XI.—*On the Composition of Mesitylole, and some of its derivatives.**By* DR. A. W. HOFMANN.

We are indebted to Sir Robert Kane for the investigation of an interesting class of compounds, arising from the decomposition of acetone.* The general result of these researches was the exhibition of a remarkable analogy in the nature of this body to that of an alcohol.

The original formula for acetone, as resulting from Dumas' and Liebig's analyses, was :

representing an equivalent of an acetate, minus an equivalent of a carbonate ; a formula which, subsequently, when Dumas determined the density of the vapour of this liquid, was doubled, on the supposition that its equivalent corresponded to 4 volumes of vapour.

The products of decomposition of acetone, afforded an additional support to the formula :

as representing the equivalent of this body, which, according to the experiments of Kane, we have to consider as the hydrated oxide of a compound radical, mesityl, analogous to methyl, ethyl, and amyl :

In fact, Sir Robert Kane succeeded in isolating the oxide of this radical, as also in combining it with sulphuric and phosphoric acids, and in preparing the chloride and iodide(?) corresponding to the oxide. He, moreover, obtained a liquid hydrocarbon, which he described under the name of mesitilene (mesitylole), and which he considered as representing, in his new series, the olefant gas of common alcohol.

So far the analogy is complete ; we may add even, that since that period an acid has been discovered which, in the mesityl-series, would correspond to the acid terms of the other alcohols. We know that all true alcohols, by losing two equivalents of hydrogen, and assuming two equivalents of oxygen, pass into a class of acids of which formic, acetic, and valerianic acids are familiar instances. Now *acrylic acid* (acronic acid, Berz.), which Prof. Redtenbacher discovered among the derivatives of glycerin, stands to acetone exactly in the relation which exists between common alcohol and acetic acid.

* "On a series of combinations derived from Pyroacetic Spirit," Dublin, 1838.

Acrylic acid has not yet been prepared from acetone, which, when subjected to oxidizing agents, is converted into acetic and formic acids; but if we consider the great facility with which, according to Redtenbacher's experiments, acrylic acid is itself converted into these two acids, we may still, perhaps, hope to arrive at this result by a judicious selection of the proper oxidizing agent.

These observations sufficiently prove that acetone exhibits, in a remarkable manner, the characters of an alcohol; nevertheless, our views respecting the nature of this compound appear to be by no means settled. Indeed, the progress of science has not failed to raise a series of objections to the opinion, which, at the time of Sir Robert Kane's experiments, appeared most probable.

The extreme instability of the mesityl compounds, at once distinguishes this group of bodies from the derivatives of the regular alcohols, from which it differs, moreover, in the ratio of the carbon and hydrogen equivalents. The impossibility of reproducing acetone from these derivatives, and the difference in the constitution of sulphomesitylic and sulphovinic acids, likewise appeared to discountenance the reception of acetone into the group of well-established alcohols. The former of these objections has lost some of its weight, since, in the cyanides of the alcohol-radicals, we have become acquainted with a class of alcohol-compounds likewise irreconvertible into the original terms, whilst the latter might, perhaps, be removed by a closer investigation of sulphomesitylic acid and its compounds. Be this, however, as it may, the state of our knowledge respecting the derivatives of acetone, clearly proves that this field has not yet been sufficiently explored.

The following pages contain a small contribution to the history of mesitolle, one of the most interesting among the acetone-descendants, which the researches of Sir Robert Kane have elicited.

To trace the analogy of acetone and alcohol, this chemist naturally directed his attention to the action of dehydrating agents on the former. He found that sulphuric acid readily decomposed acetone, giving rise to a variety of products, among which an oxygenated liquid, oxide of mesityl, according to Kane, the ether of the series, and an oily carbohydrogen (mesitylene), the representative of olefiant gas, are enumerated.

I have repeated this reaction with precisely the same results. On distilling a mixture of 2 volumes of acetone, and 1 volume of con-

centrated sulphuric acid, a distillate is obtained consisting of an aqueous solution of sulphurous acid, on the surface of which an oily liquid floats, whilst a dark-brown residue remains in the retort. Redistillation of this liquid, after washing with water and drying, evinced at once the compound nature of the oil, which commenced to boil at about 100° C. (212° F.), the boiling-point rising gradually to upwards of 250° C. (482° F.) My attention being chiefly directed to the carbo-hydrogen, which, according to Kane, boils at 135° C. (275° F.), I collected the distillate, passing over between 120° C. (248° F.) and 160° C. (320° F.) separately. On repeatedly distilling this quantity, I, however, soon found that the boiling temperature of the substance I was in search of, was much higher than 135° C. (275° F.); I was consequently obliged to fraction the whole portion, passing over in the first distillation between 120° C. (248° F.) and 200° C. (392° F.) After very numerous distillations a liquid was obtained, boiling pretty constantly between 155° C. (311° F.) and 160° C. (320° F.), which possessed all the properties Sir Robert Kane attributed to his substance, excepting the boiling-point, to the difference in which I have alluded above.

The analysis of mesitolole originally led to the ratio of carbon and hydrogen equivalents—

but both the formation of the new body, as being derived from acetone, and the products into which it is converted under the influence of various agents, proved at once that the equivalent of mesitolole was higher. In fact, the preparation of a beautiful crystalline body, by the action of chlorine upon mesitolole, and described by Kane under the name of chloride of pteyl, compelled him to double the above formula into the following expressions :

a change which rendered the transformation of acetone perfectly analogous to that of alcohol under the same circumstances :

This formula for mesitolole appeared to be confirmed by the composition of the corresponding bromine- and nitro-compounds :

which, at a later period, were discovered by M. Cahours. The determinations, however, of the density of the vapour of mesitolole, in which M. Cahours had hoped to obtain further support for this formula, gave results which induced many chemists to double again the formula of mesitolole. According to Cahours' density, one equivalent of this substance would contain only two volumes of vapour, whilst all other hydrocarbons, whose equivalents have been ascertained by metamorphoses, have been found to correspond to four volumes of vapour. In fact, we know as yet no exception to this general rule. Olefiant gas, Faraday's gas, Amilole, Cetole, Benzole, Toluole, Naphthalole, &c., substances, the equivalents of which we may consider as fixed both by their origin and by their descendants, all contain invariably four volumes of vapour in one equivalent. These considerations have pretty generally led to the adoption of the following formulæ for the mesitolole series :

All the observations which we possess respecting this group appear to find a satisfactory explanation in the assumption of the above formula : there is only one property of mesitolole which does not well agree with this expression, viz. : its boiling-point. In the present state of our knowledge respecting the boiling temperatures of liquids, the discrepancy of the actual boiling-point of mesitolole, and the temperature at which we should expect the ebullition of a liquid represented by the formula

could not fail to throw some suspicion on the exactness of this expression. If we recollect that the accurate experiments, both of

Mr. Mansfield* and Dr. Kopp,† have fixed the boiling-point of benzole at 80° C (176° F.), we cannot but be surprised to find a liquid of very similar constitution, containing the same number of equivalents of carbon, and even more hydrogen, boiling at so much higher a temperature. An increase in hydrogen almost invariably depressing the point of ebullition of a compound, we should expect to see mesitolole boiling rather at a lower than at a higher temperature. This circumstance has not escaped Leopold Gmelin, who in his Handbook‡ alludes to this discrepancy. He attributes, however, to the presence of substances possessing a higher boiling-point in the crude product after the action of sulphuric acid upon acetone, that the boiling-point of Kane 135° C. (275° F.) had been observed too high. He mentions likewise that the boiling-point would correspond more closely with a substance of the formula :

We shall see directly that this formula actually represents the composition of mesitolole.

The purification of mesitolole is attended with considerable difficulty and although working on rather a large scale, I have not been able to obtain a perfectly fixed temperature for this substance ; but numerous experiments, made both by Mr. Maule and myself, have proved that this point is decidedly between 155° C. (311° F.) and 160° C. (320° F.)

This boiling-point of mesitolole, higher even than had resulted from Kane's experiments, could not fail to invite me to a few experiments with this body, in order to obtain further data for establishing its composition. It appeared by no means impossible that, by the moderate action of decomposing agents, substances might be produced differing in composition from those hitherto obtained, and thus afford a key for the solution of the question.

Action of Bromine on Mesitolole.—The inferior affinity for hydrogen, which distinguishes bromine from chlorine, naturally directed my attention first to this powerful salt-former. Bromine was added carefully, drop by drop, to mesitolole, waiting each time until the heat evolved had subsided, and taking care to keep the hydrocarbon in excess. Mesitolole is thus converted into a white crystalline compound, which was freed from hydrobromic acid by washing with water, in which it is perfectly insoluble. Two or three crystallizations from boiling alcohol render this compound absolutely pure. It presents

* Journ. of the Chem. Soc. Vol. 1. 244. † Pogg. Ann. Bd. LXXII. 1 and 223. ‡ Vol. IV.

itself in white needles, which are volatile without decomposition, and are not changed by ebullition with either potash or ammonia.

Analysis gave the following results :

- I. 0.3595 grm. of bromine-compound gave :
 0.4048 „ „ carbonic acid, and
 0.0905 „ „ water.
 II. 0.0223 „ „ bromine-compound gave :
 0.3540 „ „ bromide of silver.

Per-centage composition :

	I.	II.
Carbon . . .	30.70	—
Hydrogen . . .	2.79	—
Bromine . . .	—	66.68

These numbers lead exactly to the composition of M. Cahours' bromine-compound, corresponding with either

	Theory.		Experiment.
12 equiv. of Carbon . . .	72.00	30.70	30.70
6 „ „ Hydrogen . . .	6.00	2.56	2.79
2 „ „ Bromine . . .	78.86	66.74	66.68
1 equiv. of Bromine-compound	156.26	100.00	100.17

The properties of the substances likewise prove their identity.

Action of Nitric Acid on Mesitylene.—The action of this acid on the carbohydrogen has been likewise studied by M. Cahours. On treating mesitylene with concentrated nitric acid, he found that a dark yellow oil was produced, which did not present a sufficiently definite character for analysis ; by employing, however, a mixture of concentrated nitric and sulphuric acids, he obtained a beautiful crystalline compound, which, when purified by washing with water and repeated crystallizations from alcohol, or by sublimation, exhibited the lustre of metallic silver in a remarkable degree. Analysis proved this compound to be either :

My experiments have led me to the same result. By acting either with the sulphuro-nitric mixture, or with fuming acid alone, I have obtained this compound with all the properties which M. Cahours has assigned to it. To his description I need only add, that this substance dissolves with extreme difficulty in boiling alcohol and ether, but is easily purified by crystallization from acetone, in which, as Mr. Maule has found, it readily dissolves.

The following numbers were obtained on analysis:

0.2210 grm. of substance gave :
 0.3415 „ „ carbonic acid, and
 0.0770 „ „ water.

The per-centage obtained from these numbers closely corresponds with the formula :

as exhibited in the following table :

	Theory.		Experiment.
12 equiv. of Carbon . . .	72	42.35	42.14
6 „ „ Hydrogen . . .	6	3.53	3.87
2 „ „ Nitrogen . . .	28	16.48	—
8 „ „ Oxygen . . .	32	37.64	—
1 equiv. of Nitro-compound	138	100.00	

So far my endeavours were attended with but little success. By employing nitric acid of inferior strength, however, I obtained at once a different result.

Mesitolole, when boiled with dilute nitric acid is very gradually attacked, it turns yellow, and loses part of its fluidity. After repeated distillations, it is converted into a yellow oil, showing a tendency to crystallize. This oil is evidently a mixture, and I have not been able to effect a separation, too small a quantity of mesitolole being at my command. By substituting nitric acid of moderate concentration, however, for the dilute acid, a few distillations were sufficient to convert the whole of the mesitolole into the crystalline compound, which presents itself in very fine needles, sometimes several inches in length.

These crystals were washed with water, and finally recrystallized from alcohol: the facility with which they dissolve in this liquid, directly showed me that I had a substance in hand perfectly

different from the previous nitro-compound, which it resembles in many other respects, especially in its outward appearance, and its volatility without decomposition.

Analysis gave the following results :

I.	0.2915	grm. of substance gave :
	0.5445	„ „ carbonic acid, and
	0.1310	„ „ water.
II.	0.2050	„ „ substance gave :
	0.3840	„ „ carbonic acid, and
	0.0915	„ „ water.
III.	0.2280	„ „ substance gave :
	0.4280	„ „ carbonic acid, and
	0.1030	„ „ water.

Per-centage composition :

	I.	II.	III.
Carbon	50.94	51.08	51.15
Hydrogen	4.95	4.95	5.01

These numbers closely correspond with the formula :

which has to be doubled into

the expression

not being reconcileable with the formulæ for the other derivatives of mesitilole.

	Theory.		Experiment.
18 equiv. of Carbon . . .	108	51.42	51.07
10 „ „ Hydrogen . .	10	4.76	4.98
2 „ „ Nitrogen . .	28	13.35	—
8 „ „ Oxygen . . .	64	30.47	—
1 „ „ Nitro-compound	—	—	—
	<hr/> 210.	<hr/> 100.00	

Its subsequent transformation into nitromesidine by Mr. Maule, altogether precluded the necessity of determining the nitrogen in this compound.

The existence of a body of this nature can leave no doubt respecting the true formula for mesitilole. It is evident that a compound of

the indicated composition can be derived only from a carbo-hydrogen of the formula :

which I consider as the true expression for the equivalent of mesitolole.

The formula of mesitolole, becomes thus identical with that of another carbo-hydrogen which is found among the derivatives of cuminic acid, viz., with cumole. These substances are, however, far from being actually identical. It is only necessary to compare the odour of the two liquids, and their comportment with reagents, in order to remove every doubt upon this head; still these substances, as might be expected, exhibit a remarkable analogy in their physical properties, their boiling points being indeed so near each other, that I do not despair of finding that they are actually identical. The boiling point of mesitolole is, as I mentioned, probably between 155°C . (311°F .) and 160°C . (320°F .) ; for the boiling temperature of cumole we possess three different observations, respectively announcing it to be at 144°C . (291°F . Gerhardt and Cahours*), 148°C . (299°F . Abel†), and 153°C . (308°F . Gerhardt‡.) It is not impossible that these two liquids boil actually at the same temperature. The compounds, too, arising from the reaction of nitric acid upon cumole present a certain analogy, although here likewise we meet with discrepancies. We have become acquainted with nitrocumole and dinitrocumole, but a trinitro-compound corresponding to trinitromesitolole, for such the nitro-compound first described must henceforth be considered, has not been formed, although M. Cahours subjected both hydro-carbons to exactly the same treatment.

In adopting the new formula for mesitolole we interfere, as is easily seen, in no way with the former results, all the analyses are perfectly correct, they have to be interpreted only in a different manner. There is, however, one observation which, at least according to principles generally admitted, is no longer reconcileable with the atomic composition of our compound. This is the determination of the density of mesitolole as made by M. Cahours. If this determination be correct, —and we have scarcely a better authority in experiments of this kind than M. Cahours,—one equivalent of mesitolole would represent not less than 6 volumes of vapour, a number which has been never observed in any similar case. All the well investigated hydro-carbons, have

* Ann. de Chim. et de Phys. 3me Série, i. p. 60.

† Memoirs of Chem. Soc. Vol. III. p. 144.

‡ Ann. de Chim. et de Phys. 3me Série, Tom XIV. 111.

given hitherto invariably 4 volumes. It is possible that the specific gravity of the mesitilole vapour is subject to similar variations as have been observed with acetic, butyric, valerianic acids, and several other compounds; it is possible, likewise, that an equivalent of mesitilole is actually represented by 6 volumes of vapour, and this anomalous condensation may assist in explaining the difference between the constitution of this body and cumole, which, like the other hydrocarbons, contains only 4 volumes of vapour. Be this, however, as it may, the subject requires further investigation. I have hitherto been prevented repeating the determination of the specific gravity, from not having obtained the hydrocarbon of a perfectly constant boiling-point.

The discrepancies existing between the theoretical and experimental density of mesitilole, when expressed by the formula :

compelled me to search for additional support for this formula from other facts. The action of sulphuric acid promised to afford some valuable results with reference to this question.

Action of fuming sulphuric acid on mesitilole.—*Mesitilo-sulphuric acid.*—Common concentrated sulphuric acid acts but very slowly upon mesitilole; fuming acid dissolves it more readily, a reddish brown liquid being produced, which, when exposed to a moist atmosphere becomes gradually crystalline. The application of heat must be avoided, as it carbonizes the compound with the evolution of sulphurous acid. The evolution of a small quantity of this gas cannot be prevented, even when operating in the cold.

On diluting with water, the brown liquid becomes colourless, and yields, when saturated with an excess of carbonate of lead, a soluble lead-compound, insoluble sulphate of lead remaining. The lead-salt is extremely soluble both in water and alcohol, which renders it difficult of purification. However, by treatment with animal charcoal, and subsequent gradual evaporation, it may be obtained in beautiful white needles of perfect purity; the analysis of this compound gave the following results :

I.	0.3180	grm.	of lead-salt	gave :
	0.1580	"	"	sulphate of lead.
II.	0.2853	"	"	lead-salt gave :
	0.1426	"	"	sulphate of lead.

III. 0.3043	„	„	lead-salt gave :
0.3979	„	„	carbonic acid, and
0.1045	„	„	water.

Per-centage composition :

	I.	II.	III.
Lead	33.95	34.15	—
Carbon	—	—	35.66
Hydrogen	—	—	3.81

These numbers lead exactly to the formula :

as exhibited in the following table :

	Theory.		Experiment.
1 equiv. of Lead	103.56	34.22	34.05
18 „ „ Carbon	108.00	35.69	35.66
11 „ „ Hydrogen	11.00	3.63	3.81
2 „ „ Sulphur	32.00	10.58	—
6 „ „ Oxygen	48.00	15.88	—
1 eq. of Mesitilosulphate of lead	302.56	100.00	

The analysis of this lead-salt proves, that the action of sulphuric acid on mesitilole gives rise to a new acid, perfectly analogous to hyposulphobenzolic and hyposulphocumolic acids, with the latter of which, our new compound is identical in composition.

The object of these experiments being only to obtain a further confirmation of the new formula of mesitilole, I have not studied the salts of this acid any further. I may mention, however, that it forms a crystallizable silver salt, which is likewise extremely soluble in water, and readily blackens when exposed to the light.

The formula :

which I propose for mesitilol, and which receives further confirmation in the study of *nitromesidine*, a beautiful alkaloid, discovered by Mr. Maule, removes this compound, to a certain extent, from the position originally assigned to it by Kane. We can no longer consider it as the representative of olefiant gas in the mesityl-series, it would much rather correspond to those liquid hydrocarbons which we invariably meet with in the dehydration of both vinic and amylic

alcohols, and which, up to the present moment, have not been sufficiently investigated, scarcely anything beyond their isomerism with olefiant gas being established.

I cannot omit here pointing out, that in mesitilole we have another instance of the remarkable tendency, exhibited in certain molecular systems, of uniting three atoms of an inferior order into one compound atom of a higher position. Similar examples we possess in the interesting transition of cyanic acid into cyanuric, in the solidification of chloride of cyanogen gas, and in the transformation of cyanide of ethyl into kyanethine. The natural product, too, which we should expect from the dehydration of acetone, is a substance of the formula :

and it is not improbable that this compound is actually formed at a certain stage of the process ; under the influence, however, of the powerful agent in the presence of which it is generated, we find it rapidly converted into a compound, containing the triple number of equivalents.

Finally, the correction of the formula for mesitilole affords a striking illustration of the valuable assistance which chemical studies are likely to derive from a more minute investigation of boiling temperatures.

The following table exhibits a synopsis of the mesitilole series :

Mesitilole	C_{18}	H_{12}
Trichloromesitilole	C_{18}	$\left\{ \begin{array}{c} \text{H}_9 \\ \text{Cl}_3 \end{array} \right\}$
Tribromomesitilole	C_{18}	$\left\{ \begin{array}{c} \text{H}_9 \\ \text{Br}_3 \end{array} \right\}$
Nitromesitilole	C_{18}	$\left\{ \begin{array}{c} \text{H}_{11} \\ \text{NO}_4 \end{array} \right\}$
Dinitromesitilole	C_{18}	$\left\{ \begin{array}{c} \text{H}_{10} \\ 2\text{NO}_4 \end{array} \right\}$
Trinitromesitilole	C_{18}	$\left\{ \begin{array}{c} \text{H}_9 \\ 3\text{NO}_4 \end{array} \right\}$
Mesitilosulphuric acid . . .	H SO_4	$\text{C}_{18} \left\{ \begin{array}{c} \text{H}_{11} \\ \text{SO}_2 \end{array} \right\}$
Nitromesidine	C_{18}	$\left\{ \begin{array}{c} \text{H}_{10} \\ \text{NO}_4 \\ \text{NH}_2 \end{array} \right\}$