

The oils obtained by steam distillation from the various parts of the plant, namely, aerial, rhizome, and roots, possess varying physical and chemical constants. The results of fractionation of these oils indicate that the components of each are present in varying amounts, also that these components vary to some extent.

Further work on the composition of these oils will be undertaken when larger supplies of oil are obtainable.

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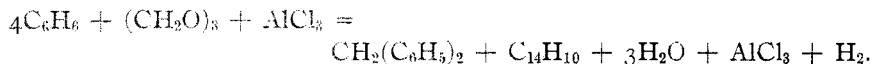
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE.]

THE ACTION OF TRIOXYMETHYLENE ON *p*-XYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE.

BY RALPH C. HUSTON AND DWIGHT T. EWING.

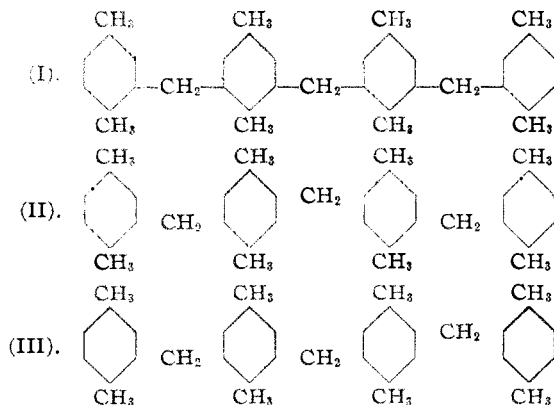
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Frankforter and Kokatnur,¹ as a result of their study of the action of trioxymethylene on benzene, toluene, *o*-xylene and mesitylene, in the presence of aluminum chloride, conclude that four benzene nuclei react with a molecule of trioxymethylene to form diphenylmethane, and anthracene or their homologues, hydrogen being liberated in the reaction.



In connection with other work on *p*-xylene which is being carried on in this laboratory an investigation of the behavior of this compound with trioxymethylene and aluminum chloride has been made.

The conditions of experiment were practically the same as those described by Frankforter and Kokatnur (see Experimental Part). From the resulting mixture, besides some unchanged xylene and a little toluene,



¹ THIS JOURNAL, 36, 1529 (1914).

three compounds were isolated. The first of these was obtained in part by filtering the ether extract, and in part from the high boiling fraction of the same. It is a yellow crystalline powder melting at 204–205°, which was proven by analysis and *molecular weight determination* to have the formula C₃₅H₄₀. It is doubtless one of the preceding three possible tetranuclear compounds.

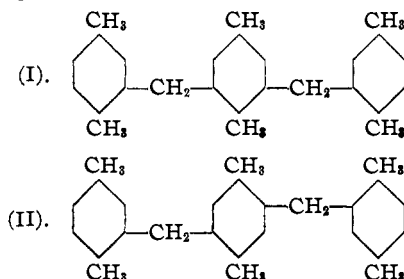
A glance at the following figures will show that simple analysis is not sufficient to fix the formula.

Calculated for tetramethyl anthracene, C₁₈H₁₈: C, 92.26%; H, 7.74%.

Calculated for the trinuclear compound, C₂₆H₃₀: C, 91.18%; H, 8.82%.

Calculated for the tetranuclear compound, C₃₅H₄₀: C, 91.24%; H, 8.76%.

The second compound formed the bulk of the fraction of the distillate from the ether extract which came over between 200° and 330°. It forms fine, colorless needles, which melt at 60° and is readily purified by recrystallization from alcohol. Analysis and molecular-weight determination correspond to the formula C₁₇H₂₀. The compound is then *di-p*-xylylmethane. The third compound distilled at a higher temperature than the *dixylylmethane*. Its melting point (157–158°) and solubility in organic solvents lies between those of the other two compounds. It forms clusters of very fine filaments which are absolutely colorless and which do not resemble the tetramethylantracene described by Anschutz¹ in any way. The compound is probably a trinuclear compound having one of the following two formulae:



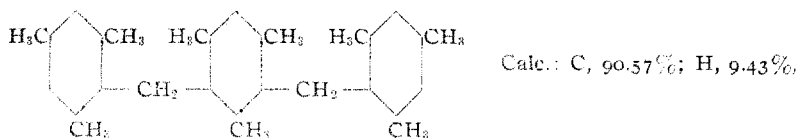
Unfortunately, it was not obtained in sufficient quantity for analysis. Aside from the fluorescence of the ether extract, there was absolutely no evidence of the presence of tetramethylantracene.

It is of interest to note in this connection that some of the experimental data of Frankforter and Kokatnur may be interpreted in a different way than they interpreted them.

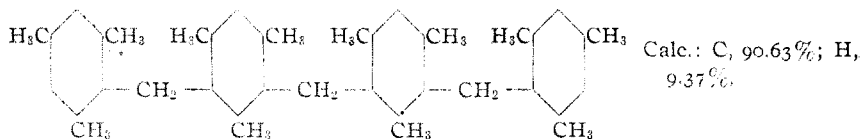
The formula assigned the compound, obtained from mesitylene, which melts at 286–287°, is especially doubtful.

The analysis given (C 89.6%, H 8.45%) agrees more closely with the calculated percentages of the trinuclear compound

¹ *Ann.*, **235**, 174 (1886).



or of the tetranuclear compound



than with those calculated for tetramethylantracene.

The description of the compound shows that it resembles closely the tetranuclear compound of *p*-xylene.

If the methyl groups of the mesitylene molecules are transformed by aluminum chloride in such a way that they form the central ring of the anthracene compound, it is difficult to conceive why Jones and Dewar¹ did not succeed in preparing it in that way.

The molecular weight of the compound was not determined.

Frankforter and Kokatnur² state that diphenylmethane and anthracene are formed in equal quantities and express in their equation the formation of a molecule of each of these from *one molecule* of trioxymethylene. In short, they assume that the molecule of trioxymethylene acts as such and not as formaldehyde, although they admit that similar condensations occur with hydrocarbons, CH_2O and H_2SO_4 . They conclude, since diphenylmethane does not yield anthracene when treated with trioxymethylene in the presence of aluminum chloride, that trioxymethylene does not act in the presence of aluminum chloride, like formaldehyde in the presence of sulfuric acid. This does not prove, however, that trioxymethylene does not act in the presence of aluminum chloride like *formaldehyde in the presence of aluminum chloride*. This last reaction has evidently never been studied. It further does not prove that the anthracene derivatives formed in certain cases, when benzene derivatives are treated with trioxymethylene in the presence of aluminum chloride, *are not formed* as the result of the decomposition of certain intermediate products such as phenylformol.³

Although we have not proven that the formation of anthracene is due to the decomposition of an intermediate product, we have proven conclusively that in the case of *p*-xylene, at least, diphenylmethane derivatives, and anthracene derivatives, *are not formed in equal molecular amounts*, as the equation of Frankforter and Kokatnur requires. We have further

¹ *J. Chem. Soc.*, **85**, 219 (1904).

² *Loc. cit.*, p. 1333.

³ Nastukoff, *J. Russ. phys. chem. Ges.*, **35**, 825 (1903).

shown the possibility of forming polynuclear compounds which contain as high as four benzene rings connected by methylene groups. This points to the dissociation of trioxymethylene into formaldehyde. It may be that steric hindrance prevents the formation of an anthracene compound from *p*-xylene, since the second connecting group must enter between two groups which are in the meta position to each other.

Experimental.

50 g. of *p*-xylene were added to 12 g. of trioxymethylene and the mixture was stirred by a motor for one hour. During this time 20 g. of anhydrous aluminum chloride were added in small portions. A large amount of hydrochloric acid was evolved. The temperature was carefully noted and was kept at approximately 45°, except for a moment, when it reached 60°. It quickly fell. If the stirring was stopped or if the aluminum chloride was added in rather large amounts a vigorous reaction would immediately commence. The color was first red but finally became reddish brown. The mass became so pasty that it was almost impossible to stir it. It was very fluorescent. After it had stood five days at about 0° the reaction appeared to be complete. Ice water was added to decompose the aluminum chloride and the mixture was treated with ether. The yellow precipitate was filtered off by suction and washed with ether.

Methylene bis-(di-*p*-xylylmethane), $C_6H_3(CH_3)_2CH_2C_6H_2(CH_3)_2CH_2-C_6H_2(CH_3)_2CH_2C_6H_3(CH_3)_2$.—The residue was air-dried for six weeks, at the end of which time the odor of formaldehyde had disappeared. The resulting yellowish brown powder was recrystallized eight times from benzene. When the purified compound is heated to 196° it begins to darken. It melts at 204–205° with partial decomposition. It is readily soluble in benzene, chloroform and carbon tetrachloride, slightly soluble in ether, and insoluble in alcohol. With benzene it forms a reddish brown, slightly fluorescent solution. Yield, 1.8 g.

The molecular weight was found by the boiling-point method to be 463; theoretical, 460.

Calc. for $C_{38}H_{40}$: C, 91.24%; H, 8.76%. Found: C, 90.69%; H, 8.7%.

Di-*p*-xylylmethane, $C_8H_3(CH_3)_2CH_2C_6H_3(CH_3)_2$.—The fluorescent ether extract was distilled, two fractions being saved. The first, which was collected between 306° and 319°, was redistilled twice when most of it came over between 313–316°. On standing twenty-four hours it solidified. The solid is very soluble in benzene, ether and chloroform. It was recrystallized repeatedly from alcohol from which it crystallizes in long, white needles. M. p. 60–60.5°. Yield, 4.2 g. A molecular-weight determination by the boiling-point method gave 231; theoretical, 224.3.

Calc. for $C_{17}H_{20}$: C, 91.01%; H, 8.99%. Found: C, 90.92%; H, 8.95%.

The second fraction, which came over between 330° and 340° tended to solidify in the air condenser. A carbon-like residue remained in the distilling flask together with a light green fluorescent solid. This was extracted with chloroform and the extract added to the distillate. On evaporation of the solvent a precipitate formed which was readily soluble in benzene and chloroform, quite soluble in ether and rather insoluble in alcohol. It was recrystallized from a mixture of benzene and alcohol. It tends to form plate-like clusters of poorly formed filaments on the sides of the beaker. It is perfectly colorless and does not show the slightest fluorescence either in the crystalline form or in solution. M. p. $157-158^{\circ}$.

Anschütz¹ prepared 1,4,5,8-tetramethylantracene from *p*-xylene and acetylene tetrachloride in the presence of aluminum chloride. It shows yellowish green fluorescence and melts at about 280° . It is evident that our compound is not identical with this tetramethylantracene. Since but one tetramethylantracene may be produced from *p*-xylene, it follows that our compound does not belong to that class. Since its properties are intermediate between those of di-*p*-xylylmethane and methylene bis-(di-*p*-xylylmethane), it is thought to be a trinuclear compound, *i. e.*, *p*-xylylmethyl di-*p*-xylylmethane. The yield was too small for a molecular-weight determination.

The mother liquor was evaporated to an oil which failed to yield more of the crystalline compound.

In a second experiment, 100 g. of *p*-xylene, 12.5 g. of trioxymethylene and 25 g. of aluminum chloride were mixed, and the above precautions were observed; the temperature rose to 62° . The upper portion of the mixture tended to take on a blue fluorescence. It was treated with cold water, and then with ether. A much larger yield of the tetranuclear compound was obtained here than in the other experiment (8 g.). This was filtered off and the ether extract was distilled. The first fraction came over between 60° and 150° and consisted of ether, benzene, toluene, and unchanged xylene. The second fraction was collected between 200° and 330° . On redistillation most of it passed over between 310° and 316° . The yield of di-*p*-xylylmethane was smaller than in the first experiment (2.4 g.). The next fraction was collected between 330° and 350° . It yielded an oily substance together with a small amount (0.2 g.) of the compound which melts at $157-158^{\circ}$. A fourth fraction was collected between 350° and 450° . This consisted of a small amount of a semi-solid mixture of an oil and solid. The oil was removed on a porous plate and the solid was recrystallized from benzene to which a little alcohol had been added. It was identified as methylene-bis-(di-*p*-xylylmethane). The residue in the flask consisted of a tarry mass with considerable carbon.

¹ *Ann.*, 235, 174.

Summary.

1. It has been shown that the reaction which takes place when *p*-xylene is treated with trioxymethylene in the presence of anhydrous aluminum chloride does not conform with the equation of Frankforter and Kokatnur.

2. Three new compounds resulting from the above reaction have been isolated and described. The molecular formulae of two of these have been determined and structural formulae are suggested.

3. It has been shown that molecular-weight determinations are essential factors in determining the formulae of substances of the types described.

4. The evidence at hand would seem to indicate that trioxymethylene is dissociated into formaldehyde, and this last is the active agent in the condensation reactions.

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

BY G. B. FRANKFORTER AND V. KOKATNUR.¹

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Through the courtesy of the editor, we have just received a copy of a paper by Huston and Ewing, entitled "The Action of Trioxymethylene on *p*-Xylene in Presence of Aluminum Chloride," representing a line of investigation begun by us and on which we are working at the present time. As the paper referred to expresses doubt as to the conclusions drawn in our preliminary work,² we feel obliged to make a statement concerning our work, so that the readers of the JOURNAL, who are too busily engaged in their own chosen field to become thoroughly familiar with the details of our own, may grasp the general outline of our work and the relation of the paper by Huston and Ewing to it.

We indicated in our preliminary paper our intention to continue the work in this special field. We were therefore somewhat surprised to find that others should have taken up this work. We thought we made it clear that we intended to continue our work with other hydrocarbons, as we have done and are doing on both the aliphatic and the aromatic hydrocarbons. We were even more surprised at some of their conclusions. It appears that they question all our work on benzene, toluene, *o*-xylene, etc., from their work on *p*-xylene. If they do, it would be equivalent to questioning the formation of phthalic anhydride from *o*-xylene, because it is not so formed from *p*-xylene.

We wish to emphasize the fact that the object of our preliminary paper

¹ An explanation of our former paper of the above title.

² THIS JOURNAL, 36, 1529 (1914).