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Oxidation of Iron(II) by Thallium(III). Rates and Equilibria

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The empirical rate law for the title reaction in aqueous perchlorate solutions is[2]

$$-\mathrm{d}[\mathrm{Fe(II)}]/\mathrm{d}t = -\mathrm{d}[\mathrm{Fe}^{2+}]/\mathrm{d}t = \frac{A[\mathrm{Fe(II)}][\mathrm{Tl(III)}]}{1 + B[\mathrm{Fe(III)}]/[\mathrm{Fe(II)}]} \tag{1}$$

This accords with a two-step process involving Tl(II) as a reactive intermediate[2]

$$\mathrm{Tl(III)} + \mathrm{Fe(II)} \underset{k'_-}{\overset{k'}{\rightleftharpoons}} \mathrm{Tl(II)} + \mathrm{Fe(III)} \tag{2a}$$

$$\mathrm{Tl(II)} + \mathrm{Fe(II)} \rightarrow \mathrm{Tl(I)} + \mathrm{Fe(III)} \tag{2b}$$

Recent workers[3-5] have measured k' and k'_- in acid solutions where Tl^{3+} and Tl^{2+} are only slightly hydrolyzed and calculated that the equilibrium constant for (2a) is in the range 4.1×10^{-8} to 8×10^{-8} M in 1 M $HClO_4$ and is 4.2×10^{-8} M when $[H^+] = 0.25$ M and the ionic strength adjusted with sodium perchlorate (I) is 3.0. A and B have been determined at 25 °C by the same experimental technique in 3 M $HClO_4$–$NaClO_4$ and also in 1.5 M $HClO_4$–$NaClO_4$.[2,6] Both A and B are $[H^+]$ dependent. We show here that this $[H^+]$ dependence can be quantitatively accounted for if there are parallel reactions represented by eq 3 and 4, where the unhydrolyzed and hydrolyzed forms for the thallium and iron oxidation states, Tl(III) and Fe(III), react as different rates. Equation 4b cannot reasonably be attributed to the reaction of Fe^{3+} with $TlOH^+$ (see below). These reactions are followed by (5).

$$\mathrm{Tl}^{3+} + \mathrm{Fe}^{2+} \underset{k_{-\mathrm{o}}}{\overset{k_\mathrm{o}}{\rightleftharpoons}} \mathrm{Tl}^{2+} + \mathrm{Fe}^{3+} \tag{3}$$

$$\mathrm{TlOH}^{2+} + \mathrm{Fe}^{2+} \xrightarrow{k_1} \mathrm{Tl}^{2+} + \mathrm{FeOH}^{2+} \tag{4a}$$

$$\mathrm{TlOH}^{2+} + \mathrm{Fe}^{2+} \xleftarrow[k_{-1}]{} \mathrm{Tl}^{2+} + \mathrm{FeOH}^{2+} \tag{4b}$$

$$\mathrm{Tl(II)} + \mathrm{Fe}^{2+} \xrightarrow{k_2} \mathrm{Tl}^{+} + \mathrm{Fe}^{3+} \tag{5}$$

We can reasonably assume that equilibria 6–8 are not

$$\mathrm{H_2O} + \mathrm{Tl}^{3+} \rightleftharpoons \mathrm{TlOH}^{2+} + \mathrm{H}^+ \tag{6}$$

$$\mathrm{H_2O} + \mathrm{Tl}^{2+} \rightleftharpoons \mathrm{TlOH}^{+} + \mathrm{H}^+ \tag{7}$$

$$\mathrm{H_2O} + \mathrm{Fe}^{3+} \rightleftharpoons \mathrm{FeOH}^{2+} + \mathrm{H}^+ \tag{8}$$

significantly disturbed by the above reactions so that the reactants and products are essentially in their equilibrium protonated configurations. By use of the preceding scheme then, the acid dependence of A and B is given by (9) and (10a)

$$0.5A = k_\mathrm{o} + \frac{(K_{\mathrm{Tl(III)}}/[\mathrm{H}^+])(k_1 - k_\mathrm{o})}{1 + K_{\mathrm{Tl(III)}}/[\mathrm{H}^+]} \tag{9}$$

$$B = k_{-\mathrm{o}}/k_2 + \frac{(K_{\mathrm{Fe(III)}}/[\mathrm{H}^+])(k_{-1} - k_{-\mathrm{o}})}{k_2} \tag{10a}$$

where $K_{\mathrm{Tl(III)}} = [\mathrm{TlOH}^{2+}][\mathrm{H}^+]/[\mathrm{Tl}^{3+}] = 0.073\ \mathrm{M}^7$ at 25 °C and $I = 3.0$ and $K_{\mathrm{Tl(III)}} = 0.086\ \mathrm{M}^6$ at 25 °C and $I = 1.5$. Recent work[8] on the hydrolysis of Tl^{2+} has shown that $K_{\mathrm{Tl(II)}} = [\mathrm{TlOH}^+][\mathrm{H}^+]/[\mathrm{Tl}^{2+}] = 2.5\ (\pm 1.6) \times 10^{-5}$ M in 0.3–1.0 M $NaClO_4$–$HClO_4$. $K_{\mathrm{Fe(III)}}$ is 1.0×10^{-3} M at $I = 3$.[4] Using (9) and referring to the variation of A with $[H^+]$[2,6] we have calculated k_o and k_1 (see Table I). No term in $Tl(OH)_2^+$ is required. We now consider (10) together with the values of B from ref 2.

Table I. Summary of Rate Constants Derived Using Eq 3–5[a]

Reactants	Symbol for rate const as used in text	Value of rate const, $M^{-1}\ s^{-1}$	
		Ionic strength 1.5	Ionic strength 3.0
$Tl^{3+} + Fe^{2+}$	k_o	0.0060	0.0078
$Tl^{2+} + Fe^{3+}$	$k_{-\mathrm{o}}$	1.4×10^5	1.8×10^5
$TlOH^{2+} + Fe^{2+}$	k_1	0.102	0.205
$Tl^{2+} + FeOH^{2+}$	k_{-1}	1.6×10^8	3.5×10^8
$Tl^{2+} + Fe^{2+}$	k_2	9.2×10^6	2.1×10^7

[a] See text.

Table II. Values of the Rate Constant for the Reaction Tl(II) + Fe^{2+} Illustrating Lack of $[H^+]$ Dependence[a]

$[H^+]$, M	0.4	0.668	1.00	1.50	1.50	2.00	2.40	2.80
$10^{-7}k_2$, $M^{-1}\ s^{-1}$	2.13	2.03	2.00	2.15	2.13	2.02	2.13	2.28
$10^{-7}k_2^*$, $M^{-1}\ s^{-1}$	1.71	1.67	1.64	1.87	1.87	1.79	1.91	1.96

[a] For calculation of k_2 see text. k_2^* is calculated using eq 10a alone.

In the highly acidic solutions in question (see Table II) $K_{\mathrm{Fe(III)}}/[\mathrm{H}^+]$ is always much less than unity. We have therefore omitted the factor $1/(1 + K_{\mathrm{Fe(III)}}/[\mathrm{H}^+])$ from the second term in (10a). The hydrolysis of Fe^{2+} is negligible under these conditions.[7]

The $[H^+]$ dependence of B at $I = 3.0$ is given[2] as

$$B = 0.0090 + 0.0215/[\mathrm{H}^+] \tag{10b}$$

From (10a) and (10b) we find $k_{-1} \gg k_{-\mathrm{o}}$ and $K_{\mathrm{Fe(III)}}k_{-1}/k_{-\mathrm{o}} = 2.39$.

If the scheme of (3)–(5) is correct, then the same ratio should be obtained from (3) to (4) which lead to

$$\frac{k_\mathrm{o}k_{-1}}{k_{-\mathrm{o}}k_1} = \frac{K_{\mathrm{Tl(III)}}}{K_{\mathrm{Fe(III)}}} \tag{11}$$

so that

$$\frac{K_{\mathrm{Fe(III)}}k_{-1}}{k_{-\mathrm{o}}} = \frac{K_{\mathrm{Tl(III)}}k_1}{k_\mathrm{o}} = \frac{0.073 \times 0.205}{0.0078} = 1.92$$

We show later in this note that the discrepancy between 1.9 and 2.4 (vide infra) is not larger than can be accounted for by the experimental errors in the data used to derive (10b) and A from the measured rates. It follows from this that reaction 5 (the k_2 step) is not significantly $[H^+]$ dependent. By substituting for $K_{\mathrm{Fe(III)}}$ in (11) then we find at $I = 3$, $k_{-1}/k_{-\mathrm{o}} = 1.92 \times 10^3$.

In 1 M $HClO_4$ the overall rate constant for the reaction Tl(II) + Fe(III) is $3.4 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. We use the symbol k'_- for this (see eq 2a). We make the following two assumptions: first, that k'_- is $3.4 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ in 1 M $HClO_4$ also when $I = 1.6$ and, second, that $K_{\mathrm{Fe(III)}}$ using the I dependence of $K_{\mathrm{Tl(III)}}$ is 1.2×10^{-3} M at $I = 1.6$. For $I = 1.6$ and $[H^+] =$

1.0 from ref 2 then $k_{-o}/k_2 + (K_{\mathrm{Fe(III)}}/k_2)(k_{-1} - k_o) = k'_-/k_2 = 0.037$ and using k'_- we find $k_{-o} = 1.4 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$; $k_{-1} = 1.6 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$ and $k_2 = 9.2 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$. This latter value is in good agreement with the directly measured values[6,7] for the reaction $\mathrm{Tl^{2+} + Fe^{2+}}$ in 1 M $\mathrm{HClO_4}$ which have been reported as $3.3 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$ and also as $6.7 \times 10^6\ \mathrm{M^{-1}\ s^{-1}}$. k_{-1} and k_{-o} are greater than k_1 and k_o, respectively, and k_{-1} is in fact only about 10 times less than the diffusion-controlled limiting rate. As this latter is of course less than that known for proton transfer and since also in all solutions $[\mathrm{Fe^{3+}}] \le 10^{-2}[\mathrm{H^+}]$, the distribution of Tl(II) is between $\mathrm{Tl^{2+}}$ and $\mathrm{TlOH^+}$ and that of Fe(III) is between $\mathrm{Fe^{3+}}$ and $\mathrm{FeOH^{2+}}$ and is overwhelmingly determined by equilibria 7 and 8.

The large increase in rate for hydrolyzed over aquo species has been noted for many other reactions of aquohydroxy cations and has been attributed to a change of mechanism from outer-sphere electron transfer (k_o, k_{-o} paths) to either inner-sphere $\mathrm{OH^-}$ bridging and/or H atom transfer.

Were the k_{-1} paths taken to reflect reaction between $\mathrm{TlOH^+}$ and $\mathrm{Fe^{3+}}$, then (using $\mathrm{p}K_2 = 4.6$) not only would the products of the reaction of $\mathrm{TlOH^{2+}}$ and $\mathrm{Fe^{2+}}$ be thermodynamically unstable but also the calculated rate constants for this path would at both ionic strengths be about $10^{10}\ \mathrm{M^{-1}\ s^{-1}}$, i.e., about 10^5 times that of the water-exchange rate[9] of the iron(III)–aquo ion.

Using the equilibrium constant $k_o/k_{-o} = K_{12} = 4.4 \times 10^{-8}$ M and also using $E° = 0.74$ V for the $\mathrm{Fe^{3+}/Fe^{2+}}$ couples[7] we find $E°_{\mathrm{Tl^{3+}/Tl^{2+}}} = 0.30$ V (cf. 0.30, 0.31, and 0.32 V from ref 3, 4, and 5).

We now consider the individual data from ref 2 which were used to construct (10b), all of which refer to $I = 3.0$. Here both A and B are available for a series of $[\mathrm{H^+}]$ values. Combining and rearranging (9) and (10a) give (12) where k_{-1},

$$\frac{(0.5A - k_o)(1 + K_{\mathrm{Tl(III)}}/[\mathrm{H^+}]}{B} = \frac{K_{\mathrm{Tl(III)}}(k_1 - k_o)k_2}{k_{-o}[\mathrm{H^+}] + K_{\mathrm{Fe(III)}}(k_{-1} - k_{-o})} \tag{12}$$

k_{-o}, and k_2 are unknown at $I = 3.0$ but $k_{-1} \gg k_{-o}$ and $k_2k_{-1}/k_{-o} = 1.92$ (see above). We make the single assumption that the ionic strength dependence of k_{-o} is the same as that we have found for k_o and calculate that at $I = 3.0$ $k_{-o} = (1.4 \times 10^5 \times 0.0078)/0.0060 = 1.82 \times 10^{-5}\ \mathrm{M^{-1}\ s^{-1}}$, $K_{\mathrm{Fe(III)}}k_{-1} = 1.92\ \mathrm{s^{-1}}$, $k_{-o} = 3.5 \times 10^5\ \mathrm{M^{-1}\ s^{-1}}$, and $k_{-1} = 3.5 \times 10^8\ \mathrm{M^{-1}\ s^{-1}}$. By substitution into (12) we have calculated k_2 for a series of $[\mathrm{H^+}]$ values. These are given in Table II. They show no trend with change of $[\mathrm{H^+}]$ from 0.4 to 2.8 M, and this demonstrates that any effects arising from different reactivities of $\mathrm{Tl^{2+}}$ and $\mathrm{TlOH^+}$ with $\mathrm{Fe^{2+}}$ are not significant but are within the experimental error of the data.

The exchange reaction $\mathrm{Fe(III)^* + Fe(II) \rightleftarrows Fe(III) + Fe(II)^*}$ also exhibits parallel paths[10] involving $\mathrm{FeOH^{2+}}$ and $\mathrm{Fe^{3+}}$ as oxidants. For the unhydrolyzed path, the exchange rate (k_{22}) is $0.87\ \mathrm{M^{-1}\ s^{-1}}$ and is now used together with K_{12} derived above to test the applicability of the modified[11] Marcus equation (eq 13) to the $\mathrm{Fe^{2+} + Tl^{3+}}$ reaction rate. ΔG_{12}^* is

$$\Delta G_{12}^* = \frac{\Delta G_{11}^*}{2} + \frac{\Delta G_{22}^*}{2} + \frac{[\Delta G_{12}°(1 + \alpha)]}{2} \tag{13}$$

$$\alpha = \frac{\Delta G_{12}°}{4(\Delta G_{11}^* + \Delta G_{22}^*)}$$

here derived using $k_{12} = 6.0 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$ (k_o in eq 3). k_{11} so calculated is $4 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$. As expected this is less than the experimental value of $3.0 \times 10^4\ \mathrm{M^{-1}\ s^{-1}}$ which was measured[3] under conditions where about 8%[7] of the $\mathrm{Tl^{3+}}$ was present as $\mathrm{TlOH^{2+}}$. We are currently attempting to correlate rates of oxidation of other reductants by unhydrolyzed $\mathrm{Tl^{3+}}$.

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Registry No. $\mathrm{Fe^{2+}}$, 15438-31-0; $\mathrm{Tl^{3+}}$, 14627-67-9.

References and Notes

(1) This work was carried out at the Chemistry Department, Stanford University, California, and at Brookhaven National Laboratory, Upton, N.Y., while on study leave (Aug 1975–June 1976).
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Ligand Distortions in Platinum(0) Complexes

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It is well-known that a ligand coordinated to a transition metal is distorted from its structure in the ground state.[1-10] There have been reported several theoretical studies of this matter.[11-14] The cis-bending distortion of acetylene coordinated to a metal atom has been investigated in moderate detail;[13] however that work involved a rather severe approximation, in that the metal ion was not included in the MO calculations. A semiquantitative study which included a metal ion was carried out by Nelson et al.,[14] using the extended Hückel MO method. They reported that the energy minimum brought about by the acetylene cis bending accorded with the maximum of the metal–carbon total overlap population. From this result, it is conceivable that the cis bending is induced by the strengthening of the metal–carbon bond. Blizzard et al. proposed that the cis bending should have little effect on the strength of the metal–acetylene interaction.[13] Thus, it appears that previous discussion of this issue is not conclusive.

In the present work, the electronic structures of platinum(0) complexes $\mathrm{Pt(PH_3)_2L}$ (L = $\mathrm{C_2H_2}$, $\mathrm{C_2H_4}$, $\mathrm{CS_2}$, $\mathrm{CO_2}$) are investigated with a CNDO-type semiempirical SCF–MO method, in order to determine why the L ligand is distorted by the coordination to the platinum atom. The conclusion we reach is different from those of both Blizzard et al.[13] and Nelson et al.[14] The carbon disulfide and carbon dioxide complexes have never been investigated theoretically.

Method and Geometries

The MO method employed is a CNDO-type approximate semiempirical SCF–MO method. This method, described elesewhere,[15-17] yields successful results on the electronic spectra of tetrachloroplatinate and on the electronic structures of various third-row transition metal complexes.[16-17]