

Catalytic Action at High Temperature and under High Pressure, V Catalytic Hydrogenation of Benzoic Acid

By

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Catalytic hydrogenation of benzoic acid in the presence of reduced nickel was tried by Sabatier & Murat¹, by which process a trace of the acid was hydrogenated at 180°–200° into hexahydrobenzoic acid, and the process was regarded as inconvenient for this purpose. However, W. Ipatiew and O. Philipow² succeeded in converting benzoic acid into its hexahydro compound with a yield of 60 % of the theory by applying 100 atmospheric pressures of hydrogen and high temperature (300°) to its sodium salt in the presence of nickel oxide.

Subsequently the catalytic hydrogenation of aromatic carboxylic acids was usually performed by converting them into the sodium salt, and Professor Sabatier³ has reported that the esters of benzoic acid are reduced more easily by his method than the free acid when the reaction is conducted at 180°, but that at higher temperatures the metal rapidly loses all its catalytic activity.

The report by R. Willstätter and D. Hatt⁴ on the hydrogenation of benzoic acid with the aid of platinum, seems to us a very exceptional case, in which the reaction proceeded with great facility in glacial acetic acid solution.

An equimolecular mixture of benzoic acid (40 gms.) and ethyl alcohol (50 c.c.) was heated at 225° for 6 hrs. in an autoclave with 92

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1. C. R., **154**, 924 (1912).
 2. Ber. D. Chem. Ges., **41**, 1005 (1908).
 3. C. R., **154**, 925 (1912).
 4. Ber. D. Chem. Ges., **45**, 1477 (1912).

atmospheric pressures of hydrogen at 34° and 5 gms. reduced nickel. 29 gms. of reaction product separated from the catalyst showed $d_4^{25} = 1.035$; $n_D^{25} = 1.496$; acid value 11. (see Fig. 1).

10 gms. of the product were treated with 5% NaOH solution and 1.2 gms. of an oily substance insoluble in the alkali solution, showing B.p. 202°–222°; $d_4^{25} = 1.034$; $n_D^{25} = 1.494$, were fractionated.

	B. p.	Yield	d_4^{25}	n_D^{25}
1	203°–206°	11 %	1.017	1.487
2	206°–209°	73 %	1.033	1.495
3	residue & loss	16 %	—	—

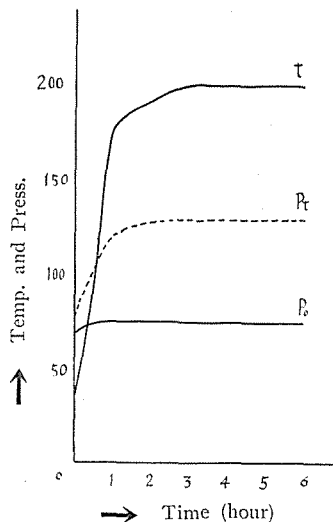
Two fractions, (1) and (2), being mixtures of ethyl esters of benzoic and hexahydrobenzoic acids, were estimated separately for the proportion of these two components in them by means of their physical constants (ethyl benzoate B.p. 208°–209°; $d_4^{25} = 1.0440$; $n_D^{25} = 1.5015$; ethyl hexahydrobenzoate B.p. 190°–193°; $d_4^{25} = 0.9524$; $n_D^{25} = 1.4392$), and the amount of hexahydrobenzoate and benzoate in the reaction product was found by calculation to be 19% and 78% respectively.

From the alkaline solution, 0.7 gm. of benzoic acid M.p. 122° was isolated, which corresponds to 3.3% for the product.

In the second experiment, 20 gms. of benzoic acid, 25 c.c. of ethyl alcohol and 5 gms. reduced nickel were mixed in an autoclave and heated at 170°–205° for 5 hrs. under 78 atmospheric pressures of hydrogen at 31°, and 18.3 gms. of reaction product ($d_4^{25} = 1.035$; $n_D^{25} = 1.494$) were isolated; it was supposed to consist mostly of esters, the acid value of the product being 10.

5 gms. of the product contained 0.3 gm. of benzoic acid and 4.6 gms. of esters, and the latter was separated into two fractions by distillation and then the proportion of ethyl esters of benzoic acid and hexahydrobenzoic acid in them calculated.

Fig. 1



	Fraction	Yield	d_4^{25}	n_D^{25}
1	201°–208°	3.1 gms.	1.028	1.491
2	208°–212°	1.5 „	1.039	1.498

The results are ethyl benzoate 80 %, ethyl hexahydrobenzoate 12 % and benzoic acid 2 %.

The benzoic acid, as seen in these experiments, was partly hydrogenated and the two acids were almost entirely esterified, and the high yield of the esters (92 %) compared with that calculated from the esterification velocity of the acid by Menschutzkin¹, must be attributed either to the catalytic action of the reduced nickel or to the high pressure of hydrogen.

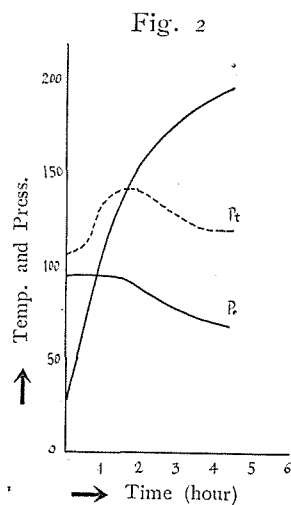
The small yield of hexahydrobenzoic acid ester by the reaction is due to the presence of free acid which acts as a negative catalyst, since the hydrogenation of benzoate runs very smoothly with quantitative yield of the hexahydro compounds.

50 gms. of ethyl benzoate B.p. 208–209°, $d_4^{25}=1.044$, $n_D^{25}=1.5015$, were heated at 115° with 5 gms. reduced nickel under 100 atmospheric pressures at 25°, and the reduction was completed with absorption of 3 mols hydrogen as may be seen in the following Fig. 2.

48.6 gms. of the product, $d_4^{25}=0.9614$; $n_D^{25}=1.4403$, were distilled and the fraction B.p. 185–193° consists of 90 % of the distillate which shows $d_4^{25}=0.953$; $n_D^{25}=1.439$ were composed of hexahydrobenzoate 87 % and benzoate 11 %.

The physical constants of the main fraction, 82 % of the product, were determined after it had been purified by distillation, and the fraction was found to consist of ethyl hexahydrobenzoate, B.p. 190°–193°; $d_4^{25}=0.9524$; $n_D^{25}=1.4392$.

In the second experiment, 30 gms. ethyl benzoate were reduced at 190° under 100 atmospheric pressures of hydrogen at 26° in the presence of 5 gms. of reduced nickel. 3.3 mols of hydrogen were

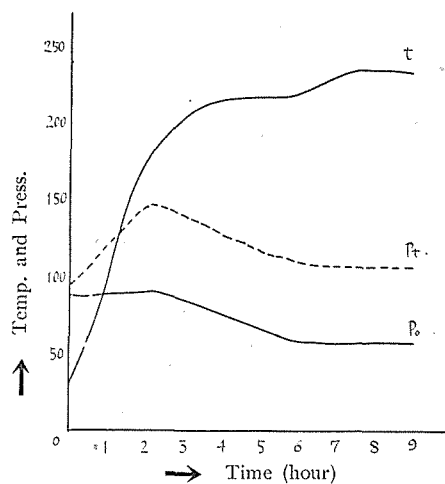


1. Ann. 195, 334; 197, 193 (1879).

absorbed in $3\frac{1}{2}$ hours, and 30 gms. of the reaction product, $d_4^{25}=0.953$; $n_D^{25}=1.439$, were fractionated and the proportion of ethyl benzoate and ethyl hexahydrobenzoate was found by calculation in the usual way to be 7% and 92% respectively.

Hydrogenation of benzoic acid ethyl ester was tried in ethyl alcohol solution and it was confirmed that the solvent has no effect on the reaction. A mixture of 50 gms. of the ester, 50 c.c. of ethyl alcohol and 5 gms. reduced nickel was heated at $175-225^\circ$ under 97 atmospheric pressures of hydrogen at 28° , and 3.3 mols hydrogen were absorbed in 4 hours by the reaction. (Fig. 3).

Fig. 3



51 gms. of the reaction product, $d_4^{25}=0.9303$; $n_D^{25}=1.432$, were fractionated with the following results:

	B. p.	Yield	d_4^{25}	n_D^{25}	Remark
1	-100°	30 gms.	—	—	Ethyl alcohol
2	$100^\circ-190^\circ$	0.9	0.882	1.436	} Benzoate Hexahydrobenzoate
3	$190^\circ-196^\circ$	17.8	0.9541	1.441	
4	$196^\circ-200^\circ$	0.6	0.9605	1.441	
5	$200^\circ-$	0.4	—	—	

The main fraction (3) was assumed from its physical constants to be composed of hexahydrobenzoate and benzoate and their proportion was found by calculation to be in the ratio of 9 : 1 ; the reaction product was assumed, therefore, to be composed of hexahydrobenzoate 95 % and benzoate 3 %.

Thus, benzoic acid was hydrogenated with quantitative yield by applying the high pressure and temperature method to its ethyl ester.

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