CXIII.—*The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part II. The Hydrogenation of Conjugated Systems.*

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THE simplest example of a conjugated system is afforded by divinyl, $CH_2{:}CH{\cdot}CH{:}CH_2$; if any of the hydrogen atoms are replaced, the properties of the derivative depend upon the number, position, and character of the substituents introduced.   One of us (Lebedev, *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249) has shown how the

nature and position of the different substituents affect the tendency to polymerisation, and in this communication a study is made of their influence on the catalytic hydrogenation of the derivatives. The addition of hydrogen in the presence of metallic catalysts has substantial advantages over the usual addition reactions, for a study of the hydrogenation curves enables consecutive reactions to be differentiated and selective catalysis to be detected.

We have studied the hydrogenation of more than a dozen substances containing conjugated systems, and have noted three different types of reaction.

Type I. This, the simplest type, consists of two consecutive phases : (1) the addition of hydrogen exclusively in the 1 : 4-position with formation of an ethylenic derivative ; (2) the addition, at a different rate, to the 2 : 3 double bond. The corresponding curve (Fig. 1) has two entirely separate sections, each representing the absorption of 1 mol. of hydrogen ; it resembles the hydrogenation curve of a binary mixture of ethylenic substances of different degrees of substitution (see Part I ; J., 1925, **127**, 417), and the break corresponds to the complete consumption of one of the active components, for, by interrupting the process at this stage, we get a homogeneous product with a double linkage in the 2 : 3-position. Processes of this kind *therefore agree with Thiele's rule.* To this type belong those substances in which all the four hydrogen atoms in the 1 : 4-position of divinyl are replaced by aliphatic radicals, *e.g.*, di*iso*butenyl, $CMe_2:CH\cdot CH:CMe_2$.

Type II. This is a very complicated type. The addition of hydrogen takes place in all the possible directions : 1 : 2, 3 : 4, and 1 : 4. This leads to the formation of two (for a symmetrical molecule) or three (for an unsymmetrical molecule) substances, containing only one double linking. The process is complicated by the simultaneous formation of fully saturated molecules. Thus, the hydrogenation curves of divinyl and of piperylene show three sharply separated sections, and the isoprene curve shows four. The curves of this type differ characteristically from those of the first type in that the end of the addition of the first mol. of hydrogen is not marked by any change in shape : this point does not coincide with a change in the number of the active components of the system. The change occurs considerably later : in the cases we have investigated, it corresponds to the addition of 68—77% of hydrogen (1·36—1·54 mols.) and to the consumption of the conjugated system.

If the process is interrupted after the addition of 1 mol. of hydrogen, a mixture of four substances is obtained in the case of symmetrical molecules and of five in the case of unsymmetrical

ones. For instance, isoprene at this stage has produced 30% of *iso*pentane, 12% of *iso*propylethylene, 13% of *as*-methylethylethylene, and 15% of trimethylethylene, 30% of isoprene being unchanged. Processes of this type *do not follow the theory of Thiele*. Of the substances we have investigated, the following belong to this type : divinyl, piperylene, di*iso*propenyl, isoprene.

Type III. We include this type in our review as a theoretically possible one, but we have not yet observed it, and possibly it is never completely realised. In this case, the addition of 2 mols. of hydrogen would take place simultaneously, or—what leads to practically the same result—the addition of 1 mol. is immediately followed by the much more rapid addition of a second. By interrupting the process at any time, a mixture of unchanged material and of completely saturated hydrocarbons should be obtained. The corresponding curves would show no break and would resemble those of simple ethylenic substances.

Paal (*Ber.*, 1912, **45**, 2221) suggested that conjugated systems are always hydrogenated in this way, and sought confirmation of this by examining the products obtained after the addition of 1 mol. of hydrogen to certain substances containing a conjugated system. He chose for this purpose piperine, piperinic acid, cinnamylidenemalonic acid and cinnamylideneacetone. We have studied the hydrogenation of piperinic acid and have found that the process does not belong to our third type, as supposed by Paal. Our results will be published later.

In the three diagrams of Fig. 1, the percentages of hydrogen absorbed are plotted as abscissæ, and the molecular composition of the mixture is given by the ordinates. The first and third types can be considered as distinct types; the second is a transition type, which includes any number of variations between the two limiting types. *In all three cases, when 1 mol. of hydrogen has been added (50% hydrogenation) the number of unchanged (conjugated) molecules is equal to the number of fully saturated molecules.* On the diagrams this is expressed by the fact that the line of the conjugated system and the line of the saturated compound cross each other at a point corresponding to 50% of hydrogen added. The continuation of the first line intersects the abscissa at a point A, which determines the moment when the whole conjugated system is consumed. We call this *the critical point of the hydrogenation of a conjugated system*. It is a characteristic point which determines fully the course of the process, and from a knowledge of its position it is possible to draw the complete diagram. Thus, it is seen from the diagram of Type II (Fig. 1) that the positions of the breaks B and C are determined by the condition (above) as to the two lines

crossing on the 50% ordinate, in conjunction with the following data :

(1) Both points lie on the ordinate of the critical point A.
(2) AB + AC = 100.

The diagram of Type II shows A at 70% hydrogenation; this is the case with isoprene, but the diagram equally represents the hydrogenation process of any conjugated system whose critical point corresponds to 70% of hydrogenation.

FIG. 1.

I TYPE

II TYPE

III TYPE

Absorbed hydrogen, %.
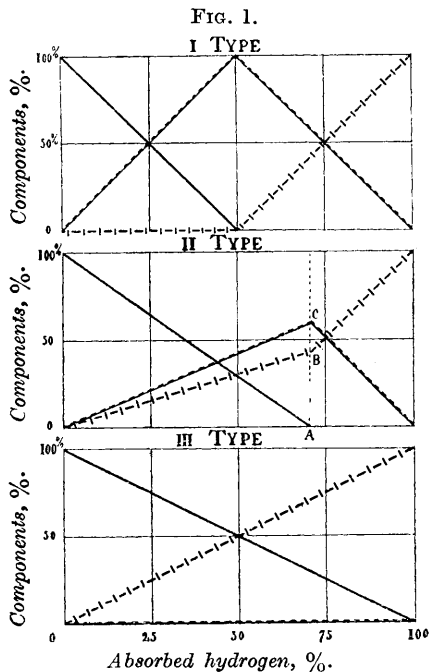
——————————— *Initial material (conjugated system).*
============= *Ethylenic substance.*   —|—|—|— *Fully saturated substance.*

The point A may be determined by several means :

1. Hydrogenation is carried up to 50%; the composition of the hydrogenation mixture is then found by determining the amount of any one of the three compounds, these amounts being connected by the relations $a = b$ and $c = 100 - a - b$, where a is the conjugated system, b the fully saturated compound, and c the mono-ethylenic compound. The diagram is then constructed on the foregoing principles.

2. In many instances the critical point is easily determined from the hydrogenation curves of the pure substance containing the

conjugated system and of its mixtures with different ethylenic substances; this occurs if the critical point corresponds to a well-defined break in the curve (see below and Fig. 2).

The three types we have dealt with comprise all the conjugated systems, but the classification of these systems will not be complete without including those cases in which 1 : 4-addition is not realised at all, the individual double linkings being hydrogenated independently. For the sake of completeness, we have gathered these cases into a special fourth type and we distinguish two varieties.

Type IV A. The double linkages differ in the degree of substitution, e.g., as in CHR:CH·CH:CRR'. In this case the linkages are hydrogenated at different rates. The hydrogenation curve has a break corresponding to the addition of 50% of hydrogen, at which stage a homogeneous monoethylenic product is formed. This case agrees in the shape of the curve and in the diagram with Type I, but differs fundamentally in that no 1 : 4-addition products are formed. *The process does not follow Thiele's rule.*

Type IV B. The linkings are equal in the degree of substitution, as in CHR:CH·CH:CHR', in which case they are hydrogenated simultaneously. The curve has the shape typical of homogeneous monoethylenic substances. When the product of 50% hydrogenation is examined, it is found to be a mixture of diethylenic, monoethylenic, and fully saturated compounds. The diagram in this case is somewhat similar to that of Type II, but the two cases differ inasmuch as 1 : 4-addition products are now absent.

In this paper we deal with the hydrogenation of isoprene.

EXPERIMENTAL.

The isoprene used was prepared by pyrogenetic decomposition of turpentine. The resulting isoprene and trimethylethylene were converted into their hydrobromides and isoprene dibromide was separated by fractional distillation, b. p. 80—82°/23 mm. The isoprene recovered by means of solid potassium hydroxide had b. p. 34·5°; $d_4^{20·0°}$ 0·6803; $n_D^{20·0°}$ 1·42207; $[R_L]_D$ 25·40 (Calc., 24·33; exaltation 1·07).

The isoprene was hydrogenated in the apparatus described in Part I (*loc. cit.*), alcohol being used as solvent, and platinum black, obtained by the method of Willstätter (*Ber.*, 1912, **45**, 1471), as catalyst; the bath temperature was in some tests 0°, and in others near to room temperature. The curves are plotted as in our former paper, the abscissæ giving time intervals and the ordinates showing the number of c.c. of hydrogen absorbed per ½ minute.

The hydrogenation of isoprene proceeds as shown in Curve 1, Fig. 3 (for details see Table IV, No. 2). The curve is horizontal

up to 70—71% of the hydrogen necessary to saturate both the double linkages; in this section the velocity is uniform. The last 30% of hydrogen is added in a very peculiar way, as shown on a larger scale in Fig. 2 (Table IV, No. 1), for which a large quantity of isoprene was used. At first the rate increases, and then it falls, showing two more or less horizontal sections. Thus the whole curve is divided into four parts, and it is obvious that isoprene is not hydrogenated at once to *iso*pentane, but that it passes through a range of intermediate stages. The amounts of hydrogen absorbed in the different sections, as calculated from Figs. 2 and 3, are :

Section	1	2	3	4
Hydrogen, %	70	8·5	9	12·5

The formula of isoprene $\overset{1}{C}H_2\overset{2}{:}\overset{2}{C}Me\overset{3}{\cdot}\overset{3}{C}H\overset{4}{:}\overset{4}{C}H_2$ indicates the following possibilities for the process of hydrogenation : (1) 1 : 2-Addition

FIG. 2.

Time (mins.).
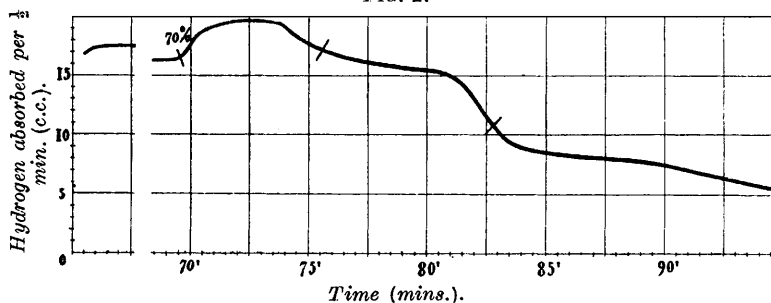
of 1 mol., giving *iso*propylethylene. (2) 3 : 4-Addition of 1 mol., giving *as*-methylethylethylene. (3) 1: 4-Addition of 1 mol., giving trimethylethylene.

Thus the formula of isoprene would explain the presence of three sections of the curve; it will be shown later that the second, third, and fourth sections correspond to the above-named three amylenes. We must obviously attribute to the first section of the curve the hydrogenation of the isoprene itself in the three possible directions. The test with sulphur dioxide shows that isoprene is present all through the first section of the curve. At the last point of this section the isoprene disappears, *i.e.*, this point is " the critical point of hydrogenation of a conjugated system." Up to this point 70—71% of hydrogen is added at a uniform rate; nevertheless, there is no doubt that in this part of the process several reactions are occurring *simultaneously*, for there are produced *iso*pentane and three different amylenes, which, on the other side of the critical point, are hydrogenated *successively*. Thus we have to deal up

to the critical point with at least four reactions. The fact that all these four reactions are summed up in one common section of the curve may be explained by assuming that they are " conjugated " by a common initial material—the isoprene. As soon as this substance is consumed (at the critical point), several *successive* reactions start, and these proceed in accordance with the rules adduced in Part I (*loc. cit.*).

The Hydrogenation Process prior to the Critical Point.

25% Hydrogenation.—In order to study the process of the hydrogenation of isoprene up to the critical point we have investigated the products formed after the addition of 25%, 50%, and 70% of the hydrogen necessary for full saturation. The mixture of hydrocarbons produced by 25% and 50% hydrogenation contains isoprene, and it was therefore removed as a solid compound with sulphur dioxide. The further information necessary was obtained by a study of the hydrogenation of mixtures of ethylenic compounds.

To 12·011 g. of isoprene, 2110 c.c. of hydrogen (25% hydrogenation) were added (see Table IV, No. 3.) The reaction product was treated with sulphur dioxide,* and allowed to stand for 6 days. The separated hydrocarbons amounted to about 3·5 g., and when freed from the residue and from sulphur dioxide they boiled at 29—36°. They were analysed by the hydrogenation method.

For this purpose 0·85 g. of hydrocarbons was fully hydrogenated and required 173 c.c., whereas if the hydrocarbons consisted only of amylenes, 293 c.c. would have been required. The composition was therefore amylene 59%, *iso*pentane 41% (see Table IV, No. 5).

From the hydrogenation curve (Fig. 3, Curve 2), we can also determine the composition of the amylenes. The sections of the curve are marked by dashes, and later we show that the first section corresponds to *iso*propylethylene, the second to *as*-methylethylethylene, and the third to trimethylethylene. In Table I we give the amount of hydrogen absorbed in different sections of the curve and the calculated composition of the reduced product; and in

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* The quantitative precipitation of isoprene is effected as follows : An alcoholic solution of the hydrogenation products is placed in a flask and saturated at 0° with sulphur dioxide; the flask is then closed. Precipitation soon commences and is complete in 2—3 days. If the concentration of isoprene is high, the contents of the flask form a colloidal mass. The liquid is distilled on a steam-bath into a vessel containing alkali at 0°, and the hydrocarbon layer which separates is again saturated with sulphur dioxide and left in a sealed vessel for some days in order to ensure that all the isoprene has been eliminated.

Table II is shown the composition of the original product of hydrogenation.*

TABLE I.

	25% Hydrogenation.		50% Hydrogenation.	
	H₂ absorbed, c.c.	Components, %.	H₂ absorbed, c.c.	Components, %.
*iso*Propylethylene	28	9·5 ⎫	116	18 ⎫
as-Methylethylethylene	28	9·5 ⎬ 59	119	18·7 ⎬ 56·7
Trimethylethylene	117	40·0 ⎭	126	20 ⎭
*iso*Pentane	0	41·0	0	43·3
Total	173	100	361	100

TABLE II.

| Degree of hydrogenation.	25%.	50%.	70%.
Isoprene	64·5% (63·9%)	30%	0%
*iso*Pentane	14·5	30	40
*iso*Propylethylene	3·3	12	17
as-Methylethylethylene	3·4	13	18
Trimethylethylene	14·3	15	25
Total	100	100	100

The isoprene was also estimated as a solid compound with sulphur dioxide.   Two weighed samples of the 25% hydrogenation product were precipitated in an alcoholic solution by sulphur dioxide, and the dried residues weighed.   These determinations gave 63·8 and 63·9% of isoprene, the latter value being that in parentheses in Table II.

50% Hydrogenation.—To 14·9 g. of isoprene, 5180 c.c. (1 mol.) of hydrogen were added (see Table IV, No. 4).   The hydrogenation product was freed from isoprene as described above, and kept saturated with sulphur dioxide for 2 months.   When freed from the residue, washed, and distilled over metallic sodium, the hydrocarbons boiled at 28—33°.   Their composition was investigated by the hydrogenation method, 1·811 g. requiring 361 c.c. as compared with 637·5 c.c. calculated for pure amylene (see Table IV, No. 6); hence there were 56·7% of amylene and 43·3% of *iso*pentane. Examination of the three sections of the curve (Fig. 3, Curve 3) as before leads to the results given in Tables I and II.

In the foregoing, we have assumed that the first section of Curves Nos. 2 and 3 (Fig. 3) belongs to *iso*propylethylene, and the last to trimethylethylene.   This conclusion is based on the rule given in Part I (*loc. cit.*), which may be stated thus : If a mixture of ethylenic derivatives of different degrees of substitution is hydrogenated, the

* The calculation is as follows : 100 Mols. of isoprene require 50 mols. of hydrogen for 25% hydrogenation; if x mols. of amylene and y of *iso*pentane have been formed, we have $x + 2y = 50$, and $x : y = 59 : 41$; hence $x = 21$, $y = 14·5$, and isoprene (by difference) = 64·5%.

monosubstituted ethylene is hydrogenated first, then follow in succession the di-substituted, the tri-substituted, and finally the tetra-substituted derivative. In order to confirm this we made two experiments in which the reaction product was further hydrogen-

Time (in mins.) for Figs. 3, 4, and 5.

Time (in mins.) for Fig. 6.
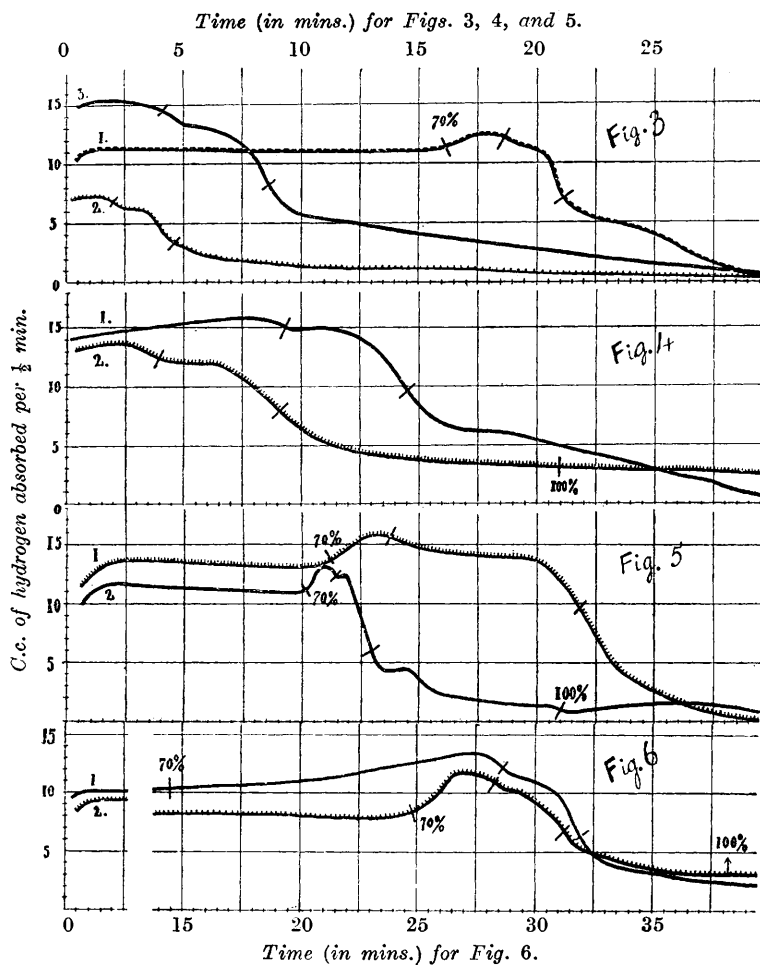
ated after admixture with (a) *iso*propylethylene and (b) trimethyl-ethylene.

(a) The weight of the product examined was 1·8053 g., requiring 351·5 c.c. of hydrogen (at 20° and 760 mm.) on the assumption that it contained 56·7% of amylenes (see Table I). The weight of *iso*-propylethylene was 0·5465 g., which required 187 c.c. of hydrogen. The corresponding curve is given in Fig. 4 (1).

(b) The weight of the product was 1·6931 g., which requires 326 c.c. of hydrogen (at 19° and 765 mm.) on the basis of 56·7% of amylenes. The weight of trimethylethylene was 0·4219 g., which required 148 c.c. of hydrogen. The curve is shown in Fig. 4 (2).

In Table III are shown (1) the amounts of hydrogen required in the various stages as calculated from the weight taken, according to Table I; (2) the amounts actually consumed in the two experiments.

TABLE III.

C.c. of hydrogen absorbed in the sections of the curve by hydrogenation in mixture with :

		(a) isoPropylethylene.		(b) Trimethylethylene.	
		Calc.	Found.	Calc.	Found.
Section 1	....	105 + 187	290	98	100
,, 2	....	116	125	107	114
,, 3	....	130	134	121 + 148	265
Total	....	351 + 187	549	326 + 148	479
		538		474	

(a) It is evident from the table and Curve 1 that the second and third sections of the curve remained practically unchanged in size. Hence, *all the isopropylethylene was hydrogenated in the first section*.

(b) From the table and Curve 2 it is similarly clear that *the third section of the curve pertains to trimethylethylene*.

The middle section therefore relates to *as*-methylethylethylene.

70% *Hydrogenation.*—In the foregoing cases it has been necessary to extract the unchanged isoprene before examining the mixture of amylenes. In this case, however, all the isoprene has become hydrogenated, and the curves after the 70% stage (" critical point ") refer solely to the hydrogenation of the amylenes which have been accumulating and have not already been reduced to *iso*pentane.

For the addition of the remaining 30% of hydrogen we have three well-defined sections of the curve. The amounts of hydrogen corresponding to each of these sections have already been given (p. 828), and the amount of the particular amylene corresponding to each section is obtained by doubling the percentage of hydrogen absorbed over that section. The composition thus calculated is given in the third part of Table II.

General Survey of the Hydrogenation of Isoprene.

The results obtained for 25%, 50%, and 70% hydrogenation of isoprene are given in Table II, and are used for plotting the diagram in Fig. 7.
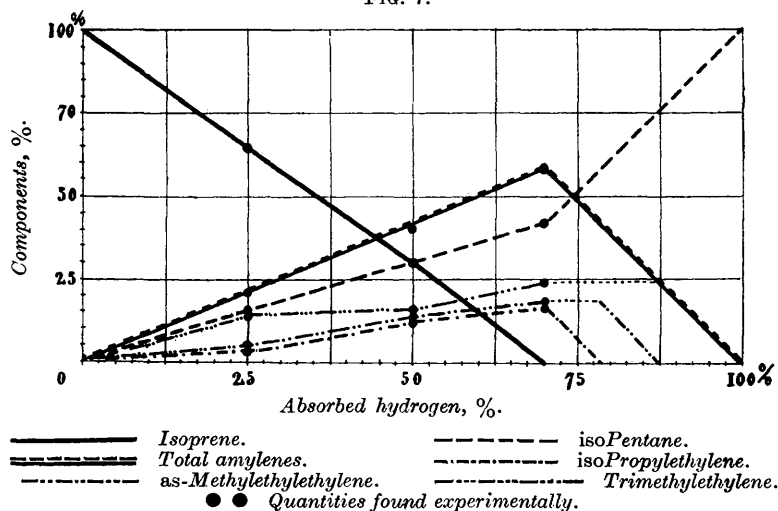
Nearly all the experimental points of the isoprene curve lie on the straight line which joins the terminal point of the axis of ordin-

TABLE IV.

Numerical data for isoprene hydrogenated totally, partially, and in admixture with monoethylenic derivatives.

Expt. No.	Material.	Weight (g.).	C.c. of H₂ calc.	obs.	Temp.	Press. (mm.).	Pt (g.).	Alcohol (c.c.).	Bath temp.	Curve No.
1	$C_5H_8 + 2H_2$	4·2390	2910	2850	11°	760	0·25	35	10·5°	Fig. 2
2	$C_5H_8 + 2H_2$	0·875	530	525	15	760	0·2	20	13·75	,, 3 (1)
3	$C_5H_8 + \frac{1}{2}H_2$	12·011	2110	2110	16	755	0·2	35	0	
4	$C_5H_8 + H_2$	14·90	5178	5178	17	755	0·2	35	15	
5	$C_5H_8 + \frac{1}{2}H_2$, freed from C_5H_8	0·85	293	173	18	758	0·1	35	0	,, 3 (2)
6	$C_5H_8 + H_2$, freed from C_5H_8	1·811	637·5	361	20	742	0·3	15	17·75	,, 3 (3)
7	{ Isoprene + isoPropylethylene	0·6920 / 0·8900	473 / 295 }	758·5	14	770	0·2	15	12·25	,, 6 (1)
8	{ Isoprene + Camphene	0·6310 / 1·3200	448 / 200 }	637	17	750	0·2	15	15·5	,, 5 (1)
9	{ Isoprene + Trimethylethylene	0·8543 / 0·4780	594 / 163 }	755	16	755	0·2	15	0	,, 6 (2)
10	{ Isoprene + Tetramethylethylene	0·4570 / 0·2896	324 / 83 }	400	17	748	0·2	15	16·25	,, 5 (2)

FIG. 7.

Isoprene. ————— isoPentane.
Total amylenes. isoPropylethylene.
as-Methylethylethylene. ————— Trimethylethylene.
● ● Quantities found experimentally.

ates (100%) with the critical point lying on the axis of abscissæ (70%). This means that the reduction of isoprene proceeds proportionally to the amount of the consumed hydrogen until it is entirely reduced.

The curves showing the total amylenes and the isopentane are straight lines up to the critical point, the experimental points lying on straight lines passing through the origin. This attests to the important fact that the accumulation, not only of amylenes, but also of isopentane is going on from the very beginning of the process. The accumulation of these two components is strictly proportional to the amount of the hydrogen consumed up to the critical point.

At this point both curves show a break, the amount of amylenes beginning to decrease towards zero, and that of *iso*pentane increasing to 100%.

The diagram does not answer the important question as to the way in which *iso*pentane is formed. During the second stage of the process, it is obvious that *iso*pentane is formed from the amylenes accumulated before the critical point, but the origin of that formed in the first phase of the process is still unknown. Two possibilities are open :

(1) *iso*Pentane is formed from the amylenes resulting from the addition of 1 mol. of hydrogen to the isoprene. In this case we must assume that it is formed neither from *as*-methylethylethylene nor from trimethylethylene, for the hydrogenation of these two amylenes in presence of *iso*propylethylene is improbable, because the last is the most readily hydrogenated of the three. This is wholly confirmed by the experimental data below. The addition to isoprene of an unsymmetrical disubstituted ethylene or of a trimethylethylene does not displace the critical point, and therefore does not change the amount of fully saturated molecules formed before the critical point is reached.

The partial formation of *iso*pentane from *iso*propylethylene is, however, a possibility. As may be seen from Curve 1, Fig. 6, the *iso*propylethylene added to the isoprene is hydrogenated, as it should be, in the second part of the curve, but the position of the critical point is too indistinct to preclude a partial hydrogenation of the *iso*propylethylene before the critical point.

(2) *iso*Pentane is formed directly from isoprene by addition of 2 mols. of hydrogen either simultaneously or in such rapid succession as to appear to be so. In this case we should have a process analogous to that taking place in the hydrogenation of benzene.

We cannot find any objection to the second hypothesis, but we cannot yet prove it, and the question must be regarded as still unsolved.

We have now to account for the relative quantities of the individual amylenes formed at the hydrogenation.

As shown by the diagram, the curves for the different amylenes depart considerably from straight lines. This is unexpected, for the sum of the three amylenes is expressed by a remarkably regular straight line. This deviation is due to the fact that in the mixture of amylenes the amount of trimethylethylene is greater than is necessary to make the lines of all three amylenes straight. This, in turn, may be due to the isomerisation of two of the amylenes into trimethylethylene. Most probably this secondary process is caused by the action of sulphur dioxide during the elimination of

isoprene from the mixture of the hydrocarbons, for we have noticed that the excess of trimethylethylene was more pronounced the longer the mixture of hydrocarbons had been kept in contact with sulphur dioxide.

Isomerisation of Amylenes by Action of Sulphur Dioxide.—A direct test has demonstrated this isomerisation : We prepared a mixture of amylenes by the decomposition of amyl alcohol (from fusel oil) by aluminium oxide at 400°. A portion was hydrogenated, and the proportion of trimethylethylene in the mixture was found, from the extent of the sections of the hydrogenation curve, to be 27%. Another portion of the mixture was saturated with sulphur dioxide at 0°, sealed, and heated at 100° for 3 days, in order to accelerate the process; it was then freed from sulphur dioxide by washing, distilled over metallic sodium, and hydrogenated, the proportion of trimethylethylene being then 41%, as determined from the curve.

There is therefore some uncertainty as to the original normal composition of the amylenes obtained as a result of the hydrogenation of isoprene. We must consider it to be the composition of the amylenes at the critical point (70% hydrogenation) as shown in the last column of Table II, for in this case the amylenes were not treated with sulphur dioxide. The composition of the amylenes obtained from isoprene hydrogenated up to 25% and 50% must, however, be considered as more or less altered by the action of sulphur dioxide.

Hydrogenation of Isoprene Mixed with Standard Ethylenic Derivatives of Different Degrees of Substitution.

When considering the process as a whole, the following questions arise : (1) How does the addition of different monoethylenic derivatives affect the general type of the isoprene curve and the position of the critical point ? (2) How is *iso*pentane formed from the products of hydrogenation ?

In order to throw light on these questions we have examined a set of isoprene mixtures with ethylenic derivatives of different degrees of substitution. The numerical data relating to these mixtures are given in Tables IV and V. In Table V are shown : (*a*) the amounts of hydrogen calculated according to the scheme on p. 828 for the four sections of the isoprene hydrogenation curve, (*b*) the amounts of hydrogen that were actually absorbed in these sections in the hydrogenation of isoprene in the various mixtures.

When examining Tables IV and V and the corresponding curves, one must note the following circumstances : The added standard

TABLE V.

C.c. of hydrogen absorbed in the sections of the isoprene curve when hydrogenated in admixture with :

		isoPropyl-ethylene.		Camphene.		Trimethyl-ethylene.		Tetramethyl-ethylene.	
		Calc.	Found.	Calc.	Found.	Calc.	Found.	Calc.	Found.
Section	1	331	328	313	305	416	415·5	228	224
,,	2	38+295	327	41	46	53·5	56·5	27	28
,,	3	41	46	·40+200	240	59·5	63	29	28
,,	4	62	59	54	46	65+163	220	40	42
,,	5	—	—	—	—	—	—	0+83	78
Total		472+295	760	448+200	637	594+163	755	324+83	400
		767		648		757		407	

ethylenic derivatives are generally hydrogenated after the critical point in the place determined by the degree of substitution of the given ethylene. Thus the isopropylethylene added is hydrogenated in the second section of the curve (Fig. 6, No. 1); camphene in the third (Fig. 5, No. 1); trimethylethylene in the fourth (Fig. 6, No. 2) ; * and tetramethylethylene is hydrogenated when all isoprene is consumed (Fig. 5, No. 2).* The critical point retains its position and is clearly defined in every case except that concerning iso-propylethylene. This circumstance allows us to assume that a monosubstituted ethylene can be partially hydrogenated simultaneously with isoprene.

Summary.

(1) In the catalytic hydrogenation of conjugated systems, the process may be of four types :

Type I. In the first phase the addition of hydrogen is directed exclusively into the 1 : 4-position. In the second phase, which proceeds at a different (lesser or higher) rate, 2 : 3-addition occurs.

Type II. In the first phase the addition of hydrogen takes place primarily in all the possible directions (1 : 2, 3 : 4, and 1 : 4), and subsequently until a fully saturated compound is formed. All these reactions proceed simultaneously. The first phase ends with the consumption of the conjugated system at the " critical point of hydrogenation." For the several substances investigated, the critical point corresponds to 68—77% of hydrogen absorbed. In the second phase are hydrogenated those monoethylenic compounds which were formed in the first phase.

Type III. One mol. of a conjugated system absorbs simultaneously 2 mols. of hydrogen, giving a saturated compound directly.

* A dash, marked 100%, on these curves indicates the point where isoprene is consumed and hydrogenation of the admixed substance begins.

Type IV. The addition of hydrogen is directed exclusively into the 1 : 2- and 3 : 4-positions. The double linkages of the conjugated system are hydrogenated independently.

(2) The process of hydrogenation of isoprene belongs to Type II. The first phase, which proceeds at a constant rate, embraces several processes—the addition of 1 mol. of hydrogen in the 1 : 2-, 3 : 4-, and 1 : 4-positions—which lead to the formation of three amylenes, *viz.*, *iso*propylethylene, *as*-methylethylethylene, and trimethylethylene. At the same time some *iso*pentane is formed.

The first phase ends at the " critical point," corresponding to the addition of 70—71% of hydrogen necessary for complete hydrogenation; at this point the whole of the isoprene has been consumed.

In the second phase the accumulated amylenes are consecutively hydrogenated : first the *iso*propylethylene, then the *as*-methylethylethylene, and finally the trimethylethylene.

(3) The hydrogenation curve of isoprene is horizontal in its first phase, but turns upwards at the critical point, denoting an increase in the rate.

In the second phase the curve shows three more or less horizontal sections corresponding to the three amylenes mentioned in (2).

(4) In the hydrogenation of isoprene in admixture with ethylenic compounds, the critical point retains its position.

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