ART. XIX.—*On the Oxidation of Alcohol and Ether by Ozone;* by Prof. A. W. WRIGHT.

IT has been stated by Houzeau,* that alcohol exposed to the action of ozone is instantly oxidized, with the formation of aldehyde, acetic acid, and hydrogen peroxide, and that ether, under similar conditions, undergoes an analogous change, being even more rapidly oxidized, with the production of hydrogen peroxide. It does not appear, however, that either the conditions of the action of ozone on these substances, or the nature of the compounds formed, have been much further studied. With a view to determine some of these points, and especially to ascertain whether ozone could be advantageously used in the production of acetic acid from alcohol, an ex-

* Comptes Rendus, lxxv, p. 142, 1872.

tended series of experiments was made by the writer, the results of some of which are here given.

As ozone is easily resolved into ordinary oxygen by heat, it appeared probable that its action would be intensified by submitting the substances examined to its influence at a somewhat elevated temperature. In the first experiments accordingly, either the alcohol was itself heated, or its vapor was subjected to the action of heat in conjunction with the ozone. In later experiments alcohol at the ordinary temperature was used, both absolute, and mixed with varying quantities of water. The ozone was produced by passing dry oxygen through an ozonizing tube under the influence of electricity. In some of the experiments Houzeau's apparatus for this purpose was employed; in others that described by the writer in a former number of this Journal, used with statical electricity. All the connections of the parts of the apparatus traversed by ozone were made with glass tubes united with perforated corks which had been soaked in melted paraffine. The determinations of the amount of acid were made volumetrically, by means of a solution of caustic potash in distilled water, and the percentages given in the results express the proportion of acid obtained relatively to commercial acetic acid, with which the comparisons were made. As the latter contains about 25 per cent of anhydrous acid, a sufficiently near approximation to the absolute percentage of acetic acid would be obtained by dividing the results by four. In all cases the amounts obtained were very small. Commercial alcohol, which contained about 8·5 per cent of water, was used in the experiments numbered 1 to 5. The volume of liquid used in each case was 100 cubic centimeters.

1. In this experiment vapor of alcohol was passed into a flask kept at 100° C., by means of a water-bath, and ozonized oxygen driven slowly through the same flask. The mixture of gas and vapor was then conducted into another flask immersed in cold water, where the alcohol and products of oxidation were condensed. The operation was continued for one hour. The alcohol at the beginning was found neutral, but at the end of the experiment it gave a decided acid reaction. The percentage relatively to commercial acetic acid, that is, the strength of the dilute acid, as compared with the former, was 1·62 per cent.

2. Ozone and alcohol vapor were passed through a porcelain tube heated to a temperature of 200° or 250° C. Percentage obtained 0·81, of which but a portion was acetic acid, as the reaction was evidently different from that at a lower temperature, and other products were formed.

3. A small quantity of alcohol was placed in a large flask, and ozone passed into it at intervals, the flask being frequently

shaken vigorously. This was continued for ten or twelve hours. The percentage obtained was 3·17, or if reduced to the amount for one hour, about 0·32.

4. Ozone was passed through boiling alcohol, and the vapor condensed in a cool flask. Percentage 1·18.

5. Ozone was passed through boiling alcohol in a flask provided with a vertical condenser, by which the condensed liquid was returned to the flask, and thus repeatedly subjected to the action of the gas. Percentage 1·22.

6. In the following series of experiments alcohol was employed which had been mixed with quick-lime, and after standing several days was then distilled off. It contained less than two per cent of water. Four determinations were made, with alcohol alone, and with alcohol mixed with different proportions of distilled water. The liquid was maintained at the boiling point during the whole operation, a vertical condenser being used, as in the preceding experiment. The results are given in the following tables, in which the first and second columns give the relative amounts of the alcohol and distilled water in the mixtures, the third shows the actual percentage of acid obtained, the fourth the amounts corresponding to equal portions of alcohol, and the fifth those amounts divided by four, giving the approximate absolute percentage.

The numbers are reduced, to correspond to a continuance of each experiment one hour.

Alcohol.	Water.	Percentage in mixture.	Percentage in alcohol.	Percentage absolute.
100	0	0·55	0·55	0·14
50	50	1·66	3·32	0·83
10	9	0·93	9·30	2·32
5	95	1·66	33·20	8·30

7. The experiments in this series were made in the same way as the preceding, except that the alcohol was not heated, and the results are as follows :—

Alcohol.	Water.	Percentage in mixture.	Percentage in alcohol.	Percentage absolute.
100	0	0·59	0·59	0·15
50	50	0·34	0·68	0·17
10	90	0·08	0·80	0·20
5	95	0·09	1·80	0·45

In the determinations it was assumed that the acid obtained was acetic acid. This would be justifiable in all cases except those where the alcohol was highly heated, as, though a small quantity of formic acid is produced, shown by its action on nitrate of silver and otherwise, acetic acid constitutes the chief portion of the product. When a quantity of the liquid was neutralized with the potash solution, evaporated, and the residue treated with dilute sulphuric acid, a strong odor of acetic acid was given off. The products of the experiment in which the alcohol was highly heated were examined in the same way, but the odor was hardly to be recognized as that of acetic acid, having some resemblance to that of formic and butyric compounds.

Although the results are not perfectly concordant, as was to be expected, considering the varying conditions of some of the cases, and the feeble proportion of acid abtained, they agree in the main very well, and show clearly enough that the action of the ozone is influenced very materially by the presence of water, and by heat.

The table in No. 7 shows that as water is added to the alcohol, the total amount of acid produced decreases, but less rapidly than the alcohol, so that with each addition to the percentage of water a larger percentage of alcohol is acidified. Both this and the preceding table show that the increase is more rapid as the proportion of alcohol becomes small.

In No. 6, with the exception of the first case, in which the amount of acid is not greatly different from that of the first in No. 7, the numbers show a large increase in the total amount of acid, and a still greater increase relatively to the proportion of alcohol. This was due in part to the fact that, by the arrangement of the apparatus, the hot vapor was mingled with the ozone, and thus more thoroughly exposed to its action. A comparison of the results in Nos. 1 and 4, however, shows that it is to be attributed chiefly to the higher temperature. It will be seen also that the effect is more strongly marked, the greater the proportion of the water. In the fourth experiment of No. 6, about eight per cent of the alcohol was converted into acetic acid, being the highest proportion obtained.

It would be of interest to determine, if possible, the nature of the reaction by which the alcohol is acidified. As considerable quantities of aldehyde and hydrogen peroxide are always produced, it seems most probable that the action proceeds in the manner commonly assumed, namely, by the abstraction of two hydrogen atoms from the alcohol molecule, forming aldehyde, and hydrogen peroxide, together with water. The aldehyde would, in part, be immediately oxidized by the ozone, and in part by the gradual action of hydrogen peroxide. This

action would be greatly facilitated by heat, which decomposes both ozone and hydrogen peroxide. If the reaction is less simple, and the alcohol molecule is broken up, we might expect to obtain carbon di-oxide as one of the products. A special experiment with alcohol which was not heated, though continued for nearly two hours, showed that, if any, only a very small amount is eliminated.

It may be observed that the proportion of alcohol in the third and fourth cases of Nos. 6 and 7, is not very different from that in the wines and other liquors used in the manufacture of vinegar. Although the application of ozone for this purpose, by the methods followed in these experiments, would be neither practicable nor economical, it is not improbable that operations on a larger scale might give better results. Especially in the German or "quick" vinegar process, where a large surface is exposed, and a considerable rise of temperature is experienced, it is hardly doubtful that the process would be materially accelerated by passing ozonized air through the apparatus, and to accomplish this an ozonizer of moderate capacity would be sufficient.

Experiments similar to those above described were made with ether and ozone. The oxygen employed was dried by passing it through a wash-bottle containing strong sulphuric acid, and thence through a large U-tube filled with small fragments of pumice-stone freshly saturated with the concentrated acid. The oxygen, after passing from this through the ozonizer, was conveyed into a flask containing the ether, and bubbled from the extremity of a glass tube immersed in the liquid. Energetic action at once took place. Each bubble of the gas gave a little cloud as it broke at the surface, and the liquid in a few minutes lost its transparency and became opalescent. This effect was caused by the production of a liquid not miscible with the ether, and dispersed through it in very minute globules. After a time they gradually fell to the bottom of the flask, and coalesced, first into drops, and finally to a thin stratum of liquid.

After the operation had been continued for an hour or more, the heavy liquid was examined, portions of it being removed with a thin glass tube. It was found to be strongly acid, and when tested, by neutralizing it with potash solution, evaporating, and treating with dilute sulphuric acid, gave an unmistakable odor of acetic acid.

Tested with lime-water, and otherwise, the liquid gave evidence of the presence of a considerable proportion of oxalic acid, while its behavior with nitrate of silver and with ferric chloride indicated a small amount of formic acid.

A small quantity of manganese di-oxide was washed with distilled water and placed in a narrow test-tube. When a

little of the liquid was dropped upon this, copious bubbles of gas were given off, doubtless oxygen, though in too small quantity to be tested. With ether (containing no hydrogen peroxide) and chromic acid the liquid produced an intense blue color. It also immediately discharged the color of indigo-solution. These tests indicate the presence of a large percentage of hydrogen peroxide. Aldehyde also appeared to be indicated, though with less certainty than the other substances. The liquid then was apparently water, formed partly by the action of the ozone and partly by the condensation in the cold ether of traces of moisture left in the gas after passing the drying apparatus, and holding in solution the other products of the reaction, namely, hydrogen peroxide, acetic, oxalic, and formic acids, and probably aldehyde.

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