XII.—*On the Oxidation of the Essential Oils.* Part II.

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IN the first part of this communication, which was brought before the Chemical Society in the early part of last year (*Journ. Chem. Soc.*, June, 1874), I described experiments which tended to show that the active agent engendered by atmospheric oxidation of oil of turpentine was not ozone, as commonly supposed and stated, or peroxide of hydrogen, but a synthetically produced compound of oxygen with the hydrocarbon.

Among the most striking experiments then detailed was that indicating the action of zinc chloride upon this body *contained in the oil*, at a temperature of 75° to 80° C., that is, at a temperature at which both ozone and peroxide of hydrogen are tolerably stable. In considering the conclusions which follow from the experiments now to be described, it is necessary to bear this in mind, as also the fact that water refuses to extract the active agent from the oxidised oil; and perhaps in the first place I may be allowed to remark briefly upon the difficulties that surround this study. This compound forms but a small fraction of the oxidised oil, and is moreover what may be called a neutral body, that is, it refuses all attempts at combination or crystallisation, and being soluble in the oil, it defies, with our existing knowledge, all attempts at isolation from the complex mixture produced by oxidising oil of turpentine. I trust that these considerations will serve as an apology for any incompleteness in the results of my endeavours to discover the nature of the body under discussion.

It was left undecided in my first communication whether water was a necessary attendant on the oxidation of turpentine to form this particular body. This question was answered by the following experiments:—

Three tubes were taken, A, B, and C, and in each 5 c.c. of oil of turpentine were placed.

To A was also added an equal volume of water, and the tube was then exhausted by an air-pump and sealed hermetically.

B was not exhausted, but only sealed, and therefore contained, besides the oil, about 20 c.c. of air.

C was simply exhausted as it was, and sealed.

After exposing these tubes to sunshine during 21 days, the ends were cut off and the contents examined by the potassium-iodide-starch test.

A and C gave no reaction for two hours, whereas B gave a deep blue coloration in a few minutes.

This experiment therefore teaches that the active agent is built up of the elements of turpentine and oxygen without the aid of water.

I next endeavoured to ascertain whether the amount of active agent produced is constant in relation to a given absorption of oxygen. Berthelot had found that one atom of oil of turpentine determined the absorption of 4.7 atoms of oxygen, using indigo solution as an index.

In two experiments which I made under parallel conditions, viz., the exposure of 10 c.c. of oil of turpentine to oxygen, standing over water on the roof of the house during summer weather, there was an absorption which averaged 28 c.c. of oxygen daily. In the one case 408 c.c. oxygen was absorbed and in the other 402 c.c.; moreover, there was some residual gas (not hydrogen, but probably carbonic acid), which refused absorption, and amounted in each case to 9 c.c. Further, in each case the oil had diminished in volume by .5 c.c. It is to be remarked that when the experiments were brought to a conclusion, the absorption of oxygen was as vigorous as ever, that is, the experiments were not allowed to proceed to the maximum result. It was not feasible to carry out the original intention of estimating the amount of active agent formed, for several reasons, primarily on account of the fact that the water over which the tubes stood contained peroxide of hydrogen (a product, as will be shown hereafter, of the decomposition of the organic peroxide produced) and that in a great state of dilution.

Assuming the original specific gravity of the oil to have been .864, then the .5 c.c. of oil, by which it had diminished in volume during the experiment, would weigh .4320 gram, and this was related to .5748 gram oxygen (equal 402 c.c. normal). According to this, 1 atom, $C_{10}H_{16}$, was related to 11 atoms of oxygen in round numbers. But this calculation has but a preliminary value, for it assumes that all the products of oxidation were in the water. Moreover, turpentine camphor, and ordinary monohydrated protoxide of turpentine were doubtless formed and dissolved, whilst in another direction acetic, formic, and carbonic acids formed, together with, as I have found, *camphoric acid*, a new oxidation product.

Berthelot's result is, as we shall see hereafter, of considerable value, especially inasmuch as it relates to the *active oxygen*, and that only.

An experiment was made at this stage as to the absorption of oxygen

by artificially prepared cymene, in order to ascertain if cymene formed this active agent by these means. I did not know at this time that the product of the distillation of ordinary camphor with zinc chloride was so impure a product as has been demonstrated, and therefore I cannot say in what degree the result is related to true cymene.

About 50 c.c. of cymene was obtained as stated and re-distilled twice over fresh chloride of zinc, by which a colourless product was obtained. In this state it gave no reaction with potassium iodide and starch, but 7 c.c. exposed in a graduated tube to oxygen over water for 18 days absorbed 52 c.c. oxygen, and meanwhile became yellow, as it was before re-distillation. During this time the oil had diminished by 1 c.c., and on testing developed blue coloration with potassium iodide and starch, which required a quantity of $\text{Na}_2\text{S}_2\text{O}_3$ solution equal 0.00489 iodine.

I have not had an opportunity of repeating this experiment with pure cymene, or of following up the questions which it raises, viz., the possible transformation of cymene into terpene by fixation of water and oxygen, and ultimate abstraction of the oxygen by means of deoxidising agents.

It will be well now if I point out in a few words the views which my more recent experiments have developed, so that that which follows may be appreciated as described.

In my first communication I expressed a notion that the active body in question was constituted on the type of a hydrated oxide, $\text{C}_{10}\text{H}_{16}\text{O} \cdot \text{H}_2\text{O}$, because it was a body already known, and I further showed how this body might lose H_2O_2 and become ordinary turpene, or how it might lose water and become terpene oxide. But since then, as indeed was to be anticipated, I have had to modify these views, and to this extent, that I regard the active agent produced in the atmospheric oxidation of turpentine as an organic peroxide of a bibasic acid, corresponding with those organic peroxides (of benzoyl and acetyl of the monobasic acids) discovered by Brodie. This organic peroxide, I believe to be Brodie's camphoric peroxide, having the composition $\text{C}_{10}\text{H}_{14}\text{O}_4$ and to be an unstable body, decomposable by water with production of peroxide of hydrogen and camphoric acid, as expressed by the equation—

Here I may point out that the relative quantitative determination of camphoric acid and peroxide of hydrogen in the product of decomposition would possibly support this expression; but as it was late in my experiments ere camphoric acid was identified, peroxide of hydrogen has alone been quantitatively determined. I give here, moreover, the formulæ for benzoic and acetic peroxides, in order to show the parallelism between these bodies—

derived from camphoric anhydride, $\text{C}_{10}\text{H}_{14}\text{O}_3$.

If this be so, the oxidation of oil of turpentine in this direction might be represented by—

and the absorption of the whole molecule of ozone by—

Here, therefore, 1 atom of $\text{C}_{10}\text{H}_{16}$ would determine the absorption of 5 atoms of oxygen, and Berthelot, as already pointed out, experimentally found it as 4.7 atoms oxygen.

Of course I cannot as yet distinctly assert the identity of the peroxidised body with camphoric peroxide; but inasmuch as it has an existence, and inasmuch also as I have discovered products of the possible reaction of water on this peroxide, the above remarks are, I submit, justifiable. Moreover, I have experiments in hand in which, imitating the procedure of Brodie, I intend if possible to ascertain more fully the action of barium peroxide upon camphoric anhydride, &c.

From what has gone before, the experiments now to follow will be intelligible, but before rendering them I will call attention to Brodie's experiments, reacting upon camphoric anhydride with barium peroxide and water, whereby an alkaline strongly oxidising solution is obtained, which appears to contain the barium salt of camphoric peroxide, $\text{C}_{10}\text{H}_{14}\text{Ba}''\text{O}_5$. Brodie states that the product does not yield H_2O_2 with acids, or BaO_2 with alkalis, and is therefore probably a product of direct union and not a camphorate of BaO_2 , represented by the formula $\left. \begin{array}{l} \text{C}_{10}\text{H}_{12}\text{O}_4 \\ \text{BaO}_2 \end{array} \right\}$.

To take oxalic acid as a starting point of comparison we have, as Brodie has shown, carbonic acid, which may be regarded as its peroxide, and its unknown anhydride would be represented by C_2O_3 . Thus—

There are two ready methods of obtaining this oxidised oil and the aqueous solution containing peroxide of hydrogen and camphoric acid. In my experiments I have employed both. The first, which is very suc-

cessful only in summer weather, consists in exposing equal volumes of oil of turpentine and water to the open air in shallow glass vessels loosely covered. In this way I have prepared several gallons of solution. After some weeks the oil has attained such a specific gravity that it sinks through the water as a viscid coloured mass.

The other method consists in placing in a series of flasks equal volumes of the oil and water and connecting them together, and the whole series with an aspirator. In this way they are heated on a sand-bath to about 30° — 50° and a current of air passed rapidly through. This operation is continued for any time, but I have always stopped at that stage when the oil fell through the water.

As already indicated, water is not a necessary adjunct; but in studying the products of the supposed reaction of water on camphoric peroxide it is advantageous, inasmuch as an aqueous solution is thus ready to hand containing them. Otherwise oil may be oxidised by itself, and then examined and extracted as will be shown.

Examination of the Oxidised Oil of Turpentine.

The oil oxidised as directed may be expected to contain much resinised oil, turpentine camphor, &c., and the excess of organic peroxide not as yet decomposed by the water. It has a strong half camphreous, half peppermint-like odour, and is of the specific gravity of water, or even greater. In all my attempts to obtain from it this peroxidised constituent I have failed, although every conceivable method has been employed; but the active agent contained in it may be estimated by heating a given volume with excess of potassium iodide and starch, and determining the iodine liberated by means of standard solution of sodium hyposulphite. The reaction, as with peroxide of hydrogen, takes a considerable time to complete, and in fact it is not improbable that, in the way already shown, it first of all decomposes into camphoric acid and peroxide of hydrogen, which decomposition is accelerated by the presence of potassium iodide. A determination was made of the active agent contained in oil which had been *oxidised in presence of water*, with the aid of heat as described.

10 c.c. treated with potassium iodide and starch in the usual manner, developed iodine sufficient to require at first .7 c.c. $\text{Na}_2\text{S}_2\text{O}_3$, but from time to time the colour returned, until 6.4 c.c. were consumed, equal to .078336 gram iodine, corresponding to .0104 gram H_2O_2 (by reaction, $\text{H}_2\text{O}_2 + \text{I}_2 = 2\text{HI} + \text{O}_2$), equal to .0605 gram $\text{C}_{10}\text{H}_{14}\text{O}_4$ (by reaction $\text{C}_{10}\text{H}_{14}\text{O}_4 + 2\text{H}_2\text{O} = \text{C}_{10}\text{H}_{16}\text{O}_4 + \text{H}_2\text{O}_2$); or, in other words, in 100 c.c. of the oil there would exist .605 gram of the body assumed to have the composition $\text{C}_{10}\text{H}_{14}\text{O}_4$.

In another case where oil was oxidised by the sunshine method in the absence of any added water, 100 c.c. gave iodine equal to 92 c.c. $\text{Na}_2\text{S}_2\text{O}_3$,

equal to 1·12608 iodine, equal to ·1507 gram H_2O_2 , equal to ·8776 gram of peroxidised body.

A portion of this same oxidised oil, of 100 c.c., was extracted by 500 c.c. water in two successive quantities of 250 c.c., and in portions of the residual oil and aqueous extract, the matter capable of liberating iodine was estimated.

Residual oil gave iodine equal to	47·5 c.c. $\text{Na}_2\text{S}_2\text{O}_3$
Aqueous extract „ „	45·0 c.c. „
Total	<hr/> 92·5 c.c. „

This result agrees with the above determination, and shows that in this extraction water had decomposed nearly one half of the peroxide, and necessarily formed an equivalent amount of H_2O_2 . This action of water probably accounts for the statements of Schönbein and others, to the effect that oxidised oil contains *two* modifications of oxygen, viz., ozone and antozone; the ozone would correspond with the peroxidised radical, and the antozone with the peroxide of hydrogen. It also embraces Berthelot's view that the active oxygen is in a state of combination similar to that of the transferable oxygen of peroxide of nitrogen.

The total acid and organic matter contained in the aqueous extract of oxidised oil were also estimated, the former by titration with standard alkali, and the latter by evaporation to dryness on water-bath in weighed vessel.

It contained acid which, calculated entirely as acetic, equalled ·300 gram, and gave an oily coloured mass on evaporation as above, equal to 2·395 grams. Therefore the results may be thus stated. The oxidised oil contained—

·8776 gram of the peroxide in 100 c.c.
 ·3000 gram acetic acid (total acid),

and on extracting this with water, such an amount of the peroxide was decomposed as was sufficient to give—

·0737 gram peroxide of hydrogen,
 and acid went into solution = ·3000 gram calculated as acetic acid,
 and 2·395 grams of organic matter.

The following experiment was made with oxidised oil left after the above extraction and determination :—

50 c.c. weighed 50 grams, and these 50 grams were boiled in a flask with a quantity of potassium bichromate and sulphuric acid in combining proportions. An energetic action took place on mixing, and great heat was evolved. After some hours' boiling, the oil became transformed into a viscous floating mass. After 13 hours the viscous

mass had disappeared, and there remained floating on the surface an oily body, which set on cooling into a hard brittle scale, which proved to be terebenzic acid, as shown by its characters. Triturated with water, it left a fawn-coloured mass, pulverulent, and entirely soluble in ammonia, from which hydrochloric acid threw down white flakes, which on isolation fused superficially and dissolved entirely in absolute alcohol, from which solution alcoholic lead acetate threw down a copious precipitate.

From the ammoniacal solution also barium chloride threw down a good precipitate, almost white. These properties precluded terephthalic acid, which was sought for in each stage of oxidation, and would seem to indicate the absence of cymene. On further boiling of this supposed terebenzic acid with fresh potassium dichromate and sulphuric acid, it was entirely split up into ultimate products, including acetic and carbonic acids.

This experiment, though not exactly relevant to the inquiry in hand, was nevertheless made, as it had a bearing on the pre-existence of cymene in oil of turpentine—a pre-existence possibly caused by some such reaction as $C_{10}H_{16} + O = C_{10}H_{14} + H_2O$. Nevertheless I do not draw any conclusions from this one experiment.

By the experiment above described relating to the extraction of the oxidised oil by means of water, much of the peroxide is, as there exhibited, resolved into camphoric acid and peroxide of hydrogen. But the whole of the oxidised oil may be dissolved in alcohol, and then reprecipitated by water, the watery-alcoholic extract decanted, and this process repeated five or six times, and even then the residual oil contains some of the active agent, and so also with boiling water. These are two good methods of obtaining the peroxide of hydrogen from oxidised oil, by proceeding as above, and concentrating the extracts on water-bath, disregarding any oily matter that may separate during such concentration. Above this, these experiments and the peculiar action of chloride of zinc upon oxidised oil, expressed in my first paper, conclusively establish the fact that peroxide of hydrogen is not an immediate product of the oxidation of turpentine, but a result of the action of water upon the peroxidised principle.

Examination of the Aqueous Solution.—When water is used in the oxidation of the oil, there results after a certain lapse of time, a solution, milky from suspension of finely divided oily globules. Filtration through Swedish paper renders it perfectly brilliant, and the filtrate has a peculiar camphreous odour, especially when hot, and consists of a solution of peroxide of hydrogen, acetic, formic, and camphoric acids, besides dissolved turpentine camphor, &c. This solution may be concentrated on a water-bath, if desirable, to a certain extent, but past this point the peroxide of hydrogen decomposes, and oily matter is deposited.

Moreover, like ordinary peroxide of hydrogen, it is decomposed entirely if the solution be agitated with animal charcoal. It gives with potassium iodide and starch a blue coloration, and with potassium iodide alone, iodine is developed.

$$\text{1st. } 2\text{CrO}_3 + 3\text{H}_2\text{O}_2 = \text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{O}_2.$$
$$2\text{CrO}_3 + 6\text{H}_2\text{O}_2 = \text{Cr}_2\text{O}_3 + 6\text{H}_2\text{O} + \text{O}_2$$

After neutralisation with soda or potash, it gives with ferric chloride a deep brown colour, and a bulky gelatinous precipitate like hydrated ferric oxide. This takes place in the cold, but if it be boiled the precipitate increases vastly. The precipitate produced in the cold is a combination of camphoric acid; whilst that formed at higher temperatures is tribasic acetate. With lead acetate in the cold it also gives a slight precipitate, whilst with copper sulphate a deep blue colour, and a light blue coloured bulky precipitate is produced in the cold, of camphorate of copper. On boiling, a further precipitate of tribasic acetate occurs.

Formic acid is present, as shown by the reduction of nitrate of silver, &c.

In one case, .082 gram peroxide of hydrogen in 100 c.c.

In another, .104 gram ,, ,,

In a third,	212 gram	"	"
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In estimating the peroxide, however, by this method, considerable time is consumed, owing to the length of time required for the peroxide to react fully upon the potassium iodide.

A much quicker and more trustworthy method is that of volume, which gives results concordant with those obtained in other methods, as is shown in the following analyses. The solution whose analysis follows was obtained by the sunshine oxidation method.

Determination of Total Solids.—50 c.c. evaporated to dryness on the water-bath left a residue oily in nature, weighing 1.188 grams. This gives 2.376 per cent. (by weight in volume).

Determination of Total Acid.—50 c.c. required 16 c.c. of standard alkali-solution; calculating acid to be entirely acetic: this corresponds with .3840 gram acetic acid in 100 c.c.

Determination of Peroxide of Hydrogen.—(a.) 40 c.c. developed iodine equal to 19.5 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ = to .23868 gram iodine = .03195 gram H_2O_2 or .0799 gram per 100 c.c. This would give by H_2O_2 = $\text{H}_2\text{O} + \text{O}$, 26 c.c. of oxygen (normal).

(b.) To check this last determination, the method of volume was resorted to. 50 c.c. of the solution treated in a measured tube over mercury with excess of acidified potassic permanganate gave an instant evolution of gas equal to 27 c.c. at 17° and 765 bar., equal 25 c.c. normal.

Now, by reaction

only one-half of this oxygen came from the H_2O_2 , viz., 12.5 c.c. = .0357 gram = .0760 gram H_2O_2 per 100 c.c., a result fairly agreeing with that in (a); moreover, this method is very rapid.

In another case, where a solution was obtained by oxidising the oil in presence of water by artificial means, the peroxide of hydrogen was determined by both methods as above.

(a.) 30 c.c. gave iodine equal to 17.5 c.c. $\text{Na}_2\text{I}_2\text{O}_3$ = .2142 iodine.

This equals .0286 gram H_2O_2 equal to .0953 gram per 100 c.c.

(b.) A determination by volume with KMnO_4 gave a closely approximating result.

In what has preceded I have stated that when such an aqueous solution as that under consideration is treated with copper sulphate or ferric chloride, slight precipitates occur in the cold, but that on heating, tribasic precipitates are formed. This was shown by making rough determinations of the metals in the salts obtained.

50 c.c. of an aqueous solution were neutralised by pure potash and treated with excess of copper sulphate, then boiled, and the precipitate was isolated by filtration, washed with boiling water, and dried at

100° C. ·138 gram, when dried, gave on ignition ·0878 gram copper oxide equal to 50·81 per cent. copper. Tribasic copper acetate, $2(\text{Cu} \cdot 2\text{C}_2\text{H}_3\text{O}_2) \cdot 4\text{CuO} \cdot 3\text{H}_2\text{O}$, requires 51·8 per cent. copper. This copper salt readily dissolved in acetic acid. The iron salt on drying lost its bulky nature and became a hard pulverulent powder. When recently precipitated it is dissolved by warm acetic acid. A quantity of it prepared from neutralised aqueous solution and ferric chloride, then washed and dried at 100°, was analysed.

·341 gram gave on strong ignition ·236 gram Fe_2O_3 , equal to 48·44 per cent. iron.

Tribasic ferric acetate, $2(\text{Fe} \cdot 2\text{C}_2\text{H}_3\text{O}_2) \cdot 2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, requires 46·02 per cent. iron.

A lead salt prepared from the neutralised solution and basic lead acetate, proved readily soluble in acetic acid and insoluble in alcohol. Washed and dried at 100°, ·4836 gram gave, on ignition with H_2SO_4 , ·5182 gram $\text{PbSO}_4 = 73\cdot1$ per cent. lead.

Tribasic lead acetate ($\text{Pb} \cdot 2\text{C}_2\text{H}_3\text{O}_2 \cdot 2\text{PbO} \cdot \text{H}_2\text{O}$) requires 78·7 per cent. lead.

I attach, of course, but little value to the analyses of these salts, as we know they must have contained a little camphorate of the metal in each case, and perhaps formate. In fact the analyses were made more as an identification of acetic acid than for any other purpose.

But now I come to the consideration of camphoric acid as a constituent of the solution, and as a product *not hitherto recognised* in this process.

About $1\frac{1}{2}$ litres of a solution obtained by the sunshine-method of oxidation of oil of turpentine was concentrated to about 100 c.c., exactly neutralised with pure soda, and the solution was treated with excess of ferric chloride, agitated, and filtered at once. The precipitate was washed first with cold, and finally with boiling water, and the gelatinous bulky precipitate dried at 100°, when it shrank considerably, and readily admitted of pulverisation. The total quantity so obtained weighed ·6 gram. It was now analysed.

Determination of Iron was made by burning in a weighed platinum crucible, when camphreous vapours were evolved, burning with a white smoky flame. Residue was strongly ignited with the aid of nitric acid, and when cooled weighed.

·3106 gram thus furnished ·0746 gram Fe_2O_3 equal to 24·01 per cent. Fe_2O_3 or 16·806 per cent. iron.

Determination of Carbon and Hydrogen was made with chromate of lead.

·1924 gram gave ·286 gram $\text{CO}_2 = 40\cdot540$ per cent. carbon, and ·116 gram $\text{H}_2\text{O} = 6\cdot756$ per cent. hydrogen.

Thus we have the following percentages :—

Theory.		Per cents.	÷ at wgt.s.	÷ Fe as 1.	÷ O as 7.
38·96	Carbon	= 40·540	3·3783	11·2	10·5
6·49	Hydrogen	= 6·756	6·7560	22·5	21·0
18·18	Iron	= 16·806	·300	1	·93
36·36	Oxygen	= 35·898	2·243	7·4	7·00

fairly agreeing with the formula $\text{Fe}''\text{C}_{10}\text{H}_{14}\text{O}_4, 3\text{H}_2\text{O}$.

To confirm the fact of this being camphoric acid, a quantity of iron salt from pure camphoric acid was prepared as above. It gave by analysis numbers approximate to those just given.

·431 gram gave ·100 gram Fe_2O_3 = 16·24 per cent. iron.

·3066 gram gave ·454 gram CO_2 = 40·639 per cent. carbon.

and ·1774 gram H_2O = 6·425 per cent. hydrogen.

Thus we have—

	Per cents.	÷ at wgt.s.	÷ Fe = 1.	O = 7.
Carbon	= 40·639	3·3866	11·5	10·3
Hydrogen	= 6·425	6·4250	21·9	19·6
Iron	= 16·240	·293	1·0	·9
Oxygen	= 36·696	2·293	7·8	7·0

fairly agreeing with $\text{Fe}''\text{C}_{10}\text{H}_{14}\text{O}_4, 3\text{H}_2\text{O}$.

Camphoric acid is certainly a bibasic acid, but books fail to give any formula for the iron salt prepared from ferric chloride. It would further appear that the iron is rather too low in each case. This is perhaps explained by the reaction $\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_4 + \text{Fe}_2\text{Cl}_6 = \text{Fe}''\text{C}_{10}\text{H}_{14}\text{O}_4 + \text{FeCl}_2 + 2\text{NaCl} + 2\text{HCl}$. The HCl would take a little iron out, and this is supported by the weight of iron salt obtained from 1 gram of $\text{C}_{10}\text{H}_{16}\text{O}_4$, viz., only ·80 gram. Theory equals 1·5 grams. But there can be no reasonable doubt that the two acids are identical, and seeing that one was known to be pure camphoric acid, it necessarily follows that the other is also.

Thus far to recapitulate, I have shown that, in the oxidation by air of oil of turpentine, there is produced a small but definite amount of what is probably an organic peroxide of formula $\text{C}_{10}\text{H}_{14}\text{O}_4$, together with other bodies; and that on heating this product with water, peroxide of hydrogen and camphoric acid pass into solution, whereas it is certain that the active agent in the original oil is *not* peroxide of hydrogen. Therefore it is highly probable that these bodies result from such a reaction as I have already expressed, viz.:

In conclusion, I may be allowed to make a few remarks on a few other points of interest in regard to oil of turpentine. In a note

which I published about two years ago (*Chem. News*, xxv, 632), I described a few quantitative experiments in regard to the oxidation of cuprous oxide in the presence of alkalis, and I considered it of some interest to substitute for the alkali oil of turpentine; but I obtained negative results, that is, it was found that in presence of the oil, in a current of air, cuprous oxide does not oxidise, neither does cupric oxide become cuprous oxide.

It was left undecided in my first communication, whether the reduction of mercuric to mercurous oxide, which is effected by oil of turpentine, was to be attributed to the active agent or not. Since then I have made many experiments in this direction. The reaction, which requires time in the cold, proceeds very rapidly at higher temperatures, the whole of the mercuric oxide becoming perfectly black. On isolation and after washing with alcohol and ether, it again becomes red oxide on heating, thus verifying the reduction. But my endeavours to estimate this reduction were failures, on account of the difficulty encountered by the fact that with the suboxide there is also a little organic matter which refuses to be washed out by alcohol or ether. So that when the matter is gently heated in a U-tube in a current of carbonic acid a slight deflagration takes place, and any calculation made for the amount of mercury obtained from a given weight of the black powder is rendered abortive by the presence of this matter. But I succeeded in ascertaining that the reduction takes place readily in tubes containing pure oil of turpentine, and exhausted by the air-pump when heated to about 70°, so that it may be stated that the possible reaction expressed in my first communication is not the cause of the reduction of mercuric oxide to the suboxide.

Finally, it becomes me to express my deep sense of gratitude to Dr. J. L. W. Thudichum for having allowed me to conduct many of these experiments in his laboratory.