combined chloride. Mercuric and zinc chloride do not form any polymerization products and, since zinc chloride is much more active than mercuric chloride, it is the best promoter of all the salts in an ether solution.

Ferric chloride is the most potent of all the salts studied in the promotion of the Tischtschenko reaction. This conclusion was reached through a study of the reaction in butanol-ether and ethanol-xylene solutions.

The aldehyde-catalyst-promoter compound is probably held together by secondary valence forces and cannot be assigned any definite configuration. The authors believe that the experimental work is not in accord with the interpretation of the mechanism of the reaction variously advanced by Nef, Claissen and Lachman.

MADISON, WISCONSIN

---

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

# ORGANIC REACTIONS AT THE SURFACE OF TITANIA ADSORPTION OF CERTAIN GASES BY TITANIA

BY FRITZ BISCHOFF[1] AND HOMER ADKINS

RECEIVED JULY 14, 1924 PUBLISHED MARCH 5, 1925

The work reported below was carried on with titania along lines analogous to those previously followed in this Laboratory with alumina catalysts. The principal method of attack has been to study a series of reactions with the same titania catalyst and a series of titania catalysts with the same reaction. Particular attention has been paid to the changes in the catalyst that modify the proportion of two simultaneous reactions, that is, to selective activation.

The reactions of formic acid, acetic acid, a mixture of formic and acetic acids, ethanol, butanol, butanol and ammonia, ether and ethyl acetate have been studied for the titanias obtained from the alkyl titanates, titanic acid, sodium titanate and titanous hydroxide. A few experiments were performed with acetone, acetaldehyde, butyraldehyde and propionic acid.

The adsorptions, by three varieties of titania, of certain products of the catalytic reactions have been measured in attempting to discover the relationship that has been supposed to exist between the adsorptive power of substances and their catalytic activity.

**The Reported Reduction of Acetic Acid by Formic Acid.**—Sabatier and Mailhe[2] stated that mixtures of formic acid and a higher aliphatic acid, when passed over titania at 300°, gave excellent yields (40 to 90%) of aldehydes; and that it was but natural that this should be the case, since

---

[1] Dr. Bischoff held a DuPont Fellowship for the year 1923–24. This paper and one entitled "The Alkyl Titanates" were abstracted from his dissertation submitted in candidacy for the degree of Doctor of Philosophy.—H. A.

[2] Sabatier and Mailhe, *Compt. rend.*, 154, 561 (1912).

the reaction was analogous to the formation of aldehydes by heating mixtures of calcium formate and the calcium salt of a higher member of the series. As we were looking for a bimolecular reaction of this type, we attempted to duplicate their results. We tried varying the proportions of formic and acetic acids from equimolecular amounts to 2.5 moles of formic acid to 1.0 mole of acetic acid at temperatures of 300°, 330°, 340° and 350°. In none of the 20 odd experiments with acetic acid and the few with propionic acid was the least amount of an aldehyde obtained. As soon as the temperature was raised to 340° some acetone was formed, as would be expected. Below 340° the only reaction that took place was the decomposition of the formic acid. Sabatier claimed that the yield of aldehyde could be calculated from the amount of carbon dioxide in the gas mixture, as formic acid alone gave carbon monoxide exclusively. At 330° the addition of acetic acid to formic acid did cause the formation of considerable quantities of carbon dioxide but this was not accompanied by the production of aldehyde. This shows that the acetic acid is capable of influencing the ratio of the products of the formic acid decomposition. The results at higher temperatures were difficult to interpret because the blank on the formic acid decomposition becomes such a large factor. At 300° the acetic acid has no effect on the formic acid decomposition. As Sabatier used a train of catalyst and we had been using but 2.5 g. in the form of pills, we duplicated his experimental conditions but with negative results.

**Formic Acid.**—The titania used by Sabatier for the production of aldehyde was prepared by hydrolysis of titanium tetrachloride, dried below 300°, and gave exclusively carbon monoxide and water with formic acid. Correcting for the blank we find that the titanias from the oxyethyl titanates, from titanous chloride and that from Will and Company (which appears to be titanic anhydride) gave the same results as obtained by Sabatier, while our own precipitated titania and that from sodium titanate gave, respectively, 5% and 14% each of carbon dioxide and hydrogen. The absolute activity of these catalysts varied only slightly, 2.5 g. of the catalyst decomposing from 20 to 25 g. of formic acid in one hour at 300°. These results are not in accord with the behavior of these catalysts with the other reactions studied, where the titania from oxyethyl titanate is most like that from sodium titanate and most unlike that from titanous chloride; such differences may be due to variations in the primary and secondary adsorbing powers of these catalysts and not to spacing of the active points. Will's titania when ignited did not lose in activity but gave much more carbon dioxide and hydrogen (16% of each) and a correspondingly less amount of carbon monoxide.

Ignition of titania reduces its activity for other reactions. Thus for ethyl acetate the activity is cut down 30% or more by ignition. From this we might gather that the production of carbon dioxide and hydrogen is the reaction fostered by secondary adsorption, that of carbon monoxide by primary adsorption. Ignition of the catalyst kills the primary effect so that the catalyst acts like powdered glass.

**Acetic Acid.**—The primary reaction of acetic acid at the surface of titania is the formation of acetone, which then undergoes further reaction. These reactions differ from the acetic acid decomposition in that they manifest a variation in behavior with the different titanias. By passing pure acetone over titania at the temperature of these reactions a high percentage of conversion of the acetone to oily condensation products was obtained; at the same time a relatively small amount of gas containing carbon dioxide, carbon monoxide, unsaturated and saturated hydrocarbons was formed. Never more than one-third of the theoretical amount of acetone calculated from the carbon dioxide collected was obtained in the experiments with acetic acid. The carbon dioxide content of the gaseous product varied from 92 to 100% by volume, the remainder of the gas consisting of a mixture of saturated and unsaturated hydrocarbons and carbon monoxide.

**Ethanol and Butanol.**—Butylene, butane, hydrogen, butanal and its condensation and decomposition products are formed when butanol is passed over titania at 430°. The proportion and yield of the products are

TABLE I

BUTANOL, ETHANOL, ETHER AND ETHYL ACETATE

The volumes (liters at NTP) of the gaseous products from butanol, ethanol, ether and ethyl acetate are shown for the series of titania catalysts. The sources of the catalysts, indicated by letters at the top of the table are as follows: A, butyl titanate; B, titanic acid; C, ethyl titanate; D, methyl titanate; E, titanous chloride; F, sodium titanate; G, Demarçay's oxytitanates; H, *iso*propyl titanate.

| Product | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| | | | BUTANOL AT 430° | | | | |
| $C_4H_8$ | 5.6 | 5.0 | 4.9 | 3.8 | 3.2 | 1.3 | 0.4 |
| $C_4H_{10}$ | 0.25 | 0.4 | 0.45 | 0.7 | 0.4 | 1.1 | .2 |
| $H_2$ | .0 | .0 | .0 | .1 | .25 | 0.95 | 1.75 |
| | | | ETHANOL AT 400° | | | | |
| $C_2H_4$ | 3.2 | 3.4 | 3.4 | 2.3 | 2.6 | 1.3 | 0.4 |
| $C_2H_6$ | 1.2 | 1.6 | 1.5 | 1.4 | 1.6 | 1.6 | 1.5 |
| $H_2$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.7 | 0.9 |
| | | | ETHYL ETHER AT 430° | | | | |
| $C_2H_4$ | ... | 3.4 | ... | 3.1 | 3.2 | 1.0 | ... |
| $C_2H_6$ | ... | 1.2 | ... | 1.3 | 1.4 | 0.8 | ... |
| $H_2$ | ... | 0.0 | ... | 0.0 | 0.1 | .3 | ... |
| | | | ETHYL ACETATE AT 450° | | | | |
| | H | | | | | | |
| $C_2H_4$ | 1.75 | 2.45 | ... | 2.15 | 2.0 | 1.4 | ... |
| $C_2H_6$ | 0.9 | 1.1 | ... | 1.0 | 1.0 | 0.75 | ... |
| $CO_2$ | 1.75 | 2.5 | ... | 2.3 | 2.35 | 2.7 | ... |
| $\frac{\text{g. } CH_3COCH_3}{\text{g. } CH_3COOH}$ | 0.8 | 1.0 | ... | 1.6 | 1.6 | 20.0 | ... |

very greatly dependent upon the history of the catalyst. The reaction is analogous to the catalytic action of titania on ethyl alcohol in which case ethylene, ethane, hydrogen, acetaldehyde and its condensation and decomposition products are formed. The variation in the production of the alkene, alkane and hydrogen by different titanias is shown in Table I.

Engelder was the first to point out that the chief product of the saturated constituent of the gas from ethanol was ethane and not hydrogen. Previous workers reported that very little hydrogen is formed from ethyl alcohol at 400°. Sabatier, working below 360°, reports hydrogen exclusively, and since Engelder worked at 400°, Reid infers that the elevation of temperature has brought about the production of the ethane. On the contrary, we have found that in certain cases elevation of temperature increases the percentage of hydrogen over that of ethane. At 430° butyraldehyde reacts at the surface of titania, giving water-insoluble condensation products as well as some gas consisting of carbon dioxide, carbon monoxide, saturated and unsaturated hydrocarbons and hydrogen. Acetaldehyde gives appreciable amounts of condensation products at a temperature as low as 300°. This explains why the amount of aldehyde found in the distillates of the alcohol experiments is considerably less than the theoretical amount calculated from the saturated hydrocarbon and hydrogen collected.

**Ether.**—It has been shown[3] that ethanol and ether over alumina yield the same amounts of ethylene at 400°. With titania, ether does not give exclusively ethylene but the same products (see Table I) as ethyl alcohol, although not in the same ratio. However, more than twice as much ethyl alcohol is decomposed at 400° as ether at 430° (see Fig. 2). Ether is not as sensitive to the activating influence of the various titanias as alcohol. (See Fig. 1.) The sodium titanate catalyst is relatively much less active toward ether than toward the alcohol. For the titania from sodium titanate more ethane and hydrogen are formed than ethylene. This proves beyond doubt that the ether breaks up to give acetaldehyde and ethane without the intermediate formation of ethyl alcohol, for if the alcohol were first formed, there must result at least twice as much ethylene as ethane. Ether, therefore, reacts over titania in the following ways: $\mathrm{EtOEt} \longrightarrow \mathrm{C_2H_6} + \mathrm{CH_3CHO}$; $\mathrm{EtOEt} \longrightarrow \mathrm{C_2H_4} + \mathrm{CH_3CH_2OH}$; $\mathrm{EtOEt} \longrightarrow 2\mathrm{C_2H_4} + \mathrm{H_2O}$.

**Ethyl Acetate.**—Sabatier[4] reported that ethyl acetate reacts at the surface of titania to yield acetic acid and ethylene. The results obtained by us are not in agreement with those of Sabatier, for in addition to acetic acid and ethylene, we obtained acetone, ethane and condensation prod-

---

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

[4] Sabatier-Reid, "Catalysis in Organic Chemistry," D. Van Nostrand Co., New York, 1922, p. 10.

ucts. Previous work in this Laboratory showed that the products depend as much upon the source and preparation of the catalyst as upon the metal in the oxide.[5] We found that the titania of Sabatier gave 40% each of carbon dioxide and ethylene with 20% of ethane and a little carbon monoxide. The distillate contained equal amounts of acetic acid and acetone, although the amount of acetone was only one-fifth of the amount calculated from the carbon dioxide obtained. Oily products, indications of ketone or possibly aldehyde condensation products, were found, as in the work on acetic acid. With the series of titanias from the alkyl titanates, titanous chloride and sodium titanate, the ratio and yield of the reaction products differed quite markedly (Table I), one sample of titania from sodium titanate yielding 59% of carbon dioxide in the gas mixture. It is significant that those catalysts which were most active in promoting the formation of acetone from acetic acid gave the highest yields of acetone and carbon dioxide and the lowest yields of acetic acid. It is highly probable that a portion of the acetone and carbon dioxide is a product of a secondary reaction of the liberated acetic acid. The high percentage of carbon dioxide from the titania from sodium titanate can only be explained on such an assumption. This does not mean, however, that a considerable part of the reaction products is not primary decomposition units of one or more molecules of ethyl acetate, reacting in two or more ways at the surface of the catalyst, in a manner analogous to the several reactions which alcohols undergo in various proportions at the surfaces of the various titanias. No aldehyde could be detected in the distillates, but this is not surprising in view of the strong condensing action titania has on aldehydes, for at 300°, that is, 150° below the temperature at which these studies were made, titania was found to condense (or resinify) appreciable quantities of acetaldehyde. Such a condensation reaction would be regarded as a secondary one as in the case of the alcohols. Ethyl acetate over precipitated titania yielded 2.3 g. of acetic acid and 1.4 g. of acetone, 39.8% of the gaseous product being carbon dioxide. Ethyl acetate over titania from sodium titanate yielded 0.2 g. of acetic acid and 4.1 g. of acetone, 59% of the gaseous product being carbon dioxide. These same catalysts decomposed, respectively, 0.40 and 0.65 mole of acetic acid, and 0.30 and 0.22 mole of ethyl alcohol.

**Formation of Butyl Amine and the Effect of Ammonia in the Reaction of Butanol.**—In our search for a reaction at the surface of titania involving two different molecules, the formation of butylamine from butanol suggested itself. Sabatier had made the observation that all of the mixed catalysts and especially thoria were excellent for the conversion of alcohols to amines. At 430°, using the titania from Demarçay's titanate we obtained no amine; at 400°, using precipitated titania, a few crystals of an

---

[5] Adkins and Krause, THIS JOURNAL, 44, 385 (1922).

amine hydrochloride (m. p., 142°) were isolated, while at 370° the yield was increased to about 0.5 g. This preliminary work indicated that the reaction took place to some extent at lower temperatures. The amount of butanol decomposed at 370° is so small that one might consider the yield of amine at this temperature fairly high. For our studies such a reaction was not feasible and further work was consequently abandoned. However, an observation of no little importance was made with regard to the runs at 400° and 430°, for while practically no amine is formed at these temperatures, the ratio of the gaseous products is materially changed, more butane and hydrogen and less butylene being formed, not only for the ordinary precipitated titania but also for that from Demarçay's titanate. In the case of precipitated titania, the percentage of butylene in the gas mixtures was lowered 12%. In fact, the effect of the ammonia was many times as great in shifting the reactions as was the equivalent of water, butanol saturated with water giving only slightly more butane and hydrogen than anhydrous butanol.

## The Adsorption of Carbon Dioxide, Hydrogen, Ethane and Ethylene by Two Types of Titania

It was impracticable to make adsorption measurements on all of the catalysts and for all of the reaction products studied, so we chose two catalysts that showed marked differences as to selective action and amount of reaction; these were the titania obtained by treating titanic chloride with aqueous ammonia and that resulting from the hydrolysis of sodium titanate. The titania obtained from titanic chloride is readily reproducible as to absolute and relative activity. On the other hand, different preparations obtained from sodium titanate fusions varied considerably as to absolute and relative activity and for this reason it was very important to have catalytic data for each sample.

The ideal temperature for adsorption measurements would be the one at which the catalytic reactions were studied, but adsorption decreases so rapidly with rise in temperature, that measurements at 400° are not possible with ordinary methods. Our measurements were made at 20° and 97°. Benton[6] differentiates between two types of adsorption, primary and secondary. He regards "selective" and "irreversible" adsorptions as primary and considers them to be determined by chemical affinity in its usual sense, while those adsorptions due to the weaker and less specific residual valences are classified as secondary. His experimental work indicates that the tendency of different gases to be held by secondary adsorption is measured by their relative boiling or melting points and that such adsorption decreases rapidly with rise of temperature. The terms "chemical" and "physical" have been used in a similar sense to "primary"

---

[6] Benton, THIS JOURNAL, 45, 887 (1923).

and "secondary." According to Langmuir,[7] however, both types are chemical. The objection will be raised by those who thus differentiate adsorption (the evidence for so doing is by no means conclusive) that at the temperature of our measurements the primary adsorption may be completely masked by the secondary. This objection is perfectly valid; nevertheless, we feel that any adsorption measurements, however meager, in connection with catalytic work, are valuable. A summary of the adsorption of four gases by three samples of titania at two temperatures is given in Table II.

TABLE II

ADSORPTION OF CERTAIN GASES BY TITANIA

Volume of gas in cc., calculated to 20° and 740 mm., adsorbed by 1.0 g. of catalyst at 20° and 97°.

| Catalyst Source | $CO_2$ 20° | $CO_2$ 97° | $H_2$ 20° | $C_2H_4$ 20° | $C_2H_4$ 97° | $C_2H_6$ 20° |
|---|---|---|---|---|---|---|
| $H_2TiO_3$ | 17.3 | 6.1 | 0.16 | 11.6 | 4.0 | 9.4 |
| | 17.4 | | | | | |
| $Na_2TiO_3$ II | 10.7 | | 0.16 | 7.5 | | 6.5 |
| $Na_2TiO_3$ III | 13.9 | 5.7 | .23 | 9.55 | 3.5 | 7.6 |

## Discussion of Results

The hypothesis has been advanced[8] that in the case of the selective activation of the alumina catalysts, the distance between the atoms, molecules, or "active points" of the catalyst had been modified by changing the size of the radical attached to the aluminum atom when the compound went into the solid state. The range of selective activation attained is represented by the values 0.35 to 1.45. Of this range only 13% was covered by the aluminas from the alkoxides, that is, from 0.35 to 0.50. In the original work no aluminas were used which were any nearer to these alkoxide aluminas than is represented by the value 1.06. Subsequent study showed that the alumina from the previously unavailable, true aluminum hydroxide gave an alumina similar to the alkoxides, one that may be represented by the value 0.64. The study of the selective activation of titania has revealed the fact that it may be modified in its activity even more markedly than alumina. The titanias from the various normal esters of titanic acid have covered a much wider section of the total range of selective activation. In the case of butanol the range is from 24.8 to 0.3. Of this range 75% (in contrast to 13% for alumina) is covered by titania from the normal esters. The range for ethanol is from 2.76 to 0.85, 56% of it being covered by the titania from the normal esters. The similarity in the order of the alumina and titania catalysts, when one is comparing the activation effect with the source of the catalyst, is striking. The analogy is carried still further, for the alkoxides of both these metals

---

[7] Langmuir, THIS JOURNAL, **40**, 1400 (1918).

[8] Adkins, *ibid.*, **44**, 2175 (1922); **46**, 131 (1924).

(although differing in physical properties), when air-hydrolyzed, are closest to the catalysts from the true hydroxides of the metals and most unlike the hydrated oxide catalysts. The titania from normal ethyl titanate is identical with the titania from titanic acid.

While there can be little doubt that the spacing of the "active points" of the catalyst is a fundamental factor in the activation of a catalyst, it is evident that the mechanism by which spacial relationships are determined involves other factors than the size and shape of the radicals attached to the metallic atom. This is shown by the fact that titania from tetra-ethyl titanate is very different in its catalytic activity from that obtained from Demarçay's oxytitanates. For butanol the difference is expressed by the

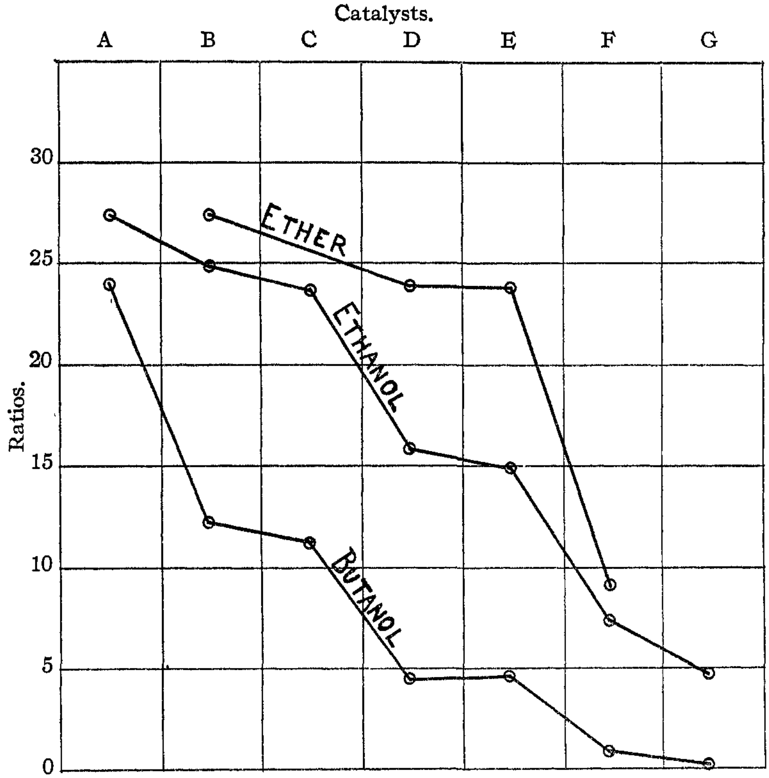

Fig. 1.

The effect of the selective activation of titania is shown by a comparison of the ratios of the percentages of the gaseous products obtained, $\frac{C_nH_{2n}}{C_nH_{2n+2} + H_2}$. The ratio figures for ethanol and ether have been multiplied by ten so as to make the graph of the same magnitude as that for butanol. The letters have the same significance as in Table I.

ratios 11.3 and 0.21; for ethanol, by 2.35 and 0.29. The experimental evidence indicates that the manner of hydrolysis and dehydration plays an important part in determining these differences. If it were not for the fact that dehydration follows hydrolysis, it is possible that the spacing of the active points in the catalyst would be the same as in the parent solid. As a matter of fact the titania obtained from the crystalline oxy-ethyl titanates has a much smaller volume than the parent substance, crumpling and shrinking during hydrolysis and dehydration. Three of the alkoxides used as parent substances in preparing the catalysts were liquids and one a solid; during the hydrolysis the liquid alkoxides became solid before all the alkoxyl groups were out and in this there was a great difference of behavior, the ethyl titanate becoming solid in a few hours while the butyl ester remained liquid for weeks. Another phenomenon, of great interest in illustrating how the selective activation of a catalyst may be brought about by changing the conditions of hydrolysis and dehydration, was brought to light when it was found that a crystalline oxytitanate which had only one ethoxyl group intact out of the possible four in the molecule, yielded a catalyst, on air hydrolysis, which had a selective effect midway between the normal ethyl titanate and the oxytitanate. For ethyl alcohol the ratio figures were: 2.35 for $Ti(OEt)_4$, 1.04 for $TiO(OH)(OEt)$ and 0.29 for $Ti_2O(OEt)_6$ and $TiO(OEt)_2$. We believe that the structural differences in the ultimate molecule of titania (to use the expression proposed by Sir James Walker), which are responsible for the difference in the spacing of the active points, may be explained in the following way. In the air hydrolysis of the titanium ethoxide the molecules do not have a chance to arrange themselves in crystalline form, nor does one molecule have the opportunity of reacting with the hydroxyl groups of another to make the most of the hydrolyzing effect of each water molecule. In the case of the oxy-ethyl titanate, hydrolysis has begun in an organic solvent with a deficiency of water. In such a solution no hydroxyl groups exist. $Ti(OEt)_3OH + Ti(OEt)_4 \longrightarrow Ti_2O(OEt)_6 + HOEt$. Moreover, the oxytitanate in crystallizing has had a chance to arrange itself in the form entailing the minimum amount of free energy. The result is that the one catalyst will resemble the titania from true titanic acid while the other resembles the hydrated oxide type.

It has been found impossible to duplicate absolute activity in the preparation of certain catalysts. Those prepared from the alkyl titanates may vary considerably in this respect. Of two samples of titania from different preparations of butyl titanate, one was able to decompose twice the amount of butanol as the other, *although the ratios of products for both were identical.* We interpret this as meaning that the active surfaces of two such catalysts are of a different magnitude, although the structure (surface lattice of the active points) is the same. The absolute activities of a series of samples of titania for acetic acid, ethanol, butanol and ether are shown in Fig. 2. It should be noted that the *order* of activities for acetic acid is markedly different from those of ethanol, butanol and ether. For the decomposition of ethanol and butanol, as well as for the reactions with acetic acid and ethyl acetate (see Fig. 1), the samples of titania preserve exactly the same order in their selective effects, namely, butyl titanate, *iso*propyl titanate, titanic acid from titanium tetrachloride, ethyl titanate, titanous chloride, mono-ethyl metatitanate,

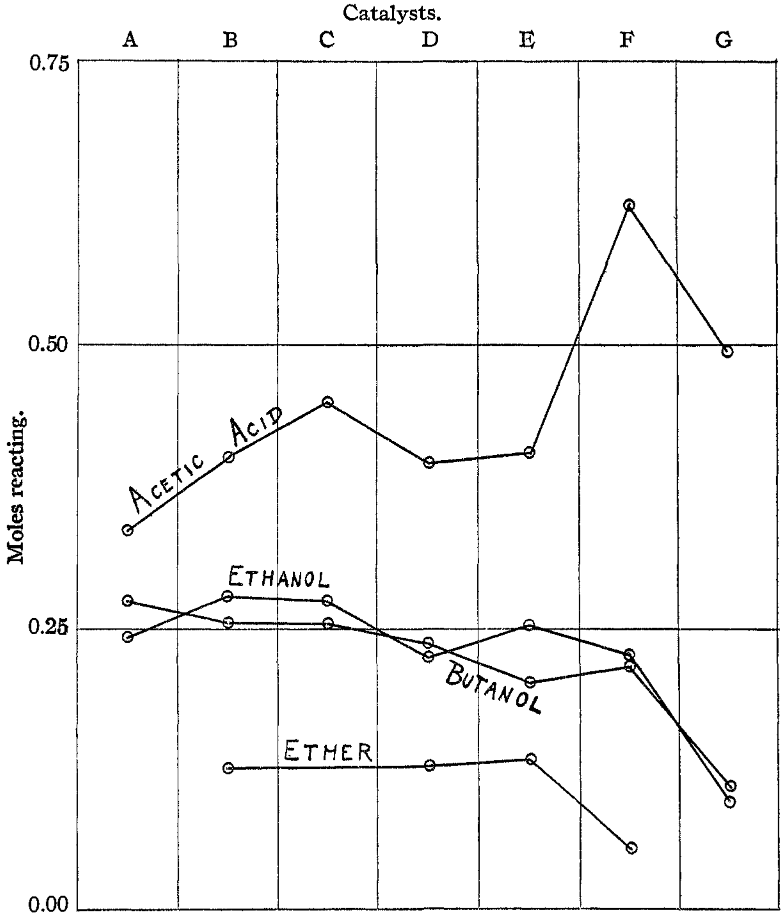

Fig. 2.—The activities of various samples of titania.

The absolute activity of the titania catalysts expressed in moles of substance decomposed per hour by 2.0 g. of catalyst is illustrated. The temperatures for the decompositions were 400° for ethanol and 430° for ether, butanol and acetic acid. The letters representing the catalysts have the same significance as in Table I.

methyl titanate, sodium titanate and Demarçay's compound. Our results, as shown in Figs. 1 and 2, indicate that there is no relationship between the relative and the absolute activities of the titania catalysts.

Engelder[9] in his work on the catalytic decomposition of ethyl alcohol by titania regarded the formation of ethane as a secondary reaction due to the hydrogenation of ethylene by hydrogen in spite of the fact that he was unable to produce ethane from ethylene when he passed a mixture of ethylene and hydrogen over titania at the temperature of his original reaction. He assumed that it was necessary to have "nascent hydrogen" in order to produce the hydrogenation. It is more probable that the reaction involves an auto-oxidation and reduction (metakliny), one molecule of alcohol being oxidized to acetaldehyde and the other reduced to the hydrocarbon. The reaction takes place either between two molecules of alcohol or between the two parts of the ether molecule, that is, $CH_3CH_2—O—CH_2CH_3 \longrightarrow CH_3CH_3 + CH_3CHO$; and, $2CH_3CH_2OH \longrightarrow CH_3CH_3 + CH_3CHO + H_2O$.

In the case of butanol and ethanol, we find that the products of reaction are strictly analogous in a qualitative sense, though the ratios of products are very different. Thus over a titania from butyl titanate, ethanol yielded 72% of ethylene and 26% of ethane, while for butanol 95% of ethylene and 4% of butane were formed. When a comparison of ratios for ether and alcohol is made, we find that they are much more alike than those for the two alcohols. Thus a sample of precipitated titania yielded 70.1% of ethylene and 27.9% of ethane for methyl alcohol, and 69.7% of ethylene and 24.2% of ethane for methyl ether. Ethanol is more reactive than either butanol or ether. At 400°, 2.0 g. of titania from methyl titanate decomposed almost exactly as much ethanol as it did butanol at 430°, the exact value being 0.23 mole per hour. The fact that ethyl ether has been found to be half as reactive as ethyl alcohol at a temperature 30° higher is not in agreement with the hypothesis of Pease[10] that ethyl ether is the intermediate compound in the catalytic dehydration of ethyl alcohol.

The adsorption measurements of the products of reaction at the surface of titania show no connection with either the activity of the catalyst or its selective effects. Whereas different titanias show differences in adsorbing powers and therefore differ from one another physically (or even chemically), these differences are apparently not the same as those factors which effect catalysis. This is evident from a comparison of the ratio of the gases in adsorption and in catalysis, as shown in Table III. It is important to note that the adsorbing powers of the three catalysts are not in the same order as their catalytic activity. Thus the catalyst from "$Na_2TiO_3$III," which shows a higher adsorbing power than that from "$Na_2TiO_3$II" in all cases, has a much lower catalytic activity, decomposing

---

[9] Engelder, *J. Phys. Chem.*, **21**, 679 (1917).

[10] Pease and Yung, THIS JOURNAL, **46**, 391 (1924).

only a third as much butanol and a half as much ethyl acetate. It is possibly a matter of chance that the catalyst from titanic acid has the highest activity as well as the highest adsorbing power. (See Table II.)

### TABLE III

### RATIOS IN ADSORPTION AND CATALYSIS

The ratios in catalysts for $CO_2/C_2H_4$ and $CO_2/C_2H_6$ are for ethyl acetate. The $C_2H_4/C_2H_6$ ratio is for ethyl alcohol.

| Source of catalyst | $CO_2/C_2H_4$ | | $CO_2/C_2H_6$ | | $C_2H_4/C_2H_6$ | |
|---|---|---|---|---|---|---|
| | Adsorp. | Cat. | Adsorp. | Cat. | Adsorp. | Cat. |
| $H_2TiO_3$ | 1.49 | 1.02 | 1.84 | 2.09 | 1.23 | 1.91 |
| II $Na_2TiO_3$ | 1.43 | 1.65 | .. | 2.96 | .. | .. |
| III $Na_2TiO_3$ | 1.45 | 1.56 | 1.83 | 7.33 | 1.26 | 0.66 |

The adsorption values for hydrogen (see Table II) on the different samples of titania are practically identical, within the limits of experimental error. Since the temperature of the adsorption measurement is far removed from the melting point of hydrogen, we can assume that this measurement is much freer from "secondary" adsorption. Here, again, there is no difference in adsorptive power to lead one to expect the great differences in the amount of hydrogen which these catalysts are able to produce from ethanol and butanol. The titania from titanic acid gives no hydrogen from butanol; the titania from sodium titanate (III) gives a gaseous product that is 68.7% hydrogen.

At 97° the adsorption measurements for carbon dioxide and ethylene have decreased almost to a third of their original value, but are still in the same order although the values have become closer for the two different catalysts studied, indicating that at still higher temperatures they might become identical and so resemble the values for the hydrogen adsorption.

## Conceptions of Hydrolysis and Dehydration of Titanium Compounds

There are three possible ways in which the hydrolysis of a titanate may proceed:

$$Ti(OR)_4 + H_2O \longrightarrow (RO)_2\,TiO + 2HOR \qquad (1)$$
$$Ti(OR)_4 + H_2O \longrightarrow Ti(OR)_3\,OH + HOR \qquad (2)$$
$$2Ti(OR)_4 + H_2O \longrightarrow Ti_2O(OR)_6 + 2HOR \qquad (3)$$

It is obvious that the final state of aggregation of the titania might be dependent upon which type of hydrolysis actually took place; according to Equation 1, single molecules of titanium dioxide would result, while according to Equation 3, the entire mass might consist of one molecule. In the case of Equation 2, the final "porosity" would be independent of the nature of the hydrolysis, as there intervenes a final step of dehydration. The hydrolysis of titanium tetrachloride in aqueous solution, giving titanic acid, illustrates Type 2. When the alkyl titanates are poured into water, titanic acid also results, as one would expect because there is a large excess of water; on the other hand, when there is present a deficiency of water for complete hydrolysis as is the case in the preparation of ethyl titanate by Demarçay's process, it is possible to show that 80% of the partially hydrolyzed titania in one sample has reacted with water according to Equation 3. We therefore suggest that the different ways in which the various titanium compounds may hydrolyze has a connection with the differences manifested in catalytic activity both as to amount and proportion of reaction products. We do not believe that this is the only factor involved, however, for the process of dehydration also plays an important role. In the process of dehydration of titanic acid there will result no one definite arrangement of titanium and oxygen atoms to give the titania molecule, but rather a series of aggregates of varying sizes. If we consider the dehydration of orthotitanic acid in the light of organic structural conceptions, we find that there will result two distinct types of oxygen linkages, analogous to the ether oxide and the carbonyl linkages in carbon chemistry and that the relative number of such linkages one to another is a variable factor. The relative number of doubly-bound oxygen atoms resulting from dehydration will decrease as the number of titanium atoms per molecule increases. It is highly probable that this number of titanium atoms going to make up the final titania molecules will be largely dependent upon the number of titanic acid molecules in the micelle of the original colloidal particles of the titanic acid.

## Experimental Part

**Apparatus and Method.**—The apparatus, method of experimentation and analysis were those previously described.[3] The iodine method could not be used for acetone, as some of the products of the reaction contained unsaturated linkages. Acetone, acetaldehyde and butyraldehyde were determined by the neutral sulfite titration method. In several instances formic acid was determined in the presence of acetic acid by a permanganate titration in boiling carbonate solution. The presence of acetone in the distillate from acetic acid was established by preparing the semicarbazone; m. p., 182°. The presence of acetaldehyde in the ethyl alcohol distillates was confirmed by the isolation of a *p*-nitrophenylhydrazone; m. p., 122°. The absence of acetaldehyde in the ethyl acetate distillates was shown by heating an equal volume of distillate with Fehling's solution in a pressure bottle at the maximum temperature of the water-bath.

In the experiments in which ammonia and butanol were used, the products were passed into water to free the gas mixture from ammonia. In the experiments in which the preparation of acetaldehyde from formic and acetic acids was sought, the gases were run into a neutral sulfite solution so that no aldehyde could be lost. From the combined distillates of the ethyl alcohol runs it was found possible to separate a water-insoluble oil, of boiling point range 64.5–194.0°. The higher fractions had all of the properties of an unsaturated hydrocarbon. The presence of such products is explained by condensation of the mesitylene type.

**Reagents.**—The ethyl acetate was dried over calcium chloride and redistilled; b. p., 76.0–77.0°. Mallinckrodt's absolute ethyl acetate which is free from acetic acid was also used. The ether was dried over sodium. The ethyl alcohol was "absolute," analyzing over 99.5%. The butanol had a boiling point range of 116.5–118°. Acetic and formic acids were analyzed by acidimetry and the purities checked by the densities.

## Preparation of the Catalysts

**Hydrolysis of Titanium Tetrachloride.**—Titanium tetrachloride was dropped into a dilute solution of ammonium hydroxide during constant stirring of the mixture, sufficient ammonia being used to keep the solution alkaline. The precipitation mixture was boiled before filtration. The precipitate was washed superficially to remove most of the ammonium chloride and then dried at 100°. Repeated washing renders the precipitate highly colloidal, thus slowing the process of filtration. By drying the precipitate and then continuing the washing, the annoyance of slow filtration is greatly reduced. The precipitate was repeatedly boiled with distilled water until entirely free from chlorides. The final drying was at 120°.

**Hydrolysis of Titanium Trichloride.**—The strongly acid solution of titanous chloride was hydrolyzed with ammonium hydroxide to give the purple, hydrated oxide. When exposed to the air this titanous hydroxide (or titanous acid) is oxidized to a white solid apparently identical with titanic acid. It was washed free from chlorides and dried below 150°.

**From Sodium Titanate.**—Unignited, dried titania was dissolved by molten sodium hydroxide. When the melt was treated with a large excess of water the greater proportion of the titania was precipitated, only a fraction remaining soluble in the alkali. The insoluble part which was a partially hydrolyzed sodium salt of titanic acid was washed for days with boiling water until neutral. By washing with dil. hydrochloric acid solution, the time of washing may be considerably reduced. The traces of nickel which had contaminated the precipitate from the fusion crucible were separated by boiling with sodium cyanide solution. The titania was finally dried at 120°.

**From Ortho Alkyl Titanates.**—A description of the preparation of the ortho-, hydroxy- and oxy-ethyl titanates has been presented in a previous paper.[11] Later work has shown that ortho-ethyl titanate, which we described as a colorless liquid, slowly solidifies at the temperature of carbon dioxide snow or when inoculated with the solid phase. The melting point of the white solid so obtained is not sharp, beginning at 36°. In the catalytic studies the solid ortho-ethyl titanate was not used because we were unaware of the fact that the liquid was in a metastable phase and could be solidified.

The ortho-ethyl, *iso*propyl, and *n*-butyl titanates were exposed to the air of the laboratory in crystallizing dishes, the depth of the liquid not exceeding 6 mm. When the liquid had been hydrolyzed to a solid,

---

[11] Bischoff and Adkins, This Journal, **46**, 256 (1924).

the latter was ground to a fine powder and further exposed to the air until the odor of alcohol could no longer be detected. In the case of the ethyl titanate this was accomplished in five days, while the butyl titanate required three weeks. In the case of the butyl titanate, the removal of the butyl alcohol was hastened by raising the temperature to 70° for several hours each day. The methyl titanate was ground to a fine powder and exposed to the air in thin layers. The samples of hydrated titania from these alkoxides were thrown into water, before using, to make certain that no unhydrolyzed portion remained. It is interesting to note that these powders are only slowly wetted by water. The final drying temperature was below 120°. The titania from ethyl titanate always had the odor of aldehyde resins; the other products were odorless.

**From Demarcay's Compounds.**—By Demarçay's compounds are meant the crystalline products resulting from the partial hydrolysis of ethyl titanate in alcohol solution, ranging from $TiO(OH)(OEt)$, through $TiO(OEt)_2$ to $Ti_2O(OEt)_6$. The products were exposed to the laboratory air, as were the ortho esters, until no odor of alcohol could be detected. In the process of hydrolysis the crystals crumbled to an amorphous powder, which was washed with water and dried below 120°. In a few instances the wash water reacted alkaline to phenolphthalein, showing that some occlusion of sodium ethoxide had taken place in the crystallization.

When dried at 120°, all these titania catalysts had a moisture content of approximately 5%. The moisture content of the titania from the ortho-alkyl titanates was less than that calculated for orthotitanic acid and nearest to that for metatitanic acid.

## Data

The experimental data summarized in the figures and tables comprise the results of over two hundred experiments. The data have been corrected for "fouling." Some catalysts lose their activity more rapidly than others and so it becomes necessary to take the "fouling effect" into consideration when comparing the weights decomposed by the different catalysts. In the experimentation, a record was taken of the amount of gas produced for each ten minutes period of the run. From these data, it has been possible to calculate what the weights would have been if the rate of decomposition effective ten minutes after the run began had remained constant. The data so obtained are significant because they show that the absolute activity of the different catalysts does not vary nearly so much as seemed apparent from the yield of products. At the beginning of the experimental work 2.5 g. of catalyst was used for a run. Later this amount was cut to 2.0 g. All the data have been calculated on the basis of 2.0 g. of catalyst functioning for one hour, a series of experiments having shown that 2.0 g. of catalyst has 93% of the activity of 2.5 g. when packed in our reaction tube as previously described. The gas volumes are always corrected to standard conditions of temperature and pressure. An excess of the compound was always over the catalyst. At least twice as much substance was passed over the catalyst as reacted. The weights distilled are formic acid, 42–50 g.; acetic acid, 39–43 g.; butanol, 31–35 g.; ethanol, 30–34 g.; ethyl acetate, 36–42 g.; ether, 31–32 g. The analysis for saturated hydrocarbons by the explosion of gas from butanol always came well within the experimental error for butane and hydrogen. In the case of the ethanol, the carbon dioxide content from the explosion often indicated some hydrocarbon with more than two carbons to the molecule, although the discrepancy was never high. In the data all the hydrocarbon is calculated as ethane or butane and the remainder of the gas as hydrogen.

The activities of the catalysts as shown in Fig. 2 were calculated as follows. The weights of ether decomposed were calculated on the basis of the least amount which could yield the products obtained; thus, $1(C_2H_5)O \longrightarrow 2C_2H_4 + H_2O$; $1(C_2H_5)O \longrightarrow 1C_2H_6 + CH_3CHO$; $1(C_2H_5)O \longrightarrow C_2H_4 + H_2 + CH_3CHO$. The reasoning back of this assumption is given in the discussion on ether. The weights of acetic acid decomposed were calculated from the weight of carbon dioxide obtained on the basis of the following equation: $2CH_3COOH \longrightarrow CH_3COCH_3 + CO_2 + H_2O$. The values so obtained agreed with the difference between the amounts of acetic acid distilled and recovered, within a gram. The weights of alcohols decomposed were calculated from the weights of the gaseous products. The blank value of the apparatus for the various compounds was: 100 cc. of gas for acetic acid at 470°, 95 cc. for butanol at 430°, 360 cc. for ethyl acetate at 450°, 30 cc. for acetone at 430°, and 1.5 g. of formic acid at 300°, on the basis of one-hour runs. These blanks are all negligible except that for formic acid.

## Miscellaneous Data not Presented in the Discussion

**Acetic Acid.**—The percentage of gas residue after the carbon dioxide was absorbed was 7.8% for the titania from butyl titanate, 8.0% for that from titanic acid, 60% for that from ethyl titanate, 4.9% for that from methyl titanate, 4.7% for that from titanous chloride, 1.2% for that from sodium titanate and 0.7% for that from Demarçay's compound. The residue from the precipitated titania consisted of 4.8% of unsaturated hydrocarbons, 1.3% of carbon monoxide and 30% of saturated hydrocarbons and hydrogen. The distribution of these gases was approximately the same in the residues for the other catalysts.

The amount of acetic acid decomposed is a linear function of the temperature. Titania from titanic acid gave the following weights of carbon dioxide for one-hour runs and 2.5 g. of catalyst: 9.9 g. at 470°, 6.5 g. at

430°, 3.9 g. at 390°, 1.0 g. at 350°. By extrapolation, 330° is obtained as the initial temperature of the reaction.

**Ethanol, Butanol, Ethyl Acetate and Ether.**—In addition to the ethane, ethylene and hydrogen, and butane, butylene and butanol, respectively, a small amount of gas soluble in sodium hydroxide was always obtained. It was less than 1% of the gas mixture for all the catalysts, except for the Demarçay catalyst, for which it was 3.6%. In the ethyl acetate and ether gas mixtures there was always present from 1 to 2% of carbon monoxide. The ether also contained low percentages of a gas soluble in caustic alkali. This gas was either uncondensed aldehyde or carbon dioxide.

**Acetone.**—At 430°, 2.0 g. of precipitated titania formed 900 cc. of gas from acetone, while the "sodium titanate" catalyst yielded only 180 cc. The gas contained 20% of carbon dioxide, 8% of carbon monoxide and 40% of unsaturated hydrocarbons. The weights of acetone in the distillates from the acetic acid experiments were 1.4 g. for the butyl titanate catalyst, 1.8 g. for the precipitated titania, 1.6 g. for the ethyl titanate catalyst, 2.5 g. for the methyl titanate catalyst, 2.0 g. for the titanous chloride catalyst, 5.0 g. for the sodium titanate catalyst and 5.1 g. for the Demarçay catalyst. The weights of butanal in the distillates from the butanol experiments were 0.3 g., 0.4 g., 0.5 g., 0.5 g., 0.7 g., 1.3 g., 1.4 g., in the same order as that given above. The weights of acetaldehyde from ethanol were 0.5 g., 0.7 g., 0.6 g., 0.9 g., 1.1 g., 1.1 g., and 0.7 g., in the same order as that given above.

## Adsorption Measurements

The receptacle for the catalyst consisted of a U-tube of about 30cc. capacity fitted with capillary stopcocks as side arms. For the measurements at higher temperatures, it was found advisable to seal the stopcocks at right angles to the ends of the U-tubes which had been drawn out. The catalyst, in the form of pellets which had previously been dried at 300° for 12 hours, was introduced into the U-tube which was then sealed off as described above. Complete drying was then effected by passing a slow current of dry air through the U-tube held at 300° for 12 hours.

In making an adsorption measurement, the U-tube was heated at 300° for one hour under a pressure of 2.5 mm. or less. The pump was then shut off from the system by one of the stopcocks, and the gas to be adsorbed was allowed to enter at the same instant through the opposite cock. Atmospheric pressure was maintained throughout the determination by adjusting the leveling bulbs of the gas buret. When the U-tube had cooled sufficiently, it was immersed in a water-bath, held within 0.1° of the desired temperature, until no more gas was adsorbed. This procedure gave a simple method for measuring the total adsorption of a catalyst without, however, measuring the rate. By introducing the gas at the high temperature immediately after turning off the vacuum, the danger of leakage through the stopcocks was entirely avoided. This procedure was also quite necessary, since the gas burets were not sealed to the adsorption bulb but connected by rubber pressure tubing. The volume of the free space in the adsorption bulb was determined by preliminary evacuation followed by filling the entire apparatus with benzene from which the volume could be calculated. The time for an equilibrium to be reached in the adsorption measurement varied from a few minutes to a quarter of an hour. The carbon dioxide used was entirely absorbable in sodium hydroxide. Commercial hydrogen was used. It analyzed over 99% by explosion. The ethylene was prepared by passing alcohol over alumina at 400°. The gas was dried over calcium chloride and freed from aldehydes with soda lime. It analyzed 99%+, by bromine absorption, the residue being inflammable (probably hydrogen). The ethane was obtained by the reaction of ethyl iodide and ethyl alcohol with the zinc-copper couple.[12] The gas was bubbled through bromine water to free it from ethylene, and finally dried with calcium chloride. The gas analyzed 98% by explosion. The data for the adsorption measurements are given in Table III. The Roman numerals following the formulas for the catalyst source indicate different preparations of the same catalyst.

Excellent checks were obtained in the adsorption measurements for all the gases except ethane, where we have only reported the highest value obtained. Duplicate determinations checked within less than 1%.

The adsorption measurements are calculated for pressures of 740 mm., which was the average atmospheric pressure during the time the measurements were made. The greatest deviation was that of a pressure of 718 mm. Measurements made at 718 mm. and 740 mm. for the same adsorption checked within the experimental error.

TABLE IV

DATA FROM WHICH ADSORPTION VALUES WERE CALCULATED

Measurements made at 20° are marked (a) and those made at 97° (b). The volumes have been corrected to 20° and 740 mm.

| Source of catalyst | Wt. of catalyst | Volume not filled by catalyst | Cc. of $CO_2$ | Cc. of $H_2$ | Cc. of $C_2H_4$ | Cc. of $C_2H_6$ |
|---|---|---|---|---|---|---|
| $H_2TiO_3$ | 12.23 g. | 28.8 cc. | 241.1 (a) | 30.7 (a) | 170.4 (a) | 143.0 (a) |
| $Na_2TiO_3$ II | 11.18 | 34.1 | 154.6 (a) | 35.7 (a) | 120.2 (a) | 106.6 (a) |
| $Na_2TiO_3$ III | 11.01 | 28.6 | 181.6 (a) | 31.2 (a) | 133.5 (a) | 112.3 (a) |
| $H_2TiO_3$ | 5.26 | 15.3 | 107.3 (a)<br>44.1 (b) | | | |
| $Na_2TiO_3$ II | 5.54 | 13.8 | 90.8 (a)<br>42.8 (b) | | | |
| $Na_2TiO_3$ III | 6.32 | 17.7 | | | 73.0 (a)<br>36.0 (b) | |

---

[12] Frankland, *J. Chem. Soc.*, 47, 236 (1885). We isolated Zn(OH)OEt.

## Summary

The reported reduction of acetic and propionic acids by formic acid to the corresponding aldehydes has not been confirmed.

Several new titania catalysts have been prepared and used with formic acid, acetic acid, ethyl acetate, ethanol, *n*-butanol and ethyl ether. These titania catalysts are markedly different from one another in their catalytic effects. Those resulting from titanic or titanous chlorides, and from the air hydrolysis of the alkyl titanates, are reproducible as to relative activity. Those obtained from sodium titanate are not precisely reproducible either as to relative or absolute activity. An extended experimental investigation of the selective activation of titania catalysts has justified the hypothesis, previously advanced for alumina catalysts, that the proportion of two or more reactions taking place simultaneously on the surface of the catalysts is determined in part by the distances between the "active points" on the catalyst.

The surface conditions that determine relative catalytic activity are apparently determined not only by the size and shape of the radical attached to titanium when the compound goes into the solid state, but also by the mechanism of hydrolysis and dehydration of the catalyst source. That is, they depend upon such factors as the type or structure of the ultimate titania molecules.

Evidence is presented that ethyl alcohol does not form ethylene at the surface of titania through the intermediate formation of ether.

There is no evidence that the saturated hydrocarbon resulting from the catalytic decomposition of the alcohols or ether is a secondary product of reaction due to the hydrogenation of the olefin. The reaction apparently involves an auto-oxidation and reduction and takes place either between two molecules of alcohol or between two parts of the ether molecule with the formation of an alkane and an aldehyde.

Formic acid has been found to be as reactive on an ignited as on an unignited catalyst, which differentiates this from the other reactions studied and has led us to classify the reaction as one due in part to "secondary adsorption."

The adsorption of carbon dioxide, ethylene, ethane and hydrogen by these samples of titania has been determined at 20° and 97°. The titanias differed greatly in absolute and relative catalytic activities but showed no similar differences in the adsorption of the gases which were the products of the reactions catalyzed. It has been shown that ammonia is much more effective in shifting the ratio of butane and butylene than is water. None of the above facts is in accord with the hypothesis that the relative activity of these catalysts is determined by factors affecting adsorption.

There is no relationship between the relative activities of a catalyst for

different reactions and its absolute activity as measured by the amount of material undergoing reaction.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

# ARSONOPHENYL-CINCHONINIC ACID AND DERIVATIVES

BY KATHARINE OGDEN[1] WITH ROGER ADAMS

RECEIVED AUGUST 12, 1924 PUBLISHED MARCH 5, 1925

In an earlier paper[2] it was pointed out that a study of arsenated derivatives of compounds containing the heterocyclic nitrogen nucleus was a promising field in which to find trypanocidal compounds. A series of derivatives of phenyl-diketopyrrolidine were made by the condensation of benzaldehyde, pyruvic acid and arsanilic acid or their derivatives. The compounds thus produced were distinctly trypanocidal but had other properties which made them useless from a practical standpoint. Phenylcinchoninic acid (Cinchophen) and its derivatives are so useful as drugs and so comparatively non-toxic, that a study of arsenated derivatives seemed of interest. This communication describes the preparation of such compounds with the arsonic acid radical substituted in the phenyl group.

The only convenient method for the preparation of phenyl-cinchoninic acid derivatives other than the benzaldehyde, pyruvic acid and amine method, which has been shown not to be applicable to arsenic compounds is that discovered by Pfitzinger[3] which consists in the condensation of isatin with acetophenone in the presence of alkalies. The method has not attracted much attention until recently, when a very convenient and cheap method was found for the preparation of isatin and its derivatives,[4,5] from primary aromatic amines, chloral and hydroxylamine.

In place of acetophenone, certain arsono-acetophenones were condensed with isatin and substituted isatins. The reactions ran normally and yielded the corresponding arsonophenyl-cinchoninic acids (I).

---

[1] This communication is an abstract of a thesis submitted by Katharine Ogden in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Johnson with Adams, THIS JOURNAL, **43**, 2255 (1921); **45**, 1307 (1923). In the first paper the condensation product of benzaldehyde, pyruvic acid and arsanilic acid was incorrectly reported as 2-phenylquinoline-4-carboxylic acid-6-arsonic acid. As shown in the second paper, it was actually a derivative of phenyl-diketopyrrolidine.

[3] Pfitzinger, *J. prakt. Chem.*, **146**, 583 (1888).

[4] Ger. pat. 301,591; *Chem. Zentr.*, 1918, I, 148; Brit. pat. 128,122; *J. Chem. Soc., Abs.*, **116**, I, 599 (1919); Ger. pat. 320,647; *J. Chem. Soc., Abs.*, **118**, I, 682 (1920).

[5] Sandmeyer, *Helvetica chim. Acta*, **2**, 239 (1919).