ART. XV.—*On the Theory of the Action of certain Organic Substances, in increasing the Sensitiveness of Silver Haloids*; by
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IN the early days of photo-chemistry, it was observed that all the silver haloids gained in sensitiveness by being in contact with a soluble silver salt; that when the soluble silver salt was removed by careful washing, a considerable diminution in sen-

sitiveness followed. After a time it was noticed that certain organic substances placed in contact with the washed haloid, appeared to take, to some extent, the place of the silver salt removed, and that the silver haloid was distinctly more sensitive when in contact, for example, with tannin, than when isolated.

In explanation of the fact, a theory was published by M. Poitevin that these organic substances acted in virtue of their affinity for the halogen. That in the case, for example, of tannin and silver iodide, the iodide was more readily attacked by light in the presence of tannin, because the affinity of tannin for iodine came into play in aid of the action of light. Shortly after, Dr. H. Vogel published the same theory.

It is a little remarkable that neither of the authors of this theory, or rather hypothesis, has at any time thought it necessary to support it by experiment or proof of any kind, but both have continued up to the present time to treat the theory as self-evident. In endeavoring to show that this explanation of the reaction cannot be received, I shall have no argument on the other side to combat, or experiments to discuss, as I can find none. I shall, therefore, state what I conceive to be the true explanation, and endeavor to support it adequately by proof.

When we examine all the substances known to be capable of increasing the sensitiveness of the silver haloids, we notice that the one property which they possess in common is, *not* an affinity for the halogen, as the Poitevin-Vogel theory would lead us to expect, but that they *are all reducing agents*. The natural view, therefore, of their action on a silver haloid is, not that they abstract the halogen from it, but that their affinity for oxygen comes into aid of the affinity of the halogen for hydrogen, and that under the influence of light, an atom of water is decomposed. That in the case of silver iodide and tannin, for example, the tannin is oxidized, the iodine is converted into hydriodic acid, and the silver salt is more or less completely reduced, probably to subiodide. According to this view, when silver iodide is exposed to light in presence of an organic body capable of accelerating the action of light, there should be traces of free acid formed, whereas, according to the Poitevin-Vogel theory the result of the action should be the formation of an iodo-substitution compound.

1. Silver iodide was precipitated in the presence of a slight excess of potassium iodide, and thoroughly washed. A small quantity of pyrogallol was added and the mixture was exposed to sunlight for fifteen minutes in contact with water. The liquid at first neutral, at the end of fifteen minutes, showed a distinctly acid reaction, increasing with continued exposure.

[Pyrogallol was used in preference to tannin (gallotannic

acid) because the former is perfectly neutral to test paper, and cannot confuse the reaction as would be the case with tannin, which of itself reddens blue litmus paper].

Again: if the Poitevin-Vogel theory were correct, it would afford a criterion as to what substances should, and what should not, exalt the sensitiveness of the silver haloids. Substances having an affinity for iodine should increase the sensitiveness, and substance not possessing such affinity, should have no such action. This is not the fact. There are substances which exalt an affinity for iodine, that do not exalt the sensitiveness of silver iodide and conversely, for example:

2. Silver iodide was exposed to light for a month under a solution of potassium carbonate, in a test tube, with another test tube, for comparison, containing silver iodide under water only. The alkali did not in the least increase the tendency of the iodide to darken.

3. Starch, which has a well-known affinity for iodine, does not appear to increase the sensitiveness of silver iodide by contact with it.

These experimental results appear to be incompatible with the Poitevin-Vogel theory.

The view which I have here offered is, moreover, very strongly supported by the phenomena of alkaline development. When a sensitive surface has been exposed to light, the image may be developed by pyrogallol, a neutral organic substance. This development is greatly stimulated by the presence of an alkali, a fact which the Poitevin-Vogel theory leaves unexplained. But according to the view here proposed, viz: that the result of the action of the organic body is not a substitution product, but a halogen acid, (e. g. HI, etc.), it is natural that the presence of an alkali should increase the tendency to form an acid for which it has a strong affinity.

Also, this new explanation is in harmony with received views of the action of the halogens in analogous cases, and particularly with that of the action of chlorine in bleaching organic substances. The modern view of the action is, not that the chlorine attracts the organic body with formation of a substitution compound, but that, by the coöperating affinity of the organic substance for oxygen, and that of the chlorine for hydrogen, an atom of water is decomposed, with formation of hydrochloric acid and peroxide of hydrogen, which latter substance attacks the oxidizable organic body. It will be observed that the reaction is exactly the same in both cases, the bleaching and the photo-chemical. In fact, the parallelism is in all respects as complete as it can possibly be, and the analogy lends a strong support to the view that I have here expressed.

I conclude, therefore, that such organic bodies as increase

the sensitiveness of the silver haloids to light, do so, not by forming substitution compounds with the halogen, but by promoting, in virtue of their affinity for oxygen, the decomposition of water by the halogen.

There is, probably, another affinity which plays some part in the tendency to form the halogen acid, and that is the tendency shown by the silver haloid to form combinations with the corresponding halogen acids, e. g. hydroargentic iodide AgIHI , etc., in the absence of an alkali.

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