STUDIES ON CATALYTIC ACTION AT HIGH PRESSURE AND TEMPERATURE.

CATALYTIC HYDROGENATION OF ETHERS.

By Shigeru KOMATSU and Masajiro MASUMOTO.

Received June 28, 1930. Published August 28, 1930.

The erroneous view that ethers are stable against chemical reagents and heat, which has been held by numerous chemists has been partly modified by the investigation conducted by K. Kashima(1) into the thermal decomposition of aliphatic ethers which are decomposed by being passed over heated Japanese acid clay, into the corresponding olefines and alcohols at low temperature (200°C.) and at high temperatures into olefines and water.

Ethers, by hydrolysis with HI, yield alcohols and iodides, which differ according to the temperature at which the ether is treated.

$$\mathrm{ROR'+HI}\begin{cases}\nearrow \mathrm{RI+R'OH}\\ \searrow \mathrm{RI+R'I.}\end{cases}$$

According to P. Sabatier(2), ethers of the aromatic series, are reduced in the presence of reduced nickel to alcohols and hydrocarbons. As he says in his book, "Les oxydes aromatiques subissent sur le nickel une scission analogue, qui à deja lieu a température peu élevée pour le oxydes mixtes phenol-alcooliques, et diminue beaucoup le rendement dans leur transformation en oxydes mixtes cycloformeniques."

The authors undertook the present research in order to get some idea concerning the affinity of alkyl or some atomic groups for oxygen, from which they might elucidate the chemical nature of ethers.

I. Catalytic Reduction of Diphenylether.

Diphenyl ether prepared(3) from chlorobenzene and phenol shows m.p. 27.5°; b.p. 138° (21 mm.), $d_4^{25}=1.0712$; $n_D^{25}=1.5781$. In the experiment, a sample with reduced nickel which had been previously prepared from nickel oxide by reduction with hydrogen at 280° was placed in an autoclave of a capacity of 600 c.c. with compressed hydrogen. The autoclave, heated

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(1) This Bulletin, **5** (1930), 25.

(2) P. Sabatier, "La catalyse en chimie organique," (1920), 186.

(3) F. Ullmann & P. Sponagel, *Ber.*, **38** (1905), 2211.

externally by electric resistance, was mounted horizontally on a shaking machine.

In the following table, the weight of the sample, the conditions under which the reaction was performed, the yield of the product and its physical constants are shown.

No.	Sample gr.	Reaction conditions			H_2 absorb. in mols.	Reaction product		
		Max. temp.	Initial press.	Time hours		Yield gr.	d_4^{25}	n_D^{25}
I	53	250°	60 atmos.	8	7.4	51	0.863	1.447
II	17	170°	60 ,,	6	5.4	17	0.918	1.476
III	50	220°	60 ,,	7	1.9	—	1.004	1.536

No. I.

	Fraction b.p.	Yield gr.	d_4^{25}	n_D^{25}	Remarks
1	73°–108°	21	0.779	1.427	Hexahydrobenzene
2	156°–168°	27	0.940	1.463	Cyclohexanol
3	Residue	2	—	—	

When purified, fraction 1 showed the constants: $d_4^{25}=0.7687$; $n_D^{25}=1.4248$, which agree with those for pure cyclohexane, and the 2nd fraction shows the constants ($d_4^{25}=0.9469$; $n_D^{25}=1.4635$) of pure cyclohexanol.

No. II.

	Fraction b.p.	Yield gr.	d_4^{25}	n_D^{25}
1	60°–110°	4	0.7795	1.4313
2	73°–115° (17 mm.)	7	0.9546	1.4712
3	115°–120° ,,	1	1.0092	1.5210

Fraction 1 and 2, as their physical constants indicate, are composed of cyclohexane and cyclohexanol respectively.

The third fraction, a mixture of diphenylether and dicyclohexyl ether, was fractionated to isolate the latter, which showed b.p. 230°–240°;

$d_4^{25}=0.9947$; $n_D^{25}=1.5080$; M.R.$=54.51$ (54.86 for $C_{12}H_{22}O$); and analytical results: $C=79.1$; $H=12.1$, (theory $C=79.1$; $H=12.1\%$ for $C_{12}H_{22}O$).

No. III.

	Fraction b.p.	Yield	d_4^{25}	n_D^{25}	Remarks
1	72°–84°	3	0.8162	1.4625	48% benzene, cyclohexane
2	75°–86° (14 mm.)	9	0.9551	1.4727	5% phenol+cyclohexanol
3	134°–138° ,,	19	1.0617	1.5702	diphenylether-cyclohexanol

Although diphenyl oxide⁽¹⁾ is said to be hardly susceptible to the catalytic action of reduced nickel in the presence of hydrogen, the conversion of the compound into cyclohexane and cyclohexanol ought to place with quantitative yield on heating it to 250° under 60 atmospheric pressures at 15°, in the presence of reduced nickel and hydrogen, in which disruption of the linking between carbon and oxygen will happen first and then the hydrogenation of the benzene nucleus of the molecules decomposed. This assumption was realized in experiment III, in which the reaction temperature was 220°, and accordingly the consumption of hydrogen is very small compared with that in the first experiment. The isolation of benzene and phenol together with their reduced substances from the reaction product is in favour of the above view. The occurrence of benzene in abundance is due to difficulty of hydrogenation under the experimental conditions, while phenol is hydrogenated with facility.

The other explanation of the formation of cyclohexane and cyclohexanol from diphenylether is shown in the scheme, in which

$$(C_6H_5)_2O \rightarrow (C_6H_{11})_2O \rightarrow C_6H_{11}OH + C_6H_{12}$$

hydrogenation of the benzene nucleus of the oxide takes place under the conditions, (lower temperature and high pressure) shown in experiment II.

The reaction products obtained from diphenyl oxide at high pressure and temperature in the presence of reduced nickel and hydrogen, are not entirely the same as those obtained by W. Ipatiew,⁽²⁾ who conducted the experiment at 230° and under 100 atmospheric pressures in the presence of nickel oxide.

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(1) A. Mailhe & M. Murat, *Bull. soc. chim.*, [4] **11** (1912), 122.

(2) *Ber.*, **41** (1908), 1001; *Compt. rend.*, **181** (1925), 793; refer W. Schrauth and W. Wege, *Ber.*, **57** (1924), 858.

II. Catalytic Reduction of Furfurol.(1)

1. Partial Hydrogenation of Furfurol. Reduction of furfurol was tried to see the behaviour of oxygen in ring, since furane forms a closely allied family with benzene from the standpoint of methods of formation and chemical behavior; the chain of four CH groups in the benzene molecule is closed as a ring by O.

M. Padoa and U. Ponti(2) performed the catalytic hydrogenation of furfurol at 190° by Sabatier's method, obtaining furfuryl alcohol with some α-methylfurane, α-methyl tetrahydrofurane, sec-n-amyl-alcohol and methyl propyl ketone, while at 270°, furane and CO were formed and these results are similar to these obtained by H. Pringsheim and H. Noth.(3)

Furfurol from Merck was used in the experiment after being purified ($d_4^{25}=1.153$; $n_D^{25}=1.522$).

(A) *Furfuryl alcohol.* (1) 50 gr. of furfurol were heated in the autoclave to 160°, with hydrogen under a pressure of 100 atmospheres, the reaction was completed with the absorption of 1 mol hydrogen in 6 hours, and the product ($d_4^{25}=1.132$; $n_D^{25}=1.498$) was fractionated:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	70°–140°	3 gr.	0.984	1.504
2	70°–80° (28 mm.)	9	1.141	1.505
3	80°–97° ,, ,,	33 (80 %)	1.136	1.498
4	97°–183° ,, ,,	6	1.154	1.506
5	Residue	trace	—	—

The first fraction consisted of furane and methyl furane, and the second fraction of furfurol and furfuryl alcohol. The main component of the reaction product was assumed to be furfuryl alcohol and confirmed to be so by purifying with distillation under 17 mm. pressure: b.p. 74° (17 mm.): $d_4^{25}=1.1317$; $n_D^{25}=1.4928$; M.R.=25.15. Combustion: C=61.5; H=6.2%. Theory: C=61.3; H=6.1% for $C_5H_6O_2$. Phenyl urethane $C_{12}H_{11}O_3N$: m.p. 43°, N=6.4%.

(B) *Tetrahydro furfuryl alcohol.* In order to get the tetrahydro compound, 50 gr. of furfuryl alcohol were subjected for 7 hours to a partial

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(1) The catalytic reductions in this part were conducted in the same autoclave and with a nickel catalyst which was prepared in the same way, as those in the former.

(2) *Chem. Zentr.* 1907, II, 570.

(3) *Ber.*, **53** (1920), 114.

hydrogenation which was carried out at around 180° and under an initial pressure of hydrogen of 85 atmospheres.

51 gr. of the product ($d_4^{25}=1.062$; $n_D^{25}=1.455$) were fractionated as usual and the physical constants of each fraction studied:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	60°–140°	2.4 gr.	0.922	1.396
2	76°–90° (16 mm.)	21	1.052	1.450
3	90°–113° ,,	3.4	1.050	1.453
4	113°–200° ,,	11	1.101	1.463

The second and third fractions were assumed from their physical constants to be composed of the tetrahydro compound, which was isolated in the pure state by fractional distillation with a yield of 70%. B.p. 79° (17 mm.); $d_4^{25}=1.0506$; $n_D^{25}=1.4509$; M.R.=26.14. Combustion: C=58.8, 58.5; H=10.1, 10.1%. Theory: C=58.8; H=9.8% for $C_5H_{10}O_2$. Its phenyl urethane $C_{12}H_{15}O_3N$ (m.p. 56°⁽¹⁾) gave N=6.3%, which agrees with theoretical value N=6.3 for $C_{12}H_{15}O_3N$.

(*C*) *Dihydro furfuryl alcohol.* Partial hydrogenation of 25 gr. of furfuryl alcohol at 144°, with hydrogen under a pressure of 80 atmospheres, was tried, and the product formed by absorbing about 0.8 mol of hydrogen showed the constants: $d_4^{25}=1.084$; $n_D^{25}=1.470$.

The product was fractionated into the following 5 parts:

	Fraction	Yield	d_4^{25}	n_D^{25}
1	50°–140°	0.5 gr.	—	—
2	77°–84° (18 mm.)	9	1.099	1.472
3	84°–90° ,,	5.7	1.098	1.472
4	90°–160° ,,	3.3	1.126	1.478
5	Residue	1.5	—	—

The second fraction seems to be a mixture of furfuryl alcohol and the tetrahydro-compound.

The third fraction was found to change its colour to yellow on exposure to air, with a characteristic odour; the physical constants of the purified

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(1) H. Wienhaus, *Ber.*, **53** (1920), 1663.

sample were determined : b.p. 79–81° (14.5 mm.) ; $d_4^{25}=1.0986$; $n_D^{25}=1.4727$. M.R.=25.52 quite agrees with the calculated value 25.80 for dihydro furfuryl alcohol and the analytical results shows: Found: C=59.9, 60.3; H=8.4, 8.2%. Calc. for $C_5H_8O_2$: C=60.0; H=8.0%.

2. Complete Hydrogenation of Furfurol. (*A*) *Complete hydrogenation of furfuryl alcohol (No. II) and tetrahydro furfuryl alcohol (No. I).* The furfuryl alcohol was subjected to complete hydrogenation under the conditions described in the table, and the behavior of tetrahydro furfuryl alcohol (No. I) in the presence of reduced nickel and hydrogen at high temperature and pressure was also studied for comparison.

No.	Sample	Reaction			H_2 absorb. in mols.	Product		
		Temp.	Initial press. at 60°	Time in hour.		Yield	d_4^{25}	n_D^{25}
I	22 gr.	300°	30 atmos.	8	0.94	18.5 gr.	0.955	1.417
II	25 ,,	300	90 ,,	13	3.72	22.0 ,,	0.948	1.410

No. I.

	Fraction	Yield		d_4^{25}	n_D^{25}
1	64°–105°	9.2 gr.	58%	0.8864	1.398
2	70°–74° (12 mm.)	3.4	21	1.053	1.447
3	75°–110° ,,	3.3	21	1.039	1.449

No. II.

	Fraction	Yield		d_4^{25}	n_D^{25}
1	64°–100°	10.5 gr.	71%	0.827	1.398
2	100°–140°	2.4		0.874	1.402
3	67°– 82° (15 mm.)	4.3	24	1.023	1.446
4	82°–105° ,,	1.0	5	1.015	1.448

A compound which was supposed to occur in the third fraction in No. I, as will be seen in experiment No. II, diminished in yield when the reaction proceeded owing to transformation of the compound into substances of low boiling point. The molecular weight of the substance ($d_4^{25}=0.999$; $n_D^{25}=1.452$) isolated in a pretty pure state, in benzene solution by the cryoscopic method, was found to be 150, which corresponds approximately to the molecular weight of polymerized hydrofurfuryl alcohol or hydrofurfuryl ether $C_{10}H_{18}O_3$ (molecular weight 186).

Both the second fraction in No. I and the third fraction in No. II, were found to be composed of tetrahydrofurfuryl alcohol. The main portion of the reaction product, the first fraction in No. I and II, was again fractionated carefully into (I) b.p. 63–70°, (II) b.p. 76–82°, (III) b.p. 113°–130° and the following compounds were isolated :

(1) Tetrahydrofurane.—The fraction b.p. 63°–70°, which forms the main portion of the product, is a colourless liquid with a characteristic odour ; $d_4^{25}=0.8669$; $n_D^{25}=1.4004$; M.R.=20.26. Combustion : Found, C=66.0, 66.4 ; H=11.5, 11.5%. Calc. for C_4H_8O, C=66.7 ; H=11.1%.

(2) Methyltetrahydrofurane.—The second fraction b.p. 76–82°, shows $d_4^{25}=0.9325$; $n_D^{25}=1.4027$, which indicates that the fraction consists mostly of methyl tetrahydrofurane with some tetrahydrofurane. For reference, the combustion was carried out : C=68.6, 68.9 ; H=12.5, 12.4%. (Theory C=69.8 ; H=11.6 for $C_5H_{10}O$ and C=66.7 ; H=11.1% for C_4H_8O).

(3) n-Butylalcohol.—The fraction b.p. 113–130° ($d_4^{25}=0.8184$; $n_D^{25}=1.402$; M. R.=22.02) was assumed to be butyl alcohol. Combustion : Found, C=64.7, 64.3 ; H=13.7, 13.4%. Calc. for $C_4H_{10}O$, C=64.9 ; H=13.5%.

Its phenyl urethane melts at 54°. The attempt to detect amyl alcohol and also amylene glycol in the reaction product failed.

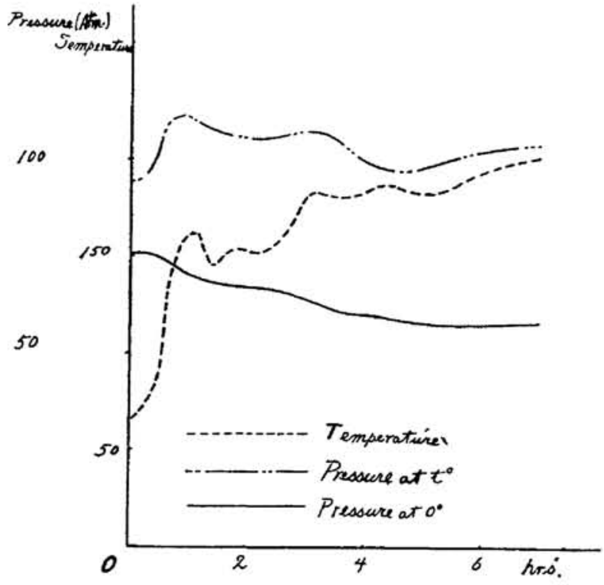
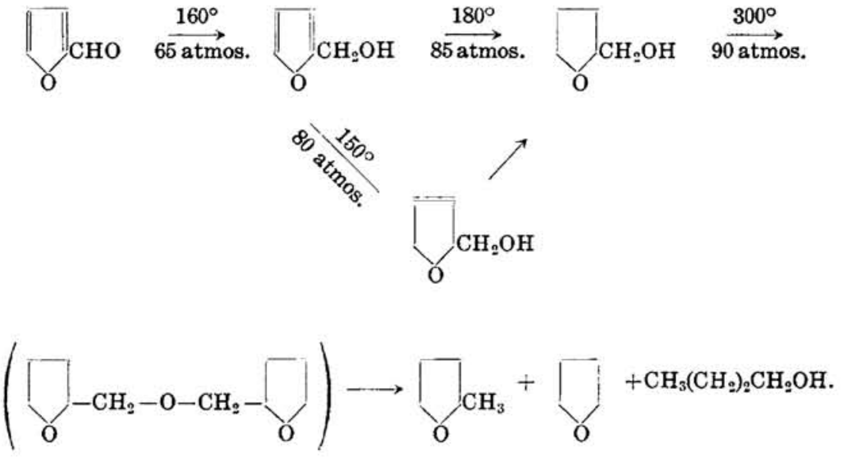


Fig. 1.

(*B*) *Complete hydrogenation of furfurol.* Furfurol was heated to 150° with hydrogen in the presence of the catalyst, under a pressure of 100 atmospheres; the pressure in the autoclave began to be depressed at 60°, and was kept constant after about one mol of hydrogen had been absorbed, the temperature being kept at 150°; it again showed the depression on the reaction temperature being raised, as is indicated in the figure.

Thus, the catalytic reduction of furfurol proceeds stepwise according to the temperature to which the reaction system is subjected.

The course of the chemical changes of furfurol on catalytic reduction in the presence of reduced nickel at high pressure and temperature is shown in the following scheme:



In the last phase of the reaction, tetrahydro furfuryl ether is assumed to occur as an intermediate reaction product which, owing to its instability towards heat or to the reducing agent, is immediately transformed by disruption of the carbon-oxygen linking into methyl furane, furane and butyl alcohol.

April, 1930.

Laboratory of Organic- & Bio-Chemistry,
Kyoto Imperial University.