THE PHOTOCHEMICAL OXIDATION OF BENZENE[1]

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In a paper published over thirty years ago, Leeds[2] showed that oxalic acid is formed and no phenol when benzene and moist phosphorus are allowed to stand in a warm place exposed to diffused light. If placed in full sunlight, considerable quantities of phenol are also formed. Ozone oxidizes benzene to oxalic acid, acetic acid, formic acid, and carbon dioxide Hydrogen peroxide oxidizes benzene to a mixture of oxalic acid and phenol, the relative amounts of phenol not being given. What really happens in Leeds' experiment is that moist phosphorus and air give rise to ozone in diffused light and to hydrogen peroxide in bright sunlight. He recognized this himself but he offered no explanation for the difference.

That the sunlight should have an effect is not surprising; but the problem is to determine why we should get hydrogen peroxide in the bright light and ozone in the diffused light. There is a rather remarkable paragraph in a paper by Wurster.[3]

"Oxygen is made active and is converted in large amounts into the permanently active forms of ozone and hydrogen peroxide only, when the rays of the sun fall upon oxygen and water simultaneously, as was first shown by Schönbein, though the fact was made use of for thousands of years in bleaching. Under these conditions of intimate contact of oxygen with drops of water the oxygen is readily made active by light and the oxygen molecule is disrupted at ordinary temperature in a way which is otherwise obtained only at a very high temperature or under the action of a very intense lime light or electric light. The oxygen is split into atoms which react to form ozone and hydrogen peroxide. This is not so remarkable

[1] A paper read before the Eighth International Congress of Applied Chemistry in New York, September, 1912.

[2] Ber. chem. Ges. Berlin, 14, 975 (1881).

[3] Ibid., 19, 3212 (1886).

when we recall that, according to Graham, we must consider dissolved gases or gases condensed on surfaces as being in the liquid state. They have therefore lost, as heat, the energy corresponding to the change to the liquid state; but, on the other hand, the readiness of the molecules to react is presumably increased by their being nearer together."

This would be admirable if Wurster had differentiated between the formation of ozone and of hydrogen peroxide, instead of lumping the two together. The action of ordinary sunlight on a mixture of oxygen and water really forms hydrogen peroxide instead of ozone.

Wilson[1] has postulated the formation of hydrogen peroxide when ultra-violet light acts on moist oxygen. I quote from J. J. Thomson.[2] "Wilson showed that the passage of ultra-violet light through a gas (as distinct from the effects produced when it is incident on a metal surface) produces very interesting effects on the condensation of clouds. If the intensity of the light is small then no clouds are produced unless the action equals that (1.25) required to produce clouds in gases exposed to Röntgen rays. If, however, the ultra-violet light is very intense, clouds are produced in air or in pure oxygen, but not in hydrogen, by very much smaller expansions, and the expansion required decreases as the time of exposure to the light increases; thus the nuclei producing the clouds grow under the influence of the light. If the light is exceedingly strong, clouds are produced in air or oxygen without any expansion at all. Wilson was even able to produce these clouds in air standing over a seventeen percent solution of caustic potash, and which therefore was not saturated with water vapor; in this case the drops lasted for three hours after the light was cut off; this, as Wilson points out, shows that the drops cannot be pure water. These clouds are probably analogous to those observed years ago by Tyndall,[3] when ultra-violet light passes through air contain-

[1] Phil. Trans., **192**, 403 (1899).
[2] Conduction of Electricity through Gases, second edition, 169 (1906).
[3] Phil. Trans., **106**, 333 (1870).

ing the vapors of certain substances of which amyl nitrite was the one which gave the most striking effects. The effects can be explained by the formation under the influence of the ultra-violet light of some substance—Wilson suggests that in his experiments it was H_2O_2—which, by dissolving in the drops as they form, lowers the equilibrium vapor pressure, and thus enables the drops to grow under circumstances which would make drops of pure water evaporate. This explanation is supported by the fact that ultra-violet light does not produce these clouds in water vapor by itself or in hydrogen; and also by the fact that, unlike the clouds due to Röntgen rays, these clouds formed by ultra-violet light do not diminish in density when a strong electric field is applied to the gas, showing that the nuclei are either not charged or that if they are charged they are loaded with foreign molecules so that they do not move perceptibly in the electric field. Vincent[1] has observed movements of these drops in a strong electric field; he found that some drops moved in one direction, others in the opposite direction, while there were some which did not move at all. Thus some drops are uncharged, others positively or negatively charged. It would thus seem that the charges have nothing to do with the formation of these drops, the drops merely forming a home for the ions produced by the ultra-violet light."

While these experiments make it probable that hydrogen peroxide is formed by the action of ultra-violet light or moist air, there is no direct proof of the presence of hydrogen peroxide and Vincent was not able to detect it. This gap has been filled by the experiments of Fischer and Ringe,[2] who have shown that the silent discharge in an ozonizer produces hydrogen peroxide instead of ozone when the air is nearly saturated with water vapor. The failure to obtain ozone under these conditions is not surprising because it is a well-recognized fact in the commercial manufacture of ozone that

[1] Proc. Camb. Phil. Soc., 12, 305 (1904).
[2] Ber. chem. Ges. Berlin, 41, 951 (1908).

the yield falls off unless the air is kept moderately dry. More recently Makowetsky[1] has shown that hydrogen peroxide is formed when a direct current glow discharge passes through oxygen or air to a water cathode. This is not an electrolytic phenomenon because the yield at low currents exceeds that called for by Faraday's law. It is just as much a photochemical reaction as is the ozone production. We should therefore expect to find that the action of sunlight on air would produce ozone when the air was moderately dry and when the sunlight was rich in ultra-violet light of wave-lengths less than 300 $\mu\mu$. We should expect to get hydrogen peroxide in presence of water. The yield of ozone would of course be negligible in case the sunlight contained almost no rays having wave-lengths less than 300 $\mu\mu$. The experiments of Bacon[2] offer a very satisfactory confirmation of this view. "When pure water or a salt solution is exposed to direct sunlight in Manila, hydrogen peroxide is formed very rapidly, strong tests being obtained after a few hours. H. D. Gibbs, of this Bureau, examined the solutions in a great number of reagent bottles exposed in the laboratory for some months to diffuse light and found considerable quantities of hydrogen peroxide in practically every case. It is evident that in the Tropics, at least in island regions, with the great quantity of vegetable growth, the vigorous transpiration of plants, and the large amounts of water continually present at the surface of the earth and in the air, all the conditions are present when the sun is shining, which are necessary to charge the water surfaces, to form peroxide of hydrogen, and in general to increase the proportion of ions in the air according to the processes which have been outlined above. Whether there is a true ionization of the air by tropical sunlight, apart from such a secondary ionization, must be determined by further studies. Considerable evidence is accumulating to show that the tropical sunlight contains more in-

[1] Zeit. Elektrochemie, **17**, 217 (1911).
[2] Philippine Jour. Sci., 5A, 271 (1910).

tense ultra-violet light than that in temperate zones. Thus I have shown in another paper[1] that the decomposition of oxalic acid or of oxalic acid catalyzed by uranium salts is very much more rapid in the Philippines than in temperate zones, and Gibbs[2] has shown that the coloration of phenol and of aniline takes place much more rapidly in the tropics than in more northern zones.

"One of the most striking effects produced by ions is the influence they exert on the condensation of clouds. I have often noted, in watching a steam jet in the open air in Manila, the remarkable way in which, as the sunlight strikes it, it becomes dense and beautifully colored, due to the interference and diffraction of the light by the small drops of water, while as soon as the sun goes behind a cloud, the jet becomes very thin, and the colors, of course, disappear. Other conditions being equal, on a cloudy day the mountains near Manila can be seen much more clearly than on one of sunshine, and I do not believe I err when I state that all days of bright sunshine in the Philippines show a decidedly hazy atmosphere, as noted by looking at objects at some distance. I believe this fact to be due to the ionization of the air by the sunlight and the consequent condensation of very minute drops of water around the ions so formed. The mountains are most clearly visible from Manila at sunrise and at sunset and on days when clouds protect the lower atmosphere from the ionizing radiations of the sun."

It does not seem very probable that the hydrogen peroxide in the reagent bottles in Manila could come from ionized air which got in when the bottles were opened. If this is not the case, then oxygen and water must react to form hydrogen peroxide to some extent under the influence of light which can pass through glass.

The matter of the ionization of the air in Manila has been discussed by Freer.[3] "Another phenomenon to be ob-

[1] Philippine Jour. Sci., 5A, 281 (1910).

[2] Ibid., 3A, 361 (1909); 4A, 133; 5A, 9,419 (1910).

[3] Philippine Jour. Sci., 5B, 10 (1910).

served in Manila in a marked degree, and which, so far as I am aware, has not been recorded in the literature from other climates, is the extensive ionization of the air when exposed to the sunlight. Doctor Bacon, using a modern electroscope, has been able to show that our atmosphere, when exposed to the direct rays of the sun, rapidly discharges the instrument, the loss of potential being 46 volts per hour, whereas, in the diffused light of a room it is only 15, and during the night 6, for the same volume of air. This is certainly a remarkable result, which deserves further study. The only comparative data on hand are a few by Elster and Geitel[1] giving us an indication of what the fall of voltage would be in northern climates. They found, in Vienna on a foggy day, a voltage of 2.77, in clear weather, 8.58, but on a day when the sky was half overcast, 13.67. These authors ascribe the phenomenon to radio-activity, but our results in Manila, where radio-active phenomena are not especially prominent, would lead to the conclusion that the air is ionized by sunlight. The presence of this ionization in so great a degree in our atmosphere would indicate a condition of the solar spectrum which might well account for many of the so-called excessive effects which have been observed."

Experiments were made in Manila to determine the extent of the solar spectrum at the ultra-violet end.[2] The spectra were obtained at noon. "They probably do not extend beyond $\lambda = 291\ \mu\mu$, and therefore not much farther than has been observed by others. Measurements undertaken by Miethe and Lehmann[3] in Assuan, Berlin, Zermatt, Gornergrat, and Monte Rosa give practically identical numbers, namely 291.55 $\mu\mu$ to 291.21 $\mu\mu$ during the latter part of August and the first part of September, these authors finding, in contradistinction to Cornu,[4] that altitude above the sea

[1] Drude's Ann., **2**, 425 (1900). The authors used an instrument of identical form with our own.

[2] Freer: Philippine Jour. Sci., 5B, 14 (1910).

[3] Sitzungsber. Akad. Wiss. Berlin, **8**, 268 (1909).

[4] Comptes rendus, **88**, 1107; **89**, 808 (1879).

level makes no great difference. As one of these places is at 24° 30′ north latitude, while the others are in northern climates, it is evident that, as the extent of the ultra-violet field does not change materially, the intensity factor in the solar spectrum must vary to a great extent in different places. However, it is possible that a considerable range of ultra-violet is absent at present (March 1) from our sunlight. Probably this area will increase as the angle of the sun diminishes and as the season advances, and it may reach a maximum in April, although these recent results would seem to indicate that even here we will not get below 288 $\mu\mu$."

These observations are important because they show that, under ordinary conditions, the sunlight reaching the earth contains practically none of the rays which cause the formation of ozone, the rays of wave-lengths less than 300 $\mu\mu$, while it does contain ultra-violet of wave-lengths greater than 300 $\mu\mu$, the rays which cause the decomposition of ozone. The bearing of this on our problem is easily shown. When phosphorus is oxidized, there is normally a production of ozone. In presence of benzene, we get the oxidation products characteristic of ozone—oxalic acid, etc., but no phenol. In bright sunlight, the ultra-violet light actually present checks the formation of ozone by making it less stable. We consequently get a certain amount of hydrogen peroxide formed. The data are not sufficient to show whether the yield of ozone drops to zero. That would depend to some extent on the intensity of the sunlight. In presence of benzene we get the decomposition products characteristic of hydrogen peroxide or of a mixture of hydrogen peroxide and ozone, namely a mixture of phenol and oxalic acid.

It is not surprising that we should also get phenol when benzene, water and palladium hydrogen are shaken up with air,[1] because hydrogen peroxide is known to be a reduction product of oxygen.

The general results of this paper are:

[1] Hoppe-Seyler: Ber. chem. Ges. Berlin, 12, 1551 (1879).

1. When benzene is oxidized by ozone, the chief product is oxalic acid, while a mixture of oxalic acid and phenol is obtained when benzene is oxidized by hydrogen peroxide.

2. When moist phosphorus oxidizes in presence of benzene, the chief oxidation product of the benzene is oxalic acid if the reaction takes place in the dark or in diffused light. A mixture of oxalic acid and phenol is obtained if the reaction takes place in bright sunlight.

3. Hydrogen peroxide is formed by the action of the silent discharge, or of bright sunlight, upon a mixture of water and air.

4. At the surface of the earth bright sunlight rarely contains any appreciable amount of ultra-violet light having wave-lengths less than 290 $\mu\mu$.

5. At the surface of the earth bright sunlight tends to destroy ozone and not to form it.

6. When moist phosphorus oxidizes in bright sunlight, the yield of ozone is decreased and that of hydrogen peroxide is increased.

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