XXX.—*The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part IV. The Hydrogenation of Conjugated Systems : Piperic Acid.*

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ACCORDING to our theory of the catalytic hydrogenation of conjugated systems (J., 1928, 823), we should expect that, if piperic acid were hydrogenated by the direct addition of 2 mols. of hydrogen, the curve representing the process would be similar to that of the hydrogenation of a monoethylenic compound and would show no discontinuity, and the reaction product at any stage during the course of the reaction would consist solely of the fully saturated and the initial compound. Paal, who investigated this reduction (*Ber.*, 1912, **45**, 2221), found no indication of the presence of dihydropiperic acid, and hence the process would appear to conform to Type III of our classification (*loc. cit.*).

We have now repeated this reduction, however, and have found that in alcoholic solution in presence of platinum black, considerable quantities of dihydropiperic acid are formed; moreover, a "critical point" was found at 76% hydrogenation, and hence the process conforms to our Type II. The contradiction might have been attributed to the difference in the conditions of the process as carried out by Paal and by ourselves, but when we repeated the reduction under Paal's conditions (*i.e.*, in aqueous solution and in presence of colloidal palladium), the results were the same, dihydropiperic acids being produced in even larger amounts than before, and the critical point then being at 68—70% of the total hydrogen required.

We therefore suggest that the material extracted by ligroin in Paal's experiments was not pure tetrahydropiperic acid but contained more than 50% of the dihydro-acid, and our contention is supported by Paal's analytical results.

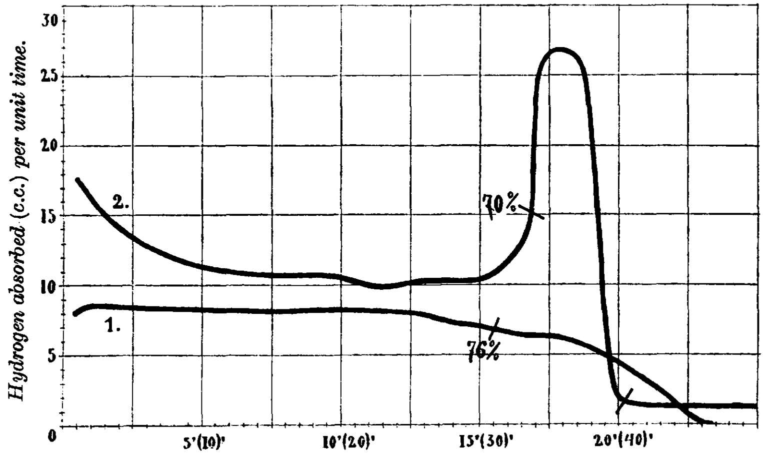
EXPERIMENTAL.

Hydrogenation in Presence of Platinum Black.

Piperic acid, obtained by saponification of piperine (Fittig and Milk, *Annalen*, 1869, **152**, 28) and recrystallised from alcohol, had m. p. 215—216·5°. 1·4338 G. of the acid, with 1·0 g. of platinum black in 250 c.c. of alcohol at 11°, absorbed 309 c.c. of hydrogen (at 18° and 765 mm.); the slight break in the curve showing the progress of absorption (Curve 1, Fig. 1) indicates a critical point at 75—77% of the total hydrogen absorbed.

The formula of piperic acid, $CH_2O_2{:}C_6H_3{\cdot}\overset{\delta}{C}H{:}\overset{\gamma}{C}H{\cdot}\overset{\beta}{C}H{:}\overset{\alpha}{C}H{\cdot}CO_2H$, indicates the following possibilities for the hydrogenation : (1) Addition of 1 mol. of hydrogen in one of the positions $\gamma\delta$, $\alpha\beta$, $\alpha\delta$, to give three isomeric dihydro-acids. (2) Addition of 2 mols. to 1 mol. of the acid, giving tetrahydropiperic acid. Thus, on the curve showing the course of hydrogenation we can expect only two sections : one during which the conjugated system is hydrogenated, and the second corresponding to the saturation of the dihydropiperic acids thus formed. The three different dihydro-acids, being symmetrical disubstituted ethylenic compounds, hydrogenate simultaneously (see J., 1925, **127**, 417), and hence are represented by a single section on the hydrogenation curve. The curve therefore shows that the process does not proceed as supposed by Paal, and that the hydrogenation is of our Type II.

FIG. 1.



Time (in minutes for curve 1, *and in* $\frac{1}{2}$ *minutes for curve* 2).

1. *Authors' method.* 2. *Paal's method.*

To confirm this we examined the product of 50% hydrogenation of the acid, 1·7569 g. in 450 c.c. of alcohol having absorbed 191 c.c. (at 18° and 760 mm.) (1 mol.) of hydrogen in presence of 1 g. of platinum black. The acids (1·7731 g.) isolated from alcohol were extracted by ligroin, in which, as shown by control experiments, piperic acid is insoluble, whereas the reduced acids are readily soluble. In this way 0·596 g. of piperic acid (m. p. 209—211°) was separated, corresponding to 33·6% of unchanged acid in the product of hydrogenation; hence, since 50% of the possible amount of hydrogen has been absorbed, the amount of tetrahydro-acid must also be 33·6% (see J., 1928, 825), and that of dihydro-acids 32·8% (by difference) (see Table I), from which, by methods explained in Part II (*ibid.*, p. 826), we find that the critical point falls at 75% of hydrogenation. The ligroin solution yielded 1·2320 g. of mixed di- and tetra-hydro-acids (m. p. 88—96°).

TABLE I.

Composition of the 50% hydrogenation product (platinum-black method).

	Calc. from amount of piperic acid.	Calc. from amount of dihydropiperic acids.	Mean.
Piperic acid	33·6%	35·0%	34·3%
Tetrahydropiperic acid	33·6	35·0	34·3
Dihydropiperic acids	32·8	30·0	31·4
Total	100	100	100

Examination of Mixed Di- and Tetra-hydro-acids.—2·5296 G. of the mixed acids thus obtained were dissolved in 35 c.c. of alcohol and treated with hydrogen in the presence of 1·2 g. of platinum black, 125·5 c.c. (at 15° and 755 mm.) being absorbed. If the mixture had consisted entirely of dihydro-acids, 272·5 c.c. of hydrogen would have been required under these conditions; hence, the composition of the mixture was 46% of the dihydro- and 54% of the tetrahydro-acid, and the composition of the original 50% hydrogenation mixture as calculated from these data is shown in the second column of Table I,* corresponding to a critical point at 77% hydrogenation.

Fig. 2 is based upon a critical point at 76% hydrogenation—the mean of the values found by the three methods above. The diagram for piperic acid hydrogenation is thus very similar to that of divinyl (see Part III, J., 1928, 2190), for the position of the critical point is nearly the same in each case; and all the criteria allocate the process to our Type II.

Hydrogenation of Piperic Acid in Presence of Colloidal Palladium.

Total Hydrogenation.—2·5121 G. of piperic acid, suspended in 90 c.c. of water and neutralised by potassium hydroxide, were hydrogenated with 0·0147 g. of colloidal palladium, previously saturated with hydrogen; 555 c.c. (at 18° and 750 mm.) of gas were required for total hydrogenation (calc., 557 c.c.). The course of the process is represented by Curve 2, Fig. 1 : the curve has a sharp break and

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* The lower proportion of dihydro-acids in the hydrogenation product (*viz.*, 30% instead of 32·8%) is attributed to partial oxidation during recrystallisation.

a peculiar shape, and the critical point is at 70% of hydrogen absorbed.

50% *Hydrogenation.*—5·0073 G. of the acid in 75 c.c. of water were hydrogenated as above in presence of 0·05 g. of catalyst; 550·5 c.c. (at 17° and 754 mm.) were absorbed (calc., 550·5 c.c.). The acids were precipitated by dilute sulphuric acid, washed, dried, and extracted by alcohol, from which 4·9691 g. of mixed acids crystallised. Treatment with ligroin as above isolated 1·2464 g. of piperic acid (m. p. 207—209°), corresponding to 25% of unchanged acid. From the ligroin solution 3·7229 g. of soluble acids (m. p. 90—116°) were obtained, and 3·1312 g. of these were hydrogenated with 0·0065 g. of colloidal palladium as before. Since 211 c.c. (at 20° and 760 mm.) of hydrogen were required as compared with a possible 341 c.c., it follows that 61·9% of dihydro- and 38·1% of tetrahydro-piperic acid were present, and the final result of the 50% hydrogenation, as calculated either from the proportion of unchanged acid or from the amount of dihydro-acids, is shown in Table II.

FIG. 2.

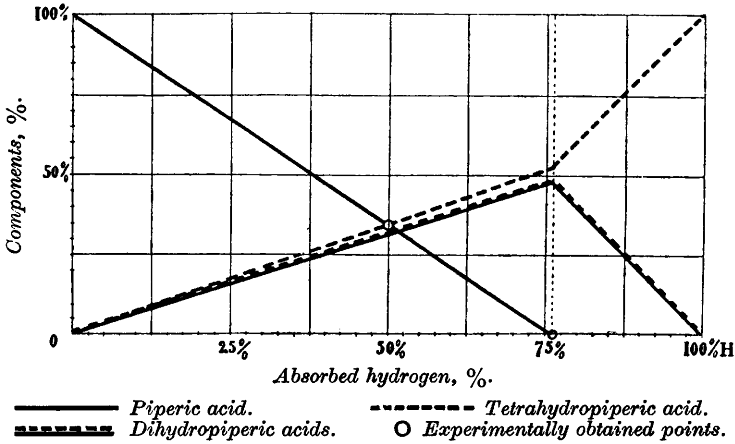


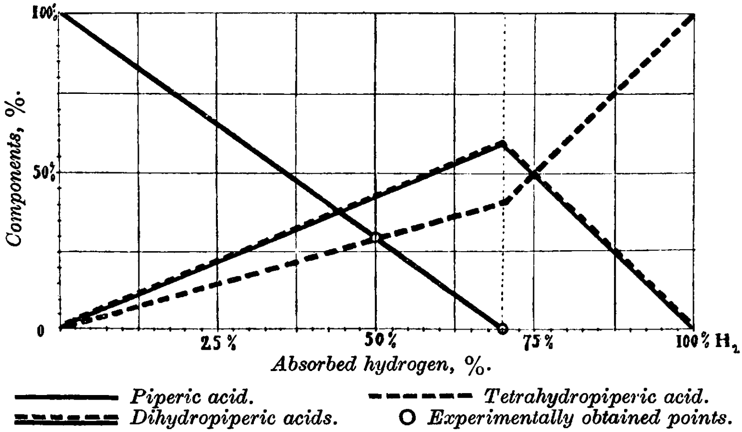
TABLE II.

Composition of 50% hydrogenation product (Paal's method).

	Calc. from amount of piperic acid.	Calc. from amount of dihydropiperic acids.	Mean.
Piperic acid	25%	27·6%	26·3%
Tetrahydropiperic acid......	25	27·6	26·3
Dihydropiperic acids	50	44·8	47·4
Total	100	100	100

The critical point of the hydrogenation, as determined graphically, is at 68% of hydrogen absorbed, and according to our views, all the piperic acid is exhausted at this point; Paal, however, states that it must be present at any moment of the process, and for, *e.g.*, 50% hydrogenation he postulates 50% of unchanged acid and 50% of tetrahydro-acid (contrast Table II). In order to settle this matter, we hydrogenated 2·4382 g. of piperic acid by Paal's method, allowing 447 c.c. (at 18° and 750 mm.) to be absorbed; since complete hydrogenation requires 541 c.c., the stage attained corresponds to 82·5% hydrogenation. The reaction product isolated dissolved completely in a small quantity of hot ligroin, which proves a total absence of piperic acid, and its m. p. was 89—93° (piperic acid has m. p. 216—217°). If the hydrogenation had proceeded as assumed by Paal, we should have found 17·5% of unchanged acid in the product.

FIG. 3.



Shapes of the Hydrogenation Curves.

In spite of the apparent total dissimilarity of the two curves in Fig. 1, they must both be related to the same type. Curve 2, according to the elements of its shape, is similar to the typical hydrogenation curves of conjugated systems of Type II (*e.g.*, the curves of di*iso*propenyl and piperylene): it differs only in the exceedingly sharp manifestation of its elements. The first section of the curve (prior to the critical point), corresponding to the hydrogenation of conjugated systems, has a clearly marked minimum. Such minima, often slightly marked, are to be found on the curves of conjugated systems of Type II (those for piperylene and its mixtures being, however, more definitely marked). The minimum corresponds to the moment when the predominance of one kind of molecule gives way to that of another kind on the surface of the catalyst. This subject will be discussed in a future communication.

The second part of Curve 2, corresponding to a greater rate, is typical of most of the conjugated systems already studied (divinyl, isoprene, di*iso*propenyl, etc.). The third part represents the hydrogenation of the benzene ring.

Curve 1 differs from the other in that its second stage proceeds at a reduced rate instead of a higher one. This peculiarity might be attributed to the low rate of the process as well as to the thermal exchange with the surrounding medium, since we have often found that alteration in the conditions of the hydrogenation process, such as change of temperature, affects the shape of the curves. This question also will be dealt with later.

All our methods prove that the conjugated system is more rapidly exhausted under Paal's conditions than under our own; after the addition of 1 mol. of hydrogen, 26·3% of the piperic acid is unchanged in the former case and 34·3% in the latter. For this reason the position of the critical point is not the same, being at 68—70% and 75—76% in the two cases, respectively.

Summary.

(1) The hydrogenation of piperic acid in presence of platinum black, as well as in presence of colloidal palladium, proceeds according to Type II of our classification.

(2) The position of the critical point depends upon the catalyst chosen; in the former method, in alcoholic solution, it is at 75—76% of hydrogen absorbed, whereas in the latter it is at 68—70% if the potassium salt is used in aqueous solution.

(3) The hydrogenation curves obtained with either catalyst must be related to the same type, although they differ in shape.

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