

LXXXVI.—*Note on the Action of Light on Ether.*

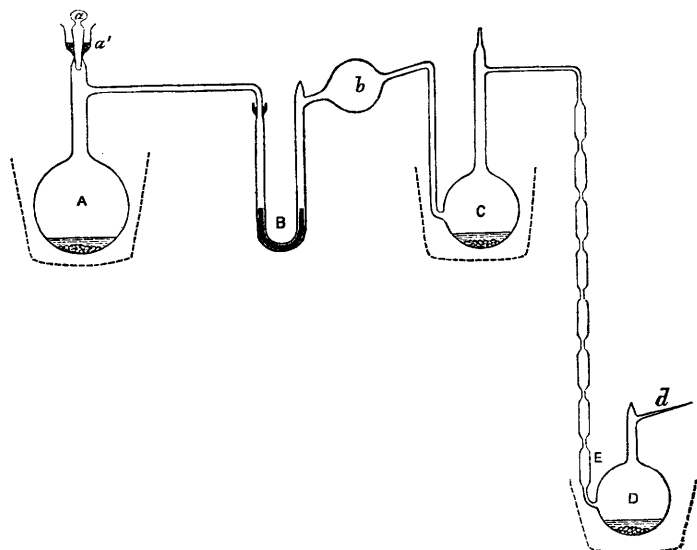
By ARTHUR RICHARDSON, Ph.D, and EMILY C. FORTEY, B.Sc.,  
University College, Bristol.

THE researches already published by one of us (Trans., 1891, **59**, 51) on the formation of hydrogen peroxide in pure ether showed that when the ether was dried by long contact with metallic sodium, it still yielded considerable quantities of hydrogen peroxide when exposed to sunlight, in presence of dry oxygen. Experiments have since been undertaken with still further precautions to remove the last traces of moisture, and the results give a full confirmation of the previous work.

The ether used in this investigation was prepared from pure alcohol and pure sulphuric acid, and, after repeated washing with water to remove traces of alcohol, was shaken with potassium dichromate according to the method of purification described by Dunstan and Dymond (Trans., 1890, **57**, 574). After being dried over phosphorus pentoxide, it was distilled into tubes without contact with the air by means of the following arrangement.

The flask A, fitted with an air-tight stopper, *a*, is connected with the flask C by means of the U-tube B. C is connected with a series of tubes drawn out, as shown in the figure, and terminating in the bulb D. In the first place the ether was distilled into A and allowed to stand over phosphorus pentoxide for two days, the stopper having been inserted and made air-tight by means of mercury in the cup *a'*, and the connection between A and C being cut off by means of a column of mercury in the U-tube. The exit tube at *d* being open, the ether was then distilled over into C, which also contained phosphorus pentoxide, and was kept cool by a freezing mixture, the mercury in the U-tube being forced into the bulb *b* by the pressure of the vapour in A. It was next distilled from C (which was again shut off from A by the falling back of the mercury into the U-tube) into the flask D, which also contained phosphorus pentoxide. The

whole system was thus filled with ether, and its vapour issued at *d*, and at this stage the latter exit was sealed. Then, by cooling C and slightly warming D, the whole of the ether was caused to collect in C, and the reverse process returned it again to D. After the end of



a week, during which time the apparatus had been kept in the dark, the whole of the liquid was transferred to C, and the last tube, E, was sealed off from D. Ether was now distilled into E by immersing the tubes in a freezing mixture, and, when nearly full, it was sealed off at the capillary neck. The rest of the tubes were filled in a similar way, and were sealed off ready for use. It is evident that by this process the desiccation of the ether can be effectually carried out, and samples obtained in hermetically sealed tubes without risk of condensation of aqueous vapour from exposure to air.

One of the tubes was placed in a larger one filled with dry oxygen and containing phosphorus pentoxide. The tube was left standing in the dark for nine weeks, and was then sealed off at a constriction shown in the figure at A.



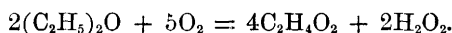
The inner tube was then broken, and the whole exposed to sunlight. After three days, the tube was opened and the ether tested

with titanin acid. A deep orange coloration was produced, proving conclusively that hydrogen peroxide was present in considerable quantity. It is thus seen that the utmost precautions to remove all traces of moisture do not prevent the formation of hydrogen peroxide when ether is exposed to sunlight in presence of oxygen, nor do they appear to diminish the quantity produced.

It may be of interest to note here that two experiments mentioned in a previous paper by one of us (Trans., 1891, 59, 51) to test the influence of temperature on the formation of hydrogen peroxide in ether kept in the dark have been repeated and the results confirmed. A flask containing ether and oxygen was heated for some days in the steam chamber at  $100^{\circ}$ . The contents were then found to be acid to litmus, and to contain hydrogen peroxide. A second flask, containing so small a quantity of ether that all was vaporised on placing it in the steam chamber, was treated similarly, and on opening it the contents were found to be acid, but no trace of hydrogen peroxide could be detected. The latter result might have been anticipated from the fact that hydrogen peroxide is unstable in the state of vapour. It should thus be borne in mind, in studying the formation of hydrogen peroxide in organic compounds, that its stability under the conditions of experiment has an important bearing on the matter when deciding whether it is formed in any particular liquid or not. Taking advantage of the intensity of the sunlight this year, an experiment was made with the object of determining how far solar heat alone would bring about the decomposition of ether. To this end, a tube containing ether and oxygen was exposed to the heating effect of the sun's rays, being, however, carefully protected from light. After an exposure of six weeks, the ether was found to contain minute traces of hydrogen peroxide, but in no way approaching the quantity formed when it has been exposed to light for a very much shorter period. Dunstan and Dymond have laid considerable stress on the influence of *temperature* in addition to that of sunlight in bringing about the formation of hydrogen peroxide in ether (Trans., 1890, 57, 988). It has, however, been shown (Trans., 1891, 59, 51) that ether exposed to light at  $0^{\circ}$  yields hydrogen peroxide freely, thus proving that decomposition can be effected under the influence of sunlight at comparatively low temperatures.

No special study having been previously made of the other products of the decomposition of ether when exposed to light in presence of oxygen, it seemed now of interest to determine this point. A quantity of ether, which had been exposed for five weeks in presence of water and oxygen, and which now contained large quantities of hydrogen peroxide, was tested and found to be strongly acid, as was also the aqueous solution. Sodium carbonate was then added, and

the excess of ether, together with any other volatile products which might have been formed, distilled off on the water bath. The distillate smelt strongly of aldehyde, and this was proved to be present by its reducing action on ammoniacal silver nitrate, and also by its restoring the colour to a solution of rosaniline hydrochloride decolorised by sulphurous acid. The aqueous solution was then evaporated down, and, after the addition of dilute sulphuric acid, it was distilled. The distillate was neutralised, and a portion tested for acetic acid with ferric chloride, and the presence of the acid was proved by the red coloration produced. This was confirmed by heating another portion of the distillate with alcohol and sulphuric acid, when a strong smell of ethylic acetate was observed. Experiments also showed that no carbon dioxide was formed during the decomposition of ether in sunlight, and it seems probable that the change consists in the oxidation of the ether first to aldehyde and then to acetic acid, together with the formation of hydrogen peroxide. The final result may, therefore, be represented by the equation



It seems, then, that in this case, as in the case of oxalic acid (Trans., 1894, **65**, 450), amyl alcohol, and certain other organic substances, hydrogen peroxide is formed in the place of water, which would be a normal oxidation product.

---