σ-Bonded Organotransition-metal Ions. Part XVI.[1] Oxidation, Complex Formation, and Electrophilic Substitution in the Reactions of Tricarbonyl(η-cyclopentadienyl)(pyridiniomethyl)-molybdenum and -tungsten with Thallium(III) and Mercury(II) Species in Aqueous Solution

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The reaction of tricarbonyl(η-cyclopentadienyl)(pyridiniomethyl)-molybdenum and -tungsten with thallium(III) perchlorate in aqueous acidic solution involves a rapid (probably two-electron) oxidation followed by a series of reactions leading to the corresponding pyridinioacetic acid as the main organic product. The marked increase in the rate of oxidation as the acid concentration is decreased is ascribed to the reactivity order $[Tl(OH)_2]^+ \gg [Tl(OH)]^{2+} \gg Tl^{3+}$. These reactions are compared with the corresponding oxidations induced by the hexachloroiridate(IV) ion. The reaction of dilute solutions of the same substrates with mercury(II) perchlorate in aqueous acidic solution involves initial rapid but reversible co-ordination of the substrate to the mercury(II) species. In the case of the molybdenum substrates, the final organometallic product is the corresponding pyridiniomethylmercury(II) ion. The rates of reaction of these substrates are indicative of a normal bimolecular electrophilic-substitution reaction between the mercury(II) species and the uncomplexed substrate. The influence of chloride ion on the above reactions is briefly explored and it is noted that a different course is taken in the reactions with the mercury(II) species when higher concentrations of reagents are employed.

SEVERAL thallium(III) and mercury(II) species, including Tl^{3+}, $[Tl(OH)]^{2+}$, Hg^{2+}, $[TlCl_n]^{(3-n)+}$, and $[HgCl_n]^{(2-n)+}$ $(1 \leqslant n \leqslant 4)$ have been shown to act as conventional electrophiles towards a number of cationic, anionic, and neutral σ-bonded organotransition-metal complexes, including the alkyl-metal carbonyl ions (1) and (2).[2-8] These reactions are believed to involve the bimolecular attack of the electrophile at the α-carbon of the organometallic complex with subsequent or synchronous displacement of the transition-metal ion [equation (1)].

$$M'^{n+} + M(CH_2R) \longrightarrow M^+ + [M'(CH_2R)]^{(n-1)+} \qquad (1)$$

(1)—(5)

(1)[2] $R = Hpy^+, M = Fe(cp)(CO)_2$
(2)[3] $R = Hpy^+, M = Mn(CO)_5$
(3)[4] $R = Hpy^+, M = Cr(OH_2)_5{}^{2+}$
(4)[5] $R = Hpy^+, M = Co(CN)_5{}^{3-}$
(5)[6-8] $R = Ph, M = Co(Hdmg)_2(aq)$
Hpy^+ = 3- or 4-substituted pyridinium ion
$M' = Hg^{II}$ or Tl^{III}
$cp = \eta\text{-}C_5H_5$

From the detailed kinetics of several of these reactions[2-5] it was possible to assign rate coefficients to each of the mercury(II) and thallium(III) species. Only in the case of the pentacyanocobaltate(III) species, (4), was any alternative reaction path detected,[5] and this was ascribed to attack of $[HgCl]^+$ on co-ordinated cyanide rather than at the β-carbon. However, both mercury(II) and thallium(III) species are also oxidising agents and a number of alkylcarbonylmetal complexes, including (1), (6), and (7), have also been shown to be susceptible to one-electron oxidation[9,10] with subsequent interesting carbonyl-insertion and nucleophilic-displacement reactions (2).

$$\begin{tikzcd}
{\begin{array}{l}[M(cp)(CH_2R)(CO)_3] \\ \text{(6a—c),(7a—c)}\end{array}} \arrow[r, "e^-"] & {[M(cp)(CH_2R)(CO)_3]^+} \arrow[d, "-e^-"] \\
{\begin{array}{l}RCH_2CO_2H \\ \text{(8a),(9a),(17)}\end{array}} & {[M(cp)(CH_2R)(CO)_3]^{2+}} \arrow[l]
\end{tikzcd} \qquad (2)$$

(6a) $R = 3\text{-}Hpy^+, M = Mo$
(6b) $R = 4\text{-}Hpy^+, M = Mo$
(6c) $R = Ph, M = Mo$
(7a) $R = 3\text{-}Hpy^+, M = W$
(7b) $R = 4\text{-}Hpy^+, M = W$
(7c) $R = Ph, M = W$
(8a) $R = 3\text{-}Hpy^+$
(9a) $R = 4\text{-}Hpy^+$
(17) $R = Ph$

The tricarbonyl(η-cyclopentadienyl)(pyridiniomethyl)-molybdenum and -tungsten complexes (6a) and (6b), and (7a) and (7b), respectively, therefore provide interesting substrates for the investigation of the mechanistic borderline between electrophilic-substitution and oxidation processes involving metallic reagents.

In this paper are described studies of the kinetics and products of reaction of complexes (6) and (7) with several thallium(III) and mercury(II) species.

RESULTS

Reactions of Thallium(III).—(a) *Spectrophotometric changes.* The reactions of thallium(III) perchlorate (10^{-4}—10^{-5} mol dm^{-3}) with (6a), (6b), (7a), and (7b) in aqueous perchloric acid (0.1—0.5 mol dm^{-3}) were studied spectrophotometrically in the 220—450 nm region using conventional and stopped-flow techniques. In each case there was an initial decrease in the intense broad absorption maximum of the organometallic substrate with the con-

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TABLE 1

Kinetics of reaction of pyridiniomethylmetal complexes, [MR], with thallium(III) perchlorate in aqueous perchloric acid at 25 °C and I = 0.5 mol dm^{-3}

Complex	Metal	$10[H^+]$	$10^5[MR]$	$10^4[Tl^{III}]$	$10^3k_{2obs.}$[a]	$10^3k_{2calc.}/m^3\ mol^{-1}\ s^{-1}$	
		mol dm^{-3}			m^3 mol^{-1} s^{-1}	(b)	(c)
(6a) [d]	Mo	5	2.5	2.5	4.43		
		5	1.25	2.0	5.38	5.4	5.9
		5	2.5	10.0	6.00		
		5	1.25	10.0	6.11		
		4	1.25	2.0	7.71	7.8	8.1
		3	1.25	2.0	12.6	11.6	12.2
		2	1.25	2.0	24.2	23.4	21.3
		1	1.25	2.0	48.6	48.4	48.1
		1 [e]	1.25	2.0	45.0		
		1 [f]	1.25	2.0	49.7		
(6b) [g]	Mo	5	2.4	2.5	5.1		
		5	1.25	2.0	5.4	5.4	5.7
		5	2.4	10.0	4.4		
		5	1.25	10.0	4.6		
		4	1.25	2.0	7.1	7.3	7.2
		3	1.25	2.0	9.9	9.7	9.8
		2	1.25	2.0	15.5	16.7	14.9
		1	1.25	2.0	28.7	27.2	28.2
(7a) [h]	W	5	2.5	2.5	25.6		
		5	1.25	2.0	28.9	27.0	28.6
		5	2.5	10.0	21.3		
		5	1.25	10.0	21.3		
		4	1.25	2.0	42.1	37.5	38.4
		3	1.25	2.0	57.2	60.1	53.9
		2	1.25	2.0	87.6	97.1	85.7
		1	1.25	2.0	174	182	173
7(b) [i]	W	5	2.5	2.5	23.5		
		5	1.25	2.0	22.7	23.4	23.3
		5	2.5	10.0	20.5		
		5	1.25	10.0	19.8		
		4	1.25	2.0	32.8	31	30
		3	1.25	2.0	50.3	42	41.3
		2	1.25	2.0	77.8	74	64
		1	1.25	2.0	123	125	123
		1 [e]	1.25	2.0	147		

[a] Calculated from first-order rate coefficients and the total thallium(III) concentration. [b] Calculated from rate coefficients k', k'', and k''' of Table 5 using $K_1 = 0.04$ and $K_2 = 0.1$ [c] Calculated as in (b) but using $K_1 = 0.125$ and $K_2 = 0.038$. [d] Observed at 293 nm. [e] In the presence of 4.8×10^{-4} mol dm^{-3} Tl$^+$. [f] Using Li[ClO$_4$] in place of Na[ClO$_4$]. [g] Observed at 308 nm. [h] Observed at 300 nm. [i] Observed at 303 nm.

current appearance of a much weaker absorption due to the organic pyridinium ion products. In the case of the molybdenum complexes (6), the broad relatively weak spectrum of an initial inorganic product was observed in the 220—350 nm region and this subsequently disappeared slowly, revealing more clearly the spectrum of the organic products. In the case of the tungsten complexes (7), only a single smooth reaction was observed (Figure 1).

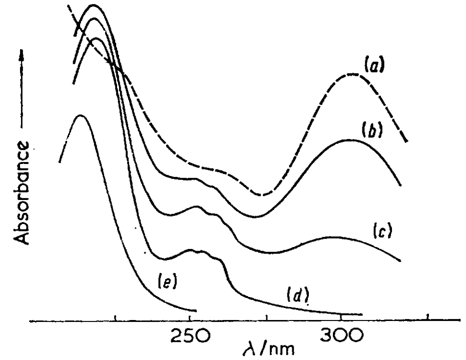

FIGURE 1 Spectral changes [(b)—(d)] during the reaction of tricarbonyl(η-cyclopentadienyl)(4-pyridiniomethyl)tungsten(II) [2.5×10^{-5} mol dm^{-3}, spectrum (a)] with Tl[ClO$_4$]$_3$ [2.5×10^{-4} mol dm^{-3}, spectrum (e)] in 0.1 mol dm^{-3} aqueous perchloric acid

(b) *Kinetics.* The kinetics of the initial reaction of the thallium(III) species with the four substrates were measured from the changes in absorbance at wavelengths close to the $\lambda_{max.}$ of the substrates, at 25 °C in aqueous perchloric acid, using a ten-fold, or larger, excess of Tl^{III}, with sodium perchlorate to maintain a constant ionic strength, I = 0.5 mol dm^{-3}. The reactions were all first order and the first-order rate coefficients were a linear function of [Tl^{III}]. The kinetics were studied as a function of the acid concentration (0.1—0.5 mol dm^{-3} perchloric acid) and, in the case of complex (6a), with lithium perchlorate as well as with sodium perchlorate. The second-order rate coefficients, which are the first-order rate coefficients divided by the total thallium(III) concentration, are shown in Table 1. The reactions of complexes (6a) and (7b) were also studied in the presence of an excess of Tl^I.

(c) *Products.* The products of the reaction of thallium(III) perchlorate with complexes (6a) and (7a), and with (6b) and (7b), were identified spectrophotometrically as predominantly ($\geqslant$70%) the corresponding 3- and 4-pyridylacetic acids, (8) and (9), respectively. These products have characteristic spectral changes with pH corresponding to the formation of the conjugate acids (8a) and (9a), the zwitterions (8b) and (9b), or the conjugate bases (8c) and

(9c), respectively.[11] The formation of a small percentage of other pyridinium products could not be ruled out. No evidence was obtained for the formation of the pyridiniomethylthallium(III) ions (10a) or (11a) [see also (d) below].[12] Because of the difficulties involved in the isolation of the very water-soluble pyridylacetic acids from dilute solution, corresponding experiments were carried out with more concentrated solutions of the benzyl derivatives (6c) and (7c) in aqueous acidic tetrahydrofuran (thf) solution. The organic products isolated from these experiments were shown by ^1H n.m.r. to contain phenylacetic acid (17) and benzyl alcohol in the ratios 41 : 9 and 67 : 33, respectively.

	$H\overset{+}{N}C_5H_4CH_2CO_2H$	$H\overset{+}{N}C_5H_4CH_2CO_2^-$	$NC_5H_4CH_2CO_2^-$
3-isomers	(8a)	(8b)	(8c)
4-isomers	(9a)	(9b)	(9c)

	$[Tl(CH_2C_5H_4\overset{+}{N}H)]^{2+}$	$[Tl(CH_2C_5H_4\overset{+}{N}H)Cl]^+$	$[Tl(CH_2C_5H_4\overset{+}{N}H)Cl]Cl$
3-isomers	(10a)	(10b)	(10c)
4-isomers	(11a)	(11b)	(11c)

	$H\overset{+}{N}C_5H_4CH_2OH$	$H\overset{+}{N}C_5H_4CH_2Cl$
3-isomers	(12a)	(13a)
4-isomers	(12b)	(13b)

	$[Hg(CH_2C_5H_4\overset{+}{N}H)]^+$	$[Hg(CH_2C_5H_4\overset{+}{N}H)]Cl$
3-isomers	(14a)	(14b)
4-isomers	(15a)	(15b)

TABLE 2

Kinetics of reaction of 4-pyridiniomethylmetal complexes (1.25×10^{-5} mol dm^{-3}) with thallium(III) perchlorate in the presence of chloride ion at 25 °C in 0.5 mol dm^{-3} perchloric acid

Substrate	Metal	$10^4[Tl^{III}]$ [a] mol dm^{-3}	$10^4[Cl^-]$ [b] mol dm^{-3}	10^4k_1 s^{-1}	10^5k_2 [c] m^3 mol^{-1} s^{-1}	Thallium species (%) [d] Tl^{3+} [e]	$[TlCl]^{2+}$	$[TlCl_2]^+$	$TlCl_3$	$[TlCl_4]^-$
(6b) [f]	Mo	10	0	61 [g]	460	100				
		8	8	68.4	855	8	85	7		
		8	16	6.01	75		7	88	5	
		4	12	3.15	74		7	88	5	
		100	400	6.0	6			19	51	30
		50	250	4.5	9			17	50	33
		100	1 100	3.0	$\leqslant 3$			1	17	82
		100	1 800	2.1	$\leqslant 2$				9	91
(7b) [h]	W	10	0	198 [g]	1 980	100				
		8	8	1 100 [g]	13 700	8	85	7		
		8	16	153	1 910		7	88	5	
		4	12	73.8	1 840		7	88	5	
		100	400	489	489			19	51	30
		50	250	264	527			17	50	33
[i]		100	1 100	145	145			1	17	82
[i]		100	1 800	78.5	79				9	91

[a] Total thallium(III) species. [b] Total chloride ion, free and complexed. [c] $k_1/[Tl^{III}]$. [d] Calculated from data of ref. 27. [e] Mixture of Tl^{3+} and $[Tl(OH)]^{2+}$. [f] Measured at 313 nm. [g] Using stopped-flow method. [h] Measured at 303 nm except where stated. [i] Measured at 320 nm.

(d) *Reactions in the presence of chloride ion.* The reactions of thallium(III) perchlorate with complexes (6b) and (7b) were also studied spectrophotometrically using various concentrations of chloride ion (Table 2). The products of reaction, determined spectrophotometrically, were also substantially the corresponding pyridylacetic acids (8) and (9), but the presence of pyridylmethanols (12a) and (12b) and chloropyridylmethanes (13a) and (13b) could not be ruled out. The corresponding reaction of the benzyl complex (7c) with thallium(III) chloride in aqueous thf gave a mixture of phenylacetic acid (17), benzyl alcohol, and benzyl chloride in the ratio 4 : 4 : 7. Spectrophotometric studies of the reactions of thallium(III) perchlorate (2×10^{-4} mol dm^{-3}) in the presence of chloride ion (4×10^{-4} mol dm^{-3}) in perchloric acid (0.04—0.4 mol dm^{-3}) with (7b) and with (3) (both 3.5×10^{-5} mol dm^{-3}) clearly showed that, although the chloro(4-pyridiniomethyl)thallium(III) ion [(11b) $\rightleftharpoons$ (11c)], formed quantitatively from (3), is stable under these conditions,[13] it is not formed from (7b).

Reactions of Mercury(II).—(a) *Spectrophotometric changes.* The reaction of mercury(II) perchlorate (2×10^{-5} — 8×10^{-3} mol dm^{-3}) with the pyridiniomethylmolybdenum ions (6a) and (6b) (2×10^{-5} mol dm^{-3}) showed three distinct spectrophotometric changes (Figure 2). The first change was extremely rapid and involved a large increase in absorbance in the $\leqslant$290 nm region and a concurrent decrease in absorbance (*ca.* 40%) in the region of the intense broad $\lambda_{max.}$ of the substrates [303 and 318 nm for (6a) and (6b), respectively]; the second, fairly rapid, change involved the disappearance of the latter absorption; the final very slow change ($\geqslant$20 h) involved a decrease in the intense absorption ($\leqslant$290 nm) which may be accelerated by the addition of chloride ion. This intense absorption masked the spectra of the organic products. In the case of the tungsten complexes (7a) and (7b), only the rapid first change was clear cut.

(b) *Kinetic studies.* The kinetics of the first two stages of the reactions of (6a) and (6b) (2.5×10^{-5} mol dm^{-3}) with mercury(II) perchlorate in aqueous acidic solution were followed spectrophotometrically using the stopped-flow method. In the presence of a four-fold, or larger, excess of

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[11] D. Dodd and M. D. Johnson, *J. Chem. Soc.* (*B*), 1970, 1337.

[12] M. D. Johnson and D. Vamplew, *J. Chem. Soc.* (*B*), 1971, 507.

[13] R. G. Coombes, M. D. Johnson, and D. Vamplew, *J. Chem. Soc.* (*A*), 1968, 2297.

mercury(II) perchlorate the initial reduction in absorbance in the region of the principal bands of the substrates was a first-order process and, although the first-order rate coefficients (Table 3) increased with mercury(II) concentration, the apparent second-order rate coefficients, calculated from the first-order coefficients and the total mercury(II) concentration, decreased until the excess of Hg^{II} was *ca.* 40-fold and then remained effectively constant.

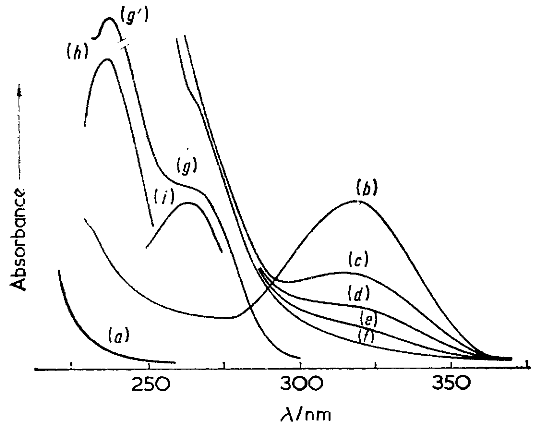

FIGURE 2 Spectral changes [(*c*)—(*f*)] during the reaction between $Hg[ClO_4]_2$ [10^{-4} mol dm^{-3}; spectrum (*a*)] with tricarbonyl-(η-cyclopentadienyl)(4-pyridiniomethyl)molybdenum(II) [2.5×10^{-5} mol dm^{-3}; spectrum (*b*)] in 0.1 mol dm^{-3} aqueous perchloric acid. Spectrum (*g*) [reduced in concentration as spectrum (*g'*)] is with added chloride ion after 20 h. Spectrum (*h*) is of $Hg_2[ClO_4]_2$ (3×10^{-5} mol dm^{-3}) and (*i*) is of the chloro(4-pyridiniomethyl)mercury(II) ion (2.5×10^{-5} mol dm^{-3})

TABLE 3

Kinetics of reaction of mercury(II) perchlorate with 3- and 4-pyridiniomethyl-tungsten and -molybdenum complexes [(6) and (7), 2.5×10^{-5} mol dm^{-3}] in 0.5 mol dm^{-3} aqueous perchloric acid at 25 °C

Substrate	$10^5[Hg^{2+}]$ / mol dm^{-3}	First stage [a]		Second stage
		$^1k_1$/s^{-1}	$10^{-1}(^1k_2)$/m^3 mol^{-1} s^{-1}	$10^3(^2k_1)$/s^{-1}
(6b)	5.0			7.8
	7.5			8.2
	10			9.1
	15			10.3
	25	19.2	7.7	11.6
	50	24.6	4.9	14.4
	100	39.7	4.0	15.9
	200	67.8	3.4	16.3
	400	119	3.0	15.7
	600	259	3.2	15.4
(6a)	25	11.6	4.7	15.0
	400	122	3.0	18.3
	800	240	3.0	18.0
(7a)	25	24.8	9.9	*b*
	400	188	4.7	
	800	352	4.4	
(7b)	25	24.3	9.7	*b*
	400	250	6.3	
	800	496	6.2	

[a] Using stopped-flow method. [b] Simple second stage not observed.

The second change in absorption in the region of the principal bands of each substrate was also a first-order process, but the first-order rate coefficients increased slightly with increasing mercury(II) concentration and remained constant when the excess of Hg^{II} was 40-fold or more (Table 3). Only the first stage of the reaction of (7a) and (7b) was studied in detail.

(c) *Product studies: dilute solutions.* The large absorption in the ⩽290 nm region completely obscured the spectrum of the organic products in each case. However, the addition of an excess of chloride ion to the solution 20 h after starting the reaction caused a marked decrease in this absorbance (Figure 2) and revealed a spectrum consistent with a mixture of 3- or 4-pyridiniomethylmercury(II) ions [14] (14b) or (15b) in 70% yield, respectively, and Hg^I. These products are stable and each has an ultraviolet spectrum which is not only substantially different from those of organic pyridinium ions but which also shows a characteristic reversible change with change of pH. The presence of some (⩽30%) organic pyridine products cannot be ruled out.

(d) *Reaction of* (6b) *in the presence of chloride ion.* In the presence of an excess of chloride ion there was a steady decrease in the intense broad absorption due to the substrate with a concurrent increase in absorption below 290 nm, such that the final spectrum was similar to that after the second stage of the reactions with mercury(II) perchlorate. A good isosbestic point was observed for the first 50% of this reaction, but this drifted when the slow incursion of the final stage became apparent. After several hours the spectrum was consistent with that of the chloro(pyridiniomethyl)mercury(II) ion [14] (15b) mixed with Hg^I. The kinetics of the first stage of this reaction were measured spectrophotometrically using an excess of mercury(II) reagent, and first-order rate coefficients were estimated. These, and the second-order rate coefficients calculated from the first-order rate coefficients and the total mercury(II) concentration, were determined as a function of the total chloride-ion concentration and are shown in Table 4.

(e) *Isolation of products.* Attempts to isolate the organomercury(II) products from more concentrated solutions of the above reagents were unsuccessful. First, because of the marked precipitation which occurred on mixing concentrated solutions of the reagents, and secondly because, under these different conditions, only organic pyridinium products appeared to be formed. Spectrophotometric studies of the supernatant liquid and of solutions made from the precipitate indicated that the final product was a mixture containing pyridylmethanols (12) [probably with the chloropyridylmethanes (13) in reactions in the presence of chloride ion]. Only benzyl alcohol could be obtained from the corresponding reaction of mercury(II) perchlorate with (7c) in aqueous acidic thf. When the corresponding reaction of (6c) was carried out in aqueous thf using mercury(II) chloride as the reagent, benzyl alcohol and benzyl chloride were obtained in the ratio 17 : 3. When mercury(II) perchlorate was used in methanolic solution only benzyl methyl ether was obtained.

(f) *Reaction with mercury*(I). The reaction of (6a) (8×10^{-5} mol dm^{-3}) with mercury(I) perchlorate (4.8×10^{-4} mol dm^{-3}) in the absence of chloride ion was approximately first order with a rate coefficient of *ca.* 3×10^{-4} s^{-1}. However, after removal of the excess of Hg^I with peroxodisulphate ion, no organomercury(II) could be detected and the final spectrum was consistent with the presence of 4-pyridylmethanol and/or 4-pyridylacetic acid.

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[14] D. Dodd and M. D. Johnson, *J. Chem. Soc.* (*B*), 1969, 1071; J. R. Coad and M. D. Johnson, *ibid.*, 1967, 633.

DISCUSSION

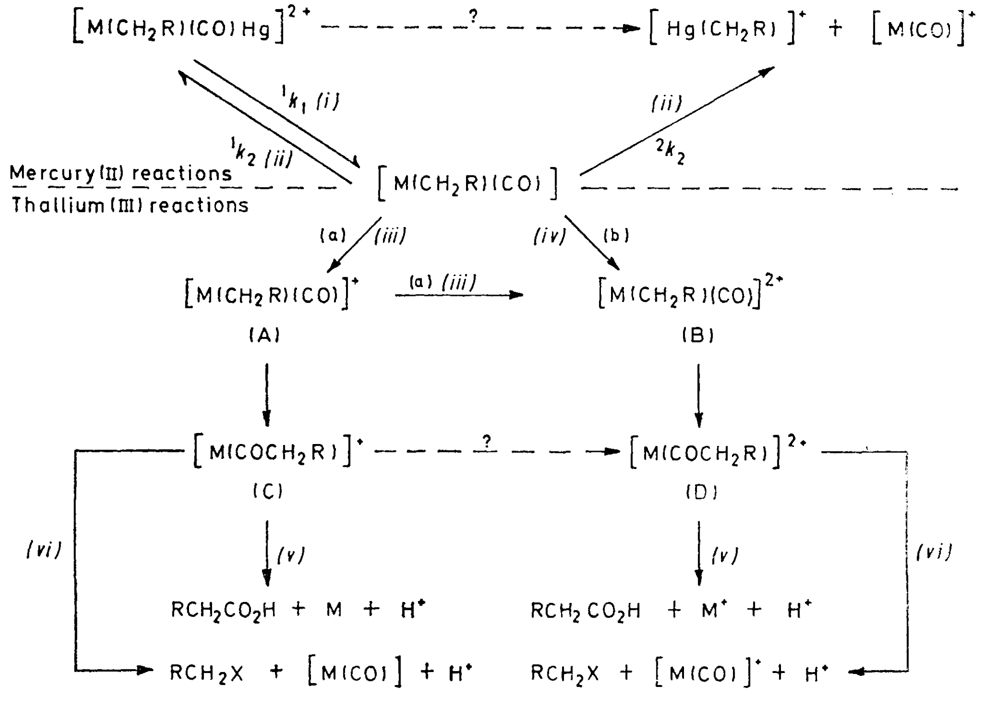
Reactions of Thallium(III).—The reactions of both molybdenum and tungsten complexes (6) and (7) with all the thallium(III) species show clearly that the latter are not behaving as conventional electrophiles as was observed with complexes (1)—(5). Since the organometallic substrates are stable for many hours in acidic solution in the dark in the absence of metallic electrophiles, even at elevated temperatures in the presence of oxygen,[15] the formation of pyridylacetic acid as the predominant organic product is indicative of a redox reaction comparable with that observed between the same organometallic substrates and the hexachloroiridate(IV) ion.[10] The products can be adequately rationalised (Scheme) by one or two initial electron transfers followed by rapid alkyl-migration reactions and subsequent nucleophilic cleavage by attack of water at the α-acyl carbon of (C) or (D). Some interception of the oxidised organometallic complexes (A) or (B), involving nucleophilic attack by water or chloride ion at the α-(methylene)carbon atom prior to the intramolecular alkyl migration, would account for the formation of the observed pyridyl-methanols and -chloromethanes. Similar interpretations have been proposed for the reaction of related organometallic complexes with Ce^{IV} in methanol in the presence of added chloride ion.[9]

TABLE 4

Kinetics of reaction of the 4-pyridiniomethylmolybdenum complex (6b) (2.9×10^{-5} mol dm^{-3}) with mercury(II) perchlorate in the presence of chloride ion at 25 °C in aqueous perchloric acid at $I = 0.5$ mol dm^{-3}

$10^4[Hg^{2+}]$	$10^4[Cl^-]$ [a]	$10^4[HgCl_2]$	$10[H^+]$	10^4k_1	10^5k_2	Hg^{II} species present (%)				
mol dm^{-3}				s^{-1}	m^3 mol^{-1} s^{-1}	Hg^{2+}	$[HgCl]^+$	$HgCl_2$	$[HgCl_3]^-$	$[HgCl_4]^{2-}$
4			5		2.5×10^7 [b]	100				
20	25		5	58	*c*	18	38	44		
4	6		5	35	*c*	9	32	59		
		3.6	1	4.3	120 [d]	0.05	3	97		
		3.6	5	4.3	120 [d]	0.05	3	97		
		50	5	10	20 [d]	0.004	0.8	99		
		200	1	18	9 [d]	0.001	0.44	99		
		200	5	18	9 [d]	0.001	0.44	99		
	200	100	4.8	$\leqslant 2.5$	$\leqslant 2.5$ [d]		0.001	84	14	3
	4 900	100	0.1	$\leqslant 2.5$	$\leqslant 2.5$ [d]			4	15	81

[a] Added chloride ion. [b] Calculated from steady-state approximation. [c] Not calculated owing to overlap of the two stages complexing and substitution. [d] Calculated from k_1 and total $[Hg^{II}]$.



SCHEME (*i*) $-Hg^{2+}$; (*ii*) Hg^{2+}; (*iii*) $-e^-$; (*iv*) $-2e^-$; (*v*) $+H_2O$; (*vi*) $+HX$ or X^-

However, despite the similarity between these reactions of Tl^{III} and those of Ir^{IV}, the latter are believed to involve two sequential electron transfers [with (6a)

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[15] M. D. Johnson and N. Winterton, *J. Chem. Soc.* (*A*), 1970, 511.

and (6b)] [see path (a), Scheme],[10] whereas the former may also act directly through a two-electron-transfer mechanism [16-19] [path (b), Scheme]. Whilst a definitive choice between these two mechanisms cannot be made from the present results, the comparable ease of the two separate electron transfers to $[IrCl_6]^{2-}$ {$k_2 = 3.7 \times 10^2$ and 1.3×10^2 m^3 mol^{-1} s^{-1} for the two steps in the reaction between (6a) and $[IrCl_6]^{2-}$ in aqueous solution at 25 °C} and the much greater oxidising ability of Tl^{2+} than of Tl^{3+} (ref. 17) suggests that the two-electron-transfer mechanism is the more likely.

The overall rate coefficients for the thallium(III) oxidation may be dissected [2,3] into the individual rate coefficients for the several thallium(III) species {Tl^{3+}(aq), $[Tl(OH)]^{2+}$, and $[Tl(OH)_2]^+$} present in the dilute aqueous acidic solutions, provided the hydrolysis constants K_1 and K_2 for Tl^{3+}(aq) are known. As there is some uncertainty in the magnitudes of these equilibrium constants [*e.g.* the literature shows K_1 (ionic strength) to be 0.066—0.333 (0.1—1 mol dm^{-3}),[20] 0.073 [21] and 0.066 (3 mol dm^{-3}),[22] 0.086 (1.5 mol dm^{-3}),[23] 0.078 (1 mol dm^{-3}),[24] and 0.045 mol dm^{-3} (0.5 mol dm^{-3})],[25] we have analysed the rate data of Table 1 in three distinct ways. First, we selected a range of values of K_1 and K_2 close to those calculated by several groups of workers and we used these to calculate several sets of values of the rate coefficients k', k'', and k''' {for Tl^{3+}(aq), $[Tl(OH)]^{2+}$, and $[Tl(OH)_2]^+$, respectively} in order to establish reasonable limits for the values of K_1 and K_2 which are consistent with our kinetic data. Secondly, we used the values of K_1 and K_2 from ref. 20 to calculate the individual rate coefficients. Thirdly, we optimised K_1, K_2, k', k'', and k''' to give the 'best' fit with our data.

Fortunately, the methods give comparable results for the rate coefficients and the values of the constants k', k'', and k''' quoted in Table 5 are appropriate to well within an order of magnitude. In particular, the results of these three sets of calculations show that: (*i*) reasonable values of the individual rate coefficients can only be obtained within the limits $0.25 \geqslant K_1 \geqslant 0.022$ and $0.25 \geqslant K_2 \geqslant 0.015$; (*ii*) irrespective of the values of K_1 and K_2 which are chosen within the limits in (*i*) above, and including those of ref. 20, the value of k' is very small compared with those of k'' and k'''; (*iii*) irrespective of the values of K_1 and K_2 chosen within the limits of (*i*) above, and including those of ref. 20, the magnitude of k''' is comparable with, or larger than, that of k''; (*iv*) the 'best' value of K_1 is *ca.* 0.04, which is comparable with that (0.045) [25] estimated for $I = 0.5$ mol dm^{-3}, and with those for $I = 3.0$ mol dm^{-3}, but lower than that (0.125) calculated in ref. 20; (*v*) the 'best' value of K_2 is 0.1 which is comparable with that determined for $I = 1.0$ mol dm^{-3}, but greater than that (0.038) from ref. 20; and (*vi*) the 'best' values of K_1 and K_2 are equally applicable to the reactions of all four of the organometallic substrates [(6a), (6b), (7a), and (7b)] considered in this work.

TABLE 5

Individual rate coefficients [a] calculated by two methods for reaction of the aqua- and hydroxo-thallium(III) species with the organometallic complexes (6) and (7), and with the 3-pyridiniomethyl derivatives (1) and (2)

Thallium(III) reagent	Organometallic reagent					
	(6a)	(6b)	(7a)	(7b)	(1)	(2)
Tl^{3+}(aq) (k') [b]	0.5	0.7	3	3	2	1
[c]	0 [d]	0 [d]	0 [d]	0 [d]		
$[Tl(OH)]^{2+}$ (k'') [b]	40	60	260	250	20	10
[c]	10	20	90	80		
$[Tl(OH)_2]^+$ (k''') [b]	175	60	530	300	10	11
[c]	260	115	790	520		

[a] All 10^{-3} m^3 mol^{-1} s^{-1}. [b] Using $K_1 = 0.04$ and $K_2 = 0.10$, *i.e.* 'best' values. [c] Using $K_1 = 0.125$ and $K_2 = 0.038$, from ref. 20. [d] Small compared with k'' and k'''.

The low value of k' is not unexpected in view of the results obtained in a number of other oxidations by thallium(III) species.[17,24,26] However, although the reactivity of $[Tl(OH)_2]^+$ is unexpectedly high, this may be because a great many of the studies of oxidation of inorganic species by Tl^{III} have been carried out in the presence of high concentrations of perchloric acid, when the reactivity of the low concentration of $[Tl(OH)_2]^+$ can usually be ignored. In some cases, as in the oxidation of hydroxylamine and hydrogen peroxide in 0.1 mol dm^{-3} perchloric acid, the reactivity of this species was undoubtedly small.[24]

Our studies using lithium perchlorate in place of sodium perchlorate (Table 1) rule out the possibility that the apparent reactivity of $[Tl(OH)_2]^+$ is an artefact of the salt character, and the very weak acidity of the substrates [(6a), (6b), (7a), and (7b) have pK_a 6.5, 7.9, 6.4, and 7.8, respectively] [27] ensures that any reaction of the unprotonated pyridylmethylmetal complexes would have to take place at or near to the encounter rate in order to account for the observed rate coefficients.

In our previous studies of electrophilic substitution by thallium(III) [2,3] we also neglected detailed consideration of the species $[Tl(OH)_2]^+$ and ascribed to it a 'small'

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rate coefficient. We have recalculated the corresponding individual rate coefficients k', k'', and k''' for the electrophilic-substitution reactions with (1) and (2) under comparable conditions, using the 'best' values of K_1 and K_2 estimated in this work. These rate coefficients (Table 5) suggest that the reaction of $[Tl(OH)_2]^+$ may also be significant in electrophilic-substitution reactions and hence that an examination of the rate profile k' to k''' is not a useful criterion for distinguishing between oxidation and substitution.

Reactions with Thallium(III) *in the Presence of Chloride Ion.*—The addition of chloride ion to aqueous acidic solutions of thallium(III) perchlorate results in the formation of mixtures containing progressively $[TlCl]^{2+}$, $[TlCl_2]^+$, $TlCl_3$, and $[TlCl_4]^-$ The reactivity down this series generally decreases in both electrophilic-substitution reactions and in oxidation reactions. In view of the limited data for the reactions of (6b) and (7b), detailed calculation of the individual rate coefficients for each of these species is not appropriate, but approximate values calculated using the known equilibrium constants[28] are as follows: 9.6×10^{-3} and 1.6×10^{-1} ($[TlCl]^{2+}$) and 10^{-4} and 10^{-3} m^3 mol^{-1} s^{-1} ($[TlCl_2]^+$) for (6b) and (7b), respectively. The rate coefficients for $[TlCl]^{2+}$ are therefore slightly smaller than those for $[Tl(OH)]^{2+}$, but those for $[Tl(OH)_2]^+$ are appreciably more than those for $[TlCl_2]^+$.

(c) *Reaction of Mercury*(II) *Species in the Absence of Chloride Ion.*—The kinetic and product studies on the very dilute solutions of mercury(II) perchlorate and the organomolybdenum ions (6) show quite different characteristics not only from those of the thallium(III) reactions but also from those of the corresponding reactions of mercury(II) perchlorate with (1) and (2). The main final organometallic products in the reactions of mercury(II) perchlorate with (6), as with (1) and (2), under the conditions used for the kinetic studies, are clearly the organomercury(II) ions (14) and (15). However, whilst reactions of (1) and (2) are one-step bimolecular displacements,[2,3] that of complex (6) appears to involve an initial rapid and substantial complexation of the Hg^{II} with the organomolybdenum ions. Not only does the apparent second-order rate coefficient (${}^1k_2$), calculated for the fast first stage of this reaction, decrease to reach a constant minimum value as the concentration of Hg^{II} is increased but the extent of this first stage, as measured by the initial decrease in absorbance, reaches a maximum value in the same region. Moreover, the apparent first-order rate coefficients (${}^2k_1$), calculated for the second stage, also increase with increasing $[Hg^{II}]$ and reach a maximum value in that same region.

The changes in ${}^1k_2$ and ${}^2k_1$ and in the extent of the first fast decrease in absorbance in the *ca.* 310 nm region with changes in the concentration of both mercury(II) perchlorate and the organomolybdenum ion show that a 1 : 1 complex (16) is formed between the two species; *e.g.*, the value of $[(16)]/[(6b)][Hg^{2+}] = K_c$ is sensibly constant. The equilibrium constant K_c [$= {}^1k_2/{}^1k_1$, equation (3)] has the value 1.6×10 m^3 mol^{-1} for the ion

$$[Mo(cp)(CH_2C_5H_4\overset{+}{N}H\text{-}4)(CO)_3] + Hg^{2+} \underset{{}^1k_1}{\overset{{}^1k_2}{\rightleftharpoons}} \underset{(16)}{[Mo(cp)(CH_2C_5H_4\overset{+}{N}H\text{-}4)(CO)_3Hg]^{2+}} \qquad (3)$$

(6b). Since ${}^1k_2$ (Table 3) is 3.2×10 m^3 mol^{-1} s^{-1} (the minimum value observed under conditions when the back reaction is negligible), ${}^1k_1 = 2$ s^{-1}. The limited data for (6a), (7a), and (7b) indicate that the values of K and of ${}^1k_1$ are of the same orders of magnitude as those calculated for (6b).

Three questions remain: the nature of the complex formed; its role, if any, in the formation of the organomercury product; and the nature of the steps forming Hg^I. Unfortunately, the kinetic form alone does not allow us to distinguish between the formation of the organomercury(II) product by (*a*) a direct unimolecular collapse of the complex (16) [equation (4)] or (*b*) a prior dissociation of the complex to reagents which then react again either to reform the complex or, more slowly through a normal bimolecular electrophilic-displacement reaction similar to that described for the reaction of electrophiles with (1)—(5), to give the observed organomercury(II) product [equation (5)].

$$[Mo(cp)(CH_2C_5H_4\overset{+}{N}H)(CO)_3Hg]^{2+} \xrightarrow{{}^2k_1} [Hg(CH_2C_5H_4\overset{+}{N}H)]^+ + [Mo(cp)(CO)_3]^+ \qquad (4)$$

$$[Mo(cp)(CH_2C_5H_4\overset{+}{N}H)(CO)_3] + Hg^{2+} \xrightarrow{{}^2k_2} [Hg(CH_2C_5H_4\overset{+}{N}H)]^+ + [Mo(cp)(CO)_3]^+ \qquad (5)$$

Application of the steady-state approximation to the low concentration of the organomolybdenum ion (6b) shows that, for equation (5), ${}^2k_2 = 2.5 \times 10^{-1}$ m^3 mol^{-1} s^{-1}, which is very close to the corresponding rate coefficients observed for the direct electrophilic-substitution reactions between mercury(II) perchlorate and the 4-pyridiniomethyl derivatives of (1) (${}^2k_2 = 1.6 \times 10^{-1}$),[2] (2) ($5 \times 10^{-2}$),[3] and (3) ($5 \times 10^{-1}$ m^3 mol^{-1} s^{-1}).[4] Moreover, under conditions in which no rapid initial complex formation between (6b) and Hg^{II} is observed, *i.e.* in solutions containing mainly $HgCl_2$ and higher chloromercury(II) species, the rate profile as a function of the free chloride ion in solution is closely similar to that of the carbonyl(pyridiniomethyl)iron complex (1).[4]

In view of the close similarity between the reaction of (6b) with those of the corresponding pyridiniomethyl-iron, -manganese, and -chromium complexes, there seems to be no reason to invoke a new mechanism [*i.e.* equation (4)] for the formation of the organomercury(II) product and it seems likely that complex (16) is not an intermediate in the reaction path to the organomercury complex, but may well be important in the alternative reaction observed with higher concentrations of reagents,

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[28] G. Nord Waind, *Proc. Symp. Co-ordination Chem.*, Tihany, Hungary, 1964, ed. T. M. Beck, p. 443.

leading to the organic products. Other workers[29] adopted a contrary view in a related system having a similar ambiguity.

The nature of complex (16) is uncertain. There was no evidence for the formation of a complex between Hg^{II} and a carbonyl group with substrates (1) and (2). The high rate of formation, the large equilibrium constant, and the substantial spectral changes therefore suggest that the complex formed involves a mercury–molybdenum bond, although the instability of this complex in the solid state hinders the determination of its structure. Four isomers of a complex involving a mercury–molybdenum bond can be postulated, in one of which the alkyl group and the mercury are not in mutual *cis* positions.

The formation of Hg^{I} during the overall reaction sequence is probably largely a result of the subsequent reactions between the excess of Hg^{II} and the molybdenum products. Molybdenum 'blues' characteristic of an oxidation reaction are always observed towards the end of the reactions indicating that several oxidation steps have occurred. Owing to the intense spectrum of the initially formed complex (16) in the $\leqslant 290$ nm region, it is not evident whether any Hg^{I} is formed in the earlier stages of the reaction.

(d) *Formation of Pyridylmethanols and Benzyl Alcohol in the Reactions of* (6) *and* (7) *with Mercury*(II) *and Mercury*(I).—The formation of organic products from the more concentrated solutions of reagents is not yet resolved and requires a separate detailed study. Clearly the change in concentration and the accompanying precipitation have an influence on the course of the reaction, since the organomercury complexes are stable under the conditions of these reactions. The formation of alcohols and chlorides is, however, compatible with an oxidative mechanism similar to that observed with Tl^{III}, but without the incursion of the carbonyl-insertion reaction.

However, these latter reactions are in accord with recent studies[30] on the reaction of other organoiron complexes $[Fe(cp)R(CO)_2]$ with mercury(II) chloride which could be of first or second order in the concentration of the mercury(II) species, depending on the nature of the group R. For the former the product was consistent with a normal displacement reaction [equation (1)]; for the latter, organic products, notably alkyl chlorides, were formed. Since our product studies on the reactions of (6) and (7) with Hg^{II} involved the use of more concentrated solutions and led to pyridylmethyl chlorides and pyridylmethanols, it is probable that similar third-order reactions are involved even in aqueous solution, but only become noticeable in the presence of high concentrations of reagents.

Clearly, the borderline anticipated at the outset of this work is complex and has a number of different frontiers besides those observed in detail in this work. The interpretation of the results of the reactions between organometallic complexes and electrophilic reagents requires detailed consideration of the exact nature of the various species present in solution, the concentration range, the nature of the group R, and the solvent, and great care must be exercised in extrapolation of results from one set of conditions to another.

EXPERIMENTAL

Materials.—Mercury(I), mercury(II), thallium(I), and thallium(III) solutions were prepared as described in earlier parts of this work (*e.g.* refs. 2, 3, and 13). The benzyl-[31] and 3- and 4-pyridiniomethyl-tricarbonyl(η-cyclopentadienyl)molybdenum complexes, the benzyl-[31] and 3-pyridiniomethyl-tricarbonyl(η-cyclopentadienyl)tungsten complexes, and solutions of the penta-aqua(4-pyridiniomethyl)chromium(III) ion[32] were prepared as described previously. Tricarbonyl(η-cyclopentadienyl)(4-pyridiniomethyl)tungsten was prepared in a similar manner to the 3-isomer[15] (Found: C, 39.5; H, 2.6; N, 3.1. $C_{14}H_{11}MoNO_3$ requires C, 39.5; H, 2.6; N, 3.3%), $\lambda_{max.}$ (0.1 mol dm^{-3} $HClO_4$) 303 nm ($\log_{10} \varepsilon$ 4.26).

Kinetic Studies.—The reactions of thallium(III) species with the pyridiniomethylmetal complexes were monitored spectrophotometrically by the methods described in earlier papers, at the wavelengths in Tables 1 and 2. The reactions of mercury(II) species with the same substrates were carried out similarly or, in the case of the faster reactions, using a Durrum stopped-flow spectrophotometer associated with a pen recorder and a digital memory. In the case of the two-step reactions of the mercury(II) perchlorate the fast first step was recorded on the digital unit and the slower second step was recorded directly. All the runs were replicated and many were later repeated using different solutions of reagents. The values shown in Tables 1—4 are, in each case, the average of the observed values.

Product Isolation.—The pyridiniomethyl- or benzyl-tricarbonyl(η-cyclopentadienyl)-molybdenum or -tungsten complex was dissolved in a small amount of tetrahydrofuran or methanol and slowly added to a solution of the thallium(III) or mercury(II) reagent in aqueous thf or methanol, respectively, containing perchloric acid (0.1—0.5 mol dm^{-3}). Addition was carried out slowly with stirring in order to minimise precipitation of intermediate complexes. When reaction was complete, the solution was diluted with water (and made alkaline in the case of the pyridiniomethylmetal complexes), the excess of volatile solvent was removed *in vacuo*, and the organic product was extracted with diethyl ether and identified by n.m.r. spectroscopy.

[6/069 *Received, 12th January*, 1976]

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