

XIX. *On the mutual action of sulphuric acid and alcohol, and on the nature of the process by which ether is formed.* By HENRY HENNELL, Esq. Communicated by WILLIAM THOMAS BRANDE, Esq. F.R.S.

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1. I WAS some time since engaged in an investigation of the nature of oil of wine and of the salts called sulphovicates: the results I obtained were considered of sufficient importance to be honoured with a place in the Philosophical Transactions*. The oil of wine and sulphovinic acid are substances produced during the mutual action of sulphuric acid and alcohol in the well-known process adopted for the preparation of ether; and an important point with me, during the above investigations and since that time, has been to develop the particular changes which take place when ether is formed from sulphuric acid and alcohol. I perceive by the Annales de Chimie for November last, that MM. DUMAS and BOULLAY have been engaged on the same subject, and have experimented on and considered, not only the formation of ether, but also the nature of sulphovicates, and, as they supposed, though incorrectly, of oil of wine†. That our results with regard to sulphovicates and oil of wine differ, may be seen from the published accounts; and there is not less difference between their conclusions with regard to etherification, and the results I have obtained, which I have now to describe.

2. When alcohol and sulphuric acid in equal weights are put together without the application of any heat beyond that generated during the mixture, the most abundant and important product is sulphovinic acid, above one half of the sulphuric acid being converted into that peculiar acid by union with hydro-carbon‡. But when such a mixture containing so large a proportion

* Phil. Trans. 1826. Part 3rd.

† The substance which these gentlemen operated upon appears, from their own account of its preparation, to have been the hydro-carbon separable from oil of wine by the action of alkalies, and not that peculiar substance which has hitherto been called oil of wine.

‡ The sulphuric acid loses half its saturating power by the union, and all the salts formed by the new acid are soluble.

of sulphovinic acid is distilled, the most important product is a new substance, namely ether, and the sulphovinic acid disappears. The questions which then arose were, whether the ether was formed altogether from the direct action of the remaining alcohol and sulphuric acid in the mixture, or whether the sulphovinic acid might not also assist, or whether it might not be an essential state of the elements intermediate between the mixture of the acid and alcohol and the development of the perfectly formed ether. MM. DUMAS and BOULLAY, who have considered the same questions, or at least some of them,—decide, that the portions of materials which form ether, are altogether independent of those which produce sulphovinic acid: but the following facts prove in my opinion the contrary of this conclusion.

3. A portion of oil of vitriol was selected for some comparative experiments, and also some alcohol of specific gravity 0.820: five hundred grains of the oil of vitriol precipitated by acetate of lead, gave 1500 grains of sulphate of lead.

4. Five hundred grains of the oil of vitriol were mixed with five hundred grains of the alcohol, and after forty-eight hours, diluted and precipitated by acetate of lead; only 616 grains of sulphate of lead were produced; so that very nearly three-fifths of the sulphuric acid had become sulphovinic acid by the effect of mixture, and little more than two-fifths remained to act as sulphuric acid upon the remaining alcohol, full two-thirds of the quantity employed.

5. Another mixture of acid and alcohol in the same proportions, and made at the same time as the above, was then distilled until 117 grains had passed over, consisting of water, alcohol, and a portion of ether. The residue in the retort had not undergone any charring effect; and being diluted, was precipitated by the acetate of lead: the quantity of sulphate of lead obtained, amounted to 804 grains, indicating an increase in the quantity of sulphuric acid equivalent to 188 grains of sulphate of lead.

6. A similar mixture of alcohol and sulphuric acid, made at the time and in the same proportions as the two former, was then distilled until two hundred grains had been received, the greater part of which was ether; the uncharred residual matter in the retort being then diluted, was precipitated by acetate of lead as before; 986 grains of sulphate of lead were obtained. This contained

nearly two-thirds of the sulphuric acid first added, and the increase by distillation had been much more than one-half of that which existed before the application of heat: so that during the distillation, and simultaneously with the formation of ether, a quantity of sulphovinic acid had been re-converted into sulphuric acid, and the latter appeared to increase in quantity in proportion to the increase of ether in the distilled products.

7. A similar mixture of alcohol and acid, made at the same time and in the same proportions as the three former, was then distilled until two hundred grains had passed over. Two hundred grains of water were added to the contents of the retort; 160 grains were distilled off; a second addition of two hundred grains of water was made, and the distillation continued: a further addition of five hundred grains of water was made, and the operation continued until as much product had been separated as equalled the water added;—the object was to separate all the ether and alcohol possible, for the purpose of ascertaining to what extent the conversion of sulphovinic acid into sulphuric could be carried. No smell of sulphurous acid was produced during the operation, nor did any charring of the contents of the retort occur; when precipitated by acetate of lead, 1480 grains of sulphate of lead were obtained. This is very little short of the 1500 given by the acid when unacted upon by alcohol, and shows that nearly the whole of the sulphovinic acid had been changed back into the state of sulphuric acid; and is completely at variance with the opinion, that when sulphuric acid and alcohol act upon each other, hypo-sulphuric acid is formed.

8. From these experiments it appeared probable that the ether was the product of the decomposition of the sulphovinic acid: but a mixture of equal weights of alcohol and sulphuric acid contains, besides the sulphovinic acid, a considerable quantity of unaltered acid and alcohol; for in such a mixture three-fifths (4) of the sulphuric acid would be converted into sulphovinic acid by combination with the hydro-carbon of less than one-third of the alcohol employed. I next proceeded to ascertain, whether, when no alcohol was present, ether would be produced. A quantity of the sulphovinate of potash was therefore prepared. The composition of this salt has been given in the paper in the Philosophical Transactions before referred to, and one hundred parts contain 28.84 of potash. Five hundred grains were mixed with 150 grains of sulphuric

acid, being nearly the equivalent of the potash in the salt, and then heat applied. The experiment therefore may be considered as the distillation of sulphovinic acid mixed with sulphate of potash, which it may be presumed remained inert during the process, and also with the water of the acid and of the salt. The proportion of water, it is found, has an important influence; but in the present experiment about a drachm of fluid distilled over, and left a blackened and acid salt in the retort, having the smell of sulphurous acid. A few grains of carbonate of potash being added to the distilled product, abstracted a little water: the clear decanted liquor was then mixed with a little dry muriate of lime, and by agitation separated into two portions; the upper one being decanted, amounted to nearly half a drachm, and was found to be pure ether. This result proves that ether may be formed from a sulphovinate or sulphovinic acid when no alcohol is present.

9. An experiment similar to the last in the nature and proportions of the substances used, was made, except that the sulphovinate was dissolved in its own weight of water previous to the addition of the sulphuric acid. The experiment is one therefore of the distillation of dilute sulphovinous acid, in place of that which is concentrated. The distilled product had no smell of ether, nor could any be discovered in it. About nine fluid drachms were obtained; to these, carbonate of potash was added, which separated the water, and left three drachms of a supernatant liquid, appearing by taste, smell and flame, to be alcohol: this was decanted, and poured upon muriate of lime; no ether separated, but the whole formed one solution; being distilled from the muriate it was evidently alcohol; and being mixed with its weight of sulphuric acid, gave sulphuric ether or sulphovinic acid again.

In this experiment there was no charring of the contents of the retort; and by precipitation by acetate of lead, the whole of the sulphuric acid was obtained;—not only the portion added to decompose the salt, but the double portion evolved from the sulphovinic acid upon the separation and re-arrangement of the hydrocarbon.

10. In the former paper it was shown that oil of wine when heated in water is resolved into hydrocarbon and sulphovinic acid: an experiment was therefore made upon it. Two hundred grains of oil of wine were placed in a retort, a little water added, and heat applied: about a drachm was received, which being

redistilled from carbonate of potash the product appeared to be principally alcohol, but the presence of ether was very evident.—This experiment proves the formation of ether from sulphovinic acid when no sulphuric acid was present as such at the commencement of the distillation.

With regard to the questions at the commencement of this paper, it appears to me from the facts detailed, that in the usual process for obtaining ether, the ether is not formed altogether from the direct action of the alcohol and sulphuric acid considered independently of the sulphovinic acid present; for the quantity of free sulphuric acid is small compared to the quantity of alcohol present, two-fifths only of the acid remaining, while of the alcohol more than two-thirds remain; and further, sulphovinic acid alone is readily converted into ether and sulphuric acid, (see 8.) and during the distillation of ether in the ordinary way the sulphovinic acid is always re-converted more or less completely into sulphuric acid (4. 5. 6.) it probably therefore assists much in the process. With regard to the third question, the opinion may be supported that the formation of sulphovinic acid is a necessary and intermediate step to the production of ether from alcohol and sulphuric acid; and although I do not mean to assert this view, yet it deserves a few remarks.

In no manner which has yet been devised can ether be formed from alcohol and sulphuric acid without the presence of sulphovinic acid. Whenever ether has been formed, sulphovinic acid has been present; whenever the sulphuric acid is diluted so far as not to form sulphovinic acid with alcohol, it also refuses to form ether with alcohol. Sulphovinic acid will produce ether without the assistance of alcohol. And although the ether produced when a mixture of equal weights of alcohol and sulphuric acid are distilled, appears to be in greater quantity than can arise from the decomposition of the sulphovinic acid existing in the mixture previous to the action of heat, it is not I think inconsistent to suppose, that at the same time that one portion of sulphovinic acid is resolved into sulphuric acid and ether, another may be formed from alcohol and sulphuric acid; and that sulphovinic acid is formed in a mixture of sulphuric acid and alcohol by heat, is proved by the following experiment. Five hundred grains of oil of vitriol were diluted by five hundred grains of water; when cold, to the dilute acid was added two thousand grains of alcohol, specific gravity 0.820. The following day this mixture was examined for sul-

phovinic acid, but none had been formed: it was placed in a retort, and a quantity distilled off nearly equal to the weight of the alcohol employed: this had a specific gravity of 0.842. Carbonate of potash separated a considerable portion of water, the original alcohol would not even moisten that salt; the residue in the retort was examined, and now sulphovinic acid was found; the evidence of which was, carbonate of lead being dissolved in considerable quantity; here sulphovinic acid had been formed by heat, where it did not previously exist. This result appears also opposed to the opinion, that in the formation of ether the sulphuric acid acts simply by abstracting water from the alcohol; for the dilute acid here gave up a portion of its water during the distillation, and separated from the alcohol a portion of hydro-carbon.

It has already been shown (9.) that the production of ether is materially influenced by the quantity of water present, and that the same sulphovinic acid will yield either ether or alcohol, as it is in a concentrated or dilute state. The hydro-carbon which, as was shown in the former paper, has the extraordinary power in oil of wine of neutralizing the whole of the acid properties of sulphuric acid, and in sulphovinic acid of neutralizing the half of them, being in the latter body in so peculiar a condition that it will unite either with that proportion of water necessary to form ether, or with the larger proportion requisite to form alcohol, according to circumstances.

In the experiments (8. 9.), in the production by distillation of ether or alcohol from sulphovinic acid more or less diluted, it appeared that sulphovinic acid might easily have its proximate elements separated and restored to their original state of sulphuric acid and alcohol. The following experiment was made with a view to illustrate this point. Five hundred grains of acid and five hundred grains of alcohol were mixed as before, and left for several days: by previous experiment it is known that more than half the sulphuric acid in this way becomes sulphovinic acid (4). By distillation and dilution at proper periods this would have given ether and alcohol, and nearly the whole of the sulphuric acid (7.): but instead of doing this, it was mixed with one thousand grains of water, and then distilled until 1400 grains had passed over. No charring or decomposition of the sulphuric acid took place; no ether was formed; but nearly the whole of the original alcohol and sulphuric acid were recovered. It may be a question whether the production of alcohol and ether

in those and similar experiments is altogether determined by the proportion of water present, or whether the difference of temperature consequent upon its variation may not have an effect.

When ether and sulphuric acid are heated together, oil of wine and sulphovinic acid are amongst the products obtained; and as this sulphovinic acid is readily converted when diluted into alcohol and sulphuric acid, so it affords a method of converting ether into alcohol: thus ether may be formed from alcohol, and alcohol from ether at pleasure, by throwing the hydro-carbon of these bodies into that peculiar state which it assumes when combined with sulphuric acid in sulphovinic acid. We may even proceed beyond this, and form either alcohol or ether, using olefiant gas as the hydro-carbon base: for I have shown in my last paper, that olefiant gas by combining with sulphuric acid, forms sulphovinic acid, and the acid so produced forms either ether or alcohol, according to circumstances which are under perfect command.

It can hardly be necessary to refer to the extraordinary remark at the end of MM. DUMAS and BOULLAY'S second paper, except to state that it is singularly at variance with the facts and opinions given throughout the former part of that and the preceding paper by the same authors. Those persons who read both papers, and also those of Mr. FARADAY and myself, which were published long before the appearance of the former, will be able to decide without further comment from whom the particular views contained in those papers first emanated.

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