

XXV.—*Oxidation of Hydrocarbons of the Benzene Series.*

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IN recent papers we have shown (*Trans. Faraday Soc.*, 1905, 1, 31, 251) that by the electrolytic oxidation of toluene, the three xylenes, ethylbenzene, mesitylene, cumene, and ψ -cumene in acid solution aldehydes were formed. In the case of toluene and *m*-xylene in alkaline solution, the hydrocarbons were oxidised to carbon dioxide and water.

In the present paper we describe experiments made on the oxidation of these hydrocarbons by purely chemical methods in which the reagents employed were lead peroxide, manganese peroxide, chromyl dichloride, and persulphates. In the latter case oxidising action was accelerated by the addition of a silver salt as catalytic agent, because,

in the absence of such a catalyst, practically no oxidation takes place.

Lead Peroxide.—When a mixture of toluene or other hydrocarbon of the benzene series and 50 per cent. sulphuric acid is treated with lead peroxide according to the equation



a very energetic reaction takes place, and unless the lead peroxide is very slowly added or the mixture very thoroughly cooled, the oxidation is so vigorous that the mixture boils over. We found that by this method the hydrocarbons toluene, the xylenes, mesitylene, ψ -cumene, and cymene all gave varying quantities of the mono-aldehydes.

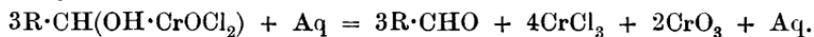
In the first experiments freshly precipitated lead peroxide was employed, but it was not found to be any more reactive than the ordinary commercial product.

Manganese Peroxide.—Fournier (*Compt. rend.*, 1901, 133, 634) studied the action of manganese peroxide in presence of sulphuric acid of sp. gr. 1.53 on hydrocarbons of the benzene series, and found that aldehydes were produced; *o*-xylene, for example, yielded about 30 per cent. of *o*-tolualdehyde. We have repeated Fournier's experiments, and in most cases obtained results corresponding very closely to those described by him.

Chromyl Dichloride.—Étard (*Ann. Chim. Phys.*, 1881, [v], 22, 218) and Bornemann (*Ber.*, 1884, 17, 1463) have shown that when chromyl dichloride acts on hydrocarbons of the benzene series an additive compound of the hydrocarbon and the chromyl dichloride is produced, in which two molecules of the chromyl dichloride unite with one molecule of the hydrocarbon:



This substance is decomposed by water with production of an aldehyde:



In the majority of cases we have obtained better yields of aldehydes by this method than by any other which we have tried. Owing to the vigour of the reaction, however, special precautions must be employed.

*Persulphates.**—When toluene is agitated with a mixture of ammonium persulphate and 4*N*-sulphuric acid, no oxidation takes place. Now, although persulphuric acid alone does not oxidise hydro-

* Since we commenced this work, our attention has been directed to the work of R. Kempf (*Ber.*, 1905, 38, 3963; 1906, 39, 3715), who has investigated the action of persulphates in presence of a silver salt on benzene and *p*-benzoquinone. He has, however, allowed the oxidation to proceed to the furthest possible limit, whilst we have been chiefly concerned with the preparation of the aldehydes.

carbons of the benzene series, it occurred to us that if a metallic salt were present oxidation might take place. Marshall (*Proc. Roy. Soc. Edin.*, 1900, 23, 163) and Marshall and Inglis (*Proc. Roy. Soc. Edin.*, 1902, 24, 88) have shown that when a persulphate is acted on by a soluble silver salt, a black precipitate of silver peroxide is formed. This is probably due to the hydrolysis of the silver persulphate first produced.* When ammonium persulphate is employed, a portion of the ammonium residue is oxidised to nitric acid, $8(\text{NH}_4)_2\text{S}_2\text{O}_8 + 6\text{H}_2\text{O} = 7(\text{NH}_4)_2\text{SO}_4 + 9\text{H}_2\text{SO}_4 + 2\text{HNO}_3$.

This mixture will bleach indigo and oxidise chromic salts. We find that when toluene or other benzene hydrocarbons are agitated with a mixture of a persulphate in sulphuric acid and a small quantity of a silver salt that oxidation takes place and that an aldehyde is the first product. If the alcohol is formed, we have not so far succeeded in isolating it.

At first sodium persulphate was employed, but the results were very contradictory. With some specimens the oxidation was very complete; with others there was practically no action. We found that when oxidation did not take place the persulphate was always contaminated with chloride; therefore in all the later experiments ammonium persulphate free from chloride was used.

The persulphate reaction is rather difficult to control, and the results in various experiments with the same hydrocarbon under apparently similar conditions were not very concordant.

EXPERIMENTAL.

Oxidation of Toluene.

I. *With Lead Peroxide.*—Two hundred and eighty grams of lead peroxide (theory requires 260) was mixed in a lead vessel, surrounded by ice, with 300 c.c. of sulphuric acid (equal volumes of concentrated acid and water, sp. gr. 1.52). The top of the vessel was closed with a sheet of lead, through which a lead stirrer was passed and a tube connected with a carbon dioxide generator, so that the operation could be carried out in an atmosphere of the gas. The mixture was vigorously agitated until the temperature had fallen to about 2°. Then 50 grams of toluene were added and the agitation continued. The temperature rapidly rose to 40°, but soon fell again and remained between 10° and 15° during three hours, when the agitation was

* The oxidation is probably brought about by the unstable silver peroxide, and is not directly due to the persulphuric acid. It will, however, proceed as long as there is any persulphuric acid present, because as soon as the silver peroxide has parted with its oxygen, it will react with the persulphuric acid and thus silver peroxide will again be formed.

stopped. The mixture, which had a strong odour of benzaldehyde, was now transferred to a round-bottomed flask and heated on the water-bath for about half an hour, when it was distilled in a current of steam. We found it always desirable to heat the mixture in this way before subjecting it to steam distillation in order that the reaction might be completed. When this was not done there was a tendency for the mixture to froth over when steam was passed into it.

The distillate was extracted with ether and the aldehyde converted into the hydrogen sulphite compound, in order to separate it from any unchanged toluene. On decomposing the hydrogen sulphite compound 24 per cent. of benzaldehyde was obtained.

When ice was not used and the toluene was added in small quantities at a time, taking care not to allow the temperature to rise above 35 to 40°, we never obtained more than about 18 per cent. of benzaldehyde.

II. *Manganese Peroxide*.—One hundred grams of commercial manganese peroxide (theory requires 83 grams MnO_2) were mixed in a lead vessel with 300 c.c. of sulphuric acid, sp. gr. 1.52, and then 50 grams of toluene added. The mixture was vigorously agitated for five hours. After heating on the water-bath and distilling with steam, only 0.5 per cent. of benzaldehyde was obtained.

The experiment was then repeated, taking, however, 100 grams of freshly precipitated manganese peroxide and agitating for 6.5 hours. In this case 5 per cent. of benzaldehyde was obtained.

III. *Chromyl Dichloride*.—One hundred and forty grams of chromyl dichloride were dissolved in 200 c.c. of chloroform and placed in a glass jar fitted with a glass stirrer, and surrounded by cold water. Forty grams of toluene were dissolved in twice its volume of chloroform and allowed to run slowly into the well-agitated solution of chromyl dichloride. When the whole of the toluene had been added, the mixture was agitated for half an hour longer (altogether two hours) and allowed to stand overnight. It was then transferred to a round-bottomed flask containing a little water, and sulphurous acid was carefully added in excess. During the addition of the sulphurous acid, the flask and its contents were gently agitated. The mixture was distilled with steam, the chloroform containing the dissolved aldehyde separated from the water, and the chloroform evaporated. The oily product was shaken with a concentrated solution of sodium hydrogen sulphite. The hydrogen sulphite compound was washed with ether to free it from any unchanged toluene and the aldehyde recovered in the usual manner. Yield of benzaldehyde, 44 per cent.

IV. *Persulphates*.—Two hundred grams of ammonium persulphate were mixed with 500 c.c. of 4*N*-sulphuric acid, and 2 grams of silver sulphate and 40 grams of toluene added. The top of the vessel was

closed with a sheet of lead, through which passed a glass stirrer and a tube in connexion with a Kipp's apparatus for generating carbon dioxide. The mixture was vigorously agitated without cooling, so as to form an emulsion. The temperature rose to 45°; after seven hours, it had fallen to that of the atmosphere and the mixture was distilled with steam. The benzaldehyde was separated as usual by means of the hydrogen sulphite compound, the yield being 78 per cent.

With 2*N*-acid, the yield of aldehyde was poor.

p-Xylene.

Lead Peroxide.—Fifty grams of *p*-xylene were added to 300 c.c. of sulphuric acid, sp. gr. 1.52, and the mixture thoroughly agitated in an atmosphere of carbon dioxide. Two hundred and fifty grams of lead peroxide were then added in quantities of about 50 grams at one time, by which means the temperature of the mixture was kept at about 45°. The whole operation took about three hours. The mixture was then transferred to a flask and heated on the water-bath for about half an hour, after which it was distilled with steam. The yield of aldehyde was 27.5 per cent.

Manganese Peroxide.—Fifty grams of *p*-xylene were mixed so as to form an emulsion with 100 grams of manganese peroxide and 300 c.c. of sulphuric acid, sp. gr. 1.52. The mixing was continued for about six hours, during which time the temperature did not rise above 25°. The mixture was then heated on the water-bath for half an hour and distilled with steam. The yield of aldehyde was 14.5 per cent.

Chromyl Dichloride.—The preparation was exactly similar to that described under toluene, and the yield of aldehyde varied between 70 and 80 per cent.

Persulphate.—In this case, it was found essential to cool the mixture during the time the reaction was taking place. In one case, taking 40 grams of *p*-xylene, 190 grams of ammonium persulphate, 500 c.c. of 4*N*-sulphuric acid, and 2 grams of silver sulphate, the temperature at the commencement was 15°; in fifty minutes it had risen to 29°, and ten minutes later the mixture boiled over, the temperature having risen to 102°. When the above mixture was well agitated in an atmosphere of carbon dioxide, the vessel being placed in cold water so that the temperature did not rise above 25°, yields of *p*-tolualdehyde varying from 35 to 48 per cent. were obtained.

The methods of procedure with *o*- and *m*-xylene were similar to those employed for *p*-xylene; the yields obtained by the different processes of oxidation are tabulated on page 263. Mesitylene and *ψ*-cumene also behaved in a normal manner, but the yields of aldehyde were less than in the cases of the xylenes.

Cymene was found to be very difficult to oxidise, even when the temperature, in the case of oxidation with lead peroxide, manganese peroxide, and persulphates, was allowed to rise unchecked. This was from 40 to 50° in the case of the peroxides, using acid of sp. gr. 1.53. With persulphates the temperature, using 4*N*-acid, rose to about 35°. In this case the reaction showed a tendency to proceed beyond the aldehyde stage and a considerable quantity of cuminic acid was obtained, the yield of cuminaldehyde being very small. The aldehyde is probably first produced and then undergoes oxidation, for a considerable amount of unchanged cymene was always recovered.

Although the main product of oxidation of all the hydrocarbons was the mono-aldehyde, on working up the residues from a large number of experiments small quantities of the alcohols were obtained. The amounts, however, were so small that they certainly did not represent more than 0.1 per cent. of the hydrocarbon employed. At the same time the fact that these small quantities of alcohols are obtained would point to the probability that the alcohol is the first product, and that by further oxidation the aldehyde is formed. In some cases a considerable quantity of resin was produced, and this was particularly marked when persulphates were employed.

Percentage yield of aldehydes with different oxidising agents.

	Electrolytic oxidation.	Lead peroxide.	Manganese peroxide.	Persulphates.	Chromyl di- chloride.
Toluene	10—20	18—21	5	78	44
<i>o</i> -Xylene	25—30	28	38	—	65
<i>p</i> -Xylene	25—35	27.5	14.5	35—48	70—80
<i>m</i> -Xylene	10—15	20	—	44	60
Mesitylene	10—15	8.5	16	5.8	5.5
ψ -Cumene	10—12	11	17	—	5
Cymene	{ 10, aldehyde } { 20, alcohols }	10	1	0.5	8

It should also be mentioned that when the hydrocarbons were oxidised with chromyl dichloride, in some cases considerable quantities of chlorinated products were obtained. This was usually the case when the yield of aldehyde was small and was particularly noticeable with mesitylene and *m*-xylene.

The authors desire to express their thanks to the Committee of the Government Research Fund of the Royal Society for a grant which, in part, defrayed the expenses in connexion with this investigation.

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