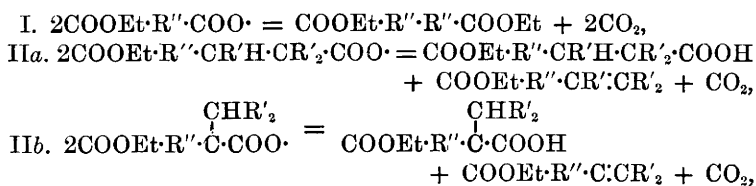


XXXVI.—*The Electrolysis of Sodium Ortho-ethyl Camphorate.*

By JAMES WALKER, D.Sc., Ph.D., F.R.S.E.

It has been shown by Crum Brown and Walker (*Annalen*, **261**, 107; and *Trans. Roy. Soc. Edin.*, **36**, 211; **37**, 361) that the potassium ethyl salts of bibasic organic acids, on electrolysis of their concentrated aqueous solutions, yield an ethereal product which consists in most cases principally of the diethyl salt of a bibasic acid and of the ethyl salt of an unsaturated monobasic acid. The changes in virtue of which these ethereal substances are produced take place at the anode, and may be represented by the following general equations:—



in which R'' represents a dyad alkylene radicle (which may also be zero in equations IIa and IIb), and R' represents hydrogen or an alkyl radicle. These substances seem always to be formed in the electrolysis when their formation is theoretically possible, but their relative amounts vary in the different cases, and they are usually accompanied by larger or smaller quantities of other ethereal products.

As the true bibasic nature of camphoric acid has recently been called in question by Friedel, it appeared to me of interest to investigate its behaviour on electrolysis. Aqueous solutions of its alkaline salts had previously been electrolysed by Bourgoin (*Jahresbericht*,

1868, 576), who found that at the anode only oxygen, carbonic anhydride, and carbon monoxide were formed, the anion being thus oxidised without formation of any synthetic product. The behaviour of the sodium ethyl salt examined by me is very different: the change is quite analogous to that which takes place in the case of the potassium ethyl salts of acids of the malonic series, the diethyl salt of a bibasic acid and the ethyl salt of an unsaturated acid being the chief products.

The salt used for electrolysis was prepared by the direct union of camphoric anhydride and sodium ethoxide in the manner I have already described for the preparation of orthomethyl sodium camphorate (*Trans.*, 1892, **61**, 1089). 23 grams of sodium are dissolved in 400 c.c. of absolute alcohol, the resulting solution of sodium ethoxide is cooled to the ordinary temperature, and to this is added gradually 182 grams of finely crystalline or powdered camphoric anhydride, which at once dissolves with formation of ethyl sodium camphorate. The temperature should not be allowed to rise during the reaction, and the solution should stand for some hours before being heated. Unlike the corresponding methyl salt, ethyl sodium camphorate is freely soluble in alcohol, and does not separate in the crystalline state even when the solution is very concentrated, a circumstance which occasions considerable trouble in the further treatment of the alcoholic solution. As much of the alcohol as possible is distilled off on the water-bath, and the thick, faintly yellow syrup which remains is poured into a basin, the evaporation being continued on the water-bath with constant stirring until all the alcohol has been driven off and a white, solid mass is left. This operation is very tedious, but cannot be hastened in any way by raising the temperature, or by adding water, without prejudicial effects on the succeeding electrolysis. The amorphous mass of sodium ortho-ethyl salt is then dissolved in 120—150 c.c. of water. Although the salt is excessively soluble in water, it dissolves in the cold solvent with extreme reluctance, so that it is usually necessary to warm slightly, and work up the tough, pasty mass with the water by squeezing through the fingers. In this way an almost colourless and somewhat viscid solution of the sodium ethyl salt is obtained, which may be at once submitted to electrolysis. As a rule, the solution is slightly alkaline, but it is not advisable to avoid this alkalinity by taking excess of camphoric anhydride at the beginning of the operation.

The electrolysis was conducted as prescribed by Crum Brown and Walker (*Annalen*, **261**, 112—114), a large platinum crucible being used as anode, and a spiral of stout platinum wire as cathode. The electromotive force of the current was 12 volts, and the average

strength 4 ampères. The successful production of ethereal substances in the electrolysis seems to depend on circumstances which I have been unable precisely to define. Two batches of ethyl sodium camphorate, prepared as far as I could judge in exactly the same way, would occasionally show great differences in their behaviour—one would give an excellent yield of ethereal product; the other, under the same conditions of electrolysis, scarcely any. As a rule, however, some slight alteration in the current strength, temperature, or concentration of the solution was sufficient to ensure a fair yield of the ethereal salts even from a portion which, to begin with, produced nothing but carbonic anhydride and water. If the directions I have given for the preparation of the sodium ethyl salt are strictly adhered to, I have no doubt that in all cases a successful result will be attained, after a preliminary experiment on the most favourable conditions of electrolysis has been made.

Each charge of solution electrolysed weighed about 40 grams, and the operation generally lasted an hour and a half. At the expiration of that time the current was stopped, and the lighter ethereal layer removed from the aqueous solution, which, on continued electrolysis, yielded a further small quantity of ethereal product. The aqueous solutions from a number of charges were finally united and extracted with ether. The ethereal extract was added to the original ethereal layer, and the mixture was then dried with calcium chloride, after which the ether was distilled off. On the average, the total yield of ethereal product was equal to half the weight of camphoric anhydride taken.

During the electrolysis, the escaping gases carry with them the vapour of the unsaturated ethereal salt, the odour being not at all unpleasant at the time. But when the vapours become diffused and diluted, their smell is very offensive and clings persistently for weeks and even months to the clothing, and especially to any leather articles which may have been exposed to them. It is, therefore, advisable to conduct the electrolysis either in the open air or in a good draught.

On fractionation, very little of the ethereal product passed over below 180° ; on reaching that temperature, however, the thermometer rose more slowly, and at 212° remained for a long time constant. Nearly half passed over between 210° and 220° . Above 225° the thermometer again began to rise rapidly, but the distillation was stopped at 240° , as decomposition then set in, the brownish residue being subsequently fractionated under reduced pressure. At a pressure of about 15 mm., the chief portion, nearly one-eighth of the whole ethereal product, passed over between 135° and 140° . When the temperature reached 160° , the distillate partially solidified in the condenser, and the solid continued to come over up to 230° , at which

temperature decomposition became very rapid, a large quantity of tarry matter remaining behind in the flask.

The yellowish, semi-crystalline solid which distilled between 160° and 220° was spread on a porous tile, and the white crystals which remained after the absorption of the yellow syrup were recrystallised from ether; they separated from this solvent in colourless needles and prisms. From its melting point, 216° , and its general chemical behaviour, the crystalline substance was proved to be camphoric anhydride, probably a decomposition product of some complex ethereal substance formed in the electrolysis (compare *Trans. Roy. Soc. Edin.*, **37**, 375).

On subsequent investigation, the fraction boiling under the ordinary pressure at 210 — 220° proved to be the ethyl salt of the unsaturated acid, and the fraction boiling under reduced pressure at 135 — 140° , the diethyl salt of the synthetic acid, formed according to the general equations already given. These two acids are both new, and I propose to name them *campholytic acid* and *camphothetic acid* respectively, in order to indicate, to some extent, their nature and their mode of formation.

Campholytic acid, $C_9H_{14}O_2$.

On refractionation, the portion of the original ethereal product which boiled between 210° and 220° came over almost entirely at 212 — 213° (uncorr.). The ethyl salt of campholytic acid obtained in this way still contained traces of the ethyl salt of camphothetic acid as its further behaviour showed, but it was found impossible to remove these by repeated fractionation.

Ethyl campholytate is a colourless, moderately mobile oil, having the sp. gr. 0.962 at $15^{\circ}/4^{\circ}$. It is optically active, and at 10° has the specific rotatory power $[\alpha]_D = +5.04$. Its solution in carbon bisulphide at once decolorises bromine in the cold.

A combustion gave the following results.

0.1318 gave 0.3496 CO_2 and 0.1202 H_2O . $C = 72.34$; $H = 10.14$.

$C_{11}H_{18}O_2$ requires $C = 72.52$; $H = 9.89$ per cent.

This ethereal salt may be saponified by boiling for three hours with half its weight of potash in alcoholic solution. Even after prolonged boiling, however, the saponification is not complete, and considerable quantities of the volatile ethyl salt are recovered when the alcohol is distilled off from the alkaline solution, to which a little water has been added. As the potassium salt of campholytic acid is soluble in alcohol, there is no separation of a solid during the saponification. On acidifying the aqueous solution of the potassium

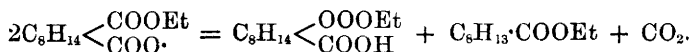
salt, the crude campholytic acid rises to the surface as a brown oil; this is removed, and the aqueous solution shaken up with ether to extract further quantities of the acid. After drying with calcium chloride, and distilling off the ether on the water-bath, the acid may be fractionated, at the ordinary pressure. Very little passes over below 230° , the thermometer remaining constant for a long time at 240 — 242° , and then rising slowly to 250° , at which temperature evident decomposition sets in. The residue in the flask is a brownish mass, which is very viscid while warm, and becomes hard on cooling. It probably consists of a polymeride of the unsaturated acid. Its formation may be to a great extent avoided if, instead of being fractionated at once, the crude acid is previously distilled over with steam; as, however, campholytic acid is not very volatile, this operation occupies considerable time, but the product is practically pure, for, on rapid distillation, it nearly all passes over between 240° and 245° . The last portions of acid that came over with the steam solidified in the condenser, and on examination proved to be camphothetic acid, the ethyl salt of which had been present in the ethyl campholytate as an impurity.

Campholytic acid is a colourless, somewhat viscous liquid, which boils undecomposed at 240 — 242° (uncorr.) under the ordinary pressure. Like its ethyl salt, it is optically active, but rotates the plane of polarisation in the opposite sense, having the specific rotatory power $[\alpha]_D = -5.00^{\circ}$ at 10° . Its density at $15^{\circ}/4^{\circ}$ is 1.017. In water it is only sparingly soluble, but it dissolves readily in alcohol, ether, and other organic solvents.

The following results were obtained on analysis.

- I. 0.1833 gave 0.4706 CO_2 and 0.1514 H_2O . C = 70.02; H = 9.18.
 II. 0.1625 „ 0.4174 CO_2 „ 0.1342 H_2O . C = 70.05; H = 9.17.
 $\text{C}_9\text{H}_{14}\text{O}_2$ requires C = 70.13; H = 9.09 per cent.

The composition of campholytic acid is, therefore, that of camphoric acid *minus* the elements of formic acid, and the formation of its ethyl salt from sodium ethyl camphorate may be represented by the equation



As an unsaturated acid it combines readily with bromine in the cold, but it depends on the conditions under which the reaction takes place, whether a definite dibromide is formed or not.

The dissociation constant of the acid was determined from the electrolytic conductivity of its solution at 25° .

Campholytic Acid, C₉H₁₄O₂.

$$\mu_{\infty} = 352.$$

<i>v.</i>	$\mu.$	100 <i>m.</i>	100 <i>k.</i>
94.5	10.33	2.93	0.00094
189.0	14.44	4.10	0.00093
378.0	20.0	5.68	0.00091
756.0	28.8	8.04	0.00093

$$K = 0.00093.$$

This constant is very low for a monocarboxylic acid. But, as I have already pointed out (Trans., 1892, **61**, 1096), nearly all the acids derived from camphor have similar small constants. Thus the constants for the two methyl hydrogen camphorates (allo- and ortho-) are 0.00108 and 0.00079 respectively, so that campholytic acid occupies a place midway between them, which is, roughly, the position it might be expected to assume.

The salts of campholytic acid are all soluble in water, a concentrated neutral solution of the ammonium salt giving no precipitates with neutral solutions of the ordinary metallic salts. For the preparation of the calcium salt, a portion of the acid was neutralised by boiling it with calcium carbonate. The filtered solution showed no tendency to crystallise on evaporation, but on keeping for a long time in a desiccator over sulphuric acid, a viscous scum formed on the surface of the liquid, and small, hard, nodules on the walls of the vessel; neither of these, however, seemed to be crystalline. The barium salt was prepared in the same way, and behaved in an analogous manner. When evaporated in a vacuum over sulphuric acid, a sticky mass was left, which did not completely part with its water even after weeks in the desiccator.

0.4078 barium salt dried at 130° gave 0.2125 BaSO₄. Ba = 30.7.

(C₉H₁₃O₂)₂Ba requires Ba = 30.9 per cent.

Dibromide of Campholytic acid, C₉H₁₄Br₂O₂.

When bromine in chloroform solution is added at the ordinary temperature to campholytic acid dissolved in the same solvent, the colour of the bromine instantaneously disappears, hydrogen bromide being evolved, and, on further addition of bromine, the solution turns black. On evaporating the solvent in a current of air at the ordinary temperature, a tarry mass is left, which shows no signs of crystallisation even on long keeping. A very different result is obtained, however, when the addition of bromine is carried out under the conditions recommended by Wislicenus (*Annalen*, **272**, 13). Bromine (7 grams) was dissolved in 20 c.c. of dry carbon bisulphide in an Erlenmeyer

flask provided with a cork through which passed a tap-funnel and a calcium chloride tube. The flask was immersed in cold water contained in a large beaker which had previously been blackened externally by a smoky gas flame in order to exclude the light. Through the tap-funnel there was gradually added a solution of 5 grams of campholytic acid in 20 c.c. of dry carbon bisulphide, the temperature during the operation never being allowed to rise above 12° . The mixture was then left over night in the dark, and on the following morning the carbon bisulphide and the excess of bromine were removed by means of a current of dry air. There remained on the bottom of the flask a brownish solid mass, which became very nearly white when small quantities of light petroleum were successively added, and then removed by the air current at the ordinary temperature. The substance was finally dissolved in ether, in which it is very soluble, and the ethereal solution mixed with about its own bulk of light petroleum, in which the bromide is much less soluble. On evaporation, the substance separated in nodules of small, ill-formed, colourless crystals, and although these were recrystallised several times, no crystals of definite form could be obtained, feathery aggregates of small plates being most frequently observed.

Dibromide of Campholytic acid.—The crystals when spread on a porous tile and dried in a vacuum in the dark remain colourless, but some of them were observed to blacken superficially on prolonged exposure to light. The melting point depends somewhat on the manner of heating. As a rule, on heating slowly, the substance was found to melt at $106\text{--}107^{\circ}$ with blackening, but if the tube containing it was plunged into a liquid already at that temperature, the substance melted quite sharply as soon as it reached 110° , and solidified again without blackening if at once removed. It is very little soluble in water, easily soluble in alcohol, ether, chloroform, and carbon bisulphide, and only slightly soluble in cold light petroleum, although it dissolves more freely in the boiling solvent. On keeping for some time at 100° , the dibromide blackens with slight evolution of hydrogen bromide. Very little hydrogen bromide is given off during its formation in the manner above described, the weight of the crude dibromide obtained being almost equal to the theoretical quantity.

A determination of the bromine by Carius' method gave the following result.

0.1752 gave 0.2075 AgBr. Br = 50.4.

$\text{C}_9\text{H}_{14}\text{Br}_2\text{O}_2$ requires Br = 50.9 per cent.

It was only after I had used up almost all the campholytic acid in my possession on experiments in other directions that I discovered

the special interest attaching to its dibromide, so that here and in what follows, I am unable to give full details of the properties of the substances described. As the preparation of a new supply of the acid will, however, take some considerable time, I now give a preliminary account of the results I have arrived at, and hope soon to be in a position to supplement them from experiments made with larger quantities of material.

As has already been stated, the dibromide dissolves very sparingly in water, but if a drop of ammonia is added to its solution in hot water, the liquid becomes turbid after a few moments, and the turbidity does not disappear either with excess of alkali or on the addition of acid. If, instead of a solution of the acid, a suspension of it in hot water is taken, and a drop of ammonia is added, the portions of the liquid reached by the ammonia become clear for a moment and then suddenly turbid again. A slight evolution of gas may also be observed if the quantity of ammonia taken is not too large; the gas given off is carbonic anhydride.

The same change takes place in the cold when sodium carbonate solution is used instead of ammonia. 5 grams of the dibromide were allowed to stand over night with an equal weight of crystallised sodium carbonate in aqueous solution. In the morning, the oil which had separated was distilled off in a current of steam, in which it was very volatile; about 1.5 grams of the oil were thus obtained. The residue contained sodium bromide in large quantity and also the sodium salt of an acid which was free from bromine, and melted at 186°.

The oil, which was heavier than water, was separated and dried with calcium chloride. It possessed a characteristic, pleasant smell somewhat resembling that of oil of turpentine, but sweeter. An attempt was made to distil it at the ordinary pressure; the thermometer rose at once to 176°, at which temperature the substance began to boil, undergoing considerable decomposition. The operation was therefore interrupted, the substance redistilled with steam, dried, and purified by distillation in a vacuum. The distillate was only slightly yellow and a bromine determination gave the following numbers.

0.3050 gave 0.2970 AgBr. Br = 41.4.

$C_8H_{13}Br$ requires Br = 42.3 per cent.

From the boiling point, the insolubility in acids and alkalis, the great volatility with steam, and the nature of the reaction in which it was produced, it seemed very probable that the substance was a brominated unsaturated hydrocarbon formed by the decomposition of the alkaline salt of the dibromo-acid, according to the equation



The amount of bromine found in the substance, although falling somewhat short of the theoretical amount, is sufficient to confirm this view, when we take into consideration the small quantity of substance which had to be dealt with, and also the detection of both the other products of the reaction.

Decompositions such as the above, in which an alkaline salt in aqueous solution is resolved into an alkaline bromide, carbonic anhydride, and an unsaturated bromohydrocarbon, are confined to $\alpha\beta$ -dibromo-acids, a fact of considerable importance in fixing the relative position of the carboxyl groups in camphoric acid.

The brominated hydrocarbon readily absorbs bromine in carbon bisulphide at the ordinary temperature. A small portion was thus treated with excess of bromine and allowed to stand one hour, after which the solvent and the remaining bromine were driven off by a current of dry air. A thick, slightly yellow liquid was left, which was easily soluble in ether, but insoluble in water, and only sparingly soluble in alcohol. When dissolved in a large quantity of alcohol, it separated in heavy, oily drops as the alcohol evaporated. All the alcohol was removed at 80° , at which temperature the oil is not at all volatile. It smells pleasantly, but has a more pungent odour than the compound $C_8H_{13}Br$. On heating, it boils with decomposition, blackening, and evolving large quantities of hydrogen bromide. A volatile liquid, probably a hydrocarbon, is formed, but the quantity obtained was so small as to preclude further investigation for the present.

Ethyl campholytate absorbs bromine under the same conditions as campholytic acid itself. In this case, however, the tendency to decomposition with blackening and evolution of hydrogen bromide is not so great, so that the addition of bromine may be effected in the ordinary way. Wislicenus' method, however, is preferable, the quantity of hydrogen bromide formed being then very small.

The bromine addition compound is a heavy, yellow liquid, with a characteristic penetrating odour. It gives off hydrogen bromide slowly at the ordinary temperature, and on keeping becomes much darker in colour. It decomposes when boiled, but may be distilled with steam.

A determination of the bromine in the undistilled product gave the following results.

0.2040 gave 0.2256 AgBr. $Br = 47.1$.

$C_{11}H_{18}O_2Br_2$ requires $Br = 46.8$ per cent.

The dibromo-ethereal salt, when shaken up with cold, moderately concentrated caustic potash solution, at once gives the characteristic smell of the hydrocarbon $C_8H_{13}Br$.

Camphothetic acid, $C_{16}H_{28}(COOH)_2$.

The portion of the original ethereal product of electrolysis boiling at 135–140° under reduced pressure (about 15 mm.) was refractionated. It then contained very little of the ethyl salt of campholytic acid, as it did not decolorise bromine in the cold, even after standing for some time. A determination of the molecular weight of the liquid by the depression of the freezing point of benzene gave the following result.

0.682 gram of substance dissolved in 17.90 grams of benzene lowered the freezing point of the solvent 0.642°, corresponding to a molecular weight of 310. The molecular weight of diethyl camphothetate, $C_{20}H_{34}O_4$, is 338.

The diethyl salt is a pale-yellow liquid (probably colourless when pure), and has a sp. gr. of 1.019 at 18°/4°. It is dextrorotatory, having a specific rotation $[\alpha]_D = +30.6^\circ$ at 10°.

As the saponification of diethyl camphothetate by means of alcoholic potash did not yield a satisfactory result, the ethereal salt was heated in sealed tubes for five hours at 130° with its own volume of hydrobromic acid of sp. gr. 1.7. On cooling, two layers were found in the tubes, the upper being black and containing crystals, the lower aqueous layer being brown and transparent; the bulk of the upper layer consisted of ethyl bromide. The crystals which had separated were filtered off, and all the liquid contents of the tube were distilled over with steam after the hydrobromic acid had been partially neutralised with sodium carbonate. Ethyl bromide came over first, then the diethyl camphothetate which had been unattacked, and finally camphothetic acid crystallised in the condenser. The crystals were united with those which had separated out in the tube, and the whole was recrystallised from alcohol, and then from light petroleum.

Camphothetic acid obtained in this way is a colourless substance, which crystallises in small, rectangular tables, and melts at 132°. It is very sparingly soluble in water, easily in alcohol or ether, and moderately in hot light petroleum, but only slightly in the cold solvent. It volatilises with steam, and may be distilled at a high temperature apparently unchanged.

0.1044 gave 0.2675 CO_2 and 0.0900 H_2O . $C = 69.88$; $H = 9.59$.
 $C_{18}H_{30}O_4$ requires $C = 69.68$; $H = 9.68$ per cent.

The following numbers were obtained for the electrolytic conductivity at 25°.

Camphothetic acid, $C_{16}H_{28}(COOH)_2$.

$$\mu_{\infty} = 350.$$

<i>v.</i>	μ'	μ''	μ	100 <i>m.</i>	100 <i>k.</i>
1700	57.1	57.5	57.3	16.4	0.0018

$$K = 0.0018.$$

Here again we observe the small value of the dissociation constant peculiar to camphor derivatives. The constant 0.0018 is just equal to that of acetic acid, and much smaller than we should expect for the constant of a dicarboxylic acid. Camphoric acid itself, however, has a constant of only 0.00225, so that the value for camphothetic acid when compared with that number is normal, as far as the relation of the two acids to each other is concerned, for in camphoric acid the two carboxyl groups are separated by a smaller number of carbon atoms than in camphothetic acid; consequently the dissociation constant of the former ought to be somewhat greater than that of the latter.

The alkaline salts of camphothetic acid are fairly soluble in water, and can be crystallised from that solvent. A saturated solution of ammonium camphothetate behaved as follows when solutions of metallic salts were added to it.

Magnesium Chloride.—No precipitate.

Calcium Nitrate.—No precipitate in the cold, but on heating a granular precipitate comes down, which redissolves on cooling.

Barium Nitrate.—White precipitate, which dissolves in a little cold water. It may be reprecipitated from the solution by heating.

Zinc Nitrate.—Curdy, white precipitate, slightly soluble in boiling water.

Cadmium Nitrate.—Crystalline, white precipitate, soluble in cold water.

Mercuric Chloride.—White, insoluble precipitate, which coagulates on heating.

Mercurous Nitrate.—Dense, white precipitate, which turns grey on heating, and at once blackens with ammonia.

Silver Nitrate.—Dense, white precipitate, soluble in much hot water. Does not blacken on boiling, but becomes coloured on exposure to light. Soluble in ammonia.

Copper Nitrate.—Bluish-green precipitate, quite insoluble in water; easily soluble in ammonia.

Lead Nitrate.—White, opalescent precipitate; soluble in hot water.

Stannous Chloride.—Dense, white, flocculent precipitate, slightly soluble in boiling water.

Ferrous Sulphate.—Faintly yellow precipitate, slightly soluble in boiling water.

Ferrie Nitrate.—Flocculent, yellow precipitate, which becomes brown on boiling. Insoluble.

The silver salt obtained by precipitation was analysed, with the following result.

0.2274 gave 0.0936 Ag. $\text{Ag} = 41.2$.

$\text{C}_{18}\text{H}_{28}\text{O}_4\text{Ag}_2$ requires $\text{Ag} = 41.2$ per cent.

The barium salt was prepared by boiling the acid, in aqueous solution, with barium carbonate until it was completely neutralised. The filtered solution was concentrated first by heating, and afterwards in a vacuum. The crystals which separated were collected and dried over sulphuric acid.

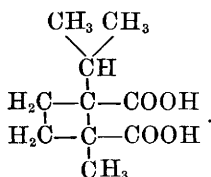
0.2444 lost 0.0420 at 130° and yielded 0.1052 BaSO_4 . $\text{Ba} = 25.3$; $\text{H}_2\text{O} = 17.2$.

$\text{BaC}_{18}\text{H}_{28}\text{O}_4 \cdot 5\text{H}_2\text{O}$ requires $\text{Ba} = 25.6$; $\text{H}_2\text{O} = 16.8$ per cent.

Constitution of Camphoric acid.

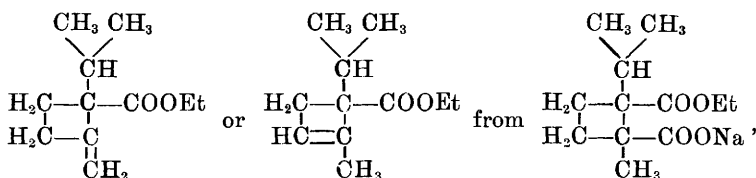
That camphoric acid is in reality a dicarboxylic acid may now be taken for granted. The recent work of Brühl, Haller, Angeli, and others bearing on this point has led all these observers to that conclusion; and, as I have shown (*loc. cit.*), the magnitudes of the dissociation constants of the acid itself and of its acid methyl salts are explicable on no other assumption. If further proof were required, it is furnished by the behaviour of the sodium ethyl salt on electrolysis. The course of the reaction and the nature of the products formed are normal for a dicarboxylic acid of the ordinary succinic acid type. First of all it must be conceded that the acid contains one carboxyl group, which in the sodium ethyl salt is converted into the group $\cdot\text{COONa}$, as otherwise the normal decomposition as a salt of the acetic acid type could not be explained. Then the chief products of the electrolysis are the ethyl salts of two acids, one undoubtedly a monocarboxylic acid, and the other undoubtedly a dicarboxylic acid. Thus the residue of the camphoric acid after the removal of one carboxyl group still contains another carboxyl group, so that in the parent substance there must have been two of these groups originally present. Any other view involves great straining, and the assumption of atomic rearrangements within the molecule, which, in view of the simple and normal course of the action, are quite inadmissible.

The formula for camphoric acid which is at present most in vogue is that advanced by Victor Meyer and Von Ballo, which represents the substance as a dicarboxylic acid derived from tetramethylene,

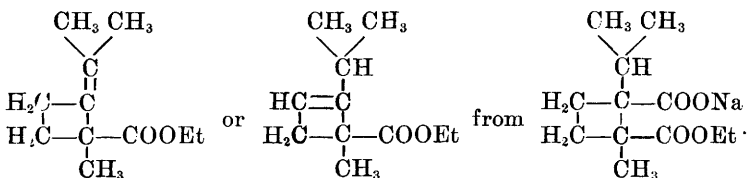


This formula perfectly well explains the behaviour of sodium ethyl camphorate on electrolysis, but, as I shall endeavour to show, it fails to account for the nature of the products formed.

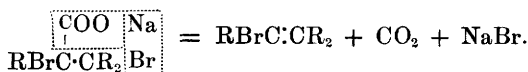
Referring back to the general equations IIa and IIb for the formation of an unsaturated ethereal salt by electrolytic decomposition, we find that the carbonic anhydride attached to one carbon atom leaves the molecule along with a hydrogen atom attached to the neighbouring carbon atom; thus the anion $\text{R}_2\text{HC}\cdot\text{CR}_2\cdot\text{COO}\cdot$ becomes $\text{R}_2\text{C}:\text{CR}_2\cdot$. Applying this principle to Ballo's formula, the possible unsaturated ethereal salts we may obtain are



and



It will be observed that these are all salts of $\beta\gamma$ -unsaturated acids, and therefore the acids obtained from them, by the addition of bromine, ought to be $\beta\gamma$ -dibromo-acids. But the alkaline salts of $\beta\gamma$ -dibromo-acids do not, in aqueous solution, yield unsaturated hydrocarbons; it is only the salts of $\alpha\beta$ -dibromo-acids which behave in this manner, the decomposition being represented by the general equation



(Compare Fittig, *Annalen*, **268**, 55.)

Since the dibromo-acid from campholytic acid decomposes according to the above equation, and is therefore an $\alpha\beta$ -acid, it follows that

campholytic acid itself is an $\alpha\beta$ -unsaturated acid, and consequently that Ballo's formula for camphoric acid is incapable of explaining the observed facts.

It might indeed be urged that by internal rearrangement a $\beta\gamma$ -unsaturated acid originally formed would pass into the corresponding $\alpha\beta$ -acid, for changes of this kind are by no means infrequent. We must consider, however, that the reagents employed and the conditions of the reactions are all extremely unfavourable to such an intramolecular transformation. The electrolytic decomposition was conducted at a temperature not exceeding 30° at the highest and in a solution only slightly alkaline with sodium carbonate and bicarbonate. Again, the addition of bromine took place under conditions shown by Wislicenus to exclude almost entirely the possibility of an internal atomic rearrangement. The only operation where such a change would be possible is the saponification of the ethereal salt of the unsaturated acid by means of alcoholic potash. That an isomeric transformation did not occur at this stage is, I think, sufficiently shown by the formation of the unsaturated bromhydrocarbon from the dibromide of ethyl campholytate and aqueous potash. Here the addition of bromine takes place before there is any chance of intramolecular rearrangement, and the action of cold aqueous potash is certainly insufficient to bring about such a process in a dibromo-compound. The ethyl salt is directly saponified, the sodium salt produced at once splitting up into sodium bromide, carbonic anhydride, and the unsaturated bromhydrocarbon.

Even admitting, however, that the possibility of intramolecular change is not excluded, Ballo's formula still fails to explain the facts, as a glance at the possible formulæ derived from it for the unsaturated ether will show. In order that a transformation from a $\beta\gamma$ -acid to an $\alpha\beta$ -acid may take place, it is necessary that there should be a hydrogen atom attached to the α -carbon atom, but in all the formulæ for the unsaturated acids the α -carbon atom is quaternary, so that no transformation of the required type can possibly occur.

We may now look at what kind of formulæ will admit of the direct formation of an $\alpha\beta$ -unsaturated acid by electrolysis of a dicarboxylic acid. The bibasic acid cannot be a glutaric acid derivative, for in the most favourable case the acid



could only give $\text{COOH}\cdot\text{CR}_2\cdot\text{C}:\text{CR}_2$, a $\beta\gamma$ -unsaturated acid. *A fortiori*, derivatives of adipic acid and higher normal acids of the same series are excluded. The only possibilities remaining, then, are that the bibasic acid should be derived from malonic or succinic acid. A

malonic acid derivative of the formula $\text{CR}_2\text{H}\cdot\text{RC} \begin{smallmatrix} < \text{COOH} \\ < \text{COOH} \end{smallmatrix}$ would

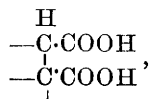
yield an unsaturated acid $\text{CR}_2\text{:CR}\cdot\text{COOH}$, in which the double linking is in the $\alpha\beta$ -position. But camphoric acid is assuredly not a derivative of malonic acid; its whole chemical behaviour contradicts such an assumption. It can only, therefore, be a succinic acid derivative, and to this extent Ballo's formula is correct. But it must be a succinic acid derivative of a special type. One of the atoms to which a carboxyl group is attached must have a hydrogen atom attached to it also, otherwise an $\alpha\beta$ -unsaturated acid cannot be formed. Thus, from



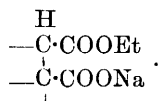
it is impossible to obtain an $\alpha\beta$ -acid by removal of a carboxyl group and a hydrogen atom from one of the radicles R, which is the normal reaction during electrolysis. The acid must be of the type



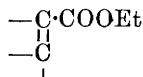
which becomes $\text{COOH}\cdot\text{CR}\cdot\text{CR}_2$, an $\alpha\beta$ -unsaturated acid, on electrolysis. Camphoric acid, therefore, must contain the group



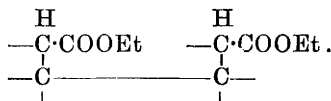
and the sodium ethyl salt formed from its anhydride and sodium ethoxide the group



This sodium ethyl salt, on electrolytic decomposition, yields ethyl campholytate containing the group

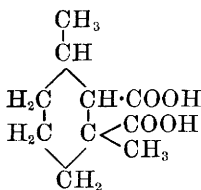


and diethyl camphothetate with the group

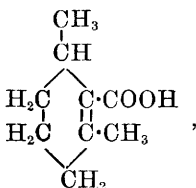


The only published formula for camphoric acid known to me which satisfies the above requirements is that proposed by Collie (*Ber.*, **25**, 1116).

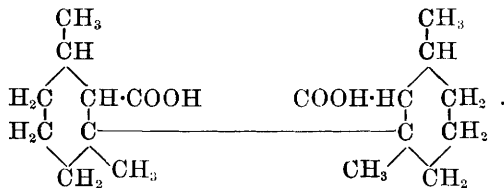
510 ELECTROLYSIS OF SODIUM ORTHO-ETHYL CAMPHORATE.



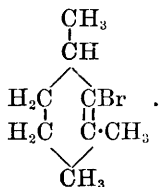
Campholytic acid, on the basis of this formula, would be



and camphothetic acid



The unsaturated bromhydrocarbon would receive the formula



A more extended investigation of the new acids and their derivatives may serve to throw further light on the question as to whether these formulæ are valid or not.

University College, London,
February, 1893.