CXL.—*Electrolytic Oxidation.*

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IN carrying out experiments on the electrolytic oxidation of organic compounds it is advantageous to employ a solvent which mixes with water in all proportions and at the same time does not interfere to any considerable extent with the conductivity of the solution. It must not of course be readily oxidisable. Three classes of compounds suggest themselves, of which acetone, acetic acid, and pyridine may be taken as types. Of these, acetone is by far the most useful, as it can be readily removed by distillation. Pyridine has the characteristics of an unsaturated or aromatic compound, and as a consequence readily forms tarry products which, however, are soluble in water and may be easily removed. It also forms complex soluble tars with other aromatic compounds, which often causes a serious loss of material. In these three solvents the electrolytic oxidation of compounds represented by the general formula

was conducted. Many such compounds are known, of which benzoin is the most important. By changing the groups denoted by X and Y

it was hoped to gain a clear idea of the reactions taking place at the anode. Two reactions are possible and may be represented by the following equations :

Two of these products may be oxidised still further according to the equations

Thus, in the case of benzoin the three products obtained, namely, benzil, benzoic acid, and benzaldehyde, are all accounted for in the above equations. When the groups represented by X and Y contain an unsaturated carbon atom, however, a further reaction takes place which cannot be indicated in the form of an equation. Complex resinous substances are formed, the constitution of which is quite unknown. These are extremely interesting, and to gain some knowledge of their mode of formation the oxidation of the unsaturated aliphatic compounds was studied. On comparing the structure of the three aldehydes, namely, benzaldehyde, furfural, and acrolein, a striking similarity of grouping will be seen :

It will be noticed that each compound contains the group
—CH:C·CHO,

and as a consequence each might be expected to have some common characteristic. Each of these substances yields complex products at the anode, this being very marked in the cases of furfural and acrolein. That this is due to the unsaturated carbon atoms is borne out by the fact that neither the saturated aliphatic aldehydes nor such saturated ring compounds as camphor possess the same property. It is interesting to note that similar complexes are formed also under the influence of a silent discharge or where a high frequency discharge is used. This again occurs only when unsaturated compounds are employed or are formed during the reaction. It is very probable therefore that a similar phenomenon is taking place at or near the anode, which may be the result of a variable electrical strain set up between the moving molecules and the anode.

The presence of these tars makes the final separation very tedious and the conditions necessary for their formation were studied with a view to their final elimination. The potential of the anode discharge has a very marked effect on their formation, the amount produced

being greatest when the *E.M.F.* reaches the highest value. This is seen very clearly in the cases where the acids sulphuric, hydrochloric, and hydrobromic are used as electrolytes. The potential of discharge of the anions is as follows :

$$\text{SO}_4'' = -0.7 \text{ volt, Cl}' = -0.31, \text{Br}' = +0.06.$$

In sulphuric acid solutions, tarry matter is always formed, but is often absent in the case of hydrochloric acid, and in no case is it formed where hydrobromic acid is employed. Very strong solutions of sulphuric acid also favour the formation of these complex substances, but this is probably a purely chemical reaction and independent of the current.

The stability of compounds containing the unsaturated carbon atom is very remarkable. Very little reaction takes place at all when the oxidation is conducted at a low potential, the double link apparently having a retarding influence on the velocity of the oxidation. This protective influence becomes less as the chain is lengthened, the saturated part of the molecule predominating. This retarding action is even greater where a ring compound is introduced. As the potential of the anode is increased, the stability becomes less, and considerable quantities of carbon monoxide are evolved.

This throws a great deal of light on the purely chemical methods of oxidation. The double link is always considered the weakest part of the molecule, and its position is determined by means of such oxidising agents as potassium permanganate. The latter is very vigorous in its action and has, probably, a high oxidation potential which accounts for the decomposition at this point.

Having investigated the mechanism of these reactions, the method was applied to determine the molecular structure of benzofuroin. Two formulæ are possible, represented by (i) and (ii) :

The half of the molecule containing the furfural group most readily decomposes with formation of tarry products, but the remaining part will form benzaldehyde or benzoic acid according to which of the above formulæ is assumed to be correct.

In the actual experiment, benzaldehyde was completely absent, which points to formula (ii) as being correct.

From the compounds anisoin and piperonyloin, nothing but tarry matter could be isolated. This might have been due to the difficulty of separating the reaction product, but otherwise this fact shows that

the potential of the complex formation is either lower or very near that of the simple oxidation.

In a paper by James (*J. Amer. Chem. Soc.*, 1899, **21**, 889) it was observed that benzoïn on oxidation in alcoholic solutions gives a small quantity of benzoic acid, but the chief product was of a tarry nature. If, however, hydrochloric acid was used as an electrolyte a good yield of benzil was obtained and the tar formation was small. This confirms the work of the present paper, that these complex bodies are formed preferably at high potentials.

Benzoïn.

The anode compartment consisted of a porous pot of about 400 c.c. capacity, round which was wound a stout platinum wire to serve as cathode. The porous pot was placed in a stout glass jar containing 10 per cent. sulphuric acid to act as electrolyte in the cathode compartment. This in turn was placed in another glass jar containing cold water to keep the whole apparatus cool during each experiment. The porous pot was fitted with a cork bored at the centre, through which a platinum stirrer could be freely rotated. This stirrer, whose superficial area was 37.5 sq. cm., was used also as the anode. In each of the following experiments 15 grams of benzoïn were dissolved in the solvent used. In the first five experiments acetone was employed and the benzoïn dissolved in 300 c.c. of this substance. Dilute sulphuric acid was then added gradually to this mixture, shaking the whole time, until the total volume measured 375 c.c. In this way most of the benzoïn remained in solution. The mixture was then poured into the porous pot and the current started. The oxidised product was invariably dark in colour, due to the formation of some tarry matter. The acetone was then removed by distillation from a water-bath and the non-volatile residue separated. This consisted of a mixture of unchanged benzoïn, benzaldehyde, benzil, benzoic acid, and tarry substances. The whole was distilled in steam for several hours. Benzaldehyde rapidly passed over, followed by the benzil, benzoic acid, and a little benzoïn. The distillate was made alkaline with sodium carbonate and filtered, the benzil and benzoïn remaining on the filter paper. To remove the benzaldehyde, the filtrate was extracted with ether and the ethereal layer dried and evaporated on a water-bath. The remaining solution was acidified with sulphuric acid and the benzoic acid also extracted with ether. The mixture of benzoïn and benzil was shaken with a little alcohol to dissolve the benzil, and filtered. In this way these two substances were separated almost completely. The mixture of benzoïn and tarry matter in the distilling flask was rendered alkaline with sodium hydroxide and filtered. The

filtrate contained the tar, and the benzoin remained on the filter paper. The tarry matter was again precipitated with dilute sulphuric acid and filtered. In this way most of these substances could be removed from solution, and any small quantity still remaining in solution was extracted with ether. In experiment (6), 300 c.c. of acetic acid were employed instead of acetone. Here the oxidised product was distilled in steam after partial neutralisation of the acetic acid. In this case the ethereal solution of benzoic acid contained also acetic acid, which was removed by careful distillation. In experiment (7), the solvent consisted of 250 grams of pyridine, to which was added 160 c.c. of dilute sulphuric acid. After the oxidation, the product was acidified with sulphuric acid and steam distilled as before. Any pyridine in the distillate was removed from the ethereal solution of benzaldehyde with a little sulphuric acid. The small quantities of benzil obtained in these experiments were mixed together and crystallised once from alcohol. The product melted sharply at 91° , whilst pure benzil melts at 90° . The benzoic acid melted at 121° after being twice recrystallised from alcohol, and was undoubtedly pure. Part of the benzaldehyde was allowed to oxidise in the air to the corresponding acid, which melted at 121° . Another portion was treated with phenylhydrazine and gave a product melting at 154° after being four times recrystallised from alcohol.

TABLE I.

Number of the experiment.	Solvent.	Strength of the acid, per cent.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Benzoic acid in grams.	Benzaldehyde in grams.	Benzil in grams.	Benzoin in grams.	Tar in grams.	Total oxygen absorbed by the benzoin, per cent.
1	Acetone	10	1.0	6	5.5	5.2	4.6	0.5	4.5	1.3	19.6
2	"	10	4.0	6	9.5-10	4.8	3.2	0.5	6.0	1.5	16.8
3	"	30	4.0	6	9.5-10	3.0	1.8	0.5	6.5	5.0	17.6
4	"	3	4.0	6	9.5-10	5.5	3.0	0.5	6.0	1.3	17.2
5	"	10	0.25	6	2.75	5.5	3.7	0.5	4.5	1.0	17.9
6	Acetic acid	10	1.0	6	4.0	2.2	2.2	0.5	10.0	0.5	9.0
7	Pyridine	5	1.0	6	5.0	2.2	1.8	0.25	9.7	0.0	7.9

In Table I the results of seven experiments under varying conditions are given. The last column shows the total amount of oxygen absorbed by the benzoin to form the substances tabulated, the tar being calculated as benzaldehyde. This absorption does not vary much where the same solvent is used, although the products of decomposition do not show the same constant value. The figures of experiment (1) indicate the greatest amount of reaction, and for this reason the conditions used here were adhered to as near as possible in the concluding work. Apparently the tarry colouring matter is most

readily obtained when a large amount of sulphuric acid is present, as is the case in experiment (3). On the other hand, a low current density acts very unfavourably to the formation of this substance, as is seen in number (5). The amount of benzaldehyde and benzoic acid present is greatest where the current density and the concentration of the sulphuric acid are kept low, the former being the most variable. In experiments (6) and (7), different solvents were used. In both cases the total reaction was much less than in the former ones.

In experiment (6), where acetic acid was used as solvent, the percentage amount of benzoin converted into benzaldehyde, benzoic acid, and tar is almost the same as in (1), under the same conditions, but with a different solvent.

The method of obtaining the gaseous products is described later. These experiments gave results agreeing with those conducted with benzaldehyde, and for that reason are not given in detail. Very small amounts of carbon monoxide were formed and even smaller quantities of carbon dioxide. Benzoin is not so soluble as benzaldehyde in acetone, however, and these results are therefore not so accurate as the former, as it is necessary to employ very concentrated solutions.

In the next series of experiments the three products, benzaldehyde, benzoic acid, and benzil, were in turn oxidised and the results tabulated in the following tables.

Benzil.

In these experiments the method of manipulation was exactly the same as in the previous ones. In each case 10 grams of benzil were oxidised and the results are tabulated in Table II. As before, the greatest amount of action was obtained in acetone solutions, whilst in the case of acetic acid this was reduced to half, and to an even smaller amount where pyridine was employed. In each case benzoic acid was produced, accompanied by small quantities of tar, the quantity of the latter being very small in pyridine solutions.

TABLE II.—*Benzil.*

Number of experiment.	Solvent.	Volume of the solvent, per cent.	Strength of the acid, per cent.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Benzoic acid in grams.	Tar in grams.	Unchanged substance in grams.	Amount of oxygen absorbed, per cent.
1	Acetone	66	6·6	1·0	6·0	4·5	7·6	1·3	1·9	14·0
2	Acetic acid	66	6·6	1·0	6·0	6·0	3·5	1·0	4·6	7·1
3	Pyridine	66	6·6	1·0	6·0	9·0	0·4	0·0	8·7	0·7

TABLE III.—*Benzoic Acid.*

1	Acetone	50	5·0	1·0	6·0	3·5	—	1·1	8·9	—
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Only one experiment was conducted with benzoic acid, as the action proceeded very slowly, and the only product formed was a small amount of tarry matter.

TABLE IV.—*Benzaldehyde*.

Number of experiment.	Solvent.	Volume of the solvent, per cent.	Strength of the acid, per cent.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Benzoic acid in grams.	Tar in grams.	Unchanged substance in grams.	Amount of oxygen absorbed, per cent.
1	Acetone	50	5.0	1.0	6.0	4.0	2.1	1.5	2.6	11.3
2	Acetic acid	36	9.6	1.0	6.0	4.0	1.1	0.5	6.3	3.4
3	Pyridine	28	2.8	1.0	6.0	4.5	2.1	0.0	7.0	6.5

The method of manipulation was the same as in the previous cases, benzoic acid and tar being the products. In each case 10 grams of benzaldehyde were oxidised and the results are tabulated in Table IV. The tarry matter was calculated as benzoic acid and the total oxygen is given in the last column. As in the previous cases, the largest amount of reaction took place in acetone solutions, due probably to the small internal friction of the solute. Thus the diffusion of the benzaldehyde into the oxidising layer round the anode will be much greater than in the other experiments. Experiment (3) shows that the activity of the oxidising material is greater in pyridine solution than in those experiments where acetic acid was used. This, however, is contrary to the previous experiments.

In the next series (Table V), the gaseous products obtained on oxidising benzaldehyde electrolytically are given. These were determined in Hofmann's apparatus for the electrolysis of water described in a previous paper (Trans., 1905, **87**, 198). In each case two experiments were conducted. In the first a mixture of sulphuric acid and solvent was electrolysed, and then a fresh solution containing a small quantity of benzaldehyde. The gases at the anode consisted of a mixture of carbon dioxide, oxygen, and carbon monoxide, which were analysed in Hempel's bulbs, the differences in each set being due to the decomposition of benzaldehyde. To determine the strength of the current, a gas coulombmeter was coupled in series with the above apparatus. The results were calculated for 500 c.c. of oxygen liberated, and tabulated for comparison. In each case the oxidising surface of the anode was 12.5 sq. dcm. These results could never be quantitative where the solvent was readily attacked by the oxygen liberated at the anode, as is the case with acetone and pyridine, for then it is very probable that the introduction of benzaldehyde interferes with the oxidation to a considerable extent. Thus, as the solvent diffuses into the active zone round the anode it is decomposed

by the oxygen available at that point, but when benzaldehyde is present only a part is used in this way, the rest being absorbed by the solute. In this way the amount of some of the gaseous products may be less in the presence of benzaldehyde than when the pure solvent is used. This is seen in the case of pyridine in experiments (3) and (3a), where actually less carbon dioxide is obtained when the aldehyde is present.

TABLE V.—*Benzaldehyde. Gaseous Products.*

Number of experiment.	Solution.	Current in amperes.	E.M.F. in volts.	Pressure in mm. of Hg.	Temperature.	Oxygen liberated in the coulombmeter in c.c.	Total volume of mixed gases in c.c.	Carbon dioxide in c.c.	Oxygen in c.c.	Carbon monoxide in c.c.	Oxygen reacting with the benzaldehyde, per cent.
1	Acetone = 50 % sulphuric acid = 5 %	0.048	6.0	760	17°	500	189.4	4.1	134.5	6.2	8.3
1a	Benzaldehyde = 3.3 % conditions as in 1	0.044	6.0	760	17	500	159.4	5.1	102.3	13.7	
Difference between 1 and 1a								1.0	32.2	7.5	
2	Acetic acid = 36 % sulphuric acid = 9.5 %	0.040	4.0	778	16°	500	457.0	10.3	421.7	5.1	1.4
2a	Benzaldehyde = 3.5 % conditions as in 2	0.050	4.0	770	16	500	450.0	11.1	418.4	7.1	
Difference between 2 and 2a								0.8	3.3	2.0	
3	Pyridine = 28 % sulphuric acid = 2.8 %	0.050	16.0	757	16°	500	218.6	22.3	170.6	6.0	6.5
3a	Benzaldehyde = 2.5 % conditions as in 3	0.050	16.0	760	17	500	187.5	21.9	149.1	9.0	
Difference between 3 and 3a								- 0.4	21.5	3.0	

TABLE VI.—*Cuminoin.*

Number of experiment.	Solvent.	Strength of the acid.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Acid in grams.	Aldehyde in grams.	Unchanged substance in grams.	Tar in grams.
1	Acetone	5 per cent.	1.0	6	4.5	3.5	3.3	2.3	1.0
2	Pyridine	5 „	1.0	6	10.0	0.5	0.3	2.4	0.0

In experiment (1), ten grams of cuminoin were dissolved in 200 c.c. of acetone, and the whole made up with dilute sulphuric acid to 300 c.c. After the oxidation, the aldehyde was separated by steam distillation,

the acid and unchanged product passing over only very slowly. The latter were separated by means of sodium carbonate, as was also the tar from the unchanged substance in the distilling-flask.

In experiment (2), the amount of pyridine was 200 c.c., made up to 300 c.c. with dilute sulphuric acid. After the oxidation, the pyridine was neutralised with hydrochloric acid, and the whole filtered after standing overnight. The filtrate was extracted with ether and added to the portions already obtained.

The aldehyde and acid were driven off in a current of steam and weighed. As might have been predicted, the oxidation proceeds much in the same way as benzoin, with this difference, however, that cuminoïn appears to be rather more stable than in the former case.

Furoïn.—Ten grams of this substance were dissolved in 150 c.c. of pyridine; 150 c.c. of 10 per cent. sulphuric acid were then added to the solution and the mixture electrolysed. The product was distilled in a current of steam for several hours. Pyridine quickly passed over, followed by bright yellow needles of furil. Sulphuric acid was added to the distillate until it no longer had an odour of pyridine, and the whole was extracted with chloroform. The extract was dried over calcium chloride, and the chloroform evaporated. The residue, after being crystallised once from alcohol, melted sharply at 162° , and was undoubtedly furil. The residue from the steam distillation was acidified, diluted with water, and filtered. The filtrate was extracted with chloroform, and this portion added to the residue on the filter paper. The tar was removed with a solution of sodium carbonate from the unchanged furoïn, and each substance weighed. In this experiment no furfural was detected, and only a trace of furan carboxylic acid was present. The following table gives the details of this experiment :

TABLE VII.

Amount of sulphuric acid.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Furil in grams.	Tar in grams.	Unchanged furoïn in grams.	Oxygen absorbed.
5 per cent.	1	6	4.5—5.0	3	1.5	3	21.1 per cent.

In order to calculate the total amount of oxygen reacting with the furoïn, the tar was reckoned as furil. This quantity agrees very closely with that obtained in the case of furfural in acetic acid solution. Experiments were also tried with acetone and acetic acid solutions, but in each case the amount of tar was much larger, and for this reason this method was abandoned.

TABLE VIII.—*Benzfuroin*.

Number of experiment.	Solvent.	Strength of the acid.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Acid in grams.	Aldehyde in grams.	Benzfural in grams.	Unchanged product in grams.	Tar in grams.
1	Acetone	5 per cent.	1.0	6	3.0	3.2	0.0	0.0	—	2.0

In this experiment, 10 grams of benzfuroin were dissolved in 150 c.c. of acetone, sufficient water and hydrochloric acid were added to make the whole up to 300 c.c., and the mixture subjected to the action of the current as in the previous cases. The acetone was evaporated on a water-bath, and the dark mixture distilled in a current of steam for several hours. In this way a white, crystalline solid was obtained in the receiver. The distillate was made strongly alkaline with sodium hydroxide and filtered, the filtrate acidified with hydrochloric acid and extracted several times with ether. The ethereal extract, on evaporation, yielded benzoic acid, melting at 120° , quite free from any furan derivatives. The part insoluble in alkali was unchanged benzfuroin, and the substance left in the distilling-flask was tar. Similar experiments were conducted in acetone solutions, using sodium hydroxide, sodium sulphate, and sulphuric acid as electrolytes, but in these cases the result was the production of nothing but tarry matter. This was also the case when acetic acid was used as solvent with sulphuric acid as electrolyte.

In pyridine solutions with either lead or platinum anodes, most of the substance was obtained unchanged, but there was invariably a small loss in weight not to be accounted for. The absence of benzaldehyde and benzfural points to the following as being the correct formula for benzfuroin, $C_6H_5 \cdot CO \cdot CH(OH) \cdot C_4H_3O$, and not $C_6H_5 \cdot CH(OH) \cdot CO \cdot C_4H_3O$, for it has been shown that the group $C_6H_5 \cdot CH(OH) \cdot CO-$ is readily oxidised to $C_6H_5 \cdot CHO$ and $C_6H_5 \cdot CO \cdot CO-$, whilst the group $C_4H_3O \cdot CH(OH)-$ forms tarry products with extreme ease. In all cases where acetone was used as a solvent, except when hydrochloric acid was the electrolyte, very considerable quantities of tarry matter were formed. These were somewhat less when acetic acid was used as a solvent. In pyridine solutions the loss in weight is due to the formation of a tarry substance readily soluble in water, as will be shown in a later part of the paper. In these experiments the potential of the oxidation is evidently too high, and it is only when the *E.M.F.* of the discharged anion is lowered, as in the case of hydrochloric acid, that any substances are formed capable of being identified.

Piperonyloin and Anisoin.

In acetone solutions with either sulphuric or hydrochloric acid as electrolyte, both piperonyloin and anisoin were converted almost completely into dark tarry products. Those obtained from sulphuric acid solutions were completely soluble in sodium hydroxide, and could thus be readily separated from the unchanged product. On acidifying, these were partly reprecipitated in the form of brown, amorphous powders and partly remained in solution. Thus the total product was always less than the amount of substance at the beginning of the experiment. The tarry matter obtained in the case of hydrochloric acid was almost insoluble in sodium hydroxide, and could not, therefore, be separated from the unchanged product. With hydrobromic acid as electrolyte, practically no reaction took place, whilst when pyridine was used the whole of the product remained in solution. In this case the solution obtained when the oxidation was complete was almost black. This was treated with sodium carbonate, and the whole evaporated on a water-bath to dryness. The residue obtained in this way consisted of sodium sulphate, unchanged sodium carbonate, and a dark semi-solid tarry substance. This was shaken up with a small quantity of water, filtered from the sodium salts, and again evaporated to dryness. In this way, 8—9 grams of tar were obtained, a quantity in excess of that taken for the experiment, the excess being supplied by the pyridine itself.

TABLE IX.—*Piperonyloin.*

Number of ex- periment.	Solvent.	Strength of acid.	Acid used.	Current in am- peres.	Ampere hours.	E.M.F. in volts.	Tarry matter in grams.	Unchanged pro- duct.
1	Acetone	5 per cent.	Sulphuric acid	1·0	3·0	6·0	3·0	1·0
2	"	5 "	Hydrochloric acid	1·0	3·0	13·0	4·5	—
3	"	5 "	Hydrobromic acid	1·0	3·0	5·0	0·4	4·6
4	Pyridine	5 "	Sulphuric acid	1·0	3·0	3·5	—	—

TABLE X.—*Anisoin.*

1	Acetone	5 per cent.	Sulphuric acid	1·0	3·0	6·0	3·0	1·0
2	"	5 "	Hydrochloric acid	1·0	3·0	4·5	4·5	—
3	"	5 "	Hydrobromic acid	1·0	3·0	3·5	0·5	4·5
4	Pyridine	5 "	Sulphuric acid	1·0	3·0	11·0	—	—

Ethyl Benzoin and Benzoin Acetate.

In all the preceding experiments, the group $\text{-CO}\cdot\text{CH(OH)-}$ has remained constant, and the groups attached to the free links only have been altered. These exercise a very important influence on the products of decomposition, and it became of interest, therefore, to determine the action of a substituent in other parts of the molecule. Ethyl benzoin and benzoin acetate are both readily procurable, and were chosen for the experiments. In (1) and (2), ten grams of substance were dissolved in 200 c.c. of acetone, and made up to 300 c.c. with dilute sulphuric acid. After the current had passed for six hours through the mixture, the acetone was removed on a water-bath and the residue distilled in a current of steam. In this way the benzaldehyde passing over was obtained in the first fractions and kept separate. This was followed by benzoic acid and a little unchanged ethyl benzoin or benzoin acetate. These were separated exactly as has been described in previous experiments. It was thought that some product containing the groups $\text{=CH}\cdot\text{O}\cdot\text{C}_2\text{H}_5$, or $\text{=CH}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ might be formed, but none was discovered, the ethyl and acetyl radicles apparently being eliminated either by hydrolysis or by oxidation during the formation of benzaldehyde. In experiment (3), ten grams of benzoin acetate were dissolved in 200 c.c. of acetic acid, and made up to 300 c.c. with dilute sulphuric acid. After the oxidation, the acetic acid and benzaldehyde were quickly removed by steam distillation and separated as in previous cases. The residue in the flask was made alkaline with sodium hydroxide and filtered when cold. In this way the tar and benzoic acid were removed together. These were precipitated from the alkaline solution with hydrochloric acid and extracted with ether, and the benzoic acid finally obtained by sublimation. It will be seen from these experiments that the course

TABLE XI.—*Ethyl Benzoin.*

Number of experiment.	Solvent.	Strength of the acid.	Current in amperes.	Ampere hours.	E.M.F. in volts.	Benzoin acid in grams.	Benzaldehyde in grams.	Unchanged substance in grams.	Tar in grams.
1	Acetone	10 per cent.	1.0	6	4.0	3.2	2.2	5.0	0.2

TABLE XII.—*Benzoin Acetate.*

2	Acetone	10 per cent.	1.0	6	4.5	1.3	2.2	4.6	2.1
3	Acetic acid	5 „	1.0	6	4.5	0.9	0.5	7.0	0.7

of the oxidation is interfered with in no marked manner by the introduction of the ethyl and acetyl radicles into the hydroxyl group. The most noticeable feature is the small amount of tar formed in experiment 1.

Unsaturated Aliphatic Compounds.

Experiment I. Allyl Alcohol.—These experiments were conducted in the same apparatus as in the case of benzoin. Thirty grams of allyl alcohol were made up to 400 c.c. with 10 per cent. sulphuric acid and a current of 1 ampere passed through the solution for twenty-four hours. After a short time an insoluble rubber-like substance was formed, which at the end of the experiment amounted to 2 grams. The mixture was extracted several times with ether and fractionated. Several grams were obtained at 45—65°, consisting of acrolein, and a similar quantity at 65—110°, which was chiefly allyl alcohol. A small amount was obtained above this temperature and the residue charred. The viscid, rubber-like substance was insoluble in water, sodium hydroxide, alcohol, or ether. The fraction above 110° was an acid which decolorised bromine and probably consisted of acrylic acid.

Experiment II.—The same experiment was made with acrolein with the same result.

Experiment III. Crotonaldehyde.—Thirty grams of this substance made up to 300 c.c. were treated as in Experiment I. On the anode there were obtained 2 grams of a viscid substance resembling in all respects that obtained in Experiment I. The ethereal extract on fractionation gave a small quantity of unchanged substance distilling below 150°, and the remainder passed over below 200°, consisting chiefly of crotonic acid. Both these fractions were small. In these experiments the *E.M.F.* was 3.5 volts on commencing, but this rose during the experiment. The anode was the one used in previous cases and measured 37.5 sq. cm.

Unsaturated Compounds.

Gaseous Products.—These experiments were carried out as the previous ones and the results calculated and tabulated for comparison in Table XIII. It will be seen from experiments (2) and (4) that allyl alcohol is by no means readily oxidisable, but is acted on to about the same extent as benzoin in acetone solutions under similar conditions. As the potential increases, however, the stability of this unsaturated compound decreases very considerably, as is seen in experiments (3) and (5), the actual amount of oxygen taking part in these reactions being three times as great. The amount of carbon dioxide liberated remains nearly constant all through, but the carbon monoxide formed increases considerably with the potential. It has been shown by

several authors that the alcohol group decomposes in contact with electrolytic oxygen to form small quantities of carbon dioxide and carbon monoxide (Elbs and Brunner, *Zeit. Elektrochem.*, 1900, **6**, 604), and the same applies to the aldehyde group (*loc. cit.*). These quantities vary very slightly with the potential. The small amount of carbon dioxide liberated in these experiments is due then to the normal decomposition of the alcohol and aldehyde groups, but the large increase in the amount of carbon monoxide is formed by the rupture of the double bond. In experiments (4) and (5) this increase is from 2·7 per cent. to 13·3 per cent. of the total oxidation. This explains the instability of the double linking to ordinary chemical oxidising agents. The potential of the oxygen liberated from such substances as potassium permanganate and nitric acid is very high, and consequently the chain of carbon atoms is attacked at the double bond. The same result is observed in the case of crotonaldehyde, as experiments (6) and (7) show, but not to such a considerable extent. The lengthening of the chain may, however, increase the stability of this substance just as in the case of saturated compounds (*loc. cit.*). Experiments (1) and (8) show the effect of a change in concentration of acrolein. The amounts of carbon dioxide and carbon monoxide are only slightly affected, but the total oxygen reacting is changed very considerably. A comparison of these experiments with corresponding ones conducted with saturated compounds gives very remarkable results. Elbs and Brunner (*loc. cit.*) have shown that in the case of propyl alcohol the amount of oxygen reacting with this substance varies from

TABLE XIII.—*Unsaturated Compounds.*

Number of experiment.	Solution.	Current in amperes.	E. M. F. in volts.	Pressure in mm. of Hg.	Temperature.	Oxygen liberated at the anode in c.c.	Volume of mixed gases in c.c.	Carbon dioxide in c.c.	Oxygen in c.c.	Carbon monoxide in c.c.	Oxygen reacting with the substance, per cent.
1	Acrolein = 8·5 %, sulphuric acid = 10 %	0·25	5	750	16°	500	294·1	21·9	243·4	13·5	52·4
2	Allyl alcohol = 5·0 %, sulphuric acid = 10 %	0·08	4	764	15	500	442·0	16·0	402·0	13·0	19·6
3	Conditions as in 2	0·30	10	764	13	500	336·4	12·6	273·1	44·2	45·4
4	Allyl alcohol = 15 %, conditions as in 2 & 3	0·08	4	760	17	500	454·5	13·5	415·0	13·5	17·0
5	Conditions as in 4	0·31	10	760	17	500	251·5	13·5	174·2	66·9	65·4
6	Crotonaldehyde = 5 %, sulphuric acid = 10 %	0·024	4	760	18	500	395·0	10·0	365·0	5·0	27·0
7	Conditions as in 7	0·23	8	760	18	500	378·6	16·5	332·5	14·5	33·6
8	Acrolein = 3 %, sulphuric acid = 10 %	0·20	4·5	750	15	500	360·4	16·9	317·0	11·6	34·6

70 to 100 per cent. of the total amount liberated, whilst in the case of allyl alcohol only 20 per cent. is used in the oxidation at low potential. Again, in the case of acrolein, this amount varied from 35 to 50 per cent., whilst propaldehyde reacts with 95 per cent. of the total oxygen (Law, Trans., 1905, 87, 202). Apparently the double bond increases the stability of the rest of the molecule. In these experiments it was noticed that both the anode and the glass became coated with a white, viscous substance.

Furfural.

This substance is undoubtedly an unsaturated aldehyde. For example, it combines readily with bromine, and on oxidation the ring is opened. It behaves in most respects, however, as an aromatic aldehyde, and for this reason these experiments were undertaken. From its general behaviour it ought to fall intermediate between the aromatic and the unsaturated aliphatic aldehydes. Thus the total oxygen reacting with this substance in acetic acid solution is in round numbers 20 per cent., with benzaldehyde 2 per cent., and with acrolein and crotonaldehyde from 30 to 50 per cent. No carbon dioxide and only small quantities of carbon monoxide are liberated in this case, and thus furfural behaves like benzaldehyde. On the other hand, however, the carbon monoxide is doubled on increasing the potential of the decomposition, as in the cases of acrolein and crotonaldehyde. In these experiments, the solvent plays very little part in the reaction, absorbing only from 5 to 15 per cent. of the total oxygen liberated, and the numbers given in Table XIV may therefore be regarded as quantitative. The following table gives the amount of oxygen reacting with four classes of aldehydes.

Benzaldehyde in acetic acid solution.	Furfural in acetic acid solution.	Unsaturated aliphatic aldehydes.	Saturated aliphatic aldehydes.
2 per cent.	20 per cent.	30—50 per cent.	95 per cent.

Benzaldehyde behaves then as an unsaturated compound, being largely influenced, however, by the stable ring formation of the benzene nucleus. The influence of the ring formation is not so apparent in the case of furfural, and the effect of the unsaturated linking predominates. The unsaturated aldehydes are remarkably stable compounds, and the saturated ones are almost completely decomposed.

TABLE XIV.—*Furfural*.

Number of experiment.	Solution.	Current in amperes.	E.M.F. in volts. Pressure in mm. of Hg.	Temperature.	Oxygen liberated in the coulombmeter in c.c.	Total volume of mixed gases in c.c.	Carbon dioxide in c.c.	Oxygen in c.c.	Carbon monoxide in c.c.	Oxygen reacting with the furfural, per cent.
1	Acetic acid = 16 % sulphuric acid = 8 %	0.053	4 755	17°	500	500.0	0.0	472.7	13.6	19.2
1a	4 grams of furfural, conditions as in 1	0.042	4 754	16	500	431.7	0.0	380.8	18.5	
Difference between 1 and 1a								91.9	4.9	
2	Solution as in 1	0.71	12 754	16°	500	452.0	2.0	420.0	24.0	20.0
2a	Solution as in 1a	0.55	12 754	16	500	363.5	2.1	318.7	32.3	
Difference between 2 and 2a								101.3	8.3	

Menthol and Camphor.

Both these substances are derivatives of six carbon atom ring compounds. They differ from benzene, however, in that they contain no double linking between two carbon atoms. They should therefore form no tarry matter on oxidation, and for this reason the following experiments were undertaken.

Experiment I.—Camphor (10 grams) was dissolved in acetone (20 c.c.) in a beaker, and water and sulphuric acid added until the total volume was 75 c.c., containing 5 per cent. of acid. In this was placed a small porous pot containing 20 per cent. sulphuric acid and a coil of platinum wire to serve as the cathode. The anode was a coil of stout platinum wire 15 cm. long and 1 mm. diameter. A current of one ampere was passed through the solution for twelve hours, at the end of which time the solution in the anode compartment had become slightly yellow, but was apparently free from resinous matter. The acid was partly neutralised with sodium hydroxide and the acetone removed on a water-bath. On cooling, the residue was extracted with ether, dried, and fractionated. The total quantity of product obtained weighed 9 grams, the remainder being lost probably during the experiment. Most of the substance distilled between 200° and 210°, and partly solidified. This was for the most part unchanged camphor. A smaller fraction was obtained below 240°, and there remained in the flask a small oily residue which had darkened somewhat during the distillation. No tarry matter was formed.

Experiment II.—Precisely the same experiment was conducted with

10 grams of menthol. After twelve hours the solution was still quite colourless, and the experiment was allowed to continue overnight. After thirty-six hours the mixture had darkened somewhat, and the experiment was stopped. The product was treated as before and distilled. The bulk of the product which did not solidify was obtained at 200—240°, and there remained behind a small quantity of a dark oily residue. The darkening in this case was entirely due to the accumulation of sulphuric acid in the anode compartment, as was proved in the following experiment. A small quantity of menthol was dissolved in a small quantity of acetone and a few c.c. of 60 per cent. sulphuric acid added. This on standing became brown in a few hours. It was noticed also in the case of benzoin that the presence of large amounts of sulphuric acid favoured the formation of tarry matter. In both these experiments the *E.M.F.* was four volts at the beginning, but towards the end rose considerably owing to the dilution of the acid in the cathode compartment.