

positive values of ${}^2J_{P-P}$ in *cis*-[PdCl₂(P(OMe)₃)₂] and *trans*-[PdI₂(PMe₃)₂]. However our results are in agreement with general ideas that large *trans* couplings are positive while the smaller *cis* couplings can have either sign.¹⁵

A similar line of reasoning gives the signs shown in Table II for the couplings in the *trans*-[PtH(PEt₃)₂(PPh₃)]⁺ cation. However, the symmetry of the [PtH(PPh₃)₃]⁺ spectra precludes the determination of any sign information except that J_{AX} and J_{BX} must be of opposite sign.

Conclusions

The above discussion clearly shows that the unusual spectra reported by Roundhill and coworkers¹ for [PtH(PPh₃)₃]-[(CF₃COO)₂H] can be completely interpreted on the basis of an ionic structure having a square-planar cation. Thus, the previous workers were correct in suggesting that non-first-order effects offer a better explanation of the spectra than does the postulate of chemical nonequivalence of the B phosphorus atoms caused by ion association. More generally our results show that different side- and center-band multiplets are expected to be common for any A_nB_mX or similar spin system. These become A_nB_mMX systems in molecules containing ¹⁹⁵Pt and the side- and center-band patterns are similar only when $|\delta_{AB}| \gg \frac{1}{2}|J_{AM} - J_{BM}|$. An example of an AB system showing these effects was recently observed by us in the ³¹P spectrum of the [PtCl(*o*-phen)(PEt₃)₂]⁺ cation which has chemically nonequivalent triethylphosphine groups. The spectrum consists of a poorly resolved central doublet (AB system) with the ¹⁹⁵Pt side bands having a quartet structure (ABM system).¹⁶

Our analysis also demonstrates that when δ_{AB} is close to

(15) E. G. Finer and R. K. Harris, *Progr. Nucl. Magn. Resonance Spectrosc.*, **6**, 61 (1971), and references therein.

(16) $J_{AB} = 22$ Hz, $J_{AM} = 3680$ Hz, $J_{BM} = 3490$ Hz, and $\delta_{AB} = 14$ Hz at 40.5 MHz.

certain critical values,¹⁷ it is not possible to neglect the effect on the X spectrum of remote magnetically active nuclei which are coupled to A or B. Thus in tertiary phosphine complexes it may not be possible to neglect the effects of remote hydrogens in the alkyl or aryl groups.

Experimental Section

The complexes [PtH(PEt₃)₃][BPh₄]¹⁸, [PtH(PEt₃)₃][ClO₄]¹¹, *trans*-[PtH(PEt₃)₂(PPh₃)][ClO₄]¹¹, [PtH(PPh₃)₃][(CF₃COO)₂H]¹ and [PtH(PPh₃)₃][BF₄]¹⁹ were prepared as previously described. Nuclear magnetic resonance spectra were recorded in dichloromethane solution using tetramethylsilane as internal reference for proton spectra and phosphoric acid as external reference for phosphorus spectra. Chemical shifts are reported in Hz or ppm as appropriate and positive values indicate resonances to high field of the reference. Proton spectra were recorded at 60 MHz on a Varian HA60 spectrometer and at 220 MHz by the Canadian 220 MHz NMR Centre, Sheridan Park, Ontario. Phosphorus spectra were recorded at 19.3 MHz on a Varian HA60 spectrometer and at 40.5 MHz on a Varian XL100 spectrometer. Simulated spectra were calculated using the UEAIR program²⁰ on an IBM 370/145 computer and plotted on a Calcomp 563 Drum Plotter using a program based on the NMR PLOT program.²¹

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Registry No. [PtH(PEt₃)₃]⁺, 48074-87-9; *trans*-[PtH(PEt₃)₂(PPh₃)]⁺, 47757-13-1; [PtH(PPh₃)₃]⁺, 47899-53-6; P, 7723-14-0; ¹⁹⁵Pt, 14191-88-9.

(17) $\frac{1}{2}|J_{AX} - J_{BX}| - |J_{AB}|$ in the particular case of the AB₂X system studied here.

(18) H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, **91**, 596 (1969).

(19) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, **5**, 1128 (1966).

(20) R. B. Johannesen, J. A. Ferretti, and R. K. Harris, *J. Magn. Resonance*, **3**, 84 (1970).

(21) J. D. Swalen in "Computer Programs for Chemistry," Vol I, D. F. Detar, Ed., W. A. Benjamin, New York, N. Y., 1968.

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Kinetics and Mechanism of the Electron-Transfer Reactions of Aquo- and Coordinated Thallium(III). VII. Reduction of Chlorothallium(III) Complexes by Hypophosphite

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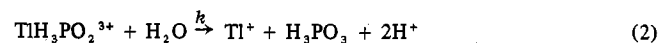
The Tl^{III}-H₃PO₂ reaction is catalyzed by chloride ions. The rate first decreases, reaches a minimum at $[Cl^-]_T/[Tl^{III}]_T \approx 1$, and then increases to a limiting value when this ratio is *ca.* 50. The reactivity of various thallium(III) species follows the order TlCl₄⁻ > TlCl₃ > TlCl₂⁺ > Tl³⁺ > TlCl²⁺. The reactive hypophosphite species is H₃PO₂. The complicated rate law for the reaction is

$$-d[Tl^{III}]/dt = (kK[Tl^{3+}] + k_1[TlCl^{2+}] + k_2[TlCl_2^+] + k_3[TlCl_3] + k_4[TlCl_4^-])[H_3PO_2]_T[H^+]/([H^+] + K_d)$$

where K_d is the dissociation constant of H₃PO₂, k , k_1 , k_2 , k_3 , and k_4 are the rate constants for the various reactive species of Tl^{III}, and K is the formation constant for the complex of Tl³⁺ and H₃PO₂.

Introduction

A kinetics study of the oxidation of hypophosphite^{1,2} has recently been made and the following mechanism was suggested



The rate law is

$$\frac{-d[Tl^{III}]}{dt} = \frac{kK[Tl^{III}][H_3PO_2]}{1 + K[H_3PO_2]} \quad (3)$$

(1) K. S. Gupta and Y. K. Gupta, *J. Chem. Soc. A*, 256 (1970).

(2) K. S. Gupta and Y. K. Gupta, *Indian J. Chem.*, **8**, 1001 (1970).

This reaction is catalyzed by chloride ions. Chloride ion catalysis has been reported for the exchange reaction^{3,4} of $Tl^{III}-Tl^I$ and the main catalytic activity was attributed to $TlCl_4^-$. The oxidation⁵ of Fe^{II} is also catalyzed and an intermediate formation of $Tl^{II}-Cl^-$ species has been suggested. For the oxidation of 1,2-cyclohexanedione by thallium(III) in the presence of chloride ions, Favier and Zador⁶ have reported that $TlCl_2^{2+}$ is more reactive than Tl^{3+} and the higher chlorothallium(III) complexes. On the other hand many reactions are known where the chloride ion has the opposite role. The oxidations of hydrazine,⁷ As^{III} ,⁸ formic acid,⁹ and vanadium(III)¹⁰ are considerably slowed by its presence. Chloride ions form strong complexes and in some cases they are highly reactive. Other ions which form complexes and accelerate the rate without themselves being oxidized are bromide,¹¹ cyanide,¹² sulfate,^{13,14} and nitrate.¹⁵ On the other hand substances such as thiocyanate,¹⁶ formic acid,⁹ oxalic acid,¹⁷ and olefins¹⁸ etc. coordinate and subsequently reduce Tl^{III} .

So far no thallium(III) electron-transfer reaction involving a net chemical change in a chloride-containing system has been studied in detail. The chloride-catalyzed oxidation of Fe^{II} by Tl^{III} is complicated by the formation of chloro complexes of Fe^{III} in addition to those of Tl^{III} . The present study has a distinct advantage insofar that no complexes other than those of Tl^{III} are formed and hence a less ambiguous chloride dependence can be shown.

Experimental Section

The chemicals and the procedure for preparing solutions and following the rate were same as described earlier.^{1,2,19} In most cases 70–80% of the reaction was followed. The treatment of present data is based on the initial rates obtained by the plane mirror method.²⁰ The duplicate rate measurements were reproducible to $\pm 5\%$.

All the reactions were studied at 28° unless otherwise stated.

Results

Stoichiometry. A number of reaction mixtures containing sodium hypophosphite and thallic perchlorate in varying proportions with appropriate concentrations of perchloric acid and sodium chloride were thermostated at 28° for about 1–3 hr. Excess thallium(III) was determined iodometrically.¹ One mole of thallium(III) is required for each mole of hy-

Table I. Stoichiometry of the $Tl(III)-H_3PO_2$ Reaction in the Presence of Chloride Ions^a

$10^2 \times [Tl(III)]_T$, <i>M</i> (initial)	$10^2 \times [NaH_2PO_2]_T$, <i>M</i> (initial)	$10^2 \times [Tl(III)]_T$, <i>M</i> (unused)	$\Delta[Tl(III)]/\Delta[NaH_2PO_2]$
2.4	1.0	1.40	1.00
2.4	2.0	0.38	1.01
3.2	2.0	1.16	1.02
3.2	3.0	0.20	1.00
4.8	2.00	2.75	1.02

^a $[HClO_4] = 1.0 M$; $[Cl^-]_T = 0.2 M$; temperature 28°.

pophosphite. The same stoichiometry was found in the absence of chloride ions.¹

Thallium(III) Dependence. The concentration of thallium(III) was varied from 5×10^{-4} to $1.88 \times 10^{-2} M$ at $[Cl^-]_T = 5 \times 10^{-3} M$ and $[H_3PO_2]_T = 5.0 \times 10^{-2} M$, where $[Cl^-]_T$ and $[H_3PO_2]_T$ are the analytical concentrations of all the chloride and hypophosphite species. A plot of rate *vs.* $[Cl^-]_T/[Tl(III)]_T$ (hereafter referred to as *R*) gives a curve with a minimum at $R \approx 1$ and a maximum at $R \approx 4$. A simple order in thallium(III) in the presence of chloride ions is not obvious because it forms a number of complexes of different reactivities whose proportions vary with *R*. However if chloride is also varied along with thallium(III) in order to maintain *R* constant (experiments 1–9), a log-log plot of rate and thallium(III) concentration yields a straight line with slope of 1.03. The order in thallium(III) is thus 1. This indirectly shows that the formation constants of the complexes are large enough so that concentration of a particular complex increases almost in proportion to the increase in $Tl(III)$ and chloride. When chloride concentration is sufficiently large, a particular complex of thallium(III) is formed and no further complexation occurs (experiments 10–15). In such a situation thallium(III) variation has a clear-cut first order dependence. All these results are shown in Table II.

Hypophosphite Dependence. The concentration of hypophosphite was varied in the concentration range (2.5–50) $\times 10^{-3} M$ at $R = 1.4$ and $R = 10$, and a log-log plot of rate and H_3PO_2 yielded a straight line with a slope of 1.07. The rate can be represented by experimental rate law (4) at constant

$$\frac{-d[Tl(III)]}{dt} = k_{\text{obsd}} [Tl(III)]_T [H_3PO_2]_T \quad (4)$$

R and hydrogen ion concentration.

Hydrogen Ion Dependence. The concentration of hydrogen ion was varied with perchloric acid in a fixed 1.0 *M* perchlorate medium, adjusted with lithium perchlorate to avoid medium effects.^{1,2} The rate increases sharply in the hydrogen ion concentration range of 0.064–0.5 *M* and then tends to attain a limiting value. This is in conformity with rate law (5) at constant chloride, thallium(III), and hypophosphite

$$\frac{-d[Tl(III)]}{dt} = \frac{k'_{\text{obsd}} [Tl(III)]_T [H_3PO_2]_T [H^+]}{[H^+] + K_d} \quad (5)$$

concentrations, where $[H^+]$ is the equilibrium concentration, K_d is the dissociation constant of H_3PO_2 (see later), and

$$k_{\text{obsd}} = k'_{\text{obsd}} \left(\frac{[H^+]}{[H^+] + K_d} \right)$$

By using $K_d = 0.135 M$, at $\mu = 1.0 M$ and 25°, reported by Espenson *et al.*,²¹ the values of (rate)/ $([H^+] + K_d)/[H^+]$ given

(21) J. H. Espenson and D. F. Dustin, *Inorg. Chem.*, **8**, 1760 (1969).

- (3) G. Harbottle and R. W. Dodson, *J. Amer. Chem. Soc.*, **73**, 2442 (1951).
 (4) S. Gilks, T. E. Rogers, and G. M. Waind, *Trans. Faraday Soc.*, **57**, 1371 (1961).
 (5) F. R. Duke and B. Bornong, *J. Phys. Chem.*, **60**, 1015 (1956).
 (6) R. Favier and M. Zador, *Can. J. Chem.*, **47**, 3539 (1969); **48**, 2407 (1970).
 (7) K. S. Gupta and Y. K. Gupta, *Indian J. Chem.*, in press.
 (8) P. D. Sharma and Y. K. Gupta, *J. Chem. Soc. A*, 52 (1973).
 (9) H. N. Halvorson and J. Halpern, *J. Amer. Chem. Soc.*, **78**, 5562 (1956).
 (10) N. A. Daugherty, *J. Amer. Chem. Soc.*, **87**, 5026 (1965).
 (11) L. G. Carpenter, M. H. Ford-Smith, R. P. Bell, and R. W. Dodson, *Discuss. Faraday Soc.*, **29**, 92 (1960).
 (12) E. Penna-Franca and R. W. Dodson, *J. Amer. Chem. Soc.*, **77**, 2651 (1955).
 (13) C. H. Brubaker, Jr., J. P. Mickel, and C. P. Knop, *J. Inorg. Nucl. Chem.*, **4**, 55 (1957).
 (14) D. R. Wiles, *Can. J. Chem.*, **36**, 167 (1958).
 (15) R. J. Prestwood and A. C. Wahl, *J. Amer. Chem. Soc.*, **71**, 3137 (1949).
 (16) L. Triendl and M. Fico, *Collect. Czech. Chem. Commun.*, **34**, 2873 (1969).
 (17) L. B. Monsted, O. Monsted, and G. Nord, *Trans. Faraday Soc.*, **66**, 936 (1970).
 (18) P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990, 4423 (1965); **88**, 1597 (1966).
 (19) H. G. S. Sengar and Y. K. Gupta, *J. Indian Chem. Soc.*, **43**, 223 (1966); I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience, New York, N. Y., 1957, p 370.
 (20) M. Latshaw, *J. Amer. Chem. Soc.*, **47**, 793 (1925).

Table II. k_{obsd} for the Tl(III)- H_3PO_2 Reaction at Various R Values^a

Expt no.	$10^3[\text{H}_3\text{PO}_2]_T$, M	$10^3[\text{Tl(III)}]_T$, M	$10^3[\text{Cl}^-]_T$, M	R	$10^7(\text{rate})$, $M \text{ sec}^{-1}$	$10^2 k_{\text{obsd}}(\text{eq 4})$, $M^{-1} \text{ sec}^{-1}$
1	10	0.48	0.48	1	0.41	0.87
2	10	0.96	0.96	1	0.93	0.97
3	10	1.92	1.92	1	1.87	0.97
4	10	2.88	2.88	1	2.70	0.93
5	10	3.84	3.84	1	3.75	0.97
6	10	0.48	0.96	2	1.55	3.1
7	10	0.96	1.92	2	3.33	3.3
8	10	1.92	3.84	2	5.73	3.0
9	10	3.84	7.68	2	11.2	3.0
10	10	0.96	40.0		18.8	19.5
11	10	1.45	40.0		30.1	20.1
12	10	1.93	40.0		39.5	20.0
13	10	2.41	40.0		50.0	20.1
14	10	2.89	40.0		59.3	20.0
15	10	3.84	40.0		77.0	20.0
16	2.5	1.90	20.0	10	6.25	13.1
17	5.0	1.90	20.0	10	13.1	13.8
18	10	1.90	20.0	10	28.3	14.8
19	20	1.90	20.0	10	56.7	14.8
20	5.0	2.50	3.50	1.4	2.30	1.87
21	15	2.50	3.50	1.4	7.47	1.98
22	30	2.50	3.50	1.4	1.46	1.97

^a $[\text{HClO}_4] = 1.013 M$; temperature 28° .

in the last column of Table III are seen to be fairly constant at a particular chloride ion concentration. The plots of $1/(\text{rate})$ vs. $1/[\text{H}^+]$ yielded straight lines at different chloride ion concentrations with identical slopes, equal to K_a in accordance with eq 5.

Chloride Ion Dependence. The rate first decreases slightly and then increases to attain a limiting value as the concentration of chloride ion is varied from 2.5×10^{-4} to $8.0 \times 10^{-2} M$. The characteristic curve has been given in the earlier paper.¹

Ionic Strength Dependence. The ionic strength was varied by use of lithium perchlorate. The rate slightly decreases with the increase of ionic strength from $21.7 \times 10^{-7} M \text{ sec}^{-1}$ at $\mu = 1.01$ to $20.7 \times 10^{-7} M \text{ sec}^{-1}$ at $\mu = 3.01$, $[\text{Tl(III)}]_T = 2.4 \times 10^{-3} M$, $[\text{H}_3\text{PO}_2]_T = 5.0 \times 10^{-3} M$, $[\text{Cl}^-]_T = 3.0 \times 10^{-2} M$, and a temperature of 28° .

Product Dependence. Variation of the concentrations of reaction products thallium(I) ($(1-4) \times 10^{-3} M$) and H_3PO_3 ($(0.1-1.0) \times 10^{-2} M$) did not affect the rate, showing thereby that the rate-determining step has no preequilibrium steps involving thallium(I) and H_3PO_3 .

Temperature Dependence. A few kinetics experiments were made at 28 , 32 , and 36° , and values of initial rates were found to be 21.7×10^{-7} , 33.3×10^{-7} , and $40.0 \times 10^{-7} M \text{ sec}^{-1}$, respectively, at $[\text{Tl(III)}]_T = 2.4 \times 10^{-3} M$, $[\text{H}_3\text{PO}_2]_T = 5.0 \times 10^{-3} M$, $[\text{Cl}^-]_T = 3.0 \times 10^{-2} M$, and $[\text{HClO}_4] = 1.01 M$.

Reactive Species, Mechanism, and Rate Constants.

Thallium(III) Species. The simplest interpretation of the results is that the thallic ion forms various chloride complexes which differ in their reactivities and that the overall rate is a function of the concentrations of these complexes. The interconversion between hydrated Tl(III) and the various complexes is rapid compared to the rates of reactions followed in the present work. A detailed consideration of these complexes, therefore, becomes necessary before any rate law can be suggested. At present there is disagreement with respect to the number of chloride complexes formed. Some authors^{22,23} reported thallium(III) species containing as

Table III. Hydrogen Ion Dependence of the Rate of the Tl(III)- H_3PO_2 Reaction^a

$10 \times$ $[\text{HClO}_4]_T$, M	$10^3 \times$ $[\text{Cl}^-]_T$, M	R	$10^7(\text{rate})$, $M \text{ sec}^{-1}$	$10^7 \times$ $(\text{rate}) \times$ $([\text{H}^+] +$ $K_a)/$ $[\text{H}^+]_T$, $M \text{ sec}^{-1}$
3.44	2.0	0.83	0.33	2.1
6.63	2.0	0.83	1.67	2.0
3.44	2.5	1.04	2.18	3.0
10.1	2.5	1.04	2.67	3.0
0.64	4.8	2.0	1.15	3.7
0.90	4.8	2.0	1.80	4.3
2.00	4.8	2.0	2.29	3.8
3.44	4.8	2.0	2.78	3.8
5.00	4.8	2.0	3.00	3.8
10.1	4.8	2.0	3.53	4.0
0.90	7.2	3.0	3.08	7.7
2.00	7.2	3.0	4.17	7.0
3.44	7.2	3.0	5.58	7.8
10.1	7.2	3.0	7.08	7.8
0.90	9.6	4.0	4.67	11
2.00	9.6	4.0	6.33	10
3.44	9.6	4.0	7.83	11
5.00	9.6	4.0	9.66	12
10.1	9.6	4.0	10.6	12
0.90	30.0	10.25	7.87	25
2.00	30.0	10.25	12.0	21
3.44	30.0	10.25	16.6	23
5.00	30.0	10.25	18.3	23
6.63	30.0	10.25	20.4	25
8.53	30.0	10.25	21.2	25
10.1	30.0	10.25	21.6	25

^a $[\text{Tl(III)}]_T = 2.4 \times 10^{-3} M$; $[\text{H}_3\text{PO}_2]_T = 0.5 \times 10^{-2} M$ except for the first four experiments where it was $1 \times 10^{-2} M$; $\mu = 1.013 M$; temperature 28° .

many as six chlorides per Tl^{3+} whereas others regarded pentachlorothallium(III) as the ultimate chloride complex.²⁴ Many workers have not confirmed the formation of penta- and hexachloro complexes,²⁵⁻²⁸ nor did we find any evidence

(24) D. F. Shriver and I. Wharf, *Inorg. Chem.*, **8**, 2167 (1969).

(25) R. Benoit, *Bull. Soc. Chim. Fr.*, 518 (1949).

(26) B. Baysal, *Actes Congr. Int. Catal.*, **1**, 559 (1960).

(27) S. Ahrland, I. Grenthe, L. Johansson, and B. Noren, *Acta Chem. Scand.*, **17**, 1567 (1963).

(28) J. M. Woods, P. K. Gallagher, Z. Z. Hugus, Jr., and E. L. King, *Inorg. Chem.*, **3**, 1313 (1964).

(22) D. Peschanski and S. Vallades-Dubois, *Bull. Soc. Chim. Fr.*, 1170 (1956).

(23) T. G. Spiro, *Inorg. Chem.*, **4**, 731 (1965).

from kinetics. The present discussion is based on the work of Woods and coworkers,²⁸ who reported the stepwise formation constant values 5.22×10^6 , 1.25×10^5 , 482, and $65.3 M^{-1}$ ($\mu = 0.5 M$, temperature 25°) for $TlCl^{2+}$, $TlCl_2^+$, $TlCl_3$, and $TlCl_4^-$, respectively. By use of the procedure of Woods, *et al.*,²⁸ these values were corrected to 1.0 M ionic strength and the values are 4.2×10^6 , 1.1×10^5 , 450, and $65.3 M^{-1}$. These values were used to work out the results of the present investigation.

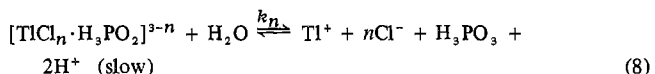
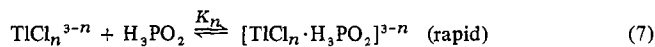
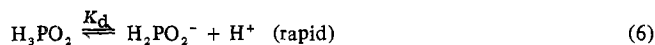
The hydrolysis constant²⁹ of Tl^{3+} is reported to be 0.073 at 25° and hence only a small fraction of Tl(III) would exist as $TlOH^{2+}$ in 1.0 M $HClO_4$ (used in most of the experiments) and in presence of chloride ions. The only mixed hydroxy species reported in chloride medium is $TlOHCl^+$.²³ Since the rate increases on increasing hydrogen ion concentration under all conditions, the hydroxy species cannot be considered to be reactive to any significant extent. Likewise these have not been considered reactive in earlier oxidation studies.³⁰ Hence the only species of Tl(III) considered reactive for the construction of the rate law are Tl^{3+} , $TlCl^{2+}$, $TlCl_2^+$, $TlCl_3$, and $TlCl_4^-$.

The concentrations of the free chloride and various thallium(III) species were calculated by successive approximations from the equilibrium and mass balance relations.^{30,31} The fractions of thallium(III) present as Tl^{3+} , $TlCl^{2+}$, $TlCl_2^+$, $TlCl_3$, and $TlCl_4^-$ were plotted against $\log [Cl^-]_T$ (Figure 1). The figure also includes a log-log plot of rate and chloride concentration. A correlation of rate and the concentration of the various species and the reactivities can be easily made. The order of reactivity is $TlCl_4^- > TlCl_3 > TlCl_2^+ > TlCl^{2+}$.

The role of chloride ions with respect to the formation of different reactive species is shown in a single experiment (Figure 2). As the reaction proceeds, thallium(III) decreases and consequently R increases. The decrease in Tl(III) is compensated by the formation of more reactive chloro complexes and hence the rate is almost constant until R becomes greater than 2. Normal Tl(III) disappearance is observed only after $R = 4$.

Hypophosphite Species. Based on the above argument, it is likely that the hydrogen ion effect is linked with hypophosphite. In aqueous solutions it will be present as $H_2PO_2^-$ and H_3PO_2 . Increasing the hydrogen ion concentration will increase the concentration of H_3PO_2 . Thus the hydrogen ion effect can be explained by assuming H_3PO_2 is the reactive species and the limiting rates can be ascribed to the complete conversion of $H_2PO_2^-$ into H_3PO_2 .

On the basis of the above arguments the rate-determining steps possibly involve chlorothallium(III) complexes and undissociated acid molecule H_3PO_2 . A general mechanism for all the species of thallium(III) and H_3PO_2 could be written as



There is no evidence from the kinetics for step 7 but in any

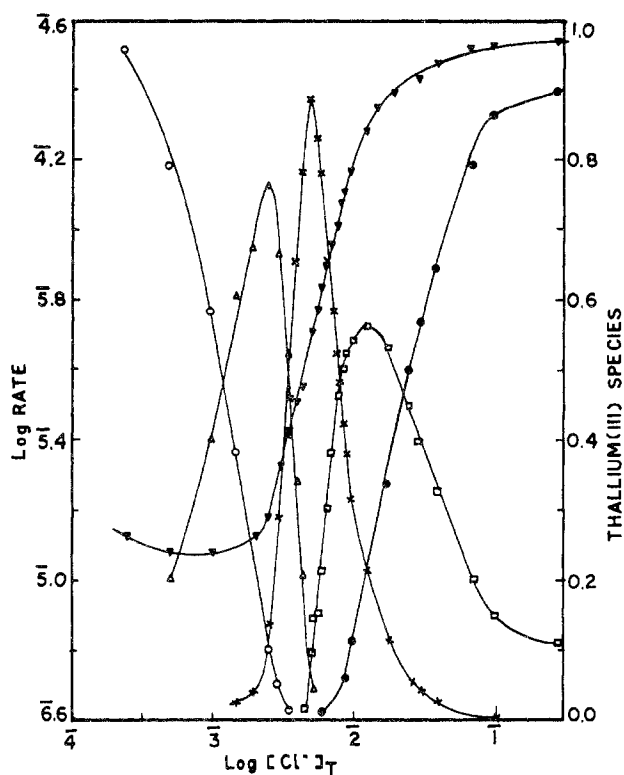


Figure 1. The rates and distribution of Tl(III) species at various chloride concentrations for the Tl(III)- H_3PO_2 reaction with $[Tl(III)]_T = 2.42 \times 10^{-3} M$ and $[HClO_4] = 1.01 M$. Fraction of $Tl(III)_T$: \circ , Tl^{3+} ; Δ , $TlCl^{2+}$; \times , $TlCl_2^+$; \square , $TlCl_3$; \bullet , $TlCl_4^-$.

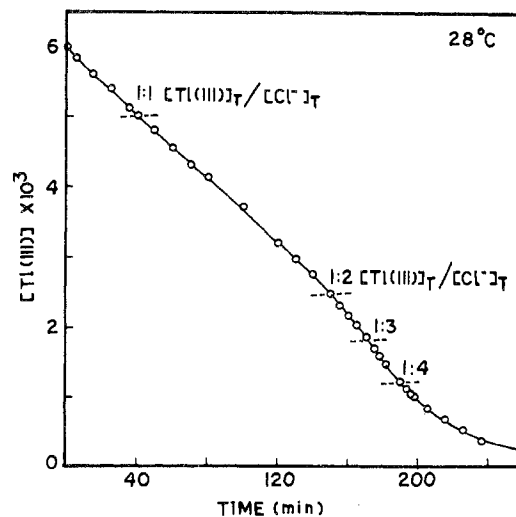


Figure 2. A plot showing the course of a single kinetics experiment for the Tl(III)- H_3PO_2 reaction with $[Tl(III)]_T = 6.0 \times 10^{-3} M$, $[Cl^-]_T = 5.0 \times 10^{-3} M$, $[HClO_4] = 1.01 M$, and $[H_3PO_2] = 1.0 \times 10^{-2} M$.

case the formation constant of the $[TlCl_n \cdot H_3PO_2]^{3-n}$ complex is small. Step 7 may find support from the reported results that $TlCl_3$ forms the complex $TlCl_3 \cdot 2OPCl_3$ with $POCl_3$ ³² and the addition compound $[PCl_4^+][TlCl_4^-]$ with PCl_5 .³³

The rate law (9) for the reaction can be written on the basis

(29) G. Biedermann, *Ark. Kemi*, 5, 441 (1953).

(30) G. M. Waind, *Discuss. Faraday Soc.*, 29, 136 (1960).

(31) K. S. Gupta, Ph.D. Thesis, University of Rajasthan, 1970.

(32) V. E. W. Wartenberg and J. Goubeau, *Z. Anorg. Allg. Chem.*, 329, 269 (1964).

(33) V. P. Petro and S. G. Shore, *J. Chem. Soc.*, 336 (1964).

$$\frac{-d[\text{Tl(III)}]}{dt} = (kK[\text{Tl}^{3+}] + k_1[\text{TlCl}_2^{2+}] + k_2[\text{TlCl}_2^+] + k_3[\text{TlCl}_3] + k_4[\text{TlCl}_4^-]) \left(\frac{[\text{H}_3\text{PO}_2]_T [\text{H}^+]}{[\text{H}^+] + K_d} \right) \quad (9)$$

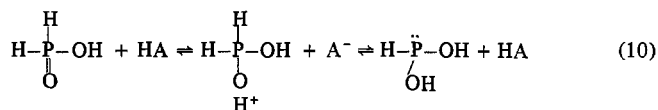
of reactions 1-3 and 6-8.

It can be seen from Figure 1 that at any particular chloride ion concentration not more than three chloro complexes are present in significant amounts in the system. By making suitable plots in $[\text{Cl}^-]_T$ ranges of $(2.4-4.5) \times 10^{-3}$, $(5-7) \times 10^{-3}$, and $(9-14) \times 10^{-3} M$ and employing $k = 7.1 \times 10^{-4} M^{-1} \text{sec}^{-1}$ and $K = 15 M^{-1}$ at 28° for the uncatalyzed reaction, various rate constants were calculated. These are given in Table IV. However it must be noted that the different rate constants are not pure rate constants but possibly include formation constants of step 7 also.

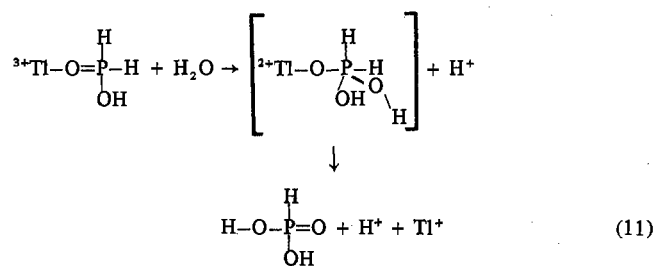
Some of the observed and calculated rates given in Table V are seen to be in good agreement.

Discussion

A common feature of the reduction of chlorothallium(III) complexes and aquothallic ion by hypophosphite is the reactive H_3PO_2 species. Reduction of Tl^{3+} by phosphorous acid³⁴ is also interpreted by considering H_3PO_3 as the reactive species. Similar kinetics behavior has been noted in the H_3PO_2 oxidation by vanadium(V)³⁵ and chromium(VI).³⁶ If P-H bond breaking occurs in these reactions, it would appear that the labilization of the P-H bond,³⁷ followed by proton exchange with the medium, and the presence of the unprotonated pair of electrons of P greatly facilitate oxidation. This is supported by the rapid oxidation of $(\text{C}_2\text{H}_5\text{O})_3\text{P}$ by Cr(VI) .³⁷ In case of H_2PO_2^- (or H_2PO_3^-) proton attack from any acid HA simply stabilizes the acid species and the P-H bond is not labilized.



An alternative mechanism for the oxidation of H_3PO_2 by aquothallic ion is



This is analogous to olefin oxidation.¹⁸

The most important aspect of this reaction is the acceleration of rate by chloride ions. Reductions of thallium(III) on the basis of chloride ion effect may be divided in two classes.

(A) One class includes the oxidations of hydrazine,⁷ formic acid,⁹ and arsenious acid,⁸ etc., which are decelerated by chloride ions. All these reactions proceed through the for-

(34) K. S. Gupta and Y. K. Gupta, *J. Chem. Soc. A*, 1180 (1971).

(35) J. N. Cooper, H. L. Hoyt, C. W. Buffington, and C. A. Holmes, *J. Phys. Chem.*, 75, 891 (1971).

(36) G. P. Haight, Jr., M. Rose, and J. Preer, *J. Amer. Chem. Soc.*, 90, 4809 (1968).

(37) G. P. Haight, Jr., F. Smentowski, M. Rose, and C. Heller, *J. Amer. Chem. Soc.*, 90, 6325 (1968).

Table IV. Rate Constants at 28°

Reactants	$10^2 \times$ rate constants, $M^{-1} \text{sec}^{-1}$
$\text{Tl}^{3+}-\text{H}_3\text{PO}_2$	$kK = 1.08$
$\text{TlCl}_2^{2+}-\text{H}_3\text{PO}_2$	$k_1 = 0.67$
$\text{TlCl}_2^+-\text{H}_3\text{PO}_2$	$k_2 = 2.8$
$\text{TlCl}_3-\text{H}_3\text{PO}_2$	$k_3 = 12.5$
$\text{TlCl}_4^--\text{H}_3\text{PO}_2$	$k_4 = 24.0$

Table V. Observed and Calculated Rates of the $\text{Tl}^{III}-\text{H}_3\text{PO}_2$ Reaction in Different Chloride Media^a

$10^3[\text{Cl}^-]_T,$ M	$[\text{Cl}^-], M$	$10^7(\text{rate}), M \text{sec}^{-1}$	
		Obsd	Calcd
0.0	0.0	2.27	2.25
0.25	2.88×10^{-8}	2.17	2.18
0.5	7.13×10^{-8}	2.01	2.08
1.0	1.64×10^{-7}	2.01	2.00
2.0	5.26×10^{-7}	2.21	2.00
2.5	1.67×10^{-6}	2.50	2.43
3.0	3.87×10^{-6}	3.50	4.00
3.5	8.02×10^{-6}	4.50	4.80
4.0	1.75×10^{-5}	5.25	5.16
4.5	3.54×10^{-5}	5.83	5.75
5.0	2.50×10^{-4}	8.33	8.41
5.5	5.00×10^{-4}	9.58	9.00
6.0	6.65×10^{-4}	11.2	11.8
9.0	2.00×10^{-3}	21.0	20.2
10.0	3.19×10^{-3}	24.0	24.7
12.5	5.70×10^{-3}	32.3	30.8
17.5	1.02×10^{-2}	36.7	36.7
30.0	2.19×10^{-2}	44.0	45.1
40.0	3.10×10^{-2}	48.3	47.3
70.0	6.07×10^{-2}	54.1	53.3
100	9.07×10^{-2}	55.1	54.1
140	13.06×10^{-2}	55.1	55.1

^a $[\text{Tl}^{III}]_T = 2.42 \times 10^{-3} M$; $[\text{HClO}_4] = 1.01$; $[\text{H}_3\text{PO}_2]_T = 1.0 \times 10^{-2} M$; temperature 28° .

mation of an intermediate complex between thallic ion and the substrate in the absence of chloride ions. The same mechanism probably operates in the presence of chloride ions too. Chloride ions block the coordination sites on Tl^{3+} and thus inhibit the formation of an intermediate complex and the rate of thallium(III) reduction.

(B) The other class of thallium(III) reactions includes oxidation of Fe(II) ⁵ and Sb(III) ³⁸ and the $\text{Tl(III)}-\text{Tl(I)}$ exchange reaction,³⁰ where chloride ion accelerates the rate of reaction. The catalysis by chloride ions can be explained by invoking a bridge-activated mechanism with chlorine as the bridge atom.

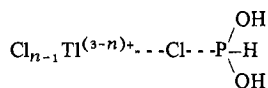
The hypophosphite reaction is unique. Like class A reactions, in absence of chloride ions, it proceeds through the formation of an intermediate complex. From kinetics studies,¹ the equilibrium constant for the formation of $\text{TlH}_3\text{PO}_2^{3+}$ has been estimated to be $15 M^{-1}$ at 28° . In the presence of chloride ions there is no evidence from kinetics for the formation of this intermediate complex. This is in line with the findings for class A reactions that the chloride ions inhibit the formation of an intermediate complex. Since the rate is accelerated by chloride ions, the most reasonable way to explain this is by assuming that the reaction proceeds through a chloride-bridged mechanism (class B behavior). This is likely in view of the fact that the active form³⁹ of hypophosphorous acid

(38) P. D. Sharma and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.*, 789 (1973).

(39) W. A. Jenkins and D. M. Yost, *J. Inorg. Nucl. Chem.*, 11, 297 (1959).

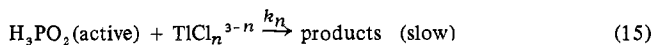
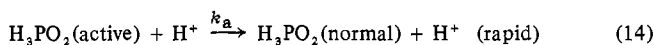
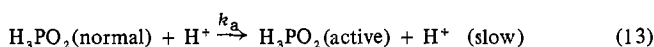
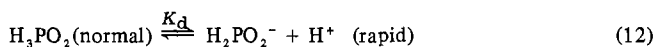


is a better electron donor. Formation of an activated complex



may find support from the fact that a similarly bridged complex $\text{Cl}_3\text{Ti} \cdots \text{Cl} \cdots \text{Cl}_2\text{PO}$ has been considered to be a possibility in chloride-exchange kinetics between TiCl_3 and POCl_3 .⁴⁰

The mechanism on the basis of an active form of hypophosphorous acid³⁹ could be



Assuming a steady state for $\text{H}_3\text{PO}_2(\text{active})$, rate law (16) is

$$\frac{-d[\text{Ti(III)}]}{dt} = \frac{k_n K_d k_a [\text{Ti(III)}]_T [\text{H}^+]^2 [\text{H}_3\text{PO}_2]_T}{([\text{H}^+] + K_d)(k_a' [\text{H}^+] + k_n [\text{Ti(III)}])} \quad (16)$$

obtained. If $k_a' [\text{H}^+] \gg k_n [\text{Ti(III)}]$, the rate law (16) reduces

(40) J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 1305 (1963).

to (17). This is same as the experimental rate law (5) with

$$\frac{-d[\text{Ti(III)}]}{dt} = \frac{k_n K_d k_a}{k_a'} \frac{[\text{H}^+][\text{Ti(III)}]_T [\text{H}_3\text{PO}_2]_T}{[\text{H}^+] + K_d} \quad (17)$$

$$k'_{\text{obsd}} = k_n K_d k_a / k_a'$$

For $\text{Ti(III)}-\text{Ti(I)}$ exchange reaction it has been shown that the reaction is decelerated by small amounts of chloride,³⁻⁵ bromide,¹¹ and cyanide¹² ions but strongly accelerated by larger amounts. It has been concluded that the species TiCl_2^{2+} , TlBr^{2+} , and TiCN^{2+} are least reactive. In the present investigation, too, the overall rate appears to decrease with the increase in chloride ion until $R \approx 1$. This may suggest TiCl_2^{2+} to be least reactive (Table IV).

In contrast is the oxidation of 1,2-cyclohexanedione⁶ in which the TiCl_2^{2+} species has been reported to be most reactive, *i.e.*, more reactive than Ti^{3+} , TiOH^{2+} , and higher chloro complexes. The opposite role of TiCl_2^{2+} in the two oxidations probably indicates that the two reactions occur through entirely different mechanisms.

It appears that TiCl_2^{2+} is less reactive than aquothallic ion because chloride inhibits the formation of an intermediate complex of Ti^{3+} and H_3PO_2 and at the same time the thallium(III) reduction does not occur *via* a bridged activated complex. This probably becomes operative with the formation of TiCl_2^{2+} and subsequent complexes.

Two implications are thus obvious: (1) chloride ions inhibit the formation of intermediate complexes in all cases and (ii) chloride ions accelerate the redox processes in those cases where a bridge-activated mechanism can operate.

Registry No. Ti^{3+} , 14627-67-9; TiCl_2^{2+} , 23715-56-2; TiCl_2^+ , 23172-38-5; TiCl_3 , 13453-32-2; TiCl_4^- , 18616-42-7; H_3PO_2 , 6303-21-5; Cl^- , 16887-00-6.

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Microwave Spectrum, Barrier to Internal Rotation, Dipole Moment, and Molecular Structure of Methyl difluorophosphine^{1,2}

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The microwave spectrum of methyl difluorophosphine has been assigned in the ground state and the three lowest excited vibrational states. From the splittings of the ground and first excited torsional states the barrier to the methyl group internal rotation was found to be 2300 (50) cal/mol. Stark effect measurements gave the following values for the dipole moment and its components: $\mu_a = 2.047$ (2) D, $\mu_b = 0.0$ D, $\mu_c = 0.195$ (62) D, and $\mu = 2.056$ (6) D. With judicious assumptions for the methyl group geometry and the PF bond length, the PC bond length was found to be 1.82 Å.

Introduction

A study of methyl difluorophosphine was undertaken as a result of recent interest in difluorophosphine derivatives in our laboratory and elsewhere.³⁻⁷ Determination of the

barrier to internal rotation of the methyl group would provide an interesting comparison to the previously reported values for methylphosphine,⁸ methylamine,⁹ methyl-

(1) This work was supported in part by grants from the National Science Foundation.

(2) A preliminary account of this work was presented at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1971.

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