CLXXV.—*Studies with the Microbalance. Part IV. The Photochemical Decomposition of Silver Iodide.*

By ERNST JOHANNES HARTUNG.

EXPERIMENTAL investigation of the action of light on silver iodide has hitherto furnished no definite result; when insolated in air, the substance slowly becomes greenish-grey, but the actual amount of chemical change appears to be very small and no free halogen has been detected. Koch and Schrader (*Z. Physik*, 1921, **6**, 127) illuminated very minute particles of silver iodide, suspended between the charged plates of a condenser, but could find no changes in weight greater than 1—2%. Koch and Vogler (*Ann. Physik*, 1925, **77**, 495) examined the space lattice of silver iodide by *X*-ray methods; after exposure to sunlight for 4 months, no free silver could be detected, although this was readily found on illumination of silver chloride and bromide for much shorter periods. Various other methods have given negative or indefinite results, although the consensus of opinion appears to be that the change is different in nature from the decomposition of the bromide and chloride Some years ago, the author showed (J., 1922, **121**, 689) that very thin films of silver iodide deposited on vitreous silica lost weigh appreciably when exposed in air to sunlight; the losses were very much smaller than those found for the bromide and chloride, but there was no doubt as to their reality. A thorough study of the question has now been made by means of the Steele-Grant microbalance, on the general lines used successfully in the cases of the bromide and chloride (J., 1924, **125**, 2198; 1925, **127**, 2691) and it has been found that the photochemical decomposition of silver iodide is analogous to that of the other halides of silver; iodine is liberated and, under suitable conditions, the action may be made almost complete. The microbalance employed carried a load of 105 mg. and weighed with precision to 10^{-4} mg.; it had been thoroughly tested for 2 years and was used in very favourable circumstances. The general plan of the work was to iodinate thin films of chemically deposited silver until pure iodide had been formed. The films were then exposed to sunlight for various periods in oxygen, hydrogen, or nitrogen in the presence of a suitable iodine absorbent and subsequently reweighed. The insolated material was then treated in various ways in attempts to discover its nature. A series of experiments on the rate of iodination of silver, and of previously insolated silver iodide, was also made.

Preparation of Films of Pure Silver Iodide.—Light vitreous silica sheets were silvered in the well-known tartrate solution and ignited at 400° in a small electric furnace to drive off all occluded matter. After weighing, these films were hung over carefully purified iodine at room temperature; pearly-yellow iridescent silver iodide was rapidly formed and the films were then reweighed. Comparison of the weights with those calculated from the weight of silver taken showed an average discrepancy of 1 part in 1300 parts; the average weight was 0·34 mg. and the thickness about 0·0002 mm. Precipitated silver iodide is known to adsorb iodine readily, but no evidence of adsorption, or of the formation of polyiodides, was obtained in these experiments.

Photochemical Decomposition of Silver Iodide.—The glass apparatus in which the films were sealed, prior to insolation, was similar to that employed for silver bromide and has already been described (*loc. cit.*). Great care was necessary to prevent damage to the films by flame gases during sealing operations, but repeated tests showed that a good counter-current of purified air gave adequate protection. Before exhaustion, the vessel was filled with oxygen, hydrogen, or nitrogen, which had been specially purified and filtered. Experiments showed that at atmospheric pressure decomposition of the silver iodide was very slow, even after prolonged exposure to strong sunlight, but was hastened by diminution of pressure. The apparatus was therefore exhausted either to 10 mm. pressure or as completely as possible. As heating of the glass walls was inadmissible owing to the sensitive nature of the films, adsorbed gas must have been released slowly during insolation; this is denoted by " res." (*i.e.*, " residual ") in Table I, to indicate that the pressure in the apparatus was less than 0·001 mm. at the time of sealing off from the pump. As absorbent for the liberated iodine, a roll of clean copper gauze was employed at first; this metal is particularly efficient in removing chlorine and bromine from a gas phase, but it was not successful with iodine. Inspection of the gauze after prolonged irradiation of the iodide film showed only slight evidence of tarnish, and at the same time the decomposition of the silver iodide had been very slow. Thus, after more than 6 months' exposure on the roof of the laboratory in an exhausted vessel containing copper gauze, a film of silver iodide weighing about 0·4 mg. had lost only 16·6% of its total iodine. This tardiness of decomposition indicated that the partial pressure of iodine vapour above strongly illuminated silver iodide is very small, for copper tarnishes readily above solid iodine at room temperature (partial pressure of vapour 0·2 mm.). It was subsequently found that silver absorbs iodine vapour with extreme readiness, even when the partial pressure of the halogen is very small, and consequently the lower portion and side-tube of the apparatus were silvered internally before introduction of the photosensitive film. During insolation, this silver deposit was shielded from radiation by opaque wrappings and a marked increase in the rate of decomposition of the halide was observed at once. In all subsequent experiments, therefore, silvering was adopted in order to render the absorption of iodine as complete as possible. The amount of radiant energy absorbed during insolation could not be measured, owing to the progressive change in the colour, opacity, and reflecting power of the films, but a fair indication is given in each case by the length of exposure in days. After a definite period of insolation, during which the film became deep slate-grey, the apparatus was opened under exhaust and purified nitrogen gradually admitted. The film was then removed and weighed; subsequent treatment consisted usually of re-iodination, but attempts were also made to analyse the product of insolation. Table I summarises the results of the experiments, weights being given in mg., and the columns headed F_1 and F_2 denoting the weights of the films after exposure and after re-iodination, respectively. It is evident that decomposition of the silver iodide proceeded very extensively, but only when the apparatus was exhausted;

TABLE I.

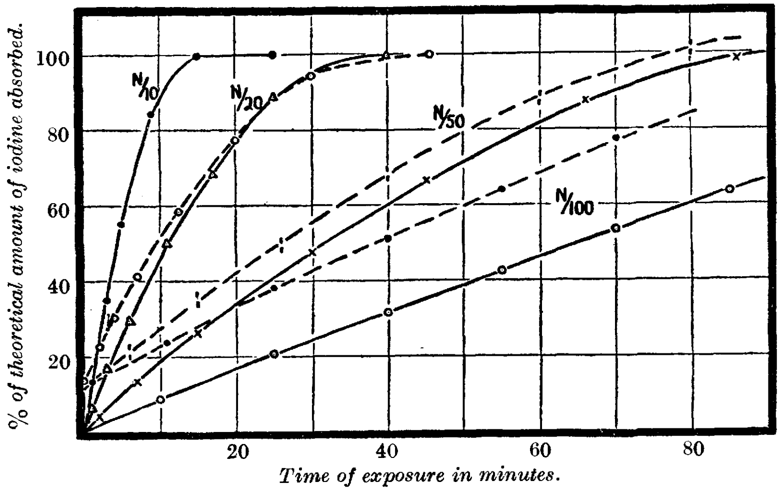
	Ignited	AgI.				% I		Gas in
Expt.	Ag.	Found.	Calc.	F_1.	F_2.	lost.	Days.	apparatus.
1	0·1137	0·2475	0·2476	0·1250	0·2564	91·6	84	H_2 res.
2	0·1814	0·3954	0·3948	0·2102	0·3966	86·5	42	,, ,,
3	0·1120	0·2439	0·2438	0·1300	0·2452	86·3	52	N_2 ,,
4	0·1175	0·2558	0·2557	0·1335	0·2571	88·4	44	,, ,,
5	0·0701	0·1521	0·1526	0·0795	0·1552	88·5	36	,, ,,
6	0·2622	0·5705	0·5707	0·3355	0·5721	76·2	83	Air ,,
7	0·1095	0·2386	0·2383	0·1172	0·2402	94·0	89	O_2 ,,
8	0·1884	0·4101	0·4100	0·2548	0·4116	70·0	81	,, ,,
9	0·1884	0·4095	0·4100	0·4040	0·4153	2·5	86	O_2 10 mm.
10	0·1561	0·3396	0·3398	0·3341	0·3439	3·0	80	,, ,,
11	0·1797	0·3907	0·3911	0·3686	0·3905	10·5	90	N_2 ,,
12	0·1775	0·3863	0·3863	0·3775	0·3869	4·3	40	,, ,,

at 10 mm. pressure, the change was hindered in a remarkable manner. The nature of the residual gas in the apparatus seems to exert little influence and, in particular, the claim that oxygen is necessary is seen to be unfounded. Moreover, the extent of decomposition depends less on the period of exposure than on the thickness of the film, this being approximately proportional to the weight in each case. When all the factors are favourable, as in Expt. 7, decomposition is nearly complete. Certain minor irregularities in the results find a ready explanation in small variations in shape of the apparatus, which affect the ease of diffusion of the liberated iodine to the absorbing silver surface. There can be no doubt, however, that the products of insolation of silver iodide are silver and iodine, and the reason why extensive change is found only in very thin films is because of the opacity of the liberated silver and its very powerful attraction for iodine vapour. There is no evidence of the formation of any sub-iodide.

On re-iodinating the product of insolation, rapid restoration of the former yellow colour of the film took place and the weight was then usually rather greater than that of the original silver iodide. This behaviour was found with the chloride and bromide also and is believed to be due to slight oxidation of the insolated film during manipulation; the discrepancies are usually slight and, except for Expt. 1, are largest when oxygen in appreciable amount has been present in the exposing vessel (Expts. 9 and 10). Many attempts were made to analyse the product of insolation by methods which were devised for the filtration of very small amounts of material (this vol., p. 840), but no procedure for the accurate estimation of silver, or of silver iodide, in less than 0·5 mg. of a mixture of the two could be found. It was hoped to effect separation by suitable reagents, but solvents for silver (*e.g.*, nitric acid) removed the metal imperfectly from the iodide, whilst solvents for silver iodide (*e.g.*, silver nitrate, thiosulphates, cyanides) all attacked thin films of silver rapidly in the presence of oxygen. Solution of both silver and silver iodide was easily effected by ammonium cyanide, which was then treated with acetic or hydrochloric acid; this precipitated all the iodide, and the remainder of the silver as either cyanide or chloride, but in each case the ammonium salt left in solution increased the solubility of the silver salts so markedly that no accurate results could be obtained. Also, estimation by simple evaporation of the ammonium cyanide solution to dryness was rendered useless by the formation of ammonium formate. Another attempted method consisted in evaporating the product of insolation with hydrochloric acid; the iodide was not affected by this treatment, but conversion of the silver presumably present into the chloride was so slow and imperfect that success was impossible. Finally, the attempts at analysis had to be abandoned, after showing that treatment of the product of insolation with silver iodide solvents left a residue of practically pure silver.

Rate of Iodination of Silver Films.—Further evidence as to the nature of the product of insolation of silver iodide was obtained by comparing its rates of re-iodination with those of pure silver. The apparatus and method have been described previously for the case of silver bromide (J., 1924, **125**, 2204); the experiments were carried out in a thermostat at 25° (regulated to 0·1°) and at first solid iodine was placed in the iodinator, giving a partial pressure in the vapour phase of 0·3 mm. However, silver films were attacked so rapidly that conversion into iodide was complete in less than 2 minutes and accurate measurements were impossible. Solutions of iodine from $N/10$ to $N/100$ were therefore made in N-aqueous potassium iodide, and the partial pressures of the halogen above these solutions (not measured) were sufficiently small to give convenient rates of iodination. The results obtained are shown in Fig. 1, in which the iodine absorbed, as percentage of that necessary to form pure silver iodide, is plotted against the total time of iodination in minutes. The continuous curves indicate iodination of pure silver, and the broken curves iodination of the product of insolation of silver iodide, which contained an average of 14% of the total original iodine at the start. In each case, the total area of the film was 146 sq. mm. and the thickness about 0·00015 mm., so that the curves are fairly comparable. The rapid increase in the speed of addition of the halogen as the solution increases in concentration is shown, as well as the striking similarity in speed between silver and insolated silver iodide for the same concentration of iodine which is evident from the approximate parallelism of each pair of curves. This is strong presumptive evidence that one of the products of insolation is silver itself, although, of course, differences in the physical state of the liberated metal may be expected to alter the rates of iodination very considerably, and indeed do so in the cases of the chloride and bromide. The peculiar phenomenon of an optimum halogen concentration which was discovered in the case of chlorine (J., 1925, **127**, 2696) has no parallel with iodine, where the rate of addition of the halogen steadily increases as the concentration in the gas phase rises. No evidence of the formation of sub-iodides or poly-iodides is indicated.

FIG. 1.



Summary.

1. The photochemical decomposition of silver iodide has been studied by means of the microbalance.

2. The maximum percentage loss of total iodine in thin films of silver iodide when suitably insolated was: in hydrogen 91·6%, in nitrogen 88·5%, and in oxygen 94·0%.

3. Evidence is adduced to show that the photochemical decomposition products are silver and iodine, that oxygen is not necessary for the change, and that extensive action is found only with extremely thin films at low gas-pressure in the presence of silver as iodine absorbent.

4. The rates of iodination of silver and of previously insolated silver iodide have been studied; close agreement exists between them for similar concentrations of iodine vapour.

5. No evidence of the formation of silver sub- or poly-iodides has been found.

UNIVERSITY OF MELBOURNE. [*Received, April 7th,* 1926.]
