Photo-oxidation of Thallium(I) with the Production of Hydrogen Peroxide

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Examination of the photolytic destruction of luminescence of aqueous thallium(I) solutions containing chloride has revealed that luminescence is lost through oxidation, following the equation: $Tl^{I} + 2H^{+} + O_2 \longrightarrow Tl^{III} + H_2O_2$. Cl^- is necessary for the reaction which is assisted by Tl^{III}. Under similar conditions Sn^{II} is also oxidised with the production of H_2O_2. Pb^{II} does not react in this way.

THE u.v. absorption maximum of thallium(I) in solution shifts to longer wavelengths on addition of chloride ion,[1-3] as does its luminescence,[4,5] while the quantum efficiency of the process decreases slightly.[6] Thallium(I) is determined fluorimetrically in chloride medium [7-9] as more intense sources are available at the longer wavelengths. With the halide concentration greater than 4M the luminescence is weaker in HCl than $CaCl_2$;[10] however analysts [7-9] use solutions containing HCl. Irradiation of a solution of Tl^{I} in an HCl + KCl medium results in a rapid loss of luminescence attributed to the oxidation $Tl^{I} \longrightarrow Tl^{III}$.[9] Loss of luminescence from Sn^{II} solutions on irradiation has been attributed to oxidation,[10] and a similar observation with Pb^{II} has also been reported.[11]

That oxidation is responsible for luminescence decay was inferred from the observation that Sn^{IV} and Tl^{III} do not luminesce. It seems unlikely that Pb^{IV} is so readily produced in solution. Bely and Ochrimenko [12] state that ' chemical analysis ' revealed Tl^{III} in their exposed Tl^{I} solutions, and that the oxidation occurred in solutions containing either chloride or bromide. They found that Sn^{II} and Sb^{III} were similarly photo-oxidised.

If the luminescence can be assigned to discrete complexes of Tl as many workers have supposed,[4-6,10] then an alternative mechanism for the loss of luminescence on irradiation would involve the formation of a non-luminescent complex of the same oxidation state. Woodford has pointed out that it is probable that the $Tl^{I}Cl^{-}$ system does not form discrete (*i.e.*, stoicheiometric) complexes, but rather the Tl^{I} ion exists in a quasi-crystalline ionic assembly in the solution.[1]

The present work shows that a change in oxidation state is the cause of luminescence decay and that this is accompanied by the production of H_2O_2. No luminescence decay could be detected on irradiation of Pb^{II} solutions.

EXPERIMENTAL

Hopkin and Williams laboratory reagent TlCl and B.D.H. laboratory reagent Tl_2O_3 were used to prepare Tl^{I} and Tl^{III} solutions.

pH measurements were made with an E.I.L. model 23A pH-meter.

A Hersch scrubber was employed for the deoxygenation of solutions with ' white-spot ' nitrogen.[13]

A Unicam SP 800 instrument was used to obtain absorbance values for the Tl^{I} and Tl^{III} solutions in 3M-NaCl at the wavelength used for fluorescence excitation (254 nm).

Luminescence measurements were made with an Aminco spectrophotofluorimeter.

An aliquot portion (2 cm^3) of solution in a 10 mm square-section fluorimeter cell was exposed to a 500 W xenon lamp at the focus of a convex silica lens. The approximately parallel beam produced was refocused with a second silica convex lens into the fluorimeter cell through the silica window of a thermostatted (20 °C) water-bath. An iris diaphragm was placed between the two lenses, the edge of the second being viewed perpendicular to the light path with a 1P28 photomultiplier through a 250 nm interference filter. The signal from the photomultiplier was displayed on a potentiometric chart recorder and the iris diaphragm manually adjusted to give a constant standard reading. This compensated for fluctuations in arc intensity.

Oxygen was blown through a capillary tube into the solution to saturate it before exposure. The process was continued during exposure to stir and ensure saturation of the solution with oxygen.

Fluorescence decay curves were obtained by saturating the 2 cm^3 aliquot portion for 15 min with oxygen and then exposing to the arc for 2 min intervals, removing the cell from the water-bath to the spectrofluorimeter, noting the luminescence intensity of the sample, and immediately afterwards the intensity of a standard quinine sulphate solution. The second reading was used to compensate the first for fluctuations in the sensitivity of the fluorimeter. The excitation and emission wavelengths being different in both cases the maximum intensity was recorded.

A Beckman DB spectrophotometer was used to follow the reaction with ceric ion. A calibration curve for Ce^{IV} was prepared at 320 nm by use of the tungsten lamp source. The calibration was effected in 3M-NaCl by taking readings within 2 min of mixing, as Ce^{IV} reacts slowly with Cl^-.

After exposure of a 2 cm^3 aliquot portion of Tl^{I} solution for a certain period, 1 cm^3 was transferred with a dry pipette to a dry 10 mm absorbance cell, to which 0·5 cm^3 (Excelo micropipette) of standard Ce^{IV} solution was

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[1] R. C. Woodford, *J. Chem. Soc.* (*A*), 1970, 651.

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[5] R. E. Curtice and A. B. Scott, *Inorg. Chem.*, 1964, **3**, 1383.

[6] G. Steffen and K. Sommermeyer, *Biophysik*, 1968, **5**, 192.

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[9] G. F. Kirkbright, T. S. West, and C. Woodward, *Talanta*, 1965, **12**, 517.

[10] P. Pringsheim and H. Vogels, *Physica*, 1940, **7**, 225.

[11] G. F. Kirkbright and C. G. Saw, *Talanta*, 1968, **15**, 570.

[12] M. U. Bely and B. A. Ochrimenko, *Bull. Kiev University*, No. 5, Series Astronomy, Physics and Chemistry, 1st edn., p. 15.

[13] D. Gilroy and J. E. O. Mayne, *J. Appl. Chem.*, 1962, **12**, 382.

added. The absorbance of this solution at 320 nm was noted by use of the residual 1 cm^3 in the fluorimeter cell in the reference beam.

The polarograms were obtained with a Radelkis type OH 109 polarograph in conjunction with an internal mercury pool reference electrode.

RESULTS

The rate at which luminescence was destroyed depended on the pH. Figure 1,A shows the decay for 4×10^{-4}M-Tl$^{\mathrm{I}}$ in 3M-NaCl + $4{\cdot}08 \times 10^{-2}$M-HCl. The decay was much slower in neutral solution and faster in 3M or 6M-HCl. An increase in pH during exposure was noted for solutions 3M in NaCl, 4×10^{-4}M in Tl$^{\mathrm{I}}$ + 5·1, 7·0, and $9{\cdot}0 \times 10^{-4}$M-HCl. Exposure of a solution of Tl$_2$SO$_4$ in 2M-H$_2$SO$_4$ for 2 h showed no reduction in luminescent intensity.

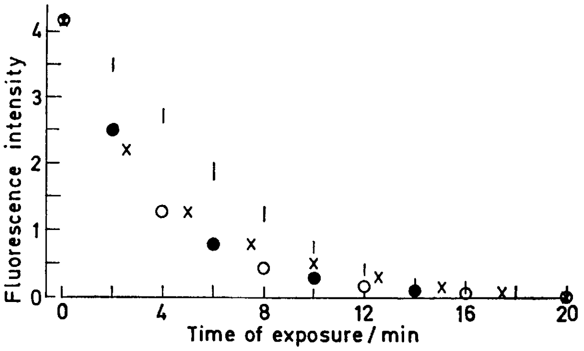

FIGURE 1 A, Vertical bars, luminescence decay on exposure of 4×10^{-4}M-Tl$^{\mathrm{I}}$ in 3M-NaCl + $4{\cdot}08 \times 10^{-2}$M-HCl. The length of the bar gives the standard deviation for five runs; B, filled and open circles, luminescence of mixtures of Tl$^{\mathrm{I}}$ and Tl$^{\mathrm{III}}$ (total concn. = 4×10^{-4}M) in 3M-NaCl; abscissa values = 0 min = 4×10^{-4}M-Tl$^{\mathrm{I}}$, 20 min = 0M-Tl$^{\mathrm{I}}$; filled circles, no H$_2$O$_2$; open circles, +H$_2$O$_2$ equal in concentration to [Tl$^{\mathrm{III}}$]; and C, crosses, calculated luminescence of mixtures of Tl$^{\mathrm{I}}$ and Tl$^{\mathrm{III}}$

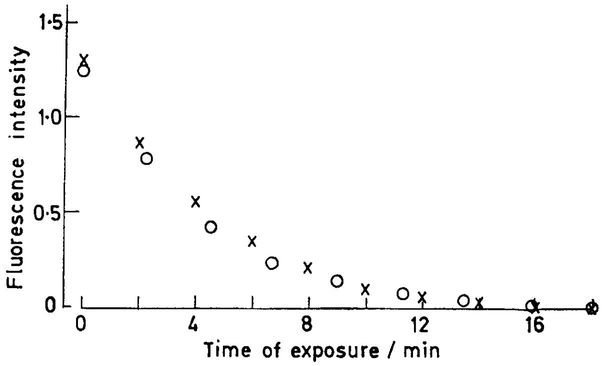

FIGURE 2 A, Crosses, luminescence decay on exposure of 4×10^{-4}M-Tl$^{\mathrm{I}}$ in 3M-NaCl + $4{\cdot}08 \times 10^{-2}$M-HCl containing $0{\cdot}8 \times 10^{-4}$M-Tl$^{\mathrm{III}}$; B, circles, luminescence of mixtures of Tl$^{\mathrm{I}}$ and Tl$^{\mathrm{III}}$ (total concn. = $4{\cdot}8 \times 10^{-4}$M) in 3M-NaCl; abscissa values: 0 min = 4×10^{-4}M-Tl$^{\mathrm{I}}$; 18 min = 0M-Tl$^{\mathrm{I}}$

Oxygen was required for the decay since on deoxygenating a 4×10^{-4}M-Tl$^{\mathrm{I}}$ solution in 6M-HCl in a Hersch cell for 1 h with ' white-spot ' nitrogen and exposing in an oxygen-free cell, no reduction in luminescence could be detected after 3 h.

The unexposed O$_2$-saturated solutions did not react with Ce$^{\mathrm{IV}}$,[14] except slowly by oxidation of Cl$^-$. Exposed O$_2$ saturated solutions reacted rapidly.

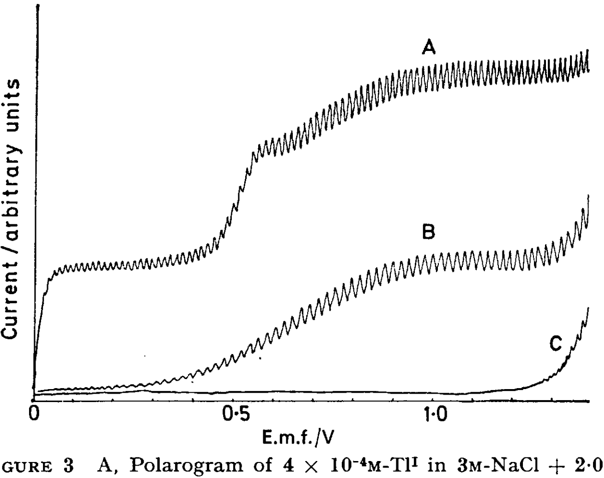

FIGURE 3 A, Polarogram of 4×10^{-4}M-Tl$^{\mathrm{I}}$ in 3M-NaCl + $2{\cdot}04 \times 10^{-3}$M-HCl after exposure for 20 min; B, polarogram of unexposed 4×10^{-4}M-H$_2$O$_2$ in 3M-NaCl + $2{\cdot}04 \times 10^{-3}$M-HCl; and C, blank; 3M-NaCl + $2{\cdot}04 \times 10^{-3}$M-HCl

Figure 3,A shows the polarogram of a 4×10^{-4}M-Tl$^{\mathrm{I}}$ solution in 3M-NaCl + $2{\cdot}04 \times 10^{-3}$M-HCl after exposure to the arc for 20 min. It shows clearly the Tl$^{\mathrm{III}} \longrightarrow$ Tl$^{\mathrm{I}}$ reduction at around 0 V and the Tl$^{\mathrm{I}} \longrightarrow$ Tl^0 reduction at 0·5 V, both superimposed on an irreversible wave identical with that in Figure 3,B which is the polarogram of a 4×10^{-4}M-H$_2$O$_2$ solution in 3M-NaCl + $2{\cdot}04 \times 10^{-3}$M-HCl. Hydrogen peroxide, therefore, seems to be the species responsible for the reductive power of the solution after exposure.

To obtain the maximum range on the polarograms, and the minimum oxidation of Cl$^-$ conducive with rapid luminescence decay, exposures were conducted on solutions $2{\cdot}04 \times 10^{-3}$M in HCl. In this case luminescence was destroyed after exposure for 26 min.

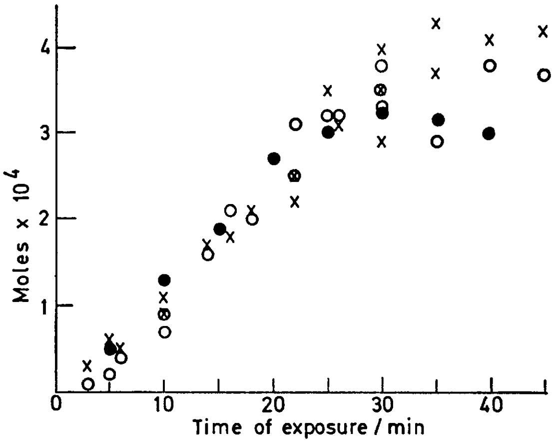

FIGURE 4 Plots against time of exposure of 4×10^{-4}M-Tl$^{\mathrm{I}}$ in 3M-NaCl + $2{\cdot}04 \times 10^{-3}$M-HCl of A, filled circles, 0·5 × moles Ce$^{\mathrm{IV}}$ consumed; B, open circles, moles H$_2$O$_2$ produced measured polarographically; and C, crosses, moles Tl$^{\mathrm{III}}$ produced measured polarographically

The concentration of Tl$^{\mathrm{III}}$ was determined directly

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[14] P. A. Shaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 2169.

from the wave-height at 0·2 V and is shown in Figure 4,C. The H_2O_2 values were obtained by subtracting from the total wave height at 1·1 V the Tl^{III} wave-height on the same polarogram and also the constant Tl^{I} wave-height measured on the unexposed solution. These are shown in Figure 4, B. Figure 4,A shows the H_2O_2 determined cerimetrically.

254 nm was the wavelength used to excite luminescence. That this wavelength does not correspond to the absorption maximum of Tl^{I} in 3M-NaCl is due to the steep dependence of light output on wavelength for the xenon arc source in the spectrofluorimeter. The excitation wavelength (*i.e.*, excitation maximum) was not constant throughout the decay, shifting to shorter wavelength during the final 20%. This is to be expected as the absorption maximum of $Tl^{III}Cl^-$ lies at a longer wavelength than the $Tl\text{-}Cl^-$ absorption maximum.

In an attempt to simulate the luminescence decay curve of Figure 1,A, mixtures of Tl^{I} and Tl^{III} of total concentration 4×10^{-4} were prepared in 3M-NaCl. Alternative solutions ($[Tl^{I}] = 4{\cdot}0, 3{\cdot}2, 2{\cdot}4, 1{\cdot}6$, and $0{\cdot}8 \times 10^{-4}$M) were prepared containing H_2O_2 in equal concentration to $[Tl^{III}]$. To plot these points on the same axes as Figure 1,A, was necessary to assign a concentration scale to the abscissa. Since the luminiscence was destroyed after exposure for 20 min it was concluded that $[Tl^{I}] = 0$M at 20 min, so that intermediate concentrations could be assigned to the other abscissa times, it being assumed that the oxidation proceeded at a constant rate (*i.e.*, 5 min = 3×10^{-4}M-Tl^{I} + 10^{-4}M-Tl^{III}, 10 min 2×10^{-4}M-Tl^{I} + 2×10^{-4}M-Tl^{III}). The observed values for the mixtures are plotted in Figure 1,B, and calculated values plotted in Figure 1,C, it being assumed that Tl^{I} and Tl^{III} are the only absorbing and Tl^{I} the only luminescent species.

The continuous nature of the points in Figure 1,B indicates that H_2O_2 has no effect on the luminescence. That Figures 1,B and 1,C are quite different from Figure 1,A indicates that an incorrect assumption has been made in assigining concentration values to the abscissa, *i.e.*, the luminescence decay shows that the oxidation does not proceed at a constant rate, but is initially slow.

The decay of Tl^{I} luminescence was unchanged by adding up to 10^{-4}M-H_2O_2. Figure 2,A shows the decay when $0{\cdot}8 \times 10^{-4}$M-Tl^{III} was added before exposure. Figure 2,B shows mixtures of Tl^{I} and Tl^{III}. The abscissa values for concentration of Tl^{I} have been assigned as for Figure 1,B, *i.e.*, by assuming that $[Tl^{I}] = 0$ at 18 min, and that the reaction proceeds at a constant rate. The good agreement between Figures 2,A and 2,B shows that in the presence of Tl^{III} the latter assumption is correct.

Polarographic examination of a freshly prepared 4×10^{-4}M-$SnCl_2$ solution in 3M-NaCl + 4×10^{-4}M-HCl, before and immediately after exposure for 20 min, showed that the Sn^{II} had been completely oxidised and that some H_2O_2 had been produced. As no precaution was taken to exclude O_2 during preparation of the solution, the polarogram of the unexposed solution showed some Sn^{IV} to be present initially. The whole operation, preparation of solution, exposure, polarographic analysis was effected within 1 h.

Attempts to destroy the luminescence of a 4×10^{-4}M-Pb^{II} solution failed despite working in 3·3M-HCl + 0·8M-KCl,[11] and in 6M-HCl. Polarograms revealed that no H_2O_2 was produced on exposure. The 20% loss in irradiation for 2 h in the fluorimeter[11] referred to a 4×10^{-6}M solution in which the luminescence is only just discernable above the background.

DISCUSSION

The polarography and cerimetry show that Tl^{III} and H_2O_2 are produced simultaneously. That H^+ and O_2 are required for the reaction suggest that it follows the stoicheiometry (1). The production of H_2O_2 on irradiation by u.v. light may seem incompatible with its use as an actinometer[15] but the absorption band of H_2O_2 is completely blanketed by those of Tl^{I} and Tl^{III}. The redox potential for thallous–thallic salts is reduced with increasing chloride concentration,[16] and this explains why the oxidation does not occur in the absence of chloride.

$$Tl^{I} + 2H^+ + O_2 \xrightarrow{h\nu} Tl^{III} + H_2O_2 \tag{1}$$

Bely and Ochrimenko[12] suggested a free-radical mechanism following charge-transfer absorption. However they did not report the production of H_2O_2, and it is difficult to see a radical reaction giving so high a yield of H_2O_2 for Tl^{I} oxidised. To explain the 1 : 1 ratio of $Tl^{III} : H_2O_2$ the mechanism shown in reactions (2)—(5) is suggested; this mechanism does not account for the influence of Tl^{III} on the rate of the oxidation.

$$Tl^{I} + h\nu \longrightarrow Tl^{I*} \tag{2}$$

$$Tl^{I*} + O_2 \longrightarrow Tl^{I}O_2^{*} \tag{3}$$

$$Tl^{I}O_2^{*} + H^+ \longrightarrow Tl^{III} + HO_2^- \tag{4}$$

$$HO_2^- + H^+ \longrightarrow H_2O_2 \tag{5}$$

[1/2346 *Received, 7th December*, 1971]

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