Evidence for Formation of a $[TlOH]^+$ Complex

By PETER O'NEILL and DIETRICH SCHULTE-FROHLINDE

(*Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, 433 Mülheim a.d. Ruhr, Stiftstrasse 34—36 W. Germany*)

Summary Using pulse radiolysis with conductivity and spectrophotometry as a detection system evidence was found for the formation of the monocharged complex $[TlOH]^+$ which is in equilibrium with Tl^{2+} (pK 4·6±0·2); $k(H^+ + [TlOH]^+)$ and $k(Tl^{2+} + H_2O)$ are 1·4 (±0·5) × 10^{10} l mol^{-1} s^{-1} and 3·5 × 10^5 s^{-1} respectively.

Tl^{2+} HAS been suggested to be an intermediate formed in the radiolysis of aqueous solutions[1,2] of Tl^+ and in the oxidation[3] of Fe^{2+} by Tl^{3+}. However, there appears to be a discrepancy in the literature[1,2] concerning the optical absorption spectrum of Tl^{2+} expected to be formed *via* reaction (1) or formed *via* photolysis[4] at different pH values.

$$OH + Tl^+ \longrightarrow Tl^{2+} + OH^- \qquad (1)$$

In pulse-irradiated neutral solution an absorption maximum of a transient was observed at 360 nm[1] which was absent in 1M perchloric acid.[2] A transient spectrum produced in the flash photolysis[4] of a 1M perchloric acid solution containing Tl^{3+} showed an absorption maximum at *ca.* 270 nm.

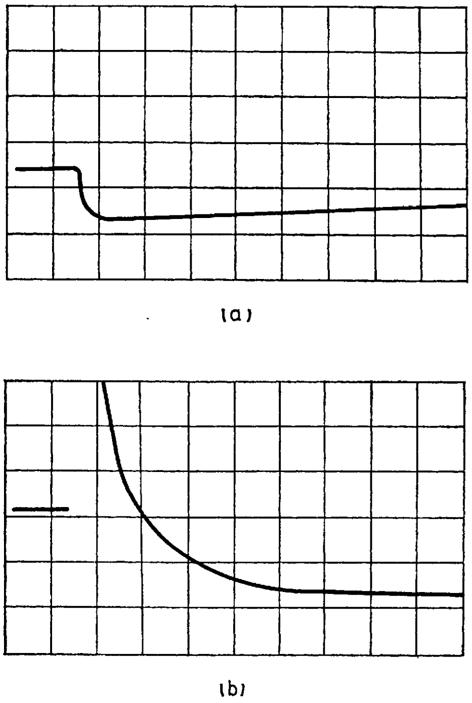

FIGURE 1. Oscillograms showing the time dependence of the conductivity in pulse irradiated aqueous solutions of 10^{-4} M Tl_2SO_4 saturated with N_2O at 21 °C (500 rad per pulse): (a) pH 4, sweep 10 μs/div., sensitivity 34 mV/div; (b) pH 5·45, sweep 10 μs/div., sensitivity 2 mV/div.

We have performed pulse radiolysis and pulse conductivity measurements[5] using thallium(I) sulphate solutions saturated with N_2O at 21 °C. In such a solution the primary effect of electron irradiation produces OH· radicals (90%) and H atoms (10%). The H atoms have been shown[6] to reduce Tl^+ to Tl^0. The OH· radicals are expected to react according to reaction (1), in which an ion pair is generated. At pH 4 the OH^- formed disappears very rapidly (*ca.* 2—4 μs) by reaction with H^+ and, experimentally, an overall removal of conductivity was observed (Figure 1a). Taking a mobility of 1·6 × 10^{-3} V^{-1} cm^2 s^{-1} for Tl^{2+} and using the known mobilities for all the other ions involved a G (Tl^{2+}) of *ca.* 5 was obtained from the removal of conductivity at pH 4.

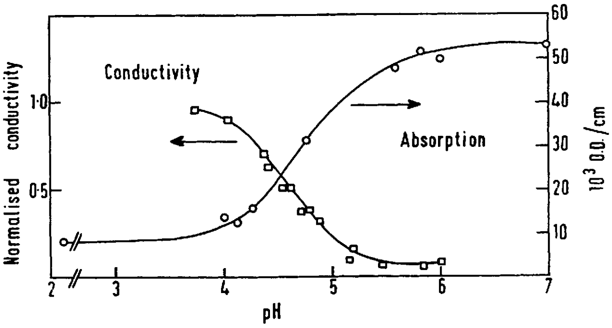

FIGURE 2. The dependence of the optical absorption (○—○—○) 5 μs after pulse (10^{-3} M Tl_2SO_4, N_2O saturated, 360 nm) and the removal of conductivity □—□—□ (10^{-4} M Tl_2SO_4, N_2O saturated) as a function of pH using 1 μs electron pulses of *ca.* 500 rad. The OD values are normalised to a dose of 3 krad. Temperature 21 °C. The pH was adjusted with perchloric acid.

However, at pH >5·5 the amount of the removal is reduced by 90% (Figure 1b). This effect is explained by assuming that the reaction of OH with Tl^+ at pH 5·5 leads to the monocharged complex $[TlOH]^+$ and not to Tl^{2+} and OH^-. From the dependence on pH of the removal of the conductivity a pK value of 4·6 (±0·2) for the formation of the $[TlOH]^+$ complex was obtained (Figure 2). Schwarz *et al.*[2] have suggested that the absorption maximum at 360 nm observed by Cercek *et al.*[1] could be due to $[TlOH]^+$. Our transient spectrum at pH 2 in N_2O-saturated perchloric acid containing 10^{-3}M Tl_2SO_4 is similar to that observed in 1M perchloric acid by Schwarz *et al.*[2] From absorption measurements (λ 360 nm) after the pulse as a function of pH we obtained a pK value for a protonic equilibrium of the transient of 4·7 (±0·2) (Figure 2) [equation (2)]. From optical measurements a value for k_2 was obtained of 1·4 (±0·5) × 10^{10} l mol^{-1} s^{-1}. Thus from the pK value and k_2 the pseudo-first-order rate constant k_{-2} is 3·5 × 10^5 s^{-1}. A value of $2k$ = 5 × 10^9 l mol^{-1} s^{-1} was measured for the bimolecular disappearance of $[TlOH]^+$.

$$Tl^{++} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [TlOH]^+ + H^+ \qquad (2)$$

From the agreement between the pK values observed by conductivity and by optical methods it is suggested that the species responsible for the change in conductivity is in fact the same as that which is responsible for the change in absorption at 360 nm. We therefore conclude that the species responsible for the absorption at 360 nm is the complex $[TlOH]^+$. Since this species is only formed at pH > *ca* 4 it further follows that the pure spectrum of Tl^{2+} is observed only in solutions at pH < *ca.* 4.

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