Catalytic Reduction of Aromatic Carboxylic Acid Esters under High Pressure and Temperature

By **Keisaku Mitsui**

Prof. P. Sabatier succeeded in reducing ethyl benzoate into hexa-hydrobenzoate by applying a temperature of $180°$ and hydrogen in the presence of reduced nickel.[1] Using copper-chromium, copper-barium-chromium, or copper-calcium as catalyst, H. Adkins and K. Folkers,[2] however, obtained benzyl alcohol from ethyl benzoate. The same reaction had been obtained by Bowveault and G. Blanc,[3] who used ethyl alcohol or amyl alcohol[4] with sodium as reducing agent. Consequently aromatic carboxylic acid esters can be converted into their hexahydro-compounds or aromatic alcohols according to the catalysts employed.
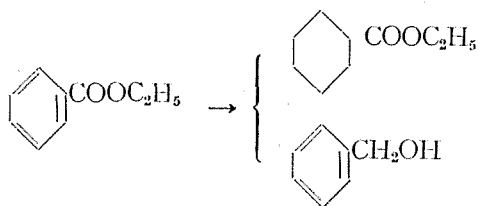

Using reduced nickel, which was prepared from nickel nitrate converted into oxide by heat of about $350°$, and reduced in the hydrogen stream at $290° - 320°$, the author endeavoured to reduce aromatic carboxylic acid esters under high pressure of hydrogen and at high temperature into hexahydro-compounds. The following is the report of the experiment.

(I) Ethyl benzoate (B.p. $= 208° - 212°$; $D_4^{25} = 1.0441$; $n_D^{25} = 1.5625$) was heated under 100 atmospheric pressures of hydrogen with 10 percent of reduced nickel. At $100°$, hydrogen began to be absorbed and the reaction at $150°$ was remarkable and was completed with the absorption of 3 mols hydrogen by being kept at $150° - 190°$ for 2 hours. 90 mol percent of the reaction product consisted of ethyl hexahydro-benzoate (B.p. $= 190° - 195°$; $D^{25} = 0.9524$; $n_D^{25} = 1.4396$) but neither benzyl alcohol nor benzoic acid was present. Repeating the reaction in

(1) P. Sabatier: Compt. rend., **154**, (1912), 925.　　(2) H. Adkins, K. Folkers: J. Amer. Chem. Soc., **53**, (1931), 1095, **54**, (1932), 1145.　　(3) L. Bowveault, G. Blanc: Bull. Soc. Chim., **31**, (1904), 666.　　(4) V. Markownikow: Ber., **25**, (1892), 3357.
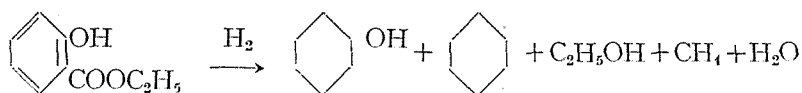
ethyl alcohol solution, it was confirmed that the solvent has no effect on the yield and reaction velocity.
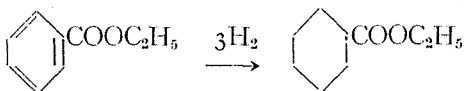
Subsequently, ethyl phenyl acetate (B.p.$= 111°/20$ m.m.; $D_4^{25} = 1.0277$; $n_D^{25} = 1.4949$) was reduced in hydrogen which began to be absorbed at about $150°$, and after keeping the temperature $180° - 200°$ for 15 hours, $2\frac{1}{2}$ mols hydrogen were absorbed. The reaction product consisted of 90 mol percent of ethyl cyclohexyl acetate. (B.p.$= 100° - 102°/20$ m.m.; $D_4^{25} = 1.1255$; $n_D^{25} = 1.5206$)

(II) From the fact that the reduction velocity of phenol was greater than that of benzene, it was supposed that the hydroxyl group might have some effect on the reduction velocity of catalysis. The writer therefore conducted an experiment with ethyl salicylate (B.p.$= 132° - 133°/35$ m.m.; $D_4^{25} = 1.1255$; $n_D^{25} = 1.5206$), which was heated under 100 atmospheric pressures of hydrogen, it being expected that the reaction would occur more easily than in the above cases. But even at $200°$ no reaction occurred, so the temperature was raised to $240°$ and hydrogen began to be absorbed, and by maintaining this temperature for 6 hours $4\frac{1}{2}$ mols hydrogen were absorbed. The reaction product consisted of 75 mol percent cyclohexanol, cyclohexane, and ethyl alcohol. This experiment indicated that salicylic acid ester was dissociated into phenol and carbo-ethyoxyl group. The former were transformed into cyclohexanol and cyclohexane under high pressure of hydrogen and temperature.

In the next experiment, ethyl esters of meta- and para-hydroxybenzoic acid were reduced under high pressure and temperature by aid of the catalyst. From para-hydroxybenzoate (M.p $= 112°$), after 2 mols of hydrogen had been absorbed at about $200°$, 40 mol percent of para-hydroxyhexahydrobenzoate (B.p.$= 252° - 258°$; $D_4^{25} = 1.1664$; $n_D^{25} = 1.4694$) were obtained. But from the meta-isomer (M.p.$= 72°$; B.p.$= 187° - 188°/31$ m.m.) 3 mols of hydrogen being absorbed at $200°$, 75 mol percent of meta-hydroxyhexahydrobenzoate (B.p.$= 156° - 160°/33$ m.m.; $D_4^{25} = 1.0678$; $n_D^{25} = 1.4683$) were obtained. In the reaction of meta- and para-isomers as it differes greatly from that of the ortho-compound, no liberation of the carboxyl group occurred.

$$\text{C}_6\text{H}_4\genfrac{}{}{0pt}{}{\text{OH}}{\text{COOC}_2\text{H}_5} \xrightarrow{\text{H}_2} \text{C}_6\text{H}_{10}(\text{OH}) + \text{C}_6\text{H}_{12} + \text{C}_2\text{H}_5\text{OH} + \text{CH}_4 + \text{H}_2\text{O}$$

From the above mentioned experiments with ethyl benzoate, ethyl phenyl acetate and ethyl hydroxybenzoate, it is concluded that esters of aromatic carboxylic acid are converted into hexahydrocompounds by reducing at 200° under 100 atmospheric pressures of hydrogen in the presence of reduced nickel; benzene nucleus is hydrogenated by the activated hydrogen, and the reaction is altogether different from that in which copper-chromium is used as catalyst, since it chiefly activates the carboxyl group.

Experiment

(I) Catalytic Reduction of Ethyl Benzoate[1]

30 gms. of this ethylbenzoate of the physical constants B.p. $= 208° - 212°/753$ m.m.; $D_4^{25} = 1.0441$; $n_D^{25} = 1.5025$ were electrically heated in an autoclave, under 100 atmospheric pressures of hydrogen at 26° and with 10 percent of reduced nickel. The depression of the pressure in the autoclave began at 90° and became rapid at 140°, the reaction being completed in 3 hours with absorption of 3.3 mols hydrogen (Fig. 1). The reaction product ($D_4^{25} = 0.953$; $n_D^{25} = 1.439$) was examined, 30 gms. of liquid being fractionated with the following results :—

Fraction	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester-value
1	185°–190°	7.0%	0.9506	1.4374	—	—
2	190°–195°	84.7	0.9524	1.4396	43.12	364
3	195°	7.0	—	—	—	—

Fraction, B.p. $190° - 195°$, was colourless liquid found to consist of ethyl hexahydrobenzoate by being converted into hexahydrobenzoic acid (M.p. $= 30°$) by hydrolysis. From the physical constants of the fractions ; B.p. $= 185° - 190°$ and $190°$ — upwards, the reaction product was assumed to consist principally of ethyl hexahydrobenzoate. Thus ethyl benzoate was reduced into ethyl hexahydrobenzoate with a yield of 90 percent. Catalytic reduction of ethyl benzoate was tried in the ethyl alcohol solution. The conditions and the experimental result are shown in the following table and Fig. 2.

1 S. Komatsu, K. Mitsui: The Mem. of the Sci. K. I. U. A. 14 (1931), 297.

Sample	Ethyl alcohol	Initial press.	Temp.	Time	Absorption of hydrogen
50 g.	50 g.	97 atm./28°	180°–220°	$2\frac{1}{2}$ hrs.	3.3 mols

Fig. 1.

Fig. 2.
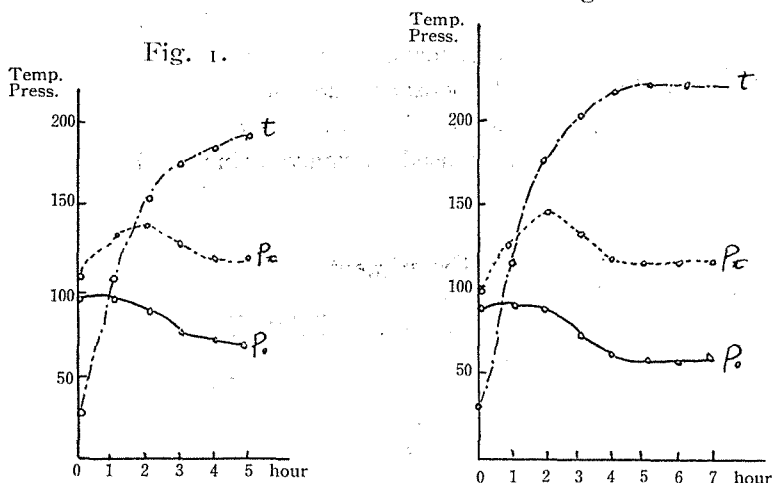
After the reaction was completed, the solvent was expelled by distillation and the physical properties of the residue (50 gms.) were measured : $D_4^{25} = 0.930$; $n_D^{25} = 1.432$

The physical constants and yield of ethyl hexahydrobenzoate purified by fractional distillation were :—

| B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester-value
190°–196°	88%	0.9531	1.4411	43.22	366

(II)   Catalytic Reduction of Ethyl Phenyl Acetate

Ethyl phenyl acetate (B.p.= $111°/20$ m.m.; $D_4^{25} = 1.0277$; $n_D^{25} = 1.4949$) was reduced in the presence of 10 percent of reduced nickel under the following conditions.

Sample	Initial press.	Reaction temp.	Time	Absorption of hydrogen
25 g.	100 atm./20°	180°–200°	17 hrs.	2 mols

Absorption of hydrogen began at 140° and became rapid at 150°, as will be seen from Fig. 3, and 2 mols of hydrogen were absorbed in 17 hrs.

Fig. 3.
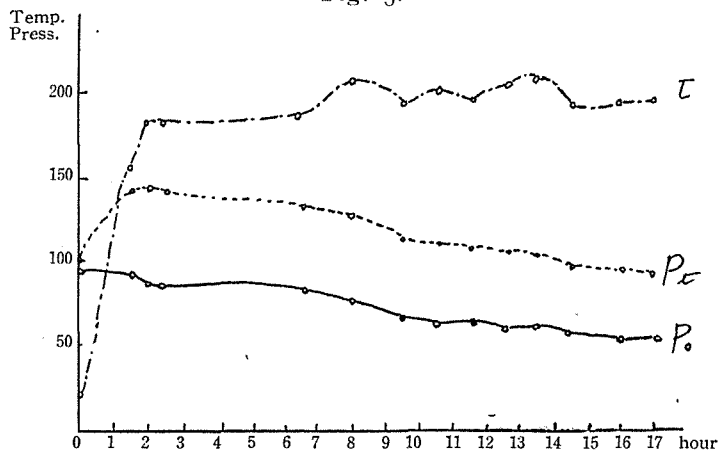
The reaction product was a weak acidic yellowish liquid and the yield was 23 gms. and the physical constants were: $D_4^{25} = 0.924$ $n_D^{25} = 1.446$.

After the reaction product was neutralized with caustic alkali and dried, 20 gms. of the neutral part, separated from the acidic part, were fractionated under reduced pressure and the physical properties of the fractions obtained:

Fraction	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester-value
1	90°–100°/20m.m.	6.5%	0.9321	1.4455	—	300
2	100°–102°/20m.m.	75.0	0.9415	1.4456	48.0	315
3	residues and loss	14.0	—	—	—	—

The second fraction was assumed from its physical constants to be ethyl cyclohexyl acetate, and was confirmed to be so by combustion analysis.

Sample	CO_2	H_2O	C%	H%
0.1145 g.	0.2994 g.	0.1070 g.	71.1	10.4
	Calc. for $C_{10}H_{18}O_2$		70.6	10.6

The first fraction, as will be seen by the constant, contained some ethyl cyclohexyl acetate and the third fraction consisted of ethyl phenyl acetate.

(III) (a) Catalytic Reduction of Ethyl Salicylate

31 gms. of ethyl ortho-hydroxybenzoate (ethyl salicylate) (B.p. = $132° - 133°/35$ m.m.; $D_4^{25} = 1.1255$; $n_D^{25} = 1.5216$) were reduced under the

Fig. 4.
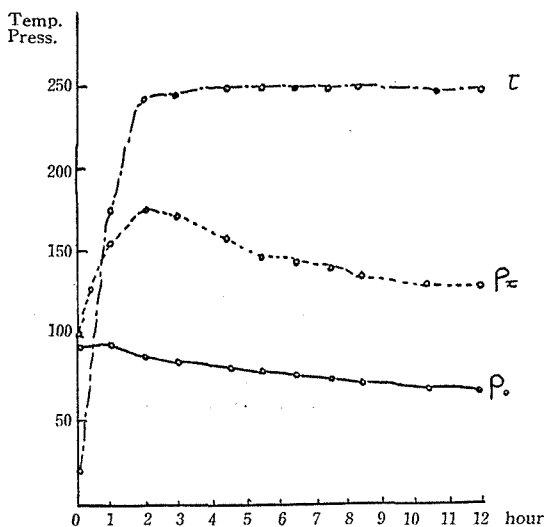
similar conditions with the former cases and the reduction began at $160°$ and became rapid at $200°$. (cf. Fig. 4.) During about 10 hours heating at $250°$, $4\frac{1}{2}$ mols hydrogen were absorbed. 28 gms. of reaction product of constants D_4^{25} $=0.916$; $n_D^{25}=1.426$ were separated by fractional distillation into 6 gms. of ethyl salicylate (B.p.$=$ $230°-232°$; $D_4^{25}=1.1220$; $n_D^{25}=1.5200$; ester value 308), an other fraction of 22.0 gms. The latter was again fractionated :—

Fraction	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.
1	$75°-85°$	5.7%	0.7784	1.4248	27.58
2	$85°-95°$	20.0	0.8596	1.3658	—
3	$95°-160°$	6.7	—	—	—
4	$160°-165°$	42.0	0.9407	1.4605	29.16
5	residues & loss	4.3	—	—	—

The first fraction was confirmed to be cyclohexan by analysis after it had been distilled with sodium.

Sample	CO_2	H_2O	C%	H%
0.1430 g.	0.4497 g.	0.1841 g.	86.6	14.3
	Calc. for C_6H_{12}		85.7	14.3

The second fraction was distilled again and was ascertained to be ethyl alcohol from the iodform reaction and formation of acetic acid ester. The 4th fraction which showed the physical constants of cyclohexanol, was confirmed to be so by measurement of its melting point $(79°)$ after changing it into phenylurethane, and by analysis after purifying it.

Sample	CO_2	H_2O	C%	H%
0.2471 g.	0.6467 g.	0.2600 g.	71.4	11.7
	Calc. for $C_6H_{12}O$		72.0	12.0

(b) Catalytic Reduction of Meta-Hydroxybenzoate

20 gms. of ethyl meta-hydroxybenzoate (M.p. $= 72°$; B.p. $= 187° -$ 188°/31 m.m.) were dissolved in 20 gms. of absolute ethyl alcohol, and the mixture was reduced with 10 percent of reduced nickel under the following conditions similar to the case of ethyl salicylate. As will be seen in Fig. 5, some of hydrogen was absorbed at 140° and most of it while the temperature was raised from 150° to 180°, and 3 mols of hydrogen were absorbed in 5 hours. 18 gms. of reaction product of physical properties $D_4^{25} = 1.049$; $n_D^{25} = 1.470$ were obtained.

Fig. 5.
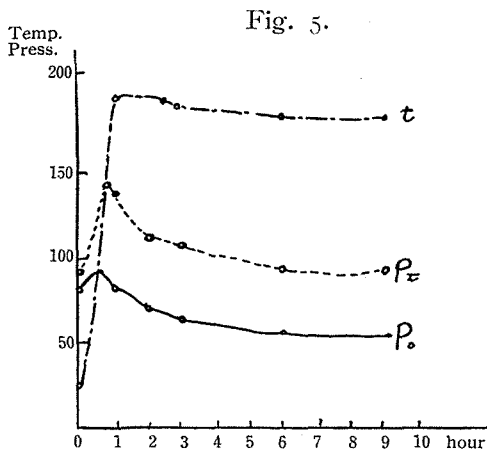
By fractional distillation 17.8 gms. of the higher fraction were separated from the lower fraction of ethyl meta-hydroxybenzoate and were fractionated again into fractions with the following physical properties.

Sample 20 g.	Initial press. 92 atm./23°	Temp. 170°–190°	Time 5 hrs.	Absorption 3.0 mols

Fraction	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester value
1	135°–156°/33m.m.	5.8%	1.0055	1.4647	—	220.8
2	156°–160°/33m.m.	82.0	1.0678	1.4683	44.8	310.6
3	residues & loss	9.3	—	—	—	—

The first fraction was found to be meta-hydroxyhexahydrobenzoate containing some of other lower boiling part. From its physical properties and ester value, the second fraction seemed to be meta-hydroxyhexahydrobenzoate, which was confirmed by elementary analysis.
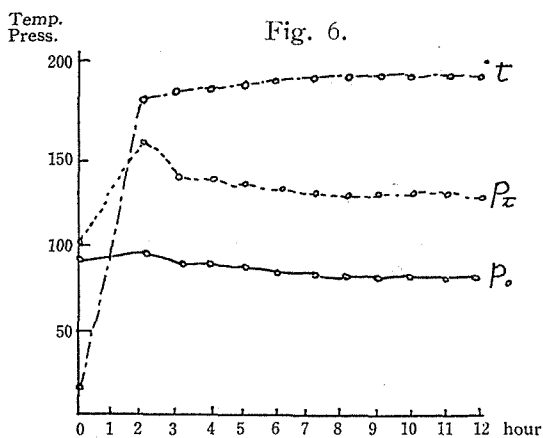
Sample 0.4106 g.	CO_2 0.9371 g.	H_2O 0.3478 g.	C% 62.2	H% 9.4
	Calc. for $C_9H_{16}O_3$		62.8	9.3

(c) Ethyl Para-Hydroxybenzoate

The ester of the constants M.p. $= 112°$; Ester value $= 332$ was

reduced with the same amount of absolute ethyl alcohol under the following conditions :

Sample 20 g.	Initial press. 100 atm./$17°$	Temp. $180° - 200°$	Time 8 hrs.	Absorption 2.0 mols

Temp.
Press.

Fig. 6.

The absorption of hydrogen began suddenly at $180°$ and 2 mols of hydrogen was absorbed in 9 hours. (cf. Fig. 6) The product was separated into ethyl para-hydroxybenzoate.   18.0 gms. of the fraction (B.p. $= 255° - 258°$; $D_4^{25} = 1.065$; $n_D^{25} = 1.468$), were fractionated into fractions with the following results :—

Fractions	B.p.	Yield	D_4^{25}	n_D^{25}	M.R.	Ester value
1	$-252°$	4.7%	1.0593	1.4784	—	—
2	$252°-258°$	40.0	1.0664	1.4694	44.9	322
3	residues & loss	1.4	—	—		

The second fraction was confirmed to be ethyl para-hydroxyhexahydrobenzoate by its physical properties and chemical elementary analysis.

Sample 0.2011 g.	CO_2 0.4625 g.	H_2O 0.1625 g.	C% 63.0	H% 9.0
	Calc. for $C_9H_{16}O_3$		62.8	9.3

The first fraction contained, as will be seen from the physical constants, a small amount of the same substance as the second fraction. Ethyl hydroxybenzoate (9.1 gms.) was confirmed by converting it into para-hydroxybenzoic acid (white crystal, M.p. $= 210°$) by hydrolysis.