the pinacol yield should be proportional to the square of the acetone concentration, and does not account for the observed change from this to a linear dependence on acetone concentration. Neither does his mechanism account for the large effect of hydroxyl ion concentration.

However, the following mechanism, which is quite similar in many respects to that of Müller, seems to account for most of the observed phenomena.
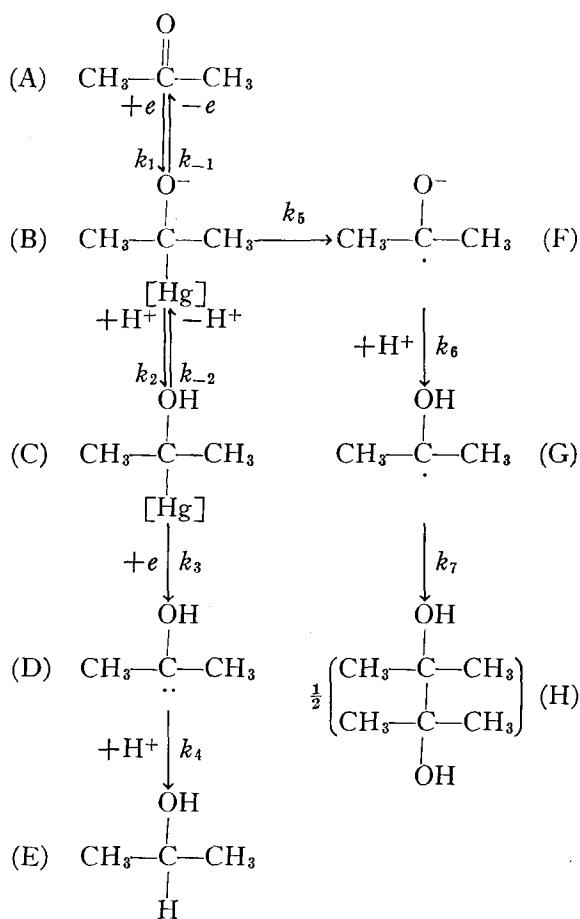
The first step in this process (reaction 1) is the attachment of acetone to the mercury surface. The polar character of the C=O group in acetone causes the positive carbon atom to be attracted to the negative mercury surface. A pair of unshared electrons on a mercury atom is donated
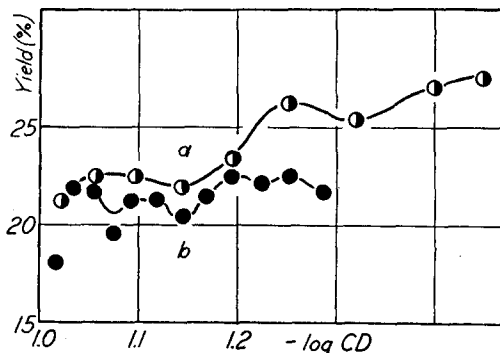

FIG. 5a. Yield of alcohol plotted against the log of the current density. a, 3.3 M acetone, 0.46 N sodium hydroxide. b, 3.8 M acetone, 0.5 N sodium hydroxide.
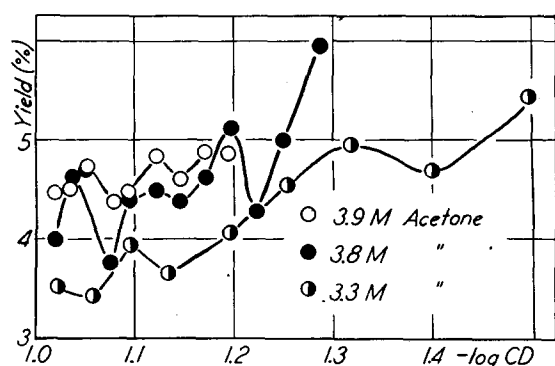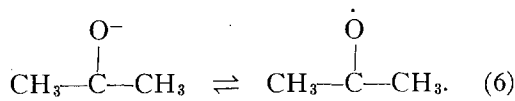
FIG. 5b. Yield of pinacol plotted against the log of the current density in 0.5 N sodium hydroxide.

to this carbon atom, forming a covalent bond, and displacing one of the electron pairs of the double bond to the oxygen, giving the oxygen atom a negative charge. This negative oxygen atom is strongly basic, and in the presence of water an acid-base equilibrium is set up (reaction 2). Under the influence of the electric field the acid (C) may ionize away from the surface (reaction 3) to form the carbanion D. This in turn is strongly basic and will capture a proton from water (reaction 4) to form isopropyl alcohol.

If the basic form of the adsorbed acetone (B) dissociates from the surface, it will ordinarily form acetone, but when the surface is sufficiently negative it may form an ion (F) which is simply an acetone molecule with an extra electron (reaction 5). This ion is stabilized to some extent by the resonance between structures

$$
\begin{matrix} O^- \\ | \\ CH_3\!-\!C\!-\!CH_3 \end{matrix} \rightleftharpoons \begin{matrix} O \\ | \\ CH_3\!-\!C\!-\!CH_3 \end{matrix}. \quad (6)
$$

This ion, however, will soon pick up a proton (reaction 6) to form (G), which dimerizes (reaction 7) to form pinacol (H).

It might be thought that (B) could also ionize from the surface to form an ion

$$
\left[\begin{matrix} :\!\ddot{O}\!: \\ | \\ CH_3\!-\!C\!-\!CH_3 \end{matrix} \right]^{=},
$$
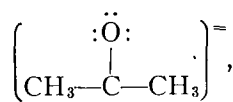
but this would violate the adjacent charge rule by having negative charges on two adjacent atoms, and would therefore be very unstable. Likewise, the dissociation of (C) from the surface

to form (G) directly is unlikely since the negative charge of the surface no longer aids the reaction, and in any case leads to kinetics which differ from those observed.

In setting up the kinetics of this mechanism a number of points must be observed. In alkaline solutions the protons for reactions 2, 4, and 6 will come from water. In the reverse of reaction 2 the formation of the base (B) will occur only by the reaction with OH$^-$. The concentration of OH$^-$ involved in this process is not the bulk concentration, but the concentration near the surface, which we shall denote by $[OH^-]_e$. Furthermore, reactions 1 and 3 involve electron transfers from the electrode, and therefore have rates which are affected by the potential of the electrode.

If the rate equations for this mechanism are now set up in the usual way, assuming that a steady state is reached in which the intermediates (B), (C), (D), (F), (G) all have constant concentrations, then the following equations are found for the rates of formation of isopropyl alcohol and pinacol, $I_{alc.}$ and $I_{pin.}$:

$$
I_{alc.} = \frac{k_1 k_2 k_3 [A]}{k_3(k_{-1}+k_2+k_5)+k_{-2}(k_{-1}+k_5)[OH^-]_e}, \quad (7)
$$

$$
I_{pin.} = \frac{k_1 k_5 (k_{-2}[OH^-]_e+k_3)[A]}{k_3(k_{-1}+k_2+k_5)+k_{-2}(k_{-1}+k_5)[OH^-]_e}. \quad (8)
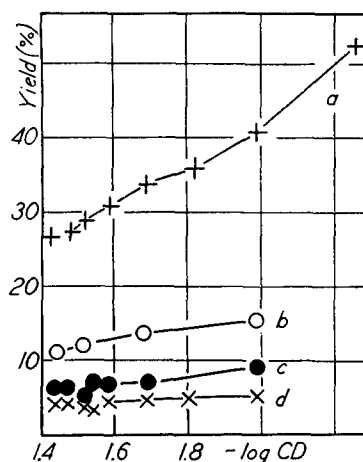$$

FIG. 5c. Yield of alcohol plotted against the log of the current density. a, 0.13 N sodium hydroxide, 2.3 M acetone. b, 0.35 N sodium hydroxide, 1.2 M acetone. c, 0.8 N sodium hydroxide, 1.1 M acetone. d, 1.1 N sodium hydroxide, 1.3 M acetone.

The rate of the acid-base equilibrium (k_2 and k_{-2}) is much larger than the rate of any of the dissociation reactions (k_{-1}, k_3, k_5) so that these equations may be approximated by the simpler equations

$$I_{\text{alc.}} = \frac{k_1 k_2 k_3 [A]}{k_3 k_2 + k_{-2}(k_{-1}+k_5)[\text{OH}^-]_e}, \quad (9)$$

$$I_{\text{pin.}} = \frac{k_1 k_5 k_{-2}[\text{OH}^-]_e[A]}{k_3 k_2 + k_{-2}(k_{-1}+k_5)[\text{OH}^-]_e}. \quad (10)$$

Before these equations can be applied an expression must be found for $[\text{OH}^-]_e$ in terms of measurable quantities. An exact treatment of this would be very complicated, but the following argument shows the important features. If no acetone is present, the discharge of Na^+ is controlled by the diffusion of NaOH to the electrode surface, and at the surface itself the NaOH concentration is practically zero. If acetone is present, on the other hand, the reduction produces OH^-, and the current of OH^- from the surface together with the current of Na^+ to the surface produces an ordinary transport process with no necessity of diffusion if the Na^+ current and the OH^- current are in the proper ratio. Under these circumstances the OH^- concentration would be equal to the bulk concentration right up to the electrode surface. In these experiments the situation is intermediate. The acetone reduction current is present, but the OH^- produced is not sufficient to eliminate the diffusion completely. Hence the OH^- concentration at the electrode is less than in the bulk of the electrolyte, but not zero.

In the most dilute acetone solutions, the OH^- concentration near the electrode is nearly zero, and one would expect the small deviation from zero to be proportional to the acetone current. Since this is owing mainly to the formation of isopropyl alcohol, it leads to a proportionality between the value of OH^-_e and the acetone concentration. If we put $[\text{OH}^-]_e = b[A]$, the equations for $I_{\text{alc.}}$ and $I_{\text{pin.}}$ in dilute solutions become

$$I_{\text{alc.}} = \frac{k_1 k_2 k_3 [A]}{k_3 k_2 + k_{-2}(k_{-1}+k_5)b[A]}, \quad (11)$$

$$I_{\text{pin.}} = \frac{k_1 k_5 k_{-2}b[A]^2}{k_3 k_2 + k_{-2}(k_{-1}+k_5)b[A]}. \quad (12)$$

We thus obtain results in agreement with the observed proportionality between $I_{\text{alc.}}$ and the acetone concentration and $I_{\text{pin.}}$ and the square of the acetone concentration.

In the more concentrated solutions the OH^- concentration is not reduced very much near the electrode, and we may assume that the value of $[\text{OH}^-]_e$ is approximately equal to the bulk con-
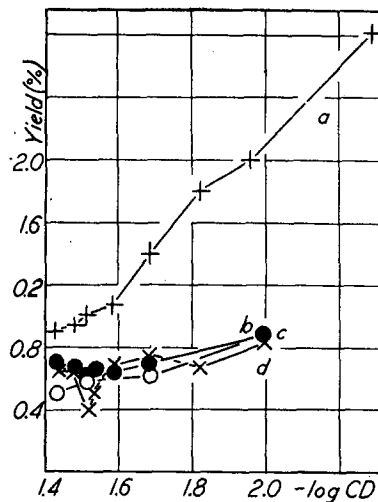

FIG. 5d. Yield of pinacol plotted against the log of the current density. a, 0.13 N sodium hydroxide, 2.3 M acetone. b, 0.8 N sodium hydroxide, 1.1 M acetone. c, 0.35 N sodium hydroxide, 1.2 M acetone. d, 1.1 N sodium hydroxide, 1.3 M acetone.

centration. Under these assumptions

$$I_{\text{alc.}} = \frac{k_1 k_2 k_3 [A]}{k_3 k_2 + k_{-2}(k_{-1}+k_5)[\text{OH}^-]}, \quad (13)$$

$$I_{\text{pin.}} = \frac{k_1 k_5 k_{-2}[\text{OH}^-][A]}{k_3 k_2 + k_{-2}(k_{-1}+k_5)[\text{OH}^-]}. \quad (14)$$

Thus both $I_{\text{alc.}}$ and $I_{\text{pin.}}$ should become proportional to the acetone concentration. This accounts for the straightening out of the plot of $I_{\text{pin.}}$ against acetone concentration.

These same equations predict that in all but the most dilute acetone solutions, the reciprocals of $I_{\text{alc.}}$ and $I_{\text{pin.}}$ should be linear functions of $[\text{OH}^-]$, which is in approximate agreement with the observations. They also explain why increasing the concentration of OH^- decreases the yield of isopropyl alcohol and increases the yield of pinacol.

These equations do not explain the leveling off of the plot of $I_{alc.}$ against acetone concentration. This may be owing to the fact that the solutions are nearing saturation. In this region an increase in concentration of acetone does not necessarily mean a corresponding increase in the activity of acetone. It would be interesting to plot these currents as functions of acetone activity rather than concentration, but the necessary data are not available.

The effect of substituting other negative ions for OH^- is explained by the fact that the concentration of OH^- affects the equilibrium of reaction 2. The effects are all in the direction predicted by this mechanism, but cannot be explained quantitatively because of the difficulty of analyzing the complex diffusion-conduction systems set up near the electrode in these systems.

The effect of changing the cation is tied up with the fact that such charges affect the electrode potential quite strongly. In the Ba^{++} solutions the potential necessary to reduce Ba^{++} is below that necessary to reduce the acetone. In K^+ the electrode is more negative than in Na^+. As a result k_1 and k_3 are increased, while k_{-1} is decreased. This results in an increase in the values of both $I_{alc.}$ and $I_{pin.}$.

The effect of current density is similar. At higher current densities the electrode is made more negative. This increases $I_{alc.}$ and $I_{pin.}$ and also the sodium current. In the discharge of Na^+ the whole of the electrode potential assists the discharge rate, but in the reduction of acetone on the surface the electrons do not immediately pass all the way through the electrical double layer. In reaction 1 the reduction electron moves only from the metal to the oxygen atom, and is completely removed from the surface only by reaction 3 or reaction 5. Thus the effect of the electrode potential is divided between the two steps. Because of this none of the k's is increased as rapidly as the sodium current, and hence it is easily seen that the increase in $I_{alc.}$ and $I_{pin.}$ is less than the increase in sodium current. The fraction of the current going into the reduction of acetone is decreased by increasing the current density.

The ratio $I_{pin.}/I_{alc.}$, which is given by

$$\frac{I_{pin.}}{I_{alc.}} = \frac{k_5 k_{-2}[OH^-]_e}{k_2 k_3}, \qquad (15)$$

is affected by the electrode potential only through k_3. Hence we would expect an increase in current density to decrease this ratio, which again is in agreement with experiment. This is also in agreement with the prediction of Semerano[10] that at very low current densities only pinacol would be formed.

[10] G. Semerano, Gazz. chim. ital. 62, 959 (1932).