

XLIV.—ON THE PRODUCTION OF OZONE BY HEATING SUBSTANCES CONTAINING OXYGEN.

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In his excellent "Historisch-Kritische Studien über das Ozon," published December, 1879, Prof. C. Engler enumerates among the modes of formation of ozone, that of heating substances containing oxygen. This statement is founded upon the experiments published by Schönbein, as far back as 1855*, and which, although rendered of doubtful probability by the fact established by Andrews, that the decomposition of ozone into ordinary oxygen occurs at (and below) 270°, have never been formally refuted.

Schönbein was led to anticipate the results of his experiments by certain peculiar views concerning the state in which the oxygen existed in the bodies experimented upon. He thought that they contained the oxygen either partly or altogether in an ozonized condition, and he included in the number of such bodies the oxides and superoxides of all the noble metals, the superoxides and some acids of the common metals, and a number of the states of oxidation of non-metallic elements, *e. g.*, the peroxide of hydrogen, the various acids of nitrogen, of chlorine, bromine, and iodine, or in general, *all those substances which evolve oxygen on heating.* Furthermore, the reason, according to Schönbein, why these bodies underwent decomposition under the influence of heat, was that the ozone which they contained was partly resolved into ordinary oxygen on heating.

In the conduct of his experiments, Schönbein thought that he amply provided against the presence of oxides of nitrogen in the gas liberated on heating, by due care in the preparation of the bodies experimented upon. The peroxide of lead, for example, he prepared from minium by means of acetic acid, the mercuric oxide from mercuric chloride, the argentic oxide from the sulphate, and so on. And while he recognized that the chlorates, bromates and iodates would evolve traces of chlorine, bromine and iodine, he ascribed to these substances only a part of the effect produced, assuming that the rest was due to ozone set free, on heating, at the same time. The apparatus employed was of the simplest description, merely in fact a test tube 6 in. in length and $\frac{1}{2}$ in. in breadth, in which the body was heated, and strips of moistened potassium-iodide-starch paper, or

* *Verhandl. d. naturf. Gesell.*, Basel, 1, 252; *Journ. f. Prakt. Chem.*, 66, 286; *Phil. Trans.*, 1860, 113.

paper dipped in freshly prepared guaiacum tincture held in the upper end of the tube.

Tried in this manner, all the substances experimented upon by Schönbein which gave off oxygen, gave at the same time the ozone reaction; the oxides of the noble metals, like argentic oxide, giving the reaction in the most striking manner, the peroxide of manganese very feebly.

In conclusion, Schönbein remarks that the escape of a portion of the liberated oxygen from the deozoneing action of heat, is a striking fact, beyond his power to explain.

Apparently unaware of the extended research of Schönbein, and of the theoretical grounds upon which that research was founded, Mr. Kingzett published in 1872, a preliminary note upon ozone*, in which he obtained results similar to those detailed above. After stating that the gas, evolved on heating mercuric oxide, even after its passage through a considerable depth of potash solution, turned potassium-iodide-starch papers blue, and that the same effect was produced by the gas liberated from native or artificial manganic dioxide, even when the dioxide was heated to redness, Mr. Kingzett states that "in short, from every source I have tried, the oxygen produced never lacked these properties."

In his critical history of ozone, Prof. Engler imputes to Mr. Kingzett the statement that the gas given off in these decompositions is ozone, but in justice to Mr. Kingzett it should be said that this is a slight misrepresentation, and that the latter states that he has no proof to offer that it is ozone.

In the same place, Prof. Engler states† that periodic acid on heating to 130–135° gives off ozonized oxygen, and quotes the experiments of Croft‡, that iodic acid, in the act of crystallization, gives off ozone. Also the statement of Bellucci§, that during the concentration of the aqueous solution of iodic acid, and also during the crystallization of the syrup obtained by concentrating, ozone is given off.

I have elsewhere shown that the apparent evolution of ozone from iodic acid, in process of concentration and crystallization, ceases when the iodic acid has been recrystallized a sufficient number of times to obtain it free from those traces of chlorine or nitrous acid,

* *Chem. News*, 25, 242.

† *Historisch-Kritische Studien über das Ozon*, p. 26.

‡ *Chem. News*, 25, 87.

§ *Ber. d. deutsch. chem. Gesell.*, 1875, 8, 905.

or possibly some lower oxide of iodine formed in the process of manufacture, and gradually eliminated by successive recrystallizations of the acid.

In the conduct of the experiments detailed below, two considerations were kept very prominently in view: 1st. To obtain the material experimented upon in as nearly as possible a state of purity. 2d. To absorb any gases, other than ozone, by washing.

To this end mercuric oxide was prepared by precipitation from the chloride by caustic potash, and washing by decantation and filtration, until no traces of either potash or hydrochloric acid could be detected in the filtrate. The oxide, weighing 54 grms after complete drying, was introduced into a piece of hard glass tubing, sealed at one end, and so cautiously heated in a combustion furnace, that the liberated gas came over at the lowest temperature of evolution and very slowly. The oxygen was passed first through a flask containing strips of filter paper, moistened with a two per cent. solution of fresh, unaltered resin of guaiacum in alcohol. These were gradually turned of a deep blue. The flask was then disconnected directly from the combustion tube, and a series of three Geissler absorption bulbs, each containing a very small amount of water (15 c.c.), was inserted between. After allowing the oxygen to bubble through the bulbs for six hours, fresh strips of moistened guaiacum paper placed in the flask were entirely unchanged. Upon the addition of silver nitrate to the wash waters, they gave an unmistakable reaction for chlorine.

It follows, therefore, that it is practically impossible to wash out from the mercuric oxide prepared as above, every trace of chloride, and that sufficient remains to give on heating a reaction for chlorine, or as Schönbein thought, for ozone.

Manganese dioxide was prepared by digesting the sulphate with chloride of lime. After the decomposition was complete, the precipitate was washed *more than thirty times*, until finally no trace of chlorine could be detected in the wash water. The dried peroxide was then heated in the combustion furnace to such a temperature, that a slow evolution of oxygen took place during eight hours. No change of the moistened guaiacum papers occurred in contact with the evolved oxygen, either before or after its passage through the Geissler bulbs, neither could any reaction for chlorine be obtained with the wash water. It may be stated, accordingly, that artificial-manganic peroxide prepared with due care, gives on heating no reaction for ozone, or for any gas which could be mistaken for ozone.

Native manganic peroxide, on the contrary, heated for six hours in like manner, affected the guaiacum test when placed before the wash bottles, but not when it was put after. In the latter case, the wash water itself gave the reaction for chlorine.

Plumbic peroxide was prepared from the acetate by digesting with chloride of lime, and washing between thirty and forty times, or until the filtrate gave no reaction for hydrochloric acid. On cautious heating for six hours, the evolved gas affected the guaiacum when placed before the wash water, but not when it was put after; the wash water, in the latter case, giving the chlorine reaction.

Some argentic oxide was prepared from pure silver, obtained by reduction from the chloride. After conversion of the silver into sulphate, the oxide was thrown down by potash, and washed with boiling water, until no traces of chlorine, etc., could be detected in the filtrate. The argentic oxide was then transferred to a small retort, which was heated by an oil bath. Air, passed previously through a train of purifiers, was drawn through the retort in a slow stream during the heating. After leaving the retort, it passed over a strip of moistened guaiacum paper, then through three Geissler bulbs, containing water, and finally through a flask containing another strip of guaiacum paper. In the first experiment, the first guaiacum paper became strongly colored when the temperature of the oil bath was raised to 190° , the second when the temperature had reached 213° .

This result made it appear probable that the air of the laboratory was not sufficiently purified, and the experiment was again repeated with outside air. Identical results were obtained, the first paper changing at 190° , the latter at somewhat higher temperature, and the heating being continued until the oil bath had risen to 280° . An experiment was then made in blank, purified air being drawn through the train of apparatus without heating the argentic oxide, when it was found that both papers altered in contact with the air alone, though at a slower rate than in the previous experiments, when the air was heated.

Having established in this manner, that the change of color of the guaiacum tests was insufficient to prove the presence of ozone, they were replaced by zinc-iodide-starch papers. On raising the temperature of the retort containing the argentic oxide to 284° , the first iodide paper turned blue, the second, which was placed after the series of Geissler bulbs, remained entirely unaffected. The reaction was due to the presence of a trace of chlorine, but some difficulty was experienced in demonstrating this to be the fact. The

wash water gave so faint an indication, that it was not until the whole amount of wash water in the three bulbs, amounting in all to 45 c.c., had been evaporated down to 5 c.c., that an unequivocal reaction for chlorine was obtained.

Some periodic acid was then prepared by digesting 1 pt. of iodine with 20 pts. of sodium carbonate in 200 pts. of water, and passing a stream of chlorine through the liquid until no further precipitate was formed. The sodium periodate was then filtered, slightly washed with cold water, dissolved in dilute nitric acid, and decomposed with argentic nitrate. The resulting diargentic periodate was crystallized out of its solution in hot nitric acid, decomposed with cold water, and the aqueous solution of periodic acid thus formed evaporated to dryness six or seven times, until no trace of acid fumes could be detected in the escaping moisture. The periodic acid was heated in a retort placed in an oil bath, a slow stream of purified air being drawn over it during the course of the operation, and at no time was the temperature allowed to rise above 154°. In the first set of trials, the guaiacum papers placed before and after the Geissler bulbs containing the water employed in washing the gas, were colored blue. After the discovery that the air alone could effect this change, zinc-iodide-starch papers were employed, when the paper placed before the wash waters was turned blue, that placed after remained unaltered. The wash waters gave an unmistakable reaction for chlorine.

The conclusion to be drawn from the foregoing experiments is, that the supposed evolution of ozone upon heating certain oxides of both metallic and non-metallic bodies, is in reality due to minute traces of impurities, usually chlorine, which cannot be eliminated in the ordinary course of preparation of these bodies.