

XXII.—*On Etherification.*

BY ALEXANDER W. WILLIAMSON, Ph.D., F.C.S.

PROFESSOR OF PRACTICAL CHEMISTRY IN UNIVERSITY COLLEGE, LONDON.

The question of the transformation of alcohol into ether and water by the agency of sulphuric acid, may be divided into two parts; first, the relative weight of the substances engaged in the reaction; and, secondly, the actual process by which the transformation is effected. In a preceding memoir, read before the British Association last autumn, I briefly described the formation and properties of certain new ethers, which seemed to solve at least the first part of this question, *i. e.* the relative formulæ of alcohol and ether. I now lay before the Society a more exact account of the process by which these bodies were obtained, with their analysis, to which I have to add a direct evidence of the process by which sulphuric acid effects the decomposition of alcohol; and, finally, I will describe a reaction with the acids of the adipic series, in which the formation of a peculiar series of bodies gives evidence that the formulæ of these acids should be halved similarly to those of the alcohols. But first, a few words on the previous views of the subject, as I understand them.

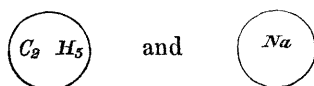
Of the relative formulæ of alcohol and ether, there have been especially two views; one of which represented ether as the compound of olefiant gas with one atom of water, and alcohol as the compound of this same hydrocarbon with twice as much water; the other considered ether as the oxide of a peculiar hydrocarbon C_4H_{10} , and alcohol as the oxide of another hydrocarbon C_2H_6 . The first of these views was derived from a consideration of the analogy of the ethers with the salts of ammonia; the second was formed rather from a comparison with metallic salts. To the French school, with Dumas

at its head, we owe the former, and the great Berzelius suggested and advocated the latter. The study of the transformations of alcohol, and especially that by sulphuric acid, led to the modification of these views, and to the formation of others containing certain points of each; and the most important of these is certainly the theory of Liebig, who, giving the name of ethyl to the hydrocarbon C_4H_{10} , represented ether as its oxide, and alcohol as the hydrate of that oxide. From novel and highly important considerations, Gerhardt arrived at the formulæ of Berzelius, and compared alcohol in its reactions to an acid. The process of etherification, of which the continuous nature had been discovered by Boullay, was, from the different points of view afforded by the above-mentioned formulæ, of course represented differently. Berzelius and the contact-school, seeing in ether a more complex atom than alcohol, and considering the apparently indefinite action of sulphuric acid, were especially struck with the difference between etherification and other cases of chemical action, and supposed some different force must be active in it, which was christened *catalysis*. It was certainly an important step towards the philosophical solution of the question, which Liebig made, in urging the resemblance to chemical action, and explaining more successfully than Hennel had been able to do, the process by chemical affinity, overcome successively by the decomposition of sulphovinic acid by heat. The mutual action of these various theories had exercised a decomposing influence upon them all, and the elegant experiments by which Graham shewed the untenable nature of the chemical theory, afford conclusive evidence of that decomposition. Now I submit that the theory here laid before you, with its experimental conclusions, combines the requisitions of the several parties in this great discussion, and may be considered as closing it amicably, by shewing that each point of view contained part, and an important part, of the facts. The explanation of the process is composed of two parts—first, proving in etherification the occurrence of decompositions strictly analogous to common phenomena usually attributed to chemical affinity, and as explicable by such a name as those phenomena may be; and, secondly, on finding that over and above the commonly observed phenomena of chemical action, there occurs in this process a new circumstance, it will be necessary to prove the occurrence of this circumstance in the more familiar cases.

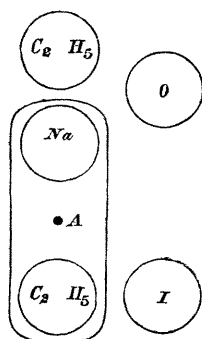
Formation of ether by double decomposition.—In the paper above referred to, I stated the fact of this reaction, which consists in the elimination by metallic sodium of the hydrogen in alcohol, which has to be replaced by ethyle, and the action of the iodide of ethyle

on the compound thus formed, which, from its analogy with the hydrate of potash, I will call *ethylate of potash*.* It is important that the alcohol used in this and all similar reactions be as anhydrous as possible; and the naphtha which surrounds the sodium must be removed completely by drying with bibulous paper and immersion for a few seconds in a small portion of absolute alcohol, which serves successively to rinse all the pieces of metal used in one experiment. The pieces of sodium thus purified are thrown, one at a time, into the alcohol which is to be transformed into ether, until the liquid is completely saturated with them; after cooling, it is treated with iodide of ethyle, and distilled, the ether passing over with alcohol vapour and some of the iodide. To remove these admixtures, the distillate should be treated with sodium, which, as long as alcohol is present in equivalent quantity with the iodide, forms more ether, and when all the iodide has been thus decomposed, forms with the remaining alcohol, ethylate of sodium, from which the ether may be distilled off in a state of perfect purity. Prepared in this manner, ether is identical in its boiling-point and all its properties with that prepared by the action of sulphuric acid.

The reaction is easily understood by the following diagram, in which the atoms



are supposed to be capable of changing places by turning round upon the central point A.



* The atomic weight of hydrogen and the metals, iodine, &c., is in this paper according to Laurent and Gerhardt's notation, assumed at half their equivalents. The compound radicals methyle (CH₃), ethyle (C₂H₅), amyle (C₅H₁₁) are of course reduced to the same unit.

It is clear that we thus get $\text{C}_2\text{H}_5\text{O}$ and NaI . The circles are merely used to separate off the atoms or units of comparison. To express the corresponding decomposition of iodide of ethyle by hydrate of potash, forming alcohol, we should replace the ethyle of the sodium-compound by hydrogen, and the same change of place between sodium and ethyle forms $\text{C}_2\text{H}_5\text{O}$ (alcohol) and NaI .

Three-carbon ether, Ethylate of methyle, or Methylate of ethyle.—This compound may be prepared by the action of iodide of ethyle on the methylate of sodium, CH_3O , or inversely, by acting on ethylate of sodium by iodide of methyle. Of these two processes, I however prefer the former, from the fact of iodide of ethyle boiling at so much higher a temperature than the ether, that any excess of it is easily separated by distillation. This ether is purified in the same manner as the preceding one. On account of its more powerful action, I generally preferred potassium to sodium for the removal of the last traces of alcohol from an ether; and in order that the action of the metal might be complete, the distilling apparatus was so arranged that the distillate constantly flowed down into the retort until the action had completely ceased, and then only was the ether distilled over from the fixed products of that action. The boiling-point of this ether is 11°C ., and it was therefore usually distilled simply by removing from the retort the frigorific mixture by which it was retained in the liquid state. In order to effect its combustion, a small quantity was introduced into a strong bulb at the extremity of a piece of thermometer tubing, about 6 inches long, which had been previously weighed, and which being bent at a right angle, could be fixed by means of a cork into the end of a combustion-tube, open at both ends, and was in the power of the operator.

By this process, the ether being burnt by oxide of copper, the following results were obtained :

0.2215 grm. of liquid gave :
 0.482 „ „ carbonic acid, and
 0.2685 „ „ water.

The percentage composition as deduced from this, is :

	By Experiment.	By Calculation.	Difference.
Carbon	59.39	60.00	0.61 —
Hydrogen	13.46	13.33	0.13 +
Oxygen	27.15	26.67	0.48 +

The density of its vapour was found to be :

By Experiment.	By Calculation.	Difference.
2·158	2·084	·074

Weight of globe and air at 12° C. and 30·05 in. bar.	= 53·6240 grms.
Weight of globe and vapour, the temp. at moment of sealing the point 23°·5 C., and bar. 30·05.	= 54·1790 „
Capacity of globe	= 438 cub. centi.
Residual air at 16° C. and 30·05 bar.	= 23 „

Hence its formula is $\begin{matrix} C_2 & H_5 \\ C & H_3 \end{matrix} O$, or empirically $C_3 H_8 O$.

Now it being thus established beyond doubt that this substance contains 1 volume ethyle, 1 vol. methyle, with 1 vol. oxygen, the three condensed into two volumes, and the two opposite modes of preparing it proving that the two atoms of hydrocarbon are contained in *like* manner in it, we may view it either as the ethylate of methyle, *i. e.* alcohol in which one atom of hydrogen is replaced by methyle, or else as methylate of ethyle. I am, however, convinced that the simplest view that can be formed of its constitution is to be gathered from a comparison with water, from which it may be produced by replacing one atom of hydrogen by ethyle and the other by methyle.

Seven-carbon ether, Amylate of ethyle, or Ethylate of amylo.—This ether is one of the most easily prepared of these peculiar bodies, and is perfectly identical when prepared from amylic alcohol and iodide of ethyle, or ethylic alcohol and iodide of amylo. I have prepared it in considerable quantity by each process, and could discover in no respect any difference of properties between the products; its boiling-point is 112° C. Combustion performed with oxide of copper.

0·2350	gram.	yielded :
0·624	„	of carbonic acid, and
0·276	„	of water ;

or in 100 parts.

	Experiment.	Calculation.	Difference.
Carbon	72·42	72·41	0·01 +
Hydrogen	13·99	13·79	0·20 +
Oxygen	13·59	13·80	0·21 —

Its formula is therefore $\begin{matrix} C_2 & H_5 \\ C_6 & H_{11} \end{matrix} O$, or empirically $C_7 H_{16} O$.

The density of its vapour was found to be :

	By Experiment.	Calculation.	Difference.
	4.042	4.031	0.011
Weight of globe and air at 11° C., bar. at 29.60 in.	= 93.7790 grms.		
Weight of globe and vapour, the temp. at moment of sealing being 135.5° C., and bar. 29.64.	. = 94.6755 „		
Capacity of globe	. = 377 cub. centi.		
Residual air at 25° C., and 29.60 bar.	. = 3 „		
Increased expansion of glass globe at 135° C.	. = 0.92 „		

Six-carbon ether.—Boils at 92° C.; analysis as follows :

0.2050 gm. of liquid gave as the produce of combustion :	
0.528 „ „ carbonic acid, and	
0.256 „ „ water.	

which gives in 100 parts :

	Experiment.	Calculation.	Difference.
Carbon . .	70.244	70.588	0.344—
Hydrogen . .	13.873	13.725	0.148 +
Oxygen . .	15.883	15.686	0.197 +

Hence the formula $C_6H_{14}O$.

The density of its vapour was found to be :

	By Calculation.	By Experiment.
	3.546	3.75
Weight of globe and air, temp. 10° C., bar. 29.72 in.	= 90.689 grms.	
Weight of globe and vapour, temp. at moment of sealing the point 110° C., and bar. 29.72 in.	. = 91.553 „	
Capacity of globe	. = 407 cub. cen.	
Residual air at 19½° C., and 29.93 inches bar.	. = 10.75 „	

A second experiment gave nearly analogous results :

Weight of globe and air, temp. 11.5° C., bar. 30 in.	= 85.0855 grms.	
Weight of globe and vapour, temp. at moment of sealing, 111.5° C., bar. 30 in.	. = 85.8925 „	
Capacity of globe	. = 377 cub. centi.	
Residual air at 22° C., and 30 in. bar.	. = 4.5 „	

Calculated density from this latter experiment = 3.73.

In my former paper, I showed how the formation of these intermediate ethers proves the atomic weight of the alcohols to be half

that which they have of late years been considered, so that their equivalent occupies in the state of vapour the same volume as that of ether, water, &c. It is of course only a *relation* which I here establish, and if any chemists prefer doubling the present formulæ of ether, water, and all the metallic oxides, they will accomplish the same object in an unnecessarily clumsy manner. But the same arguments which require me to halve the atomic weight of alcohol must of course apply to its compounds, and sulphovinic acid, which is nothing else than the sulphate of alcohol, as represented by the formula $\frac{\text{Æ}}{\text{H}} \text{SO}_4$; and the process of etherification is at once explained; for by the reaction of this sulphovinic acid upon alcohol, we have at once ether and sulphuric acid, which again reacts upon the atoms of alcohol, forming with the first, $\frac{\text{Æ}}{\text{H}} \text{SO}_4$ and $\frac{\text{H}}{\text{H}} \text{O}$, and with the second $\frac{\text{Æ}}{\text{Æ}} \text{O}$ and $\frac{\text{H}}{\text{H}} \text{SO}_4$. Thus it is that the sulphovinic acid formed at the end of a long process of etherification is not the same as that which formed at first, but being perfectly like, it cannot of course be distinguished from it. To prove this point, I made sulphuric acid react successively upon two alcohols, so that it took the hydrocarbon from the first, and gave it up to the second, forming an intermediate ether, and finding only the second alcohol to react upon, remained at last combined with its hydrocarbon alone. The experiment was performed in the following manner: Sulphamylic acid was prepared by the action of sulphuric acid upon its equivalent weight of fusel oil, and this compound was treated with vinic alcohol by the continuous process, until the distillate consisted of pure 4-carbon ether. The residue was then examined, and found to contain *no* sulphamylic acid, but only sulphovinic, the 7-carbon ether being easily separated out from the first portions of the volatile product. I next tried the action of sulphuric acid upon a mixture of equivalent weights of the two alcohols, expecting similarly to have the production of the 7-carbon ether, and the result fully justified my expectations; for on treating the mixture by the continuous process, a distillate was obtained consisting of two liquids, water and a light ethereal liquid, which, after two distillations over fused potash, was distilled with the thermometer, and rose from 40° to 180°. A considerable portion was separated by repeated distillation at the temperature of 112° C. I shewed by combustion the exact composition of the 7-carbon ether.

0·25075 grm. of ether yielded :
 0·6665 „ „ carbonic acid, and
 0·3100 „ „ water.

which gives the following percentage :

	Experiment.	Calculation.	Difference.
Carbon	72·46	72·41	0·05 +
Hydrogen	13·73	13·79	0·06 —
Oxygen	13·81	13·80	0·01 +

The last portions of the distillates were added together and re-distilled, their temperature rising rapidly to 176°, where it remained stationary for some time, and the liquid which came over at this temperature shewed the composition of amylic ether. Thus :

0·2045 grm of distillate produced :
 0·5685 „ „ carbonic acid, and
 0·2595 „ „ water.

giving the following percentage composition :

	Experiment.	Calculation.	Difference.
Carbon	75·81	75·95	0·14 —
Hydrogen	14·09	13·92	0·17 +
Oxygen	10·10	10·13	0·03 —

The smell of common ether was very perceptible in the first portions of the mixture which came over. It is thus clear that by the action of sulphuric acid on the mixed alcohols, three ethers are formed by the reaction of sulphovinic and sulphamylic acids on each of the alcohols respectively. On treating in a similar manner a mixture of equivalent parts of methylic and amylic alcohols, a corresponding result was obtained, the products being, however, more easily separated than in the preceding instance, owing to the greater difference of their boiling-points. The experiment was performed in the following manner : 17 oz. of aqueous methylic alcohol was mixed with 38 oz. of fusel oil, which had been ascertained by a previous trial to contain the equivalent quantity of amylic alcohol ; 7 oz. of this mixture were added to 5 oz. of sulphuric acid, and heated to 120°, at which temperature the etherification commenced ; the mixed alcohols were allowed to run into the retort, so as to maintain the level of the liquid in it a little higher than it had been at first, and in this manner the whole of the mixture was converted into a colourless distillate, composed of about one volume of

water to three of the mixed ethers, and possessing a faint smell of sulphurous acid. The theory of the purification of this mixture by distillation over dry hydrate of potash, is easily intelligible from the fact that that substance becomes transformed in contact with alcohol into ethylate of potash, with formation of water; and similarly into amylate of potash by the action of amylic alcohol. Thus it is that the whole of these alcohols are kept back by the potash, and the excess of it even takes up pretty completely the water, so that the mixture of ethers, after this treatment, is scarcely acted on at all by potassium. We have in these reactions the best evidence of the nature of the action of sulphuric acid in forming common ether, or in accelerating the formation of the so-called compound ethers; for acetic ether is formed from acetic acid, just as ethylic ether from alcohol, by the replacement of hydrogen by ethyle. And if the circumstance of containing hydrogen, which is replaceable by other metals or radicals, be the definition of an acid, we must consider alcohol as acting the part of an acid in these reactions. Common ether is its ethyle-salt, the 3-carbon ether is its methyle-salt, and so on, just as the potassium-alcohol or ethylate of potash is its potassium-salt.

But before proceeding further in the investigation of these circumstances, I must beg leave to direct your attention for a moment to the relation between alcohol and acetic acid, and show how the conclusions just arrived at concerning the former will be applicable to the atomic weight of the latter. You are aware that this acid is essentially monobasic in its characters like the other terms of the series to which it belongs, and that, in conjunction with other reasons, this circumstance has been urged by M. Gerhardt as a ground for halving its formula. Now as acetic acid is formed from alcohol by replacing one-third of its hydrogen by oxygen, there are strong grounds for assuming a similar atomic constitution in both, and of writing acetic acid at half its usual atomic weight, in accordance with the reduced formula of alcohol. Viewing, therefore, alcohol as water in which half the hydrogen is replaced by ethyle, $C_2 \frac{H_5}{H} O$, we shall consider acetic acid as containing one equivalent of oxygen in the place of two atoms of hydrogen of that radical, or $C_2 \frac{H_3}{H} O$. Organic chemistry is replete with instances of differences similar to those between alcohol and acetic acid, and produced by the substitution of an electro-negative element for hydrogen; take for example phenylic alcohol, a feeble acid, in which the substitution of hyponitric acid for hydrogen

produces stronger and stronger acids up to carbazotic, a very strong acid; or again, consider the diminution of the alkaline properties of aniline by the substitution of more and more chlorine for its hydrogen, until they entirely disappear in the trichloraniline, as shewn by Dr. Hofmann. Now we actually prepare acetic acid by the action of oxygen upon alcohol under certain circumstances, and observe a double decomposition perfectly analogous to that produced by chlorine in its action on hydrocarbons, water being formed, and the hydrogen thus taken out being replaced by oxygen; but it is clearly not the basic atom of hydrogen in alcohol which is thus replaced, for acetic acid retains it with its characteristic properties heightened. It is, therefore, the hydrogen of the radical which is thus replaced by oxygen, and acetic acid differs from alcohol by containing, instead of ethyle, this other radical, differing from it by having oxygen in lieu of an equivalent of hydrogen, and which may be called *oxygen-ethyle*, or *othyle*. We are thus led to consider the atom of ethyle as containing half the number of atoms which are generally ascribed to it, and as occupying in the state of vapour two volumes and not four. But I endeavoured to obtain an experimental evidence of the correctness of this conclusion, and sought it in the decomposition of the acetates by heat, by which their elements separate into acetone and carbonate. In this decomposition, the process differs according to the two views of the constitution of acetic acid; if the atom of acetate of potash be $C_4 \frac{H_6}{K_2} O_4$, acetone and carbonate are formed by the division of one atom; whereas, if the formula of the acetate be $C_2 \frac{H_3}{K} O_2$, the reaction consists in a double decomposition, by which CH_3 in one atom is replaced by KO , *i. e.* methyl by peroxide of potassium, or $C_2 H_3 O$ replaced by CKO_2 . To ascertain which of these two opposite views is the more correct, I dissolved in water equivalent weights of acetate of soda and valerate of potash, and evaporated rapidly to dryness. The mixed salts were introduced into a retort, and subjected to dry distillation, the oily distillate shaken with aqueous potash, to remove the acids which might have come over undecomposed, and after separation from the potash, distilled with the thermometer. By uniting the products of repeated distillations, a liquid was obtained, boiling with perfect regularity at $120^\circ C.$, and constituting nearly two-thirds of the original distillate. This body was found to possess the composition $C_6 H_{12} O$, as shewn by the following combustion with oxide of copper.

0.704 grm. of carbonic acid and 0.2935 grm. of water were the

results of the decomposition of 0·2690 grm. of the liquid; the percentage relations, as obtained by experiment and calculation, are as follows:

	Experiment.	Calculation.	Difference.
Carbon	71·38	72·00	0·62—
Hydrogen . . .	12·12	12·00	0·12+
Oxygen	16·50	16·00	0·50+

Hence the formula is, $\frac{C}{C_4} \frac{H_3}{H_9} CO$, or empirically, $C_6 H_{12} O$.

The same experiment was performed with various other terms of the series, and similar results obtained, the details of which I will communicate on a future occasion. On distilling equivalent parts of an acetate and formiate, the corresponding reaction would consist in the formation of a body having the composition of aldehyde, which is the hydruret of ethyle, as acetone is its methyle-compound.

The method here employed of stating the rational constitution of bodies by comparison with water, seems to me to be susceptible of great extension; and I have no hesitation in saying that its introduction will be of service in simplifying our ideas, by establishing a uniform standard of comparison by which bodies may be judged of.
