[Contributions from the Laboratory of the London Institution]

XLIV.—*The Relation between the Products of gradual Oxidation and the Molecular Constitution of the Bodies Oxidised.*

By ERNEST THEOPHRON CHAPMAN and WILLIAM THORP.

WE believe it will be generally allowed that the greatest problem now occupying the attention of chemists is that of isomerism. There are two methods by which this problem may be attacked. We may either synthetically form the isomeric compounds and compare them, or we may decompose the already formed isomeric compounds into their proximate constituents. The first method requires assistance from the second, because, as isomeric bodies frequently have almost identical physical properties, a difficulty may arise in determining whether such bodies are not really identical, and not only isomeric. All tests, such as the boiling-point, fusing-point, &c., are liable to be rendered fallacious by the presence of traces of foreign matter. We therefore require a method by which we may determine what are the proximate constituents of isomeric bodies. We believe that gradual oxidation fulfils this requirement. But before adopting this method, it is requisite to examine its action on bodies, the molecular grouping of which is well understood, and also on those products which may be termed proximate oxidation-products, more particularly the acids of the acetic series. We have made such an examination, and though at present it has been confined to substances connected with the vinic series, it has led us to the conclusion that, by the gradual oxidation of complex organic molecules, simpler groups are produced; that these simpler groups represent the radicles entering into the composition of the substances oxidized; and, finally, that these representative groups themselves can only with great difficulty be further oxidized.

1. All bodies derived from the vinic series, that we have yet oxidized, have yielded acids of the acetic series, and in some instances carbonic acid. The first step, therefore, in this investigation is to examine the action of oxidizing agents on this class of

acids. With this object, three solutions were prepared, containing respectively 3, 5, and 8 per cent. of bi-chromate of potash. They were prepared by dissolving the requisite quantity of bichromate of potash in water, and adding sufficient sulphuric acid to combine with the potash as bi-sulphate, and with the chromium as sulphate of sesquioxide. To these solutions small quantities of pure acetic acid were added, the mixtures sealed up in digestion-tubes, and heated for twelve hours in the water-bath. On examining the tubes, the 3 and 5 per cent. solutions had not sensibly altered their colour, the 8 per cent. had slightly changed, but no gas was evolved on opening any of them. All three tubes were sealed up again and heated as before for 24 hours, along with a similar tube containing the 8 per cent. mixture without acetic acid; at the end of this period the contents of the tubes had slightly altered in colour, though not perceptibly more so than the tube containing no acetic acid; still little or no gas was evolved. All four tubes were now heated for four hours to 130° C.; on opening, gas escaped from all four, though only in minute quantities from the 3 and 5 per cent. tubes; both the 8 per cent. tubes yielded rather more. The gas from the 8 per cent. tube containing acetic acid was tested for carbonic acid, of which it contained a small quantity. The contents of all three tubes were now distilled, the distillates boiled with excess of carbonate of baryta, filtered, evaporated on the water-bath, and the percentages of barium determined. The results were as follows:—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
(1) 0·4366	0·3978	53·57	53·726	Acetic acid
(2) 0·2984	0·2720	53·60	"	" "
(3) 0·3308	0·3015	53·59	"	" "
(4) 0·4082	0·3718	53·55	"	" "
(5) 0·3464	0·3154	53·54	"	" "
(6) 0·4688	0·4272	53·58	"	" "

Numbers 1 and 2 are from the 3 per cent. tube.

" 3 " 4 " 5 "

" 5 " 6 " 8 "

From the foregoing determinations it is evident that acetic acid withstands the action of this oxidizing agent very perfectly.

2. Propionic acid was the next member of this series experimented upon. It was prepared from cyanide of ethyl. It was heated with the 5 per cent. mixture for 24 hours at 100° C. The contents of the tube were diluted and distilled—diluted because the boiling-point of the mixture is considerably above that of water; therefore had this been omitted, the experiment would not have been a fair one. The distillate (free from sulphuric acid) was neutralised with standard solution of potash, enough sulphuric acid added to combine with two-thirds of the potash, the mixture distilled, the distillate converted into a baryta-salt, and the percentage of barium determined.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
0·4032	0·3306	48·22	48·41	Propionic acid
0·4648	0·3815	48·27	"	" "

This fraction of the propionic acid was, therefore, unaltered.

Now if any acetic acid whatsoever were produced, it would remain in combination with the potash in the retort; excess of sulphuric acid was, therefore, added to the contents of the retort and those contents distilled; the distillate, as before, was converted into a baryta-salt, and the percentage of barium determined.

Substance taken.	Ba ₂ SO ₄	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds
0·3975	0·3266	48·33	48·41	Propionic acid
0·3624	0·2976	48·28	"	" "

These numbers prove the absence of acetic acid. There can, therefore, be no doubt that propionic acid also will endure long-continued digestion with dilute chromic acid at 100° C.; at a higher temperature, however, propionic acid is easily decomposed by oxidizing agents. Four hours' digestion with an 8 per cent. solution of chromic acid at 130° C. is sufficient to cause a large evolution of carbonic acid.*

* In the oxidation of his ketone from carbonic oxide and sodium-ethyl, Wanklyn

3. Valerianic acid was next subjected to the action of oxidizing agents. Like the preceding acid it withstands their action at the temperature of boiling water, but at 130°C . is pretty rapidly decomposed. As in the case of acetic acid, three simultaneous experiments were made with 3, 5, and 8 per cent. solutions, the digestion being continued for twelve hours in the water-bath. The 3 and 5 per cent. tubes yielded no gas on opening, the 8 per cent. gave forth a little. The contents of all three tubes were diluted and distilled, and the distillates from the 3 and 5 per cent. tubes were at once converted into baryta-salts. The distillate from the 8 per cent. tube was neutralised with standard solution of caustic potash, and divided into three fractions by the addition of the necessary quantity of sulphuric acid, and by distillation. The first and third fractions were converted into baryta-salts. The following table contains the percentages of barium* in these salts, and also in the salts from the 3 and 5 per cent. tubes:—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which it corresponds.
From 3 per cent. tube				
0·3608	0·2457	40·05	40·413	Valerianic acid
0·4114	0·2808	40·13	"	" "
From 5 per cent. tube				
0·2998	0·2044	40·09	"	" "
0·3670	0·2504	40·11	"	" "
8 per cent. tube 1st frac.				
0·3938	0·2694	40·21	"	" "
0·3078	0·2102	40·16	"	" "
0·4054 3rd frac.	0·2773	40·22	"	" "
0·3726	0·2548	40·21	"	" "

From this table it appears that the above treatment had not affected valerianic acid.†

heated this substance, which yields acetic acid and propionic acid, for many hours in a digestion tube, together with excess of bichromate of potash and dilute sulphuric acid. No carbonic acid was formed, thereby proving that in this experiment neither acid had undergone decomposition.—(Chem. Soc. J., August, 1866, page 326 of this volume.)

* In this table the barium was determined as sulphate by precipitation.

† One sample of this acid was found to decompose on treatment like that described in the text; it decomposed readily, and produced butyric and carbonic acids. The acid which split up in this way was furnished by one of the London druggists, but we could not learn its history; it could not have been a primary acid.

4. Lastly, caproic acid was submitted to the action of oxidizing agents. Two samples of this acid were employed, the one obtained from cyanide of amyl, the other from a ketone obtained by the distillation of ricinolate of potash; this ketone, when oxidized, yields caproic and carbonic acids. Both these samples were exposed to the action of 5 per cent. chromic acid solution for twelve hours, at the temperature of the water-bath; neither underwent any perceptible change, though in both instances the bichromate was slightly discoloured. Both samples were separated by distillation from the chromic acid and converted into baryta-salts. Determinations 1 and 2, in the following table, are from the caproic acid prepared from cyanide of amyl; 3 and 4 from the other sample.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
(1) 0·4444	0·2824	37·37	37·33	Caproic acid
(2) 0·3886	0·2472	37·48	"	" "
(3) 0·4306	0·2728	37·25	"	" "
(4) 0·3946	0·2497	37·21	"	" "

It is perhaps worth while to remark that, in converting the higher acids into baryta-salts, hydrate of baryta is preferable to the carbonate.

The action of dilute permanganic acid was then investigated. This substance, when dilute, has little or no action on acetic and propionic acids, even when boiled with them. In its concentrated state, however, it decomposes them pretty rapidly. But as it was not our intention to work with this substance, we did not further investigate its action on the acids of the acetic series.

We think we are justified by the above experiments in our statement that, under ordinary circumstances, and at the temperature of the water-bath, these acids are not attacked by dilute chromic acid.

We will now mention a few exceptional circumstances which have great effect on the rapidity of the action of chromic acid. The following circumstances promote the action :—

1st. Presence of large excess of concentrated sulphuric acid.

2nd. Presence of free chromic acid, *i.e.*, chromic acid that has been actually separated from potash.

3rd. Presence of a very small quantity of binocide of manganese.

In the first case it is to be observed that acetic and propionic acids are not affected by the excess of sulphuric acid, unless this be so great as to develop heat on mixing with water. We are unable to account for the more violent action in the second and third cases.

On the other hand, if we substitute phosphoric for sulphuric acid, we obtain an oxidizing mixture which appears to be absolutely without action upon the acids of this series, though it is quite capable of oxidizing alcohol, &c.

Having now proved that, if the acids of this series be once formed by oxidation they are not destroyed by excess of the oxidizing agent, we are in a position to observe the effects of this oxidation on a series of compounds, the molecular constitution of which is well understood. The substances selected for this series of experiments were the following:—

1. Ethyl-alcohol	7. Nitrite of amyl	13. Ethylamine
2. Amyl-alcohol	8. Nitrate of ethyl	14. Propylamine
3. Acetate of ethyl	9. Nitrate of methyl	15. Amylamine
4. Acetate of methyl	10. Iodide of ethyl	16. Ethyl-amyl-
5. Acetate of amyl	11. Iodide of amyl	amine
6. Valerianate of amyl	12. Iodide of isopropyl	

We will call the products obtained by carrying this oxidation as far as we can without endangering the acids produced, *proximate* oxidation-products; and those obtained either by limiting the period of action or employing an insufficient quantity of the oxidising agent, *mediate* products.

1. *Ethyl-alcohol*.—In the first place it was necessary to obtain chemically pure alcohol. The test employed to determine its purity was to oxidize a portion of it with excess of chromic acid, distil off the acids formed, *nearly* neutralize the distillate with potash and distil again, carrying the distillation to dryness. As all the acids of the acetic series, at any rate all the lower members of that series, are expelled from their compounds by acetic acid, it follows that, had any homologues of alcohol been present, they would, by their oxidation, have furnished acids differing from acetic acid in their saturating capacity, and that these acids would

all accumulate in the small fraction described above. When, therefore, a sample of alcohol, yielded nothing but acetic acid by this treatment, it was obviously free from homologues; and as it had previously been digested with caustic potash, it must also have been free from compound ethers. It was oxidized with chromic acid in insufficient quantity to produce the proximate products of oxidation; aldehyde and acetic acid were obtained, and also a neutral liquid not completely miscible with water, and smelling of acetic ether. It was digested with potash, excess of sulphuric acid added, and the acid thus liberated distilled off: it proved to be pure acetic acid. Another portion of the alcohol was heated with excess of chromic acid in a sealed tube for about three hours; the contents of the tube were distilled, and the distillate examined by Liebig's method for fractionating acids. We could detect no product excepting acetic acid.

2. *Amyl-alcohol*.—A portion of this alcohol was digested with 5 per cent. solution of chromic acid for one hour; the contents of the tube were distilled; and the distillate saturated with sulphate of soda, whereby the oily layer on its surface was greatly augmented; this oily layer was decanted, distilled, and treated with solution of carbonate of soda, whereby a portion was dissolved. The remainder (supposed to be a compound ether) was decanted and digested with alcoholic solution of potash. It was then treated with excess of sulphuric acid and distilled. The solution in carbonate of soda was treated in the same manner. The original distillate, which had been saturated with sulphate of soda, was re-distilled; all three distillates gave an acid reaction, and smelt and tasted of valerianic acid. They were converted into baryta-salts; the percentages of barium obtained from them are tabulated below. Another sample of the amyl-alcohol was digested for six or seven hours with 5 per cent. chromic acid solution; no gas was evolved. The contents of the tube were diluted and distilled; the distillate, which was totally soluble in alkalis, divided into three fractions by Liebig's method, and the first and third fractions converted into baryta-salts; the percentages of barium obtained from these salts will be found on the next page.

As will be seen, the whole of the above percentages correspond to valerianic acid.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
(1) Free acid— 0 5732	0 3960	40 27	40 413	Valerianic acid
(2) Free acid remaining in distillate— 0 4362	0 2991	40 32	"	" "
(3) Acid from ether— 0 3774 0 3814	0 2588 0 2620	40 32 40 38	" "	" " "
(4) First fraction— 0 2998 0 3228	0 2053 0 2215	40 27 40 35	" "	" " "
(5) Second fraction— 0 3436	0 2353	40 27	"	" "

The first oxidation of both the foregoing alcohols produced a complicated result. In both the corresponding aldehyde was no doubt formed, in both we had a compound ether formed, and in both we had the acids formed. As will be seen below, we have proved that these two compound ethers—acetate of ethyl and valerianate of amyl—yield, the one nothing but acetic acid, the other nothing but valerianic acid, when oxidized. Therefore, the apparent complication of the products has in reality no effect on the ultimate result.

3. *Acetate of Ethyl*.—This compound was oxidised both with chromic and permanganic acids; by the former at the boiling-point of water, by the latter both in the cold and at the boiling-point. The products of all three operations were separately distilled, and each of the three converted into baryta-salts; the percentages of barium obtained from these salts will be found in the annexed table, all corresponding to acetic acid.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
Chromic acid— 0 4264 0 3712	0 3885 0 3384	53 64 53 67	53 726 "	Acetic acid " "
Permanganic acid, hot— 0 4212	0 3846	53 70	"	" "
Permanganic acid, cold— 0 3455	0 3153	53 66	"	" "

4. *Acetate of Methyl*.—This compound was oxidised with chromic acid; it yielded acetic and carbonic acids. Formic acid also was tested for and found, though the greater proportion of this acid had evidently split up into carbonic acid and water.

5. *Acetate of Amyl*.—This compound is not very easy to oxidize, requiring several hours' heating in the water-bath, with five per cent. chromic acid solution. If it be imperfectly oxidized, valerianic aldehyde is apparently formed. If, however, the oxidation be carried far enough, acetic and valerianic acids only are produced. This was proved by diluting the contents of the digestion tube, distilling, dividing the distillate into three fractions by Liebig's method, converting the first and last fractions into baryta-salts, and determining the percentages of barium. They corresponded, the first to valerianate, the second to acetate, as will be seen in the next table :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction —				
0.4416	0.3029	40.33	40.413	Valerianic acid
0.4764	0.3258	40.21	"	" "
Third fraction —				
0.4145	0.3768	53.46	53.726	Acetic acid
0.3624	0.3297	53.40	"	" "

6. *Valerianate of Amyl*.—This substance is even more difficult to oxidize than the corresponding acetate. It will not bear a temperature much higher than 100° C., nor the action of a very concentrated solution of chromic acid. However, by using a great excess of dilute chromic acid, the oxidation was effected pretty easily. On distillation and fractionation of the distillate by Liebig's method, it became evident that we were dealing with valerianic acid. The first and last fractions were converted into baryta-salts and the percentages of barium obtained, which we give in the annexed table :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·4286 0·3578	0·2938 0·2454	40·30 40·33	40·413 "	Valerianic acid " "
Third fraction— 0·3582	0·2454	40·28	"	" "

These numbers all correspond to valerianic acid.

7. *Nitrite of Amyl*.—This substance, as elsewhere shown,* yields, by oxidation, nitric and valerianic acids, and, if the oxidation be incomplete, valerianate of amyl.

8. *Nitrate of Ethyl*.—By oxidation this compound yields nitric and acetic acids.

9. *Nitrate of Methyl*.—From this substance we obtain nitric and carbonic acids by oxidation.

10. *Iodide of Ethyl*.—This compound oxidizes without difficulty. Iodine is liberated in abundance during the digestion. The contents of the digestion-tube were diluted and distilled, the distillate treated with mercury to remove the iodine, redistilled, and divided into three fractions. The first and last fractions were converted into baryta-salts, and the percentages of barium in the annexed statement obtained from them:—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·3989	0·3637	53·61	53·726	Acetic acid
Third fraction— 0·3838	0·3500	53·62	"	" "

Both corresponding to acetic acid.

11. *Iodide of Amyl*.—This compound is somewhat difficult to oxidize; nevertheless, by treatment similar to that described in the last paragraph, it was made to yield an acid. This acid, when

* Journal of the Chem. Soc. August, 1866.

freed from iodine, was found to be pure valerianic acid. This was proved by dividing it into three fractions, and converting the first and third into baryta-salts; from these salts the annexed numbers were obtained :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·4226	0·2899	40·34	40·413	Valerianic acid
0·4074	0·2796	40·36	„	„ „
Third fraction— 0·2788	0·1918	40·45	„	„ „

12. *Iodide of Isopropyl*.—This substance yielded much gas during its oxidation, which proved to be carbonic acid. The contents of the digestion-tube were treated as in the case of iodide of ethyl, the first and last fractions so obtained were converted into baryta-salts, and, as will be seen from the annexed barium determinations, were nothing but pure acetic acid :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·3570	0·3249	53·51	53·726	Acetic acid
Third fraction— 0·3672	0·3349	53·63	„	„ „

13. *Ethylamine*.—It has already been proved that this compound yields, by oxidation, acetic acid.*

14. *Propylamine*.—We know that isopropyl compounds do not yield propionic acid by oxidation, also that it is possible to prepare a propyl compound, viz., propylamine. Now it is probable that we shall ultimately succeed in converting the alcoholic ammonias into the corresponding alcohols, and thus effect the ascent of the alcohol series. This being the case, it was obviously most important to determine whether the propylamine obtained from

* Wanklyn and Chapman, Chem. Soc. J., August, 1866.

cyanide of ethyl was a primary or a secondary compound. If the method of investigation, above described, be of any value, it would decide this question at once. We have, therefore, oxidized propylamine. The experiment was carried on in a digestion-tube, with three per cent. chromic acid solution, at a temperature of 100°C . When the digestion was complete, the tube was opened, the escaping gas being collected over mercury. Not the slightest absorption occurred on the introduction of potash into this gas, thus proving the absence of carbonic acid. The contents of the digestion-tube were diluted, and the acid formed was distilled off. It was converted into a baryta-salt; the following table contains the percentages obtained from it, all corresponding to propionate:—

Substance taken.	Ba_2SO_4 found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
0·5072	0·4166	48·29	48·41	Propionic acid
0·3238	0·2656	48·23		

15. *Amylamine*.—The oxidation of this substance requires care; it is not very easily or rather not very rapidly effected. We found that the quickest way to oxidize it, was to treat it with concentrated chromic acid, but at a temperature not higher than 70° or 80°C . After half an hour of this treatment, the fluid was diluted and the digestion continued at the temperature of the water-bath. The first treatment with concentrated acid appears to start the reaction, after which the dilute acid easily completes it. Much time is saved by this method of treatment, both in this and the following case. The acid formed was distilled off and converted into a baryta-salt, which yielded the following numbers, corresponding to valerianate:—

Substance taken.	Ba_2SO_4 found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
0·4056	0·2784	40·35	40·413	Valerianic acid
0·2662	0·1824	40·29		

16. *Ethyl-amylamine*.—This compound is more rapidly attacked, though it takes a long time to complete the re-action. The products of the digestion were diluted, distilled, and fractionated, and the first and last fractions converted into baryta-salts, from which the following percentages were obtained. They correspond to valerianic and acetic acids :—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·3824 0·3266	0 2619 0 2240	40·29 40·32	40·413 „	Valerianic acid
Last fraction— 0·4338	0·3945	53·47	53·726	Acetic acid

Observations.—The whole of the foregoing oxidations were conducted in sealed digestion-tubes, and in no instance was the temperature employed higher than that of boiling water, generally from 10° to 20° below it. With the exception of the last two oxidations, the chromic acid employed was in no instance stronger than 8 per cent., and generally less than 5 per cent. Nearly all these experiments have been repeated twice, and some of them three times. The greatest possible care was taken to obtain pure substances. The four compound ethers—acetate of ethyl, acetate of methyl, acetate of amyl, and valerianate of amyl—were all titrated, *i.e.*, the percentage of acid which they yielded to caustic potash determined, which, it is obvious, is a complete guarantee of their purity. The acetate of amyl, and valerianate of amyl, were obtained by acting with iodide of amyl on acetate and valerianate of potash. The object in adopting this method of preparation was to eliminate any possible action of sulphuric acid on the molecular arrangement of the alcohol in question.

The fractionations were performed in the following manner:—The contents of the digestion tube having been diluted and distilled, the distillate was tested for sulphuric acid, which was invariably found to be absent when the distillation had been carefully conducted. It was then neutralized with standard solution of caustic potash, and sufficient standard sulphuric acid added to

combine with a third of the potash employed, thereby liberating an equivalent third of the acids operated upon. The liberated acid was then distilled off, a sample of it converted into a baryta-salt, and the percentage of barium in this salt determined. If it corresponded to any one of the acids of the acetic series, we proceeded no further with this fraction. If it did not, but differed considerably from any known member of the series, the process was repeated. This was, however, hardly ever requisite, as, from the nature of the substances operated on, we never had occasion to separate any acids excepting acetic and valerianic acids, and in that case the valerianic acid generally distils over in the first fraction in a state of perfect purity. A second third of sulphuric acid was now added to the original distillate, and the acid thereby liberated distilled off. Excess of acid was employed to obtain the third fraction, and this third fraction treated in precisely the same manner as the first. If the percentages obtained from the first and third fractions corresponded, it was obvious that we were dealing with a single acid, and therefore it was unnecessary to examine the second fraction. If, however, they differed, the second fraction was always examined, though we have not thought it necessary to give the details of these examinations.

The barium was, unless otherwise stated, determined as sulphate by heating the dry salt with concentrated sulphuric acid. This method is exceedingly rapid, and perhaps the most accurate known.

The annexed table will show precisely the nature of the results obtained in the foregoing portion of this paper:—

Table showing the proximate oxidation products of the following substances.

Alcohols.

Compound Ethers.

Iodides of Alcohol-radicles. *Ammonia-bases.*

The first application made by us of the knowledge acquired by the foregoing experiments was the oxidation of certain of the olefines, an account of which was read at the Nottingham meeting of the British Association.

Ethylene.—This substance is not easy to oxidise by the action of dilute chromic acid, but it yields without difficulty to hot concentrated solutions. The results are carbonic acid and water. We could not detect formic acid.

Amylene.—This substance was digested for many hours with a moderately concentrated solution of chromic acid. When the amylene had disappeared, the contents of the tube were diluted, distilled, and fractionated, the first and last fraction converted into baryta salts, from which the following percentages were obtained:—

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·4826 0·3014	0·4318 0·2720	52·61 52·67	53·726 "	Acetic acid " "
Third fraction— 0·6089	0·5566	53·75		

These numbers show that the substance in hand is acetic acid.

The determinations in fraction 1 are slightly too low. This is due, without question, to a trace of impurity in the substance employed. Carbonic acid was evolved in abundance during the oxidation. In an experiment made to determine the amount of acid produced from amylene by oxidation, 4 grm. of amylene yielded 6·12 of acetic acid, or 153 per cent. If 1 eq. of amylene

yields 2 eqs. of acetic acid, the percentage should have been 171·4. It yielded, therefore, 89·3 per cent. of the theoretical quantity. Now, as the tube had been opened to allow of the escape of carbonic acid, and as, therefore, some amylene was without doubt lost, this is quite sufficiently near to prove our point, viz., that 2 eqs. of acetic acid are formed.

The above work was repeated under circumstances the most varied as to concentration of chromic acid, &c., but always with the same result. Acid solution of permanganate produced the same result, no matter whether used cold or hot. The decomposition of amylene, therefore, by nascent oxygen, is as follows:—

β-Hexylene.—Four grammes of this substance were digested with moderately dilute solution of chromic acid in the water-bath. The tube was cooled, and opened to allow the escape of gas (carbonic acid) twice. When the digestion was completed, the contents of the tube were diluted and distilled. The distillate was free from sulphuric acid. It was neutralised with standard solution of potash, of which it required a quantity corresponding to 3·16 grammes of potassium. Had it yielded 2 eqs. of acid, it would have required 3·815. It, therefore, yielded 82 per cent. of the required quantity, which, considering the loss which must have occurred when the tube was opened, is a sufficiently close approximation.

The acids combined with the potash were now submitted to fractionation, the fractions converted into baryta-salts, and the percentage of barium determined:—

Substance taken.	Ba.S ₂ O ₄ found.	Per cent. Ba found.	The retical per cent.	Acid to which this corresponds.
First fraction— 0·3140 0·3336	0·2577 0·2734	48·26 48·19	48·41	Propionic acid
Second fraction— 0·3745	0·3144	49·36	intermediate	
Third fraction— 0·4555 0·4998	0·4159 0·4569	53·68 53·75	53·726	Acetic acid

From fraction 1 we learn the presence of propionic acid, fraction 3 proves the presence of acetic acid, and fraction 2 proves that no other acids were present.

β -Hexylene, like amylene, was oxidized in a variety of ways, and always with the same result; we therefore conclude that it is decomposed by nascent oxygen, thus—

A few weeks prior to the publication of the above results, but unknown to us, M. Truchot published a paper on the oxidation of the olefines. His results differ remarkably from ours, but we believe we can explain the cause of the difference. M. Truchot states that amylene yields acids of the acetic series when oxidized with permanganate of potash, but that butyric, propionic, acetic, and formic acids are all formed. Now it is obvious that if this were really the case, gradual oxidation would be valueless as a method of research, for no possible information could be derived as to the molecular constitution of a body if molecules of every degree of complexity were formed by such oxidation. We have repeated the experiments of M. Truchot, and can to a certain extent verify his results; *i.e.*, if we oxidize amylene with *permanganate of potash*, we find that we can isolate acids, the salts of which contain a smaller proportion of base than corresponds to acetate. This, however, occurs only when the oxidizing agent is alkaline, and we find that even when it does occur, these higher acids may be made to split up by the action of oxidizing agents into acetic and carbonic acids. We conclude, therefore, that M. Truchot has insufficiently oxidized this olefine. It is, however, possible, and indeed probable, that he may have operated upon a mixture of isomeric olefines, in which case the complicated result obtained would be fully accounted for.

The following table shows the results of the oxidation of the olefines:—

These results induce us to propose the following graphic formulæ:—

Ethylene C_2H_4 . Amylene C_5H_{10} . β -Hexylene C_6H_{12} .

Whether these formulæ be correct or not is a question for the answering of which there are no data extant. There is, however, nothing inherently improbable in them, they represent the grouping indicated by the oxidation-products, and this consideration will, we trust, derive greater weight from the foregoing work.

We would draw attention to the relation subsisting between the oxidation-products of these two olefines and those of the secondary

alcohols obtained from them. The one, amylene, yields a secondary alcohol, the oxidation-products of which are, according to Wurtz,* identical with those of the olefine itself. He obtains, as the oxidation-products of amylene, acetone and acetic acid; that is to say, he obtains acetic acid and a substance which, by further oxidation, yields acetic and carbonic acids; and, moreover, he observes that it is somewhat difficult to obtain the acetone, thus confirming our statement. From the oxidation of the corresponding alcohol he obtained the same products, and, in addition, a small quantity of a substance having the composition of butylic alcohol. The method of its formation is not very clear. The assumption that oxidation has simply removed CH_2 , and left the substance from which this molecule has been subtracted still in the form of an alcohol, appears to us untenable. It seems to us possible that the substance in question may have been a mixture, perhaps of unaltered secondary amyl-alcohol and acetone. This view derives some probability from the fact that it is rather difficult completely to remove acetone from amyl-alcohol by the action of bisulphites. We have made such a mixture, and find that, even after 24 hours' standing, separation is not complete. We desire further to point out that this butyl-alcohol, if, as assumed by Dr. Debus, it be a secondary alcohol, would yield acids of a lower carbon condensation than itself to the action of oxidizing agents.

The alcohol obtained from β -hexylene does not yield the same oxidation-products as β -hexylene itself. This may possibly arise from the fact that the alcohol is not obtained from the olefine in the same manner as in the case of amylene. If this be the true reason, we should obtain a different alcohol by using oxide of silver to convert the iodide of β -hexyl into the alcohol.

In a former part of this paper we remarked that we had met with a sample of valerianic acid which did not resist the action of oxidizing agents. It split up and yielded carbonic and butyric acids. In a similar way there exists an amyl-alcohol which does not yield valerianic acid when oxidized; at least, so we infer from the following observations.

It has long been known that amyl-alcohol is not always found to boil at 132° . In fact, one variety of it boils at 128° . When we were searching for a pure sample of amyl-alcohol to be employed in the foregoing experiments, we received a sample from a distillery

* Ann. Ch. Pharm., Oct., 1864, p. 134.

in which rice was employed, though mixed with other grain, or, at any rate, spirit from other ~~grain~~ ~~was~~ mixed with rice-spirit before rectification.* After the fusel-oil had been put through all the ordinary purifying processes, such as washing, drying, digestion with potash, and repeated fractionation, it was found impossible to get it to boil at a constant temperature. In fact, it began to boil between 127° and 128° , the thermometer going up gradually and evenly to about 131° . With so small a difference between the boiling-points, it was obviously useless to attempt anything like a complete separation of the two liquids composing this mixture. Still, by repeated fractionation, especially as we had large quantities of the substance at command, we might accumulate a larger proportion of the substances of lower boiling-point in one fraction than existed in the original mixture. After many distillations a fraction was obtained which, though its boiling-point still rose to 131° towards the close of the distillation, passed over, for the most part, at a lower temperature. On the other hand, another fraction was obtained, the boiling-points of which were from 128° to 132° , the greater proportion of the liquid passing over near the latter. The former of these fractions we will designate fraction A, the latter fraction B. Two combustions were made of fraction A. Both yielded numbers corresponding to amyl-alcohol:—

	Substance taken	CO ₂	H ₂ O
I.	0.2248	0.5604	0.2742
II.	0.2646	0.6589	0.3176.

From these numbers we deduce the percentages:—

	I.	II.	Theory
C.	67.97	67.91	68.18
H	13.55	13.33	13.63

The combustions were made with oxide of copper, chlorate of potash being employed at the close of the operation. Fraction A was then oxidized with chromic acid, in the manner so frequently before described, and the products of the operation fractionated. Carbonic acid was liberated during the oxidation.

* We state the above facts on the authority of the distiller, from whom we received this sample of fusel-oil.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Theoretical per cent.	Acid to which this corresponds.
First fraction— 0·3748 0·4164	0·2800 0·3107	43·92 43·87	44·052	Butyric acid
Last fraction— 0·3768 0·4002	0·2583 0·2757	40·34 40·51	40·413	Valerianic acid

These acids are somewhat difficult to separate, requiring several repetitions of the fractionating process before the separation can be looked upon as complete. Carbonic, butyric, and valerianic acids appear, therefore, to be the products of the oxidation of this mixture. If the substance of lower boiling-point be really a secondary alcohol, yielding carbonic and butyric acids as its oxidation-products, we ought to have equivalent quantities of these substances produced. To determine this point, 1·2128 grm. of fraction A were introduced, in a sealed bulb, into the digestion-tube, which already contained bi-chromate of potash and sulphuric acid; the neck of the tube was drawn out to a long, fine point, and the digestion proceeded with. When it was judged that the digestion was complete, an india-rubber tube was slipped over the point and connected with a Liebig's potash-apparatus containing concentrated sulphuric acid. A second potash-apparatus, charged with potash, which had been weighed, was connected with the first. The point of the digestion-tube was then snipped off, and the carbonic acid escaping through the extremely small aperture, was dried by its passage through the sulphuric acid, and absorbed by the caustic potash. As soon as the passage of gas had completely ceased, the point of the digestion-tube was broken off somewhat lower down, though still within the india-rubber tube, and the contents heated until they boiled. The steam, of course, expelled the whole of the carbonic acid, and, by judiciously cooling the india-rubber tube and, when necessary, the top of the digestion-tube, any dangerously rapid absorption by the sulphuric acid was avoided. The potash-bulbs were then detached and reweighed. Of course their increase of weight gave a most accurate measure of the amount of carbonic acid liberated.

A precisely similar experiment was performed with fraction B.

As will be seen from the annexed numbers, the amount of carbonic acid differed considerably in the two cases:—

Substance employed.	Carbonic acid found.	Per cent. of carbonic acid.
Fraction A. 1·2128	0·4096	33·77
Fraction B. 1·5728	0·3636	23·09

Samples of each of the alcohols were oxidized as before, the contents of the digestion-tubes diluted and distilled almost to dryness, and samples of each acid distillate converted into baryta-salts. The annexed table exhibits the percentages of barium contained in these salts, and also those which would have been obtained on the assumption that an amount of butyric acid equivalent to the carbonic acid was produced, and that this butyric acid was the representative of the secondary alcohol contained in the two fractions. It is further assumed that the primary alcohol produced nothing but valerianic acid.

Substance taken.	Ba ₂ SO ₄ found.	Per cent. Ba found.	Calculated per centage.
Fraction A.			Fraction A.
0·4092	0·2975	42·75	42·801
0·3834	0·2784	42·69	
Fraction B.			Fraction B.
0·3192	0·2286	42·11	42·016
0·4203	0·3002	41·97	

Finally, a portion of the valerianic acid obtained by the oxidation of one of these samples of alcohol, was digested with dilute chromic acid (five per cent). No carbonic acid was liberated, thereby proving that the butyric and carbonic acids did not owe their existence to the decomposition of the valerianic acid.

We think that we have thus fairly proved the existence of a second isomeric, amyl-alcohol in the sample we were operating upon, though we were unable to isolate it.

We will now consider what information the method of research,

by gradual oxidation, is capable of affording us with regard to the molecular constitution of bodies. This question is best answered by considering how many isomers it is capable of revealing to us in any one case. Take for instance amyl-alcohol. We know that there are many possible isomers of this body, but gradual oxidation, or at least oxidation carried far enough to produce those substances which we have agreed to term proximate products of oxidation, could only reveal to us the existence of a portion of them; for it is obvious that we may have a pseudo-primary amyl-alcohol, *i.e.*, an alcohol containing a pseudo-amyl, say for instance propyl-ethyl; and we may have a secondary amyl-alcohol containing propyl and ethyl. Both these compounds would, we believe, yield the same proximate oxidation products, though doubtless the former would, in the first instance, yield pseudo-valerianic acid. This would at once distinguish it from the real primary alcohol, but would not distinguish it from the secondary alcohol, which would yield the same oxidation-products. Still, though the so-called proximate products of oxidation would not furnish us with information on this point, the *mediate* products taken in conjunction with the proximate products would.

We have not in the foregoing paper considered the case of bodies in which the ratio of carbon to hydrogen is such as to render it impossible to account for the whole of the carbon in the form of acids of the acetic series. It is obvious that such bodies must either yield substances of an altogether different class, or the carbon must be converted into carbonic acid.