XLVIII.—*The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part V. The Hydrogenation of Cyclic Ethylenic Derivatives and of their Mixtures.*

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THE following communication is closely connected with Part I of our investigation (J., 1925, **127**, 417), in which it was shown that the rate and nature of hydrogenation of single ethylenic compounds and of their mixtures are determined by the characteristics of the type to which they belong (*i.e.*, by the degree of substitution at the double linkage in the molecule) rather than by individual characteristics. Thus, in every case, monosubstituted ethylenic derivatives are hydrogenated preferentially, and tetrasubstituted last of all, the di- and tri-substituted types being intermediate.

This property is most marked in the hydrogenation of mixtures of different ethylenic derivatives. Compounds of the same degree of substitution at the double bond are hydrogenated concurrently in a mixture and their curves show no break, but those of different types are hydrogenated consecutively in the above order, so that their curves display definite breaks corresponding roughly to the end of hydrogenation of one component and the beginning of that of another. This is probably due to the fact that the affinity of the catalyst for monosubstituted is much greater than for polysubstituted ethylenic compounds, those of the same degree of substitution being adsorbed with approximately equal readiness.

Discussion is simplified by the following classification of ethylenic compounds according to the degree of substitution at the double bond, *c* denoting a cyclic structure and R the remainder of the ring system.


$\begin{matrix}\mathrm{CHA}\\ \|\\ \mathrm{CH_2}\end{matrix}$
(I.)


$\begin{matrix}\mathrm{CHA}\\ \|\\ \mathrm{CHB}\end{matrix}$
(II*s*.)

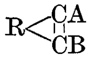

$\begin{matrix}\mathrm{CAB}\\ \|\\ \mathrm{CH_2}\end{matrix}$
(II*as*.)


$\begin{matrix}\mathrm{CAB}\\ \|\\ \mathrm{CHX}\end{matrix}$
(III.)


$\begin{matrix}\mathrm{CAB}\\ \|\\ \mathrm{CXY}\end{matrix}$
(IV.)


(II*c*.)


(III*c*.)


(IV*c*.)

The present communication deals primarily with ethylenic derivatives in a *cyclo*hexane ring, other cyclic systems being reserved for a future paper. We have studied the hydrogenation of single representatives of this class, and of their mixtures with one another and with open-chain ethylenic derivatives (in all, about forty binary mixtures were examined) and the results conform to the general rules given above for open-chain compounds. In those cases in which the hydrogenation of a mixture of two compounds shows a break in the curve, we are justified in assuming that both components are often (or perhaps always) hydrogenated simultaneously in each section, and this conclusion is supported by an examination of the distribution of hydrogen between the components in different phases of the process.

We have found that in some binary mixtures *practically* pure components are hydrogenated on both sections, whereas in other cases there are mixtures capable of being analytically separated.

We have also found that the position of the break on the curves of practically all of the binary mixtures examined of an open-chain (see Part I) and a cyclic ethylenic derivative exactly corresponds with the consecutive hydrogenation of the pure components in the mixture. As appreciable deviations from this rule are extremely rare, it is possible to calculate the composition of the mixture to within a few units % from the volume of hydrogen absorbed on the different portions of the curve.

Two such deviations are shown in Fig. 8 (curves 1 and 4), the breaks being considerably removed from the calculated positions in each case. The only other deviation is much more peculiar. It was noted in the pair carvone–camphene (Fig. 11, Curve 3); here we have a mixture of two types of substitution at the double bond, *viz.*, an *as.*-disubstituted ethylene (in both camphene and carvone) and a trisubstituted one (in carvone), yet we find on the hydrogenation curve three sharply separated sections instead of the two expected. This case requires further study.

EXPERIMENTAL.

The method of investigation was the same as described in Part I. 0·02—0·0025 G.-mol. of the substance was used, and, unless otherwise stated, the other conditions were: 0·2 g. of platinum-black, 15—25 c.c. of alcohol as solvent, and a bath temperature of 20°. The curves are plotted as before, the transverse dash in each case indicating the point at which the preferentially hydrogenated compound is calculated to be saturated. Since *rate* of absorption is plotted against time, the volume of hydrogen absorbed up to any given time is given by the *area* under the curve.

Hydrogenation of Single Compounds (Table I).

Disubstituted Compounds (Type IIc; Fig. 1).—The curves for *cyclo*hexene (Curve 1) and 1-methyl-Δ^3-*cyclo*hexene (Curve 2) are very much alike; the rate is nearly constant to the end, and the reaction ceases sharply with the absorption of 100% of the hydrogen calculated for saturation of the latter and of about 90% of that calculated for the former.* The rate of hydrogenation of indene (Curve 3) is lower, and the curve droops slightly. A fourth compound of this type examined was maleic anhydride (obtained by the method of Tanatar, *J. Russ. Phys. Chem. Soc.*, 1890, **22**, 213; m. p. 52—55·5°). Its hydrogenation gave an entirely unexpected result; for the absorption in ethereal solution was exceedingly low. Several experiments showed that the hydrogenation of *cyclo*hexene is hindered by the presence of this anhydride; and hence we conclude that maleic anhydride is an anti-catalyst, although neither the acid itself nor its esters possess this quality. Citraconic acid

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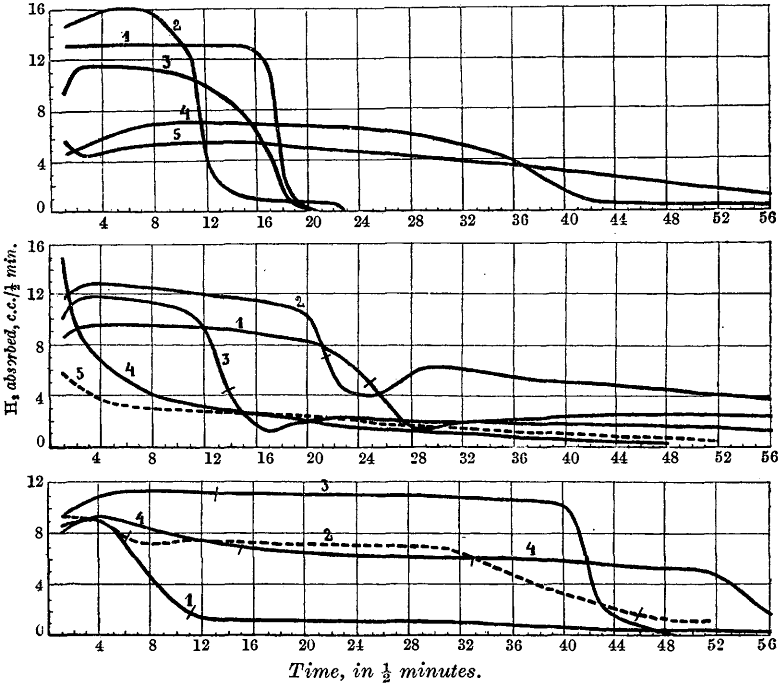
* The *cyclo*hexene contained about 10% of benzene or some other hydrocarbon very little susceptible to hydrogenation.

and its anhydride (Type III*c*) behave similarly. An investigation of this phenomenon in anhydrides and acids is being undertaken.

Trisubstituted Compounds (Type IIIc; Figs. 1 and 2).—Menthene and pinene are hydrogenated very slowly, their curves falling continuously. Both seem to contain a proportion of some compound (? dipentene) having a higher absorption rate, as shown by the initial rapid fall (Fig. 2, Curves 4 and 5).

FIGS. 1, 2, 3.



The curves of terpineol and carvotanacetone are very much alike (Fig. 1, Curves 5 and 4): the rate of absorption rises somewhat at first, and then falls continuously to the end. The latter compound was prepared by 50% hydrogenation of carvone in the absence of solvent (compare Armstrong, *Chem. and Ind.*, 1925, **44**, 701), and since its oxime (m. p. 74—76°) and semicarbazone (m. p. 171—172·5°) showed it to be pure, we are convinced that in the hydrogenation of carvone the double bond in the side-chain (Type II*as*) is reduced before that in the ring system (Type III*c*).

The absorption curves of carvone and *l*-limonene resemble one another (Fig. 2, Curves 1 and 2): in both cases hydrogenation of the bond in the side chain proceeds first and at an almost constant

TABLE I.

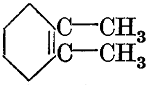
Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press. of H_2.	H_2 absorbed, c.c.	
				Calc.	Found.
*cyclo*Hexene	1; 1	0·8700	19°; 745 mm.	259	239·5[‡]
1-Methyl-Δ^3-*cyclo*-hexene	1; 2	0·747	17°; 768	183	179·3
Indene[*]	1; 3	0·8200	17°; 744	171·5	175
Carvotanacetone	1; 4	1·5409	17°; 758	241	229
Terpineol	1; 5	1·367	16°; 758	211	228
Menthene[*]	2; 4	0·763	16°; 757	124	141·5
Pinene[*]	2; 5	0·6493	17°; 757	113	122
Carvone[*]	2; 1	1·394	18°; 755	435	438
l-Limonene	2; 2	1·3800	18°; 765	481·5	491
,,	2; 3	0·8500	14°; 768	291	287
1 : 2-Dimethyl-Δ^1-*cyclo*hexene	3; 1	0·718	16°; 758	155	118[†]
,, ,,	3; 2	3·065	17°; 765	659	—[†]

[*] Bath temperature, 15°. [†] Hydrogenation incomplete.
[‡] See footnote, p. 323.

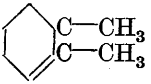
rate. The end of the absorption of the first molecule of hydrogen is marked by a sharp break in the velocity of reaction (compare Vavon, *Compt. rend.*, 1911, **152**, 1675), which falls to a minimum and then increases somewhat. The second portions of the curves are like those of carvotanacetone and terpineol, in that the rate rises slightly at first and then falls slowly till the end of the reaction. In the case of carvone, after the absorption of 2 mols. of hydrogen a very slow hydrogenation of the ketonic group sets in. A second experiment with *l*-limonene (Fig. 2; Curve 3) was carried out with platinum-black which had been used previously; the rate of hydrogenation of the cyclic bond (Type IIIc) was somewhat slower, but that of the side-chain bond (Type II*as*) remained practically the same.

Tetrasubstituted Compounds (Type IV*c*; Fig. 3).—Only one compound of this type was available, *viz.*, 1 : 2-dimethyl-Δ^1-*cyclo*hexene, prepared as follows: 2-methyl*cyclo*hexanol was oxidised to the ketone by Sabatier's method (*Compt. rend.*, 1905, **141**, 20), and this was treated with magnesium methyl iodide, and the product decomposed by 30% sulphuric acid; the required hydrocarbon was thus obtained with b. p. 132·5—134·5°, $d_{0^\circ}^{0^\circ}$ 0·8378 (Sabatier gives b. p. 132°, $d_{0^\circ}^{0^\circ}$ 0·8411). Its hydrogenation gave a very interesting result. Using small amounts, we observed only two sections in its curve (Fig. 3, Curve 1), the first corresponding to 44% of the total volume of hydrogen absorbed, but with larger amounts (Curve 2) we found three distinct sections, the first part of the curve showing an additional break, which would have corresponded to only 10—11 c.c. in Curve 1 and would therefore escape notice. The absorptions in the three sections are 7, 37, and 56%

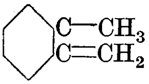
respectively of the total. The explanation of these breaks is as follows. The dehydration of 1 : 2-dimethyl*cyclo*hexanol by sulphuric acid can occur in three directions, resulting in the formation, in successively decreasing yield, of the following three hydrocarbons :



(Type IV*c*.)



(Type III*c*.)



(Type II*as*.)

Now, from the types to which they belong, it is seen that their ease of hydrogenation should be in the reverse order, the compound of Type II*as* being reduced preferentially. In order to assure ourselves that the second section of the Curve 2 corresponds to the hydrogenation of the second compound, we hydrogenated a mixture of our hydrocarbon with terpineol. The curve obtained is shown in Fig. 6 (Curve 2). Owing to the small amount of hydrocarbon taken, we can discern only two portions in it, but the first has increased in agreement with the amount of terpineol used, proving that the linkings hydrogenated in this section are both of Type III*c*.

It is clear that the hydrocarbon was too impure for use as a standard compound of Type IV*c*, so, since the impurities (Types II*as* and III*c*) are hydrogenated preferentially, the mixture was allowed to absorb 45% of the maximum hydrogen, whereby we obtained a mixture of saturated hydrocarbons together with the (presumably) unchanged hydrocarbon of Type IV*c*, which we used in subsequent experiments as a comparative standard of 55% content.

The foregoing results for individual cyclic hydrocarbons are completely analogous to those for open-chain compounds (Part I), and indicate that the absorption rates of the Types II*c*, III*c*, and IV*c* decrease in that order. Moreover, the curves of the last two types fall slowly, although that of Type III*c* shows a slight rise initially; on the other hand, the curves for compounds of Type II*c* (except indene) tend to be horizontal, pointing to a constant absorption rate.

Hydrogenation of Mixtures of Cyclic Ethylenic Derivatives (Table II).

Mixtures of Compounds of the Same Degree of Substitution.—(*a*) Type II*c* (Fig. 3). We examined two binary mixtures in this category, *viz.*, *cyclo*hexene + 1-methyl-Δ^3-*cyclo*hexene (Curve 3) and *cyclo*hexene + indene (Curve 4). In each case both components were hydrogenated concurrently, the curves showing no breaks. The curve of the first mixture is nearly horizontal, whereas that of the second slopes somewhat as in the case of indene alone. The second mixture is interesting in that it suggests that the effect of platinum-black is similar whether a 5- or a 6-membered ring is involved.

TABLE II.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press. of H_2.	H_2 absorbed, c.c. Calc.	H_2 absorbed, c.c. Found.
*cyclo*Hexene Indene	3; 4	0·8676 0·6085	17°; 762 mm.	223 114 } 337	353
1-Methyl-Δ^3-*cyclo*-hexene *cyclo*Hexene	3; 3	0·5455 1·148	18°; 749	137·5 305† } 442·5	438·5
Carvotanacetone Terpineol	4; 1	0·926 0·526	21°; 764	146 82 } 228	221
Carvone *l*-Limonene	4; 2	1·0000 0·5786	20°; 755	324 206 } 530	525
l-Limonene Terpineol	4; 3	0·8175 0·4585	21°; 752	294 73 } 367	383

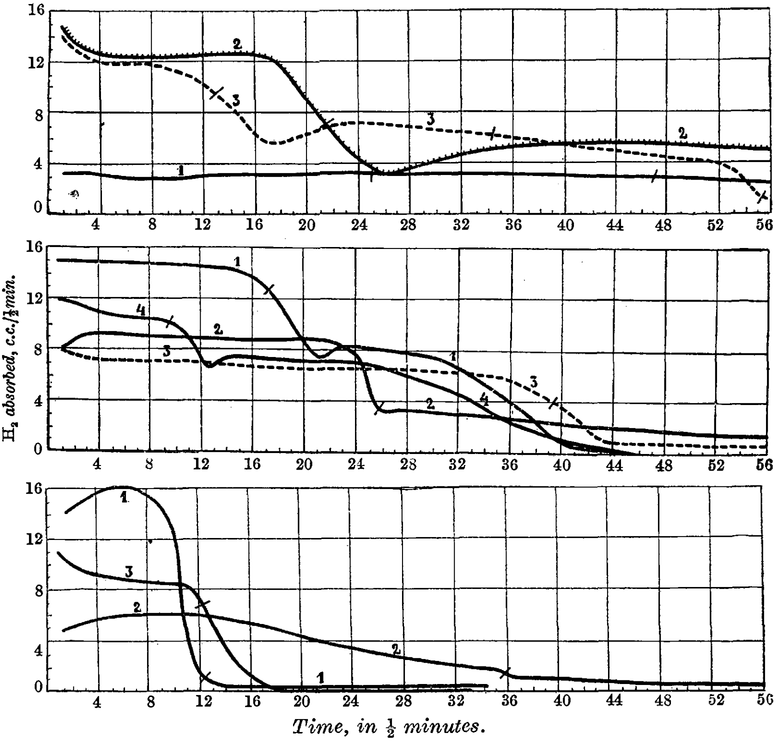
† Based on content of 90% (see p. 323).

(*b*) Type III*c* (Fig. 4). Three such mixtures were examined: carvotanacetone + terpineol (Curve 1), carvone + *l*-limonene (Curve 2), and *l*-limonene + terpineol (Curve 3). The general character of the absorption curve of the first mixture is similar to that of the individual curves of its components; it has no breaks, and apparently both components are hydrogenated concurrently. The mixture of carvone + *l*-limonene corresponds to two binary mixtures, Type II*as* as well as Type III*c* being present in each compound. The curve resembles those of the two components separately, and calculation shows that the only break corresponds with complete hydrogenation of the two Type II bonds, followed by simultaneous reduction of the bonds in the ring of each compound. We have no doubt that reduction occurs in this order, for 50% hydrogenation of carvone and of *l*-limonene produces carvotanacetone and carvomenthene respectively (Vavon; Armstrong; *locc. cit.*).

The curve for *l*-limonene + terpineol is similar to the preceding case, the stages being the hydrogenation of the bond of Type II, the abrupt fall in the rate to the minimum, and hydrogenation of the cyclic bonds simultaneously. The curve shows also the beginning of a third section, corresponding, apparently, to the very slow hydrogenation of the alcoholic group of terpineol.

Hydrogenation of Mixtures of Cyclic Ethylenic Derivatives of Different Degrees of Substitution (Table III).—(*a*) Types II*c* + III*c* (Fig. 5). We examined six binary mixtures of this type, *viz.*, (1) *cyclo*hexene + carvotanacetone (Curve 1); (2) *cyclo*hexene + terpineol (Curve 2); (3) indene + terpineol (Curve 3); (4) 1-methyl-Δ^3-*cyclo*hexene + terpineol (Curve 4); (5) *cyclo*hexene + carvone; and (6) *cyclo*hexene + *l*-limonene. The last two, being combinations of Types II*as* + II*c* + III*c*, are discussed under the head of mixtures of Types II*as* + II*c* (see p. 331). The curves of the other four mixtures are all similar, showing, first, the constant or slightly falling hydrogenation of Type II*c*, then the abrupt fall to the minimum,* and finally the slow fall characteristic of the hydrogenation of the compound of Type III*c*. The different sections of these curves are very similar to the curves for the individual components of the mixtures; moreover, each component retains its own rate of hydrogenation fairly closely, except that in the mixture indene + terpineol, the latter reacts much more slowly than when alone. Further, the breaks on the curves of these mixtures are much more pronounced than in the case of the corresponding open-chain mixtures (compare Part I, *loc. cit.*).

FIGS. 4, 5, 6.



(*b*) Types II*c* + IV*c* (Fig. 6). We examined only one mixture of this type, *viz.*, *cyclo*hexene + 1 : 2-dimethyl-Δ^1-*cyclo*hexene (Curve 1).

* The minimum rate is not noticeable in the mixture indene + terpineol, probably because of the decreased absorption rate of the latter.

As expected, *cyclo*hexene is hydrogenated first, and then the rate falls extremely sharply to a very small fraction ($\frac{1}{60}$—$\frac{1}{90}$) of its value to that characteristic of the reduction of the other compound.

TABLE III.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press. of H_2.	H_2 absorbed, c.c.		
				Calc.		Found.
*cyclo*Hexene Carvotanacetone	5; 1	0·943 0·888	16°; 752 mm.	*248 129	377	390
*cyclo*Hexene Terpineol	5; 2	0·811 0·6955	14°; 762	*209 106	315	304·5
Indene Terpineol	5; 3	1·346 0·646	18°; 760	†258 100	358	359
1-Methyl-Δ^3-*cyclo*-hexene Terpineol	5; 4	0·438 1·052	16°; 765	105 161	266	276
*cyclo*Hexene 1 : 2-Dimethyl-Δ^1-*cyclo*hexene	6; 1	0·6174 0·294	17°; 765	*160 §35	195	173‡
Carvotanacetone 1 : 2-Dimethyl-Δ^1-*cyclo*hexene	6; 3	0·6859 0·2898	18°; 760	108 §34·6	143	128‡
Terpineol 1 : 2-Dimethyl-Δ^1-*cyclo*hexene	6; 2	0·9524 0·3056	17°; 765	146 §36	182	179‡

* Based on a content of 90% (see p. 323). ‡ Process incomplete.
† Based on a content of 93%. § Based on a content of 55% (see p. 326).

(*c*) Types III*c* + IV*c* (Fig. 6). Two of these mixtures were studied : 1 : 2-dimethyl-Δ^1-*cyclo*hexene with terpineol (Curve 2) and with carvotanacetone (Curve 3). The break in the curve for the first mixture was not pronounced, but that for the second was very sharp. The hydrogenation rate of carvotanacetone was nearly double its usual value, and it will be seen later that the reduction of tetramethylethylene is similarly accelerated in the presence of 1 : 2-dimethyl-Δ^1-*cyclo*hexene.

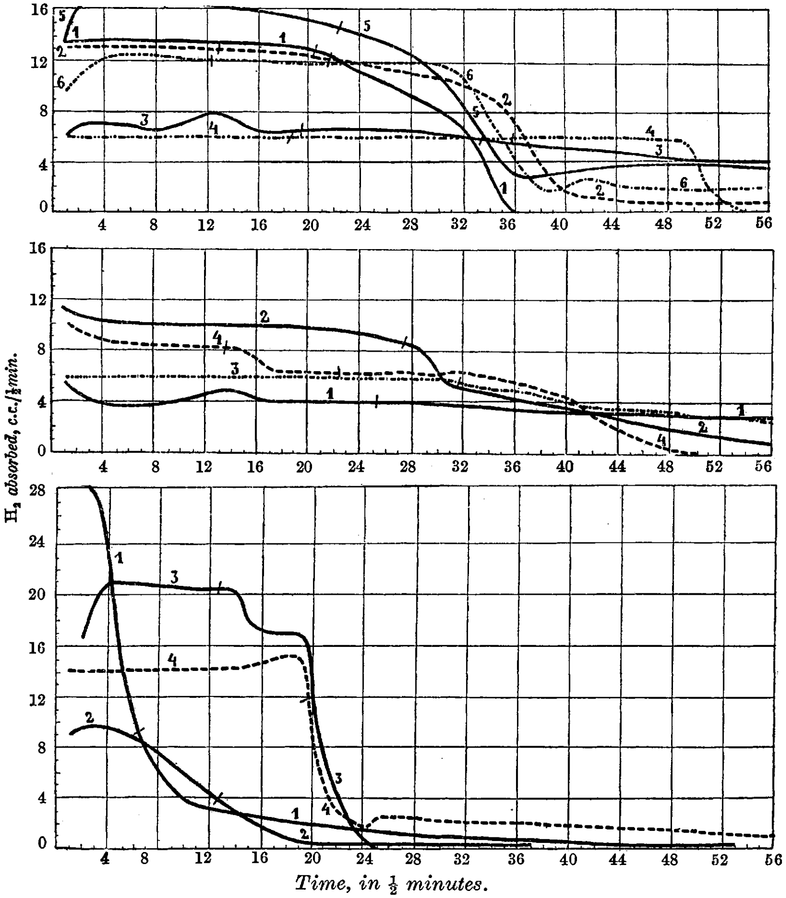
The results obtained with these mixed cyclic ethylenic derivatives show that the two components are hydrogenated concurrently if they are of a similar degree of substitution, or consecutively and at different rates if of different degrees ; the corresponding curves are accordingly continuous or discontinuous, respectively. The ease of hydrogenation decreases according to type in the order II*c*, III*c*, IV*c*, in conformity with the results obtained for open-chain compounds (Part I) and for individual cyclic compounds.

Hydrogenation of Mixtures of Cyclic with Open-chain Ethylenic Derivatives.

The results obtained in this series of experiments show that here again the degree of substitution determines the character of the hydrogenation. They also show that platinum-black acts differently upon similarly substituted derivatives of open-chain and of cyclic structure during the hydrogenation of their mixtures.

(1) *Compounds of the Same Degree of Substitution* (Table IV).—(*a*) Types IIc + II*s* (Fig. 7). In each of the three mixtures, *cyclo*hexene + anethole (Curve 1), 1-methyl-Δ^3-*cyclo*hexene + anethole

FIGS. 7, 8, 9.



(Curve 2), and *cyclo*hexene + cinnamyl alcohol (Curve 3), the components are hydrogenated at the same rate, the curves having no sharp breaks. The curves of the first two mixtures are very much like that of anethole.

(*b*) Types IIc + II*as* (Fig. 7). We examined three mixtures, *viz.*, those of *cyclo*hexene with camphene (Curve 4), with carvone (Curve

TABLE IV.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press of H_2.	H_2 absorbed, c.c. Calc.		Found.
*cyclo*Hexene	7; 1	1·0194	19°; 764 mm.	*267	386	385·5
Anethole		0·7400		119		
1-Methyl-Δ^3-*cyclo*-hexene	7; 2	0·6458	16°; 750	162	435·5	439
Anethole		1·685		273·5		
*cyclo*Hexene	7; 3	0·5673	19°; 768	*147	365	395
Cinnamyl alcohol		1·236		218		
† *cyclo*Hexene	7; 5	1·317	19°; 764	*345	611	595
Carvone		0·836		266		
*cyclo*Hexene	7; 4	0·7779	20°; 762	*204	308	297
Camphene		0·5909		104		
*cyclo*Hexene	7; 6	1·075	18°; 765	*280	543·5	528
l-Limonene		0·7556		263·5		
Carvotanacetone	8; 1	1·3953	21°; 765	220	325	329
Methylheptenone		0·5533		105		
Terpineol	8; 2	0·6324	19°; 765	98	365	373
Mesityl oxide		1·0993		267		
Terpineol	8; 4	1·132	18°; 745	179	301	300
Methylheptenone		0·6334		122		
† Carvotanacetone	8; 3	0·6883	18°; 764	107	318	305
Mesityl oxide		0·8714		211		
§ 1 : 2-Dimethyl-Δ^1-*cyclo*hexene	9; 1	0·6092	17°; 778	‡70·5	205	200
Tetramethylethylene		0·4871		134·5		
Same mixture	9; 2	0·1401	17°; 778	‡16·5	115·5	121
		0·3500		99		

* Based on a content of 90% (see p. 323). † Bath temperature, 17°.

‡ Based on a content of 55% (see p. 326).

§ For this expt. 1 g. of platinum-black was used.

5), and with *l*-limonene (Curve 6). The hydrogenation rate of the first mixture is constant throughout the whole reaction. The other two mixtures are each a combination of the types II*c* + II*as* +III*c*; the disubstituted compounds are hydrogenated together, the absorption rate being nearly constant. The end of the hydrogenation of the system II*c* + II*as* coincides with a sharp fall in the absorption rate, which reaches a minimum and then increases a little.

(*c*) Types III*c* + III (Fig. 8). Four mixtures were examined: carvotanacetone + methylheptenone (Curve 1), mesityl oxide + terpineol (Curve 2), mesityl oxide + carvotanacetone (Curve 3), and terpineol + methylheptenone (Curve 4). The curves of the two mixtures containing mesityl oxide have prominent breaks, for this compound is hydrogenated first and at an almost constant rate. The mixture of terpineol + methylheptenone is of interest because the break in the curve does not coincide exactly with the end of the hydrogenation of either of the components. Each section seems to correspond with the hydrogenation of a mixture of the two components in different proportions, and the size of the sections suggests that methylheptenone probably predominates in the first portion. This anomaly is still more prominent in the pair methylheptenone + carvotanacetone : the break is not sharp and is strikingly displaced to the left. The resemblance between curves 1 and 4, on the one hand, and between curves 2 and 3, on the other, is noteworthy. It is clear that sometimes the shape of the curves depends, not only upon the characteristics of the type, but also on those of the individual.

These examples show that in the hydrogenation of their mixtures, compounds of the types III and III*c* are not equivalent. Apparently platinum-black absorbs the open-chain type preferentially and consequently compounds of this type are usually hydrogenated first.

(*d*) Types IV*c* + IV (Fig. 9). The mixture, 1 : 2-dimethyl-Δ^1-*cyclo*hexene + tetramethylethylene (Curves 1 and 2) was studied, 1 g. of platinum-black (instead of the usual 0·2 g.) being used at first because both these hydrocarbons are hydrogenated very slowly. Two experiments showed abnormal reactivity on the part of the tetramethylethylene (Curve 1). Using only 0·2 g. of platinum-black, we obtained Curve 2, where again the end of the hydrogenation of tetramethylethylene is sharply defined and the reaction rate is abnormal, being 9·5 c.c./$\frac{1}{2}$ min.

(2) *Compounds of Different Degrees of Substitution* (Table V).—(*a*) Types II*c* + I (Fig. 9). In the binary mixture, safrole + *cyclo*hexene (Curve 3), the former was hydrogenated first, at an almost constant rate, and the sharp break on the curve coincides closely with the end of this process.

(*b*) Types II*c* + III (Fig. 10). We examined four mixtures : *cyclo*hexene + mesityl oxide, *cyclo*hexene + methylheptenone (Curve 1), *cyclo*hexene + trimethylethylene (Curve 2), and indene + methylheptenone. In all four, the cyclic compound was hydrogenated first; the breaks were somewhat like those in the mixtures of Types II*s* + III and II*as* + III (Part I, *loc. cit.*), and much less well-defined than those in the curves of mixtures of Types II*c* + III*c* and II*as* + III*c*. This difference can be explained by the fact (see above) that Type III is much more readily adsorbed by platinum-black, and therefore more readily hydrogenated, than III*c*; hence Type III is more nearly allied to Type II*c* than to Type III*c*.

In the mixture, *cyclo*hexene + mesityl oxide, we have a very complicated case, owing to the presence of the conjugated system in the latter; it seems that *cyclo*hexene is hydrogenated first. This curve, as well as that of the mixture indene + methylheptenone, is not given here.

(*c*) Types II*c* + IV (Fig. 10). We examined the binary mixture *cyclo*hexene + tetramethylethylene (Curve 3); the former is hydrogenated first at a constant rate, and a sharp break divides this process from the reduction of the other component, which, however, is markedly higher than normally.

FIGS. 10, 11.

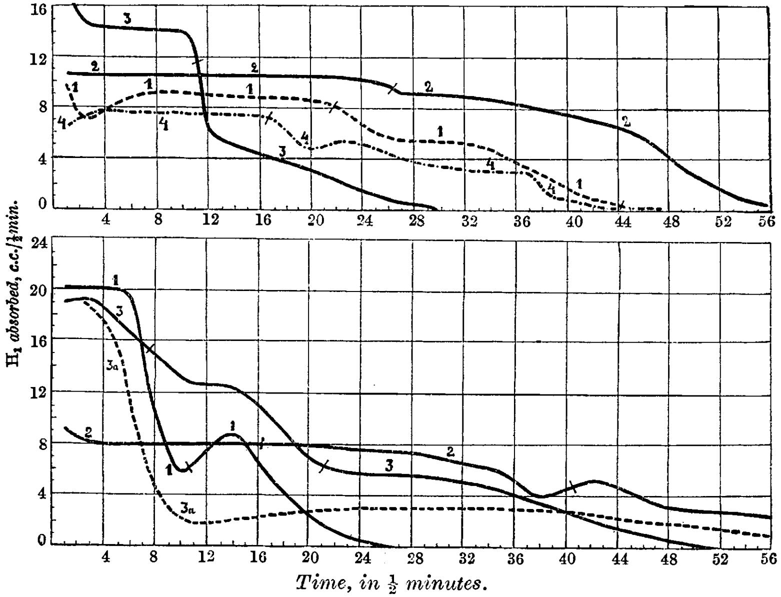


TABLE V.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press. of H_2.	H_2 absorbed, c.c. Calc.		H_2 absorbed, c.c. Found.
Safrole *cyclo*Hexene	9; 3	1·517 0·501	18°; 758 mm.	224 *131	355	367
Safrole Terpineol	9; 4	1·844 0·5875	18°; 750	275·5 92	367·5	365
*cyclo*Hexene Methylheptenone	10; 1	0·6836 0·4538	21°; 760	*181 87	268	280
*cyclo*Hexene Trimethylethylene	10; 2	1·019 0·459	19°; 757	*268 158	426	434
*cyclo*Hexene Tetramethylethylene	10; 3	0·5848 0·2036	19°; 765	*153 *58	211	206·5
Terpineol Tetramethylethylene	10; 4	0·7468 0·2796	19°; 762	116 79·5	195·5	206
Camphene Terpineol	11; 1	0·9309 0·4426	19°; 758	164 69	233	225
Camphene *l*-Limonene	11; 2	0·9200 0·6973	18°; 742	165 250	415	371
Carvone Camphene	11; 3	0·8232 0·8859	17°; 753	264 157	421	386

* Based on a content of 90% (see p. 323).

(*d*) Types IIIc + I (Fig. 9). In the mixture safrole + terpineol (Curve 4), the former is hydrogenated first and at a constant rate, slightly increasing towards the end. The curve then falls sharply to a minimum, and the reduction of terpineol sets in with a slight rise followed by a gradual fall.

(*e*) Types III*c* + II*as* (Fig. 11). This category is illustrated by 7 curves: (1) carvone, (2) *l*-limonene, (3) carvone + *l*-limonene, (4) terpineol + *l*-limonene, (5) camphene + terpineol (Curve 1), (6) camphene + *l*-limonene (Curve 2), and (7) camphene + carvone (Curves 3 and 3*a*). The curves for the first four reductions have already been given (Fig. 2, Curves 1 and 2; Fig. 4, Curves 2 and 3), since the simpler systems also contained those of the type now concerned. The mixtures of camphene with *l*-limonene and with terpineol gave curves of the same type: the minimum is very pronounced, particularly in the second case.

The mixture carvone + camphene is noteworthy. Its curve has three sharply separated sections corresponding with the hydrogenation (i) of the side chain of carvone, (ii) of camphene, and (iii) of the double bond in the ring of carvone (Curve 3). This is the first case in which a break has been found in the hydrogenation of a mixture of two bonds both of the type II*as*; and it is quite unexpected, for carvone behaved like camphene in all the hydrogenations of mixtures, and it would be anticipated that the bonds in the side chains of carvone and camphene would be equivalent in respect to platinum-black when hydrogenated in presence of one another. In this case, evidently, the course of hydrogenation is chiefly determined, not by the degree of substitution at the double bond in the compounds, but by their individual qualities and their mutual influence on adsorption at the surface of the catalyst. We therefore made the following experiment. Immediately after the mixture of carvone + camphene had been reduced, a certain amount of carvone was introduced into the hydrogenation vessel, and the course of its reduction followed (Curve 3*a*). Comparison of Curves 3 and 3*a* shows that the rate of reduction of the nuclear bond (Type III*c*) of carvone is decreased in the second case: the reduction of its side chain is abnormally rapid in both cases.

(*f*) Types III*c* + IV (Fig. 10). In the mixture terpineol + tetramethylethylene (Curve 4), the latter is attacked first; the break is clearly visible, and the curve has a minimum. The third section of the curve corresponds with the hydrogenation of the alcoholic group of terpineol.

A general survey of our experiments establishes that the degree of substitution at a double bond is the chief factor determining the order and character of the hydrogenation of mixtures of ethylenic derivatives (either cyclic or open-chain). Other factors, as, for instance, the individual characteristics of the molecules or the mutual influence of molecules of two different species on their adsorption (and hydrogenation) at the surface of platinum-black, predominate only in exceptional cases. Such phenomena occur only when one of the components of a mixture contains conjugated double bonds, as in mesityl oxide or carvotanacetone. The hydrogenation of individual compounds containing this system is anomalous, and the presence of such a component in a mixture changes the whole character of the hydrogenation.

Conclusions.

(1) Cyclic disubstituted ethylenic derivatives are hydrogenated more readily than trisubstituted ones, and these, in turn, more readily than tetrasubstituted.

(2) Mixtures of cyclic ethylenic derivatives of a similar degree of substitution are hydrogenated at a common rate, the curves showing the absorption of hydrogen being continuous.

(3) In mixtures of cyclic ethylenic derivatives of different degrees of substitution, the components are hydrogenated consecutively in the order given in (1). The curves for such mixtures always have breaks, corresponding closely to the end of the hydrogenation of the first component, and in many cases being associated with a minimum in the rate of reaction.

(4) In a mixture, the section of the curve corresponding to the hydrogenation of any one component bears a strong resemblance to the curve obtained when this component is hydrogenated alone.

(5) The individual hydrogenation rates of the compounds may be considerably modified in mixtures.

(6) The hydrogenation of mixtures of cyclic with open-chain ethylenic derivatives of the same degree of substitution proceeds on the following lines. (*a*) In mixtures of cyclic with open-chain (*s.*- or *as.*-) disubstituted compounds, the components are hydrogenated concurrently, the curves for such mixtures being continuous. (*b*) In mixtures of cyclic with open-chain trisubstituted compounds, the components are hydrogenated consecutively, the latter reacting preferentially in virtue of a somewhat greater capacity for adsorption by platinum-black; the hydrogenation curves of such mixtures show rather considerable breaks. (*c*) In mixtures of a cyclic and an open-chain tetra-substituted compound, the latter is hydrogenated considerably more rapidly than the former.

(7) Mixtures of cyclic or open-chain (*s.*- or *as.*-) disubstituted compounds with cyclic tri- or tetra-substituted compounds show much sharper breaks in their hydrogenation curves than when the more heavily substituted compounds are open-chain.

(8) Mixtures of cyclic with open-chain ethylenic derivatives of

different degrees of substitution are usually hydrogenated consecutively, the component with the lower degree of substitution at the double bond being hydrogenated first.

(9) In mixtures containing a component with a conjugated system, deviations from the above generalisations are observed.

(10) Anhydrides of maleic and citraconic acids, unlike the acids themselves, are toxic towards platinum-black.

(11) Examination of the hydrogenation curves of mixtures of cyclic ethylenic derivatives of known constitution (standard derivatives) with those of unknown constitution enables us to determine the type of substitution at the double linking in the latter, but it is essential that the standards be cyclic.

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