ON THE THERMAL DECOMPOSITION OF FATTY PRIMARY ALCOHOLS.

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M. Berthelot⑴ studied the thermal decomposition of ethyl alcohol in 1851. Since then many works on the line have been done by many different researchers. The main reactions may be expressed by the following formulas:

$R.CH_2OH = R.CHO + H_2,$ .... (1)
$R.CH_2OH = R' : CH_2 + H_2O,$ and .... (2)
$2R.CH_2OH = (R.CH_2)_2O + H_2O.$ .... (3)

Also the effects of many kinds of the catalysts on the reaction have been studied. Some of them having intimate relations with the present experiment may be mentioned as references. Sendrens⑵ perceived the formation of methyl ether and water by passing methyl alcohol upon alumina heated at 300-350° and Inoue⑶ reported the formation of ethylene, carbon dioxide and para-formaldehyde by passing the alcohol with air or carbon dioxide upon heated Japanese acid clay.

Ethylene and water were produced from ethyl alcohol by passing the alcohol on aluminium oxide at 400°,⑷ while ethyl ether and water were produced by using alumina heated at 240–260° on the reaction.⑸ When Japanese acid clay was used as the catalyst on the reaction, ethylene, ethyl ether, ester and aldehyde were produced⑹; the catalyst was used in the manufacture of ethylene in a semi-industrial scale.⑺

n-Propyl alcohol behaves similar to ethyl alcohol on the reaction. On passing upon aluminium oxide heated at 560°, n-propyl alcohol gave propylene and water as the decomposition products⑻; and propyl ether was the additional product to the above ones, when the reaction was conducted under high temperature and pressure.⑼

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(1) *Ann. chim. phys.*, [3] **33** (1851), 295; *Ann.*, **81** (1852), 108.

(2) *Compt. rend.*, **148** (1909), 928; *Bull. soc. chim.*, [4] **5** (1909), 480.

(3) This Bulletin, **1** (1926), 197.

(4) Sabatier and Mailhe, *Compt. rend.*, **146** (1908), 1376; **147** (1908), 106.

(5) Sendrens, *Compt. rend.*, **148** (1909), 228; *Bull. soc. chim.*, [4] **5** (1909), 480.

(6) Inoue, this Bulletin, **1** (1926), 198.

(7) Kashima, Mihara and Takahashi, Japanese Patent, 81,337 (1929).

(8) Ipatiew, *Ber.*, **36** (1903), 1997.

(9) Ipatiew, *Ber.*, **37** (1904), 2997.

LeBel and Greene(1) obtained a mixture of two butylenes by dropping n-butyl alcohol upon strongly heated zinc chloride and Sendrens(2) gained the mixture by passing the alcohol on aluminium phosphate.

Lemoine(3) proved the formation of n-amylene by passing n-amyl alcohol upon a coal (*braise de boulanger*) heated at 430°.

From the above results and others, the reactions may be summarised as follows: When aliphatic primary alcohols are thermally decomposed, aldehyde are formed after dehydrogenation and olefines or ethers after dehydration. And the formation of ethers seems to occur at lower temperature than that of olefines.

It was presumed, from the standpoint of thermochemistry, that ethers were produced firstly in the thermal decomposition of the alcohols and then they were further decomposed into olefines and water. The writer therefore attempted to make clear the mechanism of the thermal decomposition of the alcohols by using Japanese acid clay as the catalyst and methyl, ethyl, n-propyl, n-butyl and n-amyl alcohols as the materials.

The heat effects, Q_1, Q_2, and Q_3, in the following three reactions, (4), (5) and (6), may be calculated by the succeeding three formulas, (7), (8) and (9), respectively:

$$2R.CH_2OH = (R.CH_2)_2O + H_2O + Q_1, \quad \ldots\ldots \quad (4)$$
$$R.CH_2OH = R'{:}CH_2 + H_2O + Q_2, \text{ and} \quad \ldots\ldots \quad (5)$$
$$(R.CH_2)_2O = 2R'{:}CH_2 + H_2O + Q_3. \quad \ldots\ldots \quad (6)$$
$$Q_1 = (\text{ether}) + (\text{water}) - 2\,(\text{alcohol}), \quad \ldots\ldots \quad (7)$$
$$Q_2 = (\text{olefine}) + (\text{water}) - (\text{alcohol}), \text{ and} \quad \ldots\ldots \quad (8)$$
$$Q_3 = 2\,(\text{olefine}) + (\text{water}) - (\text{ether}). \quad \ldots\ldots \quad (9)$$

Where, (ether), (water), (alcohol) and (olefine) represent the heats of formation of ethers, water, alcohols, and olefines, respectively.

The heats of formation of organic compounds are intensively described in Berthelot's work(4) or in Stohmann's papers.(5) But those of the five alcohols and ethers and the four olefines mentioned in this paper are not given by a series of the experiment and there are some differences according to the authors. J. Thomsen's values are therefore adopted from his work(6)

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(1) *Amer. Chem. J.*, **2** (1880), 24.

(2) *Compt. rend.*, **144** (1907), 1110; *Bull. soc. chim.*, [4] **1** (1907), 692.

(3) *Bull. soc. chim.*, [4] **3** (1908), 940.

(4) "Essai de mécanique chimique," I, p. 406. Paris, Dunod, 1879.

(5) *Z. physik. Chem.*, **6** (1890), 334.

(6) "Thermochemistry," translated by K.A. Burke, pp. 369, 467, etc. London, Longman, Green & Co., 1908.

and those not obtained experimentally are calculated by his formulas. Those values and the calculated Q_1, $2Q_2$ and Q_3 are given in Table 1 ;

Table 1.

Substance	Heat of formation, Cal.	Q_1, Cal.	$2Q_2$, Cal.	Q_3, Cal.
Methyl alcohol	50.58	—	—	—
Dimethyl ether	48.19	4.67	—	—
Ethyl alcohol	57.02	—	—	—
Diethyl ether	67.43	11.03	—	—
Ethylene	−3.29	—	−5.34	−16.37
n-Propyl alcohol	63.66	—	—	—
Di-n-propyl ether	76.37	16.54	—	—
n-Propylene	2.06	—	−7.92	−4.76
n-Butyl alcohol	69.51	—	—	—
Di-n-butyl ether	90.39	18.86	—	—
n-Butylene	6.49	—	8.94	9.90
n-Amyl alcohol	74.64	—	—	—
Di-n-amyl ether	104.41	22.52	—	—
n-Amylene	12.43	—	10.56	12.06

The thermal effect, Q_1, in the case of ether-formation is always larger than $2Q_2$ and Q_3. It is therefore assumed that when the alcohols are passed over the heated Japanese acid clay, corresponding ethers are firstly produced and then the ethers decompose into olefines and water by the further action of the heated clay. Figs. 2, 3 and 4 show the mutual quantitative relations between the decomposition products at different reaction temperatures from ethyl, propyl and butyl alcohols ; that the amounts of olefines and water produced increase with the rise in the reaction temperature, while that those of ethers and alcohols in the decomposition products decrease with the rise in temperature will sufficiently explain the above assumption.

The Japanese acid clay used as the catalyst in the experiment is produced in the Province of Niigata, giving the following analytical result :

Table 2.

Composition of Japanese Acid Clay, per cent.

H_2O	Loss on ignition	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO
10.15	5.28	63.78	5.94	14.63	0.48	0.82

The clay is well mixed with about 80 per cent. water and pressed through a 8-mesh sieve obtaining prisms having wrinkles on the sides. They are dried at 100°, cut into cubes and filled in a combustion tube of 15 mm. diameter to the length of 450 mm., the weight of the clay being about 55 grams. The glass tube is inserted into a porcelain tube to be heated electrically. The clay is previously heated in the glass tube at about 350–400° for getting rid of water and for making active. When the clay thus treated attains a desired temperature, a sample is gradually dropped into a space in one end of the glass tube from a burett, which vaporises and is decomposed by the heated clay. A Liebig condenser, a special receiver for liquid and a gas-holder are attached to the other end of the tube. When the reaction is completed, the products in the receiver and the gas-holder are analysed. In the case of methyl alcohol, a washing bottle containing concd. sulphuric acid is inserted between the receiver and the gas-holder for absorbing methyl ether produced by the reaction, which will naturally also absorb one part of the olefine, though it is not desired.

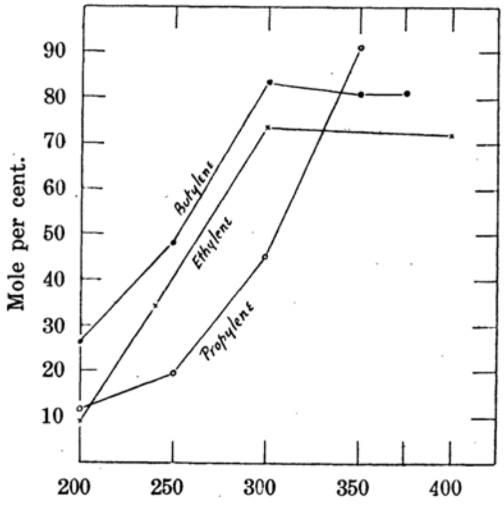

Fig. 1.

Generally, when the alcohols are passed over heated Japanese acid clay, corresponding ethers, olefines, aldehydes, water and sometimes esters are produced as the decomposition products. The amounts of olefines increase with the rise in the reaction temperature, which is shown in Fig. 1. Above a certain temperature the amounts of olefines and water become almost constant, which shows the steady progress of the reaction.

The double bond of the olefine produced belongs to the carbon atom linked with the hydroxyl group:

$$R.CH_2.CH_2OH \longrightarrow R.CH:CH_2.$$

However, in the case of n-butyl alcohol, the olefine produced is a mixture of ethyl ethylene ($C_2H_5.CH:CH_2$) and dimethyl ethylene ($CH_3.CH:CH.CH_3$), the latter being predominated (cf. Table 15). It may be assumed that the former is produced firstly and is changed into the latter stable form by the moving of the double bond by the further action of the heated clay. LeBel and Greene⁽¹⁾ and Sendrens⁽²⁾ obtained the mixture by dropping n-butyl alcohol upon heated zinc chloride or passing the alcohol over aluminium phosphate, which may be ascribed to the same cause. The ratio of the two olefines varies according to the reaction temperature, dimethyl ethylene being 2–6.5 times of ethyl ethylene.

The amounts of ethers in the decomposition products decrease with the rise in the reaction temperature and almost zero at high temperature (cf. Figs. 2, 3 and 4). They also decrease as the molecular weights of the alcohols increase. From the fact that the values of Q's are proportional to the molecular weights of the alcohols, the degree of olefine-formation from ethers will become easier according to the increasing molecular weights.

It may also be mentioned that esters are produced at generally low temperature. In the case of ethyl alcohol, the ester is formed in comparatively larger amount than the cases of the other alcohols.

Methyl Alcohol. Pure methanol of Merck free from aldehyde and distilled over quick lime is used as the material, boiling point of which being 65°. As the general procedure throughout the series, the alcohol is gradually dropped into a space of one end of the reaction tube previously heated at a certain temperature and the decomposition products are collected in a receiver and a gas-holder attached to the other end of the reaction tube through a Liebig condenser. In the case of methyl alcohol, a washing bottle containing concd. sulphuric acid is inserted between the receiver and the gas-holder. The gas produced is analysed according to the ordinary method. The identification of the olefine is generally done through its bromide. After testing some qualitative properties of the liquid part of the decomposition products, it is fractionally distilled with caution and the each fraction is examined by proper methods.

The experimental conditions, the decomposition products and the analytical results are summarised in Tables 3, 4 and 5:

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(1) Loc. cit.

(2) Loc. cit.

Table 3.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Increase of weight of H_2SO_4-bottle, gr.	C_nH_{2n} yield, mole %
				Liquid, gr.	Gas, L.		
1	51.3	200	0.4	19	0.5	29	0.51
2	41.8	200	0.4	24	0.5	15	0.62
3	149.0	270	0.6	130	1.0	11	—
4	64.0	270	0.5	26	0.5	19	—
5	46.0	270	0.9	18	0.8	19	0.65
6	135.1	400	0.4	64	12.7	60	1.18
7	83.0	400	0.4	36	5.4	9	1.73

Table 4.

Composition of the Produced Gas, volume per cent.

No.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
1	36.2	1.7	0	11.2	12.8	18.8
2	36.4	2.2	0	10.0	7.5	23.7
3	—	—	—	—	—	—
4	—	—	—	—	—	—
5	26.3	0	0.4	11.9	22.4	22.6
6	8.8	3.2	15.5	1.2	37.6	33.7
7	18.6	2.8	10.0	1.4	30.9	36.3

Table 5.

Composition of the Produced Liquid, per cent.

No.	Alcohol	Water	Aldehyde
1	31.6	52.6	0.09
2	52.1	25.0	0.09
3	74.2	9.2	—
4	59.6	26.9	0.07
5	27.2	63.9	0.06
6	32.8	56.3	0.40
7	31.7	60.6	0.68

A bromide obtained by carefully passing the gas of No. 5 into bromine water is washed, dried and distilled, two fractions being obtained. The one boils at 130–131° and the other at 140–141°. The former boiling point corresponds to that of ethylene dibromide and the latter to that of propylene dibromide. The olefine obtained is therefore a mixture of ethylene and propylene.(1)

When the sulphuric acid solution of the 7th column of Table 3 is dropped into about same amount of water, a colourless gas is produced. The gas collected over mercury dissolves into water and condenses into a colourless liquid by introducing it into a small U-tube loosely filled with glass-wool and cooled at –35°, the liquid boils at –23.5°. It is therefore dimethyl ether.

When methyl alcohol is passed over Japanese acid clay heated at 400°, a small amount of crystalline mass condensed at the inlet part of the Liebig condenser, which melted at 162-163°, after purified from alcohol, it will therefore be hexamethyl benzene.(2)

In No. 7, a washing bottle containing water is used instead of a sulphuric acid one, which resulted the increasing percentages of olefine, carbon monoxide and hydrogen in the produced gas.

Ethyl Alcohol. Pure ethyl alcohol is used after distilling over quick lime and silver oxide, boiling point of which being 78°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 6, 7 and 8 and the mutual relation of the main products (in percentages to the sample) is shown in Fig. 2:

Table 6.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Ethylene yield, %
				Liquid, gr.	Gas, L.	
8	43.3	200	0.12	28	4.5	6.81
9	37.4	200	0.13	23	2.3	3.69
10	44.6	200	0.14	31	2.0	3.27
11	86.2	200	0.11	58	9.2	8.68
12	56.8	240	0.19	30	11.5	21.51
13	57.0	240	0.18	25	11.0	21.02
14	48.7	300	0.13	19	22.6	46.46
15	54.6	300	0.15	22	22.6	43.21
16	51.6	400	0.17	20	23.5	45.83
17	42.9	400	0.12	18	17.4	41.42

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(1) LeBel and Greene, loc. cit.

(2) LeBel and Greene, loc. cit.

Table 7.

Composition of the Produced Gas, volume per cent.

No.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
8	52.4	0.1	0.7	9.6	1.8	3.2
9	47.8	0.5	1.2	11.2	1.3	3.0
10	58.4	0.6	0.8	9.4	4.2	6.2
11	64.9	3.2	0.3	7.2	3.8	8.6
12	84.9	3.6	0.3	3.7	2.2	3.1
13	87.0	2.0	0.4	3.4	2.3	3.7
14	80.0	5.5	0.2	10.9	1.0	2.4
15	83.4	5.2	0.2	6.2	1.4	3.6
16	80.4	6.1	0.4	7.3	3.3	2.5
17	81.6	5.0	0.2	9.3	1.5	0.8

Table 8.

Composition of the Produced Liquid, per cent.

No.	Alcohol	Water	Ether	Aldehyde	Ester
8	41.4	14.6	42.1	0.16	0.89
9	33.0	10.4	36.5	0.56	0.43
10	35.8	11.6	37.1	0.40	0.32
11	30.0	8.6	31.0	0.34	0.17
12	31.7	37.0	15.3	0.17	0.16
13	40.8	47.2	12.0	0.19	0.60
14	2.6	92.1	trace	0.09	—
15	2.7	92.7	0	0.05	—
16	trace	96.0	0	0.10	—
17	trace	94.4	0	0.06	—

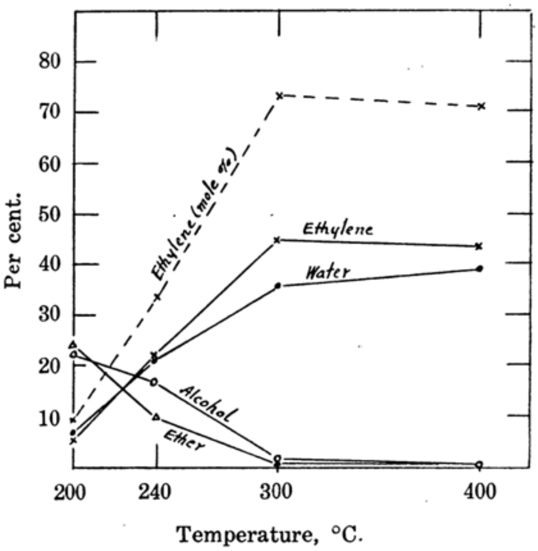

Fig. 2.

The amounts of the gas, ethylene and water produced increase with the rise in temperature and they become almost constant at above 300°. The purity of ethylene increases also with the rise in temperature. The amounts of ether and of the remaining undecomposed alcohol in the decomposition products decrease as the temperature rises.

As stated above, the above facts prove that ether is firstly produced in the reaction when the temperature is not high, one part of which being decomposed into ethylene and water, but it is almost completely changed into ethylene and water as the temperature rises and the reaction proceeds in the same mode.

n-Propyl Alcohol. Pure n-propyl alcohol of Eastman Kodak Co. was used after purifying with distillation, boiling point of which being 94°. The experimental conditions, the decomposition products and the analytical results of the products are summarised in Tables 9, 10 and 11 and the mutual relation of the main products (in percentages to the sample) is shown in Fig. 3:

Table 9.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Propylene yield, %
				Liquid, gr.	Gas, L.	
18	80.8	200	0.75	70	10.5	5.6
19	80.5	200	0.76	68	5.8	.11.0
20	151.0	250	1.67	118	14.0	14.7
21	111.0	300	1.23	63	22.4	32.5
22	53.0	350	0.75	12	19.0	65.2

Table 10.

Composition of the Produced Gas, volume per cent.

No.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
18	23.0	0	0.2	17.0	6.0	7.2
19	81.5	7.4	0.2	3.7	2.0	1.3
20	84.0	—	—	—	—	—
21	86.0	—	—	—	—	—
22	97.0	0	1.8	1.1	—	—

Table 11.

Composition of the Produced Liquid, per cent.

No.	Alcohol	Water	Ether	Aldehyde	Ester
18	77.6	3.5	12.9	0.17	+
19	68.2	7.8	17.7	0.19	+
20	79.7	5.2	3.5	0.24	—
21	46.5	—	—	—	—
22	8.3	84.2	2.5	0.09	—

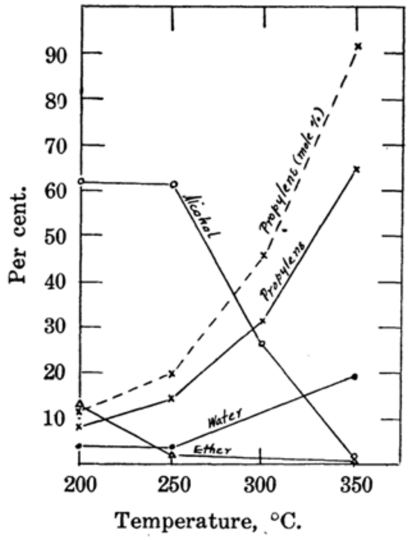

Fig. 3.

The amounts of the gas and of propylene produced increase with the rise in temperature. When the reaction temperature is not high, the amount of n-propyl ether in the decomposition products is large, but small at higher temperature. The purity of propylene increases as the reaction temperature rises, it being 97 per cent. at 350°; the method is therefore applied to the preparation of the olefine, the yield being about 93 per cent.

n-Butyl Alcohol. Pure n-butyl alcohol of Eastman Kodak Co. was used after distillation, boiling point of which being 117°. The experimental conditions, the decomposition products and the analytical results of the products are summarised in Tables 12, 13 and 14 and the mutual relation of the main products (in percentages to the sample) is shown in Fig. 4.

Table 12.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Butylene yield, %
				Liquid, gr.	Gas, L.	
23	193.0	200	0.40	165	18.3	19.9
24	48.2	250	0.40	25	7.5	36.1
25	49.9	250	0.42	28	7.8	36.8
26	64.3	300	0.53	23	16.5	62.3
27	46.6	300	0.39	15	12.8	65.1
28	51.5	350	0.47	16	13.1	60.6
29	45.0	350	0.47	14	11.8	60.6
30	52.3	370–380	0.44	16	13.5	60.9
31	48.2	370–380	0.40	14	12.3	60.4

Table 13.

Composition of the Produced Gas, volume per cent.

No.	C_nH_{2n}	CO_2	CO	O_2
23	83.7	0	0	3.0
24	92.7	0	0	1.6
25	94.2	0	0	1.2
26	96.9	0	0.4	0
27	94.7	0	0	1.1
28	95.2	0.9	0.8	1.8
29	92.4	0	0	2.0
30	94.2	0	0	1.3
31	96.1	0	0	0.8

Table 14.

Composition of the Produced Liquid, per cent.

No.	Alcohol	Water	Ether	Aldehyde	Ester
23	67.0	29.2	1.2	0.37	trace
24	38.5	45.5	trace	—	trace
25	54.1	42.4	trace	—	—
26	12.7	65.6	0	—	—
27	16.7	70.0	0	—	—
28	14.1	48.4	0	—	—
29	11.6	67.0	0	—	—
30	15.6	65.6	0	—	—
31	17.3	68.6	0	—	—

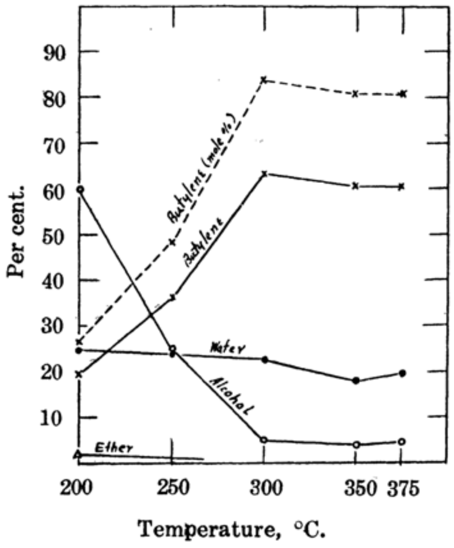

Fig. 4.

When bromine is reacted carefully at low temperature, the produced gas absorbs it. The dibromide thus obtained is washed, dried and fractionally distilled, the result being shown in Table 15:

Table 15.

Composition of Butylene Dibromide, per cent.

No.	Reaction temperature	Low-boiling fraction	α-Compd.	β-Compd.	β/α
24	250	10.2	12.8	76.9	5.9
25	250	3.8	19.2	76.9	3.9
26	300	10.0	12.0	78.0	6.5
27	300	3.1	21.8	75.0	3.4
28	350	9.6	25.8	64.5	2.5
29	350	11.7	11.7	76.4	6.5
30	370–380	8.6	30.4	60.9	2.0
31	370–380	12.7	12.7	74.5	5.9

In each case, the gas is therefore a mixture of dimethyl ethylene and ethyl ethylene; the former being about 2–6.5 times of the latter. This fact shows that the latter is produced first and is changed into the former by the action of the heated clay:

$$CH_3.CH_2.CH{:}CH_2 \longrightarrow CH_3.CH{:}CH.CH_3$$

The amounts of butylenes increase with the rise in temperature and become almost constant at above 300°. The amounts of ether and of butyl alcohol in the products decrease as the temperature rises. It is therefore assumed that the reaction proceeds steadily at above 300°.

n-Amyl Alcohol. Pure n-amyl alcohol of Kahlbaum is used after distillation, boiling point of which being 137–138° and $n_D^{13.8}$: 1.415. The experimental conditions and the decomposition products are shown in Table 16.

Table 16.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition Products		Amylene yield, %
				Liquid, gr.	Gas. L.	
32	66	260–270	0.33	55	5.2	32.0

The liquid part of the decomposition products was of two layers, the lower one was water containing a small amount of amyl alcohol. The upper layer was fractionally distilled with care first under ordinary pressure and then under reduced one, three fractions being obtained. The first boils at 35–39°, from which n-amylene is isolated, the dibromide of which boils at 187-189°. The second boils at 138-139° ($n_D^{13.8}$: 1.417) and is undecomposed amyl alcohol. And the third boils at 68-71°/12 mm. ($n_D^{13.8}$: 1.430) and is di-n-amyl ether. The above result and the gas-composition are shown in Table 17.

Table 17.

Composition of the Products.

No.	Gas, volume per cent.				Liquid, per cent.			
	C_nH_{2n}	CO_2	CO	O_2	Alcohol	Water	Ether	Amylene
32	1.6	0	0.85	15.85	14.2	19.5	4.5	38.4

June, 1929. Tokyo.