

# The Anodic Behaviour of Substituted Acetic Acids, Part I. Diphenylacetic Acid

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(Received November 27, 1928)

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As is well known, the anodic behaviour of fatty acids is not always the same; some change chiefly to hydrocarbon, saturated or unsaturated, while others are transformed into esters or alcohols. The property of an acid undergoing such an electrolytic reaction, called the Kolbe reaction, becomes greatly modified when hydrogen in the alkyl radical is substituted by other radicals. For example, mono-, di- and tri-chloroacetic acids differ from each other and also from acetic acid itself in their anodic reaction.

To see how the anodic reaction of acetic acid is effected by a phenyl radical, diphenylacetic acid was electrolyzed with direct and alternating current and the results described below were obtained.

## I. Electrolysis with Direct Current

A fifty per cent solution of potassium diphenylacetate acidified with a drop of sulphuric acid was first electrolyzed in a bath provided with a diaphragm, by passing a current of 45 amperes per 100 sq. cm. at a temperature of below 30° for an hour. As there was produced no synthesized substance, the electrolysis was renewed with a bath having no diaphragm, into which a current of air free from carbon dioxide was passed, in order to drive off carbon dioxide formed in the electrolysis (see Fig. 1). Both electrodes consisted of similar platinum spirals and the temperature of the bath was kept below 38° by cooling with a freezing mixture.

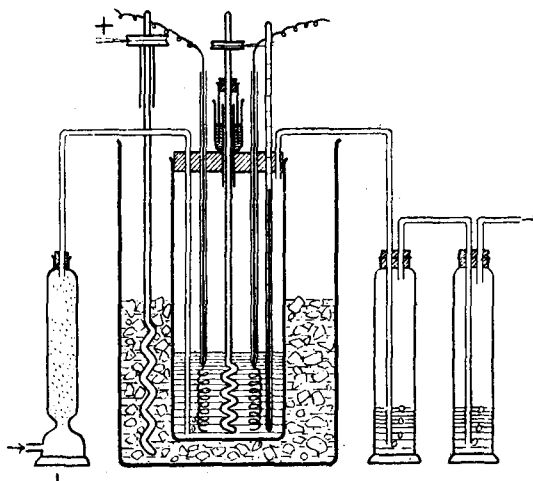


Fig. 1

After a current of 55 amperes per 100 sq. cm. had been passed for 15 hours, about 3.3 grams of a reaction-product consisting of diphenyl methyl alcohol (98%) and diphenylacetic diphenylmethyl ester (2%) were obtained. When lead was used as the cathode the yield of the alcohol, but not the ester, was increased to more than 3 times. This is no doubt due to the catalytic action of lead, for the same result may also be obtained with a platinum cathode, if some lead oxide is added to the bath.

The influence of external conditions on the electrolytic reaction was examined by measuring carbon dioxide evolved from the bath, on the assumption that the whole of the carbon dioxide is produced only by the Kolbe reaction:

(a) *Influence of the Concentration of the Electrolytic Solution*

Current density, 55 amp/100 sq. cm.; temperature, 25°

Conc. of solution (%)	CO <sub>2</sub>
20	not evolved
35	very little
50	much evolved

**(b) Influence of Current Density**

Sixty grams of 55% potassium diphenylacetate solution were electrolyzed for 4 hours.

Current density (amp./100 sq. cm.)	Temp.	CO <sub>2</sub> (gram)
2	0°	0
4	4°	0.008
20	20°	0.13
30	29°	0.25
55	39°	0.57

**(c) Influence of Acidity of the Solution**

Concentration of the solution, 55%; temperature, 29°; current density, 55 amp/100 sq. cm.

Acidity of solution	Time (hours)	CO <sub>2</sub> (gram)
Neutral	3	0
Acidified with diphenyl acetic acid	3	0
A drop of H <sub>2</sub> SO <sub>4</sub> added	3	0.41
A drop of HCl     ,,	3	0.22

From the results above stated it is seen (1) that the Kolbe reaction of diphenyl acetic acid does not take place with a solution more diluted than 20%; (2) that evolution of carbon dioxide is increased when current density increases, and as long as current density is kept below 4 amp/100 sq. cm. no appreciable amount of carbon dioxide is evolved; (3) that neither a neutral solution nor a solution made acidic with diphenyl acetic acid undergoes the Kolbe reaction, the solution acidified with a drop of sulphuric acid giving off carbon dioxide most abundantly.

**II. Electrolysis with Alternating Current**

In the electrolysis of diphenyl acetic acid, as it was found difficult to pass a direct current of high density maintaining at the same time

the temperature of the bath low, electrolysis with an alternating current in a bath having no diaphragm was undertaken, on the presumption that diphenyl acetic acid, as well as the substances which would be formed from it at the anode, would cathodically be inactive. Twenty grams of 50% potassium diphenyl acetate solution acidified with a drop of sulphuric acid were put in a U-tube cooled with a freezing mixture, and from both sides of the tube platinum spirals were inserted as the electrodes. Now an alternating current of about 3 amperes (90 am/100 sq. cm.) was passed for an hour, the temperature of the bath being kept sometimes at 10° and sometimes at 25°. During the electrolysis carbon dioxide was evolved from both electrodes, and some crystalline substance separated out. The electrolytic solution became coloured dark brown and showed a fairly strong alkaline reaction at the end of the electrolysis (see Fig. 2).

Now the crystalline substance formed by electrolysis was separated by filtration, washed well with water and recrystallized from alcohol. It crystallized in prismatic form and melted at 106°. The yield was about 1.5 grams. The results of analysis and of molecular weight determination showed it to be diphenylacetic diphenyl methyl ester.

0.1014 g taken for analysis gave 0.3181 g CO<sub>2</sub> and 0.0546 g H<sub>2</sub>O.  
C=85.57%, H=5.98% (calc. C=85.68%, H=5.86%).

The molecular weight was determined by the cryoscopic method using 16.25 grams of benzene as the solvent.

Substance taken 0.2126 g, depression of freezing point 0.176°, mol. wt. 372 (calc. 378).

It was also confirmed that the substance changes into diphenylacetic acid and diphenylmethyl alcohol, when saponified with 20% alcoholic potash solution.

The filtrate separated from the ester above stated was neutralized with dilute sulphuric acid and distilled with steam, when about 2 grams of a substance crystallizing in long needles were obtained. It melted at 65.5° and boiled at 298°. Its acetyl value was determined by acetylating 0.6444 gram of it.

Acetic anhydride required, 0.00351 mol. (calc. 0.00350). The substance was thus proved to be diphenylmethyl alcohol.

As the relation between the amount of the ester and of the alcohol produced by the direct current was seen to differ from that produced by the alternating current, experiments were performed to determine the difference definitely by electrolyzing 50% potassium diphenyl acetate solution with the current of 55 amp./100 sq. cm. at about 25°. In the case

of the direct current, about 3.2 grams of diphenylmethyl alcohol and 0.08 gram of diphenylacetic diphenylmethyl ester were produced after 15 hours' electrolysis, while with the alternating current, 0.1 gram of the alcohol and 1.0 gram of the ester were obtained after passing the current for an hour.

It might at first be conjectured that either one of the above two substances would be the primary product formed electrolytically and the other the secondary one derived from the former purely chemically. Such a conjecture was, however, proved to be quite groundless by the following two experiments.

Experiment 1.—Diphenylacetic diphenylmethyl ester was added to a concentrated caustic potash solution, and this solution was electrolyzed with a direct current of 80 amp./100 sq. cm. at 50°. Even after 10 hours' electrolysis no diphenylmethyl alcohol was yielded.

Experiment 2.—Diphenylmethyl alcohol was added to 10% potassium diphenylacetate solution and after the solution had been made faintly alkaline with caustic potash an alternating current was passed through it under conditions similar to those used for the electrolysis before described. But no ester could be obtained.

From the experimental facts so far observed, it may be concluded that the concentrated solution of potassium diphenylacetate undergoes the anodic reaction so as to yield diphenylacetic diphenylmethyl ester and diphenylmethyl alcohol which seem to be produced each independently from the other. The reason why the formation of diphenylmethyl alcohol predominates when the direct current is used, will not be difficult to understand if we admit that, in the course of electrolysis, hydroxylion in the neighborhood of the anode may possibly take such a concentration as is favourable to the formation of alcohols, even though the electrolytic solution is in vigorous agitation. As is generally known, neither a strongly alkaline solution nor an acidic solution is suitable for the formation of alcohol.

This investigation will be extended to other substituted acetic acids.

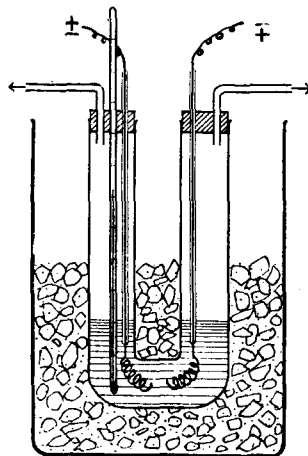


Fig.2

### Summary

1. The Kolbe reaction of potassium diphenylacetate was studied using direct as well as alternating current.

2. With the alternating current, the electrolytic reaction took place far more readily and produced diphenylacetic diphenylmethyl ester and diphenylmethyl alcohol, the amounts of which were found to differ from those produced with the direct current.

3. Experiments were conducted to see if one of the two products—ester and alcohol—is not the secondary one formed from the other purely chemically,

4. It was found that the use of an alternating current is preferable, when the substance to be electrolyzed and also the synthesized product are not reducible.

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