9. 2,4-Dimethoxybenzoyl-*o*-benzoic acid, its methyl ester and ammonium salt have been made from the dihydroxy acid.

10. The phenylhydrazone of dihydroxybenzoyl-benzoic acid has been prepared.

11. 3,5-Dibromo-2,4-dihydroxybenzoyl-*o*-benzoic acid and its tri-acetate have been prepared and studied. The action of dry ammonia gas on the dibromo acid and the formation of eosin by heating the acid have been investigated.

12. The anhydride of the mono-acetate of dibromo-dihydroxybenzoyl-benzoic acid has been prepared.

13. The diacetate of the anhydride of the dibromo acid has been prepared.

14. This investigation confirms the theory that the formation of fluorescein (like that of other phthaleins) takes place in two stages and that 2,4-dihydroxybenzoyl-*o*-benzoic acid is the intermediate product.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

ORGANIC REACTIONS AT THE SURFACES OF DEHYDROGENATING CATALYSTS

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In considering the causation of organic reactions it has seemed advisable to investigate experimentally the behavior of representative organic compounds at the surfaces of those catalysts whose most pronounced characteristic is to remove hydrogen from the organic molecule. In particular, an attempt is being made to correlate the dehydrogenating and the hydrogenating power of a catalyst. Since it has been recently demonstrated[1] that the relative proportion of reactions taking place at the surface of alumina and titania are quite dependent upon physical characteristics of the surface, it seemed desirable to find out whether the reactions taking place with nickel, copper, iron and zinc catalysts were similarly dependent or were characteristic of the metal present. To this end the behavior of ethanol, ethyl acetate, acetal, ether, acetaldehyde and acetic acid at the surfaces of various catalysts containing these metals has been investigated, as has the hydrogenation of ethylene over nickel. The data accumulated are so extensive that only an abstract of them can be presented. While possibly there is no relationship between mass and trustworthiness of data, it should be pointed out that the conclusions given in this paper are based

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[1] Adkins and Nissen, THIS JOURNAL, **46**, 130 (1924).

on the results of over 225 experiments that have involved the analysis of probably 300 samples of gas, 75 analyses of catalysts and numerous analyses of the liquid products of the reaction. Crucial experiments have been repeated again and again with various preparations of catalyst, etc.

Statement of Results

Ethanol over Nickel Catalysts.—There appear to be two distinct types of nickel catalysts, so far as our experience goes. One type is produced when nickelic or nickelous oxide (Ni_2O_3 or NiO) either with or without a support is reduced by methyl, ethyl or butyl alcohol at temperatures from 350° to 420°. The other type is produced by the reduction of the same materials with hydrogen (or carbon monoxide) at temperatures from 300° to 400°. As far as analytical methods indicate, there is complete reduction with alcohol in from 30 to 60 minutes at 420°. With hydrogen complete reduction requires perhaps 12 hours at 400°, although we have usually allowed it to proceed for a few hours longer.

There is not only a distinct difference in the time of reduction but even more marked differences in activity and in the relative efficiency for different reactions. At 420° the nickel catalyst "by alcohol" will produce an average of 13 liters per hour of gaseous products. Under the same conditions an equal amount of nickel catalyst "by hydrogen" will produce about 5.5 liters per hour. The nickel catalyst "by alcohol" causes alcohol to react to give about 1% of carbon dioxide, 30% of monoxide, 30% of ethane, 38% of hydrogen and some free carbon. If it is assumed that the hydrogen is a measure of the aldehyde formed, it may be calculated that over 80% of the aldehyde formed is decomposed into carbon monoxide and methane. This assumption is not entirely correct, for aldehyde itself gives some hydrogen over nickel; hence it is more correct to say that a nickel catalyst reduced by alcohol decomposes practically all the aldehyde that is formed at 420°. The nickel catalyst "by hydrogen" gives a gas that is about 24% of carbon monoxide, 24% of methane and 50% of hydrogen; no carbon is formed. It breaks up only about one-half of the aldehyde that it forms at 420°. There is thus a marked divergence between the catalytic activity of the nickel reduced by hydrogen and by alcohol both with respect to total activity and to the relative amount of aldehyde formed as compared to the amount that is decomposed.

The lower activity of the nickel "by hydrogen" with respect to the amount of alcohol dehydrogenated and more especially the greatly decreased power to split the aldehyde formed is not due to poisoning of the catalyst by grease, etc., during the reduction with hydrogen. This was demonstrated by reducing the usual amount of nickel oxide with alcohol at 420° for 20 minutes and then passing hydrogen over it for 15 hours at a temperature of 400°. At the end of this time the catalyst behaved towards ethyl alcohol exactly as though it had not been treated with the hydrogen at all. It behaved like a nickel catalyst reduced by alcohol.

No permanent injury is done to the catalyst when it is reduced with hydrogen. A catalyst so reduced and manifesting low activity and power to split aldehyde was re-oxidized in place and then treated with alcohol; it behaved as though it had not been treated with hydrogen and was like the nickel catalyst "by alcohol."

There was no apparent change in activity at the point where analytical methods showed that the nickel was all in the metallic condition. The activity for the decomposition of alcohol was unchanged at the end of five hours' use.

It apparently makes no difference in either the amount or manner of the decomposition of alcohol whether the catalyst is reduced by hydrogen at 300° or 400° although of course the reduction takes place more slowly at the lower temperature. Whether the decomposition of the alcohol over a nickel catalyst is carried out at 350° or 420° affects the amounts but not the relative proportions of the reaction products. The activity was about 3 liters of gaseous products per hour at 350°.

Nickel oxide without a supporting material behaves essentially like the oxide on pumice except that due to the greater density of the catalyst and concentration of the oxide it is more difficult to obtain complete reduction. After reducing such a catalyst for 15 hours with hydrogen at 400°, the initial reaction for alcohol was typical for nickel "by alcohol." However, after 30 minutes the activity had decreased markedly and the catalyst then decomposed such a portion of the aldehyde formed as to indicate that the reaction had become that induced by nickel "by hydrogen." On account of the high activity of nickel "by alcohol" it is readily conceivable that a very small amount of unreduced oxide could bring about this initial reaction, thus masking the effect of the nickel "by hydrogen."

Hydrogenation of Ethylene over Nickel Catalysts.—In order to ascertain the relationship, if any, between the ability of a catalyst to promote dehydrogenation of alcohol and its ability to catalyze a hydrogenation reaction, the two types of nickel catalysts ("by hydrogen" and "by alcohol") noted above were used for the hydrogenation of ethylene. The nickel reduced by alcohol caused the formation of 2.3 liters of ethane per hour at 300° and 4.1 liters at 200°. The nickel reduced by hydrogen overnight at 420° caused the formation of 1.5 liters of ethane at 300°, and a catalyst reduced at 300° caused the formation of 3.6 liters of ethane at 200°.

It may be seen that while a nickel catalyst reduced by alcohol is over 100% more effective for dehydrogenating alcohol and 300% more effective in breaking the aldehyde so formed, it is only from 15 to 50% more effective as a hydrogenating catalyst. These two types of nickel are being used for other hydrogenations.

Ethyl Acetate over Nickel Catalysts.—It has been stated[2] that ethyl acetate over catalytic nickel gives propane and carbon dioxide. Mr. Brynjulv H. Nissen, to whom is due credit for the earlier experimental work in this Laboratory on nickel catalysts, identified the hydrocarbon produced by the action of a nickel catalyst as methane, not propane. Very small quantities of ethane may also be produced, but by the utilization of the adsorption of hydrogen by palladium and the combustion of the pure hydrocarbon it was definitely shown that no propane was formed. This work has been verified.

The behavior of ethyl acetate over nickelic oxide, nickelous oxide, nickel reduced by hydrogen and nickel reduced by alcohol has been observed. There is apparently no difference between the activities of nickel catalysts obtained by reducing the two oxides with ethyl acetate. There is a marked difference in that while ethyl acetate begins to reduce nickelic oxide immediately at 420°, nickelous oxide is entirely unacted upon at that temperature. When, however, the oxide is raised to 450° or 460° for a minute or two, reaction begins and will continue at 420°, and thereafter there will be no difference between the catalysts from the two oxides. Such catalysts will produce at 420° about 5 liters of gas per hour, which 20 minutes after the beginning of the reaction is shown by analysis to contain 11% of carbon dioxide, 1.5% of ethylene, 27% of carbon monoxide, 27% of methane and 31% of hydrogen. Thirty minutes later the methane had increased to 40% and the hydrogen decreased to 19%. An hour after the first analysis there was 48% of methane and 11% of hydrogen, the proportion of the other gases remaining unchanged. A nickel catalyst that has been completely reduced (as far as analytical methods indicate), either by hydrogen for 12 hours at 420° or by alcohol for an hour at 420°, has quite a small activity against ethyl acetate at 420°, only a few hundred cubic centimeters of gas being produced. When, however, such an inactive catalyst is oxidized in the catalyst tube it regains the activity and the characteristics of a nickel catalyst that has not been reduced by alcohol or by hydrogen even though it is quickly reduced to a condition that analysis indicates to be metallic nickel. A considerable volume of carbon is formed by all active nickel catalysts in this reaction. Less than 0.4% of acetic acid was produced, probably through the action of the catalyst support, pumice.

Alcohol and Acetic Acid over Nickel Catalysts.—In an attempt to throw some light on the mechanism of the reaction of ethyl acetate over nickelic oxide, glacial acetic acid and an equimolecular mixture of this compound and ethyl alcohol were passed over the above catalysts at 420°. Acetic acid yielded about 2 liters of gas in an hour, consisting of 27% of

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[2] Bancroft, (a) *Trans. Am. Electrochem. Soc.*, **37**, 51 (1920). (b) "Applied Colloid Chemistry," McGraw-Hill Book Co., New York, **1921**, p. 45. (c) *J. Ind. Eng. Chem.*, **14**, 546 (1922).

carbon dioxide, 9% of ethylene, 21% of carbon monoxide, 6% of methane and 36% of hydrogen. It seems significant that when these figures are averaged with those obtained for ethyl alcohol under the same conditions, the result is almost identical with that obtained experimentally for ethyl acetate. The results obtained by passing the mixture of ethyl alcohol and acetic acid over the catalyst were not so illuminating. In this case the activity was 6 liters, a value between that obtained for the two constituents when present alone. The gas contained 6% of carbon dioxide, a trace of ethylene, 25% each of carbon monoxide and methane and 44% of hydrogen, indicating that the ethyl alcohol reaction is much more rapid than the acetic acid reaction. This is in harmony with the relative activities when these two substances were used alone.

Ethanol over Iron Catalysts.—The variation in the percentage of gaseous products and of the reactivity of ethanol over various iron catalysts is depicted in Fig. 1. The percentage of saturated hydrocarbons determined by combustion has been *calculated* as methane. It has been demonstrated by the use of palladium as an absorbent for the hydrogen and by the combustion of the hydrocarbons remaining that about equal parts of methane and ethane existed in the gas produced by the precipitated hydrated ferric oxide. The same is probably true for the similar catalysts from the ignition of the nitrate and oxalate.

The iron catalysts from the alkyl ferrites and the reduced iron are similar to each other in that they produce very little reaction other than straight dehydrogenation, being quite similar to copper. This is in marked contrast to the other iron catalysts which produce from 20 to 25% as much hydrocarbon calculated as methane as they do hydrogen. The difference between the iron catalysts from the alkyl ferrites and that from hydrated ferric oxide is not due to a greater ease of reduction of the former which would of course result in their being similar to the reduced iron. The converse is apparently true, although in both cases the extent of reduction of iron oxide by alcohol at 400° is so small as to appear to be negligible.

Ethanol and *iso*Propanol over Copper Catalysts.—Copper catalysts have been made from several different compounds, and while they vary in activity all of them give almost pure hydrogen from ethanol or *iso*propanol at temperatures below 350°. Catalysts were prepared by the reduction of cupric oxide and cuprous oxide, and by the decomposition of copper oxalate and copper formate. No answer has been obtained to the question as to whether catalysis is due to metallic copper or to an oxide on the surface present in too small amounts to be detected by chemical analysis.

The Behavior of Ethanol, Acetaldehyde, Diethyl Ether, Acetal and Acetic Acid over Various Zinc, Iron and Nickel Catalysts is summarized in Table I. These results are correlated in a later section. Outstanding facts are that zinc oxide has been selectively activated for dehydrogenation and dehydration of ethanol so that with extreme catalysts there is in one case six times and in the other four times as much dehydrogenation as dehydration. The production of carbon dioxide is also a modifiable characteristic of zinc catalysts.

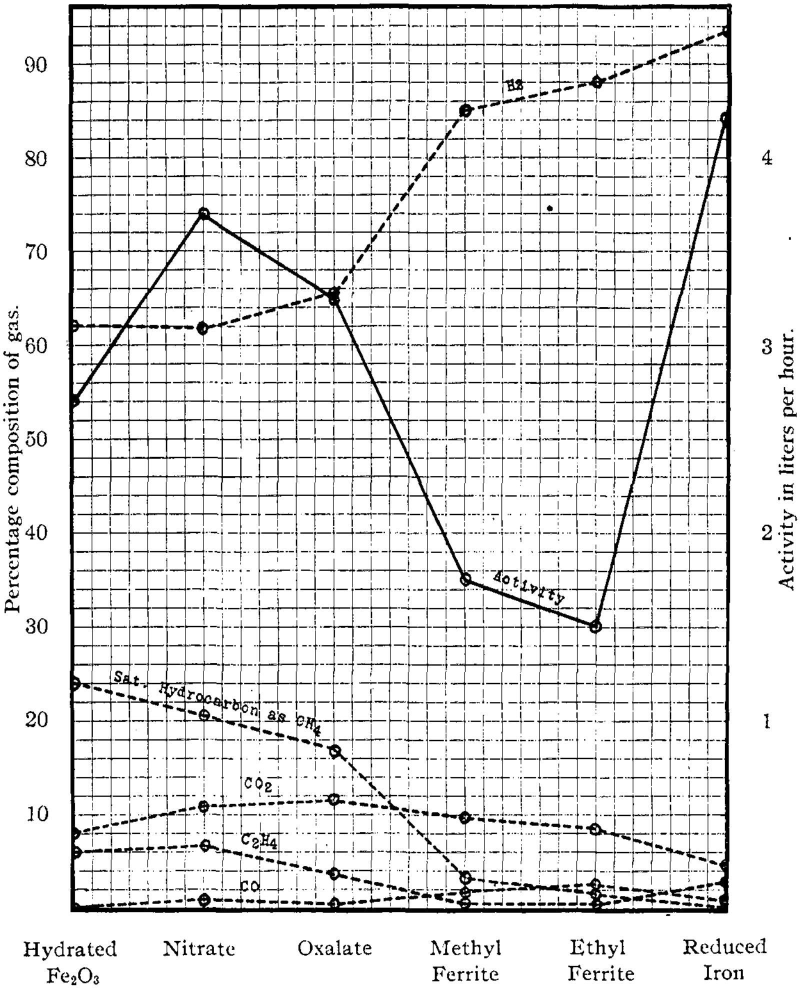

Fig. 1.—Reaction products of ethanol over iron catalysts at 400°.

The percentages of carbon monoxide, carbon dioxide, ethylene, hydrogen and saturated hydrocarbons produced by iron catalysts from various sources, indicated at the bottom, are shown by the circled dots connected by the dotted lines, the numerical values being indicated on the left. The liters of gaseous products from these same catalysts are similarly shown by the solid line, the numerical values being indicated at the right.

A nickel catalyst reduced by alcohol is five times as effective against acetaldehyde as one reduced by hydrogen. The former catalyst is quite active against ether or acetal while the latter is inactive. Very marked cases of selective activation of iron and zinc catalysts are to be found in the behavior of various types towards acetaldehyde, acetal and ether.

Table I

Various Compounds over Dehydrogenating Catalysts

Catalyst + (source)	Temp. °C.	Activity Liters	CO_2 %	C_2H_4 %	CO %	C_nH_{2n+2} %	H_2 %
Ethanol							
ZnO (*iso*propoxide)	400	2.9	5	19	0	0	76
ZnO (ethoxide)	400	2.5	4	20	0	0	76
ZnO (hydroxide)	400	1.8	0.5	13	0	0	86
ZnO (nitrate)	400	0.5	No gas analysis				
Acetaldehyde							
Ni (by alcohol)	420	10.8	2	0	44	37	17
Ni (by hydrogen)	420	2.3	4	1	44	37	13
Fe_2O_3 (hydrated)	400	16.8	40	1	4	5	50
Reduced iron	400	2.3	25	2	19	7	47
ZnO (*iso*propoxide)	400	3.6	35	1	4	5	55
ZnO (hydroxide)	400	0.9	10	1	36	36	16
Ethyl Ether							
Ni (by alcohol)	420	4.6	2	16	20	31	31
Ni (by hydrogen)	420	0.7	1	16	22	23	37
Fe_2O_3 (hydrated)	400	0.5	26	23	6	17	28
Reduced iron	400	0.8	7	19	4	5	64
ZnO (*iso*propoxide)	400	1.2	12	39	1	5	43
ZnO (hydroxide)	400	0.7	2	36	1	6	55
Acetal							
Ni (by alcohol)	420	5.3	5	3	28	33	31
Ni (by hydrogen)	420	0.7	6	7	15	50	22
Fe_2O_3 (hydrated)	400	3.2	24	3	3	29	42
Reduced iron	400	1.7	11	5	5	24	54
ZnO (*iso*propoxide)	400	1.9	19	16	4	18	43
ZnO (hydroxide)	400	0.6	7	14	7	46	27
Ethyl Acetate							
Fe_2O_3 (hydrated)	400	1.6	58	6	1	18	17
Reduced iron	400	1.1	20	7	4	2	67
ZnO (*iso*propoxide)	400	1.7	42	23	1	1	33
ZnO (hydroxide)	400	0.3	No gas analysis				

Correlation of Results

One of the outstanding facts uncovered in this work is that there are two distinct types of nickel catalysts, both of which are indicated by chemical analysis to be 100% nickel. (It is realized that chemical analysis cannot give a decisive answer to the question as to whether the real catalyst is elementary nickel or a film of oxide on the surface.) These two nickel catalysts differ according to the reducing agent used in producing them. While the nickel catalyst reduced by alcohol as compared with the one reduced by hydrogen is at least twice as active in dehydrogenating alcohol, it is so much more active in breaking down acetaldehyde to carbon monoxide and methane that it produces almost no acetaldehyde from ethanol. The nickel catalyst "by alcohol" is only slightly superior to the hydrogen-reduced nickel as a catalyst for the reduction of ethylene to ethane, but is five times as effective in splitting pure acetaldehyde, and many times as effective against ethyl ether or acetal. In contrast to this is the fact that neither of these nickel catalysts is effective against ethyl acetate, whereas a catalyst reduced by ethyl acetate itself from nickel oxide is active against the ester or the alcohol, although in this case as in the others, the nickel is completely reduced according to analytical standards.

Pease and Taylor[3] have shown that the reduction of copper and of nickel by hydrogen is a case of a reaction at an interface of metal and oxide. The reduction is slow and requires many hours to go to completion. Reduction by alcohol is a very rapid reaction and it seems possible that it is not a case of reaction at the interface of metal and oxide. Alcohol molecules certainly combine with oxygen atoms attached to metals and the evidence is conclusive that in the case of the oxides of nickel as with alumina, titania, etc., the *oxide* brings about a *catalytic* decomposition of the alcohol. That is, some alcohol molecules react at the surface of nickel oxide without removing oxygen from the nickel, although in a comparatively short time enough of the alcohol molecules do take oxygen atoms to form acetaldehyde and water to reduce the nickel oxide. It is reasonable to believe that reduction by alcohol or by other compounds which have a strong tendency to combine with oxygen linked to metals and which are themselves in a state of reactivity is not dependent upon the condition of an interface of metal and oxide.

It may readily be seen that when the two reducing agents act through these two different processes the resultant distribution of nickel atoms (or of the short chains of atoms spoken of by Langmuir) will be very different. Hence, to the extent that the "spacial configuration of the active points" of the catalyst plays a part, the relative proportions of the induced reactions will be effected.

A very worth-while contribution to the knowledge of the function of the nickel catalyst in hydrogenation has been recently made by M. C. Boswell.[4] Boswell believes that "nickel oxide partially reduced at a low temperature consists of particles of nickel oxides surrounded by metallic nickel carrying positive hydrogens and negative hydroxyls alternately arranged." Fur-

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[3] Pease and Taylor, THIS JOURNAL, **43**, 2179 (1921).

[4] Boswell, *Trans. Roy. Soc. Canada*, **16**, 1 (May, 1922).

ther reduction consists in the removal of the hydroxyl by a positive hydrogen and its replacement on the surface by a negative hydrogen, this being a very slow reaction. Oxygen is again drawn to the surface to form hydroxyl groups which are essential, according to Boswell, for catalytic activity. When no more hydroxyl groups are left in the surface the catalyst is inactive as it is covered with hydrogen.

Some support is given to Boswell's idea by the fact that it has been found that nickel reduced by ethyl ether, acetal or ethyl acetate is reactive towards the decomposition of these compounds, while a catalyst rather completely reduced by hydrogen is inactive. These compounds behave as though an hydroxyl group was on the nickel to which they were attached. That is, when they are adsorbed on this type of catalyst they behave as though the reaction $ROR + (H^+)\ (OH^-) \longrightarrow 2ROH \longrightarrow$ took place; they behave like their hydrolysis products.

Willstätter[5] among other investigators came to the conclusion that there must be oxygen at the nickel surface in order that it may function as a catalyst. On the other hand, so careful and thorough workers as Armstrong and Hilditch[6] think that there is no necessity for this belief. However much one may be inclined to agree with Willstätter and with Boswell, it must be pointed out that the type of experimentation on which the former depended is valueless and the latter's is inconclusive. Boswell's evidence is largely based on the fact that a partially reduced nickel catalyst is better for hydrogenation than a completely reduced one. Willstätter found (as did Voorhees and Adams[7] in the case of platinum) that the catalyst was much more active for hydrogenation after it had been treated with oxygen. We have found that a similar treatment of a nickel catalyst reduced by hydrogen greatly increases its activity towards any dehydrogenation or decomposition reactions. This reactivation is not due to the addition of oxygen, for the latter is quickly removed and within a few minutes there is no more oxygen on the catalyst than there was before reactivation, but the increased activity is retained during hours of use. It may well be that the beneficial effect of treating the catalyst with oxygen is that poisoned or inactivated points or atoms on the catalyst are oxidized and then reduced with the result that they are once more effective. Moreover, in the case of a hydrogen-reduced catalyst, treatment with oxygen and then reduction with an organic reducing agent gave a much more effective catalyst than it had *ever* been before. It was *activated*, not only *re*activated. Moreover, it possessed the property of producing a different *proportion* of reactions than did the catalyst before the oxygen treatment.

The utter futility of attempting to assign to any particular metallic

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[5] Willstätter and Waldschmidt-Leitz, *Ber.*, **54**, 113 (1921).

[6] Armstrong and Hilditch, *Proc. Roy. Soc.* (*London*), **102**, 27 (1923).

[7] Voorhees and Adams, THIS JOURNAL, **44**, 1398 (1922).

oxide any particular reaction or proportion of reactions has been further experimentally demonstrated. The metal present on the oxide is of less importance than the relationships existing on the surface of the oxide, and these are dependent upon various factors that are being experimentally investigated in this Laboratory.

While iron oxide as made by the drying of precipitated hydrated ferric oxide or by the ignition of the nitrate gives about 20% as much of the reactions involving the formation of saturated hydrocarbons as it does of dehydrogenation when alcohol is passed over it, yet this is not an inherent property of iron oxide, for by the use of an iron oxide prepared from an alkyl ferrite no saturated hydrocarbons are formed. This latter type of iron oxide is almost identical in its effect with copper or metallic iron in giving a straight dehydrogenation of alcohol with the formation of acetaldehyde and hydrogen.

Similarly, while the zinc oxide from zinc hydroxide dehydrogenates six times as much alcohol as it dehydrates, the zinc oxide from zinc *iso*propoxide dehydrogenates only four times as much as it dehydrates. The catalyst from the butoxide was intermediate between these two, as it was in the case of the alumina catalysts. There was also a difference in that the zinc oxide from the *iso*propoxide always produced 5 or 6% of carbon dioxide, while the other zinc catalyst produced only 1 or 2%. Pease and Young[8] believe that carbon dioxide production from ethyl alcohol by alumina is due to oxygen adsorbed on the alumina. They took certain precautions to avoid the presence of oxygen and obtained no carbon dioxide in their ethylene. No such precautions have been taken in this Laboratory and with pure alumina no carbon dioxide has appeared in the ethylene. It appears that carbon dioxide production is a function of the nature of the surface or of the orientation of molecules by the catalyst and is a reaction on a par with the dehydrogenation or dehydration of alcohol.

One of the most outstanding cases of selective activation may be noted in the case of the two zinc oxides and acetaldehyde. The zinc oxide from the *iso*propoxide is almost identical with iron oxide in the proportions of the reaction products, while the zinc oxide from the hydroxide produces 25% less carbon dioxide and more than 30% more of carbon monoxide and saturated hydrocarbons, and 40% less hydrogen. Other similar evidences are given in the table.

Bancroft[2] imputed to Sabatier the statement that ethyl acetate over a nickel catalyst produced propane and carbon dioxide. Recently careful reviews of the literature by both Dr. Bancroft and ourselves have failed to reveal any such statement by Sabatier. Dr. Bancroft[9] using the conception that the function of the catalyst is to break the organic molecules into free

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[8] Pease and Young, THIS JOURNAL, **46**, 392 (1924).

[9] Ref. 2 c.

radicals suggested that by passing ethyl acetate with hydrogen over nickel one could determine by an examination of the reduction products whether these radicals were $CH_3—$, $C_2H_5C\overset{O}{\diagup\!\!\!\diagup}—$, $C_2H_5—$, or $CH_3C\overset{O}{\diagup\!\!\!\diagup}—O—$. This suggestion like most others that are based on the hypothesis of dissociation being a precursor to reaction becomes worthless when examined in the light of experimental results. The facts of contact catalysis are so utterly at variance with the Nef ideas of dissociation that work along this line has in the past five years changed the senior author from a devout follower to a pronounced skeptic of the theoretical speculations of that distinguished chemist.

It should be emphasized that the evidence is conclusive that the reactions under consideration are not successive reactions in the sense, for example, that ethyl alcohol is first dehydrogenated and that the acetaldehyde formed comes in contact with another point on the catalyst and is decomposed to form methane and carbon monoxide. If such were the case the proportion of products would depend upon the depth of the catalyst layer and on its distribution in the tube, for these factors determine the chance of the second contact on which a chain reaction would depend. Whether a single pill of nickel oxide or several grams of catalyst is used, the proportion of the products of reaction is unchanged, although of course the amount of reaction varies greatly. The proportion of reaction products is determined by the nature of the catalyst, whereas the amount of reaction is a very variable factor.

The iron catalyst from the hydrated ferric oxide and nickel reduced by hydrogen are similar in that both produce a considerable amount of saturated hydrocarbons from ethanol. They are markedly different in that while nickel produces only methane, iron oxide like titania produces considerable amounts of ethane. As Bischoff will show in a forthcoming paper, ethane over titania is the result of auto-oxidation and reduction (metakliny), whereas it is obvious that methane is the result of the rupture of a carbon-to-carbon linkage. Nickel is the only catalyst among those studied in this Laboratory that will cause the rupture of carbon linkages at temperatures below 450°. It appears that the marked efficiency of nickel in the promotion of hydrogenation may be connected with its ability to pull electrons from their normal positions between atoms, that is, in its ability to "loosen" linkages. This is possibly another way of expressing Baly's idea that the catalyst "opens up the lines of force" connecting the atoms but it has an advantage over the latter in that the position of electron orbits may be more readily determined than that of the "lines of force."

For the sake of economy little space has been devoted to the experimental work of Sabatier and Maihle[10] which treats of much the same reactions

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[10] Sabatier and Maihle, *Ann. chim. phys.*, [8] **10,** 289 (1907).

that have been observed in this investigation. It is our opinion that their observations are somewhat lacking in value because of their experimental methods. This may be illustrated by their results with ethanol over "reduced nickel." Their nickel was partly reduced by hydrogen and partly by alcohol and their catalyst could not all have been at the same temperature; hence their reaction products were (1) partly those from nickel "by hydrogen" (2) partly those from nickel "by alcohol," (3) partly from unreduced nickel oxide acting as a catalyst and (4) partly from the reduction of the oxide. Then too, the amount of alcohol passed over the catalyst was apparently not sufficiently great to prevent secondary reactions.

Experimental Part

Preparation of Catalysts.—Seventeen catalysts were prepared and studied in this work, some of them having been modified by various modes of reduction. With the exception of two nickel catalysts, all were prepared without the use of a supporting material. Nickelic oxide "on pumice" was prepared by melting 300 g. of nickelous nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) and stirring into it 75 g. of finely ground, ignited pumice. This mixture was heated over a hot-plate until almost dry, when it was transferred to a Pyrex test-tube and ignited for five to six hours at 350–400°. Nickelous oxide "on pumice" was obtained from this catalyst by ignition at 650° for four hours and cooling in a stream of carbon dioxide. A nickel oxide catalyst "without pumice" was obtained by ignition of nickel nitrate for five hours at 450°. This catalyst had a very high density as compared with those which contained pumice.

Cupric oxide was obtained by the dehydration and ignition of copper nitrate at 450°. Cuprous oxide was prepared by the reduction of hot Fehling's solution with glucose. Addition of the calculated amount of ammonium oxalate to a solution of cupric nitrate yielded cupric oxalate as a blue precipitate, which when dried and ignited at 325° for ten minutes in the reaction tube proved to be a very active catalyst. Copper formate was prepared by solution of cupric oxide in formic acid. Crystals were obtained upon spontaneous evaporation, which when heated at 300° yielded a catalyst similar to that obtained from the oxalate.

Yellow, hydrated ferrous oxalate was prepared from ferrous chloride by treatment with ammonium oxalate. The precipitate was washed free from electrolytes. This compound when heated for 30 minutes in the reaction tube yields pyrophoric iron which is a good catalyst. Hydrated ferric oxide was prepared by the precipitation of ferric chloride with ammonium hydroxide and washing free from electrolytes. This precipitate was dried for 24 hours at 110° and ground fine in a mortar. Ignition of ferric nitrate yielded the bright red oxide. Two iron oxide catalysts were prepared from organic compounds which have not been described in the literature. These were made from ferric chloride and sodium ethoxide and are apparently methyl and ethyl ferrites or iron alkoxides. A description of these compounds and their method of preparation will be published later. These compounds were hydrolyzed by moist air to yield the oxide which was used as a catalyst.

Zinc hydroxide was prepared by precipitation from zinc sulfate with sodium hydroxide. The precipitate was thoroughly washed and dried for 24 hours at 110°. The heating of zinc nitrate to 450° yielded an oxide which had a crystalline texture and a slightly yellow color. Metallic alkoxides were again made use of in the preparation of zinc oxide catalysts. These were prepared by the action of sodium alkoxides on zinc chloride. The method of preparation and the properties of the zinc alkoxides will be described later. Catalysts were prepared from the ethyl, *iso*propyl and butyl compounds by hydrolysis in moist air.

Magnesium oxide was prepared by precipitation from one of its salts.

Reduction of the Oxides.—The iron and nickel oxides were reduced by hydrogen prepared by the electrolysis of a solution of sodium hydroxide. From the electrolytic cell the gas was passed through a tube containing a copper spiral heated to red heat and then through a drying train of calcium chloride and phosphorus pentoxide. All of the catalysts to be reduced were placed in the reaction tube in which they were to be used and the hydrogen was introduced through a 3-way stopcock so the alcohol could be later passed in without introduction of air. After the tube was filled with hydrogen, the furnace was heated to the reduction temperature. In general the reductions were conducted for about 15 hours. Hydrogen was passed through the tube at the rate of 1 liter per hour.

Activity of Supporting Materials.—Since supporting materials were used in the nickel catalysts it was important to determine whether such substances are capable of any activity themselves. Ethyl acetate was used in this study. Kaolin, diatomaceous earth and pumice were all found to produce an activity of less than 0.2 liter per hour at 425° although a small amount of hydrolysis took place. At 475° the same materials gave an activity of 0.6 liter per hour. Various organic compounds were at intervals passed through the reaction tube containing only glass wool and in every case the activity of the tube was found to be negligible.

Analysis of Catalysts.—In order to determine the extent to which reduction of the iron and nickel catalysts had taken place, these were analyzed by the ferric chloride method for the determination of these metals in the presence of their oxides.[11] After use the catalyst was cooled in a stream of carbon dioxide, transferred to a glass-stoppered bottle and covered with 100 cc. of neutral ferric chloride solution. After several days half of the liquid was drawn off with a pipet and the ferrous iron titrated with a standard solution of potassium permanganate.

The nickelic oxide catalyst "on pumice" was found to contain 38% of nickel as determined by the dimethylglyoxime method.

A number of the oxide catalysts which contained water of hydration were ignited over the Bunsen flame and the loss in weight was determined. The loss in weight is given in percentage after the name of the oxide and its source: Fe_2O_3 (hydrated), 7.0%; Fe_2O_3 (methyl ferrite), 16.3%; Fe_2O_3 (ethyl ferrite), 15.3%; ZnO (hydroxide), 23.2%; ZnO (ethoxide), 5.9%; ZnO (*iso*propoxide), 12.7%.

Four representative oxide catalysts in pill form were heated to 400° in the furnace, held at that temperature for 30 minutes and cooled in a desiccator. The loss in weight under these conditions was; Fe_2O_3 (hydrated), 4.6%; Fe_2O_3 (ethyl ferrite), 10.0%; ZnO (hydroxide), 2.3%; ZnO (*iso*propoxide), 10.0%.

Apparatus.—The apparatus and method of experimentation has been described in previous papers.[1] Two g. of catalyst in the form of small pellets was used for each experiment. The reacting materials were passed over the catalyst at a rate of 35–40 cc. per hour. The distillate was collected in a bottle immersed in an ice-bath and the gas was collected at atmospheric pressure.

Gas Analysis.—Samples were usually taken 20 and 50 minutes after the beginning of the experiment. Carbon dioxide, olefins, oxygen and carbon monoxide were removed as previously described. A 15cc. sample of the residual gas was usually exploded with 85 cc. of electrolytic oxygen for the determination of hydrogen and of saturated hydrocarbons, and "calculated as methane and hydrogen." In important cases the hydrogen

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[11] Treadwell-Hall, "Analytical Chemistry," John Wiley and Sons, New York, 1919, vol. II, p. 612.

was also determined by absorption in a solution of colloidal palladium[12] and the residual hydrocarbon determined and identified by the explosion method.

The next paper of this series will deal with the relation of the structure of alcohols to their relative ease of dehydration and dehydrogenation by the same and different catalysts. It does not seem worth while to attempt to present a formulation of the difference in the electronic rearrangement necessary for dehydration and for dehydrogenation before the relationship between structure and the ease of these reactions is clearly outlined.

Summary

It has been shown that two distinct types of nickel are produced through reduction by alcohol and by hydrogen. These two catalysts are somewhat different in their ability to promote hydrogenation of ethylene, quite different in their power to dehydrogenate alcohol and very different in their ability to break carbon-to-carbon linkages in acetaldehyde and other compounds.

The proportion of reactions taking place at the surface of zinc and iron oxides may be modified by preparing these oxides from the hydrates or hydroxides and from different metallic alkoxides. Zinc oxide may be so modified that it will give from four to six times as much dehydrogenation as dehydration of ethanol. Ordinary iron oxides give a gaseous product with ethanol that contains 20–25% of hydrocarbons at 400°, but an oxide that has been made from alkyl ferrites gives no more hydrocarbons than does copper.

In the case of alumina, titania, zinc oxide and ferric oxide the relative activities of the catalysts for the different reactions taking place simultaneously on their surfaces are determined by the solid compound which is converted into the catalyst. In the case of nickel catalysts the relative activity is not so determined but is a function of the process by which the nickel compound is reduced.

It has been pointed out that there is no trustworthy proof that oxygen must be present at a nickel surface in order that it may function as a catalyst.[13] It has been shown that the fact that oxygen activates a nickel catalyst is no evidence for this belief.

The facts summarized in the last two paragraphs indicate that the true catalyst is not a nickel oxide but metallic nickel. It appears that the spacing of the active points on a nickel catalyst is a matter of fundamental importance, as it is in the case of the non-reducible oxide catalysts.

One of the marked characteristics of all nickel catalysts is their pronounced ability to break carbon-to-carbon linkages, that is in the ability

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[12] Paal and Hartmann, *Ber.*, **43**, 243 (1910).

[13] Recently Kelber [*Ber.*, **57B**, 142 (1924)] has shown that active nickel catalysts may be prepared from nickel compounds that contain no oxygen, thereby substantiating the hypothesis that the true catalyst is nickel, not an oxide of nickel.

to pull electrons from the positions in which they function as valence electrons. The significance of this fact in hydrogenation has been considered.

Facts too numerous to recapitulate here have been discovered in an extensive and comparative study of the behavior of ethanol, acetic acid, ethyl acetate, ethyl ether, acetal and acetaldehyde at the surface of some 20 nickel, iron, copper, zinc and magnesia catalysts.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

THE ROLE OF WEIGHT OF ACYL IN THE MIGRATION FROM NITROGEN TO OXYGEN. II[1]

BY L. CHARLES RAIFORD AND JOHN R. COUTURE

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Introduction

Previous reports from this Laboratory have shown (1) that when an *o*-acetylaminophenol is benzoylated by the Schotten-Baumann method, the benzoyl radical goes to nitrogen while acetyl migrates to oxygen;[2] (2) that this migration takes place also when acid-forming substituents are attached to the nucleus of the aminophenol;[3] (3) that the acetyl-benzoyl derivatives of *p*-aminophenols do not suffer this rearrangement;[4] (4) that the migration does not take place when one of the reacting groups is situated on a side chain;[5] (5) that the presence of bromine and other heavy radicals occupying positions *ortho* to the reacting groups (amino and hydroxyl), which in many reactions have been found[6] to cause marked retardation and in some instances, complete inhibition, does not prevent the rearrangement;[7] (6) that these observations seem to hold with bases derived from condensed and multinuclear hydrocarbons, namely, 1-amino-2-napththol[8] and halogenated derivatives, and 3-amino-4-hydroxydiphenyl[9] and (7) that in the diacylated compounds studied up to this point the heavier acyl was always found on nitrogen.[10] But, in view of the fact that none of these radicals contained any substituent except hydrogen,

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[1] Condensed from a thesis presented by J. R. Couture to the Graduate College of the State University of Iowa in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1923.

[2] Raiford, THIS JOURNAL, **41**, 2068 (1919).

[3] Raiford and Couture, *ibid.*, **44**, 1793 (1922). Glavincheff, unpublished research.

[4] Raiford and Iddles, *ibid.*, **45**, 469 (1923).

[5] Raiford and Clark, *ibid.*, **45**, 1738 (1923).

[6] Stewart, "Stereochemistry," Longmans, Green and Co., 2nd ed., 1919, p. 261.

[7] Raiford and Woolfolk, THIS JOURNAL, **46**, 2246 (1924).

[8] Armstrong, unpublished research.

[9] Colbert, unpublished research.

[10] Raiford and Greider, THIS JOURNAL, **46**, 430 (1924)