Reactivity of Main-group–Transition-metal Bonds. Part 7.[1] Kinetics of the Reaction of Mercury(II) Halides with Compounds containing Tin–Chromium, –Molybdenum, –Tungsten, –Manganese, –Rhenium, and –Iron Bonds

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The kinetics of the cleavage of tin–transition-metal bonds by mercury(II) halides have been measured for the following reactions: [Cr(cp)(CO)$_3$(SnMe$_3$)] with HgBr$_2$; [Mo(cp)(CO)$_3$(SnMe$_3$)] with HgX$_2$ (X = Cl, Br, or I); [W(cp)(CO)$_3$(SnMe$_3$)] with HgBr$_2$; [Mn(CO)$_5$(SnMe$_3$)] with HgX$_2$ (X = Cl, Br, or I); [Re(CO)$_5$(SnMe$_3$)] with HgBr$_2$; [Fe(cp)(CO)$_2$(SnMe$_3$)] with HgX$_2$ (X = Cl, Br, or I) (cp = η-cyclopentadienyl). The reactions proceed *via* an adduct formed between the reactants, and the reactivity patterns resemble those for iodination.

We have reported detailed kinetic studies of the reactions of [M(cp)(CO)$_3$(SnMe$_3$)] † (M = Cr, Mo, or W), [Fe(cp)(CO)$_2$(SnMe$_3$)], and [M(CO)$_5$(SnMe$_3$)] (M = Mn or Re) with iodine and bromine,[1-4] and have shown that they involve electrophilic cleavage of the tin–transition-metal bond and proceed *via* an intermediate complex somewhat akin to the σ complex in aromatic substitution. Here we report our kinetic studies on the reactions of the same compounds with another group of electrophiles, the mercury(II) halides. No kinetic studies of these reactions have been reported. Roberts [5] has identified the products of the reactions of [M(cp)(CO)$_3$(SnMe$_3$)] (M = Mo or W) with mercury(II) halides, HgX$_2$, as [M(cp)(CO)$_3$(HgX)], and shown that mercury(II) chloride reacts with [Fe(cp)(CO)$_2$(SnMe$_3$)] to give [Fe(cp)(CO)$_2$(HgCl)].[6] Mercury(II) chloride (1 mol) reacts with [Mn(CO)$_5$(SnMe$_3$)] (x mol) to give [Mn(CO)$_5$(HgCl)] (if $x = 1$) [6] or [Hg{Mn(CO)$_5$}$_2$] (if $x = 2$).[7]

EXPERIMENTAL

Preparations.—The organometallic compounds were prepared as described previously.[1,3,4] No impurities were apparent from the i.r. and n.m.r. spectra of these compounds. Dioxan was purified by boiling under reflux with sodium for 48 h. It was then distilled from the sodium, and redistilled from fresh sodium in an atmosphere of nitrogen as required.

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† cp = η-Cyclopentadienyl.

[1] Part 6, J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J. Organometallic Chem.*, 1976, **121**, 185.

[2] J. R. Chipperfield, J. Ford, A. C. Hayter, D. Lee, and D. E. Webster, *J.C.S. Dalton*, 1976, 1024.

[3] J. R. Chipperfield, J. Ford, and D. E. Webster, *J.C.S. Dalton*, 1975, 2042.

[4] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Dalton*, 1975, 2048.

[5] R. M. G. Roberts, *J. Organometallic Chem.*, 1972, **40**, 359.

[6] R. M. G. Roberts, *J. Organometallic Chem.*, 1973, **47**, 359.

[7] R. A. Burnham, F. Glockling, and S. R. Stobart, *J.C.S. Dalton*, 1972, 1991.

TABLE 1

Products identified from the reactions of organotin–transition-metal compounds and mercury(II) halides

		This work			Literature		
Reactants		Solvent for i.r.	Carbonyl i.r. peaks (cm^{-1})	Compound	Carbonyl i.r. peaks (cm^{-1})	Ref.	Mass spectrum (ions identified)
$[Cr(cp)(CO)_3(SnMe_3)]$	$HgBr_2$	CS_2	1 995, 1 937, 1 919	$[Cr(cp)(CO)_3(HgBr)]$	1 994, 1 937, 1 920	*a*	$[Cr(cp)(CO)_3(HgBr)]^+$, $[SnBrMe_3]^+$
$[Mo(cp)(CO)_3(SnMe_3)]$	$HgBr_2$	$CHCl_3$	2 019, 1 950, 1 931	$[Mo(cp)(CO)_3(HgBr)]$	2 021, 1 950, 1 933	9	$[SnBrMe_3]^+$
	$HgCl_2$	$CHCl_3$	2 022, 1 954, 1 935	$[Mo(cp)(CO)_3(HgCl)]$	2 024, 1 954, 1 936	9	$[SnMe_3Cl]^+$
	HgI_2	$CHCl_3$	2 013, 1 942, 1 925	$[Mo(cp)(CO)_3(HgI)]$	2 015, 1 945, 1 927	9	$[SnI]^+$
$[W(cp)(CO)_3(SnMe_3)]$	$HgBr_2$	$CHCl_3$	2 014, 1 941, 1 921	$[W(cp)(CO)_3(HgBr)]$	2 016, 1 942, 1 922	9	$[SnBrMe_3]^+$
$[Mn(CO)_5(SnMe_3)]$	$HgCl_2$	$CHCl_3$	2 111, 2 056, 2 018	$[Mn(CO)_5(HgCl)]$	2 111, 2 057, 2 019	*b*	$[SnMe_3Cl]^+$
	$HgBr_2$	$CHCl_3$	2 109, 2 055, 2 020	$[Mn(CO)_5(HgBr)]$	2 110, 2 055, 2 020	*b*	$[SnBrMe_3]^+$
	HgI_2	$CHCl_3$	2 105, 2 045, 2 016	$[Mn(CO)_5(HgI)]$	2 106, 2 045, 2 016	*b*	*c*
$[Re(CO)_5(SnMe_3)]$	$HgBr_2$	CH_2Cl_2	2 129, 2 025, 2 008	$[Re(CO)_5(HgBr)]$	2 128, 2 024, 2 006	*d*	$[SnBrMe_3]^+$
$[Fe(cp)(CO)_2(SnMe_3)]$	$HgCl_2$	$CHCl_3$	2 019, 1 974	$[Fe(cp)(CO)_2(HgCl)]$	2 020, 1 974	9	$[SnMe_3Cl]^+$
	$HgBr_2$	$CHCl_3$	2 017, 1 969	$[Fe(cp)(CO)_2(HgBr)]$	2 018, 1 972	9	$[SnBrMe_3]^+$
	HgI_2	$CHCl_3$	2 014, 1 969	$[Fe(cp)(CO)_2(HgI)]$	2 014, 1 967	9	$[SnMe_3I]^+$

[a] A. R. Manning and D. J. Thornhill, *J. Chem. Soc.* (*A*), 1971, 637. [b] P. N. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc.* (*A*), 1967, 1889. [c] Trimethyltin iodide was not observed in the mass spectrum probably because of its high volatility. It was isolated from reaction mixtures and identified by its n.m.r. spectrum. [d] A. T. T. Hsieh and M. J. Mays, *J. Chem. Soc.* (*A*), 1971, 2648.

TABLE 2

Rate coefficients for the reactions of organotin–transition-metal compounds and mercury(II) halides (HgX_2)

Compound	10^3 Concentration mol dm^{-3}	HgX_2	$10^3[HgX_2]$ mol dm^{-3}	Solvent	λ nm	θ_c °C	$k_2^{obs.}$ $dm^3\ mol^{-1}\ s^{-1}$
$[Cr(cp)(CO)_3(SnMe_3)]$	0.16—0.18	$HgBr_2$	2—5	Dioxan	400	30	32.1
$[Mo(cp)(CO)_3(SnMe_3)]$	0.14—0.20	$HgCl_2$	2—6	Dioxan	395	30	0.690
						40	1.31
						45	1.94
						50	2.50
	0.17—0.45	$HgBr_2$	2—6	Dioxan	395	30	1.33
						40	2.43 [a]
						45	3.30 [a]
						50	3.72 [a]
	0.21—0.35	HgI_2	2—6	Dioxan	395	30	0.773
						40	1.34
						45	1.73
						50	2.08
$[W(cp)(CO)_3(SnMe_3)]$	0.10—0.15	$HgBr_2$	2—6	Dioxan	395	30	1.83
						40	3.14
						45	4.21
						50	5.58
$[Mn(CO)_5(SnMe_3)]$	0.16—0.23	$HgCl_2$	10—40	Ethyl acetate	285	30	0.034 1
						35	0.041 2
						40	0.056 8
						45	0.098 1
						50	0.114
	0.13—0.18	$HgBr_2$	5—40	Ethyl acetate	300	30	0.059 [a]
						40	0.090 [a]
						50	0.143 [a]
	0.15—0.26	$HgBr_2$	20—60	Dioxan	300	50	0.001 7 [a]
	5.7—6.3	HgI_2	9.9	Ethyl acetate	*b*	30 ± 1	0.033
$[Re(CO)_5(SnMe_3)]$	10.0—12.0	$HgBr_2$	20—60	Dioxan	*b*	30 ± 1	0.020
$[Fe(cp)(CO)_2(SnMe_3)]$	0.16—0.33	$HgCl_2$	2—6	Dioxan	405	30	3.20
	0.18—0.35	$HgBr_2$	2—6	Dioxan	405	30	3.32
						40	4.41
						45	5.85
						50	5.30
	0.17—0.26	HgI_2	2—6	Dioxan	405	30	5.9

[a] Extrapolated values for $[HgBr_2] = 0$, see Table 3 and text. [b] Kinetics studied by i.r. spectroscopy, see text.

AnalaR ethyl acetate was dried over molecular sieves (B.D.H., type 4A), and used without further purification. G.l.c. analysis showed it to be >99.97% pure with no detectable acetic acid impurity.

Product Analyses.—The organometallic compound (15—30 mg) was mixed with an excess of mercury(II) halide in the appropriate solvent. After reaction was complete the solvent was removed. The carbonyl-containing species in a portion of the residue was dissolved in a suitable organic solvent (see Table 1) and an i.r. spectrum was recorded. A mass spectrum was taken of another portion of the residue. The i.r. spectra showed no evidence of trace amounts of other carbonyl-containing species other than those given. The carbonyl peaks observed in the i.r. spectrum of the products, and the tin-containing ions identified in the mass spectra, are given in Table 1. Trimethyltin halides were isolated from some reactions by using a 20-fold increase in scale. The reaction solution was evaporated to dryness and the tin halide was vacuum sublimed on to a probe at −78 °C.

Reaction Kinetics.—The kinetics of most of the reactions were measured by monitoring a change in absorbance, *D*, at selected wavelengths in the ultraviolet (see Table 2) using a Unicam SP 500 or a stopped-flow spectrophotometer as already described.[3] The reactions were studied under pseudo-first-order conditions, with the mercury(II) halide in excess. Values of the observed first-order rate coefficients, $k_1^{obs.}$, were obtained from gradients of the usual plots of $\ln(D_t - D_\infty)$ against time. A second-order rate coefficient $k_2^{obs.} = k_1^{obs.}/b$ where b is the concentration of mercury(II) halide.

TABLE 3

Second-order rate coefficients for the reactions of $[Mo(cp)(CO)_3(SnMe_3)]$ and $[Mn(CO)_5(SnMe_3)]$ with $HgBr_2$

Compound (solvent)	$10^3[HgBr_2]$ / mol dm^{-3}	$k_2^{obs.}$/dm^3 mol^{-1} s^{-1}			
		θ_c = 30	40	45	50 °C
$[Mo(cp)(CO)_3(SnMe_3)]$ [a] (Dioxan)	2.0	1.33	2.28	3.24	3.59
	4.0		2.16	3.12	
	6.0	1.33	2.03	3.06	3.35
$[Mn(CO)_5(SnMe_3)]$ [b] (Ethyl acetate)	5.0	0.060 5	0.091 1		0.146
	10.0	0.061 9	0.099 9		0.156
	20.0	0.065 5	0.111		0.173
	40.0	0.072 4	0.122		0.198
$[Mn(CO)_5(SnMe_3)]$ [b] (Dioxan)	20.0				0.001 63
	28.5				0.001 48
	40.0				0.001 44
	60.0				0.001 35

[a] 1.7×10^{-4} mol dm^{-3}. [b] 1.5×10^{-4} mol dm^{-3}.

For the reactions of $[Mn(CO)_5(SnMe_3)]$ with HgI_2 and of $[Re(CO)_5(SnMe_3)]$ with $HgBr_2$ no suitable absorbance changes were found and the kinetics were measured by monitoring changes in the intensity of carbonyl bands in the i.r. spectrum. A special i.r. cell with germanium metal windows was used,[8] and the reaction was studied under second-order conditions.

RESULTS AND DISCUSSION

A stoicheiometric reaction, with cleavage of the tin–transition-metal bond, is observed for the reaction of mercury(II) halides with a range of compounds containing the trimethyltin group bonded to a transition element [equation (1) (M = Cr, Mo, or W, $m = 1$, $n = 3$; M = Fe, $m = 1$, $n = 2$; M = Mn or Re, $m = 0$, $n = 5$; X = Cl, Br, or I)]. During the kinetic studies an excess

$$[M(cp)_m(CO)_n(SnMe_3)] + HgX_2 \longrightarrow SnMe_3X + [M(cp)_m(CO)_n(HgX)] \quad (1)$$

of the mercury(II) halide was used in order to prevent any further reaction of the product $[M(cp)_m(CO)_n(HgX)]$ with starting material [equation (2)] from complicating the kinetics. If reaction (2) took place autocatalysis would be observed. We did not detect any $[Hg\{M(cp)_m(CO)_n\}_2]$. It is known that these compounds react with HgX_2 to give $[M(cp)_m(CO)_n(HgX)]$ [equation (3)] and that this equilibrium lies to the right-hand side.[9]

$$[M(cp)_m(CO)_n(SnMe_3)] + [M(cp)_m(CO)_n(HgX)] \longrightarrow SnMe_3X + [Hg\{M(cp)_m(CO)_n\}_2] \quad (2)$$

$$HgX_2 + [Hg\{M(cp)_m(CO)_n\}_2] \rightleftharpoons 2[M(cp)_m(CO)_n(HgX)] \quad (3)$$

Studies of these reactions were made difficult by the instability of solutions of the organometallic compounds in both dioxan and ethyl acetate, even though the solvents were carefully purified and degassed before use. Trace amounts of impurities appear to catalyse the reaction; consequently each reaction was studied several times and each of the results in Tables 2 and 3 is the average of reproducible runs. Table 2 lists the average $k_2^{obs.}$ values for systems where $k_2^{obs.}$ was independent of the concentration of mercury(II) halide ($k_2^{obs.}$ changed by less than 3% on doubling the concentration of mercury halide.) Table 3 contains the results for systems where $k_2^{obs.}$ is dependent on the concentration of mercury(II) halide. All except two systems (see Experimental section and Table 2) were studied under pseudo-first-order conditions. The solvents dioxan and ethyl acetate were chosen for three reasons: (*a*) suitable solubility of mercury(II) halides; (*b*) no solvolytic reactions with reagents or products; (*c*) convenient rates of reaction. Dioxan has been used as a solvent for various mercurations.[10,11] Ethyl acetate is more polar than dioxan, and mercurations which involve charge separation in the transition state (see below) are faster in the

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[8] J. R. Chipperfield, G. Collier, A. C. Hayter, and D. E. Webster, *Spectrochim. Acta*, 1976, **A32**, 659.

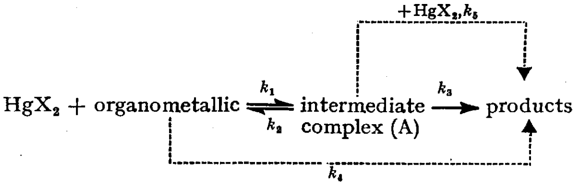
[9] M. J. Mays and J. D. Robb, *J. Chem. Soc.* (*A*), 1968, 329.

[10] B. J. Gregory and C. K. Ingold, *J. Chem. Soc.* (*B*), 1969, **276**.

[11] R. E. Dessy and Y. K. Lee, *J. Amer. Chem. Soc.*, 1960, **82**, 689.

more polar solvent {$k_2^{\text{obs.}}$ values for $HgBr_2$ + $[Mn(CO)_5(SnMe_3)]$, Table 3}.

Evidence for Intermediates in Mercuration.—Halogens react with the organometallic compounds studied here by a multistage mechanism. Charge-transfer (c.t.) complexes are formed between the reactants,[2] and reaction proceeds *via* an intermediate complex.[3,4] In the reaction of iodine with $[Cr(cp)(CO)_3(SnMe_3)]$ the formation and breakdown of the intermediate has been observed.[4] Mercury(II) halides form c.t. complexes with aromatic hydrocarbons,[12] and 1 : 1 adducts with organometallic compounds such as $[Co(cp)(CO)_2]$ [13] and $[M(CO)_3(mes)]$ (M = Cr, Mo, or W; mes = mesitylene).[14] Mercury(II) halides react with $[M(CO)_4(bipy)]$ (M = Mo or W; bipy = 2,2′-bipyridine) to give isolable adducts,[15] and the kinetics of the oxidative-elimination reaction of $[M(CO)_4(bipy)]$ with HgX_2 to give $[M(CO)_4X(HgX)]$ + CO also indicate a reaction path involving adducts.[16]



(4)

Concentration				
Initial	b	a	0	0
After time t	b	$a - c - p$	c	p
At end	b	0	0	a
Absorption coefficient	0	ε_r	ε_c	ε_p

During the reaction of mercury(II) bromide with $[Cr(cp)(CO)_3(SnMe_3)]$ in dioxan the absorbance of the solution at 400 nm decreased. However, the absorbance immediately after mixing the reactants was greater than expected from their individual absorbances. For the other systems studied initial optical densities of reaction mixtures were as expected from those of the reactants. This is consistent with very little intermediate being formed. In the reaction of $HgCl_2$ with $[Mo(CO)_4(phen)]$ (phen = 1,10-phenanthroline and 5-substituted derivatives) the formation constants of the adducts are also very small.[16]

The values of $\Delta H^\ddagger$ for mercuration of various compounds (Table 4) are low and $k_2^{\text{obs.}}$ values for the reaction of mercury(II) bromide with $[Fe(cp)(CO)_2(SnMe_3)]$ (Table 2) do not give a linear Arrhenius plot. The overall rate coefficients of multistage reactions often show this pattern of temperature dependence.

Our results suggest a reaction scheme [equation (4), full lines] where k_1 and $k_2 \gg k_3$ and $K = k_1/k_2$. The integrated rate equations for this system have been reassessed recently [17] and are given in (5) and (6). The

$$p = a\{1 - \exp[-Kbk_3t/(1 + Kb)]\}/(1 + Kb) \quad (5)$$

$$c = aKb\{\exp[-Kbk_3t/(1 + Kb)]\}/(1 + Kb) \quad (6)$$

measured absorbance, D_t, at any time is given by equation (7). If the final absorbance is D_∞ we can write equation (8). Hence the usual 'first-order' plot of $\ln(D_\infty - D_t)$ against t will have a gradient $-Kbk_3/(1 + Kb)$ $(= -k_1^{\text{obs.}})$; $k_2^{\text{obs.}}$ will equal $Kk_3/(1 + Kb)$. If $Kb \ll 1$ then $k_2^{\text{obs.}} = Kk_3$. However, if Kb is not negligible the value of $k_2^{\text{obs.}}$ will change with b, and a plot

$$D_t = (a - c - p)\varepsilon_r + c\varepsilon_c + p\varepsilon_p \quad (7)$$

$$D_\infty - D_t = \{a[(1 + Kb)\varepsilon_p - Kb\varepsilon_c - \varepsilon_r] \exp[-Kbk_3t/(1 + Kb)]\}/(1 + Kb) \quad (8)$$

of $1/k_2^{\text{obs.}}$ against b should be a straight line [equation (9)].

$$1/k_2^{\text{obs.}} = (1/Kk_3) + (b/k_3) \quad (9)$$

TABLE 4

Activation parameters for the reactions of organotin–transition-metal compounds with mercury(II) halides

Compound	HgX_2	$\Delta H^\ddagger$ / kJ mol^{-1}	$\Delta S^\ddagger$ / J K^{-1} mol^{-1}
$[Mo(cp)(CO)_3(SnMe_3)]$	$HgCl_2$	50.8 ± 2.0	−80.7 ± 6.2
	$HgBr_2$	40.4 ± 2.0	−109.0 ± 9.5
	HgI_2	38.4 ± 1.9	−120.4 ± 6.2
$[W(cp)(CO)_3(SnMe_3)]$	$HgBr_2$	42.8 ± 1.3	−98.9 ± 4.2
$[Mn(CO)_5(SnMe_3)]$	$HgCl_2$	50.9 ± 3.8	−105.9 ± 12.1
	$HgBr_2$	33.8 ± 2.3	−157.1 ± 7.4

This behaviour was found for the reactions shown in Table 5 and the derived values of K and k_3 are given.

TABLE 5

Values of K and k_3 for reactions with $HgBr_2$ in dioxan

Compound	θ_c / °C	10^3k_3 / s^{-1}	K / dm^3 mol^{-1}
$[Mn(CO)_5(SnMe_3)]$	50	0.30	6.2
$[Mo(cp)(CO)_3(SnMe_3)]$	40	74	33
	45	220	15
	50	200	19

The value of K for the reaction of $[Cr(cp)(CO)_3(SnMe_3)]$ with $HgBr_2$ in dioxan was calculated from the initial values of the optical densities of the mixed reactants as described previously.[2] The value found, *ca.* 90 dm^3 mol^{-1}, is much higher than for all the other mercurations. This is in accord with iodination of these compounds, where an intermediate complex was most stable in the reaction of the chromium derivative.[2] With a value of *ca.* 90 dm^3 mol^{-1} for K we would expect $k_2^{\text{obs.}}$ to

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[12] I. M. Vezzosi, G. Peyronel, and A. F. Zanoli, *Inorg. Chim. Acta*, 1974, **8**, 229.

[13] D. F. Shriver, *Accounts Chem. Res.*, 1970, **3**, 231.

[14] D. P. Graddon, I. K. Gregor, and I. A. Siddiqi, *J. Organometallic Chem.*, 1975, **102**, 321.

[15] K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *J. Chem. Soc. (A)*, 1968, 2851.

[16] J. W. McDonald and F. Basolo, *Inorg. Chem.*, 1971, **10**, 492; R. T. Jernigan and G. R. Dobson, *ibid.*, 1972, **11**, 81.

[17] C. W. Pyun, *J. Chem. Educ.*, 1971, **48**, 194.

decrease with increasing mercury(II) bromide concentration. However $k_2^{obs.}$ is independent of b. Possibly as b increases the expected decrease in $k_2^{obs.}$ is counteracted by an increase from a polarity effect similar to that found for mercuration of [Mn(CO)$_5$(SnMe$_3$)] in ethyl acetate (see later). It was not possible to carry out an extensive series of reactions with [Cr(cp)(CO)$_3$(SnMe$_3$)]; it is both unstable and toxic.[4]

It is possible that reaction could also take place by direct interaction of the reactants [k_4 and dotted line, equation (4)] to give rate equation (10); $k_2^{obs.}$ is then given by equation (11). From our results we cannot

$$dp/dt = k_3c + k_4ab \qquad (10)$$

$$k_2^{obs.} = (Kk_3 + k_4)/(1 + Kb) \qquad (11)$$

estimate the proportion of reaction (if any) proceeding *via* such a direct reaction, although we consider reaction *via* an intermediate most likely. If $k_3 = 0$ [no reaction *via* (A)], $k_2^{obs.} = k_4/(1 + Kb)$, and a plot of $1/k_2^{obs.}$ against b would be a straight line with intercept on the 'b' axis of $-1/K$, indistiguishable from that found when reaction is solely *via* (A) [equation (9)].

As the rate of mercuration of [Mn(CO)$_5$(SnMe$_3$)] is slow, the reaction was studied using higher concentrations of mercury(II) halides than those used for the other compounds (Tables 2 and 3). In ethyl acetate $k_2^{obs.}$ increased with [HgBr$_2$] (Table 3). There are two possible explanations for this. (*a*) Products could be formed either directly by decomposition of the intermediate (A), or by reaction of (A) with a further molecule of mercury(II) bromide [k_5 and dotted line, equation (4)] to give the rate equation (12); $k_2^{obs.}$ would then depend on [HgX$_2$] [equation (13)]. (*b*) The higher mercury(II) halide

$$dp/dt = (k_3 + k_5[\mathrm{HgX_2}])c \qquad (12)$$

$$k_2^{obs.} = K(k_3 + k_5[\mathrm{HgX_2}])/(1 + Kb) \qquad (13)$$

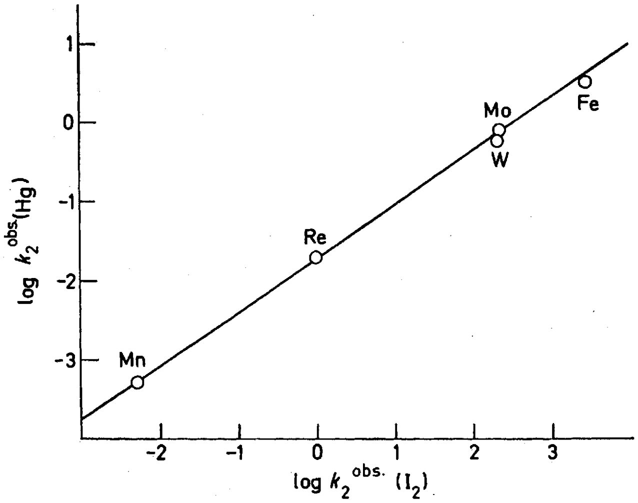
concentrations used here effectively increase the polarity of the solvent, and cause a rate increase. If (*a*) is correct we would have expected to observe similar behaviour with the other organometallic compounds when [HgX$_2$] was varied, even if the absolute [HgX$_2$] values are tenfold lower. It is likely that (*b*) would not be observed at low [HgX$_2$] and accordingly we favour (*b*) as an explanation.

The Involvement of [R$_3$SnHgX$_3$].—Abraham and Spalding[18] showed that in aqueous methanol organotin halides and mercury(II) halides rapidly react to give an equilibrium mixture containing a complex [R$_3$SnHgX$_3$] [equation (14)]. Such an equilibrium could perturb a

$$\mathrm{HgX_2 + SnR_3X \rightleftharpoons [R_3SnHgX_3]} \qquad (14)$$

kinetic study where HgX$_2$ is a reactant and SnR$_3$X a product. Although we observed a small shift in the n m.r. peak of SnBrMe$_3$ (in [^{2}H$_6$]acetone) when HgBr$_2$ was added, the u.v. spectra of SnBrMe$_3$ in the solvents used for kinetic studies, dioxan and ethyl acetate, did not change when HgBr$_2$ was added, indicating that in these less polar media the formation of the complex does not occur. A less likely alternative is that the u.v. spectrum of any complex formed is identical with the reactants. In kinetic studies we always used a ten-fold excess of HgX$_2$, so even if a little [R$_3$SnHgX$_3$] were formed the change in concentration of uncomplexed HgX$_2$ would be negligible.

The Effect of Change of Transition Metal.—The reactivity order of the organometallic complexes towards mercury(II) bromide in dioxan is [Mn(CO)$_5$(SnMe$_3$)] < [Re(CO)$_5$(SnMe$_3$)] < [Mo(cp)(CO)$_3$(SnMe$_3$)] ≈ [W(cp)(CO)$_3$(SnMe$_3$)] < [Fe(cp)(CO)$_2$(SnMe$_3$)]. This order parallels that found for iodination (Figure). The good correlation between mercuration and iodination suggests that similar mechanisms are involved. It is difficult to compare the rate of mercuration with that of iodination for [Cr(cp)(CO)$_3$(SnMe$_3$)] as this reacts with iodine by two separate steps, and there is not an overall rate coefficient analogous to $k_2^{obs.}$.[4] For those reactions where $k_2^{obs.}$ depended on the concentration of mercury(II) bromide, values of $k_2^{obs.}$ extrapolated to [HgBr$_2$] = 0 were used for comparison.



Logarithmic plot of the rate coefficients $k_2^{obs.}$(Hg) for the reaction of HgBr$_2$ with compounds containing tin–transition-metal bonds (30 °C, ethyl acetate) against the rate coefficients $k_2^{obs.}$(I$_2$) for the reactions of the same compounds with iodine (30 °C, tetrachloromethane)

The rates of mercuration of [Mo(cp)(CO)$_3$(SnMe$_3$)] and [W(cp)(CO)$_3$(SnMe$_3$)] are similar ($k^{W}/k^{Mo} = 1.3$). Similar results were found for the relative rates of iodination of these compounds.[3] It is tempting to suggest that the size of the transition metal atom is a key factor in determining reactivity.

Mechanism of the Reactions.—By comparison with iodination, and consistent with the known structure of [Co(cp)(CO)$_2$(HgCl$_2$)], we propose that the intermediate (A) [equation (4)] has the structure (I) (R = SnMe$_3$) analogous to that in iodinations.[4,19] The transition

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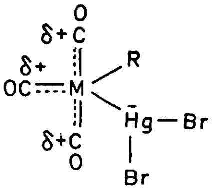
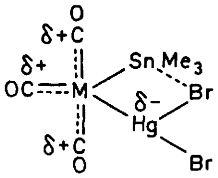
[18] M. H. Abraham and T. R. Spalding, *J. Chem. Soc.* (*A*), 1968, 2530.

[19] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Chem. Comm.*, 1975, 625 [structure (III) in this paper should have a negative charge on the I atom joined to Mn].

state for mercuration possibly has a configuration (II), similar to (I), with some interaction between the tin and halogen atoms. An intermediate similar to (A) with structure as (I) (R = alkyl) has been proposed for the mercuration of [FeR(cp)(CO)$_2$] (R = alkyl) in tetrahydrofuran, propan-2-ol, and nitrobenzene.[20]



(I)



(II)

Only representative CO groups are included

Effect of Change of Mercury(II) *Halide*.—The rates of reaction of different mercury(II) halides (HgX$_2$) with a particular organometallic compound are very similar, and show no general trend. At 30 °C with [Mo(cp)(CO)$_3$-(SnMe$_3$)] the relative rates are (X = Cl) 1.0, (Br) 1.9, (I) 1.1, with [Fe(cp)(CO)$_2$(SnMe$_3$)] (Cl) 1.0, (Br) 1.7, (I) 1.8, and with [Mn(CO)$_5$(SnMe$_3$)] (Cl) 1.0, (Br) 1.7, and (I) 1.0. This pattern of similar reactivity for all mercury(II) halides has been observed for reaction with [AuEt(PPh$_3$)] (Cl, 1.0; Br, 2.3; I, 2.5)[10] and with HgMe$_2$ (Cl, 1.0; Br, 1.4; I, 0.6).[21] The relative reactivities of our compounds vary slightly with change in temperature because the activation parameters are not the same for each reaction (Table 4). The activation enthalpies, $\Delta H^{\ddagger}$, for the reactions of HgX$_2$ with [Mo(cp)(CO)$_3$-(SnMe$_3$)] and with [Mn(CO)$_5$(SnMe$_3$)] decrease in the order Cl > Br > I. This order could reflect the decreasing strength of mercury–halogen bonds, but the multistage reaction path makes such interpretation of activation parameters unreliable.

Conclusions.—The mechanism of mercuration of compounds containing tin–transition-metal bonds parallels that of iodination. An adduct, (I), is formed between the metal complex and mercury(II) halide. The decomposition of (I) possibly involves the cyclic activated complex (II).

[6/1181 *Received*, 21*st June*, 1976]

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[20] L. J. Dizikes and A. Wojcicki, *J. Amer. Chem. Soc.*, 1975, **97**, 2540.

[21] M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, 1964, **3**, 761.