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The Preparation and the Properties of Metal Acetylides

THE PREPARATION AND THE STUDY OF THE PROPERTIES OF METAL ACETYLIDES

BY

arrie

B. DANA

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I-- INTRODUCTION

The attempts described in this thesis were made with the principal object of preparing acetylides of the type $M''C_2$ by the methods differing from previous ones. Our further intention was, in case we were successful, to prepare by new methods, not only metal acetylides already known, but also such others that have so far resisted isolation; and then to study the new situation, particularly with respect to the properties of the new acetylides.

It was found, however, that the two successful methods already devised, could not be improved upon, nor superseded by new ones without undertaking more elaborate investigations than the limited scope of the present task permitted.

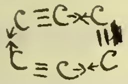
II--HISTORICAL

The lowest member of the acetylene series has the carbon residue, $-C\equiv C-$. It was first discovered in 1836 by E. Davy (1) of the Royal Soc., Dublin. Chavastelon(2) found in 1897, that $H-C\equiv C-H$ was very weakly acidic, and hence, its two hydrogen atoms were replaceable by metals primarily, forming the corresponding metal salts, or, more specifically, the metal acetylides. Authentic records of the formation of the first metal acetylides are said to go back to 1808, when Davy prepared potassium acetylide by means of electricity. This was twenty-eight years before the acetylene gas itself, H_2C_2, was known. This application of electricity to the preparation of acetylides was destined to become a most effective means toward the end of the century in the hands of Henri Moissan, the celebrated French chemist and champion of the electric furnace, who, beginning from the '90s has prepared almost all the metal acetylides that could be formed in the electric furnace, where heat up to about 4000° is said to be capable of development. It has been found, that almost all metals, that form acetylides, would do so more or less readily, by this means. A few metals, such as the metals of the platinum family, and some others, such as lead, tin, gold, cadmium, evince an ill-defined behavior toward acetylene. Keiser(3) has shown that copper and silver acetylides, Cu_2C_2, Ag_2C_2, (and even mercury acetylide), can be prepared quite easily in a cold solution of these metals by passing into it the acetylene gas itself.

What little work has been done in this field since Moissan's epoch-making carburation by means of the electric furnace, however, has been relatively of minor importance. The acetylides of

certain metals, such as that of tin, lead, platinum, gold, and others, still resist isolation, obviously awaiting the devising of methods more suitable for their carburation.

III-- THEORETICAL

The hardness of diamond, the hardest of all elemental substances, may be taken as a rough indication of the very high centripetal, cohesive property, or polymerizing tendency of the carbon atom. This force in the carbon atom is 13,400 times that in the helium atom, or, barring the inert gases, 7500 times that in the hydrogen atom. And if it has been crystallographically proved that, at least this allotropic modification of carbon consists of residual carbon of the type of benzol rings, then it is not surprising, that the hydrogen derivative of the acetylene skeleton, -C≡C-, having, in addition, to be torn out of the benzol ring,  , has proved to be about the most elusive carbon skeleton to be isolated. The amount of heat injected in overcoming this centripetal resistance of the acetylene residue, -C≡C-, in order to depolymerize it, is perhaps what Ostwald (in his Principles) calls free energy. This free energy, left behind, when H_2C_2 burns into H_2O and 2C O_2, amounts to about 68,144 cals, and which is unaccounted for in any other way except by the supposition that it was the amount of heat used originally to isolate the carbon residue, -C≡C-, of the acetylene molecule.

Although one or both of the hydrogen atoms of H_2C_2 can be replaced by almost any element or a radical, we are concerned here only with the replacement of these hydrogens by elemental atoms less acidic than the carbon atom itself. Replacement of this kind is a reaction of salt formation, pure and simple, in which acetylene must be regarded as furnishing the acid constituent of the salt molecule. Since acetylene is not generally looked upon as an acid, however, it becomes necessary, first of all, to show the acidity of this most unsaturated of all the hydrocarbons.

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Chavastelon(2) showed in 1897, that when an excess of H_2C_2 was led into an aqueous or ammoniacal solution of silver nitrate, the amount of the acetylene absorbed could be determined from the amount of the nitric acid set free. The procedure was, thus, one of simple determination of an acid. Acetylene, was, then, rightly looked upon as an acid. A reliable experimental proof is as a rule regarded as final in the establishment of a scientific contention. It may not be amiss, however, to offer the following personal observations for what little they may be worth, in further reinforcement of Chavastelon's direct proof.

Neither an acid nor a base would be the abhorent things their names suggest, were it not for the existence of water--itself the most harmless of all the chemical compaunds. It is a pity, that whenever in need of actuating reagents, we use an acid or a base, while we might use both of these, united most conveniently in the water molecule-- by far the greatest of all catalizers in existence without any exception whatsoever, because the perfectly balanced water molecule is almost equivalent to two rays of the sun. While we can not think of an acid without its hydrogen, this hydrogen itself can not be an acid, although just as many if not more arguments have been advanced to place it at the top of the seventh group of elements on the Periodic Table. The acidity of an acid is seated in the pertner of hydrogen in the molecule. The more intense the inherent acidity of this acidic atom the greater the balance shown toward the basic hydrogen, hence the greater the dissociation and finally the greater the activity of the hydrogen atom.

Though hydrogen compounds of many basic elements are known, the first element we encounter as we proceed toward the right on

the Periodic Table is boron, which is invariably acidic. Since the mutual distances of the elemtns on this table is an index of the gradation of their properties, the invariable acidity of carbon thus becomes automatically undesputable, because it lies farther inside the acidic region. To be sure, nitrogen, occupying even a more acidic position, shows the apparent anomaly in ammonia. But this may be considered as a characteristic of those elements that show variable valency. Such elements would often show basic properties in their lower valencies, that is, in those valencies which represent a proportionately larger atomic mass, or EQUIVALENT. As we proceed down any group we observe, similarly, an invariable increase of basicity with every increase of atomic weight, as if all elements overlapping in all directions formed a solid table, so-to-speak, containing all the chemical elements. Perhaps cabron itself would be found to show residual basicity if ~~the~~ methylene, H_2C_2, was ever isolated, in which carbon would then be found to have an equivalent of 6 per vlaence. Not even Gomberg's triphenyl methyl, however, would be found to exhibit any traces of basicity, for in this molecule carbon would have an equivalent equal exactly to 4. Right here one is tempted to formulate a useful little rule:- If we bar the inert helium, and if we concede the tetravalenvy of oxygen, which we must, we shall find it to be generally true, that no element exhibiting an equivalent of 4 or less per valence can be basic. Of course, this does not imply, that an element showing an equivalent of more than 4 can not be acidic. On the other hand, one feels safe to venture the statement, based solely on empirical observation, that no carbon compound can be shown, so far isolated, in which the carbon atom is basic. Once carbon is thus conceded to be invariably

acidic, then the less the carbon content of a hydro-carbon the less its acidity, or the more nearly neutral its character. The smallest carbon content of methane, then, makes it the least acidic or most nearly neutral of all the hydrocarbons. This point might be advanced, in passing, as a principal factor to account for its being a nearly ideal gas, the other factors being its large hydrogen content, and the strict monovalency of hydrogen. Acetylene, on the other hand, with its relatively largest carbon content, may be called the most acidic of all the hydrocarbons. There would be no point to bringing in the oxy-carbons in this connection, because oxygen only enhances their acidty. For instance, in

$HO\equiv\underset{\underset{O}{|||}}{C}\equiv OH$ the equivalent of carbon is 12/10.

Carbon is invariably acidic, because the nitrogen found in any carbon compound is always the basic atom of the salt residue, $N\equiv\overset{\nearrow}{\underset{\searrow}{N}}$. H. S. Fry in his series of papers in the J. Am. Chem. Soc., has shown that there are even two kinds of nitrate radicles, (No$_3^{+}$) and (No$_3^{-}$). Nor is the existence of such molecular compounds as $R_3N.RI$, $NH_3.OH$ a contradiction. The basicity of both of these molecules is due to the predominence in them of the basic component, just as HCl makes the molecule $NH_3.HCl$ acidic. Hence the nitrogen in these molecules has an equivalent of 14/3, and is, therefore, basic.

The large molecules of hydrocarbons and carbohydrates can easily be shown to be acidic. Whenever we hydrolize these carbon compounds with an acid or an alkali, we find that not only all of the products of the hydrolysis are acidic, but that they show a preference to unite with the alkai present. This tends to show pretty clearly, that these large carbon molecules are neither salts nor basic condensations, but (acid) anhydrides.

In conclusion of this discussion in favor of the invariable acidity of carbon I will say this, that we can not link up chains of, say, sodium or chlorine atoms, but we can ~~say~~ of carbon atoms (and even more easily, perhaps, of the atoms of helium), even though we may have to resort to such strenuous condensation methods as $R\boxed{Ag + I}R$. This tendency in carbon to condense becomes the more pronounced the more completely the carbon atoms of a molecule are stripped of their non-carbon diluents. This tendency of forming chains or aggregates is observed also in N_x, Si_x, S_x and others, but it culminates near the carbon position on the Periodic Table, endowing carbon with the highest melting point of all the elements(4), namely, 3873°. This shows, that in carbon, basicity and acidity are most nearly matched. This, in turn, accounts for the fact, that in the form of diamond, carbon has perhaps the smallest atomic volume of all the elements, otherwise carbon could not have been about the first element to precipitate out of the protylic magma of the fluid earth during the period of its cooling. I have brought out this point, not as a direct proof of the acidity of carbon, but as a reinforcement of evidences already presented, purporting to show how nearly balanced is the acidity of the carbon atom by its basicity.

The two outstanding characteristics brought out in the above discussion, namely, the property of extreme cohesion of carbon, and the consequent necessity of the use of high heat in order to bring its atomic activity into play, may have led Moissan into the use of his method of the electric furnace for the carburation of the metals. The intense heat of the electric furnace made the reduction of the refractory oxides also feasable--a necessary factor in carburation. Based on these assumptions, we might

further say plausibly, that the experimental fact, that such metals as bismuth, lead and tin do not absorb any carbon at their low melting point, may be due to carbon being very inactive at these low temperatures. As a matter of fact, H_2C_2 begins actually to decompose around 1500°. But at least one fact would seem to contradict this assertion. And that fact is, that while copper at its melting point, 1050°, absorbs some carbon, gold, on the other hand, having very nearly the same melting point, absorbs none whatever. What is stranger still in this respect is the fact, that the metals of the platinum family, with melting points so much nearer to that of carbon that we should look for a more favorable reaction with carbon, completely give up, however, as graphite at lower temperatures, the carbon which they take up at their melting point.

The case is differnet, however, with the alkali metals. In spite of their low melting point, they form acetylides with comparative ease from the H_2C_2 gas itself. In the preparation of these acetylides from acetylene the much greater electrolytic solution tension of the alkalis as compared with that of hydrogen may be considered as being the active factor. As is evident, our task here is not to break up a highly polymerized carbon aggregation by the application of heat. On the contrary, here carbon is already in the isolated and active form of acetylene. The problem is thus reduced to the simple matter of the electrically stronger alkalis replacing the electrically weaker hydrogen in the metathesis in a dry heat medium.

So far, the views advanced above may claim a show of plausibility in efforts at explaining the different behavior of the several metals in their carburation. But these views, even if they were conceded as being chemically sound, do not seem to be

capable of extension for the purpose of covering as many of the other metals as we might wish to include. For instance, if the law of electrolytic solution tension were a decisive factor, then every one of the metals Zn, Cd, Fe, Co, Ni, Sn, and Pb, having a larger potential than hydrogen, should form acetylides of the type $M''C_2$. But repeated attempts in this direction have completely failed. On the other hand, Cu, Ag, and Hg, although situated below hydrogen in the series, and therefore weaker potentially, readily form their well defined acetylides in aqueous solution. Here we observe, that while the acetylides of the alkali family of Group I. can not exist in water, those of the family B of the same group do so very readily. This is regular for the following reasons:- Although Cu_2C_2 and Ag_2C_2 are weaker salts than Cu_2Cl_2 and $AgNO_3$ from which they are formed respectively, they do so under the great concentration of the acetylene gas. The second favorable factor is the electro-potentially greater hydrogen replacing the electro-potentially weaker Cu and Ag. The third favorable factor is the withdrawal from the sphere of reaction of the insoluble acetylides, as fast as they are formed, thus pulling the equilibrium behind them, so-to-speak, as indicated by the heavy-faced arrow:-

$$2H_2C_2 + 2AgNO_3 \rightleftarrows Ag_2C_2 + 2HNO_3 ;$$

$$2H_2C_2 + Cu_2Cl_2 \rightleftarrows Cu_2C_2 + 2HCl.$$

Evidently, then, neither the periodic classification of the elements, nor the electro-potential series, as they stand, can lead us into a larger grasp of the periodic relationships underlying the peculiar behavior of some of the metals in their carburation. Nor yet can they help us solve and harmonize the seeming puzzles encountered in this situation of the formation of

acetylides. It is to be hoped, at least, that rightly conceived, well planned, and scrupulously executed experiments will yet help solve, in spite of hazy conception of chemical laws, many of the apparent anomalies observed in the carburation of the peculiarly behaving metals, by the aid of intense study and the application of sheer weight of adequate method.

IV-- EXPERIMENTAL

A brief survey of the mode of the composition and the end products of metal acetylides would be instructive. They afford us useful hints as to the composition and, perhaps also, the possibility of various ways in which they might be prepared. We will take up some illustrations:- Aluminum gives $Al + Al_4C_3$ in the electric furnace(5). This is the closest we have come to the genuine aluminum acetylide with the carbon residue, $-C\equiv C-$. It is decomposed by water giving H_4C. Gl_4C_3 behaves similarly. B_2C_2 is made in the electric furnace by fusing its elements together at high temperatures. It decomposes only by fusion with alkalis. Na_2C_2 is decomposed by water giving H_2C_2. Copper is prepared both in dry heat and cold solution, and is decomposed only by acids, giving H_2C_2. C_2La is decomposed by water in the cold, giving H_2C_2, $C\,H_4$, H_4C_2, etc. We observe that $Al + Al_4C_3$ and Gl_4C_3 give H_4C only; Na_2C_2 and Cu_2C_2 give H_2C_2, while C_2La gives H_2C_2, H_4C_2, and H_4C. All of these could be prepared by the same method, namely, heat. While we may feel fairly certain, that whenever a decomposition product consists of H_2C_2 and nothing else, the corresponding salt is a true acetylide, in other cases some other hydrocarbons are given off, such as H_4C_2, H_6C_2, H_4C. These may be rearrangements, or secondary formations, since only through definite methods or molecular weight determinations can we know the molecular structure of the decomposed acetylide with reasonable certainty. The case of carbides giving off only H_4C, may be considered as being doubtful with respect to containing the carbon residue $-C\equiv C-$, since all the circumstantial evidence are against their being true acetylides.

According to J. H. Vogel ("Das Acetylen", p. 20, 1911), pure H_2C_2 is completely absorbed by Al C_3 in closed vessels. The compound formed is decomposed by H Cl, giving H_2C_2. Gangloff & Henderson(6) dried H_2C_2 over sodalime, purified it from H_3P with bleaching powder, and then introduced it into a solution of Al Cl_3, dissolved in absolute alcohol till saturated. The solution was concentrated in an atmosphere of H_2C_2 in a desiccator. They received granular, light, gelatinous products which were very hygroscopic. Analysis gave the formula Al $Cl_3 \cdot H_2C_2 \cdot 2(C_2H_5OH)$. It decomposed easily on standing, losing its organic content rapidly. The rate of the composition was determined, but was considered as being unsatisfactory. Their earlier preparation gave the formula, Al $Cl_3 \cdot 2H_2C_2$ $2H_2O$. With purified methyl alcohol they obtained Al Cl_3: H_2 C_2. CH_3OH,$\cdot$ H_2O.

Although the above experiences with aluminum do not seem to have yielded a clear cut acetylide, yet our first attempt was to prepare it in a dry medium. We enclosed some pure anhydrous Al Cl_3 in a concentric, cylindrical, airtight glass apparatus, stoppered at one end with cork packed with powdered charcoal and connected with the suction pump at the other end. We let the H_2C_2, after having first passed it through Hg + Na Hg, and the charcoal, impinge right up against Al Cl_3 through glass drawn to a sharp point. The purpose of using the amalgam and the charcoal was to actuate the gas. We continued this for several consecutive hours, and we observed no visible results.

We next tried to detect the possible formation of acetylides in ammoniacal solutions below zero, and then by plotting curves from the results, we might at least detect if not isolate the formation of compounds. But the necessity of using a strong

ammoniacal medium made it difficult to obtain very low temperatures in order to freeze it. So we gave up also this mode of attack.

Then we thought of forcing acetylene gas, under pressure, into solutions enclosed in an airtight system. We had to solve three chief difficulties in the contrivance of this system. The first was to get up a means of forcing the gas into the solution under as great pressures as we could manage to obtain, and yet remain within the safe limit of explosions from the gas. We solved this by using an elevated water reservoir, from which compressed air was made to force the water down into a lower reservoir, from which, in turn, the acetylene was forced into the section of the apparatus containing the solution, closed with glass top cocks. The second difficulty to overcome, was to obtain a liquid medium which did not absorb the acetylene. This we solved by using thoroughly saturated brine. The third, and by far the most troublesome, difficulty to overcome, was to obtain a gas tight apparatus. We found that acetylene went through even thick-walled rubber tubing. For this reason we eliminated as many ~~much~~ rubber connections as we could. Common sealing wax was found to give the tightest connection, permitting a leak of only about 0.0125^{cc} per hour, which is negligible. The rest of the apparatus consisted of a graduated mercury manometer connected directly with the solution, and a common mercury manometer to measure the pressure of the gas introduced, and a gas generator. We took barometer readings twice each day, and a reading of the thermometer with every record of the gas absorption. No attempt was made to take the gas readings regularly. The reading intervals fluctuated all the way from thirty minutes to two hours.

Among others, we made six principal runs, with solutions described below. The following table will give in round figures the amount of absorption in each case.

Cuprous Ammonium Chloride,	160..........	1864.0^{cc}
Silver Ammonium Nitrate,	60..........	317.0^{cc}
Cadmium Ammonium Chloride,	60..........	207.7^{cc}
Ammonium Chloride in water,	60..........	261.0^{cc}
Cadmium Ammonium Sulphate,	60..........	849.0^{cc}
Tin Chloride in water,	60..........	827.5^{cc}

The solutions used were as follows:- Cuprous Chloride in Ammoniacal solution was prepared and used. The average of two samples of this solution analyzed by the usual thiosulphate method gave the copper content of the 160^{cc} solution taken as 7.25 grams. The precipitate was washed, dried first in the desiccator, then in an air bath. The first two weighings were more or less steady, but during the subsequent weighings the copper acetylide put on weight so rapidly, that it was difficult to weigh it accurately. We exploded a portion of this dry product in an evacuated bottle, and examined the products under a microscope. It consisted of brownish black, amorphous lumps.

A ten per cent silver nitrate solution in ammonia was next saturated with the gas in the same way. In a short time the entire silver content came down as the well known grayish white silver acetylide, leaving the supernatant liquid clear. Analysis gave 87.21% silver, which is not far from Keiser's percentage of 89.45%. Then we ran successively cadmium ammonium chloride, a blank ammonium chloride, cadmium sulphate in concentrated ammonia, an aqueous solution of $Sn Cl_4 . 2H_2O$, and,,finally a solution of

this tin chloride in absolute alcohol. All the above were 10% solutions.

The ammonium cadmium sulphate solution, when saturated with gas gave the whitecadmium hydroxide when diluted with large amounts of water. Although different portions acted rather sluggishly, we thought that every thing being equal, an equal portion acetylenated cadmium sulphate in a concentrated ammonia solution, gave up its cadmium hydroxide less readily than the corresponding aqueous solution. This may have been due to the acidic influence of the acetylene present, by forming, perhaps, a sort of fluid molecule with the cadmium.

The stannic chloride in absolute alcohol yielded, after saturation, some yellowish white, granular substance at the bottom of the solution. When we turned on the suction, several of these grains gave off small bubbles. These bubbles continued as long as the suction was kept up. It is not unlikely that a complex tin acetylide was present in the solution, but for ~~the~~ lack of time nothing further was done with it.

V--CONCLUSION

The pressure method which we tried tentatively seems to be a promising one if more perfected. Of the cadmium compounds tried, that of the sulphate seems to be the most promising for the formation of the corresponding acetylide. Tin chloride in absolute alcohol, however, seems to be the most promising of all, adn worthy of further experimentation, though for lack of time we were unable to follow up this initial attempt ~~for~~ for more tangible results.

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