In this experiment it was apparent, as in preceding ones, that the absorption of potassium from the solution of the second period was strikingly decreased when sodium was present in the solution of the first period.

The procedure employed in this paper, using the plant itself as an indicator, and transferring it from soil to solution or from one solution to another, together with the delicate analytical methods which made it possible to measure slight changes in the concentration of the solution, would seem to be applicable to the study of certain phases of the most important agricultural problems.

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REACTIONS OF ACETYLENE WITH ACIDIFIED SOLUTIONS OF MERCURY AND SILVER SALTS.

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FROM work already published on the behavior of acetylene towards neutral and acid solutions of mercury and other metals, it is fair to conclude that there is a possibility of forming compounds other than those already mentioned. Up to the present time the only acetylene derivatives of mercury that have been investigated are the nitrates (mercurous and mercuric), the chloride, bromide and the fluoride. It was expected that with acid solutions such as mercury fluosilicate, fluoborate, cyanide, nitrite, chlorate and perchlorate, compounds analogous to those discussed in the previous work,[1] would be formed under proper conditions.

While the work to be described was in progress there came to our notice an article of Hoffman[2] in which, among other compounds, he described the formation of acetylene derivatives of mercuric nitrite, chlorate and perchlorate. His method of preparing these substances is almost identical with the method by which we made them. Besides the substances mentioned by Hoffman, we have been working on a number of others about to be described. The general method of procedure was to make

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[1] Thesis: "Some Reactions of Acetylene," Notre Dame University Press, 1904.

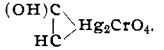
[2] Ber. 38, 1899.

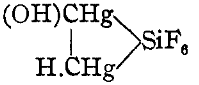
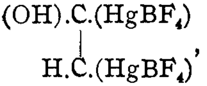
the solution of a salt of mercury by treating the acid in question with mercuric oxide and filtering. Care was taken to have these solutions acidified with the acid contained in the radical of the salt. The product was treated with purified acetylene gas that had passed through three Wolff flasks containing in the order mentioned: first, a solution of caustic potash; second, chromic acid; third, some sulphuric acid. The gas was also passed through a drying tower containing small pieces of calcium carbide. The following results were obtained:

Acetylene and Mercuric Chromate.—In a solution of mercuric chromate acidified with chromic acid, acetylene gave instantaneously a bright yellow precipitate resembling lead chromate. The acid solution of the salt was obtained in the following way. To a cold concentrated solution of chromic acid, oxide of mercury was added until no more was dissolved on shaking. After filtering the solution through asbestos, acetylene was passed into it until a precipitate was no longer formed with the gas. The compound was carefully washed for a long time both by decantation and filtration to remove the last traces of chromic acid, and the precipitate dried over sulphuric acid. But in spite of all possible care used in the process of drying, the substance turned brown, aldehyde being one of the products of decomposition. With moist iodine the compound yielded iodoform, especially in an alkaline solution, and when rubbed in a mortar or touched with a warm glass rod, deflagration took place without explosion, and carbon together with the oxide of chromium was deposited. Ordinary acids did not perfectly dissolve the chromate derivative of acetylene, but it readily went into solution in a mixture that yielded nascent chlorine. The following results were obtained in the analysis for mercury:

0.4546 gram of substance gave 0.3736 gram of mercuric sulphide.

0.4062 gram of substance gave 0.3392 gram of mercuric sulphide.

	Calculated for  $\begin{matrix}(OH)C \\ | \\ HC\end{matrix}\!\!>Hg_2CrO_4$.	Found.	
		I.	II.
Hg......................	70.42	70.85	71.12

Acetylene and Mercuric Fluosilicate and Fluoborate.—Mercury silicofluoride was prepared by dissolving mercuric oxide in fluosilicic acid to saturation. After filtering and passing in acetylene, a white precipitate was formed which towards the end of the reaction began to turn blue, while the odor of aldehyde was very strong. The same results were obtained when acetylene was passed into the fluoborate. These compounds are very unstable, decomposing spontaneously even when dry, into aldehyde and hydrofluoric acid. They respond to the iodoform reaction more readily than any of the other derivatives of acetylene formed in a similar manner. They reacted energetically with dry bromine and chlorine, apparently forming bromine and chlorine substitution products of ethane. Strong hydrochloric acid attacked them, with the formation of the hydrochloride referred to by Keiser[1] and prepared by Polleck and Thummel[2] in another way. It was expected that the following compounds,  $\left.\begin{array}{l}(OH)CHg\\ \;\;|\\ H.CHg\end{array}\right\rangle SiF_6$ and  $\begin{array}{l}(OH).C.(HgBF_4)\\ \quad\;\;|\\ \quad H.C.(HgBF_4)\end{array}$, would be obtained, but a qualitative analysis shows, however, that the boron and the silicon of the acids either took no part in the reaction, or were removed by the acetylene, so that the same substance is formed as in the reaction of acetylene with mercuric fluoride. Quite a number of analyses were made but no satisfactory coincident results could be obtained.

Acetylene and Mercuric Chlorate and Perchlorate.—Chemically pure chloric acid was prepared from pure barium chlorate by precipitation with sulphuric acid. Mercuric oxide was dissolved in the acid and acetylene passed into the solution. The white precipitate formed was washed and dried in small quantities over sulphuric acid in a desiccator. Great care had to be used in handling this compound as it was extremely explosive both on contact with sulphuric acid and by percussion or friction. When heated even the smallest quantities detonated with great violence. It gave acetaldehyde on standing in contact with water, and gave the iodoform reaction both with and without alkalies. It decomposed paper and other organic substances, and dissolved in all the acids. It does not explode in the wet state, but slowly decomposes.

Perchlorate of mercury was made from pure perchloric acid and

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[1] Am. Ch. J. 15, 535.

[2] Ber. 22, 2863 (1889).

mercuric oxide. The perchlorate of mercury and acetylene resembles the chlorate in every respect, except that it did not explode with sulphuric acid when the compound was washed for a long time, nor even when heated or rubbed in a mortar. The least trace of chloric acid or of mercuric perchlorate in the free state caused violent explosions when thus treated. Analysis of these compounds gave similar erratic results as in the case of the fluosilicate and fluoborate.

Acetylene and Mercuric Cyanide.—When pure acetylene was passed into a solution of mercuric cyanide, made acid with hydrocyanic acid, no precipitate was obtained. If, however, the impure gas that had not been passed through water or sulphuric acid was used, a cream colored precipitate was formed after a few days. As ammonia was given off from the decomposition of the calcium carbide, the solution was slowly made alkaline, causing a precipitate of mercuric carbide. Not enough of the substance was obtained for analysis or thorough examination. The compound was explosive and hence was supposed to be a carbide.

Acetylene and Mercuric Nitrite.—Acetylene gave a heavy cream colored precipitate with mercuric nitrite. If the solution of the nitrite is fairly strong, the reaction after a while becomes so energetic as to give off sufficient heat to effect the decomposition of the compound with the evolution of nitrous fumes and at the same time aldehyde is given off in considerable quantities. In a concentrated solution of nitrous acid and mercuric nitrite, the organic compound is very soluble but can be precipitated by dilution with water. Like the other compounds the nitrite gave an abundant precipitate of iodoform with iodine and an alkali. Analysis of the compound gave the following results:

0.8000 gram of the substance gave 0.7129 gram of mercuric sulphide.

0.4598 gram of the substance gave 0.4100 gram of mercuric sulphide.

	Calculated for $C{-}(HgNO_2)$ $\vert$ $C{-}(HgNO_2)$	Found.	
		I.	II.
Mercury............	77.51 per cent.	76.80	74.49

Acetylene and Mercuric Acetamide.—Acetylene gave a white gelatinous precipitate with mercuric acetamide. Mercuric acetamide was made by dissolving mercuric oxide in an aqueous solution of acetamide, also by melting acetamide, adding the oxide, and then diluting with water. The substance was found to be of the consistency of jelly, if little or no water was added to the acetamide.

Acetylene and Mercuric Bromate.—Mercuric bromate was made from pure bromic acid and mercuric oxide. It gave a very explosive white precipitate with acetylene, which was not analyzed, whereas the iodate of mercury could not be obtained in the same way.

The general properties of the above compounds may be summed up as follows: Whereas the carbides formed from acetylene in alkaline solutions are explosive, the substances formed in acid solutions are not necessarily explosive unless there is in the compound an acid grouping or radical that is itself unstable, such as that of chloric or perchloric acid. The chromic acid radical, though a strong oxidizing agent, is not violently decomposed when combined with the acetylene, though it is rather unstable. All of these compounds give off aldehyde when heated with very dilute acids or even with water. Some decomposed thus, even when kept perfectly dry in a desiccator over sulphuric acid or in tightly closed bottles. Caustic alkalies break up these compounds into two others, one soluble, the other insoluble in the reagent. The product insoluble in the alkali when treated with iodine, gave tetraiodoacetylene and diiodoacetylene, and resembled the carbide of acetylene, being somewhat explosive. The other substance, soluble in fixed alkalies, is reprecipitated by acidifying the solution containing it. It is the compound which gave the iodoform reaction. These, and other considerations seem to point to the fact that they are substances like those obtained by Polleck and Thümmel[1] by another reaction from vinyl derivatives. Therefore, we have preferred to consider them as derivatives of vinyl alcohol and not of aldehyde. Moreover, if they were acetaldehyde derivatives, the aldehyde, if it reacted with the salts of mercury, should give these compounds. Acetaldehyde forms soluble, not insoluble compounds in presence of mercury. salts.

Acetylene and Acidified Silver Phosphate.—Silver like mercury, gave insoluble products with acidified solutions. The compounds formed from acid silver fluoride, acid fluosilicate and acid fluoborate, and from solutions of silver chloride in sodium hy-

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[1] Loc. cit.

posulphite, are yellowish precipitates and are all explosive. Silver chromate, though slightly soluble in potassium bichromate and chromic acid, would not give a precipitate with acetylene. Other silver compounds have been prepared from acidified solutions.

Unlike these substances, acid silver phosphate of acetylene is not explosive, in fact it is very stable and only slowly acted upon by light. The solution of silver phosphate was prepared by precipitating from a solution of silver nitrate with disodium phosphate, and dissolving the precipitate in rather strong phosphoric acid. When acetylene was passed into the solution a cream colored substance was thrown down. The silver was quantitatively precipitated, and after saturating with acetylene, no trace of the metal could be found in the solution, which was found to be unchanged phosphoric acid. Light affected the compound only very slowly, for after standing for several months in strong diffused daylight, the color was changed only to a faint lavender. The compound did not give off aldehyde, nor did it respond to the iodoform reaction. It was soluble in potassium cyanide with evolution of acetylene and gave off the odor of hydrocyanic acid. When heated it did not explode, but puffed up, decomposing slowly, leaving finely divided carbon and silver. This substance appears in this respect, to differ from all the silver acetylene derivatives. Analysis of the compound pointed to the following composition. The silver was determined electrolytically, and there was found 44.77 and 44.77 per cent. Calculated for $3(C_2H_2)$, $2H_3PO_4.Ag_3PO_4,H_2O$, 45.3 per cent.

Other Silver Acetylene Compounds.—Besides the acetylene compound of silver phosphate, other derivatives were prepared. When acetylene gas was passed into an acidified solution of silver fluoride, a lemon-yellow precipitate was formed. The substance is paler in color when formed in dilute solution. It is extremely explosive and is probably a compound of silver carbide with silver fluoride. Silver nitrite yields a compound similar in appearance and physical properties. No results could be obtained when acetylene was passed into acidified silver chromate. No compound of silver cyanide and acetylene could be prepared. Silver cyanide was precipitated, washed carefully and redissolved in potassium cyanide. Acetylene gave no precipitate when passed into the solution to which some hydrocyanic acid had been added. The compounds of acetylene with silver bromate and silver perchlorate were also made. The gas formed precipitates in solutions of these salts acidified with pure bromic and perchloric acids respectively. The perchlorate was prepared by dissolving silver oxide in pure concentrated perchloric acid. Care was taken to have the silver salt strongly acid. When acetylene gas was passed in the solution, a fine crystalline precipitate was obtained. This substance, even in the moist condition, is almost as explosive as nitrogen iodide. On one occasion simple contact of the wet substance with a glass rod resulted in an explosion that shattered the vessel. No smoke or precipitate of carbon accompanies these explosions, thus differing in this respect from the other silver acetylene compounds. These detonations are accompanied with a flash of pale blue light. The smallest quantities of the substance are dangerous. The amount that usually "creeps" up the sides of the vessel in the preparation of the compound, has been known to pulverize the containing beaker when touched with a glass rod. The product formed in very dilute solution is, however, not quite so explosive. Owing to the dangerous nature of this compound, no analysis was attempted. None of the silver compounds of acetylene give the iodoform reaction, and all except the phosphate are quickly blackened by diffuse daylight. Investigation of other metallic derivatives of acetylene is now being made in the laboratory.

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NOTES.

A Preliminary Note on the Reactions between Acid Chlorides and Potassium Ethylxanthate.—In the spring of 1902 the author undertook to study the action of various acid chlorides on potassium ethylxanthate, $C_2H_5OCS.SK$. Owing to press of other work this study has been subject to numerous delays and postponements; it has therefore been deemed advisable to make a preliminary announcement of the work done.

Action of Acetyl Chloride.—The products obtained by the action of acetyl chloride on potassium ethylxanthate vary with slight changes in conditions. Ideally, there should be obtained the mixed anhydride of ethylxanthic and acetic acids according to the reaction