

# The Electrolytic Oxidation of Alcohols, IV. Electrolytic Oxidation of Propylalcohol in Alkaline Solutions

By

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According to Habermann<sup>1)</sup> and E. Müller<sup>2)</sup> when methylalcohol, the lowest member of the aliphatic alcohols, is subjected to electrolytic oxidation in a concentrated solution of caustic soda, hydrogen is evolved in great quantities at the anode; whereas if ethylalcohol is subjected to the same treatment there are evolved at the anode hydrogen and methane as the chief products in addition to a small quantity of ethane. As to the mechanism of the above reaction different explanations have been proposed by E. Müller<sup>3)</sup> on the one hand and Fr. Fichter<sup>4)</sup> on the other; the latter assumes the intermediate formation of a peroxide, while the former considers it more probable that alcoholate ions change temporarily to the compounds containing a pentavalent carbon atom, such as  $RCH_2:O$ .

Both of these explanations have, however, received no confirmation yet and as the elucidation of such a mechanism may lead to the clearing up of the real nature of the Kolbe reaction, the present writer has attempted to investigate the electrolytic oxidation of the higher alcohols

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1 Monatsh., **7** (1886), 540.

2 Zeit. f. Elekt. Chem., **20** (1914), 367; Ann., **420** (1920), 241; Zeit. f. Elekt. Chem., **27** (1921), 54; **27** (1921), 563.

3 Zeit. f. Elekt. Chem., **27** (1921), 54; **27** (1921), 563; **28** (1922), 101.

4 Helv. Chem. Acta, **1** (1918), 146; Zeit. f. Elekt. Chem., **27** (1921), 489.

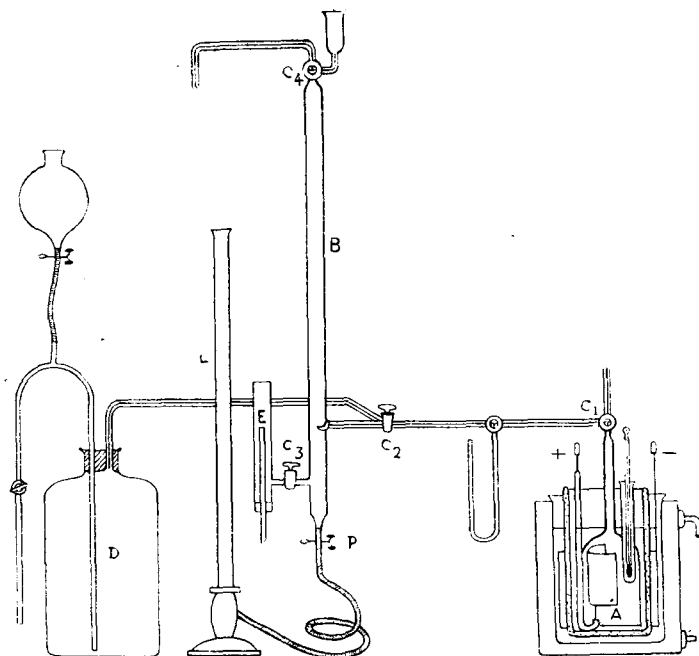
with the expectation to get some insight into the above stated relation. Furthermore, a perusal of the literature of a similar experimental study of the aliphatic alcohols reveals the fact that there are, regarding monatomic alcohols higher than propylalcohol, only the experiments made by Müller, which rather negate the previous reactions. According to him, the evolution of anodic hydrogen was extremely small, and no reaction similar to that of methyl or ethyl alcohol could be recognized, and he came to the conclusion that it was impossible to realize a reaction leading to the anodic formation of a combustible gas from monatomic alcohols higher than propylalcohol by means of the electrolysis. It is conceivable, however, that this fact is caused by the inadequacy of concentration of the higher alcohol in the anode solutions due to the scantiness of its solubility in the caustic soda solutions. Starting from this conception, the present writer attempted to examine the anodic reaction of the higher monatomic alcohols, taking methylalcohol as the solvent for increasing their concentration. Propylalcohol was first subjected to the operation and the evolution of a fairly large quantum of combustible gases such as ethane and ethylene, etc., besides hydrogen, was clearly recognized, and conclusive evidence for the production of a similar reaction to that of the lower alcohols was secured.

Methylalcohol used as the material for experiment was of B. P.  $65^{\circ}-66^{\circ}$ , and sp. gr.  $0.797\frac{15^{\circ}}{15^{\circ}}$ . It was prepared by redistillation of Merck's sample.

*n*-Propylalcohol used as the material was of B. P.  $97^{\circ}-98^{\circ}$  and sp. gr.  $0.807\frac{15^{\circ}}{15^{\circ}}$ . It was prepared by redistillation of Kahlbaum's sample.

Apparatus used for Electrolysis.

The electrolyzing apparatus as shown in the figure was thus contrived. The bell jar A carries a tube closed at one end into which a small quantity of mercury is poured and a thermometer inserted. The anode plate stands within the jar upon a glass tube bent in U-form to which its stem is firmly sealed. The jar and the anode are sunk into a porous earthenware cylinder filled with the anode solution. By filling the jar completely with the anode solution, by application of suction at the three-way cock  $C_1$ , and then beginning the electrolysis, it is possible to collect all the gases evolved at the anode in an uncontaminated state in the bell jar. The gas burette B and the gas reservoir D and all the capillary tubes connecting them with the cock  $C_1$  were completely filled



with water saturated with the anode gas before actual measurement was commenced. From time to time during the electrolysis, the anode gas evolved in the jar was transferred to the burette and the volume read off. The levelling tube E is provided for the purpose of regulating the gas pressure when it is led into the burette B. D is a provisional gas reservoir. The volume of the gas in the burette B is measured by closing the three-way cock  $C_2$  and the stop cock  $C_3$ , opening the pinch cock P, and adjusting the pressure to the prevalent atmospheric pressure by moving the levelling tube L up and down. The gas is then transferred to an ordinary gas-burette to be subjected to analysis.

### I. Methylalcohol.

Anode :	Platinum plate 36.21 sq. cm. ( $7.1 \times 5.1$ ), active surface 72.42 sq. cm.
Anode solution :	175 cc. of 8 N—NaOH mixed with 175 cc. of $\text{CH}_3\text{OH}$ .
Cathode :	Nickel gauge.
Cathode solution :	4 N—NaOH.
Temperature :	$15^\circ - 17^\circ \text{C}$ .
Current :	1 amp.
Current density :	0.0138 amp./sq. cm.

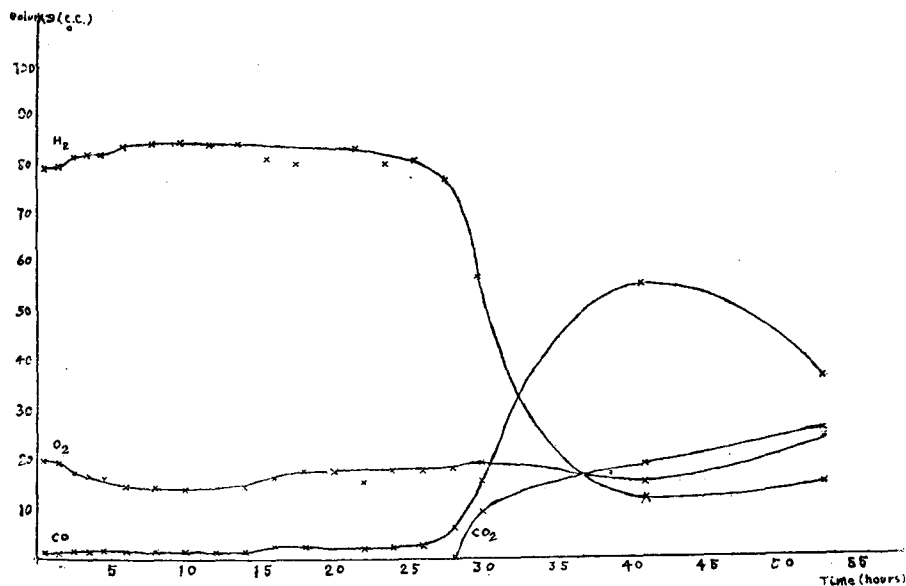
Table I.

Duration of electrolysis	Anode gas cc./hour	CO <sub>2</sub>	O <sub>2</sub>	CO	H <sub>2</sub>
0-1	25.5	0	19.5	1.2	79.0
1-2	23.9	0	19.0	1.0	79.5
2-3	22.6	0	17.0	1.5	81.1
3-4	24.7	0	16.4	1.2	82.0
4-5	25.0	0	16.0	1.6	82.0
5-7	23.5	0	14.5	1.3	83.7
7-9	23.3	0	14.2	1.3	84.3
9-11	23.0	0	13.8	1.4	84.5
11-13	22.8	0	14.4	1.3	84.0
13-15	21.9	0	14.1	1.5	84.1
15-17	21.5	0	16.2	2.6	81.0
17-19	21.0	0	17.6	2.2	79.8
19-21	20.9	0	17.5	—	—
21-23	21.0	0	15.1	2.0	82.6
23-25	19.5	0	17.9	2.1	79.0
25-27	17.7	0	17.4	2.6	79.8
27-29	14.5	0.2	18.0	6.1	75.6
29-31	14.0	9.1	19.1	15.5	56.1
31-51	21.5	18.6	15.0	54.5	11.7
51-55	22.0	25.2	23.8	35.9	14.8

The above results may be represented in curves for the individual constitute gases in the figure on the next page.

As can be clearly seen from the curves, in the neighborhood of 30 hours after the commencement of electrolysis, the evolution of anode hydrogen diminishes rapidly and that of carbon monoxide increases equally rapidly, while carbon dioxide begins to be freshly formed. This change is probably an indication of the ending of the characteristic reaction, and the sudden increase of carbon monoxide and the new evolution of carbon dioxide is due to the destructive oxidation of aldehyde and acid.

By the experiments above described it was ascertained that the particular gases evolved at the anode during the electrolytic oxidation of methylalcohol consisted of hydrogen and a small quantity of carbon-monoxide alone and that there was no production of hydrocarbons. Steps were therefore taken to examine the reactions of the anodic oxidation of



higher monoatomic alcohols in a caustic soda solution with methylalcohol as solvent.

### II. Normal Propylalcohol.

Anode : Platinum plate 72.42 sq. cm. (active surface)  
 Anode solution : 150 cc. of 8 A-NaOH mixed with 75 cc. of CH<sub>3</sub>OH and 75 cc. of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH  
 Cathode : Nickel gauge.  
 Temperature : 20° - 25°.  
 Current density : 0.0138 amp./sq. cm.

Table II.

Gas employed	100.0 cc.	
After absorption with conc. KOH soln.	73.8	26.2% CO <sub>2</sub>
"    "    "    Bromine water	61.7	12.1 C <sub>11</sub> H <sub>22</sub> n
"    "    "    Alkaline pyrogallie acid soln.	54.5	7.2 O <sub>2</sub>
"    "    "    Ammoniacal Cu <sub>2</sub> Cl <sub>2</sub>	45.4	9.1 CO
20cc. of the remaining gas were mixed with oxygen to	99.2	
After explosion	65.7	
Contraction by explosion (C <sub>X</sub> )	33.5	37.7% H <sub>2</sub>
After absorption with conc. KOH soln.	58.8	
Contraction by absorption with KOH (C <sub>KOH</sub> )	6.9	7.8% C <sub>2</sub> H <sub>6</sub>

By the electrolysis extending over 30 hours there were collected about 800 cc. of anode gases. Analysis of a portion thereof gave the results as is seen in the table II.

As the presence of saturated as well as unsaturated hydrocarbons was ascertained by the results of the analysis, the following qualitative examinations were carried out.

(1) Unsaturated Hydrocarbons.

Table III.

Gas employed	100.0 cc.		
After absorption with conc. KOH soln.	73.9	26.1%	CO <sub>2</sub>
"    "    "    Hg(CN) <sub>2</sub> reagent	73.5	0.4	
"    "    "    Hg(NO <sub>3</sub> ) <sub>2</sub> reagent	62.6	10.9	C <sub>2</sub> H <sub>4</sub>
"    "    "    Bromine water	61.7	0.9	

Table IV.

Gas employed	100.0 cc.		
After absorption with conc. KOH soln.	74.0	26.0%	CO <sub>2</sub>
"    "    "    H <sub>2</sub> SO <sub>4</sub> (sp. gr. 1.84)	72.0	2.0	
"    "    "    Hg(NO <sub>3</sub> ) <sub>2</sub> reagent	61.8	10.2	C <sub>2</sub> H <sub>4</sub>
"    "    "    Bromine water	61.6	0.2	

As is clear from Table III, among the unsaturated hydrocarbons there is almost none that is absorbed by the mercuric cyanide reagent<sup>1)</sup>, the special absorbent for acetylene. The greater part is absorbed by the mercuric nitrate reagent<sup>2)</sup>, the special absorbent for ethylene. When finally tested with bromine water for any remaining heavy hydrocarbons there was almost none detectable. As the mercuric nitrate reagent, however, absorbs propylene besides ethylene, in the experiment shown in Table IV a conc. sulphuric acid reagent<sup>3)</sup> was used as the absorbent for propylene, and it was found that a small percentage was absorbed by the reagent. The bulk of the gas, however, was absorbed by the mercuric nitrate reagent, showing that the unsaturated hydrocarbons formed in the electrolysis consist principally of ethylene.

1, 2. Treadwell u. Tauber, *Helv. Chim. Acta.* **2** (1919); 601.

3. Sutton, *Volumetric Analysis* p. 533.

(2) Saturated Hydrocarbons.

Table V.

Gas employed	100.0 cc.		
After absorption with conc. KOH soln.	73.9	26.1%	CO <sub>2</sub>
"    "    "    Bromine water	61.7	12.2	C <sub>2</sub> H <sub>4</sub>
"    "    "    Alkaline pyrogallic acid soln.	54.4	7.3	O <sub>2</sub>
"    "    "    Ammoniacal Cu <sub>2</sub> Cl <sub>2</sub>	45.2	9.2	CO
After fractional combustion with Pd-black	7.8	37.4	H <sub>2</sub>
7.8 cc. of the remaining gas were mixed with oxygen to	40.8		
After explosion	24.1	C <sub>x</sub> = 16.7	$\frac{C_x}{C_{KOH}} = 1.265$
After absorption with Conc. KOH	10.9	C <sub>KOH</sub> = 13.2	

Table VI.

7 cc. (C <sub>n</sub> H <sub>2n+2</sub> ) + O <sub>2</sub>	=	85.0		
After explosion		73.9	C <sub>x</sub> = 11.1	$\frac{C_x}{C_{KOH}} = 1.233$
After absorption with KOH		64.9	C <sub>KOH</sub> = 9.0	

Table VII.

10 cc. (C <sub>n</sub> H <sub>2n+2</sub> ) + O <sub>2</sub>	=	85.8		
After explosion		63.3	C <sub>x</sub> = 22.5	$\frac{C_x}{C_{KOH}} = 1.257$
After absorption with KOH		45.4	C <sub>KOH</sub> = 17.9	

Table VIII.

13 cc. (C <sub>n</sub> H <sub>2n+2</sub> ) + O <sub>2</sub>	=	95.6		
After explosion		67.7	C <sub>x</sub> = 27.9	$\frac{C_x}{C_{KOH}} = 1.1$
After absorption with KOH		42.4	C <sub>KOH</sub> = 25.3	

In the experiments shown in Tables VI, VII and VIII definite quantities of the gas mixture were first treated step by step with the necessary absorbents completely to remove CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, O<sub>2</sub>, and CO. Hydrogen was now absorbed with palladium black at 80°–90° and the remaining gas was then mixed with oxygen and the mixture subjected to fractional combustion of the residual hydrogen by means of palladium black. After thus removing hydrogen completely, the gas, consisting of saturated hydrocarbons mixed with air in the palladium tube, was subjected

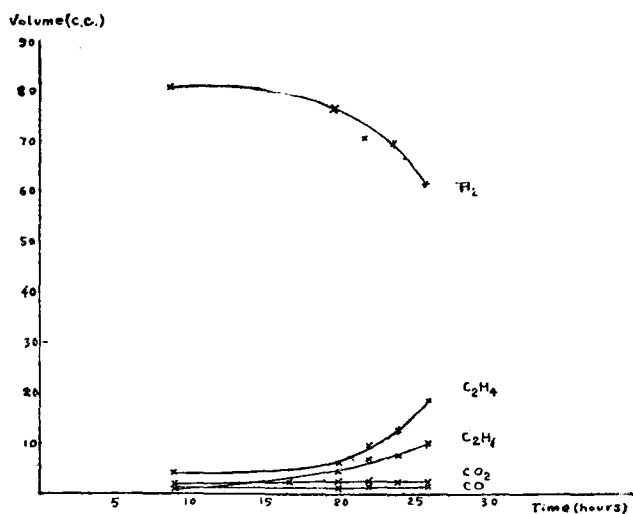
to explosion, and the contraction by explosion was compared with the contraction by subsequent absorption with a solution of caustic potash. This ratio in the case of ethane is represented in the following equation:  $C_2H_6 + 3.5 O_2 = 2CO_2 + 3 H_2O$ ;  $C_x/C_{KOH} = 1.25$ . From the figures obtained for  $C_x/C_{KOH}$ , it was concluded that the saturated hydrocarbon formed in the present instance was chiefly ethane.

(3) Change of Composition of the Anode Gas with Temperature.

Electrolysis at  $25^\circ$ , other conditions kept the same as before,

Table IX.

Duration of electrolysis	Anode gas cc./hour	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	O <sub>2</sub>	CO	H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>
0-19 hours	24.7	1.9	4.0	10.1	1.4	81.2	1.0
19-21	20.0	2.2	5.9	10.8	1.0	75.3	4.3
21-23	19.3	2.3	9.5	10.6	1.2	69.2	6.8
23-25	17.1	2.1	12.4	9.7	2.1	68.2	7.4
25-27	16.8	2.1	18.4	9.2	1.5	60.0	9.8

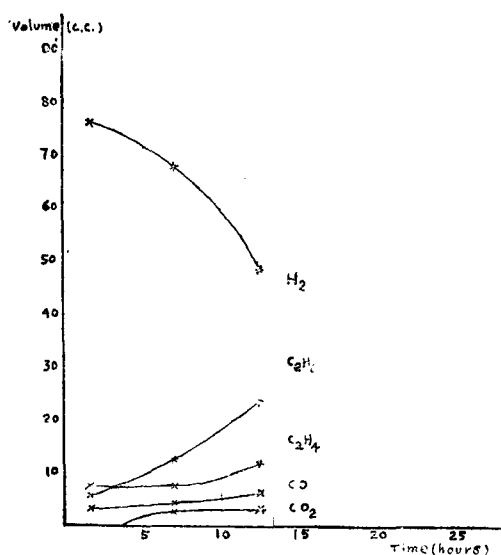




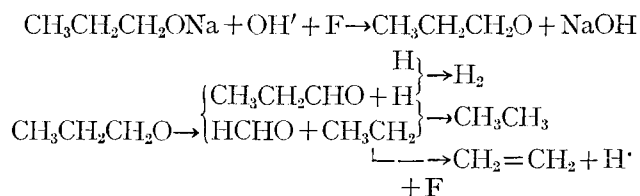
Electrolysis at 15°–18°.

Table X.

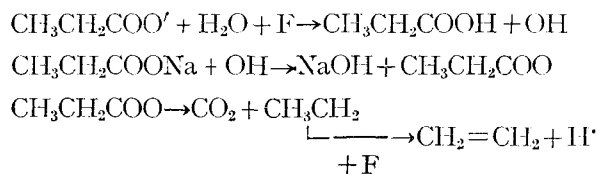
Duration of electrolysis	Anode gas cc./hour	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	O <sub>2</sub>	CO	H <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>
0–3.5 hours	30.7	0.0	7.5	7.9	3.2	76.3	5.9
3.5–10.5	27.8	2.8	7.4	5.2	4.2	67.7	12.5
10.5–14.5	25.2	3.2	11.8	6.2	6.2	48.5	23.5



From the experiments here reported the fact becomes evident that by the electrolytic oxidation of propylalcohol in a caustic alkali solution ethylene and ethane are produced together with hydrogen, and the yield of such saturated and unsaturated hydrocarbons are greatly increased by lowering the electrolysing temperature. More especially, the fact that such an unsaturated hydrocarbon as ethylene is evolved here must be intimately related to the fact that an unsaturated hydrocarbon is produced in the Kolbe reaction, for instance, ethylene from salts of propionic acid. The above phenomenon is therefore a question full of importance in considering the mechanism of the Kolbe reaction. Although there must be many more experimental explanations for the elucidation of this mechanism, the reaction is presumed to proceed through the following stages in the case of propylalcohol:



The Kolbe reaction of the salts of propionic acid may be deemed to take place just analogously as follows :



In the Kolbe reaction of the salts of propionic acid, contrary to that of propylalcohol, there is no evolution of hydrogen and the reason for the non-appearance of ethane is, therefore, self-evident.

This investigation was carried out under the direction of Professor Motooki Matsui with the aid of the fund granted to him by the Imperial Academy of Japan. The author wishes, therefore, to acknowledge his obligations to the Imperial Academy of Japan and to Prof. M. Matsui.