

5. Catalysis of the water-gas reaction thus being excluded from consideration, it has been shown that the acceleration of the reaction  $C + CO_2 = 2 CO$ , and therefore the acceleration of the reaction,  $C + 2 H_2O = CO_2 + 2 H_2$ , may be ascribed to increased adsorption of carbon dioxide by the carbon surfaces in presence of active catalytic agents.

6. Adsorption measurements have been shown to confirm this view.

7. The results obtained have been considered in view of the proposed existence of a surface complex  $C_xO_y$ , and have been found to agree with this conception.

The authors of this paper wish hereby to thank Dr. R. M. Burns for his assistance in the adsorption measurements.

This research was carried out while Mr. Neville was the DuPont Fellow in Princeton; and it is desired to express to the DuPont Company an appreciation of their aid.

PRINCETON, NEW JERSEY.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NOTRE DAME.]

## THE ROLE OF MERCURY SALTS IN THE CATALYTIC TRANSFORMATION OF ACETYLENE INTO ACETALDEHYDE, AND A NEW COMMERCIAL PROCESS FOR THE MANUFACTURE OF PARALDEHYDE.

BY RICHARD R. VOGT AND JULIUS A. NIEUWLAND.

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It is well known that acetaldehyde can be prepared commercially from acetylene and water by the use of mercury salts as catalysts. A drawback to the process lies in the ease with which the mercury salt is reduced to the metallic state, and this rate of reduction depends upon the specific mercury salt used and the acidity and temperature of the solution in which it is dissolved. It seemed desirable to determine which type of mercury salt solution can best be used in this process and to investigate the mechanism of the reactions involved as the exact nature of the changes taking place is not as yet known. A study was accordingly made of the rate and duration of the reaction of acetylene using various mercury salts in solutions of the corresponding acids at different concentrations and temperatures. Mercuric sulfate in dil. sulfuric acid solution was found to be most suitable for this purpose on account of the cheapness, activity, and lasting qualities of this catalytic solution. It was found, however, that in these solutions the mercury did not long remain in the form of the sulfate but was converted to an organic compound, and this compound acted as the catalyst.

Some reduction of mercury compounds to metallic mercury took place

in the dil. sulfuric acid solutions, and there was also a tendency for the acetaldehyde to form undesirable condensation products. With higher concentrations of sulfuric acid there was a decrease in the reduction of the mercury catalyst but an increase in the quantity of acetaldehyde destroyed. In attempting to avoid this dilemma a process was devised in which acid sulfate solutions of high concentration were substituted for dil. sulfuric acid, resulting in the production of fairly pure paraldehyde with very little mercury reduction. Since paraldehyde can readily be converted into acetaldehyde and can also be substituted for it in many reactions, it is thought that this process may be of commercial value. A process was also devised for the utilization of the acetaldehyde for the formation of quinaldine directly in a rather conc. sulfuric acid solution of the catalyst. There was slight mercury reduction and little loss of acetaldehyde by formation of condensation products. This indicates the possible advantage of using the acetaldehyde directly in the catalytic solutions for further synthesis.

A dry catalyst was also employed, consisting of a mixture of an organic mercury compound with an acid sulfate of ammonia or one of the alkali metals, and moist acetylene or a mixture of acetylene and steam was thereby slowly converted into acetaldehyde with no reduction of the mercury compound and no destruction of the aldehyde. From this and other indications it appears that the reduction of mercury salts in these processes is in some way due to their hydrolysis in aqueous solutions.

### Experimental.

#### I. Investigation of the Use of Different Mercury Salts as Catalysts.

Instead of passing a continuous stream of acetylene through the catalytic solutions and allowing the excess of gas to escape as has commonly been done, in all of these experiments the solutions were placed in a closed absorption vessel from which all air had been displaced by acetylene and this vessel was connected through a wash bottle with a gasometer filled with acetylene. The gas was rapidly absorbed on shaking the catalytic solution, and the rate, amount, and duration of absorption could be accurately ascertained by noting the reading of the gasometer and the flow of gas through the wash bottle, and by taring the absorption vessel.

It was soon found that many mercury salts in both acid and neutral solutions when shaken with acetylene would absorb it rapidly for a short time with the formation of precipitates, but that none of the neutral solutions and only a few of the acid solutions would continue to absorb readily after the precipitation had ceased.

Thus on the one hand, mercuric chloride in dil. hydrochloric acid and mercuric bromide in dil. hydrobromic acid absorb acetylene slowly for a time and then cease entirely to do so; while in stronger acid solution or in

concentrated solutions of halide salts no reaction occurs. Mercuric acetate in acetic acid solution also failed to react with acetylene after precipitation was complete, and mercuric phosphate in phosphoric acid solutions only absorbed acetylene very slowly after the initial reaction was over. *It is characteristic that the acetylene compounds of all of these salts were found to be only slightly soluble in the corresponding acids.*

On the other hand, mercuric perchlorate in perchloric acid, mercuric fluoborate in fluoboric acid, and mercuric nitrate in nitric acid, several of the mercuric sulfonates of the aromatic series in the sulfonic acids, and mercuric sulfate in sulfuric acid continued to absorb acetylene for a long time. *The acetylene compounds of all of these salts were found to be markedly soluble in the corresponding acids.* No acetaldehyde could be obtained from the nitric acid solutions, and the perchlorate, fluoborate, and sulfonates were considered too expensive for commercial use.

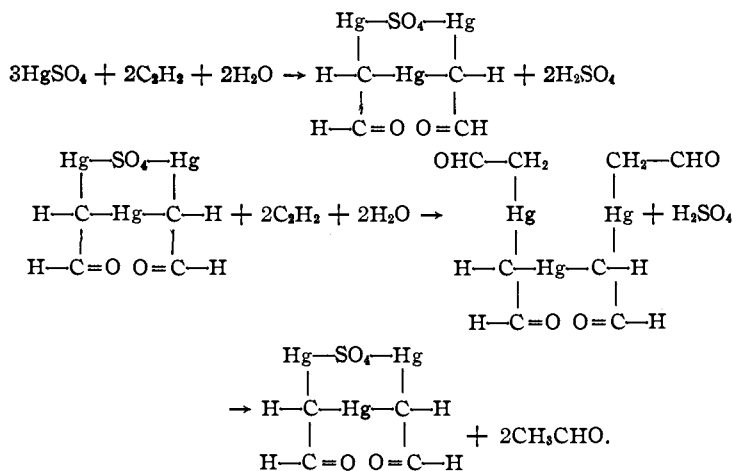
In view of these results the action of mercuric sulfate was submitted to a closer examination. It was found that in sulfuric acid of less than 20% concentration the catalyst is always reduced to metallic mercury with objectionable rapidity, on reaction with acetylene. The ratio of acetaldehyde formed to mercury salt reduced is accordingly very narrow in such a solution. With a sulfuric acid in concentrations above 20% the acetaldehyde cannot be distilled at ordinary pressure without the formation of large quantities of crotonaldehyde and tarry by-products, and the methods that have been devised for separating the acetaldehyde with organic solvents or of volatilizing it with excess acetylene or under reduced pressure are complex and expensive. We have accordingly studied the cause of these difficulties and have originated new processes in which they are at least partially obviated.

## II. The Nature of the Catalyst Compounds and the Cause of their Reduction to Metallic Mercury.

Exact information concerning the nature of the catalyst mercury compounds is very difficult to obtain by analytical methods on account of the high molecular weight of mercury, the inaccuracy of mercury determination, the constantly changing state of the catalyst, and the probability of the presence of numerous impurities in it. It has been frequently supposed that the inorganic salts of mercury acted as carriers of acetylene, but if this were the case some of the inorganic salt would be continually regenerated, especially if the supply of acetylene were shut off. However, no yellow mercuric oxide can ever be isolated from these mixtures by the addition of alkaline hydroxides; only white or gray organic substances are obtained in this way. It was not possible to detect any inorganic salts of mercury in any of the catalytic mixtures after the absorption of acetylene. The catalyst prepared from mercuric sulfate, moreover, always contained the

sulfate radical and at least one attached acetylene residue. The empirical formula,  $3\text{HgO} \cdot 2\text{C}_2\text{H}_2$ , has been fairly well established for the precipitate obtained by treating mercuric acetate in dil. acetic acid with acetylene.<sup>1</sup> When this compound is dissolved in dil. sulfuric acid it behaves in every way exactly like the compound precipitated from mercuric sulfate solutions with acetylene. It is therefore assumed that the precipitate from mercuric sulfate solutions is the sulfate of the same radical of which the precipitate from mercuric acetate is the oxide; and what appears to be a possible structural formula for this catalytic compound is given below. It is slightly soluble in strong alkaline solutions, and can be precipitated from such solutions with additional acetylene. Sulfuric acid releases a small quantity of acetaldehyde from this precipitate thus showing in two distinct stages the probable action in acid solutions. Small crystals of this catalyst can be obtained by dissolving it in warm dil. sulfuric acid and then cooling the solution.

The following reactions illustrate this point of view.



As far as is known, some acid is always liberated by the action of acetylene on the salts of mercury. It will be noted in the above reaction that the mercuric sulfate appears to supply all of the acid that is necessary, but nevertheless acid is always added to catalytic solutions in actual practice. An attempt was made to form acetaldehyde by passing moist acetylene over various mercury salts in the solid state. Mercuric chloride did not react with acetylene under these conditions. Nitrous fumes were liberated from mercuric nitrate by this method, but no acetaldehyde could be detected. From the reaction of mercuric sulfate with moist acetylene, acetaldehyde and free sulfuric acid resulted, and the acid immediately charred and polymerized a part of the aldehyde. When, however, moist

<sup>1</sup> Plimpton, *Chem. News*, **65**, 295 (1892).

acetylene at  $100^{\circ}$  was passed over a dry finely divided mixture of sodium sulfate and mercuric sulfate, the sulfuric acid which was liberated combined with the sodium sulfate to produce sodium hydrogen sulfate, there was no charring, and a considerable quantity of pure acetaldehyde was produced. It was thus demonstrated that, under these conditions, mercuric sulfate will furnish all of the acid necessary for carrying on the reaction according to theory.

As a side reaction in all of these catalytic processes we are likely to have the continual reduction of mercury compounds to the metallic state, and this is a very serious commercial disadvantage. Numerous attempts have been made to prevent the reduction of mercury salts by the use of oxidizing agents in the solution. It is understood that none of these has proved of any value in practice. The salts of iron, manganese and vanadium were tried without securing any favorable results.

In general it was found that the greater the dilution of an acid solution the more rapidly mercury salts were reduced in it by the action of acetylene; and it is to be noted that the dilution of the acid is also closely related to the hydrolysis of mercury salts. The solutions of those mercury salts which hydrolyze most readily in their corresponding acids are also those in which the most rapid reduction takes place. Thus in dil. hydrochloric acid there is little reduction; in dil. sulfuric, somewhat more; in dil. nitric or acetic, a great deal. This leads us to the conclusion that, perhaps, most of the reduction of mercury salts is due to the action of acetylene or acetaldehyde on hydrolyzed mercury compounds, containing an oxide or hydroxyl group instead of an acid radical. Moist mercuric oxide is reduced by acetylene more rapidly than any other mercury compound. We find that this theory is also supported by the fact that in alcoholic solutions both hydrolysis and reduction are less than in aqueous solutions. It should be remembered that the catalytic mercury compounds, being organic, will probably hydrolyze much more in concentrated acid solutions than the corresponding inorganic salts.

On the other hand, we find some mercuric catalytic compounds reduced in conc. sulfuric acid where there is little possibility of hydrolysis. Charring of the organic matter always takes place in such solutions with the formation of sulfur dioxide. This substance will reduce mercury salts even in strong acid solutions, and the reduction in conc. sulfuric acid is thus accounted for.

The only way in which acetaldehyde could be obtained without the reduction of any mercury salt whatever was by the action of a stream of moist acetylene at  $70^{\circ}$  to  $120^{\circ}$  on a dry mixture of the mercuric sulfate acetylene compound and sodium, potassium, or ammonium hydrogen sulfates. This mixture could be made either by the action of moist acetylene on mercuric sulfate and the normal sulfates of sodium, potassium

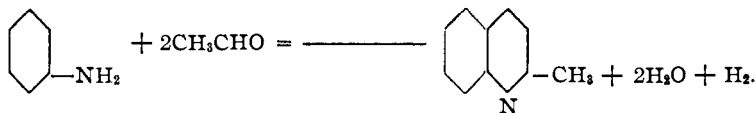
or ammonium finely ground together, as explained above; or the acid salt could be added to the washed and dried precipitate obtained from an acid mercuric sulfate solution by the action of acetylene. From such a mixture only about one gram of acetaldehyde per gram of mercury could be obtained in 12 hours, but there was no reduction of the mercury compound and the mass was perfectly soluble in water after use. When an excess of moisture or steam was used with the acetylene, a little of the mercury compound was volatilized. While this method may not be of much practical value, it serves to confirm the belief that the reduction of mercury compounds by acetylene is in some way due to their hydrolysis in dilute acid solution and points to the advantage of using stronger acid whenever possible.

It can also be shown that metallic mercury is slowly dissolved by the more concentrated solutions of sulfuric acid and the acid sulfates, but with acid strengths below 15% which have frequently been used for this purpose, this action is almost negligible.

The advantages of stronger acidity of the catalytic solutions having thus been demonstrated it became necessary to devise either a method for separating aldehyde from such strong acid solutions without the formation of undesirable by-products, or a method of utilizing the aldehyde directly in the solution for further synthesis and in this way avoiding the difficulties of separation.

### III. The Preparation of Quinaldine.

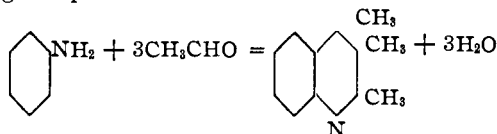
The acetaldehyde in these catalytic solutions was successfully substituted for pure acetaldehyde in the preparation of quinaldine. According to a standard process quinaldine is manufactured by treating aniline in hydrochloric acid or sometimes in sulfuric acid solution with a large excess of acetaldehyde or paraldehyde.



In the following process cheap acetylene takes the place of acetaldehyde. More concentrated sulfuric acid than can be used in making acetaldehyde from acetylene can be employed without the formation of tarry by-products. The violence of the standard quinaldine reaction is also avoided, giving more suitable conditions for manufacture on a large scale. In the old method a considerable excess of acetaldehyde was necessary, and in the new also it was found best to use an excess of acetylene. This can readily be done, since a given volume of the catalytic solution will absorb so much acetylene that the addition of a proportionate amount of aniline makes the mixture too viscous to handle.

Since quantities of a substance corresponding in properties to the

trimethyl-quinoline below indicated have been obtained in the process to be described, it is probable that under the conditions the following reaction takes place to a considerable extent in addition to the one which occurs in the regular process.



The following example will make clear the procedure.

Two g. of mercuric sulfate and 400 g. of aniline sulfate were dissolved in one liter of 40% sulfuric acid at 60° in a 2-liter flask which was then filled with acetylene, stoppered, and connected by a tube to a supply of acetylene under slight pressure. At this temperature fairly rapid absorption of the gas began at once but the speed was greatly accelerated by shaking the flask at frequent intervals. In a later experiment the same result was attained by using a drip absorption tower. In about 6 hours when 200 g. of acetylene had been absorbed, sodium carbonate was added until the solution was only slightly acid to litmus. The solution was then filtered and the precipitate contained practically all of the by-products, among them the substance thought to be trimethyl-quinoline above referred to. The filtrate was then made strongly alkaline with sodium hydroxide, causing the quinaldine and a small excess of aniline to separate as an oil. The quinaldine was purified by the ordinary methods and gave a yield of 80 g., which compares well with ordinary yields from the present commercial process.

Fifty g. of the dried by-product precipitate was heated for 5 hours at 200° with 50 g. of phthalic anhydride and 50 g. of zinc chloride, and the mass was then dissolved in hot conc. sulfuric acid and diluted in a process similar to the process for making quinophthalone from quinaldine. Considerable quantities of an orange dye were obtained showing that the original by-products were probably substituted quinaldines. The dye has properties very similar to quinophthalone, but produces an orange instead of a yellow color. The yield from the crude precipitate was only half of that calculated for trimethyl-quinoline of the same weight, on the basis that the phthalone was formed in the usual manner.

The concentration of the sulfuric acid used in these experiments varied from 10% to 95%. The temperature varied from 20° to 100°. A concentration of about 40% of sulfuric acid and a temperature of 60° seemed most advantageous. The use of phenol sulfonic and toluene sulfonic acids gave the same results as sulfuric acid. Aniline dissolved in 35% perchloric acid containing mercuric perchlorate gave very little quinaldine with acetylene and a large amount of the supposed trimethyl-quinoline. This substance separated from the acid solution and could be removed without neutralization.

The precipitate formed by the acetylene from mercuric acetate solutions was frequently used as a catalyst instead of the mercuric sulfate compound, and gave very satisfactory results.

It was found that the addition of acetone to the solution hastened the reaction, probably by increasing the solubility of the acetylene.

The aniline sulfate may be added at the beginning of the process, or while the absorption is going on, or aniline may be added when the absorption is complete, thus

neutralizing part of the sulfuric acid. It was found best to add at least part of the aniline as sulfate at the start as this tended to prevent the polymerization of acetaldehyde to tarry by-products.

It has been found possible to recover a portion of the excess acetaldehyde formed from the excess acetylene by diluting the sulfuric acid to a concentration of less than 10% and distilling the aldehyde.

The action of substituted anilines is exactly analogous; the toluidines, for example, yield the corresponding methyl-quinolines.

It will be noted that according to theory no water is used in this reaction, and this led to an attempt to carry on the process by using aniline sulfate, sodium hydrogen sulfate, mercuric sulfate, and acetylene in a nearly dry state. Acetylene was absorbed rapidly at first and some quinaldine was formed, but the mass soon became a viscous semi-solid into which the acetylene could not penetrate.

It was also found that the preparation of quinaldine could be carried on in absolute alcohol solution with dry acetylene. This points to the possibility that acetaldehyde may not be an intermediate product, but that the aniline may react directly with the mercury acetylene compound.

The preparation of aldehyde green is a related reaction that can also be performed with acetylene instead of acetaldehyde or paraldehyde. A present standard method for the synthesis of the commercial product is to treat fuchsin in rather strong sulfuric acid with about  $\frac{1}{3}$  of its weight of paraldehyde, then boil with sodium thiosulfate, filter, and treat the filtrate with sodium acetate. In this experiment 40 g. of fuchsin was dissolved in 100 g. of 50% sulfuric acid, containing 1 g. of mercuric sulfate, and the solution was allowed to absorb 7 g. of acetylene. It was then boiled with 5 g. of sodium thiosulfate, filtered, and treated with 8 g. of sodium acetate. Both a green and a blue dye were present. The mixture did not absorb acetylene very readily, but this may have been due to the presence of chloride in the fuchsin.

#### IV. Preparation of Paraldehyde.

It was often noted that when solutions containing acetaldehyde were allowed to stand for a few days an odor of paraldehyde developed, and in a few cases droplets of paraldehyde separated from perchloric and sulfuric acid solutions. It was next found that a mixture of sodium hydrogen sulfate and mercuric sulfate in a moist state became covered with a film of paraldehyde when acted upon by acetylene and this action is the basis of the process to be discussed.

The most convenient apparatus for carrying on this reaction in the laboratory is a large bottle or carboy filled with fragments of glass or porcelain. These are covered with a pasty mass made up of an acid salt, a catalytic mercury compound, and a small amount of saturated aqueous solution of the acid salt. The air in the apparatus is then displaced by acetylene, the carboy tightly stoppered, and acetylene led into the apparatus as fast as it is used. The carboy is rolled occasionally to keep the catalytic mixture evenly distributed



Mercuric sulfate, mercuric acetate, the acetylene compounds of the two salts precipitated from acid solution, and mercuric oxide were used in different experiments without markedly different results. Mercuric phosphate was not so good.

Acid phosphates and sulfates of ammonium, sodium, and potassium were experimented with. The acid phosphates were discarded because of their slow action and high mercury reduction. Sodium hydrogen sulfate is the cheapest material and is perfectly satisfactory for this purpose. Ammonium hydrogen sulfate solutions dissolved more acetylene and more of the resulting paraldehyde than any of the others.

The solution of acid salt must be saturated because reduction of mercury takes place more readily in dilute solutions, and it is best to have an excess of undissolved acid salt in the apparatus in order to saturate rapidly any water that may be added from time to time. As little solution as possible was used in most of these experiments, because larger amounts dissolved the paraldehyde and retarded its separation. Since the saturated solutions of the acid sulfates do not dissolve either acetylene or the mercury acetylene catalytic compound to a very great extent, it is necessary to have the acetylene come in direct contact with the solid catalyst, and this is prevented by the presence of much solution.

In this process acetaldehyde is first formed by the action of the mercury acetylene compounds on acetylene and water. The acid salts at ordinary temperatures and in saturated water solutions or in solid form, then rapidly and completely polymerize the acetaldehyde to paraldehyde. As paraldehyde is but slightly soluble in saturated solutions of the acid salts, it separates as a distinct layer and may be drained off in a fairly pure condition. The paraldehyde shows little tendency to cling to the catalyst mixture as long as this is protected by a film of moisture, and no solid matter is ever suspended in the paraldehyde.

The absorption of acetylene is more rapid after a certain amount of paraldehyde has been formed in the apparatus. The reason is that the paraldehyde dissolves the unconverted acetaldehyde vapor which would dilute the acetylene and thus slow up absorption and also because paraldehyde dissolves acetylene and brings it into more immediate contact with the catalysts.

The water needed in the reaction can be partially supplied by using moist acetylene, but more water must be added as often as the amount in the apparatus diminishes. It is better to add the water in small amounts and with thorough mixing, as a sudden dilution causes a sudden and notable graying and reduction of the mercury.

Considerable amount of certain impurities, especially the halides retard the absorption of acetylene greatly. Free sulfuric acid hastens absorption but the resulting paraldehyde is dark in color and contains

traces of crotonaldehyde. It should be noted that when mercuric sulfate reacts with acetylene sulfuric acid is liberated, and this will produce the same effect in a mixture as added sulfuric acid. When mercury is introduced in the form of sulfate it is best to add a small amount of the normal salt corresponding to the acid salt used to take up any free sulfuric acid that may be formed in this way. When this precaution is observed the paraldehyde is clear and colorless, and the excess of normal salt does not materially affect absorption.

The following example of laboratory procedure will serve to illustrate the process.

A 2-liter bottle was filled with clean dry glass fragments, and a mixture of 10 g. of mercuric sulfate, 40 g. of sodium hydrogen sulfate and 20 g. of water was then distributed over the surface of this packing material. The air was displaced by acetylene and the bottle tightly closed except for the inlet tube through which moist acetylene under slight pressure was continuously supplied from a gasometer. As soon as the white compound of acetylene and mercuric sulfate had been formed, acetaldehyde could be detected in the apparatus, and shortly afterward paraldehyde was also shown to be present. When about 25 g. of acetylene had been absorbed, paraldehyde began to accumulate in visible drops. Thereafter the formation of paraldehyde was practically quantitative. The production from the apparatus used was about 60 g. per day, and the total amount obtained was 287 g.

In another experiment a mixture of 295 g. of sodium hydrogen sulfate, 250 g. of water, and 75 g. of mercuric nitrate was used in the same way. Ten cc. of nitric acid was added at the end of both the fifth and ninth day, and this seemed to redissolve some of the reduced mercury and increase absorption slightly. Water was added in small quantities as needed. The paraldehyde was drained off daily, and at the end of the tenth day when the experiment was accidentally lost, the total amount obtained was 1100 g.

A mixture of 1250 g. of ammonium hydrogen sulfate, 200 g. of water, and 300 g. of mercuric nitrate was allowed to absorb acetylene for a few days before the separation of paraldehyde began. It then yielded from 300 to 500 g. of paraldehyde per day, with some interruptions due to lack of acetylene, and at the time of this writing is still running and has given a total yield of 3400 g. of paraldehyde, an aldehyde-mercury ratio of 17:1.

A mixture containing 200 g. of potassium hydrogen sulfate, and 50 g. of mercuric sulfate with frequent small additions of water absorbed acetylene for 130 days. Twenty-five g. of mercuric sulfate was then added and the experiment was carried on for 35 days longer. A total yield of 1800 g. of paraldehyde was obtained, giving an aldehyde-mercury ratio of 35:1.

The paraldehyde prepared by this method contains a small amount of dissolved water and acid salt, and, if the separation takes place immediately after absorption, unchanged acetylene and acetaldehyde may be present. These impurities were never found to run higher than 5%. The heat of formation of the paraldehyde did not appear to be as great as was expected. A 20-liter carboy of the mixture distributed over glass fragments absorbed acetylene at the rate of 2 liters per minute.

#### Summary.

It was shown by experiments on the relative value of different mercury salts as catalysts for the conversion of acetylene to acetaldehyde that

mercuric sulfate in sulfuric acid solution is the cheapest and most efficient for the purpose. It was found that the chief difficulties in its use lie in the impossibility of separating acetaldehyde from the more concentrated acid solution and in the rapid reduction of the mercury compounds in the dilute acid which is now commercially employed. The reduction of mercury compounds by acetylene and aldehyde is greatest where the conditions are the most favorable for hydrolysis, and the catalytic mercury compounds being organic are probably more readily hydrolyzed than the inorganic salts of mercury. No reduction takes place in a suitable dry mixture where there is no hydrolysis but this method is too slow for commercial use. Attention was therefore turned to methods of utilizing acetaldehyde in rather concentrated solutions of sulfuric acid or the acid sulfates.

A new method for the synthesis of quinaldine and related products has been worked out. A new paraldehyde process has been developed which is capable of being used as a substitute for the method of acetaldehyde production now in use and which has the following advantages: (1) the ratio of aldehyde to reduced mercury is much higher; (2) the apparatus is simpler and the catalyst less bulky; (3) no distillation or separation process is necessary; (4) there are no by-products and no waste products; (5) there is no excess acetylene to be recovered.

NOTRE DAME, INDIANA.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## THE EXISTENCE AND REACTIONS OF POSITIVE HALOGEN ATTACHED TO CARBON IN AROMATIC COMPOUNDS.

BY BEN H. NICOLET.

Received May 4, 1921.

The halogen atoms in certain organic compounds have the property of being replaced by hydrogen, and appearing combined with the hydroxyl group as hypohalous acids, on hydrolysis. This behavior is frequently expressed by referring to such atoms as positive halogen atoms. Most, if not all, of the compounds in which halogen replaces the hydrogen of an hydroxyl, amino, or imino group, have this halogen in the positive form.

Without doubt, halogen attached to carbon is usually negative. Nevertheless, Howell and Noyes<sup>1</sup> have recently offered excellent evidence that iodine is positive in the compound  $C_2I_2$ . Fry<sup>2</sup> had previously assigned a structure involving positive chlorine and bromine, to certain aromatic compounds, but primarily on the ground of the extreme difficulty of hydrolyzing such compounds. The negative test of non-reaction is necessarily an uncertain basis for the assignment of electronic structures.

<sup>1</sup> Howell and Noyes, *THIS JOURNAL*, **42**, 991 (1920).

<sup>2</sup> Fry, *ibid.*, **38**, 1327, 1333 (1916).