to further hydrolysis. From soluble starch downward, the hydrolysis again appears to bear a direct ratio to the acid concentration.

It would be interesting to determine the amylodextrin fraction of the over-hydrolyzed samples. With 100% conversion of starch to soluble starch, it would also be highly profitable from a theoretical standpoint to study the hydrolysis of this product in concentrations of acid below 0.75 per 100% alcohol, and to ascertain whether the soluble starch can be quantitatively converted to amylodextrin.

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE MATHIESON ALKALI WORKS, INC.]

THE INFLUENCE OF CATALYSTS ON THE CHLORINATION OF HYDROCARBONS.

BY V. R. KOKATNUR.

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The object of this paper is to show the contrasting action of light and of catalysts on the chlorination of hydrocarbons.

It is well known that chlorine acts progressively on aliphatic hydrocarbons in the presence of light, giving products of the nature of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 as in the chlorination of methane. On the aromatic hydrocarbons, on the other hand, it acts, under the same conditions, additively in the ring or substitutively in the side chain. Substitution in the ring requires the use of strong halogen carriers.

It is also known that halogen carriers can be employed in the chlorination of aliphatic hydrocarbons, giving the same ultimate products as in the chlorination under the influence of light. Halogen carriers seem to have a selective action in the substitution of aromatic hydrocarbons in preference to aliphatic. Thus in the chlorination of toluene in the presence of catalysts at a low temperature substitution is restricted to the ring without in the least affecting the side chain. At a higher temperature, however, substitution takes place in the side chain in preference to the ring. It is likely that even at a low temperature, when the substitution has gone as far as pentachlorotoluene, the side chain will then be attacked.

Regnault[1] demonstrated that chlorine acts progressively on methane in the presence of light, forming CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4, all of which can be isolated.

Bedford[2] claims to have obtained $CHCl_3$, CH_2Cl_2, CH_3Cl and CCl_4, either singly or collectively, according to the control of conditions. He made methane and chlorine to react in the presence of ice and actinic light. Masland and Sparre[3] claim to obtain mono-, di-, tri- or tetra-

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[1] *Ann.*, **33**, 332 (1840).

[2] U. S. P. 1,245,553, Nov. 6, 1917.

[3] U. S. P. 1,148,259, July 27, 1915.

chlorinated hydrocarbons according to conditions in the chlorination of petroleum under the influence of light. Brooks, Essex and Smith[1] make similar claims in the chlorination of gasolene. Blanc[2] uses both carriers and actinic light in the chlorination of petroleum and claims to have obtained similar results.

Colin[3] made attempts to burn methane in chlorine by electric sparks of proper tension, and separate the reaction mixture by fractionation, but his attempt failed completely.

Pfeifer and Szaroasy[4] proposed to expose a mixture of methane and chlorine to the action of silent electric discharge.

In 1879 Mallet[5] proposed to pass the mixture of chlorine and methane through an inert but porous material, like carbon, using it as a halogen carrier instead of light. J. Mackaye,[6] working under similar conditions, claims to have obtained the intermediate products like $CHCl_3$.

Meyer[7] showed that ethylenedibromide can be prepared from ethylbromide, by heating it with bromine in the presence of iron wire, in a sealed tube.

Burgoin[8] obtained pentabromoethane by heating tetrabromoethane with 15.6% bromine in a sealed tube for two days.

In 1893 Phillips[9] reported that in the chlorination of methane under the influence of carriers, the tendency was to form the first and the last substitution products at the sacrifice of the intermediate ones. Thus, he says, very little or no CH_2Cl_2 and $CHCl_3$ were formed in the reaction. Tokozcko[10] obtained results identical with those of Phillips. Monneyrat[11] showed that chlorination of tetrachloroethane in the presence of aluminum chloride gave hexachloroethane only, without producing any pentachloroethane.

The following experiments were tried in the attempt to make pentachloroethane by chlorinating acetylene tetrachloride, under the influence of catalysts.

General Method.

A known amount of acetylene tetrachloride was placed in a flask with or without a reflux condenser. The catalyst was either dissolved or suspended in the liquid. A known amount of chlorine was passed through

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[1] U. S. P. 1,191,916, July 18, 1916.

[2] U. S. P. 1,248,065, Nov. 27, 1917.

[3] U. S. P. 427,744, May 13, 1890.

[4] D. Anm. P. 12,058, Sept. 25, 1911.

[5] U. S. P. 220,397, Oct. 7, 1879.

[6] U. S. P. 880,900, Mar. 3, 1908 and 1,009,428, Nov. 21, 1911.

[7] *Ber.*, **24**, 4248 (1891).

[8] *Compt. rend.*, **29**, 325–327 (1875).

[9] *Am. Chem. J.*, **16**, 362 (1893).

[10] *Abhandl. Trakann. Wiss.*, 1912; *J. Soc. Chem. Ind.*, **32**, 742 (1913).

[11] *Compt. rend.*, **126**, 1805–1806 (1896).

the solution slowly. The reaction product was first washed with dil. sodium hydroxide solution and then with water to remove all hydrochloric acid and free chlorine. It was then dried over calcium chloride and distilled. The fraction passing over below 150° was regarded as acetylene-tetrachloride, b. p. 145 to 148°. The fraction above 150 to 170° was freed from hexachloroethane by either cooling the liquid and thus crystallizing out the solid, or by successive distillations whereby hexachloroethane remained in the distilling flask. This hexachloroethane-free liquid was redistilled to find out whether it was acetylene tetrachloride or pentachloroethane, b. p. 157–160°.

Experimental.

1. 25 g. of specially prepared vegetable charcoal,[1] previously tested as a catalyst, was suspended in 100 cc. of acetylene tetrachloride, $C_2H_2Cl_4$; 50 g. of chlorine was passed through this solution in 7 hours at room temperature. The reaction product was washed, dried and distilled. The first fraction, below 150°, amounted to 60 cc. and consisted of acetylene tetrachloride. The second fraction, between 150° and 170°, amounted to 30 cc. and was mostly hexachloroethane mixed with small amounts of acetylene tetrachloride.

2. 50 g. of animal charcoal was suspended in 200 cc. of acetylene tetrachloride and 180 g. chlorine was passed through in 17 hours at a temperature between 60° and 70°. The reaction product was washed, dried and distilled as before. The first fraction, below 150°, amounted to 140 cc. and was found to be acetylene tetrachloride. The second fraction, between 150° and 170°, amounted to 45 cc. and was mostly hexachloroethane mixed with small amounts of acetylene tetrachloride.

3. The results were the same as in the second experiment, except that 75 g. of hexachloroethane was added to see whether its presence would tend to make the reaction stop at the pentachloroethane stage. But results were obtained similar to those of Expt. 2.

4. 200 g. of iron was suspended in 200 cc. of acetylene tetrachloride and 140 g. of chlorine was passed through in 23 hours at room temperature. The reaction product was washed, dried and distilled. The first fraction, below 150°, amounted to 140 cc. and was acetylene tetrachloride. The second fraction, between 150° and 170°, totalled 50 cc. and was mostly hexachloroethane.

5. Duplicating (4), except at a temperature of 70 to 80°. The results were similar except that the yield of hexachloroethane was greater.

6. To 200 cc. of acetylene tetrachloride 200 g. of bleaching powder and 200 cc. of water were added and the mixture was heated on the water bath for several hours. The insoluble liquid formed was separated and

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[1] Vegetable charcoal from the market was first treated with conc. HCl and then dried in an atmosphere of chlorine for about three hours at a temp. of 600–700°.

distilled. There was a considerable loss, as some of the liquid was absorbed in the lime and could not be separated. The first fraction consisted of trichloroethylene, unsymmetrical and symmetrical tetrachloroethane. The second fraction was pure hexachloroethane.

7. Duplicating (6), but at a temperature of 130 to 140°. The results were similar but larger yields of each were obtained.

8. To 200 cc. of acetylene tetrachloride, 112 g. of anhydrous aluminum chloride was added and the mixture was heated for 3 hours at a temperature of 60 to 70°. The reaction product was treated with water, the oily liquid separated, dried, and distilled. The first fraction, below 150°, amounted to 145 cc. and was found to be a mixture of unsymmetrical and symmetrical tetrachloroethane. The second fraction, below 170°, was pure hexachloroethane.

9. Duplicating (8), but with 30 g. of aluminum chloride and heating on the water bath for several hours. Larger yields of unsymmetrical tetrachloroethane and hexachloroethane were obtained.

10. Duplicating (9), but with 20 g. of aluminum chloride and passing chlorine at room temperature. Only 80 cc. was unchanged. The rest was hexachloroethane.

Discussion.

These experiments show the influence of catalysts on the chlorination of hydrocarbons. Under their influence the chlorination is carried to the end-point without stopping at intermediate points.

Whether the production of hexachloroethane in the chlorination of acetylene tetrachloride (symmetrical tetrachloroethane) should be accounted for by the influence of catalysts or by the symmetrical structure of the compound, is difficult to say. It is true that the two hydrogen atoms in the molecule of acetylene tetrachloride have the same value, being symmetrically placed with regard to the whole molecule; hence there is no reason why one atom should be substituted and the other not. Thus it is conceivable that both hydrogen atoms are substituted simultaneously, giving hexachloroethane as the final product. Further light on this point can only be thrown when unsymmetrical tetrachloroethane is chlorinated. If it gives pentachloroethane, then it may be argued that the symmetrical nature of tetrachloroethane is the cause of not obtaining pentachloroethane as an intermediate product.

It is significant to note that the same symmetrical tetrachloroethane gives pentachloroethane when the chlorination is carried on in the presence of actinic light. This may perhaps mean that light changes the symmetrical nature of the compound while chlorinating, thus making it possible to obtain pentachloroethane; or it may mean that it dissociates chlorine into bi-atomic, mono-molecular units, which acting on tetrachloroethane gives pentachloroethane. Conversely it must be assumed, however, that the catalysts tend to associate the chlorine molecules into bi-molecules. Hence chlorination in the presence of catalysts may be called a bi-molecular reaction, while it is a mono-molecular reaction in the presence of actinic light. Thus it might be expected that methane, after chlorination, would give CH_2Cl_2 and CCl_4, though Phillips claims to have obtained CH_3Cl and CCl_4.

This is an inviting field and more definite work must be done before any hypothesis is proposed.

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THE ACTION OF CHLORINE UPON HYDRAZINE, HYDROXYLAMINE AND UREA.

BY C. T. DOWELL.

Received November 2, 1918.

In the course of an investigation of the action of chlorine upon urea, a study was also made of the action of chlorine upon hydrazine and hydroxylamine. Evidence was obtained showing that in the reaction of chlorine, with hydroxylamine and with hydrazine, nitrogen trichloride was formed. This evidence was based upon the action of a solution of nitrogen trichloride in carbon tetrachloride with potassium iodide, in which nitrogen is always liberated. When hydroxylamine and hydrazine were allowed to react with chlorine in contact with carbon tetrachloride it was found by shaking the reaction mixture and later separating the carbon tetrachloride and treating it with a solution of potassium iodide that nitrogen was given off. Precaution was taken to have a large amount of chlorine present with a small amount of the hydrazine or hydroxylamine. It was not expected that very much nitrogen trichloride would be obtained on account of the fact that this substance reacts quite rapidly with hydrazine and hydroxylamine.

After completing the work on the reactions between chlorine and urea an article[1] was found in which Chattaway had made a study of the same reactions and had isolated dichlorourea and determined its properties. My work was in the main a confirmation of Chattaway's work as far as the properties of the dichlorourea were concerned. It was found that no nitrogen is oxidized to the nitrous or nitric form. Chattaway and the writer both found that when a solution of dichlorourea was allowed to stand, it decomposed, giving as one of the products nitrogen trichloride. Chattaway supposed that the reaction took place between dichlorourea and water in which carbonic acid and monochloroamine were formed and that monochloroamine decomposed giving ammonia and nitrogen trichloride. In the early part of my work I suspected that the oxidizing properties of the solution were due to monochloroamine and made several tests

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[1] *Chem. News*, **98**, 285 (1902).