ART. XL.—*Chemical Papers from the Massachusetts Institute of Technology*.—No. III. *On the Synthesis of Hydrocarbons by the treatment of Cast Iron with Acids*; by F. H. WILLIAMS.

SINCE the day when the close relations between mineral and organic chemistry were first recognized up to the present time, the artificial production of carbon compounds from inorganic sources has occupied in a remarkable degree the attention of chemists, and the discoveries of Woehler, Kolbe, Berthelot and others, in this direction have been received with the greatest interest; it is therefore singular that the simplest possible means of preparing artificially hydrocarbons has received so little accurate study.

No synthesis in chemistry can be neater than that which joins the carbon combined in cast iron with the hydrogen evolved during the solution of the compound in an acid, and if no one has hitherto isolated and examined the products of this reaction, the reason of this neglect may perhaps lie in the erroneous assumption, that the hydrocarbons must consist in such large part of marsh gas or similar gases, as to make it impossible to separate them from the hydrogen evolved.

Dr. Schafhäütl* has given us the most precise accounts which we possess, of attempts to isolate the hydrocarbons produced during the solution of pig iron in an acid, but he does not appear to have obtained any notable quantities of substances pure enough to be recognized.

I publish here some attempts in the same direction, notwithstanding their incompleteness, in the hope that the results may be found sufficiently definite to awaken interest. They seem to point to the possibility of obtaining by the above mentioned method a great variety of hydrocarbons, belonging to the satu-

* Erdmann, Jour. der Chemie, 1859, 76, 271.

rated and non-saturated series; and these experiments, which restricted time obliges me to terminate for the present, afford the hope that some at least of those bodies may be obtained in a state of purity by operating with larger quantities. The material for the investigation was white spiegel eisen containing a very high percentage of carbon.

Of the volatile products, only those which could be separated from the hydrogen by condensation in a freezing mixture or by combination with bromine were examined, and those which could not be separated from the hydrogen by these means were lost. The compounds of carbon remaining in the liquid after the solution of the iron were collected.

The following apparatus, after several trials, was found the most convenient for the treatment of the iron with an acid, and the collection of the hydrocarbons, which could be condensed in a freezing mixture or combined with bromine.

A six liter retort was supported in a water-bath and connected with the lower end of a Liebig's condenser one meter long. To the higher end of the condenser was attached a chloride of calcium tube; from this a small glass tube carried the gas to the first of three tubes immersed in a mixture of snow and salt. From the last of these tubes the gas was conveyed to the hood, where it was passed through bromine and was allowed to escape.

The Liebig's condenser was cooled by water. It was used to condense any vapor of water which might come over, and was inclined in such a way as to cause the water to run back into the retort.

The arrangement of freezing tubes was as follows: In the bottom of an old oil cask, which was supported six or eight inches above the desk, were bored three holes. Into each was inserted, from the inside of the cask, a rubber stopper having a single perforation. Three glass tubes, somewhat less than a meter long and about thirty millimeters in diameter, were drawn out in such a way as to leave a small-sized tube three or four inches in length on one end of each; this end was pushed through the hole in the rubber stopper until the shoulder of the tube rested on the rubber; the upper ends of the tubes were stayed to the side of the cask with large copper wire. To the small lower ends of the tubes projecting through the bottom of the cask, were attached small rubber tubes closed by spring-clips.

The upper end of each tube was closed by a stopper having two perforations. Through one of these passed a small glass tube, bringing the gas nearly to the lower end of the larger tube; through the other a small tube, which took the gas to the next condensing tube, was passed just through the stopper. In this

way the gas was required to go to the whole length of the tube in the freezing mixture. Nearly all the hydrocarbons were condensed in the first of the tubes, some in the second and almost none in the third.

The cask was kept filled with a mixture of snow and salt, which gave a temperature of 15° C. nearly constant day and night during the experiments. The retort was charged with three kilograms spiegel iron, in pieces about the size of a walnut, and three liters of carboy muriatic acid 21.5 Baumé, and was quickly connected with the condenser. The disengagement of hydrogen was regulated by heat applied through the water-bath to the retort, and was kept as nearly constant as possible. About sixteen hours after, six or seven c.c. of liquid hydrocarbons were drawn off from the freezing tubes. The liquid had a very unpleasant odor and burned with a very smoky flame.

About eighteen hours after charging the retort, it was disconnected from the rest of the apparatus and the black liquid in it poured on a filter, care being taken not to allow any of the iron to go out. Two liters of fresh acid were added and the retort put back in its place. The black residue on the filter and the filtrate from it will be referred to again.

The next day the liquid was poured out of the retort; two liters of fresh acid and one kilogramme of iron were put in. The retort was charged with two or three liters of acid daily, and iron was added on alternate days for ten days; care was taken to keep the condensing tubes well cooled, and as soon as the bromine was saturated it was replaced by a fresh quantity.

The amount of iron dissolved in the first experiment was 7430 grams. 49 grams or .66 per cent. of liquid hydrocarbons and 325.5 grams of bromides were obtained.

The whole of the hydrocarbons, together with a small quantity of muriatic acid drawn from the freezing tubes, were treated with water, with dilute caustic soda, and then again with water, until they gave no reaction with litmus. The hydrocarbons were separated from these and weighed. A small quantity of chloride of calcium was added to absorb the water completely. They were allowed to stand some time in a stoppered bottle, when the most concordant analyses gave the following results:

I. Hydrocarbons,	.1764	grms.	II. Hydrocarbons	.3213	grms.
CO	.4838	"	CO	.8822	"
H ₂ O	.2172	"	H ₂ O	.3728	"
III. Hydrocarbons	.3625	"	IV. Hydrocarbons	.3555	"
Ag Cl	.1677	"	Ag Cl	.1761	"
	I.			II.	
Carbon	74.79		Carbon	74.89	
Hydrogen	13.67		Hydrogen	12.89	
Chlorine			Chlorine	11.44	
				IV.	
					
					
					
				12.25	

A portion of the hydrocarbons was distilled in a small flask fitted with a thermometer. The vapor began to go over at 93°C ., the temperature rose steadily to 135° , where it paused slightly, thence to 155° , which seemed to be the limit. The larger portion of the liquid distilled over at 135°C . There was no decomposition or disengagement of chlorhydric acid. The few drops left in the flask had a slight acid reaction.

The bromides, after being treated several times with dilute caustic soda, was washed with water until they gave no reaction with litmus paper; they were then weighed.

They were allowed to stand over night with a small quantity of solid caustic potash; in the morning they were poured into a flask and heated until the caustic potash melted. Under this treatment the liquid changed from a dirty milky to a dark, not very clear, vinegar color.

The bromides were distilled from a flask through a Liebig's condenser cooled by water. A thermometer inserted through the cork of the flask gave the following readings. The temperature rose from 20° slowly but steadily to 120°C , more slowly from 120° to 130° , still more slowly 130° to 140° , a barely perceptible motion 140° to 145° , stopped some time at 146° , motion of the mercury could hardly be seen from 146° to $148\cdot5^{\circ}$, stopped some time at $148\cdot5^{\circ}$, motion could not be appreciated from $148\cdot5^{\circ}$ to $149\cdot5^{\circ}$, stopped at $149\cdot5^{\circ}$ a short time, rose slowly $149\cdot5^{\circ}$ to 151° , rapidly 151° to 158° , slowly 158° to 163° , rapidly 163° to 169° , slowly 169° to 176° , less slowly 176° to 179° , when the lamp was taken away, as bromhydric acid was given off. About four-fifths of the liquid had distilled over.

In another experiment using the same acid with German spiegel eisen, kindly furnished by the Bay State Iron Works, 2778 grams of iron were dissolved, and 15 grams or $\cdot54$ per cent of liquid hydrocarbons were obtained; also 68.6 grams bromides.

In this experiment all residues from the retort, consisting of graphite, silica, &c., were collected on a large filter; these residues were placed with the filter and about a liter of water in a flask and distilled. There came over and was condensed with the steam a clear, yellow, oily liquid, which was collected from the surface of the water and weighed 4.37 grams or $\cdot15$ per cent of the iron dissolved; nearly all of this came over with the first half liter of distillate.

In a third experiment, using the same iron as in the second, but instead of muriatic, dilute sulphuric acid, one part to four of water, 1691 grams of iron were dissolved; 1.8 grams, or $\cdot11$ per cent, of hydrocarbons were condensed in the freezing tubes; the bromides weighed 94.7 grams.

The muriatic acid probably favored the condensation of the hydrocarbons in the first two experiments; also at times during this experiment, owing to difficulties in procuring the freezing mixture at the proper time, the condensing tubes were not as well cooled as they should have been; this would allow more of the hydrocarbons to go on to the bromine.

Just previous to the last experiment a new retort was procured and the condenser and freezing tubes were cleaned.

The heat used under the retort in the experiments with muriatic acid was very slight at first. Some time after the retort was charged and the rapidity of the current of gas slackened the temperature was raised. When sulphuric acid was used, a considerably lower temperature was sufficient to generate the gas rapidly enough.

The gas, when lighted at the end of the apparatus, always burned with a small light-giving zone indicating the presence of hydrocarbons which were not collected.

Once during the first experiment, when the retort was emptied, the liquid was poured into a stoppered bottle, the excess of chloride of iron allowed to crystallize out over night; the solution was then filtered, and four or five c.c. of nitric acid were added to about a half liter of the filtrate. The mixture was boiled, and ammonia water nearly to alkaline reaction added; the precipitate of hydrate of iron was filtered off, washed, heated with sulphuric acid and ether in a stoppered bottle, and shaken at intervals for two or three days. The ether layer was distilled, and a portion of the distillate allowed to evaporate spontaneously on a platinum dish left no residue; the lower layer was now added and distilled; no oily layer was found on the water in the receiver.

The residue in the flask was filtered, very dilute ammonia added until quite a precipitate of hydrate of iron was obtained, the solution still giving an acid reaction; the precipitate was filtered off, dried at 100° C., a portion heated in a closed tube. Steam and chloride of ammonium were given off: a small quantity of a black substance also condensed on the walls of the tube; no organic compound appeared to have been precipitated with the oxide of iron.

The chloride of calcium in the drying tube, through which the gas had passed more than three weeks, was dissolved in water and distilled; there was collected from the surface of the distillate an oily liquid, resembling in odor and appearance that obtained from the residue in the retort.

The result thus far obtained may be briefly summed up as follows: There may be obtained by the solution of cast iron in an acid, besides gaseous bodies, which escape with the hydrogen, volatile hydrocarbons, boiling between 93° and 155° centi-

grade, probably belonging partly to the saturated and partly to the non-saturated series; of this latter series, very considerable quantities may be condensed by combination with bromine after having passed through a freezing mixture. It is particularly interesting to observe that when chlorhydric acid is used, the chlorides of hydrocarbons are obtained.

Under the conditions of these experiments the quantity of hydrocarbons, which are not volatile with the vapor of water, is too small to allow them to be collected.

No formation of an organic acid could be observed.