

CLXVI.—*Electrolytic Reduction. Part VII. The Catalytic Action of Copper.*

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It has already been placed on record (Trans., 1912, 102, 1024) that citral yielded a readily volatile portion when reduced electrolytically in an acid medium. The quantity of the fraction of low boiling point varied considerably in different experiments, and amounted to 90 per cent. of the total reduction product in certain cases. The largest yield was obtained when copper cathodes were employed, and at the same time the hydrogen absorption was greatest. This was quite contrary to past experience with aromatic compounds, and seemed worthy of further investigation. It was soon discovered that the course of the reaction varied most with copper cathodes, and hardly at all with lead. Massive copper was least active, whereas thin sheets gave good yields of highly reduced products. Thick sheet copper, which had been etched with concentrated nitric acid to a fine state of division, was extremely active; but the best results were obtained by depositing finely divided metal, during reduction, on to cathodes of copper foil. Both the rate and the amount of hydrogen absorbed increased with the activity of the metal. Similar experiments were also tried with other aldehydes and ketones, and many were found to behave like citral. All aliphatic and alicyclic compounds containing an unsaturated carbon atom and a carbonyl group in the conjugated position resembled citral. Saturated and unsaturated ketones and aldehydes not included in the above class behaved like benzaldehyde, and were most readily attacked by hydrogen evolved from surfaces of high supertension.

A further peculiarity was noticed with the substances of the citral class: they all readily formed compounds with the lead of the cathodes during reduction, and yielded heavy, fairly stable, red oils containing considerable quantities of the combined metal. The members of the other class did not generally behave in this manner in the following experiments. The aromatic compounds invariably left the lead cathode quite unattacked, and the remaining members reacted in a similar manner, or yielded only very small quantities of the metallic compound. The formation of lead compounds has already been investigated by Tafel (*Ber.*, 1911, 44, 323), but under different conditions, and no comparison can be made.

EXPERIMENTAL.

Small scale experiments, in which not more than 10 grams of substance was reduced at a time, were conducted in the apparatus already described (Trans., 1909, **89**, 1512). Larger quantities of material were frequently treated, and a useful modified procedure was introduced. The cathode and anode compartments were interchanged. The cathode was the usual flag electrode, bent into the form of a cylinder, and fixed into a rubber stopper with sealing-wax. A porous pot of small diameter also passed through the rubber stopper, and served as an anode compartment. An exit for the evolved hydrogen was also provided. This apparatus was frequently used, as the progress of the reaction could be kept under strict observation, and the cathode solution could be easily maintained at a constant temperature. The solvent used throughout the following experiments was absolute alcohol. The electrolyte was sulphuric acid or potassium hydroxide, in the form of a 5 per cent. solution of the total volume of liquid. The electrodes were sheet lead or electrolytic copper foil. A small quantity of copper sulphate crystals were added to the cathode solution when copper electrodes were used. This caused a slow deposition of copper in a flocculent and finely divided state on the cathode, and exerted a powerful catalytic action.

Mesityl Oxide.

Many preliminary experiments were conducted with mesityl oxide. The cathode solution contained 5 grams of mesityl oxide, 25 c.c. of alcohol, 50 c.c. of water, and 5 per cent. of sulphuric acid or potassium hydroxide. Many forms of copper electrodes were tried in acid media. These were usually cut from commercial sheet copper, and measured from 0.5 to 0.7 mm. in thickness. The reaction was very irregular, and it was soon found that some electrodes were far more active than others. The activity of these electrodes diminished gradually after being used for several experiments without cleaning, but recovered by dipping into concentrated nitric acid. All electrodes which had worn thin by continual cleaning greatly increased in activity. The copper used in the final experiments was cut from foil made from the electrolytic metal, and varying in thickness between 0.05 and 0.1 mm. This was cleaned by dipping into concentrated nitric acid, and washed in cold water. A piece of very fine copper gauze soldered to a stout wire was also tried in some of the later experiments. The best results were obtained with the copper foil, especially if 0.5 gram of copper sulphate crystals were added to the cathode solution, in order to

keep the surface of the metal freshly deposited as long as possible. The following results were obtained in a comparative series, using sulphuric acid as electrolyte:

Cathode material.	Lead.	Copper.	Copper.	Copper.	Copper.
Thickness of cathode	2 mm.	0.7 mm.	0.5 mm.	0.06 mm.	0.07 mm.
Copper sulphate addition	none	none	none	none	0.5 gram.
Hydrogen absorbed in 4 hours.....	750 c.c.	900 c.c.	700 c.c.	900 c.c.	1000 c.c.

A similar set of experiments was also conducted in alkaline solution with a sheet lead and a copper foil cathode. The absorption was then equivalent to 700 c.c. and 600 c.c. of hydrogen respectively in four hours' time.

The constituents of the reduction product varied very considerably in different experiments. Increased activity of the cathode caused a diminution in the percentage of the fraction of high boiling point; thus the best yield of deoxymesityl oxide was obtained in alkaline solution on copper cathodes, whereas the largest quantity of readily volatile product was produced in an acid medium and an electrode of copper foil. The former experiments yielded 70 per cent. of the fraction of high boiling point, but the latter only 3—4 per cent. The readily volatile portion was examined in detail in the following experiments. A solution of 50 grams of mesityl oxide, 50 c.c. of sulphuric acid (10 per cent.), 100 c.c. of water, 100 c.c. of alcohol, and 2.5 grams of copper sulphate crystals were reduced in the bottle previously described. The apparatus was cooled in a stream of cold water. A current of 3 amperes was passed through the mixture for ten hours, which was insufficient for complete reduction. The cathode had an area of 75 sq. cm. on one side. The product had separated into two layers, which were carefully removed and treated alone. The top layer was washed with small quantities of water, dried, and fractionated. The above washings were added to the lower layer, and the mixture was distilled over a small flame to remove the alcohol, which was then used as the solvent for the next reduction. This procedure was not absolutely necessary, but it was found to be a useful method of accumulating workable quantities of product dissolved in the aqueous alcoholic portion.

The final alcoholic distillate was washed, dried, and fractionated as above. Altogether, 280 grams of mesityl oxide were reduced, and the following mixed fractions were obtained:

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|----------------------------------|----------------------------------|
| (I.) B.p. 58—71°, 61 grams. | (II.) B.p. 72—100°, 16 grams. |
| (III.) B.p. 105—140°, 140 grams. | (IV.) B.p. above 140°, 15 grams. |

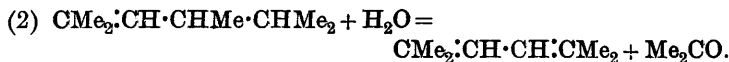
Each fraction was washed with water to remove the last trace of alcohol, dried, and redistilled.

(I) boiled chiefly at 57—67° in two portions of equal quantities above and below 62°. Both these were mixtures, and contained unsaturated hydrocarbons. The portion of lower boiling point was obtained later in a pure state, as will be described below. The fraction of higher boiling point was probably composed chiefly of *isohexylene*, $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\text{Me}$, with which it corresponded in all respects. The corresponding *isohexane* may also have been present, but the quantity was too small to isolate.

Fraction (II) was a mixture of (I) and (III), and need not be further considered. Fraction (III) was split up into two main portions, boiling respectively at 115—120° and 120—124° in approximately equal quantities. These were both treated in the same manner, and were heated on the water-bath for several hours with four times their volume of dilute sulphuric acid. The distillate was collected, washed with water, dried, and fractionated, when 10 grams of a saturated hydrocarbon were obtained, boiling at 57—58°. This substance corresponded in all respects with the hexane, $\text{CHMe}_2\cdot\text{CHMe}_2$, which was probably present in the fraction of low boiling point mentioned above. The washings of this hydrocarbon contained considerable quantities of acetone (semicarbazone, m. p. 180°), which was evidently one of the decomposition products of hydrolysis. It seemed probable, therefore, that mesityl oxide had been reduced partly according to the following equation:



This complex hydrocarbon then became hydrolysed progressively by the sulphuric acid of the electrolytic mixture, and the subsequent treatment on the water-bath:



The above reaction is similar to the formation of dibenzyl from benzaldehyde. It should be remarked, however, that the amount of acetone produced by hydrolysis was in excess of that required by the above equation, and was produced in all probability from unchanged mesityl oxide. The flask on the water-bath still contained considerable quantities of an unattacked oil. This was removed and shaken with a saturated solution of sodium hydrogen sulphite, when a white, crystalline compound was deposited, from which methyl *isobutyl* ketone was isolated. It boiled at 116—117°, and formed a semicarbazone melting at 132°. The two portions mentioned above yielded the same products, but that

of higher boiling point contained appreciably larger quantities of unchanged mesityl oxide, which was detected in the increased yield of acetone on hydrolysis. The unsaturated alcohol *isohexenol* was not isolated, but its presence was suspected in these fractions.

Fraction (IV) consisted chiefly of unchanged mesityl oxide and a small quantity of deoxymesityl oxide.

Citral.

A large number of comparative experiments were conducted with citral. Twenty-five grams of citral, 150 c.c. of alcohol, 50 c.c. of 4*N*-sulphuric acid were treated at the same time in a duplicate experiment. The cathode measured 75 sq. cm. on one side. A current of 2 amperes was employed for ten hours (overnight). The products from 50 grams of material were distilled in a current of steam, with the following results:

1. Material of cathode.	2. Weight of copper sulphate added to cathode solution.	Weight of volatile product.
Sheet lead (10 mm.)	none	7.5 grams
Sheet copper (0.7 mm.).....	none	10 "
Copper foil (0.06 mm.)	none	27 "
Copper foil (0.06 mm)	1 gram	45 "

The last experiment contained an addition of 1 gram of copper sulphate crystals dissolved in the cathode solution. The volatile product was similar in all cases, and contained chiefly the mixture of geraniols already described (*loc. cit.*).

Pulegone.

A mixture containing 15 grams of pulegone, 40 c.c. of sulphuric acid (10 per cent.), and 60 c.c. of alcohol was reduced, employing a current of 2 amperes for six hours. Two experiments were conducted, using sheet lead and copper foil as cathodes. The superficial area was 75 sq. cm. in both cases. One gram of copper sulphate was dissolved in the cathode solution when copper foil was used as electrode.

The product was diluted with water, extracted with ether, dried, and fractionated. It was noticeable that the usual lead compound was formed as a heavy, red, insoluble oil in the first experiment, and the lead cathode was considerably etched. The product boiled chiefly at 202—207°, and was menthone; but there was also present a fraction of higher boiling point. The yield of menthone was 95—100 per cent. with the copper cathode, and 50—60 per cent.

with the lead. The residue in the latter case was a complex lead containing red oil.

Carvone.

Twenty grams of carvone, 100 c.c. of alcohol, 100 c.c. of dilute sulphuric acid, and 2 grams of copper sulphate were dissolved and reduced with a current of 2 amperes for four hours. The cathode was copper foil, measuring 75 sq. cm. on one side. The product was diluted with water, and treated in the usual manner. The oil boiled at 218—222° with practically no residue, and was composed almost entirely of dihydrocarvone.

Many of the above results did not agree with those already recorded for aromatic compounds. It has been shown in several papers (*loc. cit.*) that the benzene derivatives are most readily attacked when reduced in the presence of metals of the highest super-tension. Only one record has been made (*Trans.*, 1906, **89**, 1524) of an exception to this rule, and this experiment has not been successfully repeated. The result was probably accidental, but further work will be undertaken to reproduce the correct conditions. It seemed of interest to conduct reduction experiments on closely allied compounds in order to determine the connexion between the rate of reduction and chemical constitution. This was carried out, and the results are given in the table below. Each reduction was conducted at ordinary temperature with 5 grams of substance, except in the last example, where 10 grams were used at a temperature of 50°. A set of three experiments was conducted in series, one with a sheet lead cathode, the second with copper foil, and the third as a blank, to which no reducible material was added. This series was repeated several times in most cases, and the product was sometimes extracted and examined. 0.5 Gram of copper sulphate dissolved in a small quantity of water was always added when copper foil was employed as cathode, but due allowance was made for this on recording the hydrogen absorption due to reduction. The compounds bracketed are closely allied in constitution, and differ only in respect to the unsaturated linking.

The second and third columns show the amount of hydrogen absorbed on lead and copper cathodes respectively, and the fourth column shows the result for no absorption at all.

The time of each experiment varied somewhat on account of convenience, but no experiment was stopped until the rate of hydrogen absorption had diminished almost to nothing.

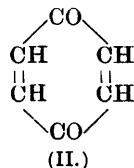
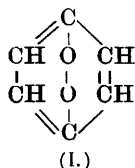
The following table shows that the $\alpha\beta$ -unsaturated aldehydes and ketones of the aliphatic and alicyclic series are more reducible in the presence of finely divided copper than with sheet lead. This

Compound reduced.	Hydrogen absorbed with electrodes.		
	1. Sheet lead.	2. Copper foil.	3. Blank.
{ Mesityl oxide	700 c.c.	800 c.c.	1400 c.c.
{ Methyl isobutyl ketone	350	200	2000
{ Citral	650	1000	1500
{ Citronellal	140	0	1800
{ Methylheptenone (natural)	750	0	1200
{ Dimethylmesityl oxide	780	850	1600
{ Pulegone	570	650	1590
{ Menthone	450	80	1600
{ Carvone	650	800	1330
{ Dihydrocarvone	300	0	1300
Cinnamaldehyde	950	490	1030
Benzil	830	600	1570
<i>p</i> -Benzoquinone	790	780	1650
{ Crotonaldehyde	620	700	1000
{ Butaldehyde	390	130	1010
Styryl methyl ketone (10 grams)	1240 (50°)	850 (50°)	1600

property was quite characteristic for copper, and no similar catalytic action was observed with any form of lead. The nature of the reaction was quite different, however, with the two metals in question. The product of the lead cathode always contained considerable quantities of a heavy, red oil. This substance was a combination of the partly reduced carbonyl compound and the lead of the cathode. The exact nature was not closely studied.

The formation of these insoluble lead salts probably accounted for the relatively slow rate of reduction. They were obtained in appreciable quantities only from the $\alpha\beta$ -unsaturated aldehydes and ketones, as previously stated. The carbonyl compounds of the aromatic series did not yield the least trace of these lead compounds, and the saturated aldehydes and ketones only small quantities. The reaction appeared to be characteristic of the aliphatic and alicyclic series, and is suggested as a test for $\alpha\beta$ -unsaturation of carbonyl compounds of these groups.

It seemed of interest to investigate the nature of the quinones according to the above relations. The constitution of these substances is still open to some doubt, but is generally accepted as one of the following:



(I) represents a peroxide of the aromatic series, which, on electrolytic reduction, should partly produce resins. The rate of reduction would be greatest on lead cathodes, and the resin formation least.

Compound (II) is obviously derived from an alicyclic unsaturated ketone, and should produce little or no resin on reduction. Reduction might take place at the carbonyl groups, the unsaturated linkings, or at both. Experience shows that only the ketone groups are attacked with the formation of a hydroxyl compound of the aromatic series. The latter fact excludes the possibility of the formation of lead salts, which are never produced with aromatic compounds. It was anticipated, therefore, that *p*-benzoquinone would resemble pulegone and carvone in its behaviour towards electrolytic hydrogen, with the exception of the formation of compounds with the lead of the electrodes. The following are some of the results recorded :

<i>p</i> -Benzoquinone reduced, grams.	Cathode material.	Copper sulphate. grams.	Hydrogen absorbed in c.c.	Control in c.c.
{ 5	Copper foil	0.0	870	1770
{ 5	" "	0.5	880	1770
{ 5	" "	1.0	880	1770
{ 5	Copper gauze	0.5	870	1820
{ 5	Lead sheet	0.0	820	1820
{ 5	Copper gauze	0.0	1060	1640
{ 5	Lead sheet	0.0	1060	1640
{ 3	Copper gauze	0.0	600	1800
{ 3	Lead sheet	0.0	550	1800

The quantity of material reduced at one time usually amounted to 5 grams. The *p*-benzoquinone was dissolved in a mixture of alcohol and ethyl acetate, and added to the requisite quantity of dilute sulphuric acid and copper sulphate solution. The cathodes measured 20 sq. cm. on one surface, and the current was maintained at 1 ampere throughout. The first product of reduction was quinhydrone, which frequently separated from solution in lustrous, greenish-brown crystals of metallic appearance. The formation of this insoluble intermediate product led to considerable irregularity in the results, and comparison is admissible only in experiments of the same series (bracketed). Even in these cases a small amount of local heating was liable to arise and affect materially the rate of reduction. The last two experiments were conducted with smaller quantities of *p*-benzoquinone to avoid this difficulty, and it was expected that no separation would take place. This anticipation was fulfilled, but did not greatly alter the comparative rates of reduction. There is a second consideration with respect to quinhydrone which should not be overlooked. This substance, according to the generally accepted formula, is no longer a ketone, and certainly not an unsaturated ketone. It is, however, an unstable combination in solution, and probably dissociates into quinol and *p*-benzoquinone. Further reduction was probably due to the

presence of the dissociated quinone, and not to the dissolved intermediate formation.

An attempt was next made to reduce pulegone on lead cathodes without the formation of the metallic compound. It was thus hoped to obtain results comparable to those of *p*-benzoquinone. This was accomplished by using sheet lead which had not been cleaned with concentrated nitric acid. It was then found that the metal sometimes remained unattacked throughout a considerable part of the experiment. The amount of hydrogen absorbed was then practically the same on both copper and lead, and amounted to 665 c.c. and 670 c.c., for the complete reduction of 5 grams of pulegone. It appears, therefore, that *p*-benzoquinone has the properties of an $\alpha\beta$ -unsaturated ketone, which, however, forms an aromatic reduction product.

In conclusion, I wish to express my thanks to the Government Grant Committee for partly defraying the cost of this work.
