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SELECTIVE HYDROGENATION BY MEANS OF CATALYSTS I:
THE HYDROGENATION OF CIS-TRANS ISOMERS WITH VARY-
ING QUANTITIES OF CATALYST (COLLOIDAL PALLADIUM)
AND SELECTIVE HYDROGENATION OF UNSATURATED
CARBONYL COMPOUNDS WITH THE AID OF PROMOTERS

BY ZOLTÁN CSÜRÖS, MEMBER OF THE ACADEMY,
THE LATE KONSTANTIN ZECH AND ISTVÁN GÉCZY

(READ BEFORE A MEETING OF THE DEPARTMENT FOR CHEMISTRY OF THE HUNGARIAN
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Different spatial arrangements render a certain control or selectivity in catalytic hydrogenation possible. This selectivity may relate to some group of atoms within a molecule, to some component in a mixture, or to geometrical isomers. In connection with selective hydrogenations of such purpose we have investigated the following points:

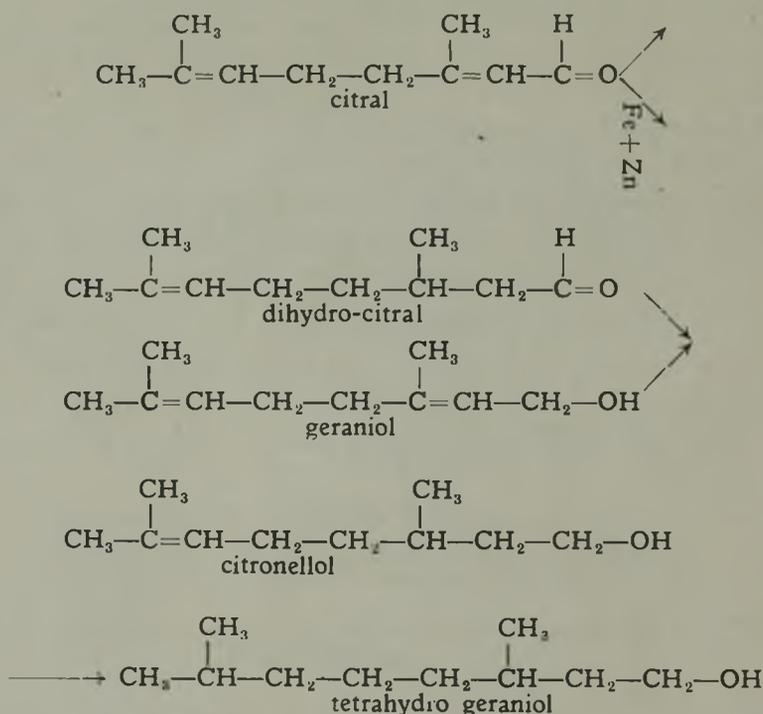
1. The controlled hydrogenation of α , β -unsaturated ketones,
2. The difference presenting itself in the hydrogenation of cis- and trans-isomers, and in connection herewith,
3. The functional relation as between quantity of catalyst and time of hydrogenation.

The substance of previous researches in connection with these researches may be summed up as follows:

1. SELECTIVE HYDROGENATION OF α , β -UNSATURATED CARBONYL
GROUPS

In order to obtain selective hydrogenation, use may be made in general of the variation of the time of reaction. In addition, selectivity may be achieved by the addition of suitable supplemental substances. Thus Faillebin (1), when reducing aldehydes and ketones by means of a Pt catalyst was able to influence the conversion by the addition of ferrous chloride, in such a manner as to ensure that the aldehydes and ketones became completely converted into the corresponding alcohols, whereas, without such addition, reaction took place in a complicated manner.

This observation was successfully employed by American investigators for the selective hydrogenation of unsaturated aldehydes and acid esters, producing from the aldehydes for instance, the corresponding unsaturated alcohols, at a pressure of 2 to 3 atmospheres, in the presence of activators. Ferrous sulphate, ferrous chloride etc. may be employed by way of such activator. Adams and Carvey (2) effected the hydrogenation of citral by means of a PtO—Pt black catalyst, with the addition of small quantities of ferro sulphate and of zinc acetate. Without the addition of promoters, the conversion takes place in such a manner that it is first the double bond adjacent to the aldehyde, next the aldehyde group and finally, the other double bond that become reduced. Under the effect of promoters it was the carbonyl group that became reduced first, and it was only following this that the two double bonds were reduced:

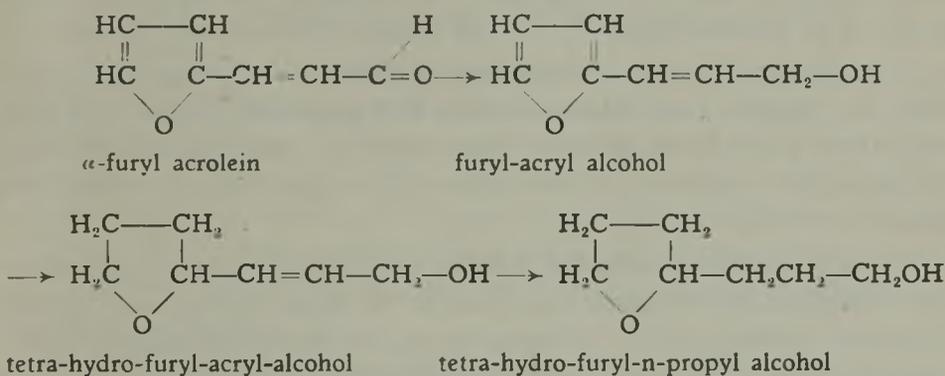


The promoters will selectively accelerate the first phase of the reaction (the formation of geraniol is more rapid, than that of dihydro citral), whilst the formation of citronellol and of tetra-hydro-geraniol taking place in the subsequent phases is slowed down.

Similarly hereto, Tuley and Adams (3) found that cinnamic aldehyde — which is capable of being slowly hydrogenated by means of Pt

black, a complicated mixture forming during the process — will with the addition of 0,01 to 0,02 millimole of ferrous chloride become smoothly converted into cinnamic alcohol. The effect is particularly striking if ferrous chloride and zinc acetate are employed jointly. The absorption of one mole of hydrogen takes place smoothly, whilst that of further quantities of hydrogen takes place very slowly only, or not at all. The cinnamic alcohol obtained was practically devoid of aldehyde. With the addition of ferrous chloride only, the absorption of hydrogen continued smoothly up to the formation of phenyl-propyl alcohol. The hydrogenations were effected at a pressure of 2 to 3 atmospheres.

Adams and his collaborators (4) obtained similar results with α -furyl-acrolein also. With the addition of ferrous sulphate and of zinc acetate, the double bond remained intact and furyl-acryl alcohol was formed, which in the presence of zinc acetate cannot be reduced any further. With the addition of ferrous sulphate only, the furyl-acryl alcohol can be hydrogenated further in the furane ring also, tetra-hydro-furyl-acryl alcohol being formed first, and tetra-hydro-furyl-n-propyl alcohol next:



As a by-product, there is also formed — with splitting of the ring — a small quantity of a kind of heptene-diol. The total quantity of hydrogen absorbed — in the presence of ferrous sulphate — amounts (instead of the 4 moles calculated) to 4,4 moles.

Sauer and Adkins (5) successfully achieved the reduction of the carbonyl group of organic acids in the case of a double bond. They have been successful in reducing unsaturated aliphatic carbonic acid esters with the aid of ZnO-CrO , or CuO-CrO catalysts, respectively, at temperatures in the vicinity of 200 to 300 $^{\circ}\text{C}$ with a yield of over 60% of unsaturated alcohols. A drawback of their method is that it requires an excessive quantity of catalyst, at least 1 part of catalyst being required for each 2 parts of ester.

The above examples established the fact that an addition of a ferrous salt will substantially accelerate the hydrogenation of the carbonyl groups, without, at the same time, accelerating the saturation of the double bonds (6) also and on the other hand the fact that the hydrogen absorption controlled by the metal oxides does not attack the double bonds but only the ester groups (5, 7).

Weidlich and Meyer—Delius (8), hydrogenating α , β -unsaturated carbonyl compounds in alcoholic solution by means of a palladium oxide catalyst observed that the hydrogen gets into an 1,2 position on the CO or C = C group under the influence of an acid supplemental substance. As against this, the addition is of the 1,4 type in the conjugated system in the case of an alkaline supplemental substance. This rule was proved by them in a number of examples.

It was possible to obtain selective hydrogenation by varying the catalyst. Thus Natta, Rigamonti and Beati (9) hydrogenated furfural and its derivatives by means of various catalysts, thus with nickel and copper, whereby, one or the other hydrogen absorption became predominant of the various possibilities. They were able to increase this effect still further by means of various promoters, as for instance, by means of Fe and Co.

Fe, frequently employed by way of promoter, is of highly selective effect as a catalyst also. Paul and Hilly (10) produced an iron catalyst of such a kind as enabled acetylene to be converted, with the absorption of hydrogen, into ethylene; the absorption of hydrogen does not proceed any further than this.

The difference presenting itself in the structure of the hydrogenatable fundamental compounds may also be the cause of a certain degree of selectivity. Golendejeff (11), hydrogenating the allyl esters of unsaturated acids by means of platinum and palladium blacks, respectively, confirmed the Lebedeff—Vavon rule, according to which it is the allyl group that becomes saturated first, and it is only following this, at a slower speed, that the unsaturated acid (crotonic, fumaric and oleic acid) becomes hydrogenated.

2. DIFFERENCE IN THE HYDROGENATION OF CIS-TRANS ISOMERES

The difference between the speed of hydrogenation of the cis- and trans-forms was observed by Paal and Schiedewitz (12) showing that in general the cis-form will become saturated more easily and more rapidly than the trans-form with a Pd catalyst, under identical conditions (aqueous or alcoholic solution, room temperature). Accordingly, as to the speed of absorption of hydrogen: maleic acid > fumaric acid, citraconic acid >

mesaconic acid, oleic acid > elaidic acid, allo-cinnamic acid > cinnamic acid, ethyl-cumarinic acid > ethyl- α -cumaric acid, iso-stilbene > stilbene; and finally β -chloro-iso-crotonic acid > β -chloro-crotonic acid. Similarly — under identical conditions — cis-phenyl butadien can be hydrogenated more rapidly, than the trans-form (13).

On the basis of the phenomenon observed, Paal and his collaborators conclude from the speed of the absorption of hydrogen on which of the two isomers they are dealing with.

Formerly (14), the explanation given for the difference in the speed of hydrogenation was that the stereo-chemical configuration of the cis-form is of such a kind, to which there corresponds a greater reaction speed, than to the trans-form. However — on the examples of di-methyl fumaric acid, di-methyl maleic acid, cis-di-methyl stilbene and trans-di-methyl stilbene — Ott and Schröter (15) established the fact that it is not to stereo-chemical, but to energetical causes that the difference as between the hydrogenation of cis- and trans-forms must be attributed.

3. THE FUNCTIONAL RELATION BETWEEN QUANTITY OF CATALYST AND TIME OF REACTION IN HETEROGENEOUS CATALYSIS

In the case of homogeneous catalysis the reaction speed is, on the whole, directly proportionate to the concentration of the catalyst. In the case of heterogeneous catalysis conditions are much more complicated. Few data can be found in this respect in the literature dealing with the subject and some of these are mutually contradictory, as for instance, that the speed of the catalyzed reaction is independent of the quantity of catalyst employed, or that the speed is directly proportionate to the quantity of catalyst.

This latter supposition seems to be natural. Heterogeneous catalytic processes are taking place on boundary surfaces and the speed of reaction is proportionate to the magnitude of the surface, that is to say, also to the quantity of catalyst employed. Accordingly, the greater the quantity of catalyst employed, the greater will be the speed of conversion, i. e. $M \cdot t = \text{const.}$ (M = quantity of catalyst, t = time required for the reaction.) It has been possible to prove the correctness of this supposition for heterogeneous gas reactions also.

According to suppositions, the surface of the catalyst does not vary in proportion with the quantity of catalyst, there existing probably a certain — as yet unknown — relation as between the quantity and the surface of the catalyst.

In the case of heterogeneous reactions of such including a liquid phase also (the majority of catalytic hydrogenations in which H_2 is present

in gaseous, the catalyst in solid, and the substance to be hydrogenated in dissolved form, is of this kind) conditions are much more intricate. Regarding such cases as definite data are available as to in what manner the quantity of catalyst will, under otherwise identical conditions, influence the time and quality of hydrogenation.

Kailan and Hartel (16) hydrogenated oleic acid by means of colloidal Ni catalyst in such a manner, that they altered the quantity of catalyst. According to their report, the speed of the absorption of hydrogen varies with the quantity of catalyst employed, and passes through a maximum. A further increase of the quantity of catalyst will already reduce the speed of absorption.

OUR OWN INVESTIGATIONS

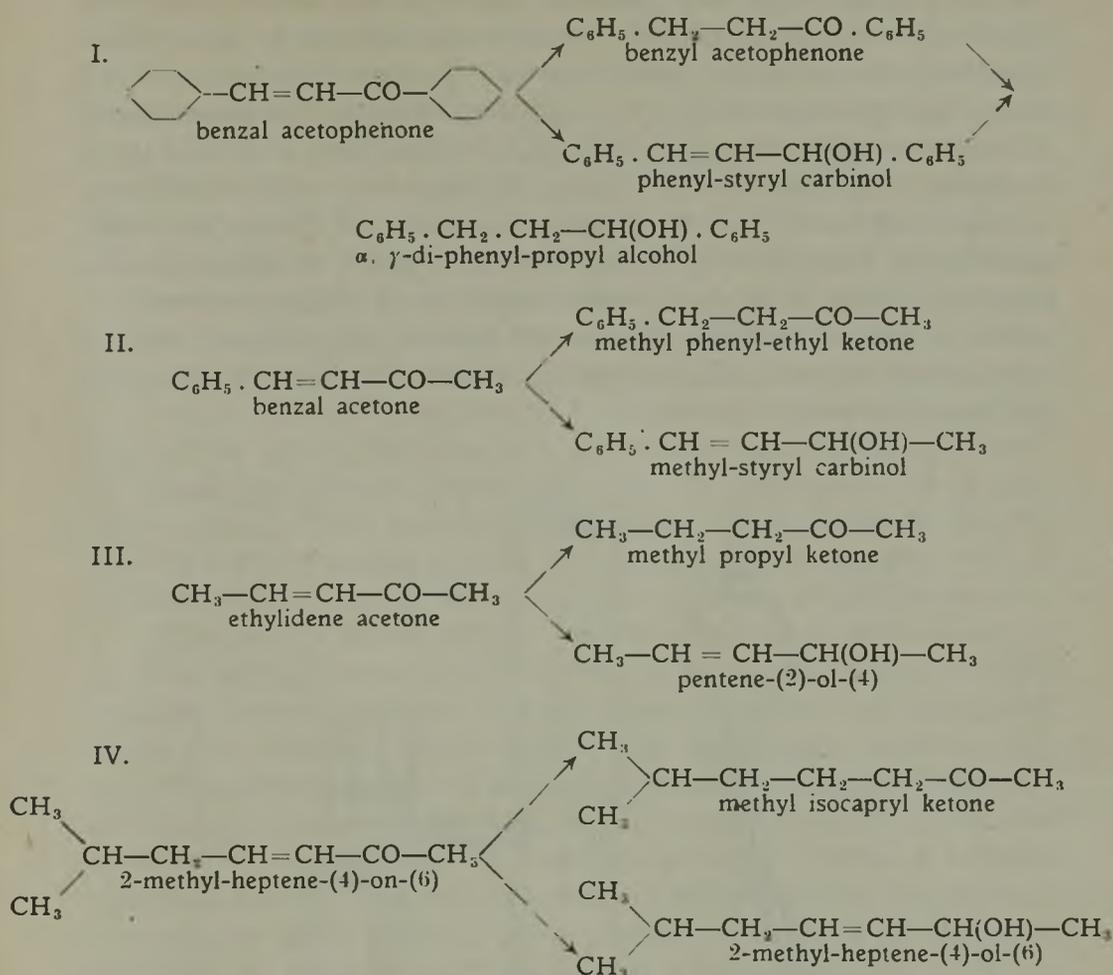
1. THE SELECTIVE HYDROGENATION OF α , β -UNSATURATED KETONES

We employed, in general, a colloidal palladium catalyst prepared according to Skita's description (17) for the experiments. The substances investigated were benzal acetone, benzal acetophenone, ethylidene acetone and 2-methyl heptene-(4)-on-(6), in alcoholic solution. Colloidal palladium, activated by means of 0,01 to 0,02 millimole of ferrous sulphate, proved a highly effective selective catalyst.

Hydrogenating benzal acetophenone (chalkon) by means of a Pd catalyst becomes converted first into saturated ketone, and following this, α , γ -diphenyl-propyl alcohol; with an addition of Fe^{++} there will first be formed phenyl-styryl-carbinol, and subsequently α , γ -di-phenyl-propyl alcohol likewise. We checked the conversion in such a manner, that we made a preparation of the compound obtained after the absorption of one mole of hydrogen, determined the unchanged double bond contained in it, and showed the sec. alcohol group by heating it with a few drops of decaline and with a small quantity of zinc chloride (18). Besides, its meltingpoint also agreed with that of phenyl-styryl carbinol.

Benzal acetone, hydrogenated by means of Pd, becomes converted into saturated ketone. With an addition of Fe^{++} and of zinc acetate it will become methyl styryl carbinol. After the absorption of the first mole of H_2 the conversion becomes slowed down in such an extent, that it can be considered as practically terminated. Under similar conditions, ethylidene acetone became converted into pentene-(2)-ol-(4), whilst 2-methyl-heptene-(4)-on-(6) became converted into 2-methyl-heptene-(4)-ol-(6). To the best of our knowledge, this last-named compound, has not been prepared previously.

The reduction of unsaturated ketones in this manner takes place smoothly at ordinary pressure and at room temperature; therefore the process can be employed with very great advantage for the preparation of unsaturated sec. alcohols. The structures shown below represent the conversions:



II. THE DIFFERENCE PRESENTING ITSELF IN THE HYDROGENATION OF CIS-TRANS ISOMERS

Paal and his collaborators investigated the difference presenting itself between cis-trans isomers with the employment of the almost same quantities of catalysts. As against this we endeavoured to find out whether their statement, according to which it is the cis-form that can be hydrogenated more rapidly, is true also in the case of varying quantities of catalyst?

From experiments carried out with solutions of fumaric acid and of maleic acid it appeared, under otherwise identical conditions, that if only the quantity of catalyst is varied, the observation of Paal and his collaborators is true for a certain interval of the catalyst quantity only. The situation is completely reversed when the quantity of catalyst is smaller or greater than this „medium“ quantity, and in such cases it is exactly the hydrogenation of the trans-compounds that is more rapid. According to experiments carried out on $\frac{1}{2}$ mole of fumaric acid and maleic acid solutions, 2,2 to 6,5 cc. of Skita's colloidal palladium catalyst solution represent the quantity for which the Paal rule is valid. Taking a quantity of catalyst less than 2,2 cc., hydrogenation will be much slower, and it will be the trans-form (fumaric acid) that will become saturated more rapidly. This will be the case also when the quantity of catalyst is greater than 6,5 cc. Thus for instance, when using 10 cc. of catalyst, the hydrogenation of fumaric acid took place in 25 minutes, that of maleic acid in 105 minutes. In the course of the experiments the quantity of catalyst was varied between 1 and 11.5 cc.

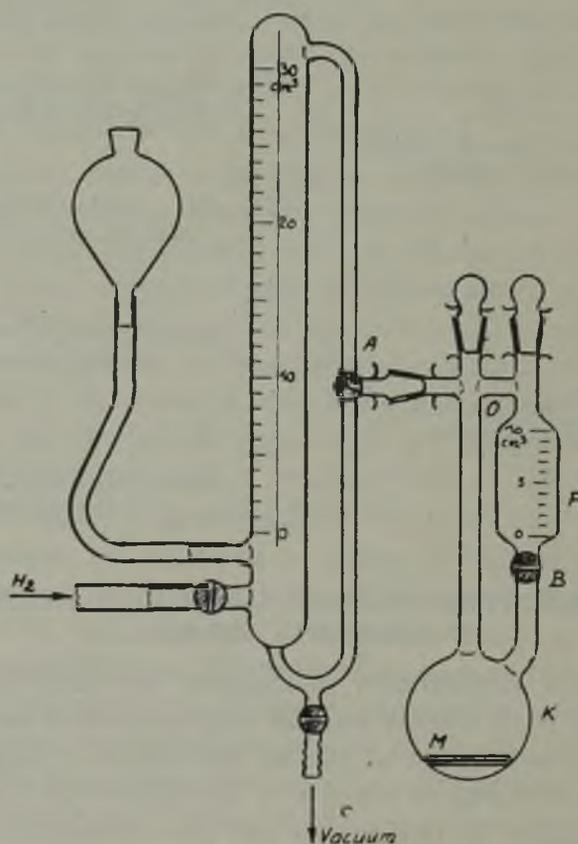


Fig. 1.

Next, we wished to extend the investigations to a number of other pairs of cis-trans compounds. To avoid unnecessary waste of catalyst, we worked in a semi-micro apparatus. The drawing of the apparatus (Fig. 1.) and the method of handling the latter are described below:

The catalyst is filled into the vessel *K*, the substance to be hydrogenated, into the part *P*. Following this the two parts are joined together at *A*, and the glass stop-cock turned into the position \curvearrowright , then the apparatus is evacuated by means of a water-jet pump. After this has been done, the apparatus is filled with hydrogen by carefully turning back the stop-cock. Setting the small iron bar (*M*) fixed into a glass tube in motion by means of a rotating magnet, the catalyst is saturated with hydrogen. When this step has been taken, the solution of the substance to be investigated is admitted through the stop-cock *B*. The quantity of hydrogen consumed is read on the milk-glass burette *L*. A partly similar apparatus has been employed by Zechmeister and his collaborators (19) to determine the content of double bonds of carotinoids. The improvement introduced by us is the milk-glass burette *L*, in order to obtain more accurate readings, the fact of dispensing with a rubber tube connection and shaking for eliminating hydrogen losses and finally, the employment of the connecting tube *O*, which facilitates the admission of the liquid and does not interfere with the hydrogen level. In employing electro-magnetic stirring instead of shaking, we followed the example of Weygand and Werner (20).

It is possible to hydrogenate 1 to 10 centigrams of substance in 5 to 10 cc. of solution in the apparatus. We carried out the saturation of the following cis-trans isomers: cumarinic acid-o-cumaric acid, oleic acid-elaidic acid, citraconic acid-mesaconic acid, allo-cinnamic acid-cinnamic acid. When hydrogenating the alcoholic solution of 0,2 mole of cumarinic and of o-cumaric acid, respectively, it was found that the catalyst interval in which the cis-form can be hydrogenated more rapidly, is between about 2.25 and 4 cc. The relation is reversed below and above this interval. Similarly, we obtained also a certain interval of this kind for the other substances for which the Paal rule is valid, whereas below and above this interval the truth is exactly the reverse of the rule.

At the same time our observations also confirmed the view of Ott and Schröter, according to which the different speed of hydrogenation of geometrical isomers is not due to stereo-chemical, but to energetical causes. Notably, it may be supposed that it is not possible for the quantity of catalyst to influence the spatial structure of the cis- and trans-forms, whereas it can easily be imagined that it will be the cis-form in one case and in another case the trans-form that will be activated in a greater extent by different quantities of catalyst.

On the basis of our experiments, the statement of Paal and his collaborators can be considered refuted, namely that it is the cis-form that can be hydrogenated more rapidly and therefore that it is possible on the basis of a single hydrogenation to decide whether the substance dealt with represents the cis or the trans-form. Both compounds must be hydrogenated several times with varying quantities of catalyst. In case of small and large quantities it is the trans-form, in that of medium quantities the cis-form that can be hydrogenated more rapidly. In our experiments we also measured the half saturation time during which one-half of the necessary quantity of hydrogen was consumed. For this time there resulted same relations, as for the time of the full absorption of hydrogen.

III. FUNCTIONAL RELATION AS BETWEEN THE QUANTITY OF CATALYST AND THE TIME OF HYDROGENATION

Investigating the speed of hydrogenation of cis-trans compounds it appeared, that the quantity of catalyst and the time of reaction do not stand in inverse proportion to each other. Plotting the data graphically (Fig. 2.), the curve obtained first decreases to a local minimum; then it rises to a local maximum and then decreases again. The product $M \cdot t$, wherein M is the quantity of catalyst, and t the time for the absorption of the calculated quantity of hydrogen, will first be smaller, when the

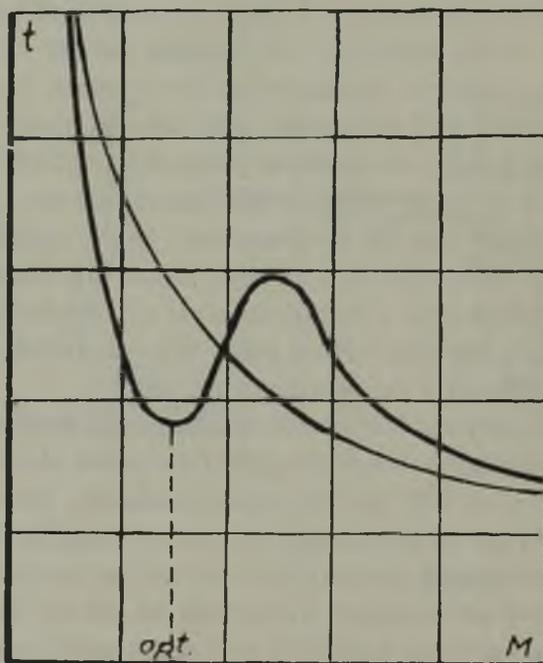


Fig. 2.

quantity of catalyst is being varied, and later on greater than the calculated figure.

The phenomenon was verified by us on the following compounds: maleic acid, fumaric acid, oleic acid, elaidic acid, cumaric acid, cumarinic acid, allo-cinnamic acid, cinnamic acid, citraconic acid, mesaconic acid, crotonic acid. We were able to find, that there always exists such a given quantity of catalyst, with which the reaction takes place relatively most rapidly.

SUMMARY

I. We have been successful in carrying out the reduction of α, β -unsaturated ketones by means of colloidal palladium with ferrous sulphate and zinc acetate promoters at ordinary pressure and at room temperature, to unsaturated sec. alcohols.

II. We established the fact that the observation of Paal and his collaborators, according to which cis-compounds can be hydrogenated more rapidly than trans-compounds, working with coll. palladium, is not quite correct, for it is true only as long as the quantity of catalyst employed remains between certain narrow limits. Where quantities different to the above are employed, it is exactly the reverse that is true. Therefore a single hydrogenation is not sufficient to determine which of two forms is the cis and which the trans-form, because the difference of the times of hydrogenation does not vary in the same sense with varying quantities of catalyst.

III. We found that the product of the quantity of catalyst and the time of hydrogenation is not constant but that this product first decreases, and subsequently increases with increasing quantities of catalyst. It follows that there exists a quantity of catalyst in each case with which the reaction takes place with the maximum of rapidity.

The experiments were carried out with the financial assistance of the Goldberger Foundation.

EXPERIMENTAL PART

Palladium catalyst (according to Skita (17)): 0,5 g of palladium chloride is dissolved during boiling in 50 cc of distilled water, following which 0,5 g of gum arabic is added to the solution. After solution has taken place, the solution is inoculated with 1 cc. of completed colloidal palladium solution, the hot solution is poured into a hydrogenating retort, the latter is filled with hydrogen and shaken during half an hour, following which it is filled up with distilled water to 100 cc.

Promoters :

a) *FeSO₄ solution* : 0,06 g of FeSO₄, dissolved in 7 cc. of H₂O of distilled water and filled up to 100 cc.

b) *Zinc acetate solution* : 0,8 g of ZnO and 1,2 g of glacial acetic acid dissolved in distilled water (shaken cold) and filled up to 50 cc.

Hydrogenation of benzal acetophenone :

1. *Production of phenyl styryl carbinol* : 4 g of benzal acetophenon, 20 cc. of alcohol, 6 cc. of catalyst, 4 cc. of FeSO₄ solution. The calculated quantity of 1 mole of H₂ (490 cc.) is consumed in 4³/₄ hours.

In order to separate the product formed, the catalyst is first of all removed. The alcoholic solution is heated in a water bath during about half an hour. A part of the alcohol evaporates and the colloidal catalyst coagulates in the mean time. The alcoholic solution decanted, or filtered off from it is diluted with water, the product separated taken up in ether and the aqueous part ethered out a few times. The united etheric solutions are dried by means of anhydric sodium sulphate, filtered and then evaporated and the rest crystallized, or distilled. The yield amounted in each case to over 90%. The product shrinks at 54 C° and melts at 57 C°. Melting-point as stated in literature: 56—57 C° (21).

2. *Production of di-phenyl propanol through phenyl styryl carbinol*. 1 g of benzal acetophenone, 10 cc. of alcohol, 2 cc. of FeSO₄ solution, 10 cc. of catalyst. The calculated quantity of 2 moles (= 250 cc.) of hydrogen was absorbed in 4¹/₂ hours. After removing the catalyst (water bath, filtering, shaking with ether, drying with sodium sulphate), the product is distilled in vacuo; boiling-point 191—193 C°/13 mm, which is in accordance with the data found in literature (192—194 C°/12 mm and 189—191 C°/12 mm. Beilstein: VI. 686; Beilstein: VI., I. Erg.-W. 331). Yield: above 90%.

Hydrogenation of benzal acetone.

1. *Production of methyl styryl carbinol by means of selective hydrogenation with the addition of FeSO₄*. 5 g of benzal acetone, 10 cc. of alcohol, 15 cc. of colloidal palladium, 5 cc. of FeSO₄ solution. The calculated quantity of 1 mole (= 840 cc.) of hydrogen was absorbed in 24 hours. After the removal of the catalyst etc. distilling in vacuo. Yield above 90%. Boiling-point 133 C° at 13 mm, figure given in literature: 131 C°/12 mm. (Beilstein: VI. 576).

2. *Hydrogenation with the addition of FeSO₄ and zinc acetate*. 0,5 g of benzal acetone, 5 cc. of alcohol, 5 cc. of catalyst, 1 cc. of FeSO₃ and 0,25 cc. of zinc acetate solutions. After the absorption of 1 mole (= 85 cc.)

of hydrogen, hydrogenation slows down very greatly. The 1 mole of hydrogen was absorbed in a quarter of an hour, further absorptions per quarter of hour: 20, 10, 5, 2.5 cc. and then during 1 hour a further quantity of 5 cc.

Selective hydrogenation of ethylidene acetone: production of pentene-(2)-ol-(4).

3 g of ethylidene acetone, 10 cc. of alcohol, 15 cc. of catalyst, 7 cc. of FeSO_4 solution. 1 mole (= 900 cc.) of hydrogen is absorbed in 9 hours. After removal of catalyst etc. distillation in vacuo. Boiling-point 123—125 C°, figure to be found in literature: 120—122 C°/735 mm. (Beilstein: I. 443.) Yield: over 90%.

Selective hydrogenation of 2-methyl-heptene-(4)-on-(6): production of 2-methyl-heptene-(4)-ol-(6).

4 g of methyl heptenone, 10 cc. of alcohol, 15 cc. of catalyst, 5 cc. of FeSO_4 and 1.5 cc. of zinc acetate solutions. Calculated quantity of 1 mole of hydrogen: 750 cc. Within 3½ hours, 730 cc. are consumed; following that hydrogenation practically stops. After removal of catalyst etc. distillation in vacuo. Yield 3.5 g, i. e. 90%, Boiling point 151 C°.

HYDROGENATION OF CIS-TRANS ISOMERS WITH VARYING QUANTITIES OF CATALYST

Fumaric acid:

0.58 g of fumaric acid, 0.53 g of Na_2CO_3 , dissolved in 10 cc. of distilled water. Calculated quantity of 1 mole of $\text{H}_2 = 125$ cc. Time of hydrogenation in dependence on the quantity of catalyst:

Quantity of catalyst:	Hydrogenation	
	half time:	full time:
1 cc.	84 min.	190 min.
2	27	72
3	30	66
4	42	78
6	42	78
8	20	42
8.5	15	33
10	12	24

Maleic acid:

0.49 g of anhydrous maleic acid, 0.53 g of Na_2CO_3 , 10 cc. of distilled water. Calculated quantity of 1 mole of $\text{H}_2 = 125$ cc. Times of hydrogenation:

Quantity of catalyst:	Hydrogenation	
	half time:	full time:
2 cc.	33 min.	78 min.
3	24	51
4	24	51
5	30	57
6	36	72
10	66	105
11,5	48	80

Cumarin :

1,46 g of cumarin is dissolved in alcohol and filled-up to 50 cc. Times of the absorption of the quantity of H_2 (= 25 cc.) for each 5 cc:

Quantity of catalyst:	Quantity of distilled water:	Hydrogenation	
		half time:	full time:
1 cc.	6 cc.	120 min.	360 min.
2	5	50	180
3	4	30	95
5	2	45	165
6	1	40	140
7	—	35	120

O-cumaric acid.

1,64 g of o-cumaric acid, 50 cc. of alcohol. Quantity of hydrogen required for the saturation of each 5 cc. of solution: 25 cc. Times of hydrogenation:

Quantity of catalyst:	Quantity of distilled water:	Hydrogenation	
		half time:	full time:
1 cc.	6 cc.	90 min.	270 min.
2	5	35	120
3	4	45	135
4	3	40	110
5	2	30	90
6	1	28	70
7	—	23	65

Citraconic acid :

1,30 g of citraconic acid, 1,10 g of Na_2CO_3 , dissolved in distilled water and made up to 50 cc. Quantity of H_2 consumed for each 5 cc. of solution = 25 cc. Times of absorption:

Quantity of catalyst:	Quantity of distilled water:	Hydrogenation	
		half time:	full time:
3 cc.	3 cc.	70 min.	180 min.
3,75	2,25	25	80
4,5	1,5	48	110
5,25	0,75	50	115
6	—	45	105

Mesaconic acid :

1,30 g of mesaconic acid, 1,10 g of Na_2CO_3 , distilled water up to 50 cc. Times of the absorption of the 25 cc. of hydrogen required for each 5 cc. of solution:

Quantity of catalyst:	Quantity of distilled water:	Absorption of hydrogen	
		half time:	full time:
1 cc.	5 cc.	55 min.	140 min.
2	4	50	110
3	3	45	105
4,5	1,5	53	115
5,25	0,75	43	100
6	—	35	90

Oleic acid :

1,40 g of oleic acid, 0,5 g of NaOH, distilled water 50 cc. For each 10 cc. of solution, 25 cc. of H_2 . Hydrogenation in solution warmed to 60 C° .

Quantity of catalyst:	Quantity of distilled water:	Absorption of hydrogen	
		half time:	full time:
1 cc.	5 cc.	45 min.	105 min.
1,5	4,5	15	45
2	4	75	180
2,5	3,5	60	130
3	3	45	120
4,5	1,5	38	95
6	—	30	80

Elaidic acid :

1,40 g of elaidic acid, 0,5 g of NaOH, distilled water, 50 cc. For each 10 cc. of solution, 25 cc. of H_2 , in solution warmed to 60 C° .

Quantity of catalyst:	Quantity of distilled water:	Absorption of hydrogen	
		half time:	full time:
1 cc.	5 cc.	45 min.	135 min.
1,5	4,5	38	105
2	4	30	80
3	3	22,5	90
4	2	30	90
5	1	22	65
6	—	16	55

Cinnamic acid:

1,48 g of cinnamic acid, 1,20 g of NaOH, distilled water, 50 cc. For each 5 cc. of solution, 25 cc. of H₂.

Quantity of catalyst:	Quantity of distilled water:	Absorption of hydrogen	
		half time:	full time:
2 cc.	4 cc.	43 min.	100 min.
3	3	28	65
4	2	16	40
4,5	1,5	23	60
5	1	30	70
5,5	0,5	23	55
6	—	13	38

Allo-cinnamic acid:

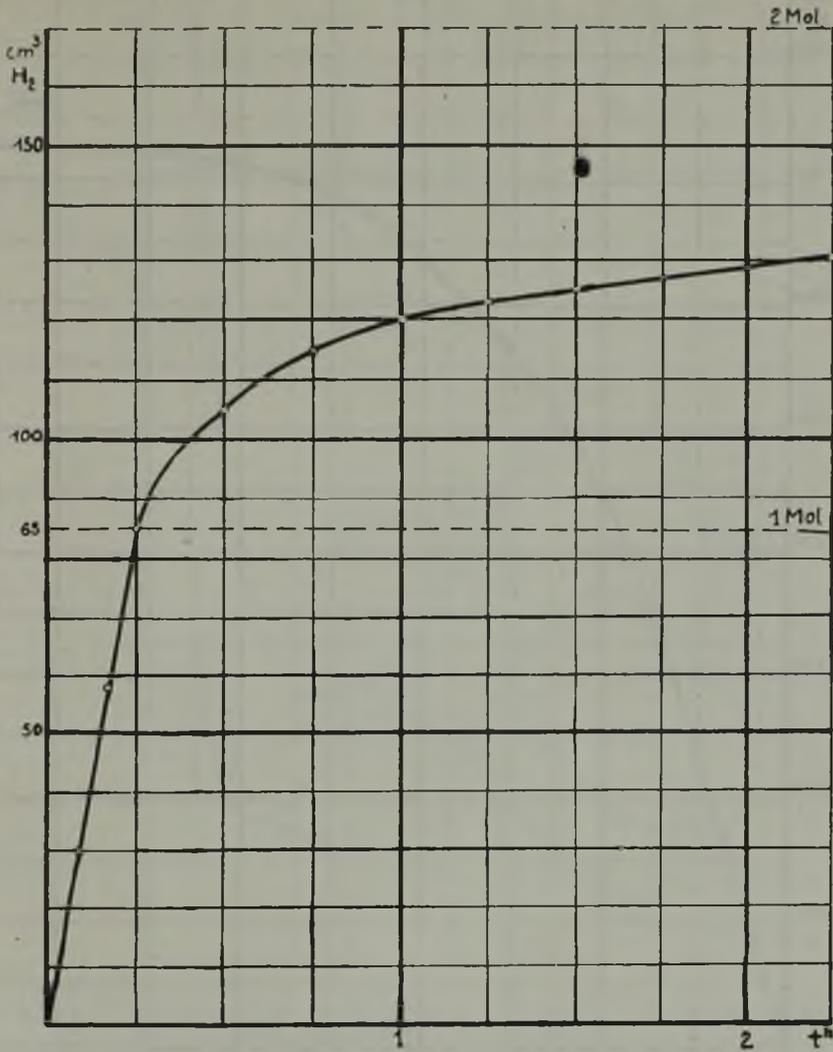
1,18 g of allo-cinnamic acid, 1,20 g of NaOH, distilled water, 50 cc. For each 5 cc. of solution 25 cc. of H₂.

Quantity of catalyst:	Quantity of distilled water:	Absorption of hydrogen	
		half time:	full time:
4 cc.	2 cc.	45 min.	105 min.
4,5	1,5	30	80
5	1	22	53
5,5	0,5	38	95
6	—	23	50

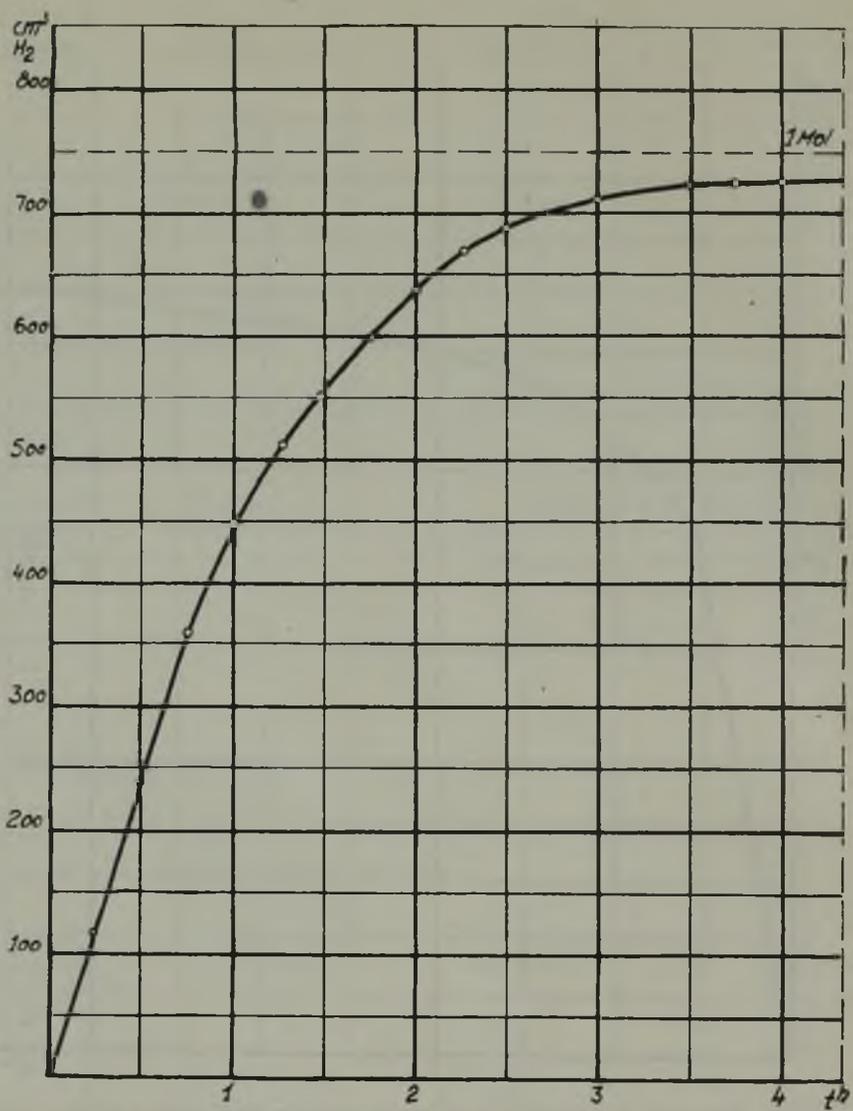
Crotonic acid:

0,86 g of crotonic acid, 0,6 g of Na₂CO₃, distilled water, 50 cc. For each 5 cc. of solution, 25 cc. of H₂.

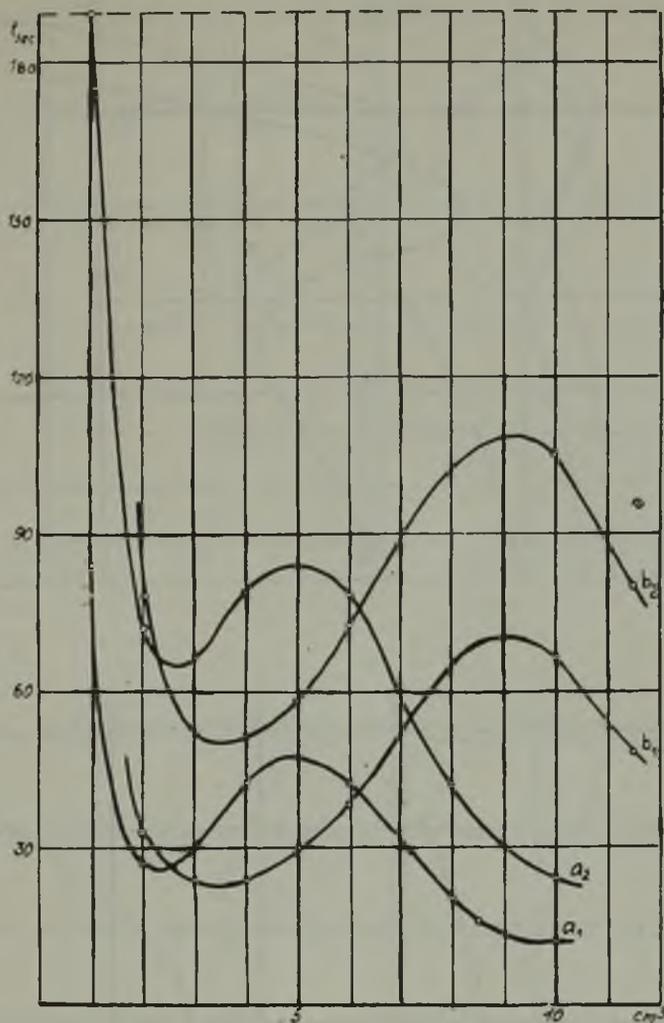
Quantity of catalyst:	Quantity of distilled water:	Absorption of hydrogen	
		half time:	full time:
2 cc.	5 cc.	42 min.	110 min.
3	4	25	70
4	3	13	33
5	2	10	23
6	1	40	90
6,7	0,3	28	60
7	—	20	40



1. Diagram: Selective hydrogenation of benzal-acetone with zinc acetate as promoter.

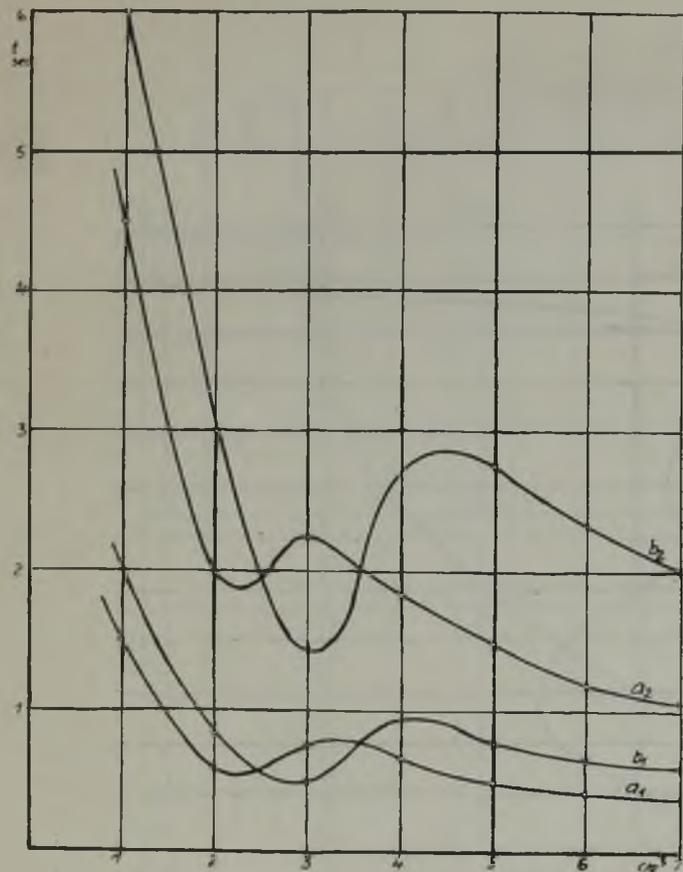


2. Diagram: Selective hydrogenation of methyl heptenon with zinc acetate as promoter.

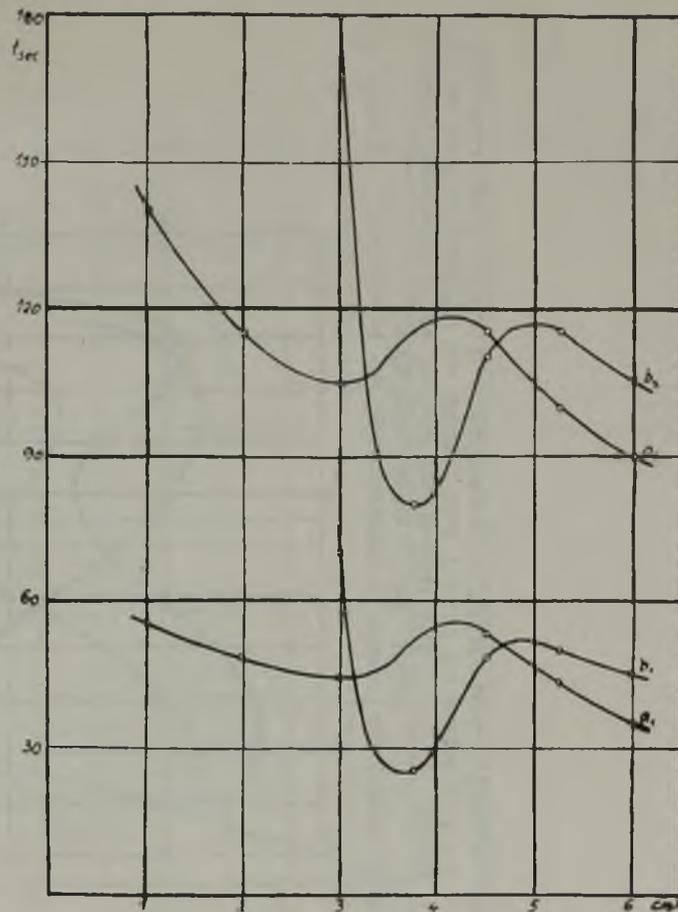


3. Diagram: The time of the hydrogenation of maleic- and fumaric-acids varying with the quantity of the catalyst.

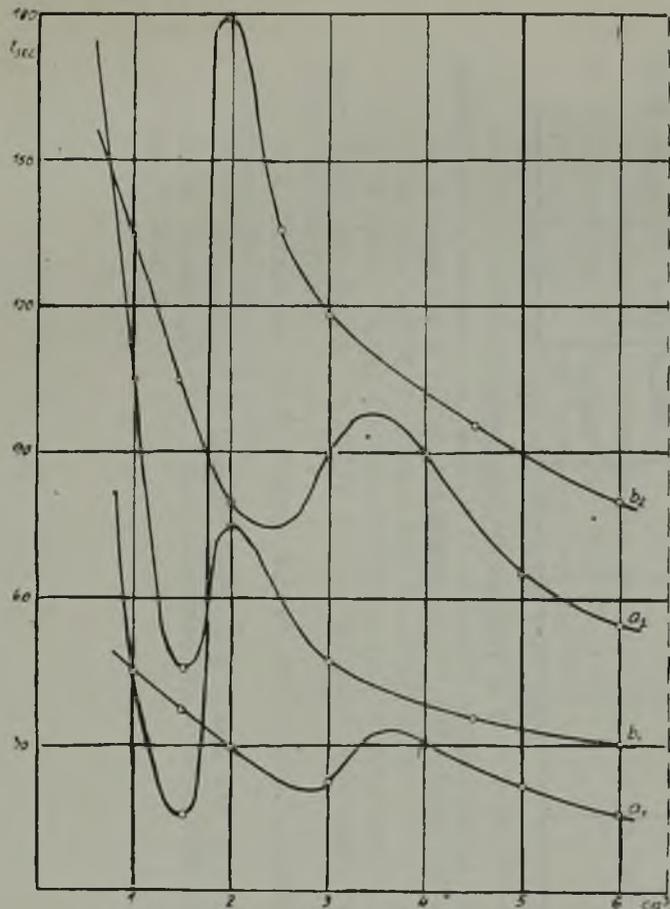
(The hydrogenation of the cis-form goes quicker with 2,2—6 cc. catalyst. Optimum of the catalyst quantity: for fumaric acid 2,5 cc., for maleic acid 3,5 cc. Notes: b_1 = maleic acid, $1/2$ time; b_2 = full time; a_1 = fumaric acid, $1/2$ time, a_2 = full time.)



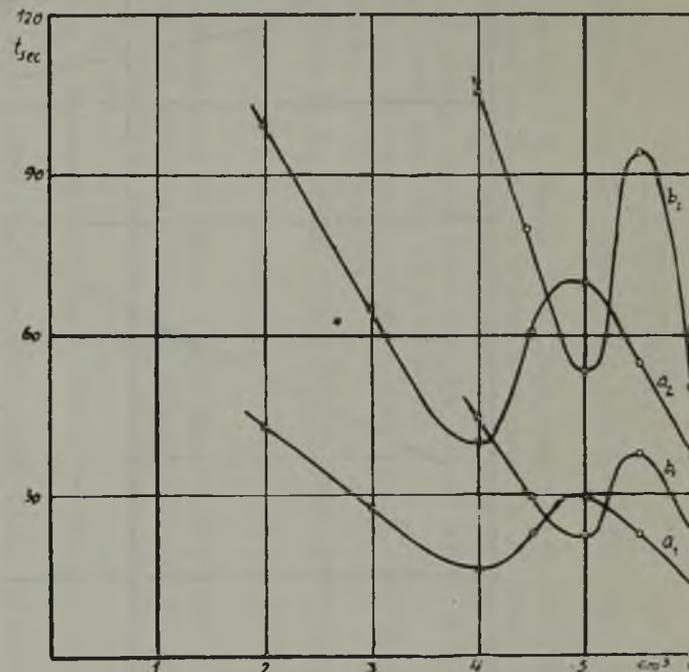
4. Diagram: Cumarin — o. cumaric acid.
 (The hydrogenation of the cis form with 2,5—3,6 cc. quicker.
 Optimums: for cumarin 3 cc., for o-cumaric acid 2.2 cc.
 catalyst. Notes: a_1 = o-cumaric acid, $\frac{1}{2}$ time, a_2 = full time;
 b_1 = cumarin, $\frac{1}{2}$ time, b_2 = full time.)



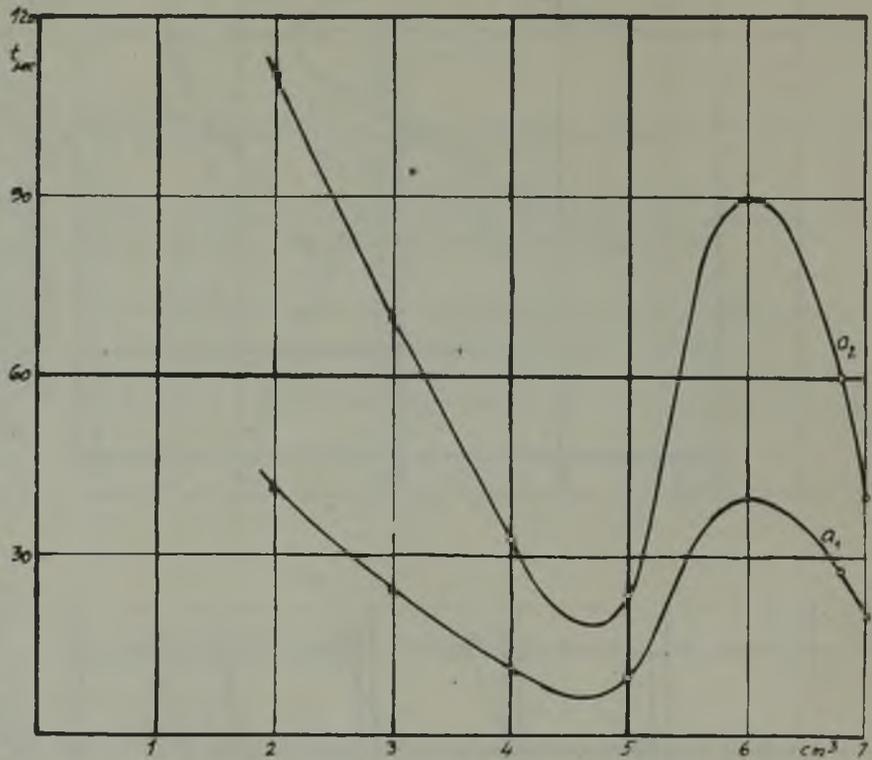
5. Diagram: Citraconic and mesaconic acids.
 (The cis form is quicker with 3,2—4,6 cc. catalyst. Optimums:
 3,75 cc. for citraconic and 3 cc. for mesaconic acids. Notes:
 a_1 and a_2 = mesaconic acid; b_1 and b_2 = citraconic acid.)



6. Diagram: Oleic and elaidic acids.
 (The hydrogenation is quicker for the cis form with 0,9—1,75 cc. of catalyst. Optimums: 1,5 cc. for oleic and 2,5 cc. for elaidic acids. Notes: a_1 and a_2 = elaidic acid; b_1 and b_2 oleic acid.)



7. Diagram: Cinnamic and allo-cinnamic acids.
 (The hydrogenation of the cis form quicker with 4,6—5,25 cc. catalyst. Optimums: cinnamic acid: 4 cc.; allo-cinnamic acid: 5 cc. Notes: a_1 and a_2 = cinnamic acid; b_1 and b_2 allo-cinnamic acid.)



8. Diagram: Crotonic acid.

(Optimum: 4,6 cc. catalyst. Notes: $a_1 = \frac{1}{3}$ time; $a_2 =$ full time of the hydrogenation.)

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SELECTIVE HYDROGENATION BY MEANS OF CATALYSTS II.:
THE HYDROGENATION OF α, β -UNSATURATED CARBONYL
COMPOUNDS BY MEANS OF VARYING QUANTITIES
OF CATALYST (COLLOIDAL PALLADIUM)

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(RECEIVED 4 SEPTEMBER 1945.)

In 1937 Kailan and Hartel (1) observed, when the quantity of catalyst varies, that it is in the case of a certain quantity of catalyst that the speed of hydrogenation reaches a maximum. The processes investigated were the hydrogenation of oleic acid, cinnamic acid and their esters, at a temperature of 180 C°, at a pressure of 1—2 atmospheres, and with a catalyst consisting of metallic nickel precipitated on a silica carrier. They found that the speed of this hydrogenation increases with increasing quantities of catalyst, passes through a maximum and finally decreases. On different materials, the maximum presents itself at different quantities of the same kind of catalyst.

Csűrös, Zech and Géczy (2) investigated the hydrogenation, by means of colloidal palladium, of stereo-isomeric unsaturated compounds (maleic acid — fumaric acid, oleic acid — elaidic acid, cinnamic acid — allocinnamic acid). They showed that a maximum indeed presents itself with the variation of the quantity of catalyst but this maximum is *of a local kind*. After having reached the local maximum, the speed of hydrogenation first drops, following which it rises again after passing through a *local minimum*. With a sufficient quantity of catalyst, the speed of hydrogenation again reaches and even exceeds the figure of the local maximum. The speed of hydrogenation (v), plotted as a function of the catalyst's quantity (M), passes through the curve shown on Fig. 1. In subsequent experiments they showed, that the variation of the speed of hydrogenation along a maximum-minimum curve of this kind refutes the Paal rule (3, 4, 5), formerly believed to be of universal validity. This rule says, that under the influence of colloidal palladium the cis-variety

can be hydrogenated more rapidly than the trans-variety. As against this, this is true only for a certain quantity of catalyst. The situation is completely reversed in the case of quantities larger and smaller than the

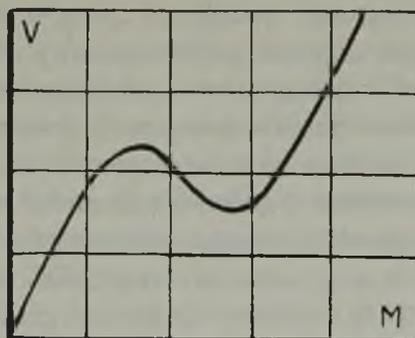


Fig. 1.

said quantity and it is the trans-variety that is capable of being hydrogenated more rapidly.

The purpose of our experiments was to investigate the application of the above principle in cases when one compound contains two groups, each of which is capable of being hydrogenated separately. We attempted to control the progress of hydrogenation by varying the quantity of catalyst on compounds of this kind.

According to existing literature on the subject, no great importance was attributed in this direction to the quantity of catalyst. It is only in a few isolated cases (Stepf (6), Daneel (7)) that any mention can be found of the fact that there exists in the case of a colloidal catalyst a certain threshold value of the catalyst's quantity, below which hydrogenation will not even start, or will not take place in a complete extent, but will suddenly stop at a certain stage. It was Skita (8) alone who described a single case in which the product obtained by the process of hydrogenation may become altered under the influence of the quantity of catalyst. Hydrogenating acetylene by means of palladium, he increased the catalyst's quantity to ten times its original figure and observed that the reaction speed becomes accelerated to $2\frac{1}{2}$ times its original value, the quantity of unchanged acetylene decreases from 21% to 14%, the quantity of ethane from 40% to 35%, whilst the production of ethylene becomes increased from 39% to 50%. According to Skita it follows when small quantities of catalyst are being employed that relatively to that of acetylene, the hydrogenation of ethylene is accelerated in a greater degree than in the case of employing large quantities of catalyst.

According to our idea the selectivity is due in such cases to the variation of the speed of hydrogenation according to the maximum-minimum curve depending on the quantity of catalyst. According to curves resembling that shown on Fig. 1., the reaction speed of the reducible groups of a compound capable of being hydrogenated through several (e. g. two) stages depends on the quantity of catalyst employed. The aggregate speed of hydrogenation is composed of the part speeds of the various stages. If the difference between the two part speeds is not so great as to permit one of the two to be neglected relatively to the other, the two groups can be reduced side by side simultaneously. It depends on the mutual proportion of the two part speeds of which group it will be possible to hydrogenate a greater quantity. With increasing quantities of catalyst, this proportion is altered. In case of groups capable of being reduced at a measurable speed, the curves of the speeds of hydrogenation of the various groups may intersect each other in various ways. After the consumption of the same quantity of hydrogen, it is therefore possible, that it will be sometimes one of the groups, and sometimes the other group that will become hydrogenated in a greater extent, depending on the quantity of catalyst. In certain cases (Fig. 2.) it is possible

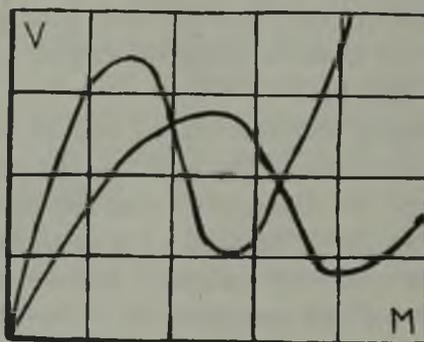
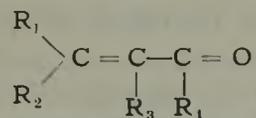


Fig. 2.

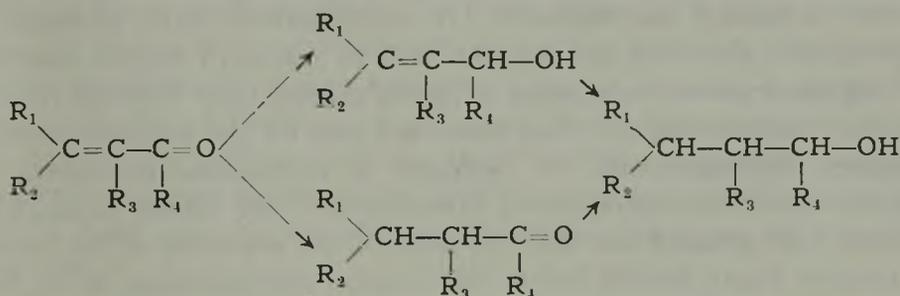
that the two part speeds may intersect each other in such a manner that it is exactly with that quantity of catalyst that one of the groups reaches the maximum of the speed of hydrogenation, with which quantity the other group passes through a minimum. In such cases the selectivity may be very high.

It was the α, β -unsaturated carbonyl compounds that we found suitable for our experiments, because their selective hydrogenation also takes place under the influence of other factors. The general structure of these compounds is



in which formula R_1, R_2, R_3, R_4 may be hydrogen, alkyls, aryls, or aralkyls. These compounds contain two groups capable of being hydrogenated, the double bond and the carbonyl group. The double bond can be completely saturated by the absorption of one mole of hydrogen. As regards the CO group, it is possible to convert it completely by means of 2 moles of H_2 into CH_2 , but by means of catalytic hydrogenation it is, generally, only possible to reduce it to the intermediate stage $=CH(OH)$ i. e. to the carbinol stage, as this group is resistant against further hydrogenation. According to Weidlich and Meyer—Delius (9) the compounds of the allyl alcohol type ($CH_2 = CH \cdot CH_2OH$) can easily be reduced to saturated hydrocarbons with colloidal platinum catalyst, whilst colloidal palladium isn't able to reduce α, β -unsaturated CO groups. This phenomenon was not observed by us, in the course of our experiments it was found in some cases that the carbonyl group became converted into $-CH_2-OH$ even with palladium.

Accordingly, the hydrogenation of the unsaturated carbonyl compounds can take place in accordance into the structures as below:



If the process of hydrogenation is interrupted after the absorption of 1 mole of hydrogen and the products obtained are investigated, in case the selectivity is of the necessary degree, the result will either be saturated ketone or unsaturated alcohol. The two intermediate products will be found side by side if the selectivity is not complete.

Up to now, it was mainly by means of various promoters that it was endeavoured to increase selectivity. Adams and his collaborators discovered the accelerating effect exercised by the ferrous ion on the hydrogenation of the carbonyl group as well as the property of zinc acetate to hinder the hydrogenation of the double bond. With the aid of

these two kinds of promoters, the effects of which mutually complement each other, they were successful in selectively hydrogenating, with a catalyst consisting of Pt/PtO, the unsaturated carbonyl compounds as for instance: citral (10), cinnamic aldehyde (11) and α -furyl-acrolein (12). With the addition of ferrous chloride, cinnamic aldehyde can be converted into phenyl propyl-alcohol, after passing through the stage of cinnamic alcohol. If at the same time zinc acetate is also employed, the reduction will practically stop at the cinnamic alcohol stage. It is in the same way that citral, too, can be hydrogenated with the addition of 0,01—0,02 millimoles of ferrous sulphate. According to Skita (13) it is impossible to hydrogenate citral so as to obtain a uniform final product without the addition of a promoter. Similarly, the hydrogenation of furyl-acrolein can also be well controlled by employing ferrous salts and zinc acetate.

In principle, all compounds containing two or more groups capable of reduction can be reduced selectively and so can also the mixtures of compounds containing a single unsaturated group. Selectivity of hydrogenation was achieved by the proper choice of the catalyst and by employing suitable promoters. Among the many examples figuring in the literature on the subject, we may mention the catalytic hydrogenation of benzonitrile, of benzaldehyde — cyano — hydrin and of benzaldoxime; these compounds, passing through benzaldehyde, become converted into primary and secondary benzyl-amines (14). Bogdanoff and Baskirova (15), as well as Ipatieff and Bogdanoff (16) hydrogenated binary mixtures of allyl-alcohol, oleic acid and cinnamic acid by means of various catalysts, but did not draw any conclusions of principal importance from the results, nor has Yuratchevsky (17) laid down any rule for the hydrogenation of mixtures. Hydrogenating the mixtures of compounds containing an ethylene bond, the distinguished three cases: 1. the various compounds became hydrogenated one after the other, 2. the reduction of the second component began already before the complete hydrogenation of the first component, and 3. the components became hydrogenated simultaneously.

Finally, it is also possible to hydrogenate selectively such compounds, which indeed contain only one group capable of reduction, this group being, however, one the saturation of which can be effected in a plurality of steps. Acetylene and its derivatives are compounds of this kind ($R_1C \equiv CR_2$; R_1 and R_2 may be H, aryl, etc.) An example was published by Skita (8) for the selective hydrogenation of acetylene. Among the derivatives of acetylene, it was chiefly the mono- and di-aryl acetylenes (phenyl acetylene, tolane, diphenyl acetylene (18, 19) as well as the γ -butinic diols, also called acetylene γ -glycols $\left(\begin{matrix} R_1 \\ R_2 \end{matrix} \right) C(OH)CR_3(OH)C \equiv CR_4$) the

catalytic hydrogenation of which formed the subject of investigations (20, 21, 22).

These last-named experiments gave rise to a difference of opinions between Salkind (20) on the one hand, and Ott and Schröter (21) on the other hand. When half hydrogenated acetylene derivatives may become converted into two stereo-isomeric (cis- and trans-) ethylene derivatives. According to Salkind the greater the speed of the reduction, the more will the formation of the cis-variety be favoured. Ott and Schröter admitted this, but believe in the case of heterogeneous catalysis that the speed of reaction is a function of the activity of the catalyst solely. Moreover, they generalize Salkind's theory by declaring in case a highly active catalyst is employed, that it is always the compound richer in energy that is formed, independently of the fact whether that compound in the various cases is the cis- or the trans variety. In their opinion, the duration of the reaction depends exclusively on the quantity of catalyst. As against this, Salkind (22) points out that if the experiments are carried out under entirely identical conditions with different quantities of the same kind of catalyst, the factor deriving from activity may be considered eliminated and it is the effect of the reaction speed that becomes predominant.

Naturally, the fact exercising the most decisive influence on catalytic hydrogenation is the nature of the catalyst itself. It is platinum and palladium that offer the widest range of possibilities in laboratory experiments, in the form of precipitates on a soft carrier or in colloidal condition. The main difference between them is that platinum is more powerful, whilst palladium is more selective. Thus for instance, by means of Skita's colloidal platinum, it is also possible to hydrogenate aromatic and heterocyclic compounds (23). Whilst colloidal palladium is highly suitable for selective hydrogenation of the ethylene bond (24, 25), particularly in those cases, where phenyl radicals are connected to a double bond (26).

It is chiefly bone black and barium sulphate that figure as carrying materials, but barium and calcium carbonate, silicagel and silica also are frequently employed. Paal (3, 4, 5) employed lizalbinat and protalbinat of sodium by way of protecting colloid for stabilizing the colloidal catalyst. Their drawback is that the colloidal solutions are separated as a precipitate in an acid medium. It is for this reason that Skita (8, 13, 25, 29) employed gum arabic in such cases. Other kinds of protecting colloids were employed in quite exceptional cases only (18).

The purpose of these experiments was always to enable hydrogenation to the desired final product to be performed as rapidly as possible. For this purpose, the following features were varied:

1. The mutual proportions of the quantities of the catalyst and of the substance to be hydrogenated.
2. The concentration of the catalyst (by using a greater or less quantity of solvent).
3. The degree of dispersion of the catalyst.
4. The temperature.
5. The pressure.
6. The quality and quantity of the promoters.
7. The hydrogen-ion concentration of the medium, and finally
8. The solvent.

As to the variation of the solvent, it is in many cases — particularly in the case of the hydrogenation of mixtures — only on the reaction speed and not on the selectivity of catalysis that it exercises any effect (27). Thus the supposition of Adkins (28) according to which the solvent also may influence selectivity, cannot be extended to all cases.

We by our experiments wished to verify whether the variation of the quantity of catalyst will influence the selectivity of hydrogenation or not. In this connection it also appeared necessary to clear up the question whether the alteration of the concentration of the catalyst may not possibly alter the degree of dispersion; if that were the case, the reaction would be influenced not by the quantity of the catalyst, but by the alteration of the degree of dispersion.

In order to clear up these questions, we conducted our investigations with two kinds of catalysts, with Skita's colloidal palladium (29) and with Schmidt's precipitate of palladium on barium sulphate (30), since it may be supposed of the latter, that it will not alter its degree of dispersion at least within a short time.

Of the α, β -unsaturated carbonyl compounds we hydrogenated croton aldehyde, as a compound of the aliphatic type, cinnamic aldehyde, as an unsaturated aldehyde containing also an aromatic portion, and benzal acetophenone, as a ketone. With each of these compounds, we carried out two comparative series of hydrogenation, in such a manner, that palladium precipitated on barium sulphate was employed as catalyst in one of the series and colloidal palladium, in the other series. By accurately keeping all experimental conditions (temperature, pressure, volume, pH, speed of stirring) unchanged all other influences were eliminated. Accordingly, it was solely the effect of varying the quantity of catalyst, on the speed of hydrogenation, that was investigated on the one hand and the manner in which the absorption of hydrogen took place, on the other hand. In each experiment, we investigated the products obtained after the absorption of one mole of hydrogen. In the experimental part of

this paper, the results were tabulated and also shown on graphs. The graphs showed the speed of hydrogenation (H consumed per cc. per minute) on the one hand and on the other hand, the gradual saturation of the double bond in the form of percentages, taking full saturation as 100%, both of them as a function of the quantity (cc., or grams) of catalyst employed. The speed curves pass through a local maximum and minimum, the saturation curves of the double bond through a local minimum. The two minima present themselves at identical quantities of catalyst.

With colloidal as well as with barium sulphate palladium, croton aldehyde became hydrogenated on its double bond only when the progress of the absorption of hydrogen was plotted on a graph, the curve obtained (graph No. 1.) was in complete accordance with those obtained by Csűrös, Zech and Géczy in connection with the hydrogenation of double-bond compounds not containing any other group capable of reduction beside the double bond. The hydrogenation of croton aldehyde practically stops after the absorption of one mole of hydrogen. Analysis proved in all cases that it was only the double bond that became saturated (see last column of Table No. I.). The reaction speed varies in exactly the same way as in the cases observed by Csűrös, Zech and Géczy (graphs Nrs. 2. and 3.) with the variation of the quantity of catalyst. In the case of colloidal palladium the medium of hydrogenation was a neutral aqueous-alcoholic, in the case of palladium precipitated on barium sulphate, a glacial-acetic acidic. In one case (Table No. I., case 13.) hydrogenation was investigated in a medium containing hydrochloric acid; in an other in a medium containing sodium hydroxide, (Table No. I., case 14.). In neither did the progress of the absorption of hydrogen alter. The carbonyl group of croton aldehyde did not become hydrogenated under the effect of an addition of ferrous sulphate either (Table No. I. 15.).

Under the given circumstances, with tiglic aldehyde the homologue of crotonic aldehyde it was likewise impossible to make it absorb more than one mole of hydrogen, either with colloidal palladium or with palladium precipitated on a carrier substance. Here also the absorption of hydrogen practically stopped after the absorption of 1 mole of hydrogen; according to the analyses, the saturation of the double bond amounted to 97—99,4% (Table No. II. 1, 2). It also was impossible in this case to obtain the reduction of the carbonyl group by an addition of ferrous sulphate (Table No. II. 3).

A different result led to the experiments carried out by us with cinnamic aldehyde and benzal acetophenone. These two compounds easily absorbed 2 moles of hydrogen also. The absorption of hydrogen

took place at constant speed up to the quantity corresponding to 2 moles. In case of different quantities of colloidal catalysts, the speed of hydrogenation varied in accordance with graphs Nrs. 4. and 8., in the case of a catalyst precipitated on a carrier substance according to graphs Nrs. 6. and 10. Interrupting the experiments after the absorption of 1 mole of hydrogen, we investigated what percentage of the double bond had become saturated. In the experiments carried out with colloidal catalyst and with catalyst precipitated on a carrier substance, it is uniformly at the same place that the saturation of the double bond is a minimum, at which point the speed of hydrogenation also is a minimum (see graphs Nrs. 5, 9 and 11). In view of checking results, in single cases, we have also determined the percentage of reduction of the carbonyl group (Table No. III. 1, 6, 7, 8, 11, 14; Table No. IV. 1, 7, 8, 11, 15, 17). The sum of the percentages of saturation of the double bond and of the carbonyl group in all cases, within the limits of error, gave 100%.

From the experiments, we may draw the conclusions set out below.

In cases when two different groups capable of reduction can be saturated with comparable speeds, it is possible to control the selectivity of hydrogenation by the mere variation of the quantity of catalyst. Of this kind are the α, β -unsaturated carbonyl compounds containing an aromatic ring also. By choosing the quantity of catalyst at a suitable figure, on these it is possible to render hydrogenation selective in such a degree,

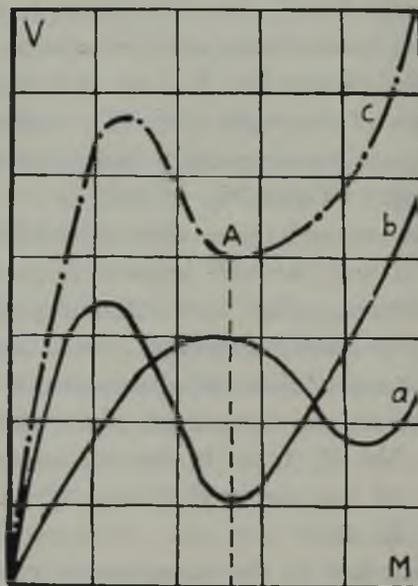


Fig. 3.

that if after the absorption of 1 mole of hydrogen, the reduction is interrupted, 77% and even 82% of the carbonyl group can be hydrogenated before the double bond. (Table No. III. 7, 14; Table No. IV. 8, 15). This phenomenon can be explained by the part the total speed of reaction (a) is composed by addition from the part speeds of hydrogenation of the double bond (b) and of the carbonyl group (c). The optimal case is denoted by the point *A*. It can be seen here that whilst the total speed reaction is indeed a minimum, but of the part speeds, the speed of saturation of the carbonyl group (which at point *A* is nearly a maximum) substantially exceeds the speed of saturation of the double bond.

In the aliphatic α, β -unsaturated carbonyl compounds there exists probably a substantial difference in order of magnitude between the speed of hydrogenation of the CO and of the C = C groups. This is the cause of the failure of all the attempts at carrying out the reduction with palladium on the CO group also, either by varying the quantity of catalyst, or by varying the pH, or by means of such supplemental substances as in other cases have given good results.

In addition to the selectivity of hydrogenation, our experiments threw light also on the function relation existing between the reaction speed and the quantity of catalyst. Notably, owing to the fact that the speed of hydrogenation varies according to a maximum-minimum curve not only in the case of a colloidal catalyst, but also in that of a catalyst precipitated on a carrier substance (graphs Nrs. 2, 3, 4, 6, 8, 10), the phenomenon may be considered universal in heterogeneous catalysis. At the same time the same fact excludes the possibility of the phenomenon caused by the alteration of the degree of dispersion of the colloidal catalyst, seeing that the catalyst precipitated on a carrier substance possesses the same effect. We may therefore declare, that the variation of the degree of dispersion cannot be the cause or, at least, cannot be the sole cause of the fact, that it is not in a linear manner, but in accordance with the curve plotted on Fig. 1. that the quantity of catalyst influences the speed of catalytic hydrogenation.

SUMMARY

In the course of our experiments, we investigated the effects exercised on the progress of hydrogenation by the quantity of catalyst. By way of catalyst we employed colloidal palladium as well as palladium precipitated on a barium sulphate carrier. Keeping all the experimental conditions constant it was exclusively the quantity of catalyst that was varied, and its influence on the speed of hydrogenation and on the product of

the reaction was investigated in the case of crotonic aldehyde, tiglic aldehyde, cinnamic aldehyde and benzal acetophenone. In the course of our experiments the carbonyl group of the aliphatic unsaturated aldehydes did not become hydrogenated, whereas the aromatic aldehydes did, notable the double bond and the carbonyl group with different selectivities. With an optimal quantity of catalyst, it is possible to control the reduction in such a manner as to ensure that the carbonyl group can be hydrogenated in its preponderant part before the double bond. With this optimal quantity of catalyst, the total reaction speed is the smallest. In all the cases investigated, the speed of hydrogenation varies with the quantity of catalyst according to a maximum-minimum curve.

Accordingly, we succeeded by further examples in proving the variation according to a maximum-minimum curve, of the speed of hydrogenation in dependence on the quantity of catalyst, and we utilized this phenomenon for the selective reduction of ketones and aldehydes containing an unsaturated bond of α, β -position. Finally, the circumstances that eventual results were obtained not only with colloidal catalysts, but also with catalysts precipitated on a carrier substance of which latter kind of catalysts it may be supposed that their degree of dispersion is constant enabled us to establish the fact that the variation of the degree of dispersion is at least not the sole cause of the phenomenon, that it is not in a linear manner, but according to the curve plotted on Fig. 1. that the speed of hydrogenation depends on the quantity of catalyst.

The experiments were carried out with the financial support of the Goldberger Foundation.

EXPERIMENTAL PART

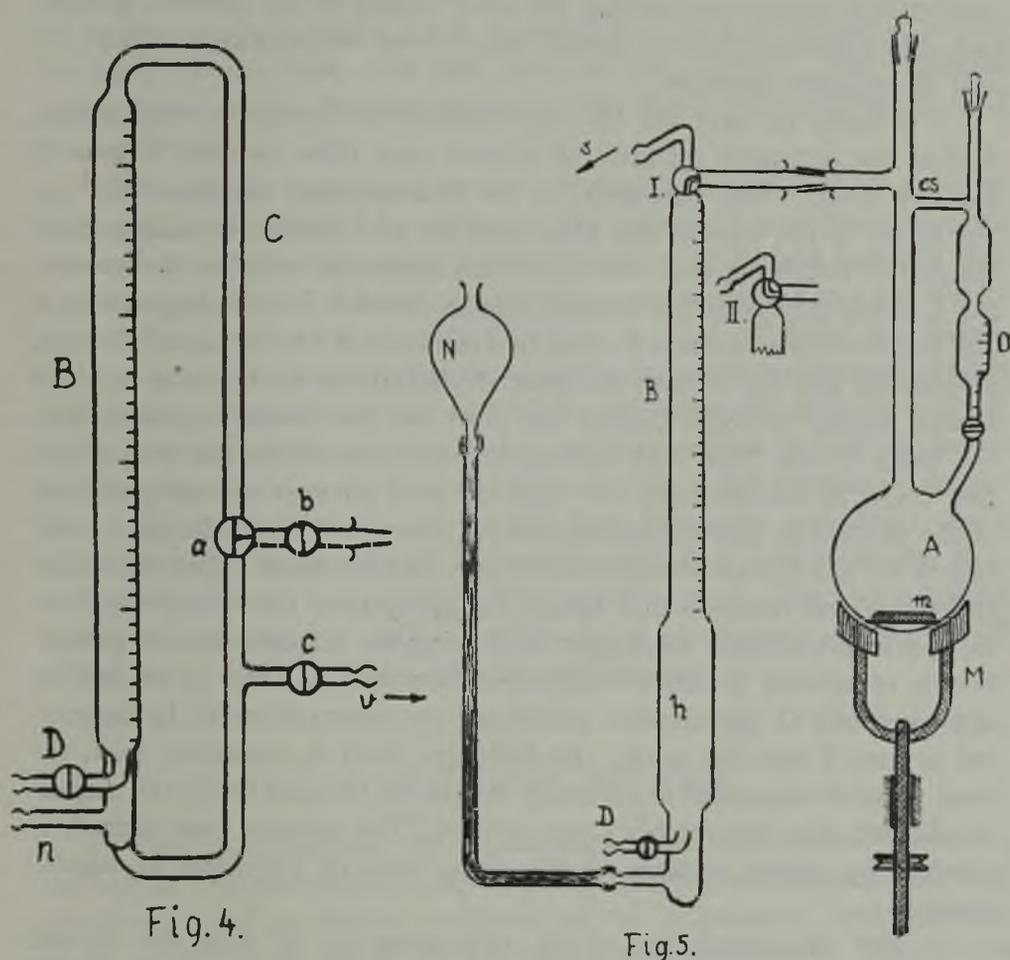
A) EXPERIMENTAL EQUIPMENT — METHOD OF CARRYING OUT THE HYDROGENATION

The hydrogenations were carried out in the semi-micro apparatus employed by Zechmeister and his collaborators (31, 32), retaining the alterations described in the previous publication (2), and indeed effecting further improvements in the various details.

The apparatus (Fig. 5) is composed of the hydrogenating retort *A*; the liquid contained is stirred with the aid of an iron bar (*m*) fixed into a glass tube which is moved by means of a rotating magnet (*M*) in accordance with the method of Weygand and Werner (38). The lateral tube *O* has a cubic capacity of 10 cc., a scale with divisions of 1/10 cc., it can be closed by means of a stop-cock and serves for the admission of the substance to be hydrogenated. With the aid of the connecting tube *cs*

the lateral tube also can easily be evacuated and the solution to be hydrogenated can be let down easily without change of volume into the retort *A*. The retort joins on through a glass joint to the gas burette *B*. The hydrogen can be introduced into this through a small tube capable of being closed by means of the stop-cock *D*, from a bombe or Deville bottle.

Our improvements are the following: 1. The lateral tube hitherto employed of the gas burette (Fig. 4. *C*) has been dispensed with. Thereby



we were able to reduce the clearance space greatly exposed to fluctuations of temperature and by employing a simple L-bored stop-cock instead of three glass stop-cocks (Fig. 4. *a*, *b*, *c*), the use of the apparatus was simplified. 2. By means of the bulge (Fig. 5. *h*) provided in the lower part of the gas burette, it was possible to ensure that a single filling with hydrogen of the gas burette should be sufficient for filling the evacuated

apparatus, whereas it was only in a number of stages that it was possible to effect such filling in the previous apparatus.

The substances to be hydrogenated employed were in aqueous, aqueous-alcoholic, alcoholic or glacial-acetic acid solutions, in quantities of 1/1000 mole. In the various series the volume was permanently kept at 20 cc., and 14 cc., respectively. On one occasion, the aqueous-alcoholic solution was rendered acid, and on another, alkaline (Table No. I. 8, 9) by adding 1 cc. of 1/10th normal hydrochloric acid, or sodium hydroxide, respectively, whilst maintaining the total volume of the solution unchanged. The experiments were carried out at room temperature (20 to 23 C^o) and at ordinary pressure.

In order to carry out the experiments, the catalyst as well as one-half of the necessary quantity of solvent were filled into the bottom of the dry retort. The substance to be hydrogenated together with the remainder of the solvent was filled into the part above the stop-cock of the part O. Following this, the retort was connected with the gas burette; the L-bored stop-cock was brought into its position II according to Fig. 5. and the retort was evacuated down to a pressure of 14—16 mm of mercury column (in case the solvent was pure alcohol, down to the point at which alcohol begins to boil). During this time the gas burette, together with the bulge h, was filled with hydrogen. After evacuation, the level-adjusting vessel N was held at a low level (so as to prevent any spraying over of the water-lock into the hydrogenating retort) and the hydrogen contained in the gas burette was allowed to pass into the retort. This evacuation and filling was repeated four times. Following this, the saturation of the catalyst with hydrogen was begun by starting the magnetic stirrer. Saturation is completed in about 5 minutes. Now the gas level is adjusted at approximately O, the solution containing the substance to be hydrogenated is passed into the retort, the hydrogen level is accurately read, the level-vessel is suspended at a constant height (60 cm) and finally the magnet is adjusted for 300 rotations per minute. The process thus started is checked by taking readings of the rising level of hydrogen, at regular intervals.

After the completion of the hydrogenation, or after the desired quantity has been consumed (25 cc. of hydrogen correspond to 1/1000 mole), the retort is evacuated, filled with air, and the product formed investigated.

B) THE PRODUCTION OF THE CATALYSTS

Our experiments were carried out with two kinds of colloidal palladium catalyst (marked *a* and *b*), prepared according to Skita's (29) method

and with a catalyst consisting of metallic palladium precipitated on barium sulphate.

The colloidal preparation marked *a* was prepared by dissolving 0,5 g of palladium chloride in 50 cc. of distilled water kept in boiling condition, adding 10 cc. of hot 5% gum arabic solution and shaking the dark brown solution, while still hot, in a shaking bottle in a hydrogen atmosphere for about half an hour. Finally, the deep black colloidal solution which presents a brilliant brownish colour in a thinner layer was filled to 100 cc. in a measuring retort.

The catalyst marked *b* was prepared in a manner similar to *a*, but its concentration was only half that of the former. The colloidal solution reduced in the shaking bottle was finally filled-up not to 100, but to 200 cc.

The metallic palladium catalyst marked *c* precipitated on a carrier substance, was prepared according to the prescription of Schmidt (30). The quantity of barium corresponding to 6,1 g of barium sulphate was suspended in 120 cc. of water, after having been separated in a hot condition; 0,7 g of palladium chloride dissolved in 30 cc. of water was added, the mixture was rendered alkaline to litmus by means of normal sodium hydroxide and was boiled during a short time after the addition of 1 cc. of 16% formaldehyde solution. The reduced palladium became deposited in a fine dispersion on the barium sulphate. First it was washed by decanting, then it was filtered and washed with hot water and dried above solid potassium hydroxide in a vacuum exsiccator, and following this, was powdered to a fine powder (in an agate mortar). Thus we obtained 6,46 g of catalyst of a kind, of which 0,1 g corresponds in content of palladium to 2,33 cc. of the colloidal solution type *a*.

C) ANALYTICAL METHODS

When carrying-out the experiments with semi-micro quantities, we had in the investigation of the products obtained, to dispense with preparation and to confine ourselves to the quantitative determination of the double bond and of the carbonyl group respectively. The double bond was determined by Mc Ilhiney's (34) method (bromine figure), the carbonyl group was determined in the easily reducible crotonic aldehyde by the argentometric method of H. Meyer (35) and in the case of cinnamic aldehyde and of benzal acetophenone by the method employing phenyl hydrazine (36).

D) HYDROGENATION EXPERIMENTS

Series I.: Hydrogenation of crotonic aldehyde.

A) A main solution of 0,5 mole of crotonic aldehyde was prepared for the experiments. 3,5010 g (0,05 mol) of aldehyde were dissolved in about 15 cc. of alcohol, and the solution filled up to 100 cc. by means of 40% alcohol. Of this main solution, 2 cc. were hydrogenated each time with varying quantities of catalyst, colloidal palladium type *a* was employed by way of catalyst. The solution was in each case made up with distilled water to 20,0 cc.

TABLE I. A.
Colloidal catalyst (type a).

No.	Quantity of catalyst	Quantity of H absorbed	Time minutes	Time up to the absorption of 12,5 cc of H	Speed of hydrogenation	Percentage of carbonyl hydrogenation	Remark
1.	1,0 cc	24,35 cc	180	82	0,15	1,1	
2.	2,0	24,38	108	28	0,45	0,0	
3.	4,0	24,40	78	24	0,52	4,0	
4.	8,0	26,00	91	32	0,40	2,8	
5.	12,0	24,82	82	25	0,51	2,0	
6.	14,0	25,04	73	20	0,63	—	
7.	16,0	25,06	48	14	0,89	—	+ 1 cc 0,1 n HCl
8.	4,0	24,66	80	29	0,43	2,0	+ 1 cc 0,1 n
9.	4,0	21,06	184	94	0,13	—	NaOH

B) In this series palladium precipitated on barium sulphate (catalyst type *c*) was employed by way of catalyst. The total volume was 14 cc., the solvent glacial acetic acid.

TABLE I. B.
Catalyst on carrier substance.

No.	Quantity of catalyst	Quantity of H absorbed cc	Time minutes	Time up to the absorption of 12,5 cc of H	Speed of hydrogenation	Percentage of carbonyl hydrogenation	Remark
10.	0,10 g	25,12	76	21	0,61	0,8	
11.	0,20	24,86	40	17	0,74	—	
12.	0,30	25,05	80	24	0,52	—	
13.	0,40	24,68	42	18	0,70	1,0	
14.	0,50	24,70	28	10	1,18	0,6	

In the experiments as above, as well as in the subsequent experiments, the absorption of hydrogen has, up to reaching complete saturation, taken place at a speed which remained constant, independently of

the concentration of the still untransformed starting substance. This is proved by the curves shown on graph No. 1., as well as by the following Table:

Progress in time of the experiment No. 3. of the series of experiments No. I. A.:

Time (minutes)	0	7	16	27	34	63	72	78
Quantity of H absorbed, cc	0	3,40	8,10	14,00	17,08	23,52	24,10	24,40

Series No. II. : Hydrogenation of tiglic aldehyde.

Of tiglic aldehyde (37), prepared from propionic aldehyde and acetaldehyde, 4,20 g (0,05 mole) were filled up with 50% aqueous alcohol to 100 cc. Of this 2 cc. were employed each time for the hydrogenations enumerated below; total volume 20,0 cc., and 14,0 cc., respectively.

TABLE II. A.
Colloidal catalyst (type a).

No.	Quantity of catalyst	Quantity of H absorbed	Time minutes	Time up to the absorption of 12,5 cc of H	Speed of hydrogenation	Percentage of carbonyl hydrogenation	Remark
1.	4,0 cc	24,35 cc	135	62	0,20	99,4	
2.	4,0	21,95	348	126	0,10	97,0	+ 4 cc 0,06% $FeSO_4$

TABLE II. B.
Catalyst on carrier substance (glacial acetic acid solution).

No.	Quantity of catalyst	Quantity of H absorbed	Time minutes	Time up to the absorption of 12,5 cc of H	Speed of hydrogenation	Percentage of carbonyl hydrogenation	Remark
3.	0,20 g	25,02	372	150	0,08	99,6	

Series No. III. : Hydrogenation of cinnamic aldehyde.

1,36 g (0,05 mol) of cinnamic aldehyde were filled-up with alcohol to 100 cc. Of the main solution, 2 cc. were employed each time for each experiment.

A) In the series employing colloidal catalysts we carried out hydrogenation with the preparation type *b*. The total volume was in each case 20,0 cc., the medium was alcoholic.

TABLE III. A.
Colloidal catalyst (type b).

No.	Quantity of catalyst	Quantity of H absorbed	Time	Speed	Percentage of saturation		Remark
					of C = C bond	of C = O bond	
1.	10,0 cc	50,82 cc	192	0,28	100,0	96,8	Informatory experiment
2.	2,0	25,00	109	0,23	98,5	—	
3.	6,0	25,05	68	0,37	94,8	—	Local maximum of speed of hydrogenation
4.	8,0	25,00	76	0,33	89,0	—	
5.	10,0	25,00	104	0,25	69,0	—	
6.	11,0	25,00	119	0,21	30,2	69,9	Maximum of C = C saturation
7.	12,0	25,00	131	0,19	17,5	82,0	
8.	13,0	24,94	113	0,22	40,5	59,0	
9.	14,0	25,00	89	0,28	88,1	—	
10.	16,0	25,05	61	0,41	83,0	—	

TABLE III. B.
Catalyst on carrier substance, total volume 14 cc., glacial acetic acid medium.

No.	Quantity of catalyst	Quantity of H absorbed cc	Time	Speed	Percentage of saturation		Remarks
					of C = C bond	of C = O bond	
11.	0,20 gr	50,32 cc	106	0,53	99,7	98,3	Informatory experiment
12.	0,10	25,06	64	0,39	91,0	—	
13.	0,20	25,00	48	0,52	60,3	—	Local maximum of speed of hydrogenation
14.	0,25	24,90	70	0,36	19,9	81,9	
15.	0,30	25,10	58	0,43	50,0	—	Minimum of C = C saturation
16.	0,40	25,00	41	0,61	89,2	—	
17.	0,50	25,10	32	0,79	89,1	—	
18.	0,60	25,00	28	0,89	77,0	—	

Series No. IV.: Hydrogenation of benzal acetophenone.

5,20 g (0,025 mole) of benzal acetophenone was filled up with alcohol to 50 cc., and 2 cc. were employed each time for each reduction. In the series A, hydrogenation was carried out with colloidal catalyst type b, in the series B, with carrier catalyst type c. The medium of the A series was alcoholic, that of the B series glacial acetic acid.

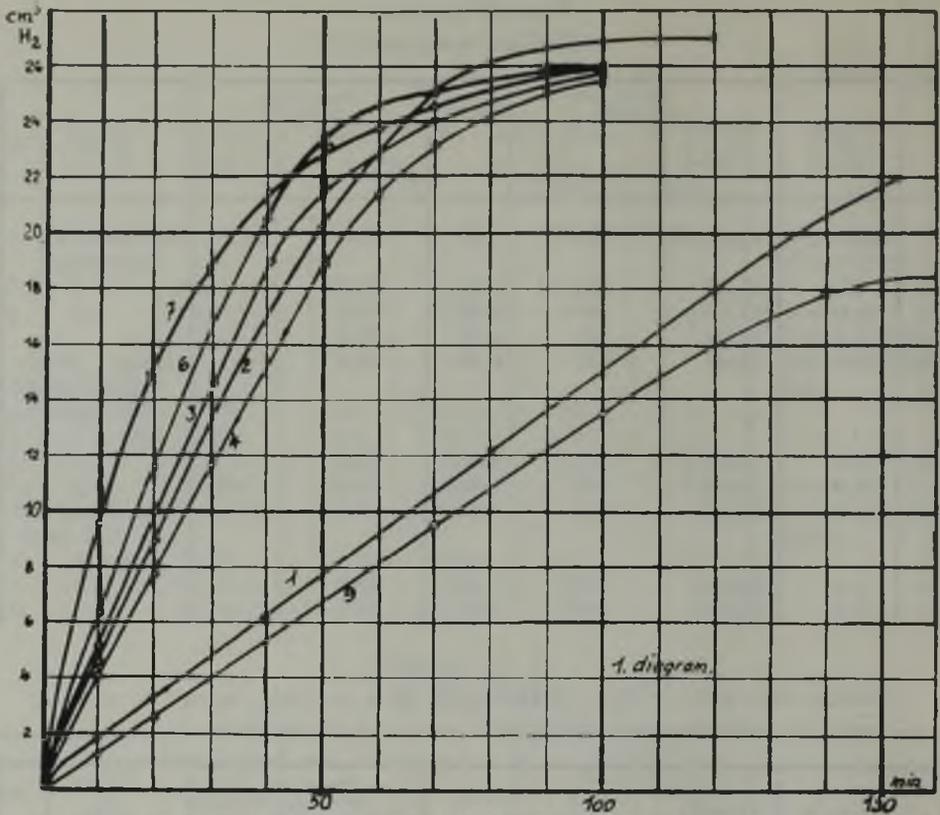
The total volume was in both cases 14,0 cc.

TABLE IV. A.
Colloidal catalyst.

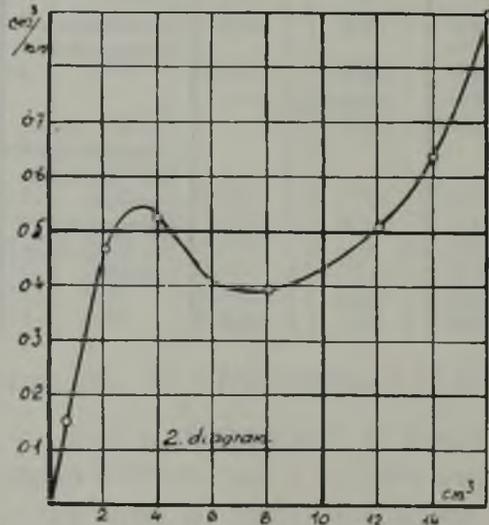
No.	Quantity of catalyst	Quantity of H absorbed	Time Speed of hydrogenation	Percentage of saturation		Remark	
				C = C	C = O		
1.	10,0 cc	49,63 cc	88	0,67	96,0	97,2	Informatory experiment
2.	2,0	25,00	104	0,24	95,0	—	
3.	4,0	25,00	56	0,45	92,8	—	
4.	6,0	25,00	41	0,61	89,5	—	
5.	8,0	24,98	36	0,69	83,0	—	
6.	10,0	25,00	37	0,68	66,7	—	Local maximum of speed of hydrogenation
7.	12,0	25,02	42	0,60	29,6	70,0	
8.	14,0	25,00	49	0,51	22,5	76,8	
9.	16,0	25,00	48	0,52	39,0	—	Minimum of C = C saturation
10.	18,0	25,00	40	0,63	58,5	—	

TABLE IV. B.
Carrier catalyst (glacial acetic acid medium).

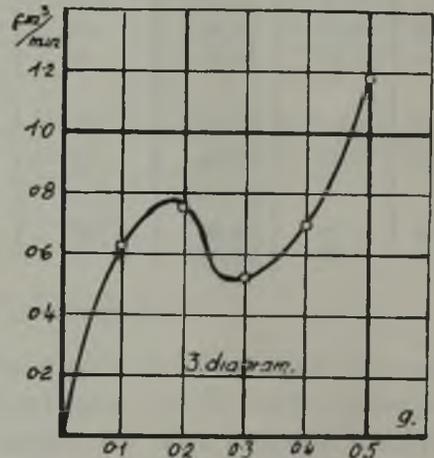
No.	Quantity of catalyst	Quantity of H absorbed	Time Speed of hydrogenation	Percentage of saturation		Remark	
				C = O	C = C		
11.	0,20 g	50,05 cc	146	0,35	99,2	96,0	Informatory experiment
12.	0,10	24,96	117	0,22	91,0	—	
13.	0,20	25,00	69	0,38	86,2	—	Local maximum of speed of hydrogenation
14.	0,30	25,00	45	0,55	76,0	—	
15.	0,40	25,04	58	0,44	21,3	75,2	Minimum of C = C saturation
16.	0,50	25,00	23	1,10	56,2	—	
17.	0,60	25,00	14	1,64	64,8	32,0	



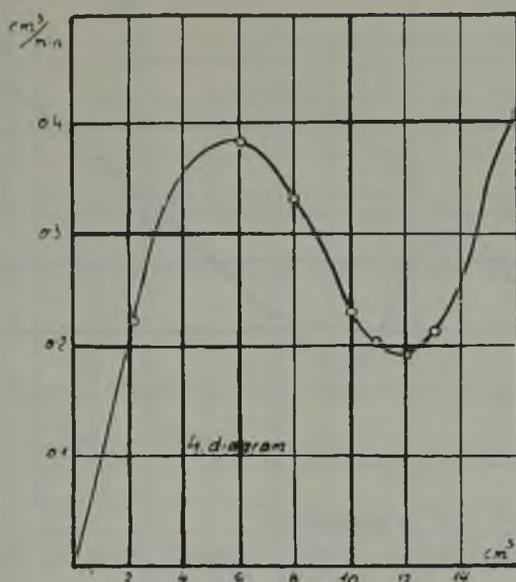
1. Diagram: See Table I. A. *Crotonic aldehyde*. The speed of the hydrogenation.



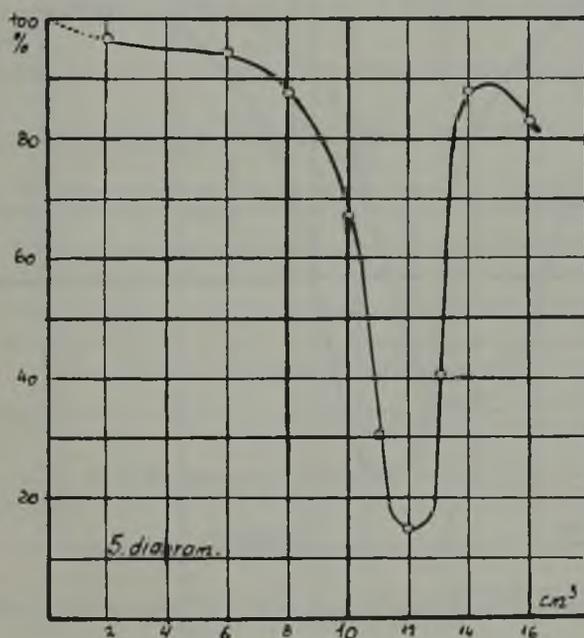
2. Diagram: The speed of hydrogenation of *crotonic aldehyde* in connection with quantities of colloidal catalyst. (See Table I. A.)



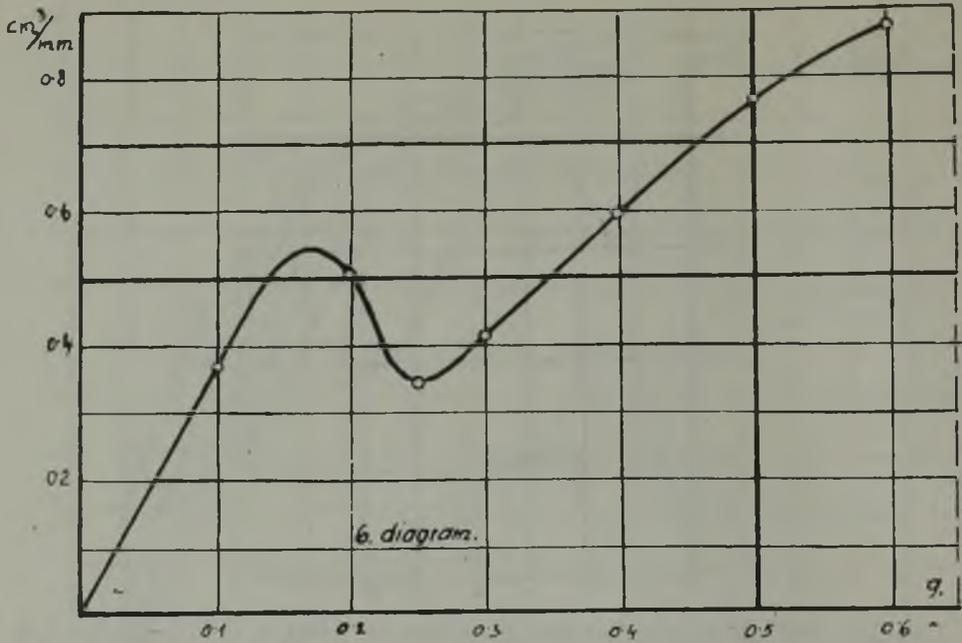
3. Diagram: The speed of hydrogenation of *crotonic aldehyde* in connection with carrier catalyst. (See Table I. B.)



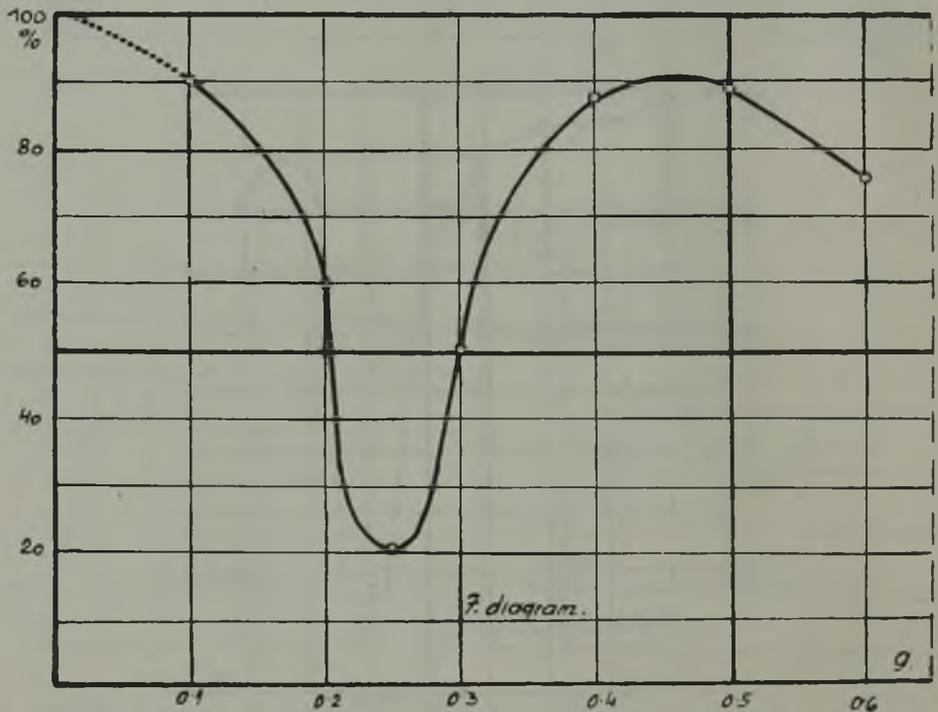
4. Diagram: The speed of hydrogenation of *cinnamic aldehyde* in connection with quantities of colloidal catalyst. (See Table III. A.)



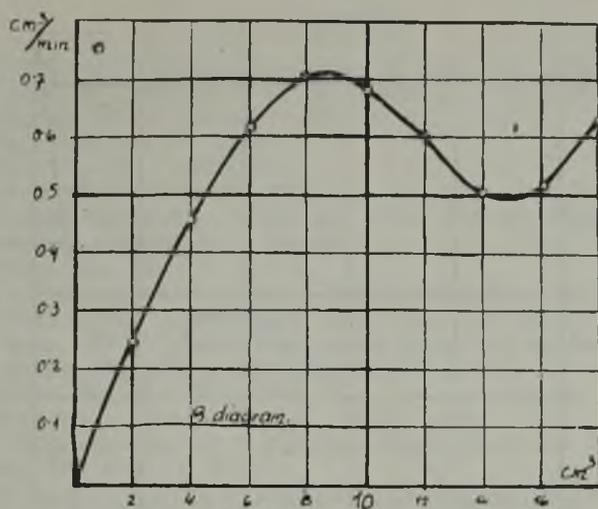
5. Diagram: *Cinnamic aldehyde*. The reduction of the double bonds with 1 mol hydrogen in connection of the quantities of colloidal catalyst. (See Table III. B.)



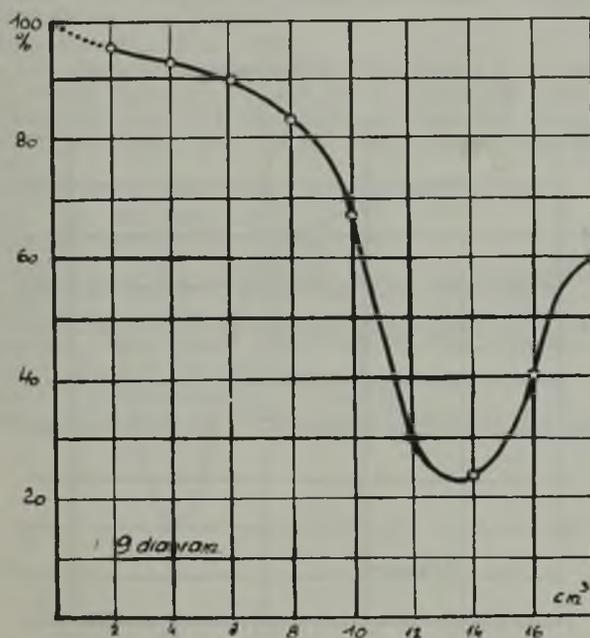
6. Diagram: *Cinnamic aldehyde*. The speed of hydrogenation with carrier catalyst (See Table III. B.)



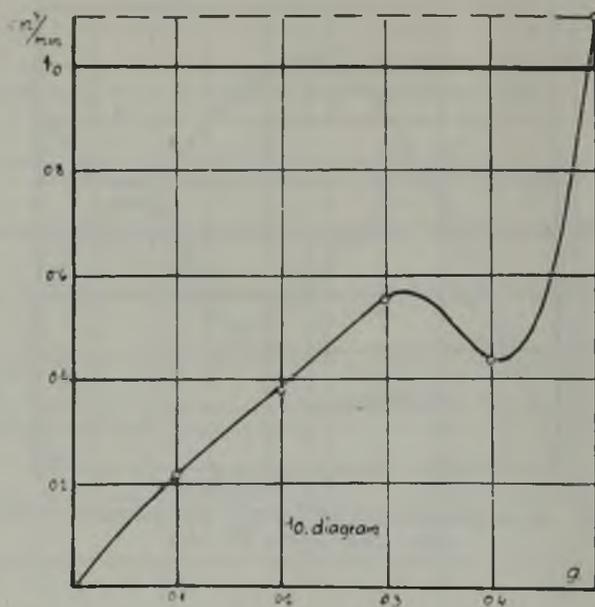
7. Diagram: *Cinnamic aldehyde*. Reduction of the double bond with 1 mol hydrogen in connection with carrier catalyst. (See Table III. B.)



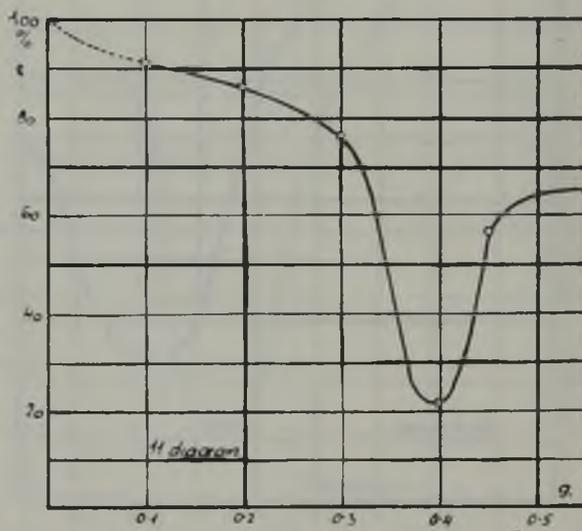
8. Diagram: Speed of hydrogenation of *benzal acetophenone* with colloidal catalyst. (See Table IV. A.)



9. Diagram: Reduction of double bond of *benzal-acetophenone* with 1 mol hydrogen, colloidal catalyst.



10. Diagram: *Benzal acetophenone*. Speed of hydrogenation, carrier catalyst. (See Table IV. B.)



11. Diagram: *Benzal acetophenone*. Reduction of double bond with 1 mol hydrogen, carrier catalyst. (See Table IV. B.)

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