Either or both of these reactions may take place inasmuch as water, hydrochloric acid and, in a few cases, aluminium oxide are liberated.

Detailed work along several lines mentioned above is now under way. So far as the work has progressed, aluminium chloride in each case unquestionably plays the part of a catalyst, whether hydrochloric acid, water, aluminium hydroxide or aluminium oxide is formed during the reaction.

THE UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

THE ACTION OF TRIOXYMETHYLENE ON THE VARIOUS HYDROCARBONS IN THE PRESENCE OF ALUMINUM CHLORIDE.

BY GEO. B. FRANKFORTER AND V. R. KOKATNUR.

Received May 13, 1914.

Ever since Friedel and Crafts discovered the reaction which bears their names, chemists have used it in various ways in order to bring about certain chemical changes, in some cases under entirely different conditions from those recorded by the authors themselves. Thus, Scholl and Seer[1] showed that anhydrous aluminium chloride, in a few cases, actually breaks off free hydrogen instead of hydrochloric acid. Recently Page[2] has shown that aluminium chloride possesses the power of transporting chlorine to certain organic compounds. Finally it has been found, under proper physical conditions, to act as a dehydrating agent like concentrated sulfuric acid. It has been shown by Kritchevsky and one of us that when an aldehyde, as chloral, and a hydrocarbon, either benzene or one of its homologs, are brought together in the presence of aluminium chloride at 0°, a reaction analogous to the Baeyer reaction takes place.

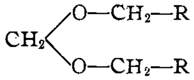
In order that the last reaction mentioned might be more thoroughly studied, experiments similar to those mentioned above with benzene and chloral were begun, using trioxymethylene, however, instead of chloral. In each case the same general condensation reaction took place. In a few cases, the reaction seemed to be comparatively simple, while in others it appeared to be extremely complex. This variation seemed to be influenced, largely, by temperature, as a result of the way in which the aluminium chloride was added, either fast or slow, or as to whether the whole mass was kept in a freezing mixture during the reaction. Finally, it was hoped that, in addition to studying the reaction itself, some light might be thrown on the constitution of trioxymethylene.

The molecular structure of trioxymethylene is generally considered to be a ring compound, in which the oxygen and the methylene groups are

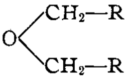
[1] *Monatsh.*, 33, 1 (1912).

[2] *Ann.*, 225, 196 (1884).

symmetrically arranged. In case the accepted theory is a fact, we hoped to prepare condensation products by breaking the ring and substituting hydrocarbon radicals for one, or more, of the oxygen atoms, as indicated by the following formulas:

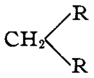


$$CH_2{<}\begin{matrix}O-CH_2-R\\O-CH_2-R\end{matrix}$$



$$O{<}\begin{matrix}CH_2-R\\CH_2-R\end{matrix}$$

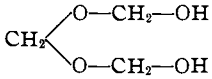
and



$$CH_2{<}\begin{matrix}R\\R\end{matrix}$$

where R represents either benzene or one of its homologs.

On going over the literature of trioxymethylene, it was found that Grassi and Masselli[1] had prepared compounds analogous to those which we had hoped to prepare by breaking the ring and substituting inorganic radicals for the oxygen. Thus by treating trioxymethylene with acetic acid and water, they obtained trioxymethylene hydrate,



$$CH_2{<}\begin{matrix}O-CH_2-OH\\O-CH_2-OH\end{matrix}$$

Then, by treating the hydrate with hydrochloric acid, the trioxymethylene chloride was formed. And finally, by treating the chloride with benzene, they obtained diphenylmethane. They assumed that the hydrochloric acid broke the ring compound down into formaldehyde, at the same time forming a hydrochloride, $ClCH_2OH$. This compound then reacted with the benzene, forming diphenylmethane. They failed to prepare any of the oxy compounds.

As has already been stated, the reaction between trioxymethylene and the hydrocarbons varies widely, depending upon the conditions under which the reaction takes place. Under none of these conditions, however, were we able to prepare any of the oxy compounds, although various complex hydrocarbons were prepared, as will be shown later. Notwithstanding the fact that no oxy compounds could be isolated, the truth remains that trioxymethylene acts differently from formaldehyde in the presence of aluminium chloride. This fact may mean that some of the oxy compounds are actually formed in the reaction and are broken down into the various hydrocarbons before equilibrium is finally reached.

Trioxymethylene has never before been used with aluminium chloride, consequently no condensation products have ever been made; neither has it been studied in connection with concentrated sulfuric acid. As a matter of fact, formaldehyde itself has never been studied in this connection. It has been used, however, with concentrated sulfuric acid, yielding compounds which, in many cases, are the same as those obtained with trioxymethylene and aluminium chloride.

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[1] *Gaz.*, **28**, 477 (1898).

Experimental Part.

Benzene and Trioxymethylene.—To 500 cc. of benzene were added 35 g. of trioxymethylene, the mixture cooled to 0° and 170 g. of anhydrous aluminium chloride added piecemeal. An automatic stirrer was used and the mixture was stirred continuously while the aluminium chloride was being added. The temperature was never more than 20°, though most of the time it was less than 10°.

After about 50 g. of aluminium chloride had been added, the color of the mixture changed to a reddish brown and copious fumes of hydrochloric acid were liberated. The stirring was continued for some time after all aluminium chloride had been added. It required 10 hrs. to complete the reaction. During this time, hydrochloric acid continued to pass off. After the reaction had apparently ceased, the whole mixture was placed in a refrigerator for three or four days. At the end of that time it was removed and ice-water added, in order to decompose all aluminium chloride without rise in temperature. After a sufficient quantity of water had been added an oily substance separated out and floated on the water. Some solid substance remained at the bottom of the flask. There was also some solid material which was lighter than water but heavier than the oil. This separated out and remained on the surface of water just below the oily layer. The whole was then extracted with ether. All, except the solid substance on the bottom of the flask, dissolved. The ether solution was then separated from the water and the insoluble substance, which was set aside for further treatment.

The ether extract was subjected to fractional distillation and the distillates were collected separately, as follows: (*a*) between 40°–80°, (*b*) 80°–130°, (*c*) 250°–280° and (*d*) 280°–360°. A preliminary examination showed that distillate (*a*) was largely ether with some benzene. Distillate (*b*) was found to contain largely benzene with small amounts of toluene. From 130° the temperature rapidly rose to 250° and an aromatic liquid continued to distil over until a temperature of 280° was reached. Then a white substance of somewhat waxy nature passed over and solidified on the walls of the condenser. This substance continued to distil over until the temperature had reached 360°. Distillation was then stopped as the tarry, resinous solid material remaining in the flask showed signs of decomposition. A peculiar blue fluorescence was observed in the distillate. The resinous material was set apart for further treatment.

As the yield of products was not entirely satisfactory, the above experiment was repeated, varying the temperature and the proportion of trioxymethylene. In each case the same products were obtained, although the yield of the liquid and solid distillates (*c*) and (*d*) varied. In the above experiment the quantity of liquid distillate (*c*) was small. When 40 g. of trioxymethylene were used under exactly the same conditions, the yield of both (*c*) and (*d*) was greater, and when 50 g. were used there was a still larger yield of both the liquid and the solid distillates (*c*) and (*d*). On the contrary, when 100 g. of trioxymethylene were used, there was a good yield of the liquid distillate (*c*) and no yield of the solid (*d*). Even when the temperature was allowed to rise to 40°–50° the same products were formed, although the yield varied.

The liquid distillate (*c*) was redistilled, after which it showed signs of crystallization. The redistilled oil was therefore cooled in a freezing mixture, when it crystallized in colorless prismatic needles. The m. p. of the substance was found to be 26°–27°. It was at once suspected to be diphenylmethane. Hence it was compared with Kahlbaum's diphenylmethane in appearance, boiling point and other characteristics. Kahlbaum's diphenylmethane, although marked "C. P.," was found to be impure. It was a yellowish colored liquid. It began to distil at 254° and continued to 261°. After distillation, however, it was colorless and at once crystallized in colorless, prismatic needles, m. p. 26°–27°.

Our diphenylmethane distilled over between 259° and 262°. It was perfectly colorless and crystallized in colorless prismatic needles. The various tests indicated that it was diphenylmethane. It also showed the characteristic blue fluorescence. Baeyer[1] first obtained diphenylmethane by treating benzene with formaldehyde in the presence of sulfuric acid; and later Nastukoff,[2] on repeating Baeyer's experiments, showed that phenylformol was formed, and this substance, by dry distillation, yielded not only diphenylmethane but also toluene xylene and anthracene.

The solid distillate (*d*) which passed over between 280°–360° was finally dissolved in a mixture of hot benzene containing a little alcohol, as this mixture was found to give best results. On cooling the solution, a leafy, white substance crystallized out. This was filtered off, washed with alcohol several times to remove the last traces of diphenylmethane and recrystallized three or four times. The pure crystals thus obtained were dried and the melting point was found to be 210°–211°. The crystals were monoclinic plates of pearly luster. The crystals both in solution and out of it showed a beautiful fluorescence. Analysis gave numbers for anthracene, although the melting point was a little low. It gave all the reactions for anthracene and on oxidation gave anthraquinone, leaving no doubt as to its identity. The yield of both diphenylmethane and anthracene was exceptionally good.

The fact that diphenylmethane and anthracene are the two principal compounds formed in the reaction throws some light on the nature of the reaction. From the amounts of these two compounds obtained, it is

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[1] *Ber.*, **5**, 1099 (1872).

[2] *J. Russ. Phys. Chem. Soc.*, **35**, 825 (1903).

evident that equal molecular quantities are formed. In view of this fact, the equation may be represented as follows:

$$4C_6H_6 + (CH_2O)_3 + AlCl_3 = CH_2(C_6H_5)_2 + C_{14}H_{10} + 3H_2O + AlCl_3 + H_2$$

As equal molecular quantities of diphenylmethane and anthracene are formed in this reaction, we were at first led to believe that the trioxymethylene molecule is not symmetrical, the methylene group forming the diphenylmethane having different molecular nature from the other two groups in the molecule. On the contrary, Baeyer obtained diphenylmethane from benzene and formaldehyde by means of sulfuric acid; and Nastukoff by the same reaction obtained both diphenylmethane and anthracene. These facts scarcely permit such a conclusion, although the reaction is none the less interesting.

Baeyer[1] showed that, when diphenylmethane was further treated with formaldehyde and sulfuric acid, condensation occurred, forming dihydroanthracene. In order to determine whether or not trioxymethylene would act the same as formaldehyde, 50 g. of diphenylmethane and 9 g. of trioxymethylene were treated with 20 g. of aluminium chloride, according to the method already given. On examining the products after the reaction had been completed a considerable quantity of diphenylmethane was recovered. There was left in the flask, after distilling off the diphenylmethane, a tarry mass which does not contain anthracene. This was set aside for examination later. Therefore, trioxymethylene does not act in the presence of aluminium chloride like formaldehyde in the presence of sulfuric acid.

In order to show whether or not trioxymethylene forms the same compound with the benzene homologs in the presence of aluminium chloride which formaldehyde does in the presence of sulfuric acid, a series of experiments was made, using toluene, xylene and mesitylene instead of benzene.

Toluene and Trioxymethylene.—Fifty grams of trioxymethylene were dissolved in 400 cc. of toluene and 100 g. of aluminium chloride added piecemeal. A large amount of heat was liberated, but the temperature was not allowed to go above 65°. The whole mass changed to a reddish brown color and fumes of hydrochloric acid were given off. The upper layer showed a deep blue fluorescence. The whole mass was kept in a cool place for four days, and after adding ice-water, subjected to the same process described under benzene. Distillate (*a*) passed over between 50° and 120°, (*b*) between 290° and 310°, and (*c*) between 310° and 400°. After the small quantity of (*a*), which on examination was found to be a mixture of ether, toluene and benzene, had passed over, the temperature immediately rose to 290°. At this point oil began to distil over and con-

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[1] *Ber.*, **6**, 222 (1873).

tinued until a temperature of 310° was reached. The distillate then began to solidify on the walls of the condenser. The solid continued to pass over until a temperature of 400° was reached. Owing to decomposition the distillation was stopped. A dark, resinous substance remained in the flask. This material was reserved for further investigation.

On redistilling the oil which was collected between 290°–310°, most of it passed over between 285–7°. It showed a brilliant blue fluorescence. It was further purified and analyzed. Analysis and physical and chemical properties checked well for ditoluylmethane.

The semisolid substance which came over between 310°–400° was then dissolved in a mixture of alcohol and benzene, from which it was obtained in a well crystallized form. It was recrystallized several times by this means, when the constant m. p. of 225°–226° indicated that it was pure. Analysis and general properties checked well for dimethylanthracene, a compound prepared by Friedel and Crafts[1] by treating toluene and methylene dichloride with aluminium chloride. As this reaction is evidently an exact duplicate of the reaction with benzene, it may be represented as follows:

$$4C_6H_5CH_3 + (CH_2O)_3 = CH_2(C_6H_4CH_3)_2 + C_{16}H_{15} + 3H_2O + H_2$$

It is also interesting to note that Anschütz[2] obtained the same dimethylanthracene by treating toluene with acetylene tetrabromide and aluminium chloride.

Xylene and Trioxymethylene.—To a mixture of 500 g. of *o*-xylene, b. p. 142°, and 50 g. of trioxymethylene, 100 g. of aluminium chloride were added, with constant stirring, The temperature rose to 65° and copious fumes of hydrochloric acid were liberated. The mass seemed to divide into two layers; the upper one showing a deep greenish blue fluorescence; the lower one was dark brown. The whole was allowed to stand at ordinary room temperature for three days, at the end of which time the reaction seemed to be complete. The whole mass was treated with ice-water, allowed to stand for some time and finally extracted with ether. The extract was drawn off, the ether removed and the residue distilled at ordinary pressure. The distillates were collected as follows: (*a*) between 70° and 150°, (*b*) 200° and 330°, and (*c*) between 330° and 400°. After these distillates had been removed there remained in the flask a tarry substance. After removing distillate (*b*) an air condenser was used and the solid distillates were thus easily collected for further examination. The first distillate (*a*) consisted of a mixture of hydrocarbons, benzene, xylene, and possibly some toluene. Distillate (*b*) was redistilled, when a large part passed over between 311°–313°. It was wonderfully fluorescent, more so even than diphenylmethane and ditoluylmethane. Analysis of

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[1] *Ann. chim. phys.*, [6] 11, 266 (1887).

[2] *Ann.*, **235**, 172 (1886).

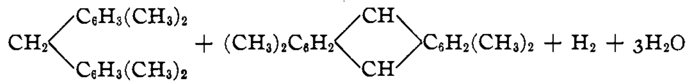
the purified substance gave numbers for $C_{17}H_{20}$ or dixylylmethane. This compound has evidently never before been made, although a substance of the same empirical formula,[1] a duryl benzyl compound, has been prepared.

Tetramethylanthracene.—Distillate (*c*), or that which passed over between 330°–400°, was now examined. It was semi-solid, evidently composed of two or more compounds, and was purified by washing with chloroform. This rapidly took out the oily substance, leaving behind most of the solid substance. The latter was then recrystallized from a mixture of benzene and alcohol. By repeating the process several times the substance was obtained in pure form. It crystallized in yellow monoclinic plates of pearly luster. In solution it possessed an intense green fluorescence. It does not appear to have a melting point but decomposes at 233°–235°. It can be sublimed, however, without difficulty, forming crystals with wonderful iridescence.

Found: C = 92.23 and H 7.22. Calc. for $C_{18}H_{18}$: C = 93.3, H = 7.7.

Friedel and Crafts[2] prepared a tetramethylanthracene from *m*-xylene with a m. p. of 162°–163°, while Anschütz[3] obtained from *m*-xylene an entirely different tetramethylanthracene with a m. p. of above 280°. Dewar and Jones[4] obtained the same compound described by Anschütz which they designated as 2 : 4 : 6 : 8 derivative. Anschütz also obtained from *o*-xylene a tetramethyl compound with a m. p. of 280°, almost the same as the meta compound. It is evident that the one prepared above is an isomeric form, the exact structure of which has not yet been obtained. From what has already been stated concerning these reactions, this one may be represented as analogous to those already given:

$4C_6H_4(CH_3)_2 + (CH_2O)_3 =$



$$CH_2\left\langle\begin{matrix}C_6H_3(CH_3)_2\\C_6H_3(CH_3)_2\end{matrix}\right. + (CH_3)_2C_6H_2\left\langle\begin{matrix}CH\\CH\end{matrix}\right\rangle C_6H_2(CH_3)_2 + H_2 + 3H_2O$$

Mesitylene and Trioxymethylene.—Two hundred grams of mesitylene were brought together with 30 g. of trioxymethylene at ordinary temperature and 55 g. of aluminium chloride added with constant, vigorous stirring. The temperature rose to 50°, hydrochloric acid gas was libera- and the color changed to a dark red. Two layers again appeared, the upper one having a deep violet fluorescence. After allowing it to stand for two days at ordinary room temperature, water was added, and finally the whole mass was extracted with ether. The addition of ether precipitated an amorphous substance which was at first thought to be an aluminium compound, but which was found to be entirely organic. It was removed

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[1] Friedel and Crafts, *Ann. chim. phys.*, [6] 1, 516 (1884).

[2] *Ann. chim. phys.*, [6] 11, 268 (1887).

[3] *Ann.*, 235, 174 (1886).

[4] *J. Chem. Soc.*, 85, 213 (1904).

and recrystallized from a mixture of benzene and chloroform. The purified substance melted at 286°–287°. It was a light yellow crystalline powder.

Found: C = 89.60 and H = 8.45. Calc. for tetramethylanthracene: C = 92.30 and H = 7.70.

It gave all the general characteristics of an anthracene derivative, notwithstanding the fact that Dewar and Jones[1] were unable to prepare anthracene derivatives from mesitylene by the Friedel-Crafts reaction. It seems perfectly evident that hexamethylanthracene cannot be made directly from mesitylene and any other reagent. On the contrary, a tetramethyl compound is not impossible, as two of the methyl groups, one from each of two mesitylene molecules, might be the means of connecting the two molecules as an anthracene derivative. This seems to have happened, forming a tetramethylanthracene which must necessarily be either a 1 : 3 : 6 : 8 or a 2 : 4 : 7 : 9 derivative. It is interesting to note that the melting point corresponds closely with the melting point of tetramethylanthracene as mentioned above m. p. above 280°.

The filtered ether extract was then distilled and the distillates collected in two parts, the first between 90°–200° and the second between 200°–350°. Above this practically nothing would distil over. At a very high temperature it began to decompose. The first distillate consisted of small amounts of benzene, toluene, xylene and mesitylene. The second distillate at first appeared as an oily liquid from which crystals formed on standing. These were separated out by adding ether, whereupon the oily substance immediately dissolved, leaving the crystals behind. They were removed, washed with ether and recrystallized from a mixture of hot alcohol and ether. Thus obtained, the crystals appeared as white monoclinic plates with a m. p. of 129°–130°.

Analysis and general characteristics showed that the substance was dimesitylmethane prepared by Baeyer[2] from mesitylene, formaldehyde and sulfuric acid.

The ether solution containing the oil was warmed in order to remove the ether and then distilled. The first fraction, boiling between 170°–325°, was so small that no attempt was made to examine it.

Durene.—The fraction between 325°–355° consisted of solids together with some oil. Both were very soluble in all the common solvents. They were finally separated by placing on unglazed porcelain plates which readily absorbed the oil leaving the crystals behind. The crystals were finally purified by crystallizing from 95% alcohol. Thus purified they melted at 79°–80°. This differed from any of the other compounds.

Found: C = 90.22 and H = 9.65. Calc. for $C_{10}H_{14}$ = 89.6 and H = 10.4.

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[1] *J. Chem. Soc.*, 85, 218 (1904).

[2] *Ber.*, 5, 1098 (1872).

There seems to be no doubt but that this substance is durene, notwithstanding the results of the analysis. In order to further identify it the dibromo and dinitro compounds were made and found to agree in every respect with the dibromo and dinitro compounds prepared by Anschütz.

That the above reaction with mesitylene is complex is evident from the formation of benzene, toluene, xylene and durene. This unusual reaction was observed by Anschütz,[1] who first showed that benzene homologs are formed from a single benzene derivative by the action of aluminium chloride. But as already stated, no anthracene derivatives had ever been prepared from mesitylene. There can be no doubt but the compound described above is an anthracene derivative. We have represented it as a tetramethyl compound, although analysis really agrees better for a hexamethyl derivative. We have so represented it because a hexa compound can only be formed from a isomer of mesitylene like pseudo-cumene or hemellithene. While we have not succeeded in identifying these latter compounds, both are within the range of possibility, and a hexamethyl derivative could therefore be formed. Experiments along this line are now under way.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

GAS ANALYSES BY FRACTIONAL DISTILLATION AT LOW TEMPERATURES.[2]

BY G. A. BURRELL AND F. M. SEIBERT.

Received April 30, 1914.

This paper describes experiments that resulted in the separation of a natural gas sample into the individual paraffin hydrocarbons present. This had not been accomplished hitherto.

Natural gases may contain only methane as the combustible constituent or may be mixtures that contain large quantities of the higher gaseous paraffins. In some samples the latter predominate. In addition, there may be vapors of the liquid paraffin hydrocarbons present, sometimes enough to warrant the installation of a plant for their extraction. The natural gas used in Pittsburgh is a complex mixture, and is typical of gas that is supplied to many cities to the extent of billions of cubic feet per year. The exact composition of this gas is of importance to the Bureau of Mines because it is used in testing explosives, safety lamps, electrical mining machinery, and other mining appliances. By the scheme shown herein, it is also possible to determine more closely the quantity of the vapors of the liquid paraffins in a natural gas mixture than has been possible heretofore.

[1] *Ann.*, **235**, 178–190 (1886).

[2] Paper presented before the spring meeting of the American Chemical Society, April 7–10, 1914, by permission of the Director of the Bureau of Mines.