INVESTIGATIONS WITH THE USE OF RANEY NICKEL CATALYST

I. CHANGES IN THE HYDROGENATION ACTIVITY OF RANEY NICKEL AS A FUNCTION OF THE TEMPERATURE AND DURATION OF EXTRACTION

By

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Introduction

Raney nickel is a much employed hydrogenating catalyst, applied mainly in batch hydrogenations in the liquid phase. Its wide-spread use is due to its cheapness and to the relatively simple way of its preparation. Another advantage is that Raney nickel is suited for the hydrogenation of many types of compounds.

The interest in Raney nickel is attested by the great number of patents and the extensive literature (see later) dealing with the preparation of its more active varieties. It is, however, rather difficult to get a clear idea of the ways and means of its preparation failing a reliable basis for comparing the papers and descriptions. Some authors describe the preparation of Raney nickel in divergent ways, without referring to model compounds. Others demonstrate the hydrogenation activity of catalysts, prepared by them, in the form of results attained with model compounds. Only a few research workers publish comparative data with catalysts prepared by other methods. In the above-mentioned cases the possibility of comparison is excluded by the sole fact that almost each research worker uses different model compounds.

In the first part of this paper an attempt is made to study, with otherwise identical experimental factors and model compounds, the changes in the hydrogenation activity of Raney nickel as a function of the conditions of preparation, and, respectively, to clear up the order of magnitude of the changes in the activity of the catalyst under altered conditions of preparation (varying the temperature and duration of extraction) and under the action of various additions.

Literature

The main phases in preparing Raney nickel are: 1. preparation of a Ni-Al alloy, 2. pulverization of this alloy, 3. extraction of aluminium and 4. washing of the catalyst.

In principle, the nickel content of the alloy Ni-Al may range from 18 to 67% [1]. The activity within these limits has been investigated by DUPONT and PIGANIOL [2] who have found no significant differences in the activity when the content of nickel is raised from 30 to 50%. When the Ni content exceeds 50%, decomposition becomes more difficult and simultaneously the activity diminishes. When, however, the content of nickel ranges below 30%, the activity somewhat increases. The degree of this rise being slight, it seems not worth to work with "dilute" alloys of this type. Recently CORNUBERT and PHÉLISSE [3] have proved that the activity of the catalyst is affected by the nickel content of the alloy (the investigations were carried out on cinnamic acid as a model substance). For the saturation of double bonds, however, a catalyst prepared from an alloy containing 20% nickel was found most active. In practice, alloys of different particle size may be applied. As the surface significantly changes with the particle size, also the conditions of extraction (temperature, duration) may alter to a considerable extent. However, experiments may be compared only in case of identical particle sizes. According to RAPOPORT and SILTSHENKO [4] the activity remains almost constant between powder fineness and a particle size of 2,5 mm, while it rapidly decreases above this value. On the contrary, CORNUBERT and PHÉLISSE [3] observed a rise in activity with the decrease of particle size.

In preparing Raney nickel, the extraction of aluminium is the phase most often subjected to variations. The crystal system formed by nickel and aluminium in the alloy is rearranged when extracted [5]. This process requires time and energy supplied in the form of heat during extraction. In this phase of preparation of the catalyst the concentration of alkali, the ratio of alkali to alloy, the duration of additon and post-treatment as well as their temperature may be varied as well. In general, alkali of concentration of 20—30% is applied, although some authors [see 6, 7, 8] use 20% alkali. According to CORNUBERT and PHÉLISSE [3] alkali concentrations of 20—30% are identical in effect. The ratio alkali : alloy ranges from 8 to 10 g to 10 g of alloy. In this connection BEREGI [9] has found that for the removal of aluminium the use of excess alkali is more efficient than the prolongation of extraction, whereas a temperature between 0° and 10° C proved best for etching, although different temperatures are recommended for this process: 115—120° by COWERT and ADKINS [6], 50° by ADKINS and BILLICA [8] and 10° by MOZINGO [7]. According to PAUL and HILLY, the activity of catalyst decreases at a temperature of about 130° and above, owing to the precipitation of aluminium-oxide-hydrate and to the reaction (oxidation) of nickel with water. Therefore, they also recommend extraction temperatures below 100°. The duration according to the extreme values published in the literature varies from 10 minutes to 48 hours, its temperature from 50 to 120° C. Subsequent to introducing the catalyst (at the last extraction) some authors [6, 7] propose the rise of temperature whereas others prefer constant temperatures [8]. BEREGI [9] found unfavourable the use of temperatures over 50° at the last extraction. The starting period of extraction ranges in the literature from 30 minutes to 12 hours. In this connection it must be noted that the complete removal of aluminium is not of advantage since the catalyst becomes inefficient [11] (quantities up to 5% remain). Suited catalyst may be obtained when 10—25% of aluminium are removed [4]. In contrast to that, SMITH and coworkers [12], investigating the rate of hydrogenation of d-limonene, have proved that the conditions of the extraction and washing do not affect the activity of Raney nickel, whereas CORNUBERT and PHÉLISSE [3] have found that even certain, apparently insignificant factors such as the rate of introducing the portions of alloy into the alkali, may considerably influence the activity. Thus, when preparing catalysts of reproducible activity, they added precisely defined quantities of alloy in each unit of time.

The preparation of catalyst is ended by the process of washing which may also affect the activity. CORNUBERT and PHÉLISSE [6], using cinnamic acid as a model substance, found washing repeated three times optimal. The activity diminished in an increasing degree with each subsequent washing. In general, washing is repeated until the water becomes neutral against phenolphthalein. According to AUBRY [11] the traces of alkali protect the active metal and inhibit the oxidizing action of water. After removing the last traces of alkali (which is an extremely difficult task) Raney nickel slowly converts under the action of water into nickel hydroxide while hydrogen is produced. Usually 0.1—0.6% of alkali is the residue in catalysts. In contrast to these, MOZINGO [7] proposes for the complete removal of alkali a ten times repeated washing after the neutral reaction of water (against litmus).

Catalyst W6 prepared by ADKINS and BILLICA [8], which proved extremely active with many compounds, deserves to be mentioned separately.

Two methods are known to increase the activity of Raney nickel: the addition of different bases, on one hand, and of various precious metals, on the other.

ADKINS and BILLICA [8] have found that the addition of some triethylamine reduces the period of hydrogenation of aldehydes and ketones to half of the original, inhibiting, however, the hydrogenation of the aromatic ring. LIEBER and coworkers [13] used sodium hydroxide as addition, DELEPINE and HOREAU [15] studied the effect of Pt, Pd, Os, etc. No systematic researches were found in literature on the effect of other metals. LIEBER and various coworkers [13, 14, 16] dealt with a systematic study of the promoting action of $PtCl_4$, stating that the addition of $PtCl_4$ has, in general, favourable effect which increase upon addition of triethylamine. The promoting action in the latter case may possibly be explained by the formation of basic chloroplatinate $[(Et_3N)_2H_2PtCl_6]$.

Finally, we quote the compilation by BEREGI [17], stating the extreme conditions of preparing Raney nickel.

Methods of preparing the catalyst in literature :

Starting extraction	20% NaOH, 41—51 ml to 10 g of alloy ; period : 30 mins. to 12 hrs. ; temperature 0—120° C.
Last extraction	20% NaOH, 41—51 ml to 10 g of alloy ; period : 10 mins. to 48 hrs. ; temperature 50—120° C.
Total duration	from 40 mins. to 60 hrs.

Conditions of the industrial production of the catalyst, on the basis of the data of an American and a German plant :

	Method of	
	Raney Catalyst Co.	A. D. 44 (German)
1. Alloy applied	50% Ni, 50% Al	42% Ni, 58% Al
2. Quantity of alloy	272,1 kg	238 kg
3. Concentration of solution of sodium hydroxide	18,58%	13,1%
4. Quantity of sodium hydroxide (100%)	224 kg	392,7 kg
5. Quantity of solution of sodium hydroxide	1205 kg	2985,4 kg
6. Temperature of extraction	boiling point	95° C
7. Period of introduction of alloy	1,5—2,0 hrs.	10 hrs.
8. Period of extraction, subsequent to adding the alloy	6,5—7,0 hrs.	3 hrs.
9. Number of washings	8	15
10. Quantity of NaOH required theoretically for dissolving the Al content of 100 kg of alloy in form of AlO_2^-	74,07 kg	85,9 kg
11. Quantity of NaOH (100%) actually applied for dissolving 100 kg of alloy	83,3 kg	165 kg

Both catalysts show about identical activities. However, the German process, using a great excess of alkali, requires considerably longer time.

Experimental technique

The apparatus used at ordinary pressure and the method of measurement are identical with those described in an earlier paper [18], with the exception that the flask was adequately modified (see Fig. 1). Benzophenone, acetone, veratrol and eugenol were applied as model substances. At room temperature 0,01 mole benzophenone, acetone and eugenol, and 0,1 mole veratrol were hydrogenated. With the former compounds, the theoretical hydrogen uptake is 242,5 ml at 23°. Veratrol was hydrogenated in a rotating Andreas Hofer autoclave of acidproof steel (under gas heating) at a starting pressure of 30 atm and at 160°. The quantity of hydrogen taken up was calculated on the basis of the fall of pressure, using the formula

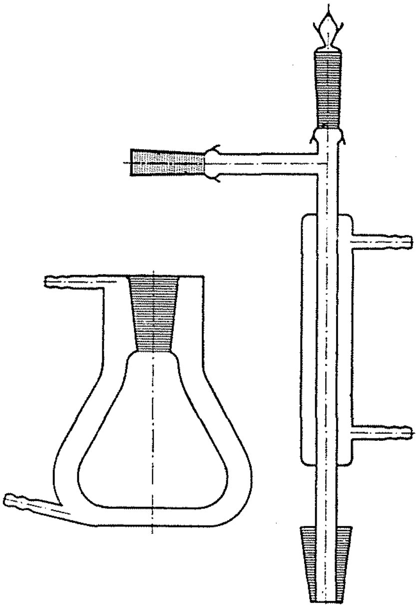


Fig. 1

$$dp = \frac{x}{a-b} \cdot 22{,}41 \text{ atm}$$

where x is the quantity of hydrogen (in moles) required theoretically, a is the total volume of autoclave and b is the volume of introduced substance.

The calculated fall of pressure was 13,4 atm at room temperature.

Veratrol (0,1 mole = 13 ml), Raney nickel (5 ml) and in certain experiments also triethylamine (2 g = 2,76 ml) were introduced in the carefully dried autoclave, then the volume of the reaction mixture was in each experiment completed to 50 ml with waterfree ethanol.

In the case of benzophenone, acetone and eugenol 1 ml of Raney nickel and in certain cases also 1 g (1,375 ml) of triethylamine were transferred into the autoclave and the total volume adjusted to 14 ml with waterfree ethanol.

In the experiments activated by precious metals, 0,125 millimole of $PtCl_4$ (dissolved in 1 ml ethanol) was added to 1 ml of 50/50 (see later) Raney nickel. Prior to starting hydrogenation, 1 ml of triethylamine was added.

The experiments proved to be reproducible within a limit of about ±10%.

Throughout the experiments, the catalysts were prepared from a commercial alloy of identical composition (50% Ni, 50% Al) and particle size, ground in a ball mill and passed through sieve Nr. 30.

Blank tests (1 ml of Raney nickel and 13 ml of waterfree ethanol) showed that the catalyst took up 9—10 ml of hydrogen in a period of 3 hours.

Experimental part

Preparation of catalysts

When preparing the catalyst, the temperature of extraction was varied (100, 50, 25 and 0° C). At 100° the catalyst was prepared according to COWERT and ADKINS [6]. At 50°, the preparation of catalyst was as follows [19]. Materials: 250 g of a 50% alloy of Ni-Al, 500 g of granulated NaOH *(purum)* and 2000 ml of distilled water. About 70 liters of distilled water are required for washing. A 5 liter beaker was placed in a 15 liter pot filled with ice water. A stirrer (an adequately bent glass rod) was inserted in the beaker. The rate of stirring was varied from 150 to 350 r. p. m. Then 500 g of NaOH *purum* was measured into a 3 liter beaker and distilled water added to obtain a 20% solution, meanwhile stirring with a glass rod. From the alkali solution 1250 ml were transferred into the 5 liter beaker and stirred until the temperature of the solution diminished to 15° (read in the thermometer located next to the stirrer). Now, the pulverized alloy was slowly dosed (possibly avoiding foam formation), care being taken to maintain the temperature below 30°. In general, the total quantity of alloy may be introduced within an hour when the pot is filled with a satisfactory amount of ice. Subsequently, the other half of the alkali solution was added to the reaction mixture, ice water was removed by suction, its volume replaced by hot water (50°) and the mixture kept at this latter temperature for 50 minutes under continuous stirring. Then the catalyst was allowed to cool and stand overnight in the solution of alkali. In the morning, the mother lye was decanted, the flask filled up with distilled water, and this process repeated 14 times. It is practical to carry out washing so as to include a complete night when the water shows already a neutral reaction against phenolphtalein. The catalyst obtained in this way may be stored under water. When a watersoluble and inexpensive substance is to be hydrogenated, the supernatant water may be decanted from the catalyst and the contact substance transferred into the compound to be hydrogenated by decantation repeated 2—3 times. When, however, a substance insoluble in water is to be hydrogenated, then decanting should be carried out with a solvent soluble both in water and in the substance to be hydrogenated (as ethanol, dioxane, acetone, etc.).

Since the model substances used in the present experiments were insoluble in water, the catalyst was washed, subsequent to decantation by water, with 95% ethanol, then with waterfree ethanol, and the ready-made substance stored under waterfree ethanol.

At 25° and 0°, catalysts were prepared according to COWERT and ADKINS [6], excepting the temperature of extraction. The flask with the alloy was kept at room temperature *i. e.* in an ice bath, respectively, for periods differing from those proposed by these authors (see later).

Preparation of catalysts by varying the duration of extraction (introduction of substance+treatment)

Three types of catalysts 25° and 0° were prepared. The periods of extraction were 50 minutes, 3 and 9 hours in the former case, and, 1,10 and 20 hours in the latter.

Catalyst W6 was prepared by a special washing process according to ADKINS and BILLICA [8].

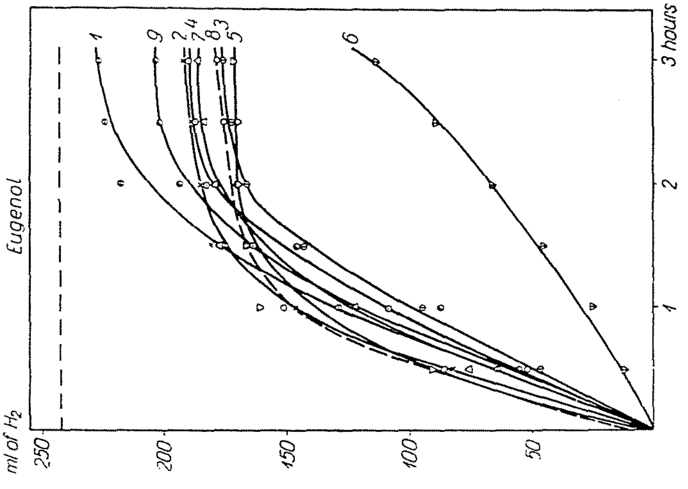
The quantity of catalyst obtained was 62 g of Ni and 7—8 g of Al. During storage, the activity of the catalyst decreased. However, when kept in ice box, it remained extremely active for about two weeks. After this period, its activity attained that of other Raney nickel catalysts prepared by other (previously mentioned) methods.

Investigation of the effect of catalysts on model substances

The best method to determine the effectiveness of catalysts is to measure their activity on various model substances. Eugenol, benzophenone, acetone and veratrol were chosen for this purpose, with the aim to compare the behaviour of compounds containing different functional groups. The given sequence simultaneously indicates also the decreasing capacity of hydrogenation. Under the conditions of the reaction (room temperature, ordinary pressure, and in the case of veratrol 160°, 30 atm initial pressure) the double bond of eugenol became saturated, the keto groups of benzophenone and acetone were hydrogenated to carbinols, whereas veratrol was converted into 1,2-dimethoxycyclohexane.

The results of the experiments are summarized in Table I and Figs. 2—5.

As the example of eugenol shows, the variation of the conditions of preparation of Raney nickel affects but slightly the hydrogenation of aliphatic


Eugenol
ml of H_2
250
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2
3 hours
1
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2
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7
8
3
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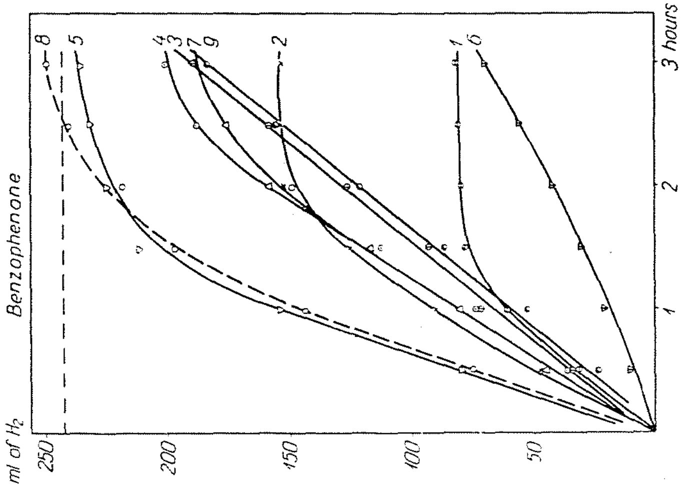
6

2


Benzophenone
ml of H_2
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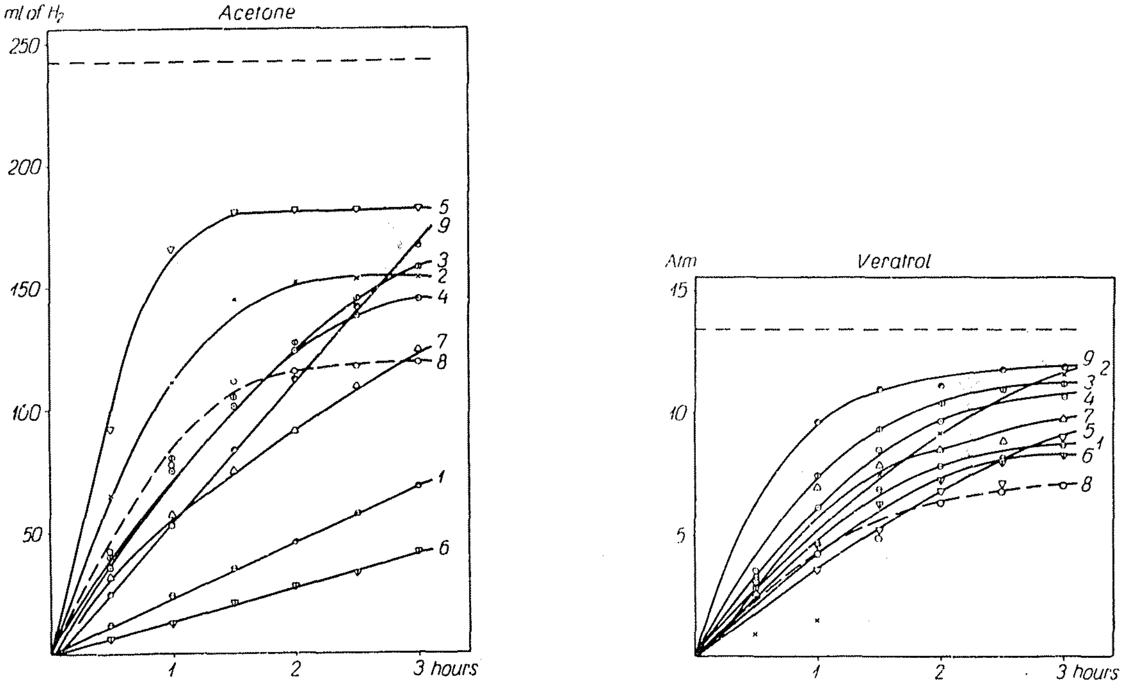

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Figs. 2—5. Hydrogen uptake of eugenol, benzophenone, acetone and veratrol with different catalysts. Curve 1 : catalyst extracted at 100°, curve 2 : catalyst extracted at 50°, curve 3 : catalyst extracted at 25° for 50 minutes, curve 4 : catalyst extracted at 25° for 180 minutes, curve 5 : catalyst extracted at 25° for 540 minutes, curve 6 : catalyst extracted at 0° for 60 minutes, curve 7 : catalyst extracted at 0° for 600 minutes, curve 8 : catalyst extracted at 0° for 1200 minutes, curve 9 : catalyst W6 double bonds. Fig. 2 indicates that the hydrogenation curves taken up with various catalysts run very close to each other which may be explained by the relatively easy saturability of the double bond. Here the catalyst extracted at 100° proved most active. The conditions of preparation of this type of catalyst are very similar to those applied in the Hungarian pharmaceutical industry. The rate of hydrogenation was only slightly affected by triethylamine.

Ketones proved considerably more sensitive against the changes of conditions of preparation of the catalyst. When the temperature of extraction was reduced, the activity of catalyst on benzophenone rose (Fig. 3). Catalyst 0/1200 was most active, followed closely by type 25/540, then 25/180 and 0/600. It is striking that type 100/420 (most active in the case of eugenol) showed here extremely weak effect. Triethylamine had, in general, favourable action, being most active when applied simultaneously with the otherwise very inefficient catalyst 100/420.

Lower extraction temperatures were more favourable in the case of acetone as well (Fig. 4). Here catalyst 25/540 proved most active, type 100/240 being among the weakest. Hydrogenation was promoted by the presence of triethylamine.

Table I

Catalyst	Eugenol	Benzophenone	Acetone	Veratrol
100/420	53/93	25/33	10/28*	35/65
100/420+T	52/96	36/88	34/75*	21/37*
50/50	61/79	37/63	46/64	11/86*
50/50+T	48/73	45/66	56/62	55/65
50/50+Pt	74/81	7/27	12/38	6/21
50/50+Pt+T	58/90	59/89	62/94	13/30
25/50	39/73	30/78*	33/65*	55/84
25/50+T	55/83	50/83	51/82	53/79
25/180	45/78	30/83	31/60	46/79
25/180+T	47/80	38/52	41/74	35/77*
25/540	67/71	63/98	68/74	22/67*
25/540+T	70/85	58/92	72/80	19/49*
0/60	10/47*	9/29*	5/17*	34/62
0/60+T	34/86	15/46*	24/64*	34/51
0/600	55/77	33/78	24/51*	52/73
0/600+T	44/77	35/73	38/65	32/67*
0/1200	63/71	59/100	33/49	33/52
0/1200+T	58/71	44/71	33/51	22/37
W6	36/84	21/77*	22/69*	72/87
W6+T	44/84	36/95	41/98	45/86

(In the first column of Table I, T signs triethylamine and Pt $PtCl_4$ as additions. The numerator of the fraction indicates the temperature (in centigrades), the denominator the duration (in minutes) of the extraction. The activity of catalyst is shown also by a fraction where the numerator indicates the percentage of hydrogen uptake in 1 hour, the denominator that in 3 hours, referred to the quantity required for complete saturation. In the case of data signed by an asterisk, hydrogen uptake was not completed in 3 hours.)

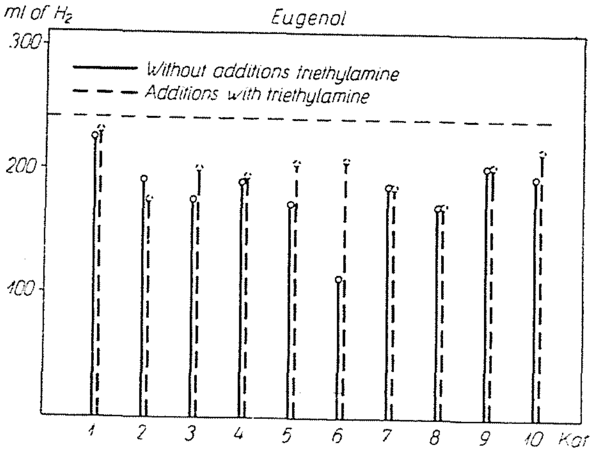
Catalyst W6 proved most active in the hydrogenation of veratrol (aromatic ring) (Fig. 5), followed next to 25/50. By applying longer periods of extraction, the activity of the 25° and 0° catalysts was reduced. Triethylamine diminished the activity in each experiment.

The bending ends of the curves of Figs. 2—5 shows that with various catalysts the process is terminated after the uptake of different amounts of hydrogen. In other words, hydrogenation proceeds with a given catalyst only to a degree characteristic of this catalyst, *i. e.* the substrate takes up solely a portion of the calculated quantity of hydrogen (indicated in the figures by a horizontal dotted line). Experiences have proved [20] that the uptake of hydrogen in the case of a given catalyst can not be increased beyond certain limits by raising the quantity of the catalyst, thus, applying excess catalyst above an optimal amount does not lead to a more complete hydrogenation.

It can be clearly seen with each model substance, excepting eugenol, that the quantity of hydrogen taken up may vary very widely by changing the conditions of preparation of the catalyst (Figs. 2—5). In general, increased hydrogen uptakes were observed with more active catalysts (where hydrogen uptake was quicker).

Figs. 6—9 shows the quantities of hydrogen taken up with various catalysts during the experimental period (with additions and without them) in the sequence of their effectiveness. The ending points of the vertical lines sign (in most cases) the termination of hydrogenation. This way, these figures clearly indicate which catalyst is most suited for the hydrogenation of a given model substance, showing also the action of addition (triethylamine).

Catalyst 50/50 (activated by $PtCl_4$) deserves to be mentioned separately. No special action has been observed with eugenol (Fig. 10). The activity on benzophenone and acetone decreased under the action of $PtCl_4$, the effect being in the presence of triethylamine stronger than that of 50/50 (Figs. 11—12). The addition of $PtCl_4$ proved unfavourable in the hydrogenation of veratrol (Fig. 13), whereas the addition of triethylamine proved efficient, although the activity ranged even in this latter case below that attained with catalyst 50/50.


ml of H_2
Eugenol
300
200
100
Without additions triethylamine
Additions with triethylamine
1
2
3
4
5
6
7
8
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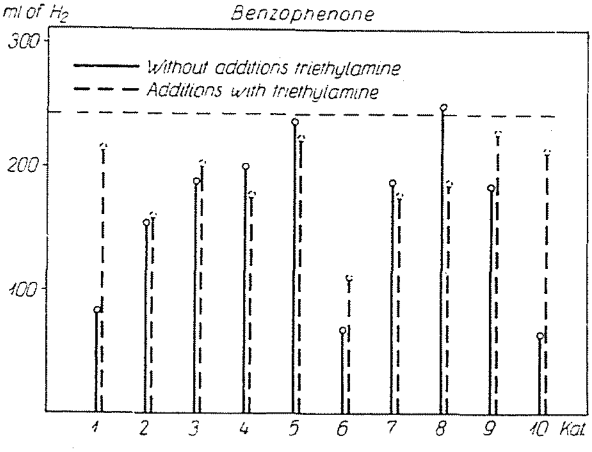
10
Kat

6


ml of H_2
Benzophenone
300
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Additions with triethylamine
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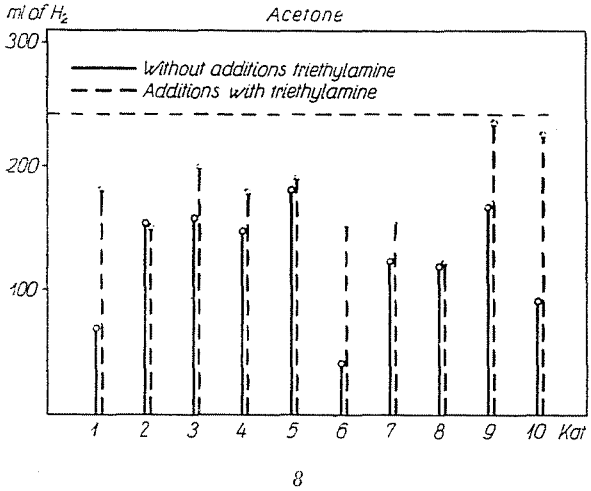
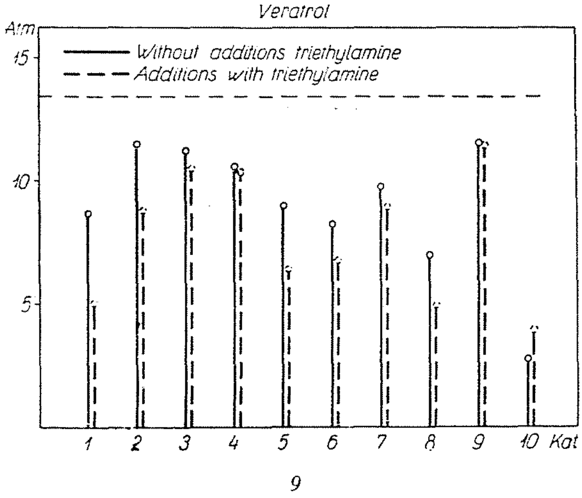
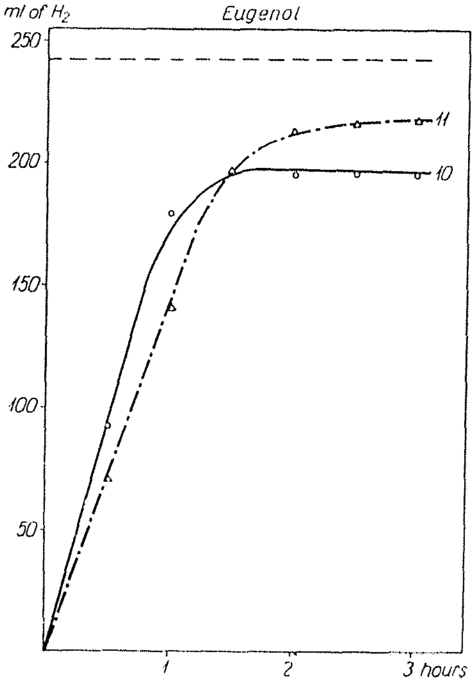




Figs. 6—9. Hydrogen uptake of eugenol, benzophenone, acetone and veratrol in 300 minutes with various catalysts without additions and with triethylamine. Legend of curves 1—9 as in Figs. 2—5. Curve 10 : catalyst extracted at 50° + $PtCl_4$, curve 11 : catalyst extracted at 50° + $PtCl_4$ + triethylamine


ml of H_2
Eugenol
250
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1
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3 hours
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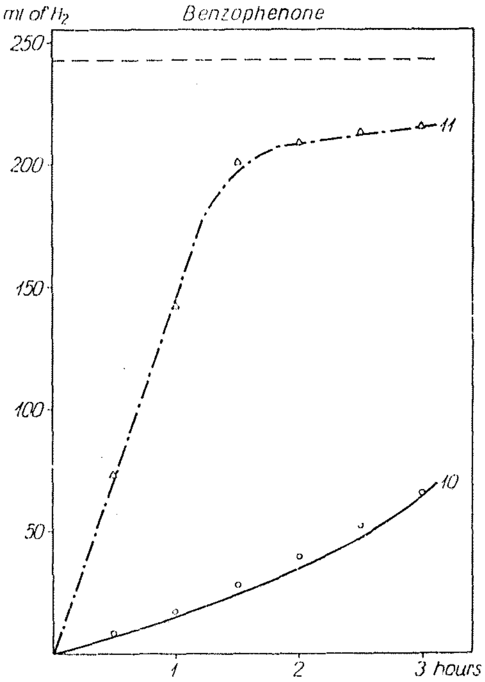
10

10


ml of H_2
Benzophenone
250
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3 hours
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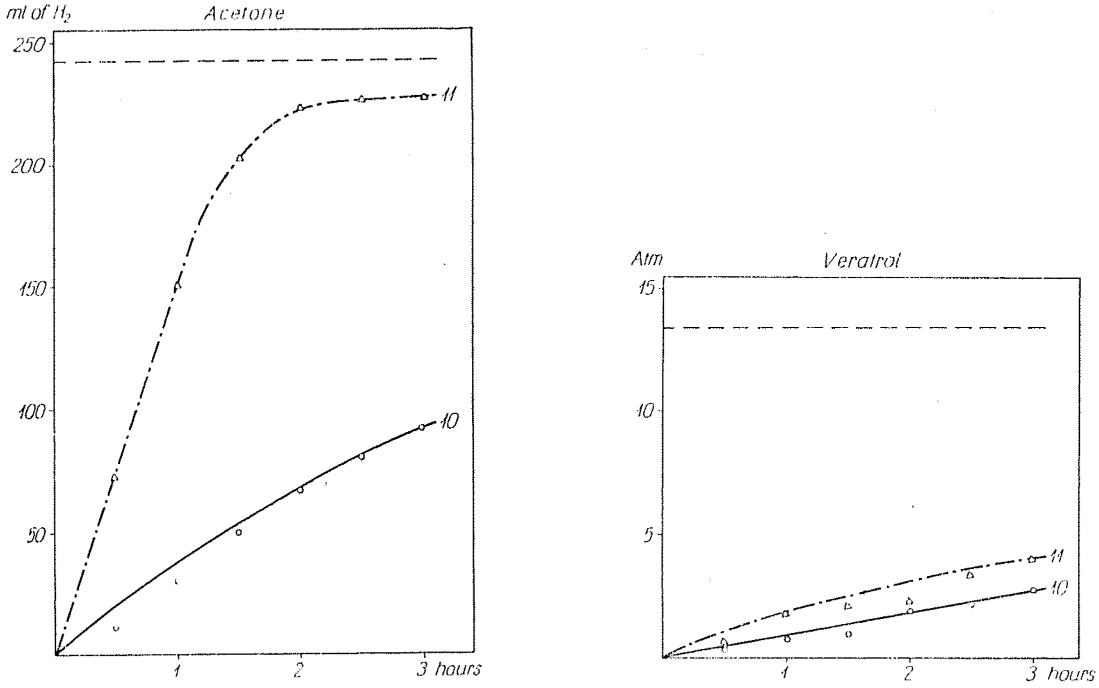

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Figs. 10—13. Hydrogen uptake of eugenol, benzophenone, acetone and veratrol. Catalyst 50/50. Additions: $PtCl_4$ (10) and triethylamine (11)

Discussion of experimental results

The present experiments have proved that the activity of the generally known and used Raney nickel catalyst may be influenced by changing the conditions of its praparation. This observation is not a new one, examples being mentioned in the literature. However, the data available refer, in general, only to the method of preparation and the action on various model substances of a given type of Raney nickel. Thus, it is impossible — in lack of a basis for comparison — to state how the activity of differently prepared Raney nickel catalysts changes.

The present investigations clearly showed that in any case it is practical to "adjust" the catalyst to the given compound, *i. e.* the hydrogenation of compounds with identical functional groups may be carried out by identical types of catalyst at a fair yield. Thus, for instance, the Raney nickel catalyst obtained by extraction at 100° (used generally in the industry) is far below the optimum degree with many model substances (excepting the hydrogenation of aliphatic double bonds). A catalyst of significantly increased activity was found to be obtainable for a given compound when the conditions of preparation are modified in a not decisive manner.

The differences in activities due to the different methods of preparation manifest themselves not only in the rates of hydrogenation but also in the degree to which hydrogenation may proceed (different states of "Equilibrium"). With the model substances studied this double property of the catalyst was, in general, parallel, *i. e.* catalysts increasing the rate of hydrogenation generally attained a higher degree of hydrogenation as well, excepting, however, certain special cases.

In accordance with data reported in the literature it has been found that the addition of bases may increase the rate of hydrogenation. However, this accelerating action may be different on various functional groups and may convert in certain cases into an inhibiting effect (*e. g.* hydrogenation of aromatic ring). Further, when the same model substance is hydrogenated by different catalysts, the action of added alkali may vary: the weaker the activity of catalyst, the stronger the effect of addition. In general, $PtCl_4$ proved efficient only when triethylamine was added.

II. EFFECT OF ALKALI ADDITIVES ON THE ACTIVITY OF RANEY NICKEL

By
Z. Csűrös, J. Petró and J. Mérész

Literature

Delepine and Horeau [15] starting from the observation that pinonic acid (a ketocarboxylic acid) may be quicker hydrogenated when the quantity of alkali exceeds the amount theoretically required, investigated the effect of alkali additions on about 40 different carbonyl compounds. Although the action of alkali was already known prior to the statements of Delepine [21], the observations had not been systematically evaluated. According to Delepine [15] the rate of hydrogenation may increase to the threefold, fourfold or in certain cases to the tenfold values. With Raney nickel activated by precious metals the action of alkali may be even stronger.

Some years later Reasenberg, Lieber and Smith [22] studied other types of compounds and found that certain quantities of sodium hydroxide might completely inhibit the reduction of nitrobenzene. Similar effects, although to a smaller degree, were observed on other, neutral nitrocompounds as well. In contrast to that, the addition of sodium hydroxide proved favourable upon the hydrogenation of methyl ethylketone, being slightly weaker upon the reduction of benzaldehyde and of some acid and basic nitrocompounds. In essence, the same results were found by Lieber and coworkers in a later communication [14], stating that alkali (NaOH) has a poisoning action on the hydrogenation of isomeric salts of nitrobenzoic acid and of nitrobenzene, whereas a promoting effect manifested itself upon the hydrogenation of the methylates and ethylates of nitrobenzoic acid.

Paul [23] found upon the hydrogenation of furfural that on the addition of sodium hydroxide not only the rate of hydrogenation increased but also the ring became partially hydrogenated which, up to this date, could only be attained by the use of platinum catalyst.

In addition to inorganic alkalies, the action of organic bases was also studied. When using catalyst W6, Adkins and Billica [8] observed that the period required for the hydrogenation of aldehydes and ketones was reduced on the addition of triethylamine to half of the original value or sometimes to yet lower values. Even certain selective action appeared insofar as the benzene ring of aromatic compounds remained intact in the presence of triethylamine and the hydrogenation of the ring was completely avoided upon the hydrogenation of a naphthylketone the aromatic portion of which is, otherwise, readily hydrogenated.

Lieber and coworkers [16] increased the promoting action of $PtCl_4$ by adding triethylamine. In hydrogenations carried out with the use of Raney

Table II

Bases	Dissociation constant at 25°
A) Inorganic bases	
Potassium hydroxide	—
Sodium hydroxide	—
Ammonia	—
B) Organic bases	
1. Aliphatic amines	—
Diethylamine	$1{,}26 \cdot 10^{-3}$
Triethylamine	$5{,}65 \cdot 10^{-4}$
Ethylene diamine	$8{,}5 \cdot 10^{5}$
Diethanolamine	—
Triethanolamine	—
2. Cyclic amines	
Piperidine	$1{,}6 \cdot 10^{-3}$
3. Aromatic amines	
Aniline	$3{,}83 \cdot 10^{-10}$
Methylaniline	$5{,}0 \cdot 10^{-10}$
Dimethylaniline	$5{,}20 \cdot 10^{-4}$
o-Toluidine	$5{,}3 \cdot 10^{-10}$
m-Toluidine	$5{,}3 \cdot 10^{-10}$
p-Toluidine	$2 \cdot 10^{-9}$
Pyridine	$1{,}4 \cdot 10^{-9}$
Quinoline	$6{,}3 \cdot 10^{-10}$
Diphenylamine	$7{,}6 \cdot 10^{-14}$
C) Other additions	
1. N-containing compounds of big molecule	
Malachitegreen	
Tetramethyl diamino diphenylmethane	
2. N-containing surface-active substances (and colloidal electrolytes, quaternary salts)	
Cetyl trimethyl ammonium bromide	
Cetyl pyridinium bromide	
Benzyl phenyl dimethyl ammonium chloride	

nickel, the combined action of $PtCl_4$ + triethylamine proved strongest on various compounds.

It is rather difficult to explain the action of alkali. The presumption that alkalies promote enolization and in this way activate the substance to be reduced, is contradicted by the fact that this effect may be observed also with carbonyl compounds not capable of being enolized. Foresti and Chiume [24] assume the activation of catalyst as an explanation of the effect of alkali.

Experimental technique

The apparatus and technique was identical with that described in an earlier communication [18].

Hydrogenations were carried out at room temperature and ordinary pressure.

Throughout the experiments 1 ml of 50/50 Raney nickel (extracted at 50° for 50 minutes) was applied as catalyst.

The substrate was throughout 0,01 mole of substance, the hydrogen uptake of which at room temperature is theoretically 242,5 ml.

The quantity of alkali added was 0,001 mole. When two types of alkali were added, 0,001 mole of each was applied.

Waterfree ethanol was used as a solvent. The total volume of the reaction mixture was completed throughout the experiments to 14 ml.

The model substances were acetone, acetophenone and benzophenone. The alkalies added are listed in Table II.

Experimental part

Acetone, acetophenone and benzophenone were chosen as model substances since, according to data reported in the literature [15, 21, 8] and to authors' own experiences, the action of added alkali is best observed upon the hydrogenation of the keto-group. Further, ketones of a structure were chosen (purely aliphatic, aliphatic aromatic and purely aromatic) to make possible certain careful conclusions on the correlation of structure and capability of hydrogenation. Another argument in favour of choosing benzephenone was that here the possibility of enolization is completely excluded. As the action of additions of alkali may perhaps be explained by enolization, this latter model substance seemed extremely promising in solving this problem.

Fig. 14 shows the hydrogen uptake of the mentioned model substances. When selecting bases, their strength and structure were considered. Both inorganic and organic bases were applied. The organic bases include aliphatic, aromatic and cyclic amines, containing primary, secondary and tertiary N-atoms. The substituting group in the aromatic amine was om-, and p-positioned against the amine-group.

Figs. 15, 16 and 17 show the hydrogen uptakes measured with these bases. The region of their activity seems to be strikingly wide-spread.

Since the quantity of base (0,01 mole referred to the substrate) was voluntarily chosen, also the amount of addition was varied in certain experiments, mainly with the best and weakest bases. The results are shown by Figs. 18 and 19.

The action of ethylene diamine and pyridine (substances showing on our model compounds strong inhibiting effects) and that of dimethylaniline and triethylamine (which had catalytic effects) were tested on eugenol as well (Fig. 20).

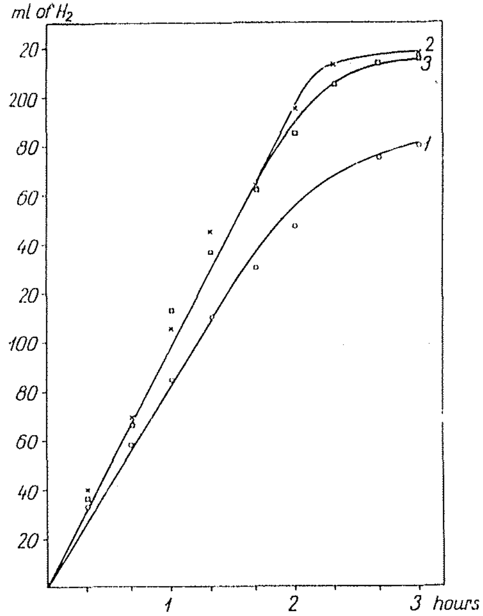


Fig. 14. Hydrogen uptake of acetone (1), acetophenone (2) and benzophenone (3)

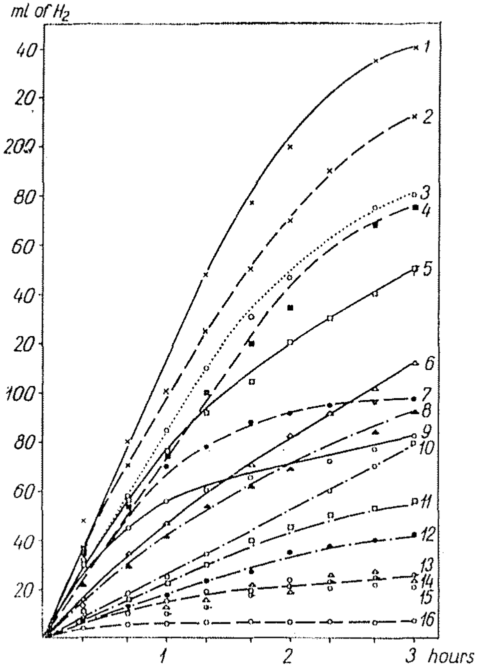


Fig. 15. Hydrogen uptake of acetone in the presence of organic bases. 1 — dimethylaniline, 2 — triethylamine, 3 — without any additions, 4 — piperidine, 5 — methyl aniline, 6 — diphenylamine, — 7 diethylamine, 8 — p-toluidine, 9 — aniline, 10 — quinoline, 11 — o-toluidine, 12 — m-toluidine, 13 — triethanolamine, 14 — diethanolamine, 15 — pyridine, 16 — ethylene diamine

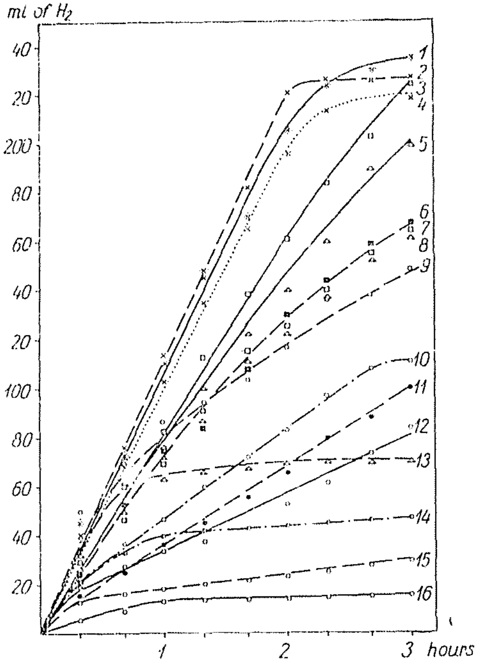


Fig. 16. Hydrogen uptake of acetophenone in the presence of organic bases. 1 — dimethyl-aniline, 2 — triethylamine, 3 — methylaniline, 4 — without any additions, 5 — diphenylamine, 6 — o-toluidine, 7 — piperidine, 8 — p-toluidine, 9 — diethylamine, 10 — m-toluidine, 11 — ethylene diamine, 12 — aniline, 13 — triethanolamine, 14 — quinoline, 15 — di-ethanolamine, 16 — pyridine

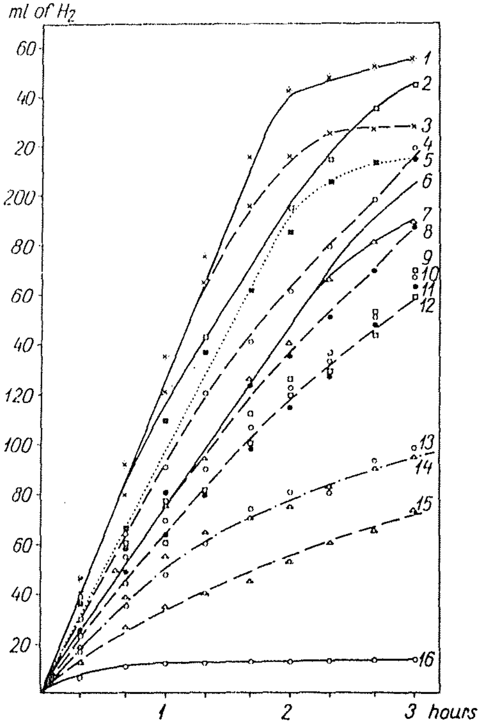


Fig. 17. Hydrogen uptake of benzophenone in the presence of organic bases. 1 — dimethylaniline, 2 — methylaniline, 3 — triethylamine, 4 — diethylamine, 5 — without any additions, 6 — aniline, 7 diphenylamine, 8 — triethanolamine, 9 o-toluidine, 10 — ethylene diamine, 11 — quinoline, 12 — piperidine, 13 — p-toluidine, 14 — m-toluidine, 15 — diethanolamine, 16 — pyridine

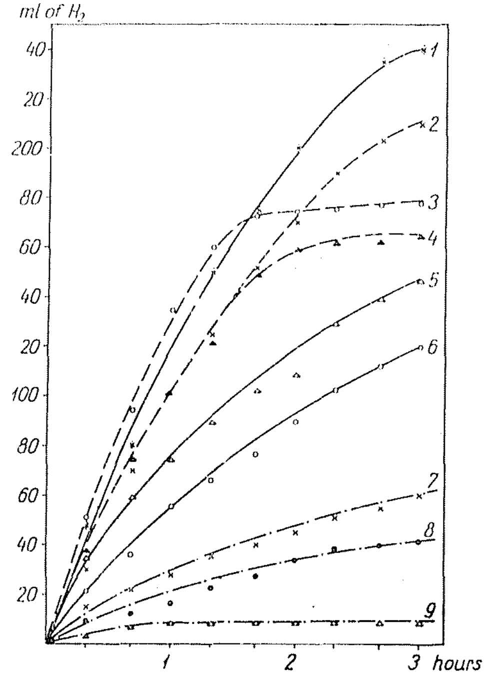


Fig. 18. Effect of various quantities of organic bases on the hydrogenation of acetone (*m* = moles added). 1 — dimethylaniline 0,001 m, 2 — triethalmine 0,001 m, 3 — triethylamine 0,01 m, 4 — triethylamine 0,0001 m, 5 — dimethylaniline 0,0001 m, 6 — dimethyl aniline 0,01 m, 7 — m-toluidine 0,0001 m, 8 — m-toluidine 0,001 m, 9 — m-toluidine 0,01 m

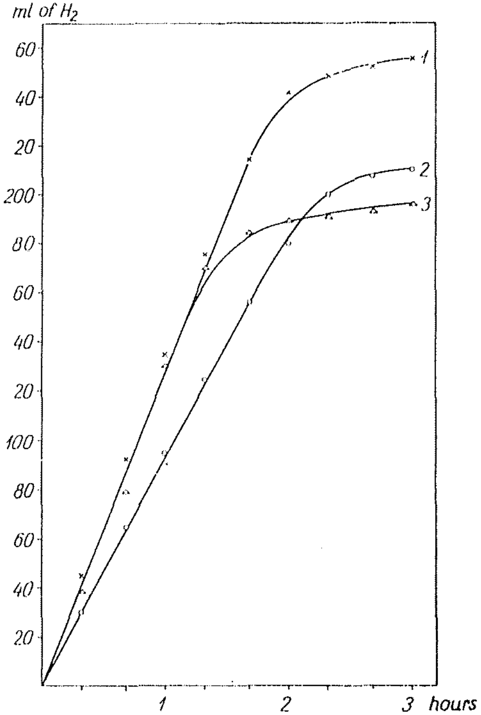


Fig. 19. Effect of various quantities of dimethylaniline on the hydrogenation of benzophenone, (m = moles added). 1 — 0,001 m, 2 — 0,01 m, 3 — 0,0001 m

Figs. 21, 22 and 23 show hydrogen uptakes measured the presence of various additions of inorganic bases (NaOH, KOH, NH_4OH).

The present experiments were carried out in a medium of waterfree ethanol where the dissociation *i. e.* the strength of various bases plays an insignificant role. Separate tests were conducted on the sole watersoluble model, acetone with various quantities of added water and strongly dissociating inorganic bases to solve the question how the action of base is affected by the dissociation (Fig. 21).

Some measurements were devoted to observing the effect of organic and inorganic bases added simultaneously (Figs. 24*a*, *b*, *c*, 25 and 26*a*, *b*). Only such couples as proved efficient with the other two models were further tested on acetophenone (Fig. 25).

Finally, also the action of other additions was investigated characterized by the presence of an N-atom. These additions included organic dyes, surface-active substances and quaternary salts of big molecule. The results are shown in Figs. 27, 28 and 29.

Discussion of the experimental results

In the group acetone, acetophenone and benzophenone, the hydrogenation of acetone was most difficult whereas both others could be almost equally hydrogenated (Fig. 14). One may draw the conclusion that the aromatic ring next to the carbonyl increases the capability of hydrogenation of this carbonyl. This seems possible since the aromatic ring or rings next to the carbonyl increase the polarized property of the carbonyl group, due to their electron repulsing action.

When evaluating the action of added alkalies, it seems striking that the statement according to which the addition of bases promotes the hydrogenation of the carbonyl group is far from being generalizable. In fact, only a few of the bases tested proved active, most of them showing an impeding or at least inhibiting effect on the uptake of hydrogen (Figs. 15, 16 and 17). Another observation of importance is that no correlation was found between basicity and activity (see also Table I indicating dissociation constants), although it must be repeatedly emphasized that the investigations were carried out in a non-aqueous medium where dissociation has but a minor significance.

The addition of dimethylaniline and triethylamine was of the strongest action in the case of each three model substances. The tertiary N-atoms of both compounds have single pairs of electrons.

The authors are of the opinion that the added organic bases, which accelerate the uptake of hydrogen, may form with the substrate an intermediate complex more capable of reacting, in addition to activating the catalyst as presumed by Foresti and Chiume [24]. This opinion seems to be confirmed by the fact that

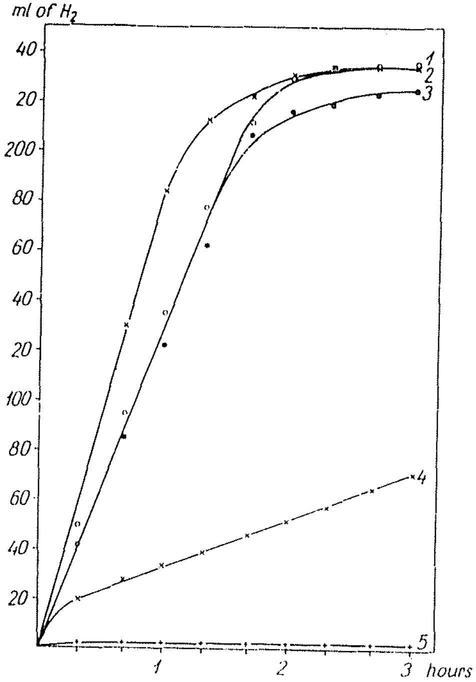


Fig. 20. Effect of organic bases on the hydrogenation of eugenol. 1 — dimethylaniline, 2 — without any additions, 3 — triethylamine, 4 — ethylene diamine, 5 — pyridine

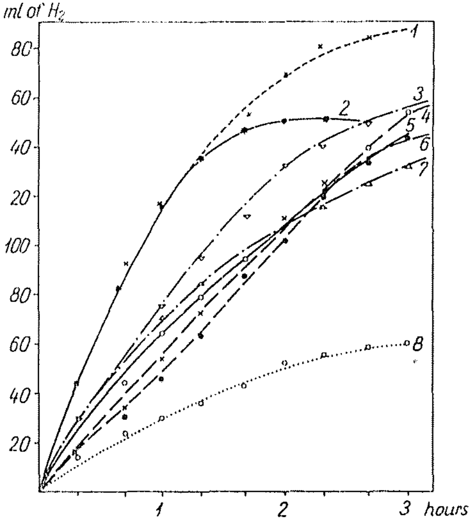


Fig. 21. Hydrogen uptake of acetone in the presence of various inorganic bases added, in non aqueous solutions and in solutions containing various quantities of water, respectively. 1 — without any additions, 2 — NaOH in waterfree ethanol, 3 — KOH in 70% ethanol, 4 — NH_3 in 70% ethanol, 5 — NaOH in 70% ethanol, 6 — NH_3 in waterfree ethanol, 7 — KOH in waterfree ethanol, 8 — NaOH in water

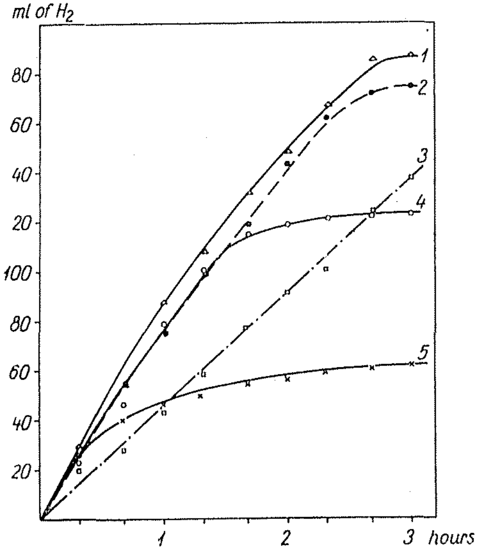


Fig. 22. Hydrogen uptake of acetophenone in the presence of various inorganic bases (m = moles added). 1 — NaOH, 2 — KOH, 3 — NH_3, 4 — NaOH (0,1 m), 5 — NaOH (0,01 m)

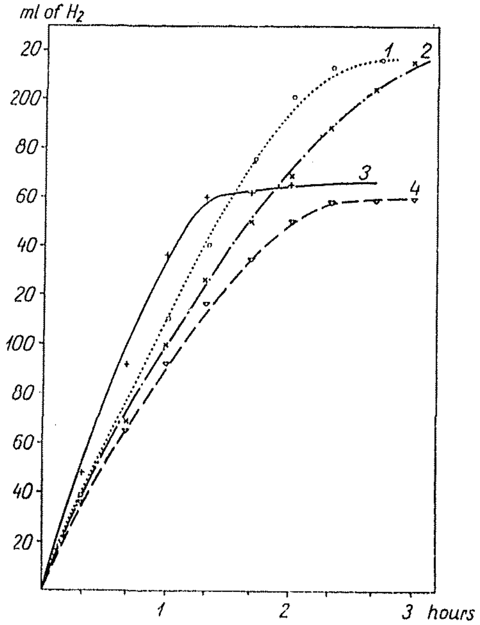
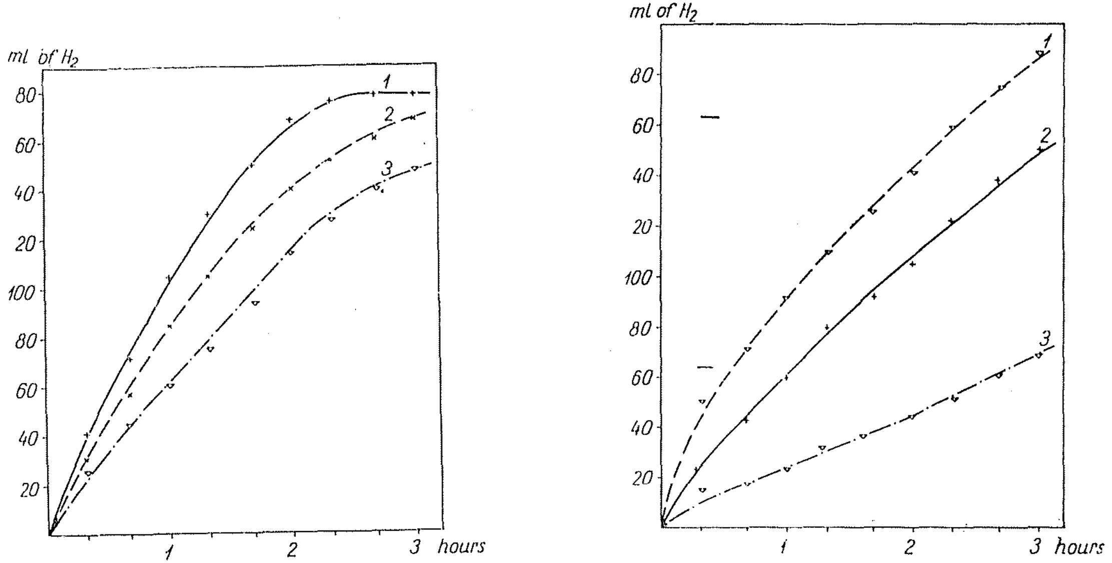


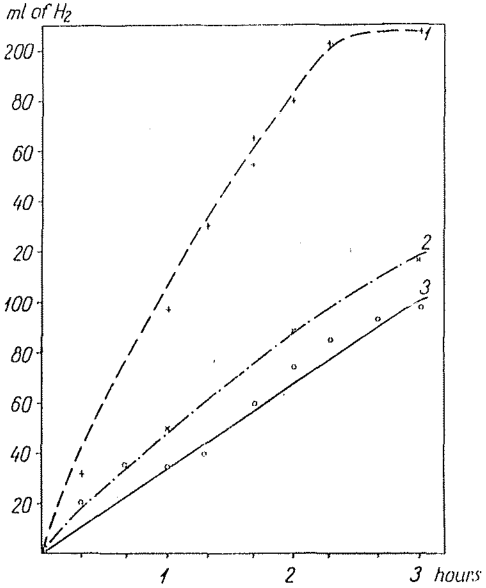
Fig. 23. Hydrogen uptake of benzophenone in the presence of inorganic bases. 1 — without any additions, 2 — NH_3, 3 — NaOH, 4 — KOH

Fig. 24. Hydrogenation of acetone in the presence of various inorganic bases and of:



24/a diethylamine 1 — NaOH+diethylamine, 2 — KOH+diethylamine, 3 — NH_3+diethylamine;

24/b quinoline 1 — KOH+quinoline, 2 — NaOH+quinoline, 3 — NH_3+quinoline;



24/c triethanolamine 1 — KOH+triethanolamine, 2 — NH_3+triethanolamine, 3 — NaOH+triethanolamine

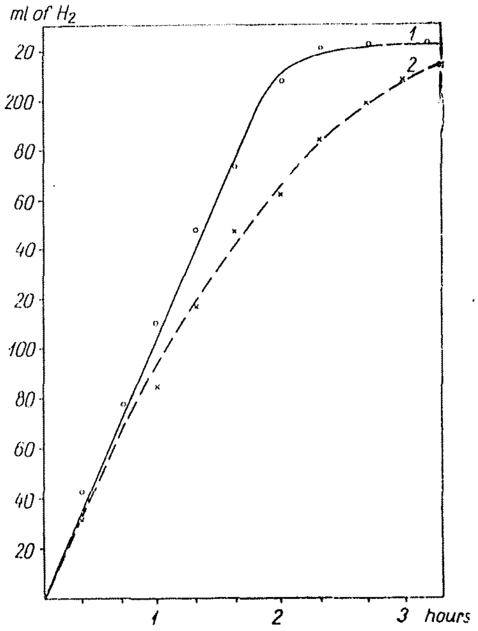
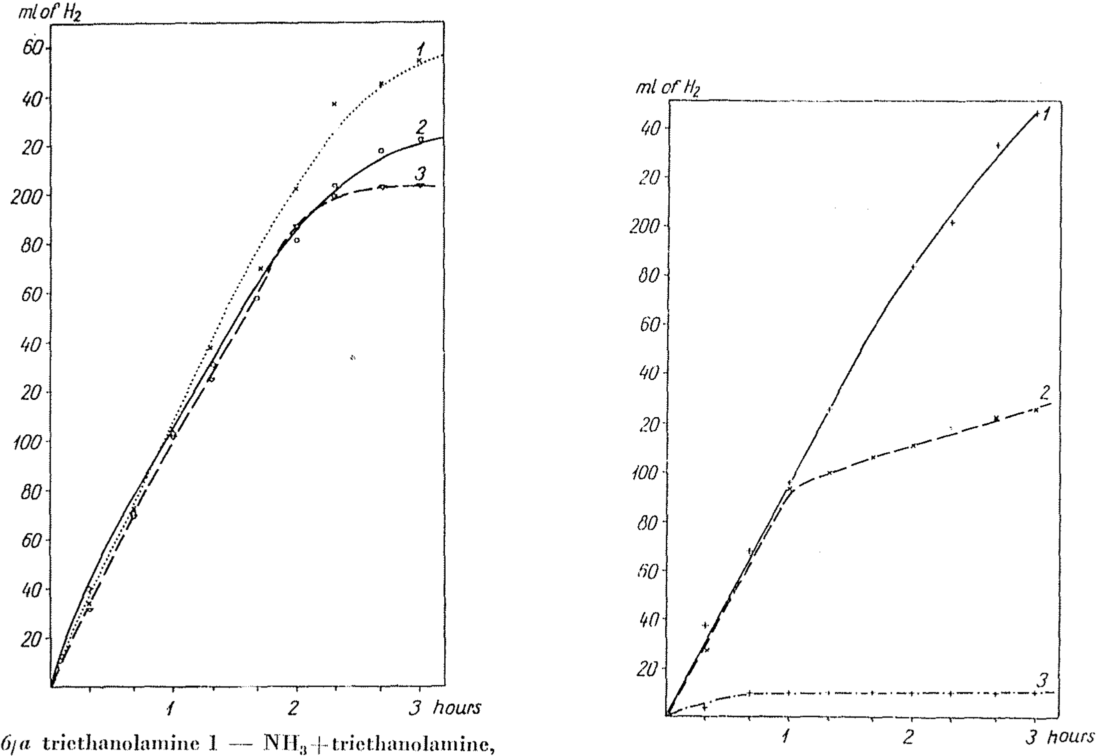


Fig. 25. Hydrogenation of acetophenone in the presence of. 1 — piperidine+NaOH, 2 — triethanolamine+NH_3

Fig. 26. Hydrogenation of benzophenone in the presence of various inorganic bases and of



26/a triethanolamine 1 — NH_3+triethanolamine, 2 — NaOH+triethanolamine, 3 — KOH+triethanolamine;

26/b piperidine 1 — NaOH+piperidine, 2 — NH_3+piperidine, 3 — KOH+piperidine the action of such organic bases [according to the literature 2, 3, 4] is quite considerable in the reduction of strongly polar functional groups (carbonyl, nitro groups) where it is easier to assume the existence of an addition complex whereas they show no or but a slight effect on less polar groups (as aromatic rings).

Thus, the action of triethylamine and dimethylaniline may be explained as follows. The carbonyl group consists, owing to the negative static inductive and tautomeric effect of the =O atom, of a C atom with a partially positive charge and of a partially negative oxygen. The tertiary N atom (with a negative static inductive and positive static tautomery action) may be linked to the partially positive carbon of carbonyl through its single pair of electrons, increasing the already existing inductive action. The increased capability of reaction may be explained this way.

Dimethylaniline exceeded triethylamine in activity. On the basis of the previously discussed presumption, this may be explained by the existence of an aromatic ring in dimethylaniline, in a position adjacent to the N-atom. The electron repulsing action of this ring may result in a motility of the sole pair of electrons of the N atom, and this way, in increasing the aforementioned effect in the addition complex of loose structure. According to the opinion of the authors, the hydrogenation of acetone is more difficult than that of acetophenone and benzophenone because in the latter, owing to the structure of the molecule the carbonyl is more polar. The addition of alkali further promotes this effect (weaker action), whereas in the case of acetone the total effect must be substituted by the molecule of the added substance which manifests itself in a more favourable action on hydrogenation.

Among the additions applied triethanolamine had a tertiary and diethanolamine a secondary N atom. The mobility of their single pairs of electrons was, however, presumably hindered by the OH groups located at the end of the chains.

The other bases presumably either stabilize the carbonyl group or poison the catalyst. To solve the problem, ethylene diamine (primary amine) and pyridine were chosen, which latter when added, almost completely inhibited the uptake of hydrogen. As a model substance, this time another functional group, the readily saturable aliphatic double bond of eugenol, was selected. Its hydrogenation was carried out with the mentioned additions both of which proved to have inhibiting action on the uptake of hydrogen (with pyridine no hydrogen was taken up) (Fig. 20). The action may be due to the poisoning of the catalyst. In contrast to that, amines promoting the hydrogen uptake of ketones (as dimethylaniline, triethylamine) facilitated also the saturation of the aliphatic double bond of eugenol (dimethylaniline) and were inefficient (triethylamine) without inhibiting the process. The activating action of dimethylaniline may be explained in a similar manner.

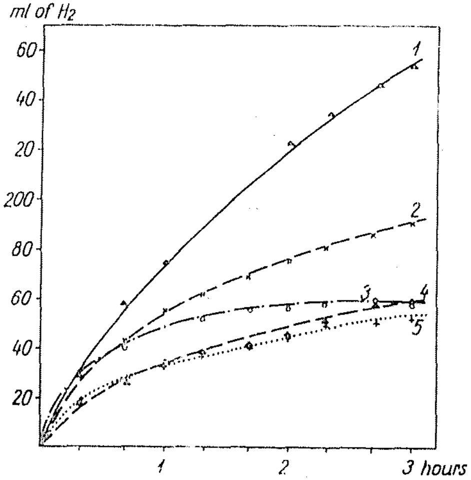


Fig. 27. Hydrogenation of acetone in the presence of other nitrogen-containing substances. 1 — tetramethyl diaminodiphenylmethane, 2 — cetyl pyridinium bromide, 3 — cetyl trimethyl ammonium bromide, 4 — malachitegreen, 5 — benzyl-phenyl-dimethyl ammonium chloride

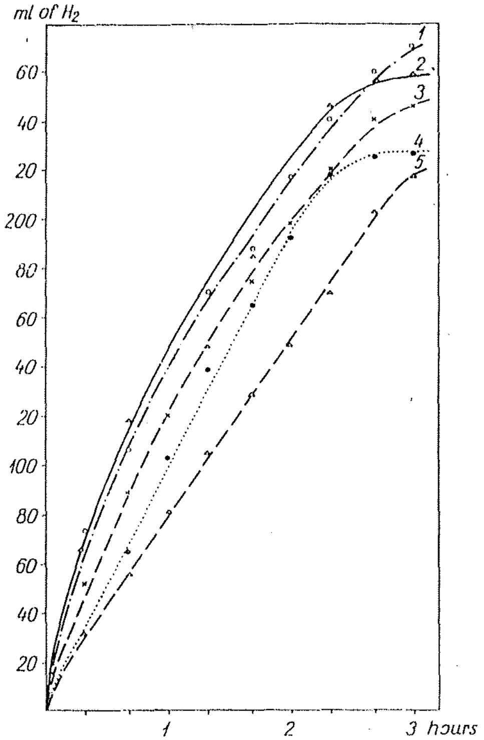


Fig. 28. Hydrogenation of acetophenone in the presence of other nitrogen-containing substances 1 — cetyl trimethyl ammonium bromide, 2 — tetramethyl diamino diphenylmethane, 3 — cetyl pyridinium bromide, 4 — benzyl-phenyl-dimethyl ammonium chloride, 5 — malachitegreen

The present experiments proved as well that certain additions are poisonous in any concentration (as m-toluidine, Fig. 18). Bases found active showed definite optimum values of concentration (as dimethylaniline, Figs. 18 and 19). When dimethylaniline is added in great quantities (as 1 : 1), it presumably gets readily adsorbed by the catalyst, acting thus as a poison to the catalyst.

The effect of added inorganic bases dissolved in waterfree ethanol was investigated as well. In contrast to data reported of the literature, their effect was rather unfavourable, inhibiting, instead of being a promoting one (Figs. 21, 22 and 23).

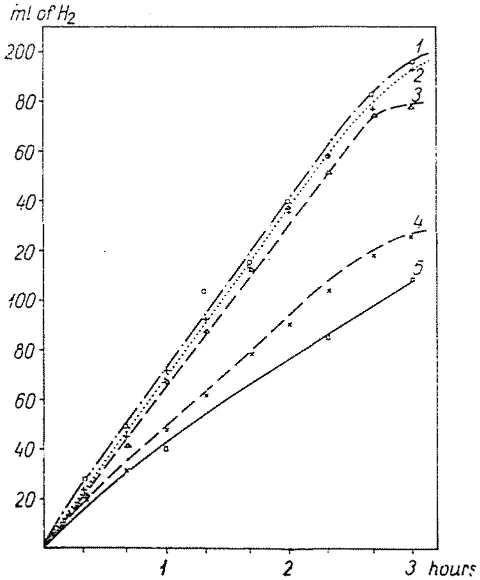


Fig. 29. Hydrogenation of benzophenone in the presence of other nitrogen-containing substances. 1 — cetyl trimethyl ammonium bromide, 2 — benzyl-phenyl-dimethyl ammonium chloride, 3 — malachitegreen, 4 — cetyl pyridinium bromide, 5 — tetramethyl diamino-diphenylmethane

Some experiments were conducted with acetone in aqueous ethanol and in water to clear up whether the action of strongly dissociating inorganic bases changes with increased dissociation. It was found that the inhibiting effect of added sodium hydroxide increases steadily with the rise of water content (Fig. 21).

Upon the simultaneous addition of inorganic and organic bases which latter proved, when applied alone, to have inhibiting effect, their action was combined and, in general, rather good results were attained. For benzophenone generally NH_3, for acetone KOH was the inorganic partner of advantageous effect (Figs. 24*a*, *b*, *c*, 25 and 26*a*, *b*).

It is of interest to note that similarly good effects could not be attained when the bases were added alone even when applied in higher concentrations.

Other additions proved to have unfavourable action on acetone excepting the almost inefficient tetramethyl diaminodiphenylmethane. Cetyl trimethyl ammonium bromide, tetramethyl diamino diphenylmethane (quaternary compounds) and benzyl phenyl dimethyl ammonium chloride were active and did not inhibit, respectively, in the case of benzophenone and acetophenone. It can be stated that compounds in this group have, generally, unfavourable effects, due presumably to their high steric demand.

Summary

I

The changes of the activity of Raney nickel were investigated as a function of the conditions of preparation. The experiments have led to following results :

1. The activity of catalyst may considerably influenced by the variation of the temperature and period of extraction.
2. The addition of bases and metal compounds (as $PtCl_4$) affects the activity of catalyst as well.
3. The degree of hydrogenation is different when the same compound is treated with Raney nickel prepared by different methods.
4. On the basis of the previous observations, in a given case the catalyst of optimum action should be selected according to the nature of the compound to be hydrogenated or at least to the functional group of this compound. A similar case exists in the case of alkali additions as well.

II

The investigations proved that the addition of organic bases may affect favourably the hydrogenation of acetone, acetophenone and benzophenone, although effects of a more or less inhibiting action were also observed. Additions of inhibiting effect act as poisons to the catalyst. In the case of additions which proved efficient, it is advisable to determine the optimum concentration. Addition of dimethylaniline in a quantity of 0,1 mole referred to the subtrate was found most active. Triethylamine proved active as well. The simultaneous use of inorganic and organic bases which, when applied alone proved inefficient or of an inhibiting action, may lead to active effects. The addition of inorganic bases and N-containing organic substances of large molecule (dyes, quaternary salts) was found inefficient and unfavourable, respectively.

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