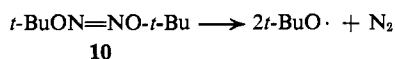


All evidence points to the mechanism of Scheme I for the decomposition of **3a**. It is interesting to consider this reaction as an analog to the decomposition of *tert*-butyl hyponitrite, **10**, studied by Traylor.¹¹ Both reactions form two *tert*-butoxy radicals, the one with loss of N₂ and the other with loss of sulfurane **5a**. The fact that ΔH^* is 10.3 kcal/mol smaller for the sulfurane reaction suggests several fascinating analogies to the chemistry of azo compounds which are currently being explored.



Acknowledgment. We gratefully acknowledge support from National Science Foundation Grant GP 30491X and from National Institutes of Health instrumentation Grants CA 11388 and GM 16864.

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A Crystalline Bilayer Adsorbed on Mercury Electrode

Sir:

There is now substantial evidence¹⁻³ that the adsorption of Pb²⁺ on mercury electrodes from aqueous halide solutions is controlled by principles quite different from those of anion-induced adsorption.⁴ In particular, the surface excess of Pb²⁺ (Γ_{Pb}) exhibits, at a solution [Br⁻] or [I⁻] which is dependent on solution [Pb²⁺] and electrode potential, a sharp increase from a modest to an exceptionally large (plateau) value (ca. 8×10^{-10} mol cm⁻²). We have shown³ that, for a given potential, the discontinuity in Γ_{Pb} occurs for the solution condition [Pb²⁺][X⁻]² = constant. We view this adsorption isotherm discontinuity as a surface solubility-controlled formation of a monolayer PbX₂ phase on the mercury surface, e.g., an adsorbed two-dimensional crystal.

This report is a preliminary description of another adsorbing system, Tl⁺ in aqueous bromide solution, which exhibits behavior similar to that of Pb²⁺ but in two stages, suggesting the existence of a bilayer surface crystal.

Data for Tl⁺ surface excess, Γ_{Tl} , as a function of [Br⁻] are shown in Figure 1 for two [Tl⁺] and two electrode potentials. These adsorption isotherms were obtained by double potential step chronocoulometry^{5,6} in the usual manner. The distinctive features of the data are the presence of two discontinuities, each followed by a plateau in Γ_{Tl} , the second plateau being twice as large as the first. Table I shows that, for a given electrode potential (-0.3 V) in 1 M KNO₃ supporting electrolyte, the solution composition at which each discontinuity in

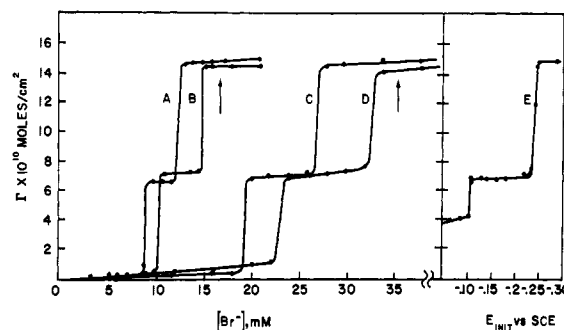


Figure 1. Surface excess for thallium adsorption from bromide in 1 M KNO₃ at 25°. $E_{\text{final}} = -0.70$ vs. sce. Data were obtained by double potential step chronocoulometry at a HMDE which was equilibrated with stirred solution for 60 sec: (A) [Tl⁺] = 1.0 mM, $E_{\text{init}} = -0.30$; (B) [Tl⁺] = 1.0 mM, $E_{\text{init}} = -0.20$; (C) [Tl⁺] = 0.5 mM, $E_{\text{init}} = -0.30$; (D) [Tl⁺] = 0.5 mM, $E_{\text{init}} = -0.20$; (E) [Tl⁺] = 1 mM, [Br⁻] = 14 mM. Arrows represent bulk solution saturation.

Table I. Adsorption Isotherm Discontinuities for Tl⁺ Adsorption from Bromide Solution at 25° on Mercury at -0.3 V vs. sce

Electrolyte	Break	[Tl ⁺], mM	[Br ⁻], mM	$K_{\text{surp}} = \frac{\Gamma_{\text{Tl}}}{[\text{Tl}^+][\text{Br}^-]}$	$K_{\text{surp}}'{}^b$
1 M KNO ₃ ^a	1	5.00	1.96	9.8×10^{-6}	2.82×10^{-6}
	1	2.00	4.6	9.2×10^{-6}	2.71×10^{-6}
	1	1.00	9.5	9.5×10^{-6}	2.82×10^{-6}
	1	0.50	19	10.4×10^{-6}	3.06×10^{-6}
	2	5.00	2.64	13.2×10^{-6}	3.88×10^{-6}
	2	2.00	6.4	12.8×10^{-6}	3.76×10^{-6}
	2	1.00	13.3	13.3×10^{-6}	3.91×10^{-6}
	2	0.50	28.8	14.4×10^{-6}	4.23×10^{-6}
0.1 M KNO ₃	1	1.00	3.75	3.75×10^{-6}	3.03×10^{-6}
	2	1.00	5.67	5.67×10^{-6}	4.57×10^{-6}
1 M KF	1	1.00	6.0	6.0×10^{-6}	2.66×10^{-6}
	2	1.00	8.75	8.75×10^{-6}	3.88×10^{-6}

^a Data are averages of two determinations. ^b Correction of K_{surp} for Tl⁺ bound by supporting electrolyte anion using association constants $K_{\text{TlNO}_3} = 2.4$, $K_{\text{TlF}} = 1.25$.

Γ_{Tl} occurs is remarkably well described by the relation $[\text{Tl}^+][\text{Br}^-] = \text{constant} = K_{\text{surp}}$.

These results, over a tenfold concentration range, leave little doubt that the discontinuities reflect control of Tl⁺ adsorption by the solubility of TlBr at the solution-mercury interface. The surface solubility of TlBr like that of PbI₂ and PbBr₂ is lower than that of "ordinary" TlBr; we have determined that the product [Tl⁺][Br⁻] for saturated TlBr in 1 M KNO₃ at 25° is 16.5×10^{-6} . We should emphasize that the Tl⁺ adsorption data represent equilibrium values; no increases in Γ_{Tl} result, on either plateau, from increasing the stirred equilibration of electrode with solution from 1 to 10 min.

K_{surp} for both discontinuities exhibit two further characteristics expected of equilibrium constants. (i) In 1 M KNO₃, K_{surp} increases with temperature. A plot of $\log K_{\text{surp}}$ vs. $1/T$ is linear, as expected for a solubility product. (ii) The value of K_{surp} is influenced by coordination of Tl⁺ by the supporting electrolyte anion in an entirely predictable manner. Thus, if [KNO₃] is lowered, or if KF electrolyte is employed, the apparent surface solubility of TlBr decreases. Application of the literature constants for complexation of Tl⁺ by NO₃⁻ or F⁻ quantitatively corrects for this effect as shown by comparison of K_{surp}' at each discontinuity for the three electrolyte solutions of Table I.

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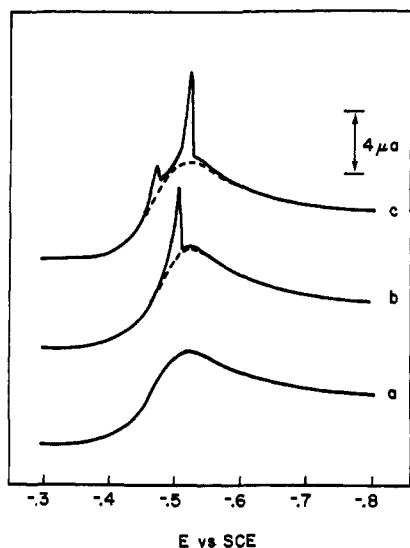


Figure 2. Linear sweep chronoamperograms of 1.0 mM Tl^+ in 1 M KNO_3 solution on HMDE which was equilibrated with stirred solution for 60 sec at -0.30 vs. sce. Sweep rate = 0.05 V/sec. $[Br^-]$ = (A) 8 mM, (B) 11 mM, (C) 15.5 mM.

Mercury electrodes equilibrated with 1.00 mM Tl^+ and various $[Br^-]$ at -0.3 V have been further examined with linear sweep chronoamperometry, with results shown in Figure 2. At $[Br^-]$ below the first Γ_{Tl} discontinuity (curve a), the shape of the Tl^+ reduction wave is little altered. At a $[Br^-]$ attaining the first Γ_{Tl} discontinuity (curve b), a sharp cathodic current spike appears superimposed on the wave for reduction of diffusing Tl^+ . This spike corresponds to reduction of the adsorbed TlBr crystals over a narrow potential range. As $[Br^-]$ is increased past the second Γ_{Tl} discontinuity (curve c), a second, more positive, current spike appears on the Tl^+ wave.

The potential sweep results qualitatively demonstrate that the TlBr adsorbed on the two plateaus are electrochemically distinct. Whether the difference in electrochemical properties has kinetic or thermodynamic roots, it clearly must mean that, from the electrode viewpoint, two *structurally* distinguishable kinds of adsorbed TlBr exist on the second Γ_{Tl} plateau.

Two pictures of the adsorbed TlBr could be drawn from the above facts. The pictures differ in whether one supposes a TlBr monolayer or bilayer. In the monolayer picture, we suppose that the second discontinuity in Γ_{Tl} corresponds to some reorientation of the original TlBr monolayer crystal so as to accommodate a large amount of additional TlBr into the monolayer. This monolayer must contain two structurally distinct kinds of Tl^+ .

In the second picture, we suppose that a second monolayer of TlBr is laid on the first. The structural arrangement of the second layer of TlBr surface crystal could be essentially identical with that of the first; the Tl^+ electrochemistries could nonetheless be nonequivalent since the second layer containing Tl^+ is not in contact with the mercury surface and will experience a different potential.

We strongly favor the second, bilayer surface crystal model, both because it requires no new and complex crystal structure for TlBr and because of further considerations of geometrical space requirements. The

values of Γ_{Tl} on the two plateaus in 1 M KNO_3 are 7.2×10^{-10} and 14.8×10^{-10} mol cm^{-2} . It is impossible to accommodate the latter Γ_{Tl} in a single monolayer of composition TlBr. For instance, if TlBr units are arranged perpendicular to the surface, with bromide contacting the surface in a simple cubic packing, a maximum Γ_{Tl} of 11×10^{-10} mol cm^{-2} is estimated for a TlBr monolayer. On the other hand, simple cubic packing of a TlBr monolayer with bond axis parallel to the surface is estimated at 7.4×10^{-10} mol cm^{-2} . Addition of a second layer, staggered over the first to form a (CsCl) body-centered cubic packing, would provide 14.8×10^{-10} mol cm^{-2} for a bilayer of TlBr. (The 110 crystal plane is parallel to the mercury surface.) While such surface space requirement estimations are not proof for the bilayer model, they do show a comfortable accommodation of experimental facts. It also happens that "ordinary" TlBr crystallizes in a body-centered cubic lattice, which was used for the estimation above.

It is evident that TlBr adsorption presents a striking example of surface chemistry. We are undertaking a further thermodynamic and electrochemical characterization of the surface crystals. The potential dependence of K_{surf} is dramatic and consonant with a surface phase formation; see the inset of Figure 1 where Γ_{Tl} is measured as a function of equilibration potential. Finally, the order and spacing of the reduction potentials for diffusing Tl^+ , first monolayer Tl^+ and second monolayer Tl^+ (Figure 2), merits careful study.

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Two-Coordinate Palladium(0) Complexes, $Pd[PPh(t-Bu)_2]_2$ and $Pd[P(t-Bu)_3]_2$

Sir:

Two-coordinate complexes still remain a rarity in transition metal chemistry. A few two-coordinate d^{10} nickel triad complexes¹ have been reported. None of them, however, has been studied by X-ray analysis. We wish to report here the X-ray structure of $Pd[PPh(t-Bu)_2]_2$ (1) and the chemical property along with that of a related complex $Pd[P(t-Bu)_3]_2$ (2). A mixture of $Pd(\eta-C_5H_5)(\eta-C_5H_5)_2$ and 2 mol of $PPh(t-Bu)_2$ ³ was stirred in *n*-hexane at room temperature for 4 hr. On cooling the reddish *n*-hexane solution, 1 was separated as diamagnetic pale yellow crystals,⁴ mp 122–126° dec,

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