ON THE THERMAL DECOMPOSITION OF ALIPHATIC ETHERS.

By Kozo KASHIMA.

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The ether has hitherto been considered to be stable to chemical reagents and to heat.(1) But the nature of the ether has not yet been made clear, as the chemistry of ether has advanced little. Recently S. Komatsu and his co-workers are exploiting the field of the chemistry.(2) The writer made some experiments on the thermal decomposition of aliphatic alcohols,(3) concluding that the alcohols are decomposed into corresponding olefines through the stages of the corresponding ethers: $R.CH_2OH \rightarrow (R.CH_2)_2O + H_2O \rightarrow R':CH_2 + H_2O$. For introducing the conclusion, the writer proved that the corresponding ethers were formed and that the thermal effects of ether-formation were always larger than those of other possible cases.

It will however be proper to discuss the problem with the result of the thermal decomposition of the corresponding ethers under the same conditions. On one side for above purpose and on the other for obtaining some data for making clear the nature of the ether, especially for getting some idea on the affinity of alkyl groups to oxygen, the writer made the present experiments as works on the field are found scarcely in the chemical literature.

In 1835, J. Liebig(4) observed that ethyl ether was decomposed into aldehyde, a burnable gas and water when its vapour was passed through a heated glass tube filled with glass pieces and the formation of acetylene in the reaction was also observed.(5) W. Tischtschenko(6) reported that the ether was mainly decomposed into aldehyde and paraffines when heated at high temperature, unsaturated hydrocarbons, carbon monoxide and hydrogen being also produced. On passing ethyl ether through a tube filled with pumice or a mixture of pumice and zinc dust at about 500°, Nef(7) observed the formation of ethylene, carbon monoxide, hydrogen,

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(1) V. Meyer und P. Jacobson, "Lehrbuch der organischen Chemie," I-1, 289, (Leipzig: Veit & Comp.), 1907; J. B. Sendrens, *Compt. rend.*, **146** (1908) 1211; J. Houben, "Die Methoden der organischen Chemie," III, 136 (H. Meerwein), (Leipzig: Georg Thieme.), 1923.

(2) Private communication.

(3) This Bulletin, **4** (1929), 177.

(4) *Ann.*, **14** (1835), 134.

(5) M. Berthelot, *Ann.*, **116** (1860), 117.

(6) *Chem. Zentr.*, (1900) I, 586

(7) *Ann.*, **318** (1901), 198:

methane and ethene with a small amount of acet- and croton-aldehydes Under high temperature and pressure, ethyl ether was decomposed into ethylene and water in the presence of iron and alumina(1); the same decomposition occurred at 200-300° in contact with alumina.(2) When ethyl ether was passed through a heated platinum tube, the principal change was the formation of ethane and acetaldehyde accompanied by ethylene and water(3). But ethyl ether in gaseous state, when heated at about 500° in a silica bulb without catalyst, did not decompose according to the formula, $C_2H_5{\cdot}O{\cdot}C_2H_5=2C_2H_4+H_2O$, but carbon monoxide separated from the molecule, the net result being thus: $CO+2CH_4+0.5C_2H_4$.(4) Ethyl ether gave ethyl alcohol when heated with alumina under ordinary pressure(5) or when treated with silicon tetrachloride(6) or with disilicon hexachloride.(7)

Propyl ether behaved similar to ethyl ether when heated.(8) The thermal decompositions of dimethyl and di-isopropyl ether and some mixed ethers were studied to some extent.(9)

As the experimental materials, ethyl, *n*-propyl, *n*-butyl, *n*-amyl and ethyl-*n*-butyl ethers and *n*-amyl alcohol are used for making comparative studies.

The experiment was conducted under the same conditions, using the same apparatus and catalyst as in the case of the alcohol. Small grains of Japanese acid clay are filled into a hard glass tube and dried and activated at 350–400°. When the temperature of the catalyst attained a desired one, the sample is gradually dropped into one end of the tube at a definite rate. It is there evaporated and acted with the clay. The produced liquid and gas are collected into proper receivers and analysed. The gas is analysed by ordinary absorption method combining a combustion one for hydrogen and paraffines. As to the liquid product, water, alcohols, ethers and sometimes aldehydes are estimated by fractional distillation, by combining the action of toluene, sodamide and others. Alcohols are proved by the formation of their phenylurethanes or benzoylesters.

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(1) W. Ipatieff, *Ber.*, **37** (1904), 2994; *Chem. Zentr.*, (1904), II, 1020.

(2) J. B. Sendrens, *Compt. rend.*, **146** (1908), 1211; *Bull. soc. chim.*, [4] **3** (1908), 823; C. J. Engelder, *J. Phys. Chem.*, **21** (1917), 698.

(3) E. Peytral, *Bull soc. chim.* [4] **35** (1924), 964.

(4) C. N. Hinshelwood, *Proc. Roy. Soc.* (London), [A] **114** (1927), 84.

(5) W. Ipatieff, loc. cit.

(6) F. S. Kipping and A. G. Murray, *J. Chem. Soc.*, (1927), 2734.

(7) F. S. Kipping and R. A. Thompson, *J. Chem. Soc.*, (1928), 1989.

(8) W. Tischtschenko, loc. cit.

(9) C. N. Hinshelwood and P. J. Askey, *Proc. Roy. Soc.* (London), [A] **115** (1927), 215; J. V. S. Glass and C. Norman *J. Chem. Soc.*, (1929), 1815; J. V. S. Glass and C. N. Hinshelwood, ibid., (1929), 1804.

When aliphatic ethers are passed over heated Japanese acid clay, they are decomposed into corresponding olefines, alcohols and water, small amounts of aldehydes, gaseous compounds, sometimes of esters and a kind of petroleum hydrocarbons (at high temperature) being also produced. A very small amount of free carbon is precipitated on the catalyst, the higher the temperature, the more the amount of carbon.

The mechanism of the thermal decomposition of aliphatic ethers in the presence of Japanese acid clay is assumed to be as follows:

$$R\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot R = 2R\cdot CH:CH_2 + H_2O.$$

Figures on the succeeding pages show the mutual quantitative relations between the decomposition products at different temperatures from ethyl, propyl, butyl, amyl and ethyl-butyl ethers and amyl alcohol. That the ratios of olefines and water produced are almost constant (2:1) at above ca. 300° and that the yields of olefines from ethers are always larger than those from corresponding alcohols will explain the above reaction mechanism, i.e., two alkyl groups are split off from oxygen at the same time at the temperatures.

In the case of ethyl-butyl ether, the decomposition product is a mixture of ethylene, butylene, ethyl and butyl alcohols and water, where the amounts of butylene and ethyl alcohol being larger than those of ethylene and butyl alcohol. The affinity between butyl proup and oxygen is therefore weaker than that between ethyl group and oxygen: $C_2H_5 > C_4H_9$.

On the formation of alcohols at low temperature, the writer wishes to assume the following reaction:

$$R\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot R = R\cdot CH:CH_2 + R\cdot CH_2\cdot CH_2\cdot OH.$$

As mentioned before, the ether has hitherto been thought as a stable compound; this conception will be correct in a certain limit, but it will not be proper to assume it very stable. Not only by the action of acids, but also even by alkalies, it is decomposed, especially at elevated temperatures.

On the hydrolysis of the ether by acids, some works(1) have been recorded, the decomposition product being different according to the temperature, at which the ether is treated:

$$R\cdot O\cdot R' + HX \begin{array}{l} \nearrow RX \;\; + R'OH, \\ \longrightarrow ROH + R'X, \\ \searrow RX \;\; + R'X. \end{array}$$

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(1) R. D. Silva, *Ann. chim. phys.*, [5] **7** (1876), 429; W. Lippert, *Ann.*, **276** (1893), 148; A. Michael. *J. prakt. Chem.*, [2] **64** (1901), 106, etc.

As the name indicates, the Japanese acid clay reacts acidic. The liquid products in the reactions are always acidic. When ethyl, propyl or butyl ether is heated in a sealed tube at 200–250° with water in the presence of the clay, corresponding alcohols are produced, the amount being however small. H. Inoue⁽¹⁾ observed the hydrolysis of acetic ester by passing it over Japanese acid clay at about 200°. And W. Ipatieff⁽²⁾ reported the formation of ethyl alcohol by the thermal decomposition of ethyl ether under the influence of alumina. A. Skrabal and H. Airoldi⁽³⁾ measured the saponification constant of ethyl ether under the influence of benzene sulphonic acid and S. K. Kulkarni Jatkar and H. E. Watson⁽⁴⁾ calculated the equilibrium constant of the reaction, $C_2H_5{\cdot}O{\cdot}C_2H_5 + H_2O \rightleftarrows 2C_2H_5OH$.

From these facts, there is a possibility to suppose that the alcohol is produced by the hydrolysis of the ether due to the special characteristics of the clay:

$$R{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}R + H_2O = 2R{\cdot}CH_2OH.$$

And it will of course be natural to suppose a very small amount of alcohol present in the liquid product is formed by the hydrolysis, but the saponification constant of Skrabal and Airoldi is only 9×10^{-5} at 98° and the equilibrium constant of Jatkar and Watson is 7.3 at 227°. Would the hydrolysis be permitted, the degree will be very small, while the amount of the alcohol determined is not small; the writer wishes therefore to propose the above reaction mechanism:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}R = R{\cdot}CH{:}CH_2 + R{\cdot}CH_2{\cdot}CH_2{\cdot}OH.$$

As will be seen from the tables and diagrams the clay represents a special characteristics to the ether, the lower the temperature, the less the decomposition to the olefines, but larger the production of alcohols. At above ca. 300°, almost complete decomposition takes place rapidly i.e., at high temperature, almost all of the ether is decomposed into olefine and water.

As in the case of the alcohol, the amounts of the produced olefines increase with the rise in the reaction temperature, which is shown in Fig. 1. At above ca. 300°, the decomposition is extremely promoted. There is almost no difference between the amounts of the produced olefines according to the difference of the ether. In the case of ethyl ether, the rate of the formation of ethylene is slightly less than the cases of other ethers.

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(1) Private communication; cf. this Bulletin, **1** (1926), 157.

(2) Loc. cit.

(3) *Monatsh. f. Chem.*, **45** (1924), 13.

(4) *J. Indian Inst. Sci.* [A] **9** (1926), 99; *Chem. Abstr.*, **21** (1927), 386.

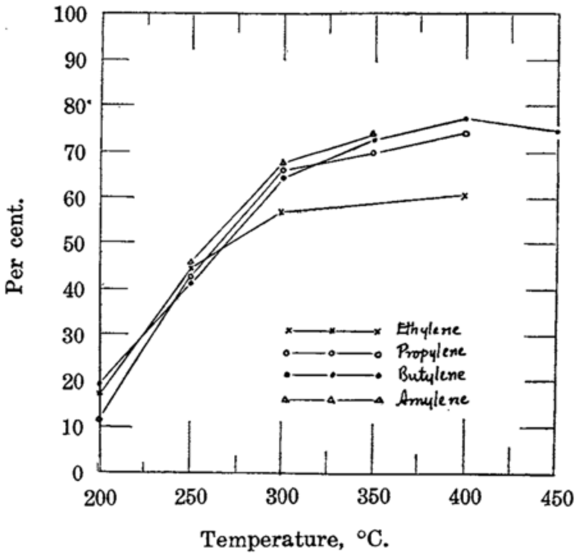

Fig. 1.

The double bond of the olefine produced belongs generally to the carbon atom linked with oxygen:

$$R\cdot CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot R \rightarrow R\cdot CH:CH_2.$$

But in the case of butyl ether, butylene is a mixture of α-and β-isomers, the latter being predominated. And amylene produced from amyl alcohol and ether is also a mixture of α-compound ($CH_3\cdot CH_2\cdot CH_2\cdot CH:CH_2$) and β-one ($CH_3\cdot CH_2\cdot CH:CH\cdot CH_3$); these will be produced by the migration of double bond by the further action of the heated clay for producing more stable isomers.

At low temperatures (mainly at 200–250°), corresponding alcohols are produced, the amount of which decreasing rapidly with the rise of temperature. Ester is produced in the case of ethyl ether, but not distinct in the cases of other ethers. Aldehyde is produced in small amounts at every cases. The amounts of carbon monoxide, hydrogen and aldehyde isolated are not large, the formation of aldehyde in the reaction will not therefore be large.

Ethyl Ether. Pure ethyl ether is used after distilling over metallic sodium, boiling point of which being 35°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 1, 2, 3 and 4, and the mutual relations of the main products are shown in Figs. 2 and 3.

Table 1.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Ethylene yield, %	Liquid yield %
				Liquid, gr.	Gas, L.		
33	73.4	200	0.35	40	11.65	16.4	54.5
34	58.3	200	0.34	28	9.87	18.6	48.0
35	87.1	250	0.34	21	39.09	50.5	24.1
36	104.4	250	0.34	29	36.22	38.4	27.8
37	126.0	250	0.33	32	58.73	53.2	25.4
38	117.4	300	0.33	25	61.49	58.8	21.3
39	118.8	300	0.32	27	63.86	55.1	22.7
40	86.4	400	0.34	19	47.57	59.0	22.0
41	104.8	400	0.35	22	56.16	62.6	21.0

Table 2.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
33	200	82.5	6.4	0.4	6.8	1.4	2.5
34	200	88.0	2.1	0.2	5.4	2.1	2.2
35	250	89.9	3.1	0.2	4.7	1.0	1.1
36	250	88.4	3.6	0.4	3.4	1.0	3.2
37	250	91.2	3.1	0.2	2.8	1.0	1.7
38	300	89.7	5.1	0.2	2.2	1.0	1.8
39	300	81.9	3.0	0.2	7.3	3.2	4.4
40	400	85.6	1.8	0.4	4.0	3.2	5.0
41	400	93.4	2.4	0.4	1.2	1.4	1.2

Table 3.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde	Ester
33	200	61.8	19.8	14.8	0.52	+
34	200	57.5	23.2	14.3	0.43	+
35	250	6.2	25.7	68.1	0.05	+
36	250	21.7	26.2	44.8	0.66	+
37	250	10.0	20.0	65.6	0.19	+
38	300	2.4	1.2	94.0	0.02	+
39	300	trace	4.1	92.6	0.02	+
40	400	0	0.5	97.4	0.02	—
41	400	0	0.3	95.5	0.01	-

Table 4.

Yields of the Main Substance, mol per cent.

No.	Reaction temp.	Ethylene	Ether	Alcohol	Water
33	200	43.4	33.3	17.2	33.3
34	200	49.6	28.0	17.8	28.0
35	250	133.6	1.7	10.2	67.2
36	250	101.5	7.7	12.1	51.1
37	250	140.6	2.4	8.2	68.8
38	300	155.3	0.6	0.4	82.7
39	300	145.4	trace	1.3	89.2
40	400	156.1	0	0.9	88.3
41	400	165.5	0	0.5	82.7

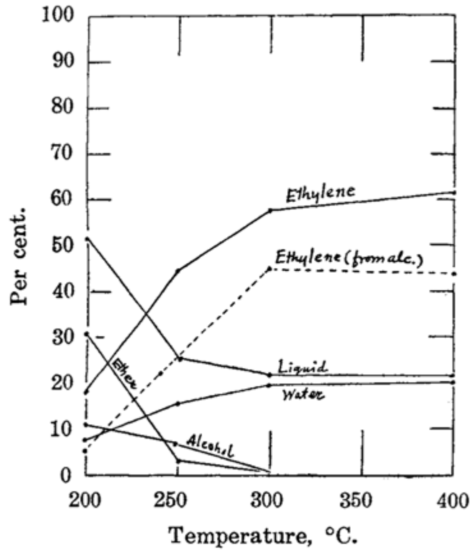

Fig. 2.

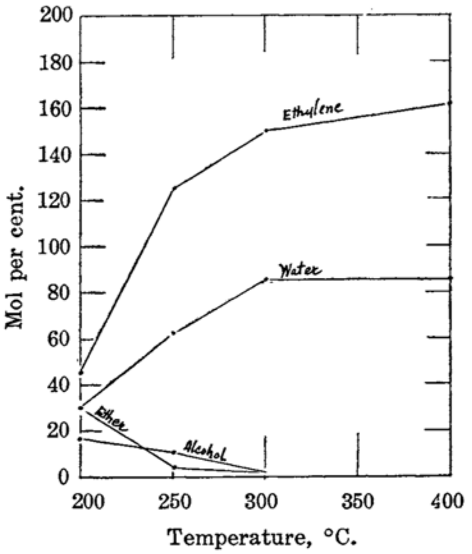

Fig. 3.

n-**Propyl Ether.** One part of the ether is prepared from n-propyl alcohol by the method of Kraft⁽¹⁾ and the other is Eastman's product. They are carefully purified by distilling over metallic sodium, boiling point of which being 90–91°. The experimental conditions, decomposition products and the analytical results of the products are tabulated in Tables 5, 6, 7, and 8, and the mutual relations of the main compounds are shown in Figs. 4 and 5.

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(1) *Ber.*, **26** (1893), 2829.

Table 5.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temerature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Propylene yield, %	Liquid, yield, %
				Liquid, gr.	Gas, L.		
42	46.0	200	0.31	33.0	2.52	9.2	71.7
43	46.0	200	0.31	30.5	4.38	13.9	66.3
44	46.0	250	0.31	20.0	10.81	41.5	43.5
45	46.0	250	0.31	20.0	10.99	43.2	43.5
46	46.0	300	0.31	8.5	16.49	65.2	18.5
47	46.0	300	0.31	8.7	17.52	68.5	18.9
48	46.0	350	0.31	8.0	17.98	67.2	17.4
49	46.0	350	0.31	8.4	18.17	70.8	18.3
50	46.0	400	0.31	8.0	18.63	73.3	17.4
51	46.0	400	0.31	8.5	19.47	75.2	18.5

Table 6.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
42	200	89.2	1.0	1.2	3.0	2.7	1.0
43	200	77.4	0.5	0.2	2.5	1.1	0.6
44	250	94.0	0.6	0.2	2.4	1.3	0.5
45	250	96.2	1.0	0.2	1.4	0.9	0.3
46	300	96.8	0.6	0.4	0.8	1.3	0.1
47	300	95.8	1.0	0.2	1.0	1.2	0.4
48	350	94.2	0.6	0	1.2	1.8	0.5
49	350	95.4	0.6	0.2	1.4	1.1	0.5
50	400	96.4	0.4	0.2	1.2	1.2	0.4
51	400	94.6	0.8	0.3	1.2	2.0	0.7

Table 7.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde
42	200	74.9	17.6	3.0	0.12
43	200	63.9	18.7	13.1	0.08
44	250	52.0	16.5	25.5	0.24
45	250	52.5	17.0	24.5	0.19
46	300	8.2	2.4	83.5	0.09
47	300	8.1	2.3	86.2	0.09
48	350	3.8	0.3	93.8	0.02
49	350	2.4	0.2	95.2	0.01
50	400	7.5	trace	90.0	0.02
51	400	3.5	trace	94.1	0.01

Table 8.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Propylene	Ether	Alcohol	Water
42	200	22.2	53.8	21.6	12.4
43	200	33.5	42.4	21.1	49.3
44	250	100.8	22.7	12.2	62.9
45	250	104.8	22.9	12.7	60.4
46	300	158.1	1.6	0.7	87.6
47	300	166.3	1.6	0.7	92.7
48	350	167.9	0.7	0.1	92.7
49	350	171.9	0.4	0.1	98.7
50	400	178.1	1.3	trace	88.9
51	400	182.5	0.7	trace	98.7

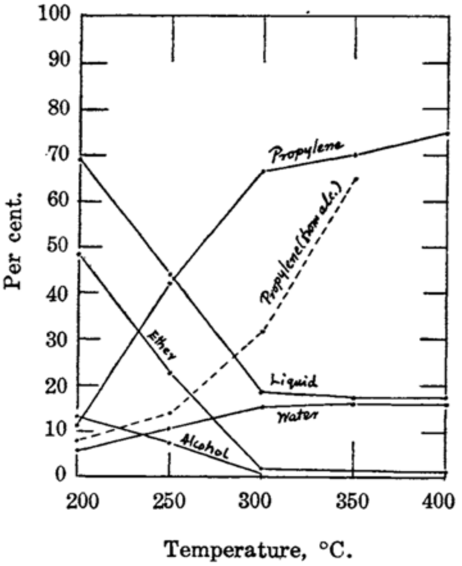

Fig. 4.

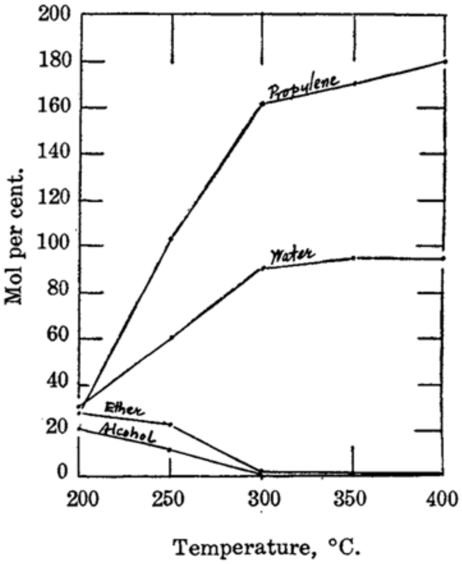

Fig. 5.

n-**Butyl Ether.** Pure ether of Eastman Kodak Co. is used after distilling over metallic sodium, boiling point of which being 140–141°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 9, 10, 11 and 12, and the mutual relations of the main compounds are diagramed in Figs. 6 and 7.

Table 9.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Butylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
52	46.0	200	0.31	34.0	3.51	15.3	73.9
53	46.0	200	0.31	30.0	4.95	23.6	65.2
54	42.5	250	0.35	22.0	6.31	33.3	51.8
55	46.0	250	0.31	21.0	9.50	49.5	45.7
56	50.0	300	0.31	13.0	13.01	61.6	26.0
57	46.0	300	0.31	9.0	13.04	67.4	19.6
58	44.4	350	0.32	8.0	14.16	78.8	18.0
59	46.0	350	0.31	8.0	13.93	71.2	18.5
60	47.0	400	0.34	8.0	19.79	83.2	17.0
61	46.0	400	0.31	8.0	14.20	72.3	17.4
62	46.0	450	0.31	6.5	14.66	74.7	14.1
63	46.0	450	0.31	6.5	14.93	74.8	14.1

Table 10.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
52	200	80.0	1.2	1.0	2.8	2.7	8.2
53	200	87.8	1.6	1.2	2.4	1.5	4.1
54	250	89.7	0.4	0.8	2.0	3.0	4.1
55	250	95.6	1.8	0.5	0.2	0.8	1.1
56	300	94.5	0	0.4	3.1	0.7	1.3
57	300	95.0	1.4	0.2	1.0	1.0	1.4
58	350	93.7	3.1	0.2	1.0	0.5	1.5
59	350	94.0	0.8	0.4	1.6	0.8	2.4
60	400	78.9	2.8	0.6	2.8	2.6	8.6
61	400	93.6	0.4	0.6	1.8	1.0	2.2
62	450	93.6	0.8	0.6	1.2	1.3	2.6
63	450	92.0	0.6	0.8	1.4	1.5	3.7

Table 11.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Alcohol	Water	Aldehyde
52	200	73.2	15.3	5.9	0.05
53	200	70.0	11.3	8.0	0.06
54	250	47.7	6.4	15.5	0.05
55	250	69.5	13.3	17.1	0.06
56	300	33.8	9.2	52.3	0.04
57	300	35.6	4.4	60.0	0.06
58	350	22.6	1.1	76.0	0.06
59	350	31.8	2.4	65.9	0.05
60	400	12.5	1.3	86.3	0.04
61	400	28.5	1.3	70.0	0.04
62	450	23.1	3.1	72.3	0.05
63	450	18.5	3.1	76.9	0.05

Table 12.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Butylene	Ether	Alcohol	Water
52	200	36.8	54.1	19.8	31.4
53	200	53.8	45.6	13.0	37.6
54	250	76.7	24.5	5.8	58.0
55	250	121.7	31.7	10.8	56.3
56	300	143.2	8.9	4.2	98.2
57	300	155.7	7.1	1.4	84.9
58	350	173.0	4.1	0.3	97.6
59	350	164.2	5.9	0.9	88.0
60	400	191.1	2.2	0.3	95.3
61	400	167.0	5.1	0.3	88.0
62	450	172.6	3.4	0.9	73.9
63	450	172.6	2.6	0.9	78.7

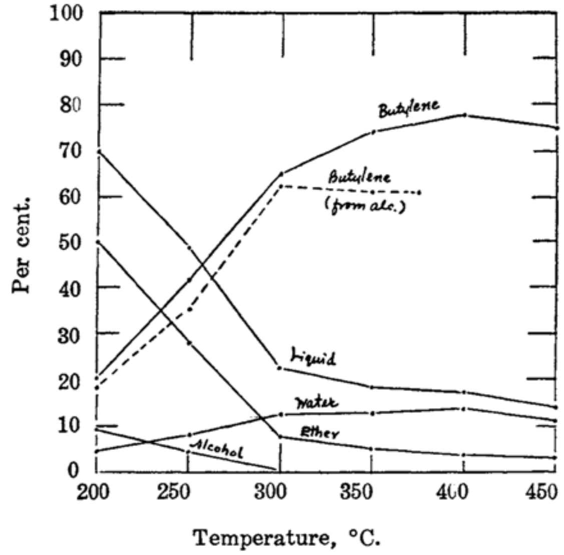

Fig. 6.

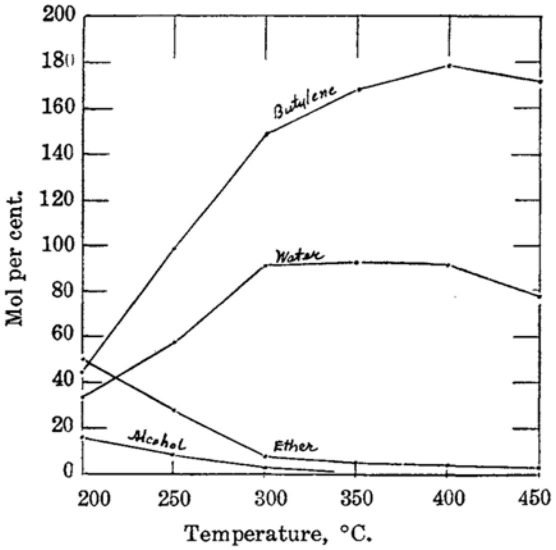

Fig. 7.

n-Amyl Ether. Pure ether of Eastman Kodak Co. is purified by distilling over metallic sodium, boiling point of which being 90–91°. The experimental conditions, decomposition products and the analytical results of the products are tabulated in Tables 13, 14, 15 and 16, and the mutual relations of the main products are shown in Figs. 8 and 9.

Table 13.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Amylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
64	45	250	0.3	41.0	0.3	45.3	91.1
65	45	300	0.3	42.0	0.4	67.1	93.3
66	45	350	0.3	42.0	0.4	74.8	93.3

Table 14.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
64	250	0	0.4	1.0	19.6	0	0
65	300	0	0.4	0	19.4	0	0
66	350	0	0	0	20.0	0	0

Table 15.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water	Aldehyde
64	250	49.7	35.4	8.1	6.8	+
65	300	71.9	17.1	2.7	8.8	+
66	350	80.1	8.1	0.8	11.0	+

Table 16.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water
64	250	102.2	32.2	13.3	54.7
65	300	162.4	15.9	4.5	68.4
66	350	180.8	7.6	1.4	89.8

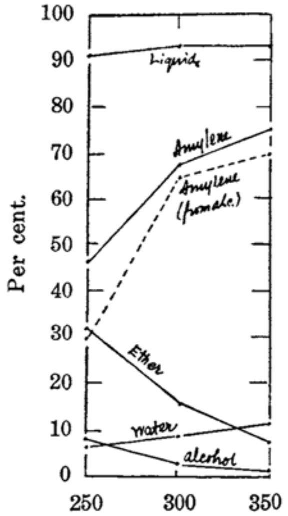

Fig. 8.

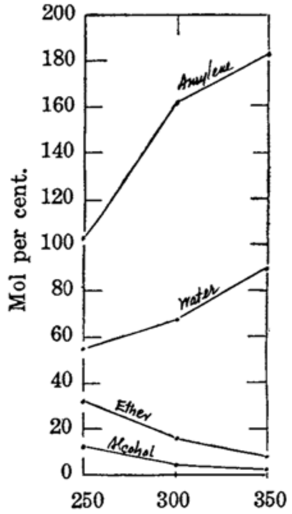

Fig. 9.

Ethyl-*n*-Butyl Ether. Pure product of Eastman Kodak Co. is repeatedly distilled over metallic sodium, boiling point of which being 91-91.5°. The experimental conditions, decomposition products and the analytical results of the products are summarised in Tables 17, 18, 19 and 20, and the mutual relations of the main products are shown in Figs. 10 and 11. The ether is also prepared from *n*-butyl alcohol and ethyl iodide using sodamide as a condensing agent, which is a good method for the preparation of the ether or of similar compounds.

Table 17.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Ethylene yield, %	Butylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.			
67	50	200	0.28	45	1.69	1.4	8.6	90.0
68	50	250	0.28	27	6.83	7.9	36.5	54.0
69	70	350	0.29	15	22.75	20.1	44.5	21.4

Table 18.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
67	200	75.4	0.4	1.0	5.0	4.2	6.2
68	250	90.2	3.0	0.4	2.2	2.0	1.2
69	350	90.2	3.2	0.6	1.4	2.4	2.2

Table 19.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Ether	Ethyl Alcohol	Butyl Alcohol	Water	Aldehyde	Low boiling fraction	High boiling fraction
67	200	46.6	7.7	1.7	6.0	+	26.9	11.1
68	250	24.2	9.6	1.1	19.3	+	36.0	9.8
69	350	9.1	1.1	trace	74.7	+	0.5	14.7

Table 20.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Ethylene	Butylene	Ether	Ethvl alcohol	Butyl alcohol	Water
67	200	5.0	15.6	41.9	15.5	2.1	30.6
68	250	28.6	66.5	13.1	11.5	0.8	59.0
69	350	73.3	80.4	2.0	4.4	trace	95.8

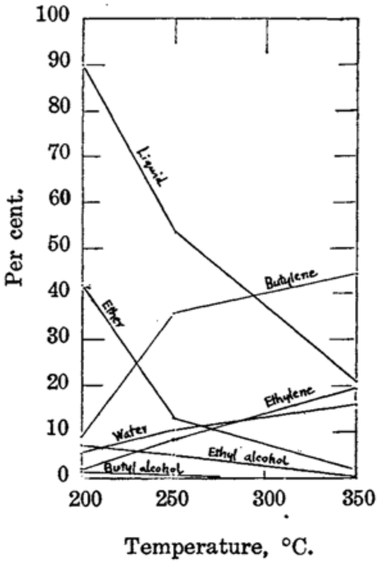

Fig. 10.

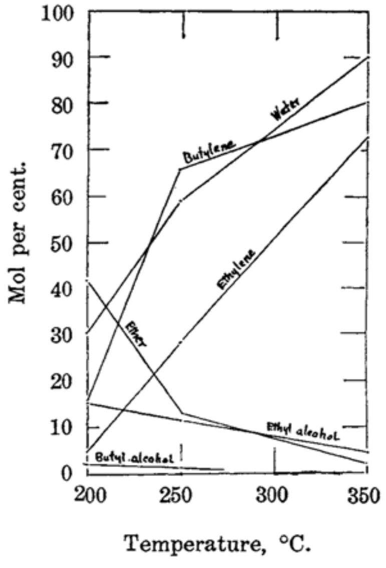

Fig. 11.

n-**Amyl Alcohol.** Pure product of Eastman Kodak Co. and of Kahlbaum is used after distilling over powdered quick lime, boiling point of which being 137-138°. The experimental conditions, decomposition products and analytical results of the products are summarised in Tables 21, 22, 23 and 24, and the mutual relations of the main products are shown in Fig. 12.

Table 21.

Experimental Conditions and Decomposition Products.

No.	Sample, gr.	Reaction temperature, °C.	Dropping rate of sample, gr./min.	Decomposition products		Amylene yield, %	Liquid yield, %
				Liquid, gr.	Gas, L.		
70	45	250	0.3	43.0	0.23	29.5	95.6
71	45	300	0.3	42.5	0.44	64.9	94.4
72	45	350	0.3	42.5	0.36	70.0	94.4

Table 22.

Composition of the Produced Gas, volume per cent.

No.	Reaction temp.	C_nH_{2n}	CO_2	CO	O_2	H_2	C_nH_{2n+2}
70	250	0	1.2	0.8	21.1	4.6	0
71	300	1.4	0.2	2.4	19.5	4.0	0
72	350	5	0.4	1.0	18.7	2.6	3.8

Table 23.

Composition of the Produced Liquid, per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water	Aldehyde
70	250	30.8	6.2	53.2	9.8	+
71	300	68.7	4.5	3.1	19.1	+
72	350	74.1	4.0	1.2	20.5	+

Table 24.

Yields of the Main Substances, mol per cent.

No.	Reaction temp.	Amylene	Ether	Alcohol	Water %
70	250	37.1	3.3	50.8	45.7
71	300	81.6	2.4	2.9	88.1
72	350	88.0	2.1	1.1	94.5

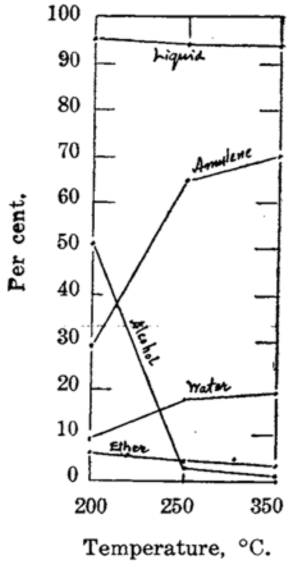

Fig. 12.

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