ATOMATION (2d PAPER). ATOMATION OF OXYGEN AT ELEVATED TEMPERATURES, AND THE PRODUCTION OF HYDROGEN PEROXIDE AND AMMONIUM NITRITE, AND THE NON-ISOLATION OF OZONE, IN THE BURNING OF PURIFIED HYDROGEN AND HYDROCARBONS, IN PURIFIED AIR.

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It has heretofore been established, by the fact of the conversion of carbon monoxide into dioxide during the slow oxidation of phosphorus, that the formation of ozone, hydrogen peroxide and ammonium nitrite, in the course of this eremacausis, is preceded by the resolution of the oxygen molecule into its constituent atoms. The converse of this proposition, viz.: That when oxidation occurs with the contemporaneous formation of the three products enumerated, this oxidation has been preceded by the production of atomic oxygen, has not as yet been satisfactorily established, and awaits experimental proof.

The object of this second paper is to present the conflicting testimony as to whether these three bodies are formed during the rapid combustion of hydrogenous substances, and the results of a new experimental inquiry.

According to Schönbein, the formation of ozone occurred in all cases of slow oxidation in presence of atmospheric air. Moreover, that when readily oxidizable metals, like zinc and iron, were agitated in contact with air and water, hydrogen peroxide was formed. Also, that ozone, in presence of air and moisture, would generate ammonium nitrite.

This last statement, after long controversy, has been satisfactorily disproven by Carius.* Satisfactorily, because Berthelot† working independently and at a later period, has entirely confirmed the results obtained by Carius. It has thus been established beyond reasonable doubt, that ozone in presence of moist atmospheric air or moist nitrogen will generate neither ammonium nitrite or nitrate.

At the same time it is no less certain that in the slow oxidation of phosphorus, the contemporaneous formation of ammonium nitrite, ozone and hydrogen peroxide takes place. And whilst the observations of Schönbein and others, as to the occurrence of the same

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*Ann. der Chem. CLXXIV, 31.

†Compt. Rend. LXXXIV, 61.

phenomena in the course of the slow oxidation of metals, have not been reinvestigated with the same minuteness as the oxidation of phosphorus, yet it is eminently probable that the correctness of his labors in these particulars will be eventually vindicated. In this connection, the recent controversy and final establishment of the fact of the production of both hydrogen peroxide and ammonium nitrite, when the hydrogen in palladium hydrogen undergoes slow oxidation in presence of air and moisture is very instructive.

After the researches of Marignac, Andrews, Soret, Brodie and others, had elucidated the true nature of ozone, a very different interpretation was put upon many of the experimental results obtained by Schönbein, from that put forth by their original observer. Instead of regarding, as Schönbein did, ozone or the fictitious antozone, as the starting point in certain sequences of phenomena, the hypothesis was advanced in various quarters, that the real starting point was an initial change in the oxygen molecule, necessarily antecedent to all the observed phenomena.

In any new investigation of this topic it is but just to previous observers to rehearse the history of their labors, and in so doing the difficulties encountered are of two kinds: 1st. To ascertain in regard to particular experiments whether the reactions noted were in reality due to their asoribed causes. 2d. To restate the thoretical explanation of these phenomena in the light of the present universally received doctrines concerning the true nature of ozone.

One of the earliest observations, relating to the subject matter of the present paper, was that contained in a brief communication made to the Lyceum of Natural History of New York in 1869, by Loew.* His experiment was of a very simple nature. He blew a strong current of air through a fine tube into the flame of a Bunsen's burner, and collected the air in a beaker glass or balloon. He stated that in the course of a few seconds, sufficient ozone could be collected in this manner to be identified by its intense odor and the common tests.

Subsequently, a large apparatus containing many jets and burners, was patented by Loew and applied to the mellowing of whiskies by means of the "ozone" thus formed.†

The production of ozone in the manner described, was immediately denied by Boeke, who substituted a blast of oxygen for the

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*Chem. News, XXII. 13.

†Wagner's Jahresb. 1874, p. 404; Dingl. polyt. Jour. CCXIII, 306.

air expired from the lungs, and obtained from the gaseous products the reactions and odor of a compound of nitrogen and oxygen.*

Böttger likewise denied the accuracy of Loew's results, but upon altogether different grounds.† He detected no ozone in air blown through the flame of a Bunsen burner, but ammonium carbonate (which he regarded as a regular constituent of air expired from the lungs), and hydrogen peroxide. In reply to these criticisms Loew repeated his experiments, using instead of expired air, a bellows and a large Bunsen burner, and stated that in this manner he filled, in a short time, a large room with the peculiar odor due to ozone, while delicate tests failed to detect any peroxide of hydrogen or ammonium carbonate.

Similar experiments were performed by Than.‡ This observer aspirated the products of combustion from the lower edge of the flame of a Bunsen burner through an acidulated solution of potassium iodide and starch. A blue coloration was speedily produced, the air in the wash-bottle smelling distinctly of ozone. When pure water was used as an absorbing solution and subsequently tested with potassium iodide and starch, no blue color was developed. From this negative result the absence of ammonium nitrite was inferred, and from the previous affirmative result the presence of ozone. But the formation of ammonium nitrite as a product of combustion of hydrogen has since that time been established beyond doubt, whilst the reactions for ozone obtained by Than permit of other explanations.

Similar objections apply to the experiments performed by Struve (1871),§ who endeavored to prove that ozone, hydrogen peroxide, and ammonium nitrite are all present in the products of combustion of hydrogen. The gas was burned beneath a long drawn-out funnel, and tests were made for ozone at the upper end of the funnel, whilst the water condensed on its sides was collected and examined for hydrogen peroxide and ammonium nitrite.

In Poggendorff's Annalen for 1872 (p. 480), a summary is given of the results obtained by Pincus upon the formation of ozone, when thoroughly purified hydrogen gas was burned in atmospheric air. The gas was burnt with the smallest possible lens-shaped flame from a metal jet. According to Pincus, when a cold and clean

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*Chem. News, XXII, 24.

†Chem. Centr. 1870, p. 161.

‡J. pr. Chem. [2] I, 415.

§Zeitsch. anal. Chem, X, 292.

beaker glass was held over the flame the contents of the beaker possessed as powerful an odor of ozone as the interior of a charged Leyden jar. When pure oxygen was substituted for atmospheric air in a properly constructed apparatus, the same phenomena occurred, showing that the nitrogen of the air was not essential to its development.

The merit of having established, by rigorous experimental proof, the formation of ammonium nitrite by the burning of hydrogen thoroughly purified in thoroughly purified air, is due to Zoeller and Grete.† In their apparatus the air and hydrogen were purified by passage through potassium permanganate, potash, sulphuric acid, and Nessler's reagent, and the absence of both nitrous acid and ammonia in the gases prior to combustion, most carefully demonstrated. The hydrogen was burnt in a jet 3 to 4 m.m. high issuing from a platinum blowpipe tip. The ammonia formed by combustion was converted into ammonio-platinum chloride, the nitrous acid was identified by diamido-benzole and other tests. Nitric acid was sought for, but no reaction for it was obtained. The authors make no mention of either ozone or hydrogen peroxide.

In entering upon the present investigation of this difficult topic, it was with the hope of constructing an apparatus in which, by the use of completely purified gases, and the elimination of all surfaces of contact with organic bodies, it would be possible to decide whether at one and the same time, ozone, hydrogen peroxide, and ammonium nitrite (and possibly nitrate) were formed in process of combustion of hydrogenous substances.

The apparatus employed is figured in the accompanying cut. The combustion chamber A consists of a tall glass cylinder 80 c.m. in height and 6 c.m. in diameter, with a globular enlargement. At the bottom it connects, by a tube passing through a stopper of ground glass, with the receiving vessel G. This vessel communicated with the bottle H, whose stopper K is provided with a platinum hook fused in to its lowest part. H communicates with the wash-flasks M and N, by tubes passing through their mouths and ground into them air-tight. The entrance-tube B passes through the ground glass joint C, and is fused to the platinum jet D. Platinum wires connected with a coil are twisted into a very small spiral E, which is interrupted so as to allow of the passage of a spark immediately above the jet. At the upper portion of the

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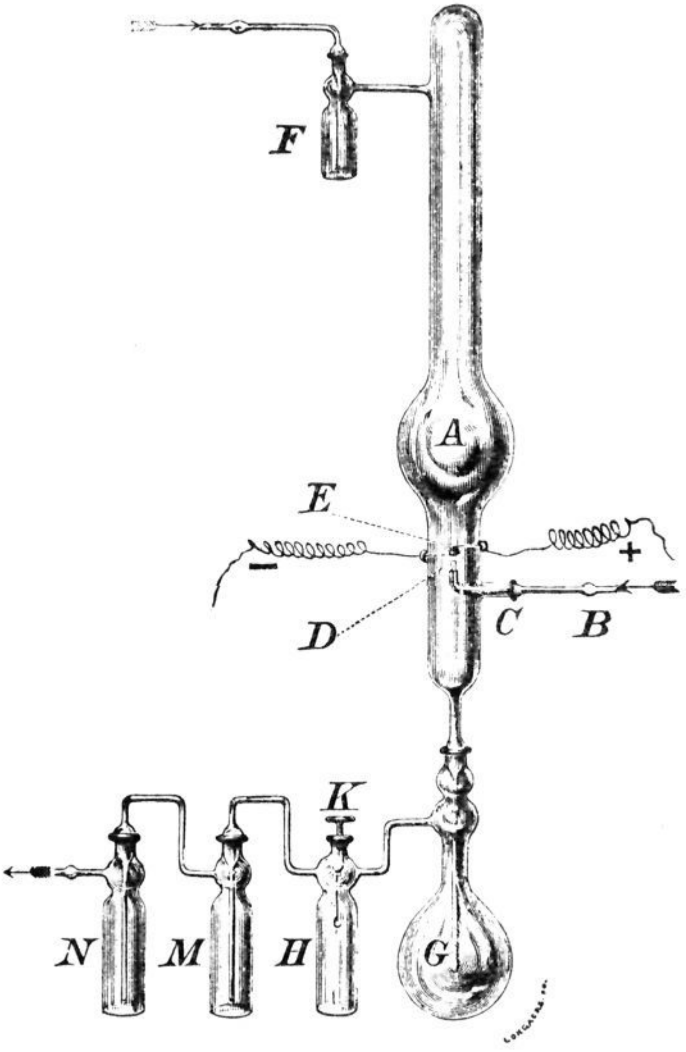
†Ber. Bericht. X, 2144.

chamber A there is a lateral tube connected with a wash-flask F, which is provided with an entrance-tube passing through its stopper of ground glass.



In the performance of the experiments, the air, after passage through a long tube filled with ignited asbestus, was passed through water, potassium permanganate, potash, sulphuric acid, and Nessler's reagent, entering at the upper end of the combustion chamber by the wash-flask F. It encountered the hydrogen similarly purified at E, and combustion was brought about by passage of the spark at this point. The platinum spiral was made very small so as to be contained within the outer surface of the flame. This was done to obviate the possible error due to the contact of platinum at high temperatures with the mixed gases. At the same time some device of this character was necessary, since the perfectly purified hydrogen gave an invisible flame and it could not be certainly known, except by the incandescence of the platinum, whether the flame had gone out or not. Without the platinum, extinction of the flame was very apt to occur, but with the platinum this never happened. The products of combustion flowed down into G, in which vessel and in H and M they were entirely condensed, these vessels being kept cold by ice. N contained a solution of potassium iodide, free from iodate and other impurities.

On opening the apparatus, in none of the trials was the odor of ozone noted. The potassium iodide alone, or after addition of starch water, was never affected when pure hydrogen was burned. When illuminating gas was used, the potassium iodide solution gave no indications of decomposition by ozone, on application of tests. If starch was added to it, a faint reddish precipitate was formed. On filtering off this precipitate, washing thoroughly with water, and allowing it to remain in contact with air, it became violet in color. Unfortunately the amount was so small that the nature of this yellow precipitate could not be determined with certainty. Aldehyde, passed into a solution of potassium-iodide starch, yielded a yellow precipitate, turning first violet and then blue on exposure to air. But these experiments are apart from the main purpose of the investigation, and the deportment of potassium iodide alone or with starch, sufficiently established the fact that no ozone passed through the wash bottle N.

The condensed water gave an intense reaction with the Griess's tests. When pure hydrogen was used the percentage of nitrous acid was 0.005 parts in 100,000, that of ammonia 0.002 parts per 100,000. These quantities are in the proportion corresponding to ammonium nitrite. The amount of hydrogen peroxide much exceeded that of ammonium nitrite, being 17 parts per 100,000. The various tests for hydrogen peroxide in which potassium iodide enters as one of the constituents, were not relied upon as conclusive, since the results obtained might have been due to other substances possibly present. But the condensed water gave in addition an intense blue color with fresh cold extract of malt and fresh guaiacum tincture. Moreover, it developed with solution of chromic acid a strong blue color, the last being regarded as the most satisfactory of the tests applied to prove qualitatively the presence of hydrogen peroxide. No nitric acid was detected.

The amounts of nitrous acid, ammonia, and hydrogen peroxide obtained when purified illuminating gas was burned, were not determined, but the qualitative tests applied to establish their presence were the same as those used in the case of pure hydrogen, and were equally satisfactory.

It should be observed that an apparatus of the character described is not well adapted to settle the question of the possible formation of ozone. The products of the combustion could not be rapidly withdrawn from the influence of the elevated temperatures in the immediate vicinity of the flame, and any ozone formed could readily have undergone decomposition. The experiment is a failure, in so far as its bearing upon the validity of the observations made by preceding observers is concerned. In all of their experiments the immediate withdrawal of the products of combustion is an essential feature. In repeating their experiments, if other evidence than that afforded by the powerful odor of ozone is sought for, it would be necessary to obtain the absorption spectrum of ozone and the blackening of silver. Under the conditions of the experiment, other qualitative tests for the presence of ozone would be open to question. The amount of ozone necessary to yield these decisive proofs however is much greater than that which could possibly be obtained in any trial where all the essential precautions are observed. For these reasons further experiments are abandoned.

The final conclusion reached is the *certain formation* of hydrogen peroxide and ammonium nitrite, and, in view of the fact that the statements of others concerning the presence of ozone have not been disproven, the *possible formation* of ozone.