IV.—*On the Action of Light upon Chloride of Silver.*

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THE blackening produced by light upon chloride of silver in the moist state was ascribed by Scheele to the liberation of chlorine, and the deposition of metallic silver. He proved that the blackened mass was only partially soluble in ammonia, and that the portion which remained undissolved by this re-agent was soluble in nitric acid. Daniell and others considered the blackening to be due to the formation of oxide of silver, imagining the decomposition of the water present by the chlorine, to be accompanied by a corresponding oxidation of the reduced silver. Others, again, have supposed the formation of a subchloride.

The few experiments which I subjoin tend, unmistakeably, to support the view originally advanced by Scheele.

(1.) Two or three grammes of dry chloride of silver were sealed in a glass tube, and exposed to direct and diffused sunlight. There was increased tension in the tube. Chlorine was shown, by the iodine test, to be present in the free state.

(2.) A portion of chloride of silver, dried at 100° , was introduced into a perfectly dry tube. The tube being then half-filled with pure and dry benzole, and heated until the boiling of the benzole had expelled all the air, was hermetically sealed, and exposed with agitation to the light. The rapid blackening which the chloride here underwent, proved the presence of oxygen to be unnecessary.

(3.) Four or five grammes of moist chloride of silver were sealed in a tube. The tube was half filled with water, and hermetically sealed. After exposure to the light for ten or twelve days, with frequent agitation, it was opened, the contents thrown upon a filter, and washed with cold water. On adding nitrate of silver to the filtrate, a precipitate of chloride of silver was formed. The grey mass on the filter was treated with strong ammonia until the latter ceased to dissolve any more of the unaltered chloride. There remained on the filter a slaty grey body, which, in the dry state, took the metallic lustre under the pestle. This body was soluble in nitric acid, not reprecipitable by ammonia, but precipitated by dilute hydrochloric acid. The non-precipitation of the nitric acid solution by the most gradual addition of ammonia, seemed already to point to the absence of chlorine.

(4.) About ten grammes of the moist chloride were introduced into a tube of $1\frac{1}{2}$ ft. in length, and $\frac{3}{4}$ in. internal diameter. After adding water and sealing, the tube was exposed as before. The supernatant liquid was poured off, and the mass washed by decantation. The hydrochloric acid was thrown down by nitrate of silver. The chloride of silver was estimated on a weighed filter

(dried at $100^{\circ}\text{C}.$) $\text{Ag Cl} = 0.2125 \text{ gm.}$

The washed material from the tube was digested with strong ammonia. The slaty-grey residue which subsided, leaving the liquid above quite clear, was collected upon a weighed filter and washed, first with ammonia, then with water

(dried at $100^{\circ}\text{C}.$) Grey substance = 0.1756 gm.

This substance assumed the metallic lustre under the burnisher. It dissolved in warm nitric acid, decomposing the latter. The substance, together with the filter, was thrown into strong nitric acid: after digestion and due dilution, it was filtered. The silver was thrown down by dilute hydrochloric acid, collected on a weighed filter and estimated.

(dried at 100°C.) $\text{Ag Cl} = 0.2254 \text{ grm.}$

Supposing, now, the grey substance obtained to have been metallic silver, it should have given 0.2333 grm. of chloride. The amount actually obtained, though too small, is yet sufficiently near to the calculated quantity to show that the original chloride of silver subjected to the light, had really undergone decomposition into chlorine and metallic silver. That the chloride of silver obtained from the hydrochloric acid, found in the tube on breaking it open, was somewhat smaller than that from the silver, was probably due to an escape of a portion of the free acid by evaporation during manipulation.

(5.) About twelve grammes of the chloride of silver were introduced into a tube; the tube was then half filled with fuming nitric acid, sealed, and exposed as before. On opening the tube it was found to contain hydrochloric acid. The chloride was found to have undergone a blackening quite as deep as that which had taken place in chloride of silver surrounded by water, which was exposed to the same light for the same time. On treating the contents as in experiment (4), there was found

Grey substance	.	.	.	=	0.1643
which gave	.	Ag Cl		=	0.2040

The quantity, supposing the substance to have been silver, should have been

$\text{Ag Cl} = 0.2183$

This is sufficiently near to show that the substance in question was nothing else than metallic silver.

(6.) Confirmatory of experiment 5.

(7.) The circumstances were as in experiment 5, excepting that the nitric acid employed was more dilute.

On treating the contents as in experiment 4, I found

Grey substance = 0.2207 grm.

and this gave

$\text{Ag Cl} = 0.2870$

instead of the calculated quantity

$$\text{Ag Cl} = 0.2932$$

In experiments 4, 5, 6, the grey substance when dry assumed the metallic lustre under the burnisher.

The fact that the chloride of silver was reduced to the metallic state, even in the presence of nitric acid, was quite unexpected. I found that neither by removing the affected mass from the light, and agitating it, nor even by warming it, was the original whiteness restored. Indeed the silver was only very gradually attacked by boiling nitric acid, unless the undecomposed chloride had been previously removed by the action of ammonia. It seems as if the light, in reducing the silver *in spite* of the nitric acid, had thereby thrown it into a more passive state, and that only after contact with the alkaline ammonia, was its original basic condition restored.

The chloride of silver used in these experiments was in every instance washed by decantation, in order to avoid the presence of organic matter.