LXXXV.—*Action of Light on Amyl Alcohol.*

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It has already been shown that ether (Trans., 1891, **59**, 51), phenol (*J. Soc. Chem. Ind.*, 1893, **12**, 415), and oxalic acid (Trans., 1894, **65**, 450) yield hydrogen peroxide on exposure to sunlight in presence of oxygen. A number of other organic substances have been tested for hydrogen peroxide after exposure to light, and among those which have been found to yield a very noticeable quantity of this substance may be mentioned amyl alcohol, palmitic, and stearic acids suspended in water, and acid solutions of some of the alkaloids.

A more detailed study of the action of light on amyl alcohol was undertaken in order to determine the nature of the change which occurs, care being taken to ensure the greatest purity in the material used; the object of the present paper is to give the results of that investigation. The sample of amyl alcohol used in the following

experiments was obtained from Kahlbaum, and after being dried for 48 hours over lime, was treated with minute quantities of metallic sodium and distilled twice. It boiled constantly at 132.6° (corr.).

Formation of Hydrogen Peroxide.—Two experiments out of a large number which were made will suffice to illustrate the ease with which hydrogen peroxide is formed during exposure to sunlight and oxygen. In the first case, a considerable quantity of water was present, whereas, in the second, the alcohol was only in contact with moist oxygen.

1. About 10 c.c. of amyl alcohol were exposed together with 50 c.c. of water in presence of oxygen. After a few days a portion was tested, and the presence of a large quantity of hydrogen peroxide in the aqueous solution was shown by a deep orange coloration with titanous acid. Another portion of the water also gave an intense blue colour with pure ether and potassium dichromate. The layer of alcohol itself gave only a faint coloration with titanous acid, hydrogen peroxide being apparently more soluble in water than in the alcohol.

2. In the next experiment, amyl alcohol was exposed in presence of moist oxygen, liquid water being absent. After only two days' exposure, the alcohol contained a large quantity of hydrogen peroxide as shown by the titanous acid test.

No hydrogen peroxide could be detected in the alcohol which had been kept in the dark either in presence of water and oxygen, or of moist oxygen alone.

Having ascertained the fact that hydrogen peroxide is formed when amyl alcohol is exposed to sunlight in presence of moist oxygen, with or without addition of liquid water, it seemed desirable to determine whether a similar result would be obtained with the dry alcohol. To this end the following experiments, among others, were carried out.

Influence of Moisture.—1. A small sealed tube containing amyl alcohol, which had been dried over metallic sodium, was broken inside a larger one through which oxygen dried over phosphorus pentoxide had been previously passed, and the tube was exposed to sunlight for 17 days. It was then opened, and the liquid, when tested, gave strong peroxide reactions, both with titanous acid and with potassium dichromate and ether.

2. To ascertain the influence of further desiccation, a quantity of pure amyl alcohol dried as before, and contained in a small sealed tube, was placed in a bent tube, containing phosphorus pentoxide at one end, and filled with dry oxygen. The inner tube was broken, care being taken not to allow the liquid to wet the pentoxide, and the tube was kept in the dark for seven weeks. The amyl alcohol so dried was then exposed to sunlight for two weeks, and when tested was found to contain abundance of hydrogen peroxide. It seems,

then, that the absence of moisture, in so far as it was ensured by the precautions adopted, does not prevent the formation of hydrogen peroxide in amyl alcohol when exposed in presence of oxygen.

Other Products.—The next point was to ascertain whether any other products were formed. A quantity of amyl alcohol which had been exposed to sunlight for some months was now strongly acid, and smelt distinctly of valerianic acid. The presence of this substance was further proved by neutralising with sodium carbonate, separating from the excess of alcohol, decomposing the sodium salt by means of dilute hydrochloric acid, and extracting with ether. On distilling off the ether, an acid liquid remained, possessing the characteristic smell of valerianic acid. The formation of this acid seemed to indicate that the change occurring was one of a comparatively simple nature, not involving the breaking down of the molecule. To further examine this point, several samples were carefully tested for carbon dioxide after long exposure to light in sealed tubes. The gas above the liquid in such cases was aspirated through solutions of barium hydroxide, which showed no signs of turbidity, proving that carbon dioxide was entirely absent. It seems, then, that the products formed by the oxidation of amyl alcohol under the influence of sunlight and oxygen only differ from those yielded when other oxidising agents are used, in that hydrogen peroxide tends to be formed instead of water. The change may, therefore, be represented by the following equation :

Effect of Temperature.—It now seemed of interest to determine whether an increase of temperature would bring about the formation of hydrogen peroxide in the dark. A tube containing amyl alcohol and oxygen was, therefore, placed in the steam chamber at 100° and heated for nine days. On opening it, the contents gave no acid reaction with litmus, and not a trace of hydrogen peroxide could be detected, showing the complete stability of amyl alcohol in the dark at temperatures below 100°. It may be mentioned that in the case of ether, oxidation had been found to take place under the above conditions (Trans., 1891, 59, 51).

The tendency of amyl alcohol to yield hydrogen peroxide on exposure to light led us to inquire into the behaviour of some of the lower alcohols. Very carefully purified methyl, ethyl, and propyl alcohols were exposed to light in presence of excess of water and of oxygen, and also in tubes containing moist oxygen only. After periods varying from a few days to six months, methyl alcohol, when tested, gave no sign of hydrogen peroxide, and remained neutral to litmus. Ethyl alcohol, which seemed to show the presence of a trace of the peroxide at the end of a few weeks, was, however, entirely free from it after

prolonged exposure, and was neutral to litmus. *n*-Propyl, isopropyl, and isobutyl alcohols were also tested, and negative results were obtained in every case. It is, therefore, surprising that the next higher alcohol, amyl alcohol, should show so marked a change in its behaviour under the same conditions. With regard to the higher alcohols, octyl alcohol alone has been tested, and the sample used was found to give a small but distinct indication of hydrogen peroxide after an exposure of two weeks.