

ART. XLVIII.—*On Photobromide and Photoiodide of Silver*;  
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*Photobromide of Silver.*

THIS substance is formed for the most part by the same reactions as the corresponding chlorine salt.

It is not however to be supposed that all reddish-brown substances resulting from the action of reducing agents on silver bromide are the photosalt. By reduction, AgBr may yield a brownish colored form of silver, which, mixed with unreduced AgBr may form a substance resembling the photosalt, but having none of its properties. The two are easily distinguished by the action of cold nitric acid which added to a brown mixture of AgBr and Ag quickly dissolves the silver leaving AgBr. On the photosalt it has no action.

A beautiful variety of photobromide is easily obtained by dissolving silver nitrate in ammonia and adding it to ferrous sulphate previously mixed with solution of soda. Then KBr is added dissolved in dilute sulphuric acid, until the mixture has a strong acid reaction.

Sometimes this method gives immediately a fine purple, sometimes a brown product. But in either case, after washing and cautiously heating with dilute nitric acid, a beautiful purple results. Much care is needed in the nitric acid treatment or particles of yellow bromide will form.

A specimen obtained in this way gave figures indicating 7.25 per cent of subbromide. Each specimen however varies in composition, often very materially.

I subsequently found it desirable in some degree to vary the method and to determine the best proportions in which the materials were used, to obtain a constant product. That which I prefer to use is as follows:

Six grams of silver nitrate are to be dissolved in 200 centimeters cube of water and ammonia added until the precipitated oxide re-dissolves easily. Twelve grams of ferrous sulphate are dissolved in 200 c. c. of water and the silver solution is poured into this. Then four grams pure caustic soda dissolved in 50 c. c. of water are added, let stand a few minutes, then five grams of KBr dissolved in a little water. Finally, dilute sulphuric acid until the whole has a strong acid reaction.

This product, well washed and then heated cautiously with nitric acid 1.36 diluted with five times its bulk of water, gives photobromide of a shade of royal purple, extremely beautiful.

Notwithstanding its fine color it proved to contain but little subbromide, not quite one per cent (0.98 p. c.).

Various other methods may be employed. Silver bromide

may be dissolved in ammonia and be treated first with ferrous sulphate and then with dilute sulphuric acid. This method, which is very good with the chloride, is less available for the bromide because of the less solubility of the normal bromide in ammonia, so that although the product is good it is small in quantity.

Very good results are obtained by dissolving silver phosphate, nitrate and probably almost any other salt of silver in ammonia, adding ferrous sulphate and after two or three minutes, hydrobromic acid.

Potash bromide and cupric sulphate may be made to act on metallic silver in fine powder, but the product is contaminated with much copper, difficult to get rid of.

When AgBr is treated with sodium hypophosphite a brown or brownish purple form of photobromide is obtained which seems to be more easily decomposed by nitric acid than most other forms of this substance.

Potash or soda with oxidable organic substances, made to react on silver nitrate and then treated with HBr gives the photobromide. With soda and milk sugar or aldehyde a rose-colored or pink product is generally obtained.

*Reactions.*—In strong solution of potassic iodide it dissolves and this solution by dilution lets fall pale yellow normal bromide. With a weaker solution it becomes somewhat lighter in color.

With acid ferric sulphate there is no action in the cold, but with a few minutes boiling the photobromide is converted into bright colored normal bromide.

In sodium hyposulphite it dissolves, leaving a little black residue of silver.

With ammonia the action at first seems slower than is the case of the corresponding chloride and if the ammonia is poured over the photobromide in small quantity, it may seem to be without effect. But the photobromide shaken well up in a test tube with a large excess of ammonia is almost instantly blackened.

Exposed to light, the red shades of photobromide darken with great rapidity. Placed along side of the corresponding chloride, the contrast is very striking:—a strong image forms on the bromide long before anything appears on the chloride; nevertheless, if these two films are thrown into a developing solution, the chloride on which nothing could be seen, gives a vigorous positive development, while the bromide which already showed a strong positive image develops a negative one. The details of this reverse development have been already considered in another paper.

As respects the direct effect of light unaided by develop-

ment, the contrast between its action on the normal haloids and on the photosalts is very striking. If a rose-colored photobromide and some normal bromide are exposed side by side the normal bromide (formed in presence of excess of alkaline bromide) darkens but very slowly while the photobromide is quickly acted on. I have seen deep purple photobromide change to brown all over its surface with less than five minutes' exposure to diffuse light in the middle of a room, an amount of exposure which would scarcely have produced a visible effect on normal bromide formed in presence of excess of KBr.

When photobromide is exposed to the spectrum, it shows the same difference in sensitiveness and darkens more rapidly than photochloride. But it gives little indication of color.

When exposed under colored glass photobromide gave distinct indications of reproducing colors, but much less favorably than photochloride. Under green glass it became bluish, under blue greenish, under yellow glass it bleached and under red glass the red of the photobromide remained unchanged.

#### *Photoiodide of Silver.*

The most characteristic color of this substance seems to be a fine rich purple. It is obtained in much the same way as the corresponding chloride and bromide, with this limitation, that an excess of alkaline haloid must not be present, as the photoiodide is quickly destroyed by it. The iodine salt differs much more from the bromide than does the bromide from the chloride and two striking distinctions are, its easy decomposition by its own alkaline salt, and its action with ammonia, as will appear beyond.

A very easy and satisfactory method of obtaining the photoiodide is the following: Silver is to be reduced from the nitrate or chloride, in fine powder in any convenient way; I have usually employed Levöl's method. To a solution of potash, iodine is to be added until the liquid becomes almost black. This iodine solution is to be diluted and poured over the silver by degrees, keeping the silver constantly agitated, until the whole mass becomes clear bright purple.

Any excess of silver present may be removed by boiling with dilute nitric acid, but this operation requires far more circumspection than in the case of the corresponding chlorine and bromine products. The acid (1.36 was used) must be diluted with twelve or fifteen times its bulk of water, and the boiling must be very short, otherwise the photoiodide is converted into normal yellow iodide.

Another method by which it may be obtained is to add ammonia to silver nitrate in considerable excess and to pour

this into solution of ferrous sulphate. Potassic iodide is dissolved in very dilute sulphuric acid and added till the mixture has a sharp acid reaction. It is necessary to observe that the KI added must be somewhat short of a proportion equivalent to that of the silver. Any excess of silver may be removed in the manner already explained.

Different specimens of the purple product in this way obtained gave various amounts of  $\text{Ag}_2\text{I}$  from 0.64 per cent to 4.63. The same remark made as to the meaning of these determinations in reference to the other haloids, applies to this.

The method of roasting silver oxide until it is black and acting on it with the hydrogen acid of the halogen, which works well in the case of the chloride, does not answer well for the iodide.

When silver iodide is boiled with solution of sodium hypophosphite, it gives a brown product, evidently indicating that reduction to some extent has taken place; the hypophosphite solution may or may not show traces of iodine. The color of the silver iodide may show a very marked darkening, and yet the solution may give no trace of iodine by the most delicate reagents.

This was very difficult to explain until I found that silver iodide has the property of taking up and retaining small portions of iodine, a reaction not very surprising in view of the tendency I have found in silver haloids to take up foreign substances of very various natures, and also of the facility with which iodine is taken up by alkaline iodides. This property in silver iodide was verified by shaking up portions of freshly precipitated and still moist  $\text{AgI}$  with iodine solutions. Alcoholic solution of iodine diluted until it has a pale sherry wine color is quickly decolorized by  $\text{AgI}$ , and the same thing happens with a very dilute solution of iodine in KI, which in a few minutes becomes as colorless as water.

This reaction I found particularly interesting, for it not only explained the action of hypophosphite in the case just mentioned, but also gave a clue to the cause of a phenomenon I observed more than twenty years ago, and which then and long afterwards seemed to me an unanswerable argument in favor of the physical nature of the latent image.

At the time referred to I formed films of pure silver iodide entirely isolated from foreign matter, by reducing metallic silver on plates of ground glass, iodizing them with alcoholic solution of iodine, or with Lugol's solution, then washing most thoroughly under a tap for hours. When these films of silver iodide were exposed to light, they received an invisible image which could be developed. But these invisible images, if the plates were laid aside in the dark, had the property of fading

out in a few days or weeks, then could no longer be developed, but the film could receive a fresh image. This seemed an unanswerable proof of the physical nature of the latent image at least on silver iodide. The argument was: If the production of this latent image is the result of chemical action involving the loss of iodine by the silver salt, how then is this iodine recovered when the image fades out? If it is formed of subiodide, where does this latter substance get back its iodine to return to the normal form, as it unquestionably does?

No answer could be given then or after, and this experiment, repeated and confirmed by others, has always seemed the strongest support of the physical theory. When, however, it appears that silver iodide can take up iodine and hold it, the course matters follow becomes evident. By the action of light a very small quantity of subiodide is formed, and combines with the normal to form photoiodide. The iodine set free evidently does not pass off but remains combined with neighboring molecules of  $\text{AgI}$ , and in the dark gradually re-combines with the photoiodide re-converting it to normal  $\text{AgI}$ . In this retention the lower tension of iodine as compared with bromine and chlorine no doubt plays its part.

In thus explaining away the fading out of the latent image on silver iodide, the last argument in favor of the physical theory is destroyed, while the chain of proof supporting this new explanation, that the latent image consists of normal haloid combined with its own subsalt, remains unbroken.

*Reactions.*—When ammonia is poured over purple photoiodide of silver, the color quickly passes to a salmon and then, even after some days, seems to undergo no further change. Of separation of metallic silver as in the case of the corresponding chloride and bromide, there is no trace.

In sodium hyposulphite it dissolves slowly, leaving a slight but distinct residue.

Dilute nitric acid mixed with dilute solution of  $\text{KI}$  slowly but completely converts it to normal silver iodide.

Light acts slowly upon it, changing the color to greenish-gray.

I have already spoken of the remarkable manner in which light acts reversely by development on photobromide. On photoiodide the effect is usually the same as on photochloride, viz: the action is direct. But occasionally it reverses and the exposed part comes out lighter in development than the part that has not been exposed. In this respect the behavior of the iodine compound is intermediate between that of the chlorine and the bromine.

*Note in Conclusion.*

The investigations of which the preceding pages are the result, are still unfinished. I have very lately observed the formation of another group of silver haloids quite different from the photosalts. The members of this new group are deeply colored, purple or red, not unlike the photosalts, but are sharply distinguished from them by very different reactions. The photosalts are unaffected by cold strong nitric acid; these new salts are by very dilute acid instantly converted into a pale pink substance which appears to be a photosalt. But the most striking difference is in the action of ferric chloride. A strong solution of this substance shows no action with the photosalts unless left in contact for many hours or days. But these new haloids are instantly converted by it into what is apparently light pink photosalt.

So energetic is this action that a solution of ferric chloride containing one part only to a thousand of water quickly attacks these dark purple salts and decolorizes them. Such a solution might remain indefinitely in contact with the substances I have called photosalts without affecting them.

Other differences exist. So far as I have yet been able to observe these new haloids are formed pure, whereas the photosalts are almost always contaminated with either free silver or free subsalt, or both. As yet there has been no time to fix with exactness their mode of formation or their properties, which I hope to do at a future day.

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