

The Electrolytic Oxidation of Alcohols, II. Electrolytic Chlorination of Ethylalcohol.

By

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ABSTRACT.

Chlorination of ethyl alcohol was studied by electrolysing it in a potassium chloride solution, and the results are as described in the summary at the end of the paper.

Electrolytic chlorination of ethylalcohol was first undertaken by Ludersdorf¹ who electrolysed a mixture of alcohol and concentrated hydrochloric acid and obtained some heavy oily substance. Afterwards E. Schering² observed the formation of chloral at the carbon anode by electrolysing alcohol with a concentrated solution of potassium chloride, using a diaphragm, and he formulated the opinion that the electrolytic process would be applicable to the technical preparation of chloral.

As far as the author is aware, further details of the electro-chemical reactions between alcohol and chlorine, however, still remain entirely unknown, while the course of the purely chemical reactions has been much studied by several investigators.³ The author was thus induced to take up the present research with the object of getting to know the progress of the reactions and of ascertaining how oxidation and chlorination take place at the anode.

¹ Pogg. Ann., **19**, 83 (1830).

² Elektro. Chem. Zeit., **1**, 70 (1894).

³ Liebig. Ann., **1**, 189 (1832); Lieben: Ibid., **104**, 114 (1857); Ber., **3**, 907 (1870); Personne: Compt. rend., **69**, 1363 (1869); Wurtz: Ibid., **74**, 777; Paternò: Ann., **150**, 253, (1869); Lobry: Ber., **26**, 271 (1893); Fritsch: Ann., **279**, 288 (1894).

I. PREPARATION OF A POROUS CELL SUITABLE FOR THE EXPERIMENTS.

On electrolysing alcohol in such a concentrated potassium chloride solution as the anolyte becomes strongly acidic and the catholyte alkaline, it was soon found that the ordinary porous cell is so severely corroded that a prolonged electrolysis can by no means be carried out. So the author was compelled first to engage in the preparation of a porous cell suitable for the intended work. It was a somewhat difficult task. The cell should resist the action of both acid and alkali; it should not be brittle and at the same time be properly porous. After several test experiments carefully conducted by paying due regard to the content of the silica, the plasticity and the degree of fineness of the clay, and also to the baking temperature it was finally found that the cell of the best quality might be procured by baking a mixture consisting of 18 parts of fire clay A, 45 parts of fire clay B and 37 parts of fire kaolin at 1230-1250° (S. K., 7-8).

Fire clay (A) (plasticity 6).

Fire clay (B), formed by baking (A) at 1350°C and crushing to fine powder (plasticity 0).

Fire kaolin (C) (plasticity 10).

Their compositions were as follows:

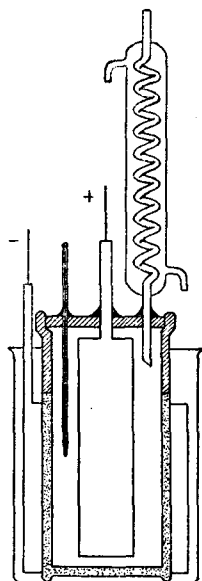
Table I.

| | Original Composition of A & B | Composition of C |
|--------------------------------|----------------------------------|------------------|
| SiO ₂ | 74.77 | 49.28 |
| Al ₂ O ₃ | 11.60 | 36.17 |
| Fe ₂ O ₃ | 1.28 | 0.48 |
| CaO | 0.50 | 0.18 |
| MgO | 0.45 | 0.06 |
| K ₂ O | 2.62 | 0.14 |
| Na ₂ O | 1.24 | 0.12 |

The upper part of the cell cylinder was glazed on both sides in order to prevent the diffusion of vapour through it.

II. APPARATUS AND METHOD USED FOR ELECTROLYSIS

Fig. 1.



Anode: Carbon plate (96.9^{sq.} cm.).

Anode solution: 250 cc. KCl solution (saturated at 70°).

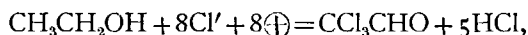
Cathode: Copper plate.

Cathode solution: The same as anode solution.

Temperature: 70–80°C.

The carbon anode and a reflux condenser were first cemented to a glazed porcelain stopper of the cell using a paste of barium sulphate and fine glass powder kneaded with water glass, and the stopper was tightly sealed with a thick solution of asphalt in chloroform.

The electrolysis was carried out by passing a current of 8 amperes for 23 hours 18 minutes (186.4 amp-h) for 50 cc. of ethylalcohol (sp. gr. 0.7952, 39.57 gms. C₂H₅OH), the theoretical electric quantities for the reaction:



being 184.2 amp. hours.

After electrolysis the anode solution containing much hydrochloric acid was added with 50 gms. of calcium carbonate and saturated with calcium chloride, and then it was repeatedly extracted with ether. The extraction must be conducted with a solution kept still sufficiently acidic, otherwise monochloroacetic acid will be missed. The ethereal extract was dehydrated with calcium chloride, and after the ether was evaporated out it was subjected to fractional distillation.

Table II.

| 60–90° | 90–100° | 100–120° | 120–180° | 180–190° |
|-------------|---------|----------|----------|----------|
| gm. 29.7 | 45.1 x | 20.1 x | 2.6 | 9.2 x |

The fraction boiling at 60–90° still contained some ether, and the next fraction (90–100°) solidified into needle crystals. From about 130° some pungent fume began to be evolved, the temperature gradually rose to 185°

x Crystalline solid was obtained from these fractions.

when the distillate solidifying to crystals was distilled, and at nearly 190° the greater part of the liquid was distilled off leaving some black residue. Sometimes a crystalline product was also obtained from the fractions boiling at 100–110° and 115–120°. Melting points and chlorine contents of the crystalline products were found as are shown in the following table.

Table III.

| Fraction | M. p. | B. p. | Subs. taken gm | AgCl gm | Cl% Found | Cl% calc. | Identified |
|-----------|---------|-----------|-------------------|-----------------------|---|--------------|-----------------------|
| 95°–100° | 54°–55° | 96°–99° | 0.2226 | 0.5756 | 63.97 | 64.30 | Chloralhydrate |
| 100°–110° | 54°–56° | 97°–99° | 0.5072 | 1.6401 | 63.75 | 64.30 | Chloralhydrate |
| 115°–120° | 46°–47° | 115°–117° | 0.2702 | 0.5910 | 54.11 | 54.99 | Chloral alcoholate |
| 185°–190° | 56°–57° | 185°–189° | 0.2581 | 0.3895 | 37.34 | 37.56 | Monochloroacetic acid |
| | | | 0.1896 | 19.90 ^{c.c.} | $\left(\frac{\text{No. of c.c. of } N/10 \text{ NaOH}}{\text{required for neutralization}} \right) 20.06 \text{ c.c. (calc.)}$ | | |

Thus it was ascertained that the crystals obtained above were chloral hydrate, chloral alcoholate and monochloroacetic acid.

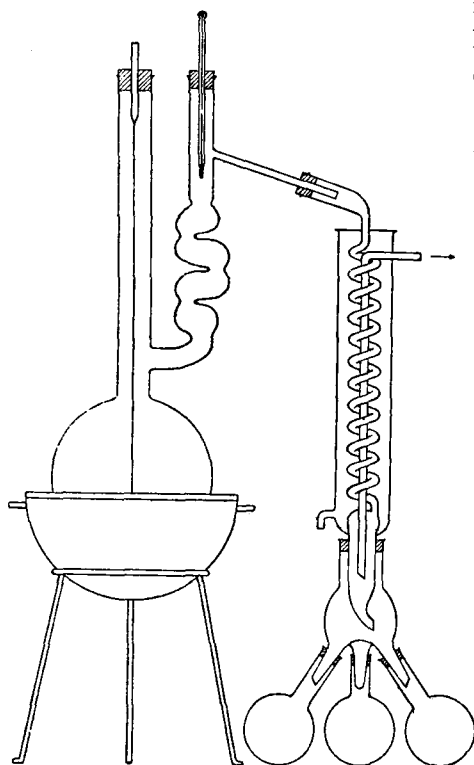
Next, to investigate the liquid which does not crystallize electrolysis was repeated several times, and about 800 cc. of it were collected. This was dehydrated over calcium chloride and fractionally distilled. But the temperature rose so slowly and gradually that it was scarcely possible to separate the liquid into the fractions of constant boiling point.

The fraction with the boiling points 60–100° seems to consist chiefly of ethylacetate, chloroaldehyde hydrate, chloroaldehyde alcoholate, chloral hydrate and chloroether, but their complete separation by means of fractionation are impracticable. Chloral hydrate was seen gradually to react with ethyl acetate so as to form chloral alcoholate. To ascertain this a solution of chloral hydrate in ethyl acetate was subjected to distillation when no chloral hydrate was separated, but instead of it chloral alcoholate was obtained, and the latter increased in quantity as the fractionation was repeated. After ten times fractionation a distillate boiling at 96–98° with a sp. gr. 1.336 (15°) was isolated. Its chlorine content was found to be 29.48% which corresponds to an ethyl acetate solution containing 45.83% of chloral hydrate.

To isolate the ethyl acetate from the products of the electrolysis, the

etheral extract obtained from the neutralized solution was first fractionated under a reduced pressure of 4–5 mm., and the portion distilling at 20–30° was shaken with a saturated solution of soda and with that of sodium bisulphite, and then rectified under normal pressure. Ethyl acetate distilled at 70–80°. It may be here noted that by a vacuum distillation at a low temperature such a condenser as is shown in Fig. 2. proved very effective.

Fig. 2.



The liquid distilling at 85°–95° may contain monochloroaldehyde hydrate, alcoholate, and chloroether. It was therefore treated with a concentrated sulphuric acid and the polymerised product was distilled. The fraction boiling at 87°–91° was proved to be monochloroaldehyde. Substance taken: 0.2780 gm., AgCl: 0.2361 gm., Cl: found, 21.01% calc., 20.26%. When 20 gm. of the fraction boiling at 95°–100° and having a sp. gr. 1.435 (15°) was treated with a caustic soda solution 4.5 c.c. of chloroform separated out from which the amount of chloral hydrate present in the fraction is calculated to be about 46%

$$\frac{4.4 \times 2.064}{20} \times 100 = 46.44.$$

Judging from its high chlorine content (about 49%) the fraction may possibly contain dichloroaldehyde hydrate, ethyl acetate and a small quantity of chloroether besides chloral hydrate.

The fraction with boiling points of 100°–110° was shaken with 60% sulphuric acid and extracted with ether. This was again rectified several times. The fraction boiling at 104°–106° was shown on analysis to be dichloroaldehyde hydrate Cl: Found, 48.21%, Calc., 47.60%.

The next higher fraction (B. p. 110°–120°) was scarcely soluble in water. When washed with water and dried over acidic clay a liquid with a sp. gr. 1.288 (18°) was obtained. From its chlorine content on the one hand and from its chemical behaviour decomposing gradually into

dichloroaldehyde hydrate and chloroacetal; and giving the iodoform reaction on the other, it was confirmed to be dichloroaldehyde alcoholate. Substance taken: 0.3483 gm., AgCl: 0.6158, Cl: 43.75% for the calculated 44.60%. In this fraction some acetic acid was also detected.

The fraction boiling at 120°-180° was small in quantity and was determined qualitatively to be an impure ethyl-chloroacetate containing a little dichloroether.

The fraction distilling above 180° was found chiefly to consist of monochloroacetic acid, a larger part of which distilled at about 190° leaving a little charred residue.

III. INFLUENCE OF VARIOUS CONDITIONS ON THE ELECTROLYSIS.

The main products of the electrolytic chlorination of alcohol having been thus confirmed, experiments were then conducted to study the influence of various conditions upon the electrolysis, the results of which are given below:

I. INFLUENCE OF TEMPERATURE.

Anode: Carbon (96.9 sq.cm.).
 Anode solution: 250 cc. KCl solution saturated at the temperature of the electrolysis, with 50 cc. alcohol (99.71% Vol.) added.
 Cathode: Platinum plate.
 Cathode solution: The same as the anode solution.
 Current density: 0.0516 amp/sq.cm.
 Electric quantity: 184.17 amp-hour.

Table IV.

| B. p. Temperature | 60-90° | 90-100° | 100-120° | 120-180° | 180-190° | |
|----------------------|-------------------|---------|----------|----------|----------|------|
| 30°-40° | 11.0 ⁸ | 1.3 | 6.2 | 17.1 | 9.9 | 45.5 |
| 50°-60° | 17.0 | 10.5 | 9.8 | 10.2 | 9.4 | 56.9 |
| 70°-80° | 19.5 | 43.7 | 22.3 | 5.1 | 8.3 | 98.9 |
| 90°-100° | 15.0 | 31.8 | 24.5 | 6.1 | 7.8 | 85.2 |

At a temperature below 40° the carbon anode was much corroded.

2. INFLUENCE OF CURRENT DENSITY.

Electrolytic solution: 250 cc. KCl solution saturated at 80°.

Temperature: 70°-80°.

Electric quantity: 184 amp-hour.

The other conditions are the same as in the previous experiment.

Table V.

| | B. p. Current density amp/sq.cm. | 60°-90° | 90°-100° | 100°-120° | 120°-180° | 180°-190° | |
|---|--|---------|----------|-----------|-----------|-----------|-------|
| | | 1 | 0.06193 | 20.0 | 47.3 | 19.8 | |
| 2 | 0.08256 | 29.7 | 45.1 | 20.1 | 2.6 | 9.2 | 106.7 |
| 3 | 0.1212 | 19.8 | 39.2 | 18.5 | 5.1 | 7.9 | 90.5 |

3. INFLUENCE OF THE ELECTROLYTE.

Current density: 0.08256 amp/sq.cm.

The other conditions are the same as in the previous experiment.

Table VI.

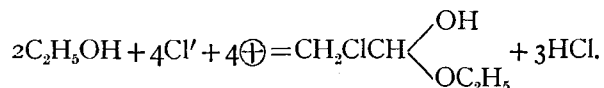
| Electrolytic solution | B. p. | 60°-90° | 90°-100° | 100°-120° | 120°-180° | 180°-190° | |
|---|-------|------------------------------|-------------------|-----------|-----------|-----------|--|
| | | 250cc KCl soln. satd. at 25° | 16.3 ^g | 15.7 | 16.3 | 22.3 | |
| 250cc KCl soln. satd. at 70° | 20.1 | 41.9 | 28.4 | 4.7 | 8.3 | 103.4 | |
| 250cc HCl sp. gr. 1.16 | 23.2 | 34.4 | 14.9 | 2.6 | 3.0 | 78.1 | |
| 250cc CaCl ₂ soln. (1:2.5) | 5.3 | 24.5 | 29.7 | 7.0 | — | 66.5 | |
| 250cc NaCl soln. satd. at 30° | 23.0 | 25.2 | 19.4 | 2.1 | 5.2 | 74.9 | |
| 250cc CuCl ₂ soln. satd. at 70° | 20.7 | 35.4 | 21.0 | 2.2 | 8.5 | 87.8 | |
| 250cc KCl soln. satd. at 70° + 10g. FeCl ₃ | 25.6 | 46.5 | 21.7 | 2.3 | 8.9 | 105.0 | |
| 250cc KCl soln. satd. at 70° + 10g. MnCl ₂ | 19.5 | 45.8 | 22.0 | 3.0 | 9.1 | 99.4 | |

The manner with which alcohol is added to the anode solution seems to have some bearing upon the results of the electrolysis. When alcohol was added drop by drop during the course of the electrolysis a better yield of chloral was obtained in comparison with the case in which alcohol was poured all at once at the beginning. To obtain the best yield of chloral the concentration of the chloride must be maintained as great as possible, alcohol should be added gradually as the electrolysis proceeds, and the temperature should gradually be raised to 70°-90° and kept at that temperature interval throughout the electrolysis. Interruption of electrolysis tends to decrease the yield. Current efficiency for chloral was found to be 33.8% and material yield 61.2%.

IV. SYSTEMATIC RESEARCH INTO THE PROGRESS OF CHLORINATION.

With the object of making the manner of the progress of chlorination and oxidation clear by tracing substances formed at each stage of the reactions, electrolysis was carried out with a limited quantity of electric current, and the substances thus formed were studied.

In the first experiment 50 cc. of alcohol were taken, and the electrolysis was conducted at 40°-50° by passing electric currents of 46.05 amp. hours just sufficient to complete the reaction



After the electrolysis was over the anode solution was extracted with ether, and the ethereal extract was fractionated in the manner previously described.

Table VII.

| 60°-90° | 90°-100° | 100°-120° | 120°-130° | |
|------------------|----------|-----------|-----------|------|
| 4.8 ^g | 10.9 | 12.8 | 3.9 | 32.4 |
| 5.5 | 9.8 | 14.1 | 4.1 | 33.5 |

With the greater portion distilled at 90°-120° and at about 130° decomposition was observed to take place. The main fraction (90°-120°) when washed with water and dehydrated showed a specific gravity of 1.07 (15°), and was analysed to contain 29% of chlorine.

Substance taken: 0.2519 gm., AgCl: 0.2953 gm., Cl: 29%.

It slowly decomposes into chloroaldehyde hydrate and chloroacetal when boiled. From these properties the fraction appears to be monochloroaldehyde alcoholate ($\text{CH}_2\text{ClCH} \begin{matrix} \text{OH} \\ \text{OC}_2\text{H}_5 \end{matrix}$ Cl=28.47%). Besides this main product, chloroaldehyde hydrate, ethylacetate and some chloroether were also formed.

In the second experiment the temperature was raised to 70°–80°, and for 50 cc. of alcohol electric currents of 50 amp. hours were passed. The products were extracted and fractionated.

Table VIII.

| 60°–90° | 90°–100° | 100°–120° | 120°–135° | |
|---------|----------|-----------|-----------|------|
| 2.75 | 4.1 | 19.1 | 4.6 | 30.5 |
| 5.0 | 3.8 | 18.9 | 4.2 | 31.9 |

The ethereal extract even in a pure and dehydrated state decomposes partly at about 125° and evolves hydrochloric acid gas. Perhaps this is due to the presence of dichloroether which changes into chloroaldehyde alcoholate and hydrochloric acid by the interaction of water liberated from the chloroaldehyde hydrates.

The main fraction (100°–120°) slightly soluble in water was washed with water and dehydrated. Its sp. gr. was found to be 1.287 (18°) and its chlorine content 43.85%.

Substance taken: 0.3423 gm., AgCl: 0.6068 gm., Cl: 43.85%.

Thus it is evident that the main product is nothing but dichloroaldehyde alcoholate ($\text{CHCl}_2\text{CH} \begin{matrix} \text{OH} \\ \text{OC}_2\text{H}_5 \end{matrix}$ Cl=44.6%). Some ethylacetate, chloroaldehyde hydrate and a little chloral were also formed in this case too.

From the results of the above experiments, it may be seen that the electrolytic chlorination of alcohol ethylacetate is also formed in the early stage of reaction, as A. Brochet¹ observed in the purely chemical process. As chlorinated substances monochloroaldehyde alcoholate, monochloroaldehyde hydrate and a small amount of chloroether are

¹ A. Brochet: Bl. (3), 17, 228 (1897).

produced, and these are further chlorinated to dichloroaldehyde alcoholate, dichloroaldehyde hydrate and dichloroether, and then to chloral alcoholate, chloral hydrate and trichloroether. The last substance will be hydrolysed to dichloroaldehyde alcoholate which is in turn chlorinated to chloral alcoholate.

Thus it is evident that the chlorination of alcohol to chloral passes mainly through the stage of chloroaldehyde alcoholate, and partially through the stages of chloroether and chloroaldehyde hydrate. It is noteworthy that chloroacetal, which is formed considerably in the purely chemical action of chlorine upon alcohol, was never found among the products of electrochemical chlorination.

V. STUDY ON THE COURSE OF THE REACTIONS WHICH GIVE RISE TO MONOCHLOROACETIC ACID.

As has been stated before, monochloroacetic acid is produced as one of the chlorination-products. To decide whether the chlorination takes place after the alcohol has been oxidized into acetic acid or into aldehyde, the following three experiments were performed.

Experiment 1.—50 grams of acetic acid were electrolysed in a potassium chloride solution at 70°–80°, using a current of the density of 0.08 amp/sq.cm. After the currents of 44.6 amp. hours were passed, the anode solution was extracted with ether, and the ethereal extract was fractionated and examined. About 70% of the acetic acid originally taken was recovered, and no chlorinated product was isolated.

Experiment 2.—The chlorination of ethylacetate was then attempted by electrolysing 50 grams of it under conditions analogous to those in the previous experiment. The total current quantity was 57.45 amp. hours. From the ether extract of the anode solution the following fractions were collected :

Table IX.

| 60°–90° | 90°–100° | 100°–120° | 120°–140° | 140°–180° | |
|------------------|----------|-----------|-----------|-----------|------|
| 8.5 ^g | 18.0 | 15.5 | 4.0 | 2.7 | 48.7 |

A very small amount of chloroacetic acid and its ethylester was produced, a larger amount of ethylacetate having been changed into chloroaldehyde, chloral, and acetic acid. Perhaps that which was chlorinated here is the alcohol produced by the hydrolysis of the ethylacetate, and not the

As is shown above hydrolysis seems to take place during the course of electrolysis. The fact that the yield of chloral is decreased, and that of monochloroacetic acid is increased when the electrolysis is interrupted, or is carried out with a dilute chloride solution, may be well regarded as the result of the hydrolysis of the intermediate products which leads to the formation of monochloroaldehyde hydrate. This latter substance is readily oxidized to monochloroacetic acid before it undergoes further chlorination.

SUMMARY.

1. Changes of alcohol at the anode by the electrolysis of its KCl solution were studied.
2. A porous cell suitable for the electrolytic experiments was newly contrived.
3. Chloroacetal which is generally formed by the purely chemical chlorination of alcohol could not be found among the products of electrolytic chlorination.
4. The presence of monochloroacetic acid as one of the chlorination-products was observed, and the course of the reactions leading to this formation was studied.
5. A general scheme showing the oxidation and chlorination reactions was proposed.

In conclusion, the author wishes to express his thanks to Professor M. Matsui for the kind interest which he has taken throughout this research.
