

IV.—UPON THE ACTION OF OXYGEN, OZONE AND NASCENT OXYGEN
UPON BENZENE.

BY ALBERT R. LEEDS.

I.—OXYGEN.

The first set of experiments was instituted to determine whether oxygen alone, in sun-light or diffused light, or oxygen together with platinum black, in sun-light or diffused light, would oxidise benzene after long-continued exposure. In every case a negative result was obtained, except in that of oxygen and platinum black brought into contact with benzene and a little water in a liter flask, and exposed to the direct sun-light. In the course of a few hours the liquid became slightly yellow, and at the end of eight days was dark yellow and intensely acid. A large amount of oxalic acid had been formed, but no acetic acid and no phenole.

II.—OZONE.

The earliest experiments upon the action of ozone upon benzene were made two years ago with the object of further studying the remarkable products obtained by Houzeau and Renard in the course of their investigation upon this subject.* Along with small amounts of formic and acetic acids, they obtained a gelatinous body which, when dried in vacuo, formed a white amorphous solid, and which they called ozobenzene. It was permanent only at low temperatures, and on gentle warming exploded with tremendous violence. Fearing the possible formation of this dangerous substance, the first experiment was made upon 1 grm of benzene, but the amount operated upon was gradually increased, until in the eighth and final trial, it amounted to 35 grms. In some experiments, the benzene was cooled by a freezing mixture; in other trials, it was ozonised at common temperatures, and in the last, the temperature was kept at 50°. The benzene was exposed to the oxygen, strongly ozonised by the silent discharge and containing about 70 mgrms of ozone in the liter, either in shallow dishes placed under a receiver through which the perfectly dry ozonised gas was kept flowing, or in Geissler bulbs connected with other bulbs to arrest the volatile products of ozonation. But in every case the results were the same. Large volumes of carbonic acid were given off, and the benzene, as it diminished in vol-

* *Compt. Rend.*, 76, 572.

ume, became converted into a dark yellow, oily mass, containing crystals of oxalic acid. In other cases, when the ozonation was performed in bulbs, an amorphous blackish mass separated out on the sides of the vessels. From these residues no crystalline bodies could be obtained either by the use of solvents or by sublimation. No indications whatsoever were noted of the white explosive body spoken of by Houzeau and Renard.

Besides carbonic and oxalic, formic and acetic acids were obtained, the latter in considerable quantity. Especial care was paid to the detection of phenole, but as far as our tests were concerned, no evidence of the presence even of a trace of this body was obtained. Hydrogen peroxide was likewise absent.

III.—NASCENT OXYGEN.

The fact that triatomic oxygen (O_3 , ozone or active oxygen) is not capable of oxidising water to the form of peroxide of hydrogen, while monatomic oxygen (O , or nascent oxygen) is, rendered it probable that a similar difference would be observed in the effects of ozone and of nascent oxygen, upon benzene. This supposition has been confirmed by experiment. The nascent oxygen was obtained by the action of phosphorus, partially submerged beneath the surface of water, upon air at common temperatures. When no benzene is present, the nascent oxygen oxidises the oxygen molecule to the form of ozone, the water molecule to hydrogen peroxide, and the nitrogen molecule in the presence of water, to ammonium nitrate. But on the addition of benzene, the ozone reaction disappears. The resulting products differ, according as the reaction takes place in sun-light or in diffused light. In the former case, after prolonged exposure, large amounts both of phenole and oxalic acid are formed, the phosphorus is converted into yellowish-red amorphous phosphorus, and the liquid remains colorless. In the latter case, the flask being kept in a warm place, the liquid becomes of a dark-brown color, and abundance of oxalic acid, but no phenole, is formed. At common temperatures the phosphorus goes into solution in the benzene, and is gradually converted into a mass of white dodecahedral crystals, the liquid remaining colorless. It is only when the temperature is above the melting point of the phosphorus (in these trials, $50-70^\circ$) that the dark brown liquid is produced. Curiously enough, though the flask becomes filled with dense white fumes, no inflammation took place at these elevated temperatures, the benzene vapor apparently protecting the phosphorus from ignition. Excess of calcium chloride was added to

the sirupy liquid, the dense precipitate of calcium phosphate and oxalate (somewhat dark from a portion of the organic matter carried down at the same time) filtered off, and the filtrate evaporated to dryness. The soluble portions were then dissolved out with the least possible amount of water, the excess of calcium precipitated out by potassium sulphate, the whole evaporated to dryness, and treated with absolute alcohol. As a small portion of the potassium chloride was taken up by the alcohol, this extract was again evaporated to dryness, and the operation repeated three times, when only the organic matter remained in solution. It was of a yellow color and pasty consistence, but as it could not be made to crystallize, and furthermore was in small amount, its further investigation was abandoned.

After my own research was in progress, I found that Prof. F. Hoppe-Seyler,* starting out from similar views as to the effects resulting from the action of nascent hydrogen upon oxygen, had performed a series of interesting experiments with hydrogenised palladium foil. A piece of such foil shaken up along with benzene, water and air, in a flask, and allowed to stand for a time, yielded an amount of phenole sufficient, after its conversion by the addition of bromine water into tribromphenole, for analysis. Besides the phenole, Hoppe-Seyler obtained a body which turned brown on the addition of potash.

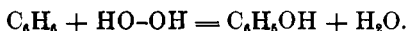
On repeating the experiment, I obtained a very abundant reaction for phenole. On addition of lime-water, the coloring matter which had been formed at the same time, was thrown down as a yellowish-brown precipitate. Not a trace of oxalic acid was present.

To my own mind, no satisfactory explanation could be given of the formation of phenole under these circumstances, except upon the supposition of the production of peroxide of hydrogen as an intermediate step. In the case of phosphorus oxidising in moist air, the contemporaneous formation of both ozone and peroxide of hydrogen, by the action of the nascent oxygen upon the oxygen and water, is a demonstrated fact.

Three suppositions therefore were admissable. Either the phenole was formed by the direct action of the nascent oxygen; or 2d. By the action of the ozone, or 3d. By the action of peroxide of hydrogen. The first supposition requires that the oxygen should produce by direct synthesis a molecule of phenole, which is in the highest degree improbable. The second supposition is inadmissable, since

* *Ber. der deutsch. Chem. Gesell.*, 12, 1551.

the non-formation of the phenole by treatment with ozone had been abundantly proven. The third supposition admitted of the rational explanation expressed by the formula,



Two modes of testing the validity of the third hypothesis presented themselves. The first was that of bringing the hydrogenised palladium foil into contact with water and air in a flask, and ascertaining if the oxygen rendered nascent by oxidation of the hydrogen, would oxidise the water to the form of hydrogen peroxide. In case an affirmative result was obtained in this experiment, it would be important to try the second test of treating benzene directly with a peroxide of hydrogen solution.

A strip of palladium, after remaining for several hours as the negative pole of a battery of six Bunsen elements, in water acidulated with sulphuric acid, was placed along with 10 c.c. of ammonia-free water in a half-liter flask filled with air. At the end of three days the water was tested with guaiacum and solution of diastase. It developed a deep blue color. On addition of cadmium-iodide-starch solution, iodide of starch was formed, and on titration with sodium hyposulphite, it was found that the total quantity of hydrogen peroxide present in the 10 c.c. of water amounted to 0.67 mgrm.

It is not improbable that both ozone and ammonium nitrate are likewise formed in the course of this reaction, but of the former no satisfactory indication was obtained, and the latter was not looked for, inasmuch as it would have required the repetition of the experiment on a much larger scale and with many additional precautions.

The successful issue of this experiment encouraged us to try what otherwise would not have been attempted, the treatment of the benzene with H_2O_2 . 20 c.c. of benzene were allowed to stand at common temperatures for two days in contact with 300 c.c. of a slightly acidulated 1.2 per cent, solution of hydrogen peroxide. The liquids remaining colorless, the flask was attached to a reflux condenser and placed in a water-bath. After the water in the bath had been kept boiling for several days, it was saturated with chloride of calcium, and the digestion continued at this temperature for two days longer. At the end of this time the liquid had become yellow, and was found to contain beside the coloring matter, oxalic acid and phenole. A very abundant precipitate was thrown down from the aqueous solution on addition of bromine water, and this precipitate of tribromphenole, after recrystallisation from alcohol, was found to weigh 0.25 grm.

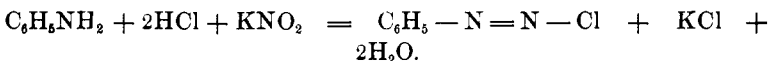
In conclusion, not only is the direct conversion of benzene into phenole by the action of hydrogen peroxide, of much interest, phenole having hitherto been obtained only by some indirect process, but it supplies a satisfactory demonstration of the validity of the third hypothesis above stated.

V.—NEW AZO COLORS BELONGING TO THE SO-CALLED TETRAZO GROUP.

BY JAMES H. STEBBINS, JR.

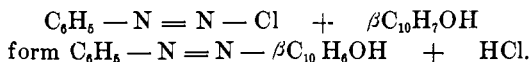
In order to give a clear understanding of this wonderful class of dyes, we will have to go back a few steps and consider the ordinary diazo compounds, their formation, and the azo dyes derived from them.

It is a pretty generally known fact, that when any of the salts of aniline (as the chloride, nitrate, etc.) or its homologues are treated with nitrous acid (either free or in the shape of a nitrite), that diazobenzole chlorides, etc., are formed, viz :



Now from Griess we learn that diazo compounds unite directly with phenoles and amines to form coloring matters which belong to the class of the so-called azo compounds.

As an example of the combination of diazo compounds with phenoles, we may take the action of diazobenzole chloride upon beta naphthole, viz :



If, on the other hand, we allow diazobenzole to react upon an amine (as aniline), we would get an amido-azo compound,



and this is the basis of the new class of colors.

Amido-azobenzole is a yellow basic coloring matter, uniting with one molecule of acids to form salts which, however, are readily decomposed with boiling water.

Now, as we have seen how nitrous acid acted upon amines, it seemed only too probable that if amido-azobenzole chloride were treated with nitrous acid, that a diazo compound would be formed, inasmuch as it contains a free amido radical (NH_2). This hypothesis was fully verified by Kekulé, who describes such a compound in his organic chemistry. This discovery, at that time, presented no value,