Notes

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Kinetics and Mechanism of Electron-Transfer Reactions of Aquothallium and Coordinated Thallium(III). XI.[1] Reduction of Chlorothallium(III) Complexes by Phosphite

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In the reduction of chlorothallium(III) complexes by hypophosphite,[2] the reactivity of different thallium(III) species follows the order $TlCl_4^- > TlCl_3 > TlCl_2^+ > Tl^{3+} > TlCl^{2+}$. The greater reactivity of chlorothallium(III) complexes has been explained by invoking a chloride-bridged activated mechanism between Tl(III) and the active form of hypophosphorous acid. In contrast the aquothallic ion is reduced via intermediate complex[3a] formation of $[TlH_3PO_2]^{3+}$ and $[TlH_3PO_3]^{3+}$ in the oxidations[3] of H_3PO_2 and H_3PO_3, respectively. In view of the close similarity between the oxidations of H_3PO_2 and H_3PO_3 by various oxidants, it is of interest to study the kinetics of the oxidation of H_3PO_3 by chlorothallium(III) complexes and to compare the rate data with those of H_3PO_2.

Experimental Section

Sodium monohydrogen phosphite ($Na_2HPO_3{\cdot}5H_2O$) was B.D.H. AnalaR grade. All other reagents and the procedure for following the kinetics were as described earlier.[3]

The present study was made at 50–60°. It was, therefore, necessary to check whether there is any decomposition[4] of $TlCl_3$. A few kinetics runs were made at 60° with $(2.5–5) \times 10^{-3}$ *M* Tl(III) and 0.1 *M* chloride, and Tl(III) was determined iodometrically[3] from time to time. No decrease in the concentration of Tl(III) was observed in 3 hr.

Initial rates were calculated with an uncertainty of ±10%.

Results

Stoichiometry. Stoichiometric determinations were made at 70°, in 1.0 *M* $HClO_4$ and 0.5 *M* Cl^-, and with excess of Tl(III) over phosphite. Excess Tl(III) was determined iodometrically. The stoichiometry corresponds to the equation

$$H_3PO_3 + Tl^{III} + H_2O \rightarrow H_3PO_4 + Tl^{I} + 2H^+ \qquad (1)$$

Rate Law. The kinetics were studied in perchloric acid solutions and the ionic strength was adjusted with lithium perchlorate. The order in Tl(III) was determined at various constant $[Cl^-]_T/[Tl(III)]_T$ ratios (hereafter referred to as *R*) as explained earlier[2] and was found to be one. Table I shows the results of the variations of thallium(III) (experiments 1–11), phosphite (experiments 12–19), and perchloric acid (experiments 20–32). At constant chloride ion concentration, rate law 2 is obeyed, where $[Tl^{III}]_T$ and $[H_3PO_3]_T$ represent

$$-d[Tl^{III}]/dt = \frac{k_{obsd}[Tl^{III}]_T[H_3PO_3]_T[H^+]}{[H^+] + K_d} \qquad (2)$$

analytical concentrations of thallium(III) and phosphite species, respectively, K_d is the first acid dissociation constant of H_3PO_3, and $[H^+]$ is the equilibrium hydrogen ion concentration. The phosphite salt Na_2HPO_3 is converted to $H_2PO_3^-$ and H_3PO_3 in acid solutions. The values of 0.076 *M* and 7×10^{-7} *M* for the first[5,6] and second[7] acid dissociation constants were employed in calculating the equilibrium hydrogen ion concentrations.[8] Although the hydrolysis constant for Tl^{3+} to form $TlOH^{2+}$ is reported[9] to be 0.073 at 25°, this equilibrium has not been considered for calculating equilibrium hydrogen ion concentrations because in the presence of chloride ions strong chloro complexes of Tl^{3+} are formed and a very small fraction of total thallium(III) is present as Tl^{3+}.

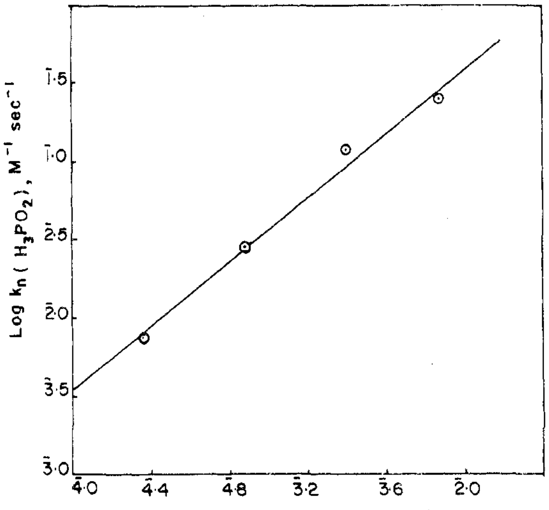


Figure 1. Plot of rate constants of reactions with H_3PO_2 against the corresponding rate constants of reactions with H_3PO_3.

The values of k_{obsd} calculated from the rate law, eq 2, are given in Table I. On increasing the concentration of chloride ions the rate first decreases, reaching a minimum at $R \simeq 1$, and then increases to a limiting value. The variation in the rate by a change in the ionic strength and by the products Tl^{I} and phosphate was within experimental uncertainty.

Rate Constants. The discussion for the reactive Tl^{III} species, active form of H_3PO_3, and hydrogen ion effect is similar to one detailed in the previous paper,[2] and the general mechanism of eq 3 and 4 for the present reaction may be suggested.

$$H_3PO_3 \overset{K_d}{\rightleftharpoons} H_2PO_2^- + H^+ \quad \text{(rapid)} \qquad (3)$$

$$TlCl_n^{\,3-n} + H_3PO_3 \xrightarrow{k_n} \text{products} \qquad (4)$$

Redox reactions also occur by a parallel path as described earlier[3] for aquothallic ion. The complete rate law is given as eq 5, where *K* is the formation constant for the complex

$$-d[Tl^{III}]/dt = \left\{kK\frac{[Tl^{III}{}_{aq}]}{[H^+]} + k_1[TlCl^{2+}] + k_2[TlCl_2^{\,+}] + k_3[TlCl_3] + k_4[TlCl_4^{\,-}]\right\}\left(\frac{[H_3PO_3]_T[H^+]}{[H^+] + K_d}\right) \qquad (5)$$

$[TlH_2PO_3]^{2+}$ (see eq 6a and 6b) and *k* is the rate constant

$$Tl^{3+} + H_3PO_3 \overset{K}{\rightleftharpoons} [TlH_2PO_3]^{2+} + H^+ \qquad (6a)$$

$$\left.\begin{array}{l} Tl^{3+} + H_2O \overset{K_h}{\rightleftharpoons} TlOH^{2+} + H^+ \\ TlOH^{2+} + H_3PO_3 \overset{K'}{\rightleftharpoons} [TlH_2PO_3]^{2+} + H_2O \\ \text{(so that } K_hK' = K) \end{array}\right\} \qquad (6b)$$

Table I. k_{obsd} for the Reduction of Thallium(III) by Phosphite at 55° and $I = 1.1\ M$

Expt no.	$10^3[Tl^{III}]$, M	$10^2[Na_2HPO_3]$, M	$[HClO_4]$, M	$[H^+]$, M	$10^2[Cl^-]_T$, M	R	10^8(rate), $M\ sec^{-1}$	10^4k_{obsd}(eq 2), $M^{-1}\ sec^{-1}$
1	2.0	5.0	1.085	0.9885	0.2	1.0	4.01	4.3
2	4.0	5.0	1.085	0.9885	0.4	1.0	7.25	4.0
3	5.0	5.0	1.085	0.9885	0.5	1.0	9.60	4.1
4	2.0	5.0	1.085	0.9885	0.4	2.0	6.03	6.4
5	2.5	5.0	1.085	0.9885	0.5	2.0	7.40	6.4
6	3.0	5.0	1.085	0.9885	0.6	2.0	10.1	7.1
7	4.0	5.0	1.085	0.9885	0.8	2.0	12.1	6.4
8	5.0	5.0	1.085	0.9885	1.0	2.0	15.0	6.4
9	2.0	5.0	1.085	0.9885	5.0	25	28.0	30
10	3.0	5.0	1.085	0.9885	5.0	16.6	43.0	30
11	4.0	5.0	1.085	0.9885	5.0	12.5	54.5	30
12	2.5	5.0	1.085	0.9885	0.6	2.4	12.0	10
13	2.5	7.5	1.085	0.9405	0.6	2.4	16.3	9.3
14	2.5	10.0	1.085	0.8928	0.6	2.4	23.5	10
15	2.5	2.0	1.085	1.0465	4.0	13	29.1	62
16	2.5	3.5	1.085	1.0175	4.0	13	48.3	75
17	2.5	5.0	1.085	0.9885	4.0	13	63.5	56
18	2.5	7.5	1.085	0.9405	4.0	13	100	57
19	2.5	10.0	1.085	0.8928	4.0	13	129	56
20	2.5	5.0	0.195	0.1150	0.75	3	12.5	16
21	2.5	5.0	0.285	0.1984	0.75	3	15.0	16
22	2.5	5.0	0.385	0.2955	0.75	3	16.3	16
23	2.5	5.0	0.485	0.3928	0.75	3	16.6	16
24	2.5	5.0	0.185	0.1055	1.1	4.4	22.5	32
25	2.5	5.0	0.285	0.1984	1.1	4.4	24.5	33
26	2.5	5.0	0.385	0.2955	1.1	4.4	30.0	30
27	2.5	5.0	0.485	0.3928	1.1	4.4	33.7	32
28	2.5	5.0	1.085	0.9885	1.1	4.4	35.1	30
29	2.5	5.0	0.085	0.0230	8.0	32	15.0	47
30	2.5	5.0	0.185	0.1055	8.0	32	38.3	53
31	2.5	5.0	0.285	0.1984	8.0	32	51.6	55
32	2.5	5.0	0.650	0.5562	8.0	32	62.0	55

Table II. Rate Constants at 55° and $I = 1.1\ M$

Reaction	Rate const, $M^{-1}\ sec^{-1}$	Reaction	Rate const, $M^{-1}\ sec^{-1}$
Tl^{3+}-H_3PO_3	$kK^a = 12.5 \times 10^{-4}$	$TlCl_3$-H_3PO_3	$k_3 = 2.7 \times 10^{-3}$
$TlCl^{2+}$-H_3PO_3	$k_1 = 2.52 \times 10^{-4}$	$TlCl_4$-H_3PO_3	$k_4 = 8.1 \times 10^{-3}$
$TlCl_2{}^+$-H_3PO_3	$k_2 = 8.2 \times 10^{-4}$		

[a] $k = 5.5 \times 10^{-5}\ M^{-1}\ sec^{-1}$ and $K = 22.8$ at 55°.

Table III. Observed and Calculated Rates for the Tl^{III}-H_3PO_3 Reaction at 55° and $I = 1.1\ M^a$

		10^8(rate), $M\ sec^{-1}$	
$10^2[Cl^-]_T$, M	$[Cl^-]$, M	Obsd	Calcd
0.06	2.703×10^{-7}	8.0	8.1
0.10	8.018×10^{-7}	7.2	6.9
0.20	2.516×10^{-6}	5.3	5.0
0.24	4.195×10^{-6}	5.0	5.0
0.32	1.01×10^{-5}	5.7	5.5
0.38	2.205×10^{-5}	6.3	6.5
0.44	4.703×10^{-5}	7.9	8.1
0.54	2.611×10^{-4}	10.7	10.7
0.60	6.841×10^{-4}	13.3	13.5
0.94	2.82×10^{-3}	26.1	27.6
1.00	3.26×10^{-3}	29.1	29.6
1.48	6.06×10^{-3}	44.6	40.2
3.50	2.612×10^{-2}	64.7	67
5.00	4.078×10^{-2}	72.5	75
6.50	5.50×10^{-2}	76.7	79.1
8.00	7.054×10^{-2}	81.3	81.6

[a] $[Tl^{III}] = 2.5 \times 10^{-3}\ M$; $[Na_2HPO_3] = 5 \times 10^{-2}\ M$; $[HClO_4] = 1.085\ M$.

for the decomposition of $[TlH_2PO_3]^{2+}$ giving products. k_1, k_2, k_3, and k_4 are the rate constants for the reactions of $TlCl^{2+}$, $TlCl_2{}^+$, $TlCl_3$, and $TlCl_4{}^-$ with H_3PO_3 as shown in the composite rate step (4). The concentrations of various thallium(III) species were calculated by successive approximations from equilibrium and mass balance relations,[10] using the stepwise formation constant values[11] of 1.85×10^6, 5.57×10^4, 3.8×10^2, and 62 M^{-1} corrected at 55° and $I = 1.1\ M$ for $TlCl^{2+}$, $TlCl_2{}^+$, $TlCl_3$, and $TlCl_4{}^-$, respectively. k_1, k_2, k_3, and k_4 were estimated by making suitable plots in $[Cl^-]_T$ ranges of $(2.4–4.5) \times 10^{-3}$, $(5–7) \times 10^{-3}$, and $(9–14) \times 10^{-3}\ M$ and employing $k = 5.5 \times 10^{-5}\ M^{-1}\ sec^{-1}$ and $K = 22.8$ at 55° determined[3b] for the reaction between thallium(III) and H_3PO_3 in the absence of chloride ions. These values have been shown in Table II. Some of the observed and calculated rates given in Table III are seen to be in fair agreement.

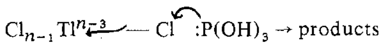
Discussion

Although the reductions of aquothallium(III) by H_3PO_3 and H_3PO_2 differ in hydrogen ion effect, reductions of chloro complexes of Tl^{III} are quite similar and have the general rate law

$$-d[Tl^{III}]/dt = \frac{(\Sigma k_n[TlCl_n{}^{3-n}])[H_3PO_m]_T[H^+]}{[H^+] + K_d}$$

where $n = 1, 2, 3$, and 4 and $m = 2$ or 3. The reactivity of chloro complexes in the two reactions follows the same order as mentioned in the introduction and the reactions probably occur by the same mechanism. It is of interest to mention that chloride ion catalysis is found elsewhere too. Mitchell[12] studied the oxidation of H_3PO_2 by $CuSO_4$ and $CuCl_2$ and found the reaction with $CuCl_2$ to be faster. The mechanism then proposed by him involves chloride ion as one of the reactants. The chloride ion catalysis in all these reactions can be explained either by invoking a chloride bridge activated mechanism or by nucleophilic attack of the phosphorus nucleophile $:P(OH)_3$ on chlorine[13] as discussed below.

For a large number of reactions of trivalent phosphorus it has been shown that phosphorus nucleophiles attack halogen where the latter is bonded to an electron-withdrawing substituent producing phosphoryl halides, halophosphines, or phosphates. Since in the oxidations under question chlorine is bonded to a highly positively charged metal ion, it is likely that a similar mechanism[14] operates here also as shown by



$$Cl_{n-1}Tl^{n-3} \leftarrow Cl \; :P(OH)_3 \rightarrow \text{products}$$

The evidence for the formation of $:P(OH)_3$ tautomer has been provided by Martin,[15] who studied the phosphonate–phosphite equilibria. Silver and Luz[16] have provided the evidence for the involvement of this tautomer in the H_3PO_3–I_2 reaction. Recently Viste et al.[17] proposed its existence to explain the results of oxidation of H_3PO_3 by silver(II). The following steps may also be considered along with (3) and (4) in order to include tautomer formation

$$H_3PO_3 + H^+ \xrightarrow{K_a} :P(OH)_3 + H^+ \quad \text{(slow)} \qquad (7)$$

$$:P(OH)_3 + H^+ \xrightarrow{K_a'} H_3PO_3 + H^+ \quad \text{(rapid)} \qquad (8)$$

These yield the same rate law as eq 2, with $k_{obsd} = k_nK_dK_a/K_a'$ and the assumption that $K_a'[H^+] >> k_n[Tl^{III}]$.

In the oxidations of H_3PO_2 and H_3PO_3 the reactivity of different chlorothallium(III) species follows the same order and probably the same mechanism. It is of interest to compare the rates of the two reactions. If the rate constants k_n of H_3PO_2 reactions are plotted against the corresponding rate constants of the H_3PO_3 reactions, a straight line with a slope of unity is obtained (Figure 1), although the rate constants refer to different experimental conditions. The rate constants of the two reactions are thus related by the equation

$$\log k_{n(H_3PO_2)} = \log k_{n(H_3PO_3)} + C$$

The simplest and most likely interpretation of the slope of unity is that the relative reactivities of various chlorothallium(III) complexes in the two reactions are the same. This will be true only if they react by the same mechanism in both the cases. It will be of interest to apply this equation in the reactions of different complexes of the same metal with two or more reagents believed to react by the same mechanism.

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Registry No. Tl^{3+}, 14627-67-9; H_3PO_3, 13598-36-2; Cl^-, 16887-00-6.

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Structural Trends of Tris(acetylacetonate)-, Tris(tropolonate)-, and Other Tris(bidentate ligand)-Metal Complexes. Additional Comments on the Trigonal Twist and Ligand-Ligand Repulsions in "Octahedral" D_3 Bidentate Ligand-Metal Complexes

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Since the structures of the majority of the first-row transition metal–tris(acetylacetonate) (acac) complexes are known,[1-4] it was of interest to us to examine structural trends and their correlations with some observed physical properties. Tris(tropolonate) (trop) structures were similarly scrutinized. Particular emphasis has been placed on comparisons with far-infrared spectra. The observed "trigonal twist" trends in these and other bidentate ligand complexes also have been examined.

Infrared Spectra of Neutral $(acac)_3$ and $(trop)_3$ Complexes. The determination of the $(acac)_3$ structures of most of the first-row transition metals allows a comparison of the M–O bond lengths with the positions of the metal-sensitive bands in the far-ir region. Figure 1 summarizes the far-ir data of neutral $(acac)_3$ complexes. A similar figure depicting the spectra of neutral $(trop)_3$ complexes is presented by Hulett and Thornton.[5b]

Theoretically,[6] seven metal–ligand (ML) vibration modes (2 a_2 and 5 e) are infrared active in D_3 site symmetry. Of these, three are stretching modes (a_2 and 2 e) and can be described as symmetric (e in D_3 correlating to e_g in O_h) and asymmetric (a_2 and e in D_3 correlating with t_{1u} in O_h). In practice, pure ML stretching bands are not observed in systems with ligands such as acac due to the extensive mixing of modes of the same symmetry. A number of investigators have recognized that certain bands in the far-ir region of $M(acac)_3$ and $M(trop)_3$ complexes were metal sensitive. For example, Thornton and coworkers[5] have pointed out that the pattern of frequency shifts in complexes where the metal is varied parallels the expected trends based on the crystal field stabilization energies (CFSE) of the metal ions. Analogously, we have observed the same pattern when the metal–ligand distances of the $M(acac)_3$ complexes (Table I) are plotted against the atomic number of the metal atoms. That is, the curve has the familiar "double-hump" characteristic.[7]

A comprehensive normal-coordinate analysis of $Fe(acac)_3$ by Mikami et al.[6c] identified the ML stretching bands as e_{sym} [found, 433 cm^{-1}; calcd, 446 cm^{-1} (48% pure)] and e_{asym} + a_2 [found, 298 cm^{-1} (unresolved); calcd, a_2 295 cm^{-1} (70%), e_{asym} 286 cm^{-1} (17%) and 222 cm^{-1} (40% pure)]. The proposed assignments were well supported by Nakamoto and coworkers[6d] using metal isotope shift techniques.

The abundance of reported structures of first-row transition series $M(acac)_3$ complexes prompted us to examine the assignments further. A plot of the frequencies of the three band series A, B, and C in Figure 1 against the metal–oxygen bond distances reveals high linear correlations, as shown in Figure 2. Series C bands show the steepest slope in the latter plot. Quite reasonably, these vibrations also reveal the largest metal isotope shifts, as noted by Nakamoto.[6d] Although the number of tropolonate structures reported is insufficient to warrant a similar plot, it seems that the same pattern also exists in that group of complexes.

The appearance of additional far-ir bands in the $Mn(acac)_3$ spectrum has long been attributed to distortions arising from