

VI.—PEROXIDE OF HYDROGEN AND OZONE.

[First Paper.]

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In the *Chemical News* (38, 224, 235, 243, 249 and 257) I published a series of articles, the chief object of which was to prove that when the so-called atmospheric ozonoscopes were prepared with the utmost precautions, and subjected in the laboratory, under known conditions, to the operation of vapors and gases other than ozone, such as nitrous acid, hydrogen peroxide, etc. (bodies existent to a greater or less extent in the earth's atmosphere), they all underwent change. Hydrogen peroxide affected all the ozonoscopes, thallous hydrate excepted. The results obtained with this were entered as doubtful. In one series of trials, operating with a very dilute solution of peroxide, the thallium paper was yellowed; in a second series, the yellow stain was upon the edge only of the paper, the centre remaining white. These results were there explained by the supposition of the "thallium peroxide undergoing reduction in contact with hydrogen peroxide, water and oxygen being liberated." In other words, while the effects of hydrogen peroxide in changing the thallium ozonoscope were visible, yet, accepting as true the generally received statement of Schoenbein, concerning the mutual decomposition of hydrogen and thallium peroxides, I attributed the final slight result to the reduction of any thallium peroxide first formed. This explanation was very unsatisfactory to me at the time, inasmuch as it necessitated the supposition of an initial oxidation, followed by a reduction effected by the continued operation of one and the same reagent, and I was engaged in its further study, when the publication of the admirable paper by E. Schoene, on this subject, definitely settled the question.* He there demonstrates the fallacy of Schoenbein's statement, and shows that hydrogen peroxide can convert thallous into thallic oxide, not only when the peroxide exists in solution, but also when it is in the form of vapor.

It may be regarded as established, therefore, that *none* of the so-called ozonoscopes necessarily indicate the presence of *ozone* in the atmosphere.

While my paper, written with the object of demonstrating the proposition just enunciated, was in course of publication, Mr. C. J.

* *Ann. der Chem.*, 196, 58.

Kingzett made the unwarranted charge (*Chem. News*, **38**, 243), that I seemed "to have fallen into an error committed by many other observers, namely, that of estimating as ozone everything in the atmosphere capable of coloring so-called ozonoscope papers." Moreover, he based this charge on a misquotation, for in the paragraph he quotes, I speak, not of the ozonic reaction, but of the "so-called" ozonic reaction, an epithet which he borrows in his own article.

In a later communication (*Chem. News*, **40**, 96), Mr. Kingzett says, "There is no known process of slow oxidation which has been established to produce ozone." Couched, as it is, in such positive terms, this assertion contravenes the statements of those who have experimentally investigated the subject during the past forty years. It might, therefore, not unreasonably be anticipated that Mr. Kingzett should bring forward some new and crucial experiments of his own. He adduces none. At the same time, he fails to recognise certain distinguishing properties of ozone and hydrogen peroxide, and apparently is not conversant with many phenomena exhibited in the oxidation of phosphorus in moist air.

Now, the property of ozone most strikingly characteristic, is its smell. This smell, so far as long-continued familiarity with it enables me to judge, and whether the ozone is derived from the oxidation of phosphorus, or results from the action of the silent discharge on pure and dry oxygen, or accompanies the electrolysis of acidulated water (and the smell in the three cases is identical), is possessed by ozone only. It is not the odor of phosphorus, nor of chlorine, nor of the oxides of nitrogen, although it is sometimes compared with these very dissimilar bodies. Concerning the odor of hydrogen peroxide, there appears to be wide diversity of opinion. Most of the works on chemistry, to which I have referred, state that it is odorless; one authority mentions that its odor is peculiar, another that it resembles chlorine. The solutions which I have prepared at different times myself, carbonic acid being employed to decompose the barium peroxide, have not evolved any odor that I was able to recognise or perceive. But when air is forced for a few minutes through a phosphorus ozonator, such as is described in *Chem. News*, **40**, 246, the atmosphere of a large lecture room becomes insupportable from the diffusion throughout it of an invisible gas (not a white smoke like the so-called antozone), and there is everywhere present the penetrating and irritating smell of ozone.

In the next place, ozone is very slightly soluble, and water through which ozone has been passed at, or below, the common temperature,

may be made to indicate the existence of dissolved ozone by appropriate tests.* It is certainly not too much to assume, that when water through which ozone has been passed, is evaporated to one-tenth of its natural bulk, its dissolved ozone is expelled. But under these circumstances, 30 c.c. of a solution which originally contained 2.7 mgrms of hydrogen peroxide, when evaporated down to 3 c.c., yielded, on titration, a result equivalent to 2.4 mgrms of the peroxide. The loss was due either to the decomposition of 0.3 mgrm of hydrogen peroxide, or to the expulsion of 0.44 mgrm of dissolved ozone. The former is by far the more probable supposition, and in either case, the body principally contained in the water was hydrogen peroxide. This water was contained in the first wash-bottle used in washing the ozone, generated by the action of phosphorus partly immersed in *aqua purissima*, upon air which had been previously purified from all pre-existent nitrogen compounds (ammonia, nitrous and nitric acids), organic particles, etc.† No nitrous acid was present in the water, as was shown by examination with Griess' test (metadiamidobenzole), but it contained 0.49 mgrm of nitric acid, and 0.066 mgrm of ammonia. This determination was made upon 481 liters of air, the amount of ozone found being 0.924 gm. The percentage of hydrogen peroxide in the first bottle of wash-water, as compared with the total weight of the air ozonised, was 0.00038 per cent.

In another trial, in which 420 liters of air were drawn over, and 0.805 gm ozone produced, the amount of hydrogen peroxide contained in the first bottle of wash-water, was 2.01 mgrms or 0.00037 per cent of the total weight of the air aspirated. It contained also 0.075 mgrm ammonia and 0.88 mgrm nitric acid, but of nitrous acid yielded not a trace to metadiamidobenzole. In a third experiment, in which 396.4 mgrms of ozone were produced, the wash-water contained 0.37 mgrm of nitric acid, no nitrous acid, and 1.3 mgrm of hydrogen peroxide, corresponding to 0.00039 per cent. of the total weight of the air ozonised. One word as to the close agreement in the percentages of hydrogen peroxide, found in the wash-water employed in the various trials. It was an agreement not anticipated at the outset, and became evident only when the actual amounts of hydrogen peroxide, found in the course of experiments continued during more than 3 months, came, at their conclusion, to be calculated up as percentages

* Ber. der deutsch. chem. Gesell., 12, 1831.

† Upon Ammonium Nitrite, and Upon the By-products Obtained in the Ozonation of Air by Moist Phosphorus. JOURN. AMER. CHEM. SOC., 1, 145. By the Author.

of the total weights of the air used. The same agreement was found to exist between the amounts of *nitric acid* present in the wash-water, when their percentages were calculated in like manner. In the first trial, 27 liters of air being aspirated, the nitric acid was 0.000318 per cent. of the total weight of the air; in the second trial, 108 liters of air aspirated, it was 0.000318 per cent.; in the fourth, 85 liters aspirated, it was 0.000303 per cent.; in the sixth, 262 liters aspirated, 0.000328 per cent. In these four experiments, water was used in the jars of the ozonator. In the third trial, 45 liters of air being drawn over, the nitric acid present in the wash-water was 0.00054 per cent; in the fifth trial, 90 liters aspirated, it was 0.00054 per cent. In these two trials, the bichromate mixture was used in the jars.

In another place,* I have shown that the amount of ozone produced by the oxidation of phosphorus, under given circumstances, is constant for any particular temperature, and consequently, the generation of ozone may be graphically represented by a curve, the production at 6° C. being nul, rising to a maximum at 24–25° C., and then rapidly diminishing as the temperature approaches 44°, the melting point of the phosphorus. The results above given, warrant, it appears to me, the formulation of another proposition, viz :

In the oxidation of phosphorus in moist air, there is formed both ozone and *hydrogen peroxide*.† The amounts of the two bodies evolved under given circumstances, bear a constant relation to one another and to the air passed over, the percentage of hydrogen peroxide being very small as compared with that of the ozone. In the experiments quoted above, the temperature being 18–21° C., the percentage of ozone, as referred to the weight of air aspirated, was 0.15 per cent.; that of the hydrogen peroxide, was 0.00038 per cent., or but one four-hundreth part of the ozone.

The amount of phosphoric acid in the wash-water, in the experiment in which 420 liters of air were aspirated, was 0.252 grm; of phosphorous acid, 0.013 grm. It was determined, by trial, that the presence of phosphorous acid in the solution, did not affect the titration of hydrogen peroxide. In this connection, it is likewise important to formulate the three following propositions:

I. No nitrous acid is present among the final products. The presence of hydrogen peroxide is, in itself, a sufficient reason.

* Chem. News, 39, 157.

† This statement is not new. Hydrogen peroxide was recognised by Schoenbein among the by-products of the oxidation of phosphorus.

II. Both ammonia and nitric acid are present in the final products, the amounts found, standing in a constant ratio to the quantity of air aspirated. In one trial, the results agreed with those corresponding to the formula of ammonium nitrate.

III. The generation of ammonium nitrate and hydrogen peroxide, is as invariable a feature of the phenomena observed during the course of the oxidation, as is the production of phosphoric and phosphorous acids. For this reason, any explanation of the phenomena which neglected the contemporaneous generation of ammonium nitrate and hydrogen peroxide, would be imperfect.

These results and the above conclusions, were arrived at and published in the early part of last year. The explanation brought forward at that time, and which as yet I have seen no reason to modify, was as follows:—“As to the reason for the formation of ozone itself under these circumstances, it may be conjectured along with Lamont † and others, that it is connected with the uneven quantivalences of the elements taking part in the reaction, which may be represented by the equation: $P_4 + O_{16} = P_2O_3 + P_2O_5 + 2O_3$. If this hypothesis be true, then we should anticipate the development of ozone whenever oxidation of a perissad occurred at temperatures compatible with the stability of the ozone molecule. Even at the temperature of combustion of hydrogen, this is supposed by C. Than ‡ to be the case. He explains in this manner the presence of the ozone, which he states he has detected in the combustion of hydrogenous substances generally, and its absence in the combustion of carbon.

“In entering into new combinations, the oxygen molecules must undergo temporary resolution into their constituent atoms. These, while *en route* to take up new positions in other combinations, and animated by their atomic energy, or energy of the nascent state, may either oxidize the oxygen molecule, or the nitrogen molecule, or the molecule of water. In the first place, ozone would be produced; in the second, regarding water as the basic body and NNO as the nitrile, there might be formed, as Hunt has indicated, § ammonium nitrate; in the third, hydrogen peroxide.”

Subsequent to the publication of these results, Prof. McLeod took up the subject, and arrived at the conclusion that || “the gas obtained

* JOURN. AMER. CHEM. SOC., I, 156.

† Chem. News, 28.

‡ Journ. Chem. Soc. [2], 9, 483; Journ. pr. Chem. [2], 1, 415.

§ Chemical and Geological Essays, T. S. Hunt, 2d ed., 472.

|| Chem. News, 40, 307.

during the slow oxidation of phosphorus, possesses the properties of ozone, and not those of hydroxyl, the only known peroxide of hydrogen." He likewise states that it is extremely improbable that ozone and hydrogen peroxide are both formed, as these substances destroy each other. The principal quantitative experiment mentioned, was that of passing the gas, first through a tube heated to various temperatures, then into a weighed sulphuric acid tube, and finally into a solution of potassic iodide and starch, acidified with sulphuric acid.

In connection with these experiments, it is to be noted in the first place, that Prof. McLeod regards the question in the light of an alternative, the presence of ozone excluding that of hydrogen peroxide, and *vice versa*. This view, though supported by the statements of Schoenbein,* that the two bodies mutually decompose one another, is much weakened by the recent elaborate experiments of Schoene,† who shows that when strongly ozonised oxygen, containing 5.2 volume per cent. of ozone, is agitated with a hydrogen peroxide solution containing 0.4 per cent. of the peroxide, or three to four times as much of the peroxide as is adequate to destroy all the ozone, it is only after the lapse of half an hour that as much as half of the ozone is destroyed.

Why then, if hydrogen peroxide and ozone were both present, did not a gradual increase in weight in the sulphuric acid dryer, as the gas was heated at various temperatures up to 200°, indicate the progressive decomposition of the former? The failure to obtain such a serial progression, is not explained. Neither is there any explanation of how an increase in weight in the cases where heat was applied, is necessarily to indicate the presence of hydrogen peroxide, when an increase (and that a much larger one) took place when no heat was used. Moreover, ozone itself undergoes decomposition at a temperature of 200°; but at this temperature, Prof. McLeod obtains by titration a result corresponding to 3.4 mgrms, which is relatively greater than the amount obtained when the ozone was not heated at all.

I shall be glad if Prof. McLeod will correct me of error, if I am mistaken in stating that the decomposition of his potassium iodide solution, under these circumstances, was due not to ozone (remaining after the air had been heated to 200°), but to the presence of free acid. In the early part of my own studies upon the subject, I investigated as an essential question, whether a current of ozonised air could be accurately

* Journ. f. prakt. Chem., 77, 130.

† Ann. der Chem., 196, 240.

titrated by an acid solution of potassium iodide, and determined that it could not.* Unless the presence of oxygen be rigorously excluded from the solution, excessively dilute acidified solutions of potassium iodide change even in the dark. In the light, the strength of the solution remaining the same, the change increases in the same ratio as the relative increase of the surface of exposure of the solution to the light's influence. But when oxygen is excluded, strong solutions containing excess of acid, may be exposed to the *direct light of the sun for days* without undergoing decomposition. Hence, when a current of air is allowed to pass through an acidified solution of potassium iodide, it is placed under conditions most favorable to its decomposition, and the amounts of iodine liberated will depend, first, upon the relative amounts of acid and iodide present; and, second, upon the intensity of the light and the relative dimensions of the surface of exposure. I have been most careful *not* to acidify the potassium iodide solution during the course of the experiment, but at its close, and then, for the reasons above-mentioned, to add only sufficient dilute acid to decompose the iodate which has been formed, and titrate at once.

In conclusion, I wish briefly to summarize the arguments above stated. The gaseous body given off in the course of the reaction between moist phosphorus and air, has a very powerful and peculiar odor, which is identical with that produced in the electrolysis of acidulated water. This is not the case with hydrogen peroxide. Ozone is very slightly soluble in water, and is readily expelled from the solution on heating. Hydrogen peroxide is miscible in all proportions with water, and solutions containing as much as one per cent. H_2O_2 , may be concentrated by evaporation on the water bath, until a higher degree of concentration is reached, without great loss of peroxide (see also Schoene, *Ann. der Chem.*, 196, 60, and Davis, *Chem. News*, 39, 221). Wash-water, through which air ozonised by phosphorus has been passed, yields, after concentration, a reaction due to hydrogen peroxide. The absence of nitrous acid in such wash-water can be readily demonstrated. No statement has been made as to the relative amounts of ozone and hydrogen peroxide *generated*, but only as to the relative amounts *evolved*. The latter amounts are those which remain after the highly dilute atmospheres of hydrogen peroxide and ozone have operated upon each other in the ozonising chamber. The absolute amounts depend upon the temperature, the period during which the ozone and hydrogen peroxide remain in con-

* *Phil. Mag.*, April, 1879; *JOURN. AMER. CHEM. SOC.*, 1, 18.

tact with one another, the rate of flow of gas, etc.; but under given circumstances, the ratio of the hydrogen peroxide in the *evolved* gas to the ozone is a definite quantity. In the experiments detailed, as determined upon the first portion of wash-water, it was approximately the $\frac{1}{100}$ th part. It must be borne in mind, that this number does not represent the total amount of hydrogen peroxide, but only that dissolved in the first wash-bottle. This is the larger amount, but some is likewise present in the second wash-bottle, still less in the third, and so on. A portion escapes solution in the water even when a number of wash-bottles are employed, and finally passes into the potassium iodide employed to titrate the ozone. During the whole of this interval, the hydrogen peroxide and ozone are slowly decomposing one another; the results obtained, on titrating with potassium iodide solution, depending on the point in the series where the titration is effected. When the current of ozonised air issues again from the potassium iodide solution, it is laden with a white cloud. This white cloud is the antozone of Schoenbein and other authors. It is, in fact hydrogen peroxide, held in a state of aqueous suspension, and *is the product of the action of the ozone upon the potassium iodide solution.* As such, it is to be discriminated from the white cloud, which is to be seen in the first two or three wash-bottles placed directly in connection with the ozonising chambers of the phosphorus ozonator. This latter white cloud is likewise suspended hydrogen peroxide, but its origin is to be sought for in the same series of changes as that resulting in the production of the ozone itself.

It follows, from the above, that the numbers obtained as the results of titrating the stream of ozone and hydrogen peroxide with potassium iodide, do not represent ozone only. They represent also the relatively minute amounts of hydrogen peroxide, which, as I have shown in the paper published in the early part of the preceding year, and previously alluded to, always accompany the ozone generated by the action of moist air upon phosphorus.

Finally, I desire to mention, in explanation of certain statements made in the latter part of the article, that they are founded upon experiments not as yet published, and that I have only been induced to make this preliminary notice of them, in order to complete an argument against what have appeared to me to be erroneous views.