

## PHOTOTARNISHING OF SILVER AND COPPER\*

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The thermal tarnishing of metals by oxygen and by the halogens<sup>1,2</sup> has been frequently studied, but there appears to be only one reported study of the effects of electromagnetic radiation on any such tarnishing reaction; thus it has been observed that the rate of oxidation of aluminium<sup>3</sup> is increased in the presence of ultraviolet light. In this communication we report experiments which show that the rates of the tarnishing reactions of silver and copper by gaseous iodine, hydrogen iodide, and methyl iodide, are greatly increased by ultraviolet radiation. Furthermore, it is shown that these phototarnishing effects result from the absorption of light by the metal iodide layer rather than the tarnishing gas.

### Experimental

Pieces of cleaned silver or copper (1 cm<sup>2</sup>) were suspended from one arm of a torsion micro-balance of sensitivity c. 2 mg per mm beam movement. The balance was enclosed in an evacuated reaction vessel; light entered the reaction vessel through a plane silica window, and the metal piece was held normal to the light beam, about 15 mm from the window. Progress of a tarnishing reaction was followed by measuring the rate of increase in weight of the metal sample. Gases were admitted to the reaction vessel from a conventional vacuum line.

Silver and copper were obtained as pure metal foils. B.D.H. methyl iodide and iodine were distilled before use. Hydrogen iodide was prepared by the dehydrogenation of tetrahydronaphthalene by iodine, and subsequently distilled.

Light was provided by a Mazda medium-pressure mercury arc, the light of which was focused onto the metal piece with a quartz lens. The heating effect on the metal piece of the resultant intense light beam was measured with a thermistor fixed to a test piece of metal. The light raised the temperature of the metal by about 1–2° at 1 atm gas pressure. The wavelength of the light incident on the metal was varied by the introduction of various filters between the reaction vessel and the light source. Those used were:

(a) Soda glass, cut-off at 325 mμ; (b) Pyrex glass, cut-off at 295 mμ; (c) narrow band pass filter, transmitted from 235 mμ to 400 mμ.

### Results

In all cases studied the plots of film thickness against time were gently curved up to film thicknesses of 200,000 Å. Thermal tarnishing rates were always < 10% of the phototarnishing rates.

(i) *Methyl Iodide*.—Results obtained with various filters for methyl iodide at 125 mm pressure, and 25°, in the presence of silver, are shown in Figure 1. Some

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<sup>1</sup> Cabrera, N., and Mott, N. F., *Rep. Progr. Phys.*, 1948, **12**, 163.

<sup>2</sup> Evans, U. R., *Rev. Pure Appl. Chem.*, 1955, **5**, 1.

<sup>3</sup> Cabrera, N., Terrien, J., and Haman, J., *C.R. Hebd. Séanc. Acad. Sci., Paris*, 1947, **224**, 1558.

additional experiments, carried out using a grating monochromator and a mercury arc, established that visible light ( $\lambda \geq 400 \text{ m}\mu$ ) was not photochemically active. It is therefore apparent from Figure 1 that the photochemically active light for the reaction of methyl iodide with silver is

$$325 \text{ m}\mu \leq \lambda \leq 400 \text{ m}\mu$$

For methyl iodide with copper it is found to be

$$280 \text{ m}\mu \leq \lambda \leq 295 \text{ m}\mu$$

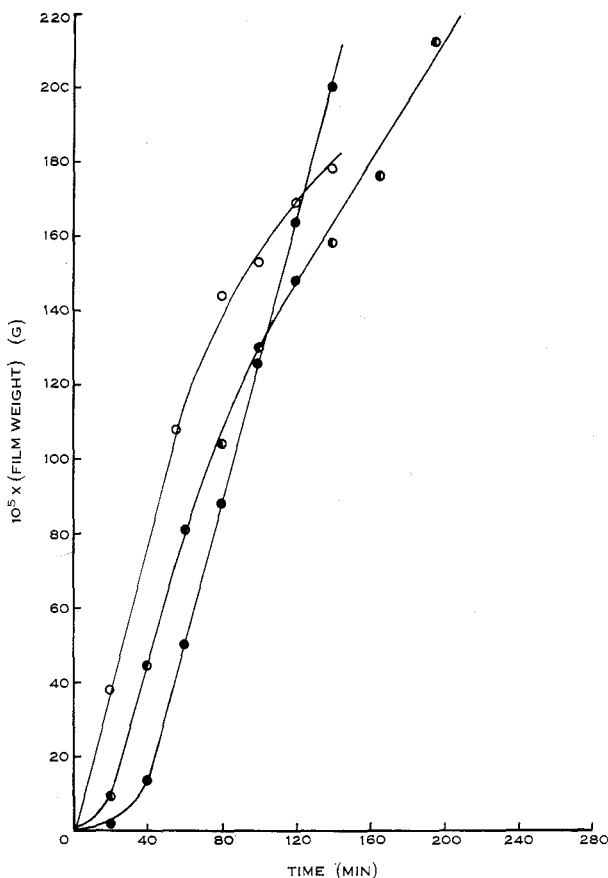


Fig. 1.—Phototarnishing of silver by methyl iodide.

○ Full arc;  
◐ Pyrex filter;  
● soda glass filter.

(In this latter case the lower limit is fixed not by an external filter, but by the internal filtering effect of the gaseous methyl iodide.)

(ii) *Iodine and Hydrogen Iodide.*—Phototarnishing reactions of iodine with silver and copper proceeded at rates comparable to those observed for methyl iodide on silver and copper. Hydrogen iodide (10 mm) phototarnished silver. For both iodine and hydrogen iodide with silver, the photochemically active light was:

$$325 \text{ m}\mu \leq \lambda \leq 400 \text{ m}\mu$$

*Discussion*

There are three lines of argument which suggest that the phototarnishing effects result from light absorption by the metal iodide layer. These are:

(i) For the phototarnishing of silver by the three gases methyl iodide, hydrogen iodide, and iodine, the photochemically active radiation lies in the region

$$325 \text{ m}\mu \leq \lambda \leq 400 \text{ m}\mu$$

This appears to eliminate the possibility that the "active" wavelength region is at all characteristic of the tarnishing gas, but rather that it is characteristic of silver iodide.

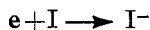
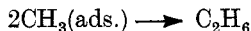
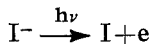
(ii) The induction periods observed for the methyl iodide phototarnishing are consistent with the necessity of establishing a layer of silver iodide on silver before the reaction can be readily propagated.

(iii) The growth of a silver iodide layer proceeds only where light is directly incident on the surface of the metal; this is consistent with the occurrence of a purely surface reaction.

Silver iodide absorbs light in the region between 300 and 400 m $\mu$ . Physically, the process of light absorption in this wavelength range is believed to correspond to the creation of a free electron and an iodine atom in the silver iodide lattice.<sup>4</sup> We therefore tentatively propose a mechanism for the phototarnishing as follows:



The mechanism implies the diffusion of electrons across the growing silver halide layer for step (4), and a parallel diffusion of silver ions across the layer to maintain electrical neutrality. The effect of the light is to produce electrons at the gas/silver iodide interface, and hence to provide a chemical potential gradient for both silver ions and electrons. Similar mechanisms would apply on copper, and to the tarnishing by methyl iodide<sup>5-7</sup> and hydrogen iodide, e.g.



<sup>4</sup> Seitz, F., *Trans. Faraday Soc.*, 1939, **35**, 74.

<sup>5</sup> Schultz, R. D., and Taylor, H. A., *J. Chem. Phys.*, 1950, **18**, 194.

<sup>6</sup> McTigue, P. T., and Buchanan, A. S., *Trans. Faraday Soc.*, 1954, **55**, 1153.

<sup>7</sup> White, P., *Proc. Chem. Soc.*, 1961, 337.