The Light-induced Blackening of Red Mercury(II) Sulphide

By R. Stephen Davidson * and Charles J. Willsher, Department of Chemistry, The City University, Northampton Square, London EC1V 0HB

The blackening of powdered red mercury(II) sulphide suspended in aqueous potassium iodide, upon illumination, has been investigated. The blackened material is shown to contain metacinnabar, the black form of mercury(II) sulphide, by electron spectroscopy for chemical analysis, photo-acoustic spectroscopy, thermal analysis, and *X*-ray powder photography.

WE have recently shown that red mercury(II) sulphide can be used as an electrode material in photoelectrochemical cells, to transduce optical energy to electrical or chemical energy.[1] Under certain conditions, the red sulphide darkens to a brown or black colour, and in this form the material is more photosensitive. Details of this and of blackening conditions have been published.[1c]

Light-induced blackening of red mercury(II) sulphide (cinnabar, vermilion) is known but not qualified. Vermilion used in paintings has been reported to blacken,[2] and the naturally occurring mineral, cinnabar, can darken upon exposure to sunlight.[3,4] This has been suggested as being due to the presence of colloidal mercury, produced by cinnabar degradation in sunlight,[3] and experiments to prove the *loss* of mercury from cinnabar under the action of sunlight failed to do so.[4] It has been noted that the percentage reflectance of red mercury(II) sulphide at 700 nm decreases as the mercury content (atomic percentage) decreases.[5] Table 1, taken from ref. 5, illustrates that a slight lowering in mercury atomic percentage causes a large decrease in percentage reflectance.

TABLE 1

Variation of percentage reflectance of red mercury(II) sulphide with composition

Mercury atomic percentage	Percentage reflectance at 700 nm
50.00	78.00
48.29	34.00
47.57	19.50

Thermally blackened red mercury(II) sulphide is known from *X*-ray powder photography to contain metacinnabar [black mercury(II) sulphide], but the black material obtained from optical blackening was not so identified.[6] Thermal blackening is reversible up to *ca.* 350 °C [7] but we have found optical blackening to be permanent.[1] The literature thus suggests that light-induced darkening is due to colloidal mercury, not metacinnabar, and the colour of the red sulphide is controlled by stoicheiometry. We now know that the blackened sulphide can be employed to effect the photo-assisted electrolysis of water using visible light, and remain stable to photo-solubilisation,[1c] so it is important to know what the black material is, and how it is formed. We have already shown how darkening can be effected, and now report on the identification of optically blackened red mercury(II) sulphide.

EXPERIMENTAL

Red mercury(II) sulphide powder (2 g) was dispersed in potassium iodide solution (0.1 mol dm^{-3}, aqueous, 500 cm^3) and the suspension irradiated by means of a Pyrex-jacketed, water-cooled, 125-W medium-pressure mercury lamp (Hanovia). The lamp was immersed in the suspension, which was stirred vigorously by a Teflon-coated magnetic bead. Blackened mercury(II) sulphide was recovered by filtration, washed with distilled water, and dried at 80 °C. The black powder was analysed by *X*-ray powder photography, photo-acoustic spectroscopy, electron spectroscopy for chemical analysis (ESCA), and thermal techniques. Photo-acoustic spectra were obtained with an OAS 400 instrument (EDT Research, London), ESCA performed with a du Pont 650 electron spectrometer, with an aluminium anode, and thermal analysis was done by a Mettler Thermo-Analyser II Thermobalance, with the sample contained in a platinum–rhodium crucible (90% : 10%) of diameter 8 mm.

RESULTS

X-Ray powder photographs of the blackened sulphide exhibit features seen in those of the black material. The red and black sulphides do have similar photographs, but the intensification of certain lines, characteristic of authentic metacinnabar, in photographs of the blackened red sulphide lead to the conclusion that metacinnabar is present here. ESCA parameters for red, blackened, and black sulphides are shown in Table 2.

TABLE 2

ESCA parameters for mercury(II) sulphide [a]

	Mercury ($4f_{7/2}$)		Sulphur ($2p_{3/2}$)		
Sample	BE/eV	AF	BE/eV	AF	Mercury (AF)/Sulphur(AF)
Red HgS	99.0	0.291	160.0	0.328	0.9
Black HgS	98.6	0.318	160.2	0.303	1.0
Red HgS after 20 h [b]	98.4	0.288	160.4	0.311	0.9
Red HgS after 70 h [b]	98.4	0.315	160.8	0.356	0.9

[a] BE = Binding energy; AF = atomic fraction. No incorporation of K, I, or O was observed. [b] This is the irradiation time of the HgS–KI suspension.

It is evident that no change in valence occurs to either mercury or sulphur; this excludes the presence of colloidal mercury or mercury(I) compounds. No change in stoicheiometry has taken place which rules out any variation in percentage reflectance as shown in Table 1. No oxygen has been incorporated, so the formation of any mercury oxides is unlikely, and no iodine is incorporated, although iodine doping is known to cause red mercury(II) sulphide to appear black.[8] ESCA results indicate quite clearly that the colour change is accompanied by no chemical change to mercury(II) sulphide.

Photo-acoustic spectra of the various materials are presented in Figure 1. Figure 1(*a*) shows the spectra of

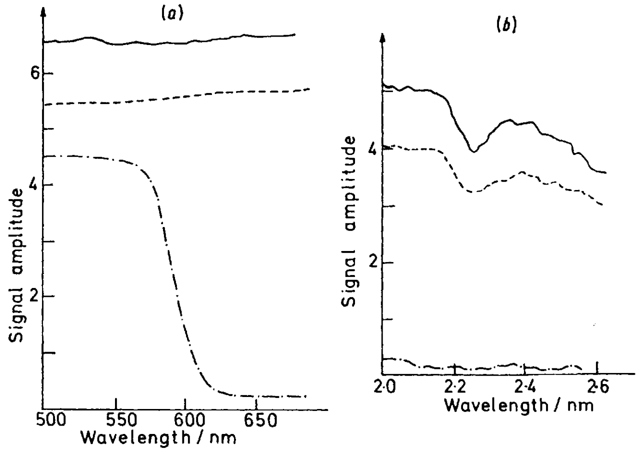

FIGURE 1 Photo-acoustic spectra of black mercury(II) sulphide (——), blackened red mercury(II) sulphide (– – – –), and red mercury(II) sulphide (— • —) for (*a*) visible wavelengths and (*b*) wavelengths in the i.r. region

red, black, and blackened mercury(II) sulphide at visible wavelengths. For the red form, the drop in signal amplitude at *ca.* 600 nm corresponds to the band gap of *ca.* 2 eV.[9,*] The authentic black sulphide shows no such drop in signal, neither does the blackened red sulphide. Figure 1(*b*) illustrates photo-acoustic spectra for wavelengths in the i.r. region; red mercury(II) sulphide undergoes little absorption of radiation, but the black sulphide gives a characteristic spectrum. Blackened red mercury(II) sulphide has a photo-acoustic spectrum very similar to that of metacinnabar, and it is concluded that the optically blackened red sulphide contains metacinnabar.

Thermal analysis of the sulphides provides more evidence for metacinnabar formation. The rate of weight loss (in mg min^{-1}) against temperature for red, black, and the red sulphide irradiated for various times is shown in Figure 2. Parts (*a*) and (*f*) are for cinnabar and metacinnabar, respectively, and exhibit very similar, but not identical plots. The red sulphide has a characteristic feature in the profile at *ca.* 375 °C, marked by an asterisk, and the black sulphide a characteristic feature, marked by a dagger, lying between 100 and 250 °C. Parts (*b*) to (*e*) represent increasing irradiation time and greater degree of blackening, and it is clear that the characteristic feature of the cinnabar profile disappears for larger irradiation times, and metacinnabar's characteristic feature correspondingly appears. It is inferred from these observations that the black sulphide is produced on illumination.

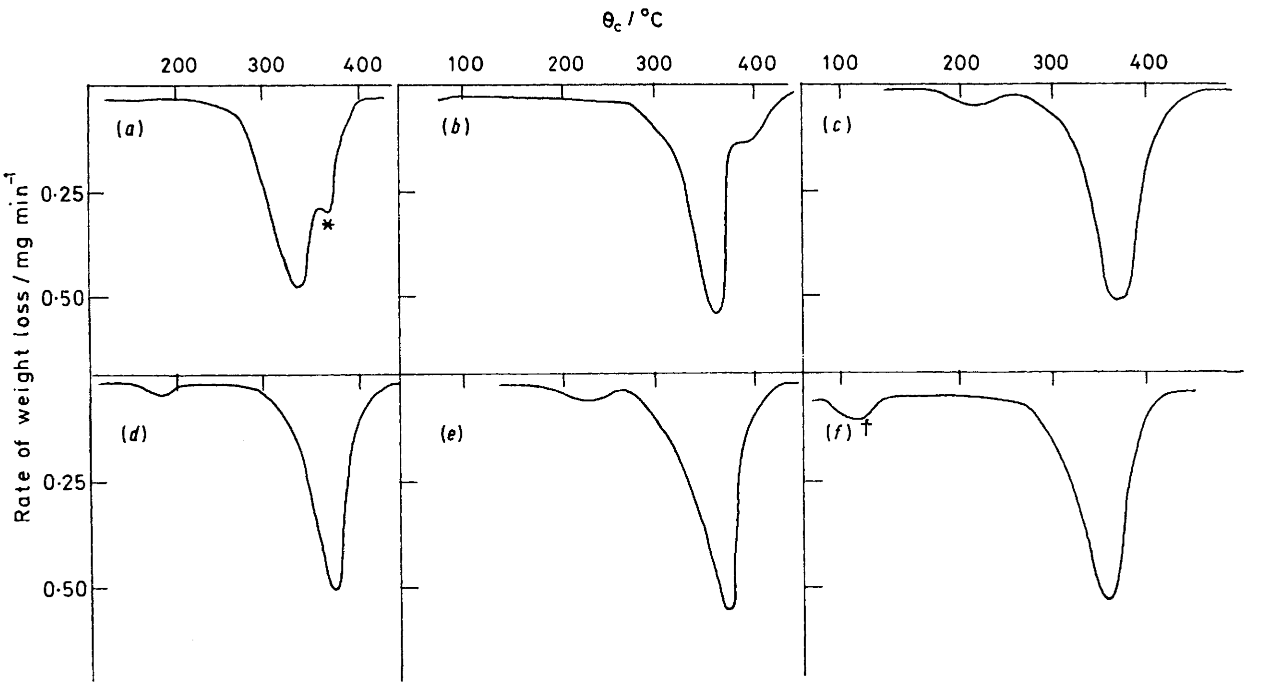

FIGURE 2 Rate of weight loss against temperature for (*a*) red mercury(II) sulphide, red mercury(II) sulphide irradiated in 0.1 mol dm^{-3} potassium iodide for (*b*) 70 h, (*c*) 100 h, (*d*) 200 h, (*e*) 240 h, and (*f*) black mercury(II) sulphide. See text for significance of asterisk and dagger

DISCUSSION

It is found that three agents, namely light, potassium iodide, and water, need to be acting simultaneously on red mercury(II) sulphide to blacken it at ambient temperatures. No darkening occurs in an irradiated mixture of red sulphide and dry potassium iodide crystals, in a stirred sulphide–iodide suspension in the absence of light, in an irradiated suspension of sulphide in pure water, or when a platinum-mesh electrode bearing red material is photoelectrochemically investigated in an electrolyte composed of anhydrous lithium iodide dissolved in dry pyridine.[10] It is known that other reducing

* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

agents, such as potassium bromide, thiocyanate, and chloride can cause darkening.[10] We are concerned with blackening effected in the conditions described above; the dark material formed when natural cinnabar is exposed to sunlight, for example, is not necessarily deemed to be metacinnabar. The mechanism of the red-black transformation is probably not straightforward, and impurities will undoubtedly play a part. It is known that the black-red transition is retarded by trace amounts of iron or zinc sulphides [11] and we consider a rigorous theoretical treatment will be necessary to adequately explain the phenomenon reported in this paper.

We thank the NRDC for a fellowship (to C. J. W.). We are grateful to Professor J. Wightman of the Chemistry Department, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, U.S.A., for performing the ESCA, and to Dr. A. W. Benbow of the Chemistry Department, The City University, for doing the thermal analyses.

[0/1129 *Received*, 17*th July*, 1980]

REFERENCES

1 (*a*) R. S. Davidson and C. J. Willsher, B.P. 7,913,420/1979; (*b*) *Nature* (*London*), 1979, **278**, 238; (*c*) *J. Chem. Soc., Faraday Trans. 1*, 1980, 2587.

2 R. L. Feller, National Gallery of Art, Report and Studies in the History of Art, Washington, D.C., 1967, p. 99.

3 R. M. Dreyer, *Am. Mineral.*, 1939, **24**, 457.

4 W. H. Cropp, *Proc. Aust. Inst. Min. Met.*, 1923, **52**, 259 [*Chem. Abs.*, **18**, 3159(5)].

5 R. W. Potter and H. L. Barnes, *Geol. Soc. Am. Abstr. Programs*, 1974, **3**, 674.

6 C. Brosset, *Naturwissenschaften*, 1936, **24**, 813.

7 J. W. Mellor, ' A Comprehensive Treatise on Inorganic and Theoretical Chemistry,' Longmans, Green and Co., London, 1964, vol. LV, p. 942.

8 M. V. Pashkovskii, V. V. Rybalka, and I. V. Savitskii, *Sov. Phys. Solid State*, 1963, **4**, 1443.

9 W. H. Strehlow and E. L. Cook, *J. Phys. Chem. Ref. Data*, 1973, **2**, 163.

10 C. J. Willsher, Ph.D. Thesis, University of Leicester, 1980.

11 N. Z. Boctor and R. H. McCallister, Year Book – Carnegie Institute, Washington, 1978 (1979), p. 582 (*Chem. Abs.*, **93**, 10842k).