

June 21, 1847.—The President in the Chair.

Four Numbers of Silliman's Journal were presented by the Editor.

The following papers were read:—

A notice from Messrs. Playfair and Joule on the next part of their paper on Atomic Volume.

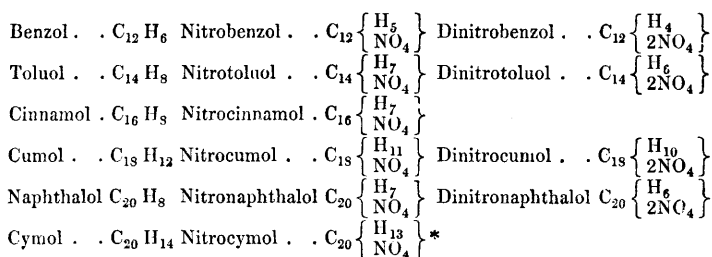
CCIII. *On some of the Products of Oxidation of Cumol by Nitric Acid.* By Mr. F. A. ABEL.

FROM the investigations on the action of nitric acid upon organic bodies, *one* result, in reference to the manner in which this acid acts, has been undoubtedly established. We know that in most cases the carbon of the organic substance remains untouched; that according to the degree of concentration of the acid a smaller or larger number of equivalents of hydrogen are expelled, and that the remaining part of the organic body combines with the remainder of the nitric acid. Thus is produced that innumerable class of neutral com-

* Erdmann's Journal, xxxiii. 29.

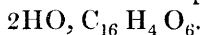
pounds considered by some chemists to be combinations of nitrous acid with organic oxides, and by others to be products of the substitution of hyponitric acid for hydrogen. It is indifferent which of these views is adopted, the fact having been established by hundreds of experiments, and we are enabled by analogy to predict with tolerable certainty the result of any new experiment.

The case is quite different when the oxidation is not confined to the hydrogen, but is extended to the carbon. The numerous experiments made on this subject do not as yet afford any general conclusion; we are far from being able to form an opinion, previous to experiment, of the nature of the product formed. This will be obvious if we examine the action of nitric acid on a class of bodies which are very nearly related to each other, both by the manner in which they are formed and in their general chemical behaviour. Benzol, toluol, cinnamol (styrol), cumol, naphthalol, cymol, are acted upon by nitric acid, the corresponding products of substitution are formed.



In the above two columns of combinations the number of equivalents of carbon will be found the same as in the carbo-hydrogens. We have however succeeded with most of these bodies, by the continued action of the acid upon them, or by the observation of particular conditions, in oxidizing also a portion of their carbon bodies with acid properties being produced which contain a smaller number of equivalents of carbon than the carbo-hydrogens from which they were derived. The composition of these acids does not however bear any constant relation to the carbo-hydrogens, such as observed in the above-mentioned products of substitution.

By the continued action of nitric acid on naphthalol, naphthalic acid, discovered by Laurent and Marignac†, is produced, the composition of which is expressed by the formula



* This substance is now under investigation by Mr. Noad.—Dr. A. W. H.

† Liebig's *Annalen*, xli, p. 98, and xlii, p. 215.

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The action of nitric acid on cinnamol (styrol) has been studied by Drs. Hofmann and Blyth*. They have shown that cinnamol may in this manner be converted into benzoic acid.

The products obtained by the action of nitric acid on toluol have been studied by Deville†. He found that the two above-mentioned products of substitution were easily formed. He moreover believes to have converted toluol, by a long treatment with oxidizing agents, into benzoic acid; he is however in doubt about the result of his experiment, as he could not always succeed in the transformation, and his method of preparing toluol did not exclude the possibility of its containing benzoic æther in admixture. If benzoic acid can in reality be obtained from toluol, we have here an instance of the formation of an acid without the original number of equivalents of carbon in the carbo-hydrogen being diminished.

In the paper lately read before this Society by Mr. Noad, he has shown that cymol is converted by the continued action of dilute nitric acid into tolylic acid.

It will be seen from these examples that we are unable to determine anything beforehand regarding the nature of these products of oxidation. The manner in which nitric acid or any other oxidizing agent acts is evidently closely connected with the constitution of the body exposed to their influence. Aided by the manner in which nitric acid acts on naphthalol, Marignac has in fact founded a view of the constitution of this body. He considers the carbo-hydrogen in question to be a combination of two others, namely, $C_{16}H_4$ and $C_4H_4 = C_{20}H_8$, naphthalic acid, $C_{16}H_4O_6$, being formed by the action of nitric acid on the first, while the other is converted by the influence of the oxygen into water and oxalic acid or carbonic acid. By this view many of the reactions of naphthalol may be explained in a very satisfactory manner. It is possible that similar views may be applied to the other carbo-hydrogens, by which their behaviour with oxidizing agents may be similarly explained; a great number of investigations are however required before we can arrive at any general result.

The following experiments, which I have instituted at the suggestion and under the direction of Dr. Hofmann, may, I hope, be considered as a slight contribution to this subject.

It is known that when cumol is treated with concentrated nitric acid it yields the usual products of substitution of the carbo-hydrogens. Gerhardt and Cahours have observed further, that by the continuous action of dilute nitric acid on

* Trans. of Chem. Soc. vol. ii. p. 334.

† *Ann. de Chim. et de Phys.* 3d Ser. t. iii. p. 168.

cumol a crystalline acid is produced*. This acid has not, however, been more closely investigated. According to the experiments on toluol, cinnamol and cymol before mentioned, this acid might be of three different kinds, according to the analogy of cumol with any one of these carbo-hydrogens. If the number of equivalents of carbon were to remain the same as in toluol, the acid obtained might be $\text{HO}, \text{C}_{18} \text{H}_9 \text{O}_3$, until now unknown (differing from toluylic or cuminic acid in containing $\text{C}_2 \text{H}_2$, more or less). Should two equivalents of carbon be eliminated, as is the case with cinnamol, the formation of toluylic acid might then be expected; and lastly, should cumol be analogous to cymol, that is, should it lose four equivalents of carbon, the acid must then be benzoic acid.

In the preparation of cumol I proceeded in the manner described by its discoverers, Gerhardt and Cahours. Pure cuminic acid was distilled with four times its weight of caustic lime in a copper retort placed in a deep sand-bath, the temperature of which was gradually raised to a red heat. The distillate obtained was colourless, possessing however an empyreumatic odour, which it did not lose on being rectified over hydrate of potash to free it from any cuminic acid that might have come over with it. I afterwards found that this peculiar odour was immediately removed on distilling the oil with a concentrated solution of chromic acid, which leaves the cumol of its agreeable aromatic smell without affecting its composition. This is a method that might perhaps prove useful in many cases where the peculiar odour of a carbo-hydrogen is disguised by the presence of a small quantity of some foreign substance.

When dried over chloride of calcium this body possessed exactly the same properties as described by Gerhardt and Cahours. Its boiling-point was found by them to be 144°C .; a later experiment of Gerhardt gave 153° as the boiling-point. The cumol that I prepared boiled at 148°C . Its analysis gave me the following results:—

0.2029 grm. burned with oxide of copper gave 0.6725 grm. of carbonic acid and 0.1804 grm. of water; corresponding to

Carbon	90.34
Hydrogen	9.88

which numbers agree with the composition of cumol.

		Theory.	Found.
18 eqs. Carbon . .	108	90.0	90.34
12 ... Hydrogen . .	12	10.0	9.88
	120	100.0	

* Liebig's *Annalen*, xxxviii. p. 67.

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On boiling cumol with concentrated nitric acid it is quickly converted into a heavy oil, which is the analogue to nitrobenzol. If the boiling is continued this oil disappears, and is gradually converted into a yellow crystalline mass, soluble in ammonia with the exception of a slight fixed residue (dinitrocumol). The ammoniacal solution gives with hydrochloric acid a white precipitate, difficultly soluble in cold water, but more easily so in hot water, from which it crystallizes on cooling. These crystals are generally somewhat coloured; recrystallization after treatment with animal charcoal removes this colouring matter.

Several combustions of the acid dried at 100° C. showed me that my substance must be a mixture. I therefore distilled another portion of cumol with fuming nitric acid for several days, and obtained a crystalline body similar to the former, which was purified in the usual manner. A combustion of this body gave me the following results:—

0·2628 grm. of substance yielded 0·4890 grm. carbonic acid and 0·0743 grm. water.

Or in 100 parts,—

Carbon	50·73
Hydrogen	3·18

These numbers correspond to the composition of nitrobenzoic acid, $\text{HO}, \text{C}_{14}\left\{\begin{smallmatrix} \text{H} \\ \text{NO}_4 \end{smallmatrix}\right\} \text{O}_3$, as is seen when compared with the theoretical numbers.

		Theory.	Found.
14 equivs. Carbon . .	84	50·30	50·73
5 ... Hydrogen . .	5	3·00	3·18
1 ... Nitrogen . .	14	8·38	
8 ... Oxygen . .	64	38·32	
	<u>167</u>	<u>100·00</u>	

On addition of nitrate of silver to the ammoniacal salt of this acid a white precipitate was formed, sparingly soluble in hot water, from which it crystallized on cooling. I had not sufficient substance to recrystallize the salt, and could therefore only purify it by washing.

Its analysis gave me the following result:—

0·1657 grm. of substance left, on being burnt, 0·0650 grm., or 39·24 per cent. of silver; which agrees sufficiently well with the composition of nitrobenzoate of silver.

		Theory.	Found.
Nitrobenzoic acid . .	158	57·67	
Oxide of silver . .	116	42·33	42·14
	<u>274</u>	<u>100·00</u>	

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In order to be perfectly certain, the small quantity remaining of the silver salt was submitted to distillation. There sublimed a portion of the acid, mixed with a few drops of an aromatic oil. The product of the distillation was therefore submitted to Dr. Hofmann's process for detecting nitrobenzol; it was dissolved in a mixture of alcohol and sulphuric acid, and reduced by means of a piece of metallic zinc. After the disengagement of hydrogen had ceased, the liquid was neutralized with potash and agitated with æther. A few drops of the ætherial solution gave, on evaporation with hypochloride of lime, the beautiful violet colour characterizing aniline.

These experiments were sufficient to identify nitrobenzoic acid, and it seemed more than probable that the excess of carbonic acid obtained in the first analysis arose from the presence of benzoic acid.

I therefore distilled a fresh quantity of cumol with nitric acid, and recollecting the difficulty Mr. Noad experienced in the preparation of toluyllic acid, I employed my acid so dilute that even on boiling the mixture no disengagement of red fumes was visible. Having continued the distillation for four or five days the cumol was converted into a crystalline mass, which was strained off from the mother-liquor and recrystallized from water. The properties of this acid distinguished it immediately from nitrobenzoic acid; it was much more soluble in cold and hot water, and might be easily recognised as benzoic acid. Not having sufficient substance for a combustion, I converted the acid into an ammoniacal salt, and precipitated this with nitrate of silver. A white flocculent precipitate was obtained, much more easily soluble in water than nitrobenzoate of silver. On cooling, beautiful crystals separated, having all the properties of benzoate of silver.

The analysis of this salt gave me the following results:—

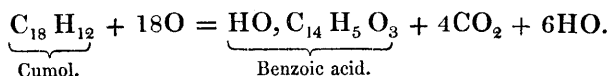
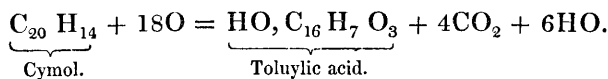
I. 0.1837 grm. of substance yielded 0.1138 grm. chloride of silver, corresponding to 0.0857 grm. or 46.65 per cent. of silver.

II. 0.1658 grm. yielded 0.0780 grm., or 47.04 per cent. of silver, which numbers correspond with the formula AgO , $\text{C}_{14}\text{H}_5\text{O}_3$, as may be seen when compared with the theoretical numbers.

		Theory.	Found.	
			I.	II.
Benzoic acid .	113	49.35		
Oxide of silver .	116	50.65	50.08	50.50
	229			

These results were sufficiently near, considering the small amount of substance employed.

From these experiments we see that cumol on being boiled continuously with nitric acid is converted into benzoic and nitrobenzoic acids. The oxidation of cumol is therefore analogous to that of cymol.



The behaviour of cumol under the influence of the continued action of dilute nitric acid induced me to submit benzol, so nearly related to cumol, to a similar treatment. After having however continued the distillation for about a week I could not obtain an acid from benzol. On employing highly diluted acid, the benzol was gradually converted into nitrobenzol.

Neither benzol nor nitrobenzol is attacked by pure chromic acid, or the oxidizing mixture of bichromate of potash and sulphuric acid. Results quite as unsatisfactory as these were obtained on boiling a solution of hyposulphobenzolic acid with chromic acid or peroxide of manganese.
