Mechanism of Electrophilic Substitution at a Saturated Carbon Atom. Part XVII.[1] Mercury(I) as an Electrophile towards Some Transition Alkylmetals

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The penta-aquochromium(III) ion is readily displaced from penta-aquopyridiniomethylchromium(III) ions by direct attack of mercury(I) ion, Hg_2^{2+},aq., on the α-carbon, according to the S_E2 mechanism. The rates of reaction of the 2-, 3-, and 4-pyridiniomethylchromium(III) ions are comparable with those for the corresponding displacements by the mercury(II) ion Hg^{2+},aq. In contrast, the reaction of mercury(I) with some alkyls of iron(II), manganese(I), and cobalt(III), is negligible compared with that of the small concentration of mercury(II) present in equilibrium with mercury(I).

THE reactions of mercury(II) species with organic compounds, such as olefins,[2] and with organometallic compounds,[3] have been studied in considerable detail. A number of the latter studies have involved organic compounds of the transition metals and these have assumed greater importance with the belief that the high concentrations of methylmercury(II) compounds recently detected in fish found in the coastal and inland waters of a number of industrial countries are a result of a reaction between mercury compounds and naturally occurring methylcobalt(III) complexes.[4] However, very few of these studies have involved mercury(I) species despite the fact that there is no inherent reason, other than the instability of organomercury(I) compounds, why they should not be effective electrophiles.

This paper describes studies of the kinetics and products of reaction of mercury(I) species with several organotransition metal complexes. The relationship between these results and those for the reaction of the same organotransition metal complexes under comparable conditions with mercury(II) species is discussed.

RESULTS

The rates of reaction of penta-aquo-2-, -3-, and -4-pyridiniomethylchromium(III) ions (I)—(III), dicarbonyl-π-cyclopentadienyl-3- and -4-pyridiniomethyliron (V) and (VI), pentacarbonyl-4-pyridiniomethylmanganese (VII), and methylbis(dimethylglyoximato)aquocobalt(III) (VIII) in the presence of mercury(I) nitrate and/or perchlorate were measured spectrophotometrically in aqueous solution at wavelengths >280 nm (see below) as described earlier for reactions with mercury(II) perchlorate.[1,5,6] The reactions with the pyridiniomethylchromium(III) ions were very fast and were measured under second-order conditions using equivalent or near equivalent concentrations of reactants. Other reactions were followed under first-order conditions with at least a ten fold excess of mercury(I). All the initial studies on the penta-aquochromium(III) ions were carried out using mercury(I) nitrate in order to determine the order of reaction, the stoicheiometry, and the variation of rate with acidity and ionic strength (Table 1). It was later found that mercury(I) nitrate contained a

TABLE 1

Kinetics of reaction of mercury(I) nitrate [a] with penta-aquo-*X*-pyridiniomethylchromium(III) ions in 0·5M-perchloric acid at 25 ± 0·2° and ionic strength 0·5M

X	10^6[Substrate]/M	$10^6[Hg_2(NO_3)_2]$/M	k_2/l mol^{-1} s^{-1}
4	9·12	9·12	219
4	37·6	18·8	240 [b]
4	37·6	37·6	226
4	9·12	60	256
4	37·6	60	233
4	9·12	100	253
4	9·12	140	272
4	37·6	140	200
4	9·12	100 [c]	36·7
4	9·12	100 [d]	105
4	9·12	100 [e]	199
4	9·12	100 [f]	203
4	9·12	100 [g]	216
3	12·8	60	131
3	12·8	100	125
3	12·8	140	143
2	16·4	60	11·0
2	16·4	100	12·4
2	16·4	140	12·2

[a] Contained 7·6% Hg^{II}. [b] ± 50. [c] 0·010M-$HClO_4$. [d] 0·010M-$HClO_4$; 0·090M-$NaClO_4$. [e] 0·010M-$HClO_4$; 0·490M-$NaClO_4$. [f] 0·100M-$HClO_4$; 0·400M-$NaClO_4$. [g] 0·010M-$HClO_4$; 0·800M-$NaClO_4$.

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[1] Part XVI, D. Dodd, M. D. Johnson, and D. Vamplew, *J. Chem. Soc.* (*B*), 1971, 1841.

[2] J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, 1967, **89**, 6427.

[3] M. H. Abraham, 'Comprehensive Chemical Kinetics. Vol. 12. Electrophilic Substitution at a Saturated Carbon Atom,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1973.

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[5] D. Dodd and M. D. Johnson, *J. Chem. Soc.* (*B*), 1971, 662.

[6] D. Dodd, M. D. Johnson, and N. Winterton, *J. Chem. Soc.* (*A*), 1971, 910.

small percentage of mercury(II) nitrate, but comparison of the results obtained with those for mercury(II) nitrate[7] and mercury(II) and mercury(I) perchlorate (Table 2) shows that this impurity does not affect the validity of the conclusions reached, only the absolute magnitude of the rate coefficients concerned. Mercury(I) perchlorate was used in the reactions of methylbis(dimethylglyoximato)-aquocobalt(III) and the dicarbonyl-π-cyclopentadienyl-pyridiniomethyliron and pentacarbonylpyridiniomethyl-manganese ions (Table 3). For comparative purposes, the reaction of mercury(II) perchlorate with methylbis-(dimethylglyoximato)aquocobalt(III) was also studied under comparable conditions (Table 3).

TABLE 2

Kinetics of reaction of mercury(I) perchlorate with penta-aquo-*X*-pyridiniomethylchromium(III) ions in 0·5M-perchloric acid at 25 ± 0·2° and ionic strength 0·5M

X	10^6[Substrate]/M	10^6[$Hg_2(ClO_4)_2$]/M	k_2/l mol^{-1} s^{-1}
4 [a]	8·53	25	166
4	8·53	50	178
4	8·53	100	183
4	9·12	100	181
3 [b]	10·3	25	103
3	10·3	50	111
3	10·3	100	118
2 [c]	16·5	25	8·43
2	16·5	50	8·33
2	16·5	100	8·25

[a] $k_2(Hg^{2+})$ [d] = 500 l mol^{-1} s^{-1}; $k_2(Hg^{2+})/K_0$ = 3·8 l mol^{-1} s^{-1}. [b] $k_2(Hg^{2+})$ [d] = 205 l mol^{-1} s^{-1}; $k_2(Hg^{2+})/K_0$ = 1·5 l mol^{-1} s^{-1}.[e] [c] $k_2(Hg^{2+})$ [d] = 30 l mol^{-1} s^{-1}; $k_2(Hg^{2+})/K_0$ = 0·23 l mol^{-1} s^{-1}.[e] [d] Rate coefficient for reaction with $Hg(ClO_4)_2$ under comparable conditions. [e] Expected rate coefficient if all reaction were through low equilibrium concentration of $Hg(ClO_4)_2$.

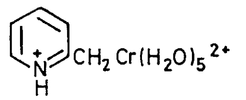
TABLE 3

Kinetics of reaction of mercury(I) perchlorate with several alkyltransition metal compounds (RM) in 0·5M-perchloric acid at 25 ± 0·2° and ionic strength 0·5M

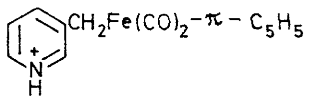
M	R	10^6[Substrate]/M	10^4[$Hg_2(ClO_4)_2$]/M	k_2/l mol^{-1} s^{-1} [a]	k_2/l mol^{-1} s^{-1} [b]
$Fe(CO)_2$-π-C_5H_5	3-$\mathrm{H\overset{+}{p}yCH_2}$ [c]	20	5·0	0·51	300
$Fe(CO)_2$-π-C_5H_5	4-$\mathrm{H\overset{+}{p}yCH_2}$ [c]	17	2·5	0·39	155
$Fe(CO)_2$-π-C_5H_5	4-$\mathrm{H\overset{+}{p}yCH_2}$ [c]	17	5·0	0·46	155
$Mn(CO)_5$	4-$\mathrm{H\overset{+}{p}yCH_2}$ [c]	6	15	0·19	47
$Mn(CO)_5$	4-$\mathrm{H\overset{+}{p}yCH_2}$ [c]	6	25	0·17	47
$Co(dmgH)_2$,aq [d]	Me	100	20 [e]		15·0 [f]
$Co(dmgH)_2$,aq [d]	Me	100	10 [e]		14·4 [f]
$Co(dmgH)_2$,aq [d]	Me	100	10	0·022	
$Co(dmgH)_2$,aq [d]	Me	100	25	0·017	

[a] Observed rate coefficient for reaction with $Hg_2(ClO_4)_2$. [b] Rate coefficient for reaction with $Hg(ClO_4)_2$ under comparable conditions. [c] $\mathrm{H\overset{+}{p}yCH_2}$ = Pyridiniomethyl. [d] dmgH = Conjugate base of dimethylglyoxime. [e] $Hg(ClO_4)_2$. [f] Direct measurement with $Hg(ClO_4)_2$.

The Figure shows a typical spectrophotometric change accompanying the reaction of a pyridiniomethylchromium-(III) ion with mercury(I) perchlorate. It demonstrates, as was apparent in most of the reactions of the pyridiniomethylchromium(III) ions, that the formation and subsequent nucleation (or, less likely evaporation[8]) of mercury(0) during the reaction prevents the attainment of a good isosbestic point at *ca.* 250 nm and precludes the use of wavelengths <275 nm for accurate rate measurements. In water, Hg^0,aq. absorbs[9] at 252 and 260 nm at 140° and has a solubility of *ca.* 3 × 10^{-7}M at 25°, though this is increased in the presence of air.[8] When more concentrated solutions of reagents were used, the nucleation of the mercury(0) was sufficiently rapid that its u.v. spectrum was not apparent during the reaction.



(I)



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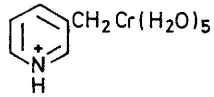

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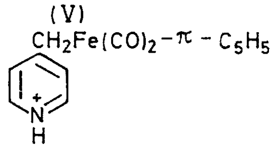
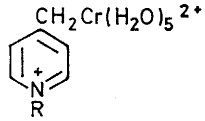
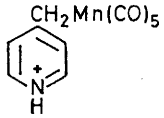


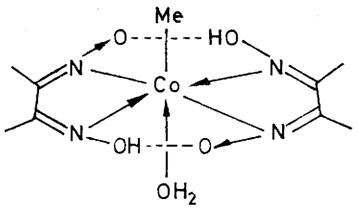
(VI)



(III) R = H
(IV) R = Me



(VII)



(VIII)

The organic products of the reaction of mercury(I) with the pyridiniomethylchromium(III) ions and with dicarbonyl-π-cyclopentadienyl-3-pyridiniomethyliron ion were identified as the corresponding pyridiniomethylmercury(II) ions from their characteristic u.v. absorption in the region 230—290 nm.[10] The inorganic products from the reaction of the pyridiniomethylchromium(III) ions were mercury(0) and the hexa-aquochromium(III) ion, but the inorganic products from the other reactions were not examined in detail.

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[7] R. G. Coombes and M. D. Johnson, *J. Chem. Soc.* (*A*), 1966, 1805.

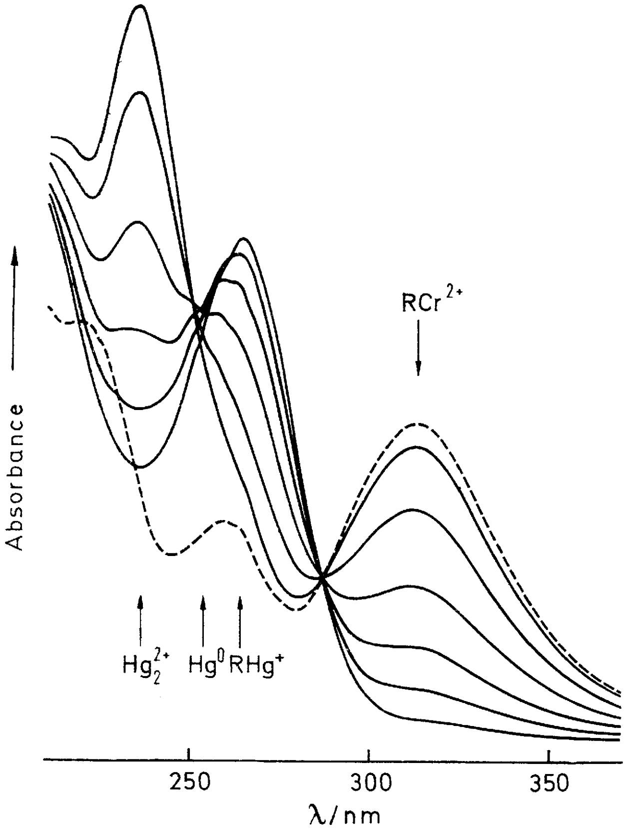
[8] D. N. Glew and D. A. Hames, *Canad. J. Chem.*, 1971, **49**, 3114.

[9] H. Reichardt and K. F. Bonhoeffer, *Z. Elektrochem.*, 1930, **36**, 753.

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

DISCUSSION

All the organometallic complexes described here are known to react readily with mercury(II) species,[1,5,6,11] the reactions of the pyridiniomethylchromium(III) ions being particularly rapid.[1] These reactions are all believed to involve a bimolecular displacement at the α-carbon with retention of configuration, as shown in equation (1). The same organomercury(II) products are formed in these and in the corresponding reactions with mercury(I) studied here [equation (2)]. However, though the binuclear mercury(I) dication Hg_2^{2+} is relatively stable in aqueous acidic solution having only weakly co-ordinating anions, it undergoes partial disproportionation according to equation (3). The equilibrium constant K_0, defined as in equation (4), has a value of 132·4 in aqueous perchloric acid at 25° and an ionic strength of 0·5M.[12]



Spectral changes accompanying the reaction between mercury(I) perchlorate (9·2 × 10^{-6}M) and penta-aquo-1-methyl-4-pyridiniomethylchromium(III) (9·2 × 10^{-6}M) in 0·5M-perchloric acid. · · · · ·, Spectrum before addition of mercury(I) perchlorate. Maxima of individual components are as indicated on the figure. With higher concentrations of reagents the mercury(0) component is not apparent due to its more rapid nucleation

$$RCH_2M^{n+} + Hg^{2+} \longrightarrow RCH_2\begin{matrix}\cdot Hg^{(2-\delta)+}\\ \cdot M^{(n+\delta)+}\end{matrix} \longrightarrow RCH_2Hg^{+} + M^{(n+1)+} \qquad (1)$$

$$RCH_2M^{n+} + Hg_2^{2+} \longrightarrow RCH_2Hg^{+} + M^{(n+1)+} + Hg^0 \qquad (2)$$

$$Hg_2^{2+} \rightleftharpoons Hg^{2+} + Hg^0 \qquad (3)$$

$$K_0 = [Hg_2^{2+}]/[Hg^{2+}] \qquad (4)$$

Therefore, two reaction paths can be envisaged: (i) a direct reaction of the mercury(I) dication, and (ii) a reaction involving the small equilibrium concentration of mercury(II). Clearly, if the observed second-order rate coefficient for reaction of the stoicheiometric mercury(I) at 25° and μ 0·5M in aqueous acidic solution is $\leqslant 7{\cdot}6 \times 10^{-3}$ times that observed for the corresponding second-order rate coefficient for the reaction with mercury(II), then the reaction through the small proportion of mercury(II) present at equilibrium must predominate and any direct reaction through mercury(I) will be difficult to detect. Such is the case in the reaction of mercury(I) with the dicarbonyl-π-cyclopentadienyl-3- and -4-pyridiniomethyliron ions, with pentacarbonyl-4-pyridiniomethylmanganese ion, and with methylcobaloxime, for which the ratios of the stoicheiometric second-order rate coefficients have the values $1{\cdot}7 \times 10^{-3}$, $2{\cdot}5 \times 10^{-3}$, $3{\cdot}8 \times 10^{-3}$, and $1{\cdot}4 \times 10^{-3}$, respectively.

In fact, these are all lower than the critical value of $7{\cdot}6 \times 10^{-3}$, but this decrease, and the variation amongst the several values, may be ascribed to the very considerable influence of even minute traces of impurities, such as chloride ion in the perchloric acid, on the low equilibrium concentration of mercury(II). These reactions parallel a similar study on methylcobalamin with mercury(I) for which the reaction through a direct attack of mercury(I) could not be detected.[13] Similar reactions through the low equilibrium concentrations have also been detected in the reaction of mercury(I) with olefins, in which mercury(II) is the effective reagent,[2] and in the reaction of mercury(I) with weak oxidising agents such as manganese(III)[14] and thallium(III),[15] in which cases the effective reagent is the small concentration of mercury(0) present in equilibrium.

On the other hand, the ratios of the rates of reaction of stoicheiometric mercury(I) to that of mercury(II) with the 2-, 3-, and 4-pyridiniomethylchromium(III) ions are 0·28, 0·53, and 0·35 respectively, which are much greater than the critical value of $7{\cdot}6 \times 10^{-3}$. Thus, if we neglect those small and less predictable changes due to minor impurities in solution, the reaction through the mercury(I) species is some 37, 70, and 46 times more important, respectively, than that through the low concentration of the mercury(II) species present in equilibrium. In these cases, therefore, *ca.* 98% of the reaction proceeds through a direct attack of

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[11] A. Adin and J. H. Espenson, *Chem. Comm.*, 1971, 653.

[12] W. Forsling, S. Hietanen, and L. G. Sillen, *Acta Chem. Scand.*, 1952, **6**, 901.

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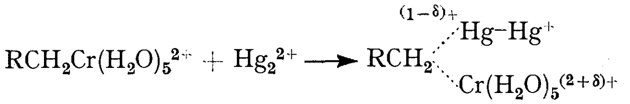
mercury(I) on the pyridiniomethylchromium(III) ion. These reactions are first order in stoicheiometric mercury(I) and in the pyridiniomethylchromium(III) ion and their rates are independent of a 50-fold change in acid concentration and increase with increasing ionic strength. Though some of the reactions were studied using mercury(I) nitrate containing *ca.* 7—8% mercury(II) nitrate, this impurity is insufficient to reduce the predominance of the reaction through mercury(I) below 75% of the total reaction and its presence does not affect our conclusions about the second-order character of the mercury(I) reaction.

Comparison of the rates of reaction of mercury(I) and those of mercury(II) with the three pyridiniomethylchromium(III) ions show that each decreases in the order 4- $\sim$ 3- $>$ 2-pyridiniomethyl. This order has also been observed for the electrophilic attack of mercury(II) complexes, of nitrosating species, and of thallium(III) complexes, on several pyridiniomethyltransition metal ions which are all believed to involve a direct electrophilic attack of the reagent on the β-carbon atom of the pyridiniomethyl group with synchronous displacement of the transition metal ion.[1,5,6] A similar displacement in which mercury(I) attacks the α-carbon atom with synchronous displacement of the penta-aquochromium(III) ion therefore seems appropriate in this case [equation (5)]. No evidence could be obtained for the formation of an intermediate organomercury(I) species. The variation in the absorption, ascribed to mercury(0), with the concentrations of reagents rules out the possibility that this is due to an organomercury(I) intermediate.



$$\mathrm{RCH_2Cr(H_2O)_5}^{2+} + \mathrm{Hg_2}^{2+} \longrightarrow \mathrm{RCH_2}\overset{(1-\delta)+}{\cdots}\begin{matrix}\mathrm{Hg{-}Hg^+}\\ \mathrm{Cr(H_2O)_5}^{(2+\delta)+}\end{matrix}$$

$$\longrightarrow \mathrm{RCH_2Hg{-}Hg^+} + \mathrm{Cr(H_2O)_5}^{3+} \quad (5)$$

$$\mathrm{Cr(H_2O)_5}^{3+} + \mathrm{H_2O} \longrightarrow \mathrm{Cr(H_2O)_6}^{3+} \quad (6)$$

$$\mathrm{RCH_2Hg{-}Hg^+} \longrightarrow \mathrm{RCH_2Hg^+} + \mathrm{Hg^0} \quad (7)$$

The inorganic product of this reaction is believed to be the penta-aquochromium(III) ion which would rapidly co-ordinate a sixth water molecule to give the stable hexa-aquochromium(III) ion [equation (6)]; this was identified as the main inorganic product of these reactions from its visible spectrum.[16] Though organomercury(I) compounds are believed to be highly unstable and may dissociate as shown in equation (7) to give the observed organomercury(II) product, it is also conceivable that the cleavage of the mercury–mercury bond may be synchronous with the carbon–chromium bond cleavage. Alternative mechanisms involving mercury(I) as an oxidising agent or as a reducing agent seem most unlikely.

The subtle change in mechanism from reaction through mercury(I) to reaction through mercury(II) can readily be understood from the fact that mercury(II) is more reactive towards *all* the organometallic substrates described here, and only with the most reactive and least selective substrates [*e.g.* the pyridiniomethylchromium(III) ions] is the reactivity difference sufficiently small for a reaction through mercury(I) to be detected. Similarly, despite the fact that mercury(II) is more reactive than mercury(I) towards hydrogen, the difference is sufficiently small for reaction through the latter to be detected,[17] but there are, unfortunately, few other well studied examples of reactions of both mercury(I) and mercury(II) with reducing agents.

A similar consideration of mercury(0) being a more effective reducing agent than mercury(I) can also be used to accommodate the fact that reactions through the former predominate with weaker oxidising agents, and reactions through the latter are only detected in the reaction with strong, relatively unselective, oxidising agents, such as cobalt(III),aq.,[18] manganese(IV),[14] and silver(II).[19]

Therefore, though mercury(II) appears to be a more effective electrophile than mercury(I), the latter is in fact much more reactive than a great many other reagents commonly thought of as effective electrophiles, such as thallium(III) reagents. For example, towards the 2-, 3-, and 4-pyridiniomethylchromium(III) ions, the mercury(I) ion $\mathrm{Hg_2}^{2+}$,aq. is $4{\cdot}2 \times 10^3$, $3{\cdot}7 \times 10^3$, and $1{\cdot}3 \times 10^3$ times more reactive than is the thallium(III) ion Tl^{3+},aq. The inability to detect many reactions through mercury(I) therefore merely disguises its inherent electrophilicity. We may therefore anticipate that there may be other examples in which the direct reaction of mercury(I) predominates, particularly where an excess of mercury(0) is present, or in the presence of low concentrations of ligands which may appropriately influence the proportions and reactivity of the mercury(I) and mercury(II) species. Clearly, without careful consideration of the exact conditions concerned, a direct reaction of mercury(I) with methylcobalamin under biological conditions cannot be ruled out from studies of this nature.

EXPERIMENTAL

Materials.—Chromatographed perchloric acid solutions of the penta-aquo-2-, -3-, and -4-pyridiniomethylchromium(III) ions were prepared from the respective chloromethylpyridinium chloride (Emanuel) and chromium(II) perchlorate as described previously.[20] The fluoroborate salts of dicarbonyl-π-cyclopentadienyl-3- and -4-pyridiniomethyliron ions and of the pentacarbonyl-4-pyridiniomethylmanganese ions were prepared as described earlier.[21] Methylbis(dimethylglyoximato)aquocobalt(III) was prepared by the method of Yamazaki and Hohokabe.[22] Mercury(I)

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[17] G. J. Korinek and J. Halpern, *J. Phys. Chem.*, 1956, **60**, 285.

[18] D. R. Rosseinsky and W. C. E. Higginson, *J. Chem. Soc.*, 1960, 31.

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[20] R. G. Coombes, M. D. Johnson, and N. Winterton, *J. Chem. Soc.*, 1965, 7029.

[21] M. D. Johnson and N. Winterton, *J. Chem. Soc.* (*A*), 1970, 507.

[22] N. Yamazaki and Y. Hohokabe, *Bull. Chem. Soc. Japan*, 1971, **44**, 63.

nitrate was B.D.H. AnalaR grade. The proportion of mercury(II) impurity in this sample was calculated from the increase in absorption due to Hg_2^{2+} at 236·5 nm [23] when a stock solution of the nitrate in perchloric acid was treated with an excess of metallic mercury. The calculated value of 7·6% mercury(II) is supported by the kinetic results. Stock solutions of mercury(II) perchlorate were prepared as described previously.[5] Stock solutions of mercury(I) perchlorate were prepared from the latter by vigorous stirring with metallic mercury for two days. The concentration of mercury(I) was confirmed by measurement of the absorbance at 295 nm.[23] Perchloric acid was Fison's Analytical reagent, sodium perchlorate was Koch–Light Puriss grade.

Kinetics.—The runs carried out with the organo-chromium, -iron, and -manganese substrates were performed as described previously for reactions with mercury(II) species.[1,5,6] Runs using the organocobalt substrate were performed by the addition of a stock solution of the methylcobaloxime (1 ml) to an appropriate solution of the mercury(I) reagent (9 ml) in a thermostatted spectrophotometer cell and observation of the absorbance at 445 nm as a function of time. Rate coefficients were calculated by standard graphical methods for first- and second-order processes. All the observed reactions were several powers of ten faster than the decomposition of the respective substrates under the same conditions in the absence of the mercury reagent.[24,25]

Products.—The organic products from the chromium runs were identified as the 2-, 3- and 4-pyridiniomethylmercury(II) cations from their characteristic u.v. spectra [10] [2-$H\overset{+}{p}yCH_2Hg^+$, $\lambda_{max.}$ 285 nm (log ε 4·0); 3-$H\overset{+}{p}yCH_2Hg^+$, 238 and 278 nm (log ε 4·3 and 3·7); 4-$H\overset{+}{p}yCH_2Hg^+$, 261·5 nm (log ε 4·3)]. The yields, estimated from the extinction coefficients, were quantitative. Other products are described above.

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