On the Equilibrium between Thallium(II) Hydroxide and Hydroxothallium(II) Ion: A Pulse-radiolysis Study

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The oxidation of Tl^+ by $OH^\bullet$ radicals leads to an addition product $[Tl(OH)]^+$ which exists in the equilibria $[Tl(OH)]^+ \rightleftharpoons Tl^{2+} + [OH]^-$ and $Tl[OH]_2 \rightleftharpoons [Tl(OH)]^+ + [OH]^-$. The previously unrecorded pK of the latter equilibrium has been determined as 7.7 ± 0.2. The optical-absorption spectrum of $Tl[OH]_2$ shows a maximum at 370 nm (ε 3.8×10^3 dm^3 mol^{-1} cm^{-1}) and a band rising towards the u.v. below 300 nm. Thallium(II) hydroxide, in contrast to Tl^{2+} and $[Tl(OH)]^+$, does not exhibit good oxidizing properties. It may even transfer an electron to suitable acceptors such as tetranitromethane.

THE formation of Tl^{2+} ions has been observed during the oxidation of Tl^+ by $OH^\bullet$ radicals,[1] the reduction of Tl^{3+} by H atoms and by other reducing agents,[2,3] and u.v. photolysis of thallium(III) perchlorate solutions.[4] Recently O'Neill and Schulte-Frohlinde,[5] using a pulse-radiolysis–conductivity technique, were able to demonstrate that the initial step of the Tl^+ oxidation is the formation of an addition product [equation (1)] which is in equilibrium with Tl^{2+} ions [equation (2)]. A pK of

$$Tl^+ + OH^\bullet \rightleftharpoons [Tl(OH)]^+ \qquad (1)$$

$$[Tl(OH)]^+ + H^+(aq) \rightleftharpoons Tl^{2+} + H_2O \qquad (2)$$

4.6 was determined. The ions Tl^{2+} and $[Tl(OH)]^+$ not only differ with respect to their charge but also exhibit different optical-absorption spectra. Both show a strong band rising towards the u.v. ($\lambda_{max.} < 250$ nm), but only $[Tl(OH)]^+$ has an additional band peaking at 360 nm. Both these ions have been found to act as oxidants, *i.e.* they accept electrons from for example dimethoxybenzenes with approximately equal rate constants.[6]

In the present paper we report the further equilibrium (3) and some physicochemical properties of the hydroxo-complexes of thallium(II).

$$Tl[OH]_2 \rightleftharpoons [Tl(OH)]^+ + [OH]^- \qquad (3)$$

EXPERIMENTAL

All the experiments were made using a combined optical and conductivity pulse-radiolysis technique described in detail elsewhere.[7,8] Interpretation and quantitative analysis of such data is also well documented.[7,8]

Irradiations were with 1 μs pulses of high-energy electrons from a 1.5-MeV Van de Graaff generator (absorbed energy: *ca.* 700 rad per pulse).† Solutions were prepared from $Tl_2[SO_4]$ and Millipore-filtered water at room temperature. The samples were also saturated with N_2O. The latter converts hydrated electrons, formed in the irradiated aqueous system, into hydroxyl radicals *via* $N_2O + e^-(aq) \longrightarrow N_2 + [OH]^- + OH^\bullet$. Under these conditions, $OH^\bullet$ radicals are formed with $G = 5.5$ (yield of species per 100 eV of absorbed energy) and account for *ca.* 90% of the primary reactive species in the irradiated system (the remaining 10% are H atoms). The thallium(I)-ion concentration was generally kept to 10^{-3} mol dm^{-3}. Owing to the high rate constant for reaction (1) [$k(Tl^+ + OH^\bullet) = 7.6 \times 10^9$ dm^3 mol^{-1} s^{-1}] [1] the $OH^\bullet$ addition to Tl^+ occurs quantitatively within the duration of the pulse.

RESULTS AND DISCUSSION

The reaction of Tl^+ ions with hydroxyl radicals leads to changes in the conductivity, $\Delta\Lambda$, over most of the pH range. Figure 1 (circles) shows the pH dependence of $\Delta\Lambda$ (in S cm^2 mol^{-1}) the latter being measured immediately after the pulse, *i.e.* completion of the $Tl^+ + OH^\bullet$ reaction. Both in acid and in basic solutions, $\Delta\Lambda$ was negative which means that a decrease in conductivity is observed as a result of the pulse irradiation. No change in conductivity was observed at pH *ca.* 5.5—6. The left-hand side (pH <6) of the curve essentially shows the results published by O'Neill and Schulte-

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† 1 rad = 10^{-2} J kg^{-1}.

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[8] K.-D. Asmus, *Internat. J. Radiation Phys. Chem.*, 1973, **4**, 417; 'Fast Processes in Radiation Chemistry and Biology,' eds. G. E. Adams, E. M. Fielden, and B. D. Michael, The Institute of Physics, Wiley, 1973, pp. 40—59.

Frohlinde.[5] At pH *ca.* 6 reaction (1) leads to $[Tl(OH)]^+$ which has about the same specific conductivity as Tl^+ and consequently $\Delta\Lambda$ *ca.* 0. With decreasing pH the dissociation reaction (2) of $[Tl(OH)]^+$ requires one $H^+(aq)$ for every Tl^{2+} formed. Assuming that Tl^{2+} has about twice the specific conductivity as Tl^+ [$\Lambda(Tl^+)$ 65 S cm² mol⁻¹], the overall change in conductivity accompanying the Tl^{2+} formation is calculated as $\Delta\Lambda = \Lambda(Tl^{2+}) - \Lambda(Tl^+) - \Lambda[H^+(aq)] = 130 - 65 - 315 = -250$ S cm² mol⁻¹. This value ties in well with the experimental result at low pH. The p*K* value of 4.65 for equilibrium (2) is in excellent agreement with that reported in ref. 5.

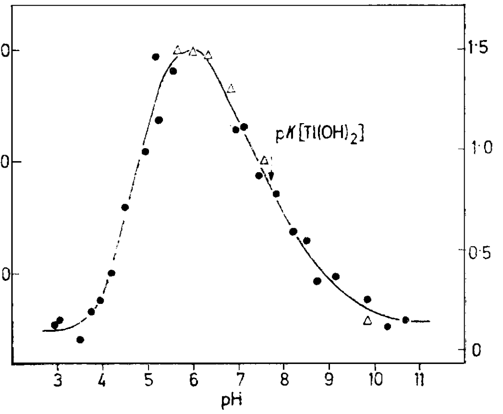

FIGURE 1 p*K* Curves for $[Tl(OH)]^+ \rightleftharpoons Tl^{2+} + [OH]^-$ and $Tl[OH]_2 \rightleftharpoons [Tl(OH)]^+ + [OH]^-$ from (●) conductivity measurements, and (△) rate constants for the reaction $[Tl(OH)]^+/Tl[OH]_2 + S_2Me_2$

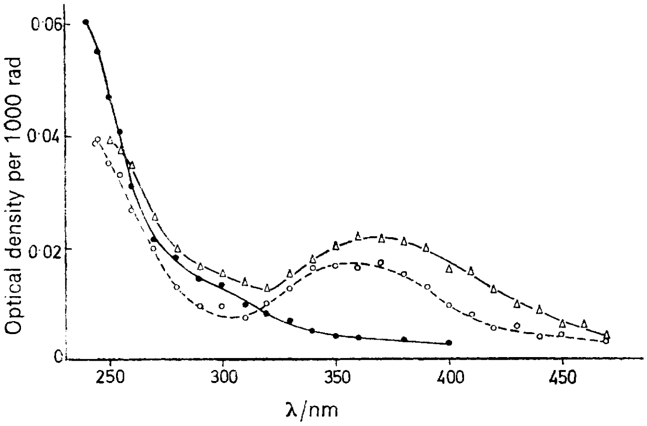

FIGURE 2 Optical absorption spectra of Tl^{2+} (●), $[Tl(OH)]^+$ (○), and $Tl[OH]_2$ (△)

On extending the experiments to basic solutions (pH >6) an increasingly negative change in conductivity was observed and another p*K* can be derived. If only reaction (1) occurred, *i.e.* if $[Tl(OH)]^+$ were stable at pH >6, $\Delta\Lambda$ should remain constant at *ca.* 0. Our results can only be interpreted in terms of an additional removal of ions. The most likely process is neutralization of $[Tl(OH)]^+$ by $[OH]^-$ according to the reverse reaction of the equilibrium (3). Since the reaction product, $Tl[OH]_2$, is an uncharged species, $\Delta\Lambda = -\Lambda(OH^-) - \Lambda[Tl(OH)^+] \approx -180 - 65 \approx -245$ S cm² mol⁻¹. This value expected for solutions at high pH is in fact in good agreement with the experimental result. The p*K* value of 7.7 ± 0.2 is attributed to the dissociation equilibrium of $Tl[OH]_2$.

The optical-absorption spectra of Tl^{2+}, $[Tl(OH)]^+$, and $Tl[OH]_2$ observed in irradiated solutions at pH 3.6, 5.6, and 9.0, respectively, are shown in Figure 2. Those for Tl^{2+} and $[Tl(OH)]^+$ are in good agreement with documented spectral data.[1-5] The spectrum of $Tl[OH]_2$ is very similar to that of $[Tl(OH)]^+$, *i.e.* it also exhibits an additional band at *ca.* 360 nm compared with Tl^{2+}. (Absorption coefficients are listed in the Table.) The appearance of an additional absorption band at longer wavelengths on addition of a hydroxyl group or a halide function to a metal ion has recently been described also for the mercury system Hg^+–$Hg[OH]$–$HgCl$.[9-12] It seems to be indicative of the establishment of a covalent structure in the hydroxylated metal ion.

From inspection of the absorption spectra it will be appreciated that determination of the p*K* of $Tl[OH]_2$ by optical measurements is difficult. Further evidence for equilibrium (3) is afforded, however, by kinetic data. Thallium(II) generally seems to decay by a bimolecular disproportionation process. This is indicated by a linear relation between the half-lives of the optical absorptions and the reciprocal concentrations of the reactive species {Tl^{2+}, $[Tl(OH)]^+$, and $Tl[OH]_2$}. The corresponding 2 k_2 values are listed in the Table. The highest rate constant is found for the reaction of two $Tl[OH]_2$ species, whereas the charged entities react more slowly, as expected. {A p*K* curve is not very meaningful since the disproportionation may also occur *via* $Tl[OH]_2 + [Tl(OH)]^+$ and $[Tl(OH)]^+ + Tl^{2+}$.}

Some physicochemical properties of $[Tl(OH)]^+$ and $Tl[OH]_2$

				$10^{-9}(2\,k_2)$/dm³ mol⁻¹ s⁻¹		
X	pH	$\lambda_{max.}$ * / nm	ε / dm³ mol⁻¹ cm⁻¹	no salt	0.25 mol d⁻³ Na[ClO₄]	$10^{-9}k(X + S_2Me_2)$ / dm³ mol⁻¹ s⁻¹
$[Tl(OH)]^+$	5.6	360	3.0×10^3	3.7	5.9	1.5
$Tl[OH]_2$	9.0	370	3.8×10^3	6.3	6.3	0.1

* An additional band in the u.v. was not resolved.

Kinetic-salt-effect experiments with added Na[ClO₄]

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[11] N. B. Nazhat and K.-D. Asmus, *J. Phys. Chem.*, 1973, **77**, 614.

[12] H. Jungbluth, J. Beyrich, and K.-D. Asmus, *J. Phys. Chem.*, 1976, **80**, 1049.

(which is radiolytically inert) showed a considerable increase in 2 k_2 at pH 5.6 whereas no effect on 2 k_2 was observable in basic solutions (see Table). This clearly demonstrates the existence of a charged and a neutral species at pH 5.6 and 9.0, respectively.

The ions Tl^{2+} and $[Tl(OH)]^+$ have been found to exhibit strong oxidizing properties.[6] We measured the rate constants for the oxidation of an organic disulphide, S_2Me_2, by the thallium(II) species at different pH. Reaction (4) can easily be followed by pulse radiolysis

$$Tl^{II} + S_2Me_2 \longrightarrow Tl^+ + [S_2Me_2]^+(+[OH]^-) \quad (4)$$

through the decay of the thallium(II) absorption $\{Tl^{2+}, [Tl(OH)]^+$, or $Tl[OH]_2\}$ and/or the formation of the $[S_2Me_2]^+$ absorption[13] ($\lambda_{max.}$ 440 nm). The reactions of Tl^{2+} and $[Tl(OH)]^+$ with S_2Me_2 occurred with very similar rate constants, $k \approx 1.5 \times 10^9$ dm^3 mol^{-1} s^{-1}. A similar finding, *i.e.* about equal reactivity of Tl^{2+} and $[Tl(OH)]^+$, has been reported[5] for the corresponding reactions with dimethoxybenzenes. A dramatic change in the rate constant for the oxidation of S_2Me_2 was observed in basic solutions, where an upper limit of $k = 1 \times 10^8$ dm^3 mol^{-1} s^{-1} is derived for the reaction of undissociated $Tl[OH]_2$. Under experimentally available conditions, the greater part of the $Tl[OH]_2$ seems to disappear by disproportionation. The measured rate constants for reaction (4) at pH >5 are also plotted in Figure 1 (triangles). The curve obtained essentially follows the pK curve from the conductivity measurements and thereby substantiates equilibrium (3).

The oxidizing properties of Tl^{II} are explained by the possibility of accommodating another electron in the free second 6*s* orbital. A stable electronic configuration is also achieved, however, if Tl^{II} loses an electron and is oxidized to Tl^{III}. It was therefore of interest to investigate whether Tl^{II} could also act as a reductant, *e.g.* towards tetranitromethane which is known to be an excellent electron acceptor. Reaction (5) was indeed

$$Tl[OH]_2 + C(NO_2)_4 \longrightarrow Tl^{III} + C(NO_2)_3^- + NO_2 \quad (5)$$

observed. In irradiated N_2O-saturated solutions (pH 8—9) of 2×10^{-3} mol dm^{-3} Tl^+ and *ca.* 10^{-4} mol dm^{-3} $C(NO_2)_4$ the $Tl[OH]_2$ absorption at 410 nm decayed and the $C(NO_2)_3^-$ absorption at 350 nm was formed expotentially with the half-lives of these processes being dependent on the $C(NO_2)_4$ concentration. Reaction (5) is not quantitative, however, which may be due to the relatively low transfer rate constant [$k_5 = (4 \pm 2) \times 10^8$ dm^3 mol^{-1} s^{-1}]. The results also indicate some reduction of $C(NO_2)_4$ by $[Tl(OH)]^+$ but the yield and particularly the corresponding rate constant are much lower. No reducing properties were observed for Tl^{2+}. It therefore appears that, in particular, $Tl[OH]_2$ has a much higher tendency to be stabilized by donating rather than by accepting an electron.

[6/578 *Received*, 26*th March*, 1976]

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