The Formation and Disproportionation of 2,2′-Bipyridylthallium(II) Complexes at a Dropping-mercury Electrode

By OLE FARVER and GWYNETH NORD*

(*Inorganic Chemistry Department, H. C. Ørsted Institutet, Universitetsparken 5, Copenhagen*)

WE have found that bivalent thallium is formed at a dropping-mercury electrode† when thallic complexes of 2,2′-bipyridyl in 0·1 M-potassium nitrate solution are reduced at low thallium concentrations (< 1 mM) and pH > 5. Under these conditions three distinct polarographic waves appear. We have furthermore shown by solvent extraction that in solutions of the composition given under Figures 1 and 2, thallium(III) is almost completely present as the bis-2,2′-bipyridylthallium(III) cation

---

† The oxidation of mercury by thallium(III) is extremely slow under the conditions of this study. The solutions were prepared using solid bis-2,2′-bipyridylthallium(III) nitrate and measured with a Radiometer Polariter Type PO4.

$[Tl(bipy)_2^{3+}]$, so that the following electrode reaction scheme applies:

$$Tl(bipy)_2^{3+} \xrightleftharpoons[E_{\frac{1}{2}}\ +\ 0{\cdot}06v]{1e}$$

$$Tl(bipy)_2^{2+} \xrightleftharpoons[E_{\frac{1}{2}}\ -\ 0{\cdot}125v]{1e}$$

$$Tl(bipy)_2^{+} \xrightleftharpoons[E_{\frac{1}{2}}\ -\ 0{\cdot}45v]{1e} Tl/Hg$$

The half-wave potential values ($E_{\frac{1}{2}}$) are given relative to the standard calomel electrode. With increase in thallium concentration the first wave grows at the expense of the second until only two waves (height 2 : 1) arise (see Figures 1 and 2). The total diffusion current obeys the Ilkovic equation throughout.

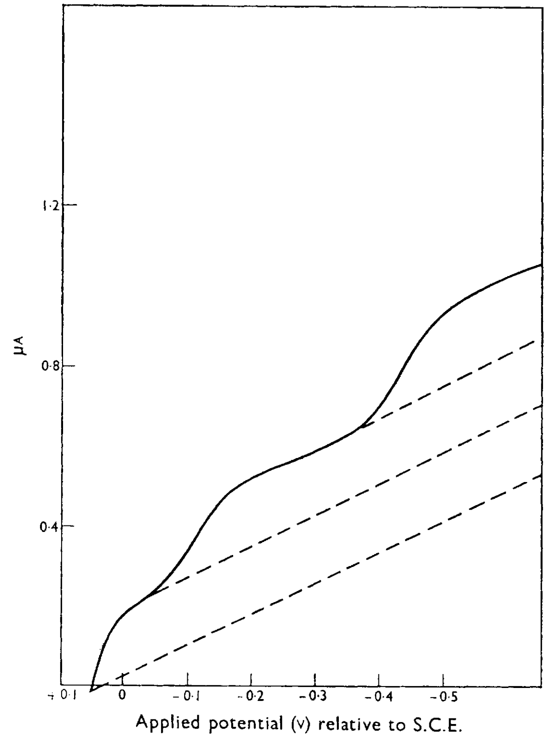

FIGURE 1. $C[Tl(bipy)_2(NO_3)_3]$ 0·04 *mM*; C_{bipy} 8·00 *mM*. *pH* = 5·0. m = 3·485 *mg./sec.*, t = 2·31 *sec./drop, damping* 4.

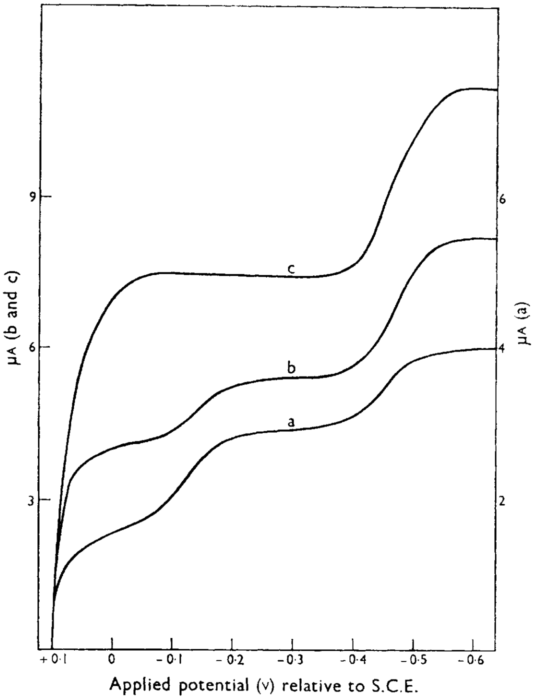

FIGURE 2. (a) $C[Tl(bipy)_2(NO_3)_3]$ 0·200 *mM*; C_{bipy} 8·00 *mM*. *pH* = 5·0 *damping* 4. (b) $C[Tl(bipy)_2(NO_3)_3]$ 0·600 *mM*; C_{bipy} 8·00 *mM*. *pH* = 5·0 *damping* 4. (c) $C[Tl(bipy)_2(NO_3)_3]$ 1·00 *mM*; C_{bipy} 10·00 *mM*, *undamped*. *pH* = 5·51.

Solutions which contained thallium(III) co-ordinated to both hydroxyl ions and bipyridyl‡ (pH + p*bipy* 7·5—8·6; pH 6·5—5·4) behaved similarly. In these cases a reaction scheme like that above is appropriate if the $Tl(bipy)_2^{n+}$ species are replaced by $[Tl(bipy)_xOH_y]^{(n-y)+}$ where $x = 2-y$. A typical solution was used to construct Figure 3, which shows that the usual analysis gave, within experimental error, the theoretical slope expected for three successive polarographically "reversible" one-electron changes.§ The expected square-root dependence on the mercury pressure was also found.

The concentration dependence of the relative heights of the first and second waves is that expected if the Tl^{II} species formed on addition of one electron at the electrode had two fates: it may diffuse away from the electrode, or while still in the electrode surface layer, it may disproportionate, a fraction of the Tl^{III} species from the disproportionation reaching the electrode and being reduced once more. This is the disproportionation mechanism

---

‡ No polymers were detected in the concentration range studied, *viz.*, 0·1—56 mM.

§ As Tl^{III} is reduced to Tl^{II} at potentials near that of the anodic dissolution of Hg, only the second half of the first wave was analysed.

used by previous workers[1] to interpret the "hydrodynamic voltammetry" of acid thallic perchlorate on platinum, although others[2] postulate stepwise reduction for acid thallic sulphate solutions.

Decreasing the pH of thallic bipyridyl solutions caused the Tl^{III}–Tl^{II} plateau to disappear, the total limiting diffusion current remaining unchanged (see Table). Here an extra competing reaction in the electrode solution layer must be considered. Rapid dissociation of the Tl^{II} chelate by proton attack could result in further reduction to Tl^{I} and it is relevant here that such rapidly dissociating protonated intermediates have been suggested to explain the results of studies of other metal bipyridyl complexes.[3]

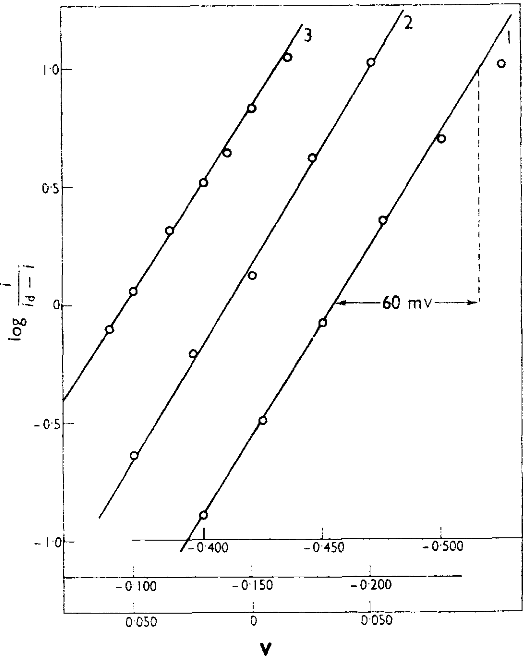

FIGURE 3. $C[Tl(bipy)_2(NO_3)_3]$ 0·134 *mM*; C_{bipy} 8·00 *mM*. *pH* = 6·07. m = 3·485 *mg./sec.*, t = 2·31 *sec./drop. undamped.* 22°.

TABLE

Solution	$i(d_1)$	$i(d_2)$	$i(d_3)$	pH
α	0·34	0·32	0·37	5·25
β	0·34	0·29	0·34	4·98
γ	$i(d_1) + i(d_2)$ 0·65		0·35	4·29

C_{Tl}(mM) = 0·069; C_{bipy} (mM) + 8·00.
i(d) = limiting diffusion current (μA).
Capillary characteristics: m = 3·485 mg./sec.; t = 2·31 sec./drop. For solution γ, two waves only appeared.

The Tl^{II} chelate detected by us would seem to be analogous to that suggested by Anbar[4] to explain the fact that Tl^{2+} ions, formed radiolytically from Tl^{+} ions, selectively oxidise ethylenediamine rather than undergo disproportionation. In this case the complete inhibition of the reaction in acid solution was attributed to the fact that, although under these conditions thallous ions do act as scavengers for hydroxyl radicals, Tl^{2+} disproportionates to Tl^{3+} and Tl^{+} rather than interact with the protonated form of the ligand.

It would seem likely that Tl^{II} complexes with other chelating agents (N and O donors) can be detected polarographically.

(*Received, June* 9*th*, 1967; *Com.* 581.)

---

[1] H. A. Catherino and J. Jordan, *Talanta*, 1964, **11**, 159.
[2] K. J. Vetter and G. Thiemke, *Z. Elektrochem.*, 1960, **64**, 805.
[3] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1953, **75**, 5102.
[4] M. Anbar, *J. Phys. Chem.*, 1963, **67**, 2708.