Reactivity of Main-group–Transition-metal Bonds. Part V.[1] Kinetics of Reactions of Halogens and Interhalogens with Pentacarbonyl(trimethylstannyl)manganese, Tricarbonyl(η-cyclopentadienyl)(trimethylstannyl)molybdenum, and Dicarbonyl(η-cyclopentadienyl)(trimethylstannyl)iron, including the Effects of Solvents on Reactivity

By **John R. Chipperfield,* James Ford, Andy C. Hayter, David J. Lee, and David E. Webster,** Department of Chemistry, The University, Hull HU6 7RX

The kinetics of the reactions of [Mn(CO)$_5$(SnMe$_3$)], [Mo(cp)(CO)$_3$(SnMe$_3$)], and [Fe(cp)(CO)$_2$(SnMe$_3$)] (cp = η-cyclopentadienyl) with bromine in tetrachloromethane (first compound), with iodine monochloride and iodine monobromide in tetrachloromethane (first two compounds), and with iodine in various solvents (all three compounds) have been studied. Bromine is *ca.* 4 000 times more reactive than I_2, the iodine monohalides form charge-transfer complexes prior to reaction and appear to react at approximately the same rate as I_2, and the reaction rate depends on solvent polarity. The reaction is akin to an aromatic substitution; a mechanism involving an intermediate complex that is stabilised by vertical hyperconjugation is in accord with the experimental results.

N earlier papers [2,3] we discussed the reactions of [Cr(cp)(CO)$_3$(SnMe$_3$)], [Mo(cp)(CO)$_3$(SnMe$_3$)], [W(cp)(CO)$_3$(SnMe$_3$)], [Fe(cp)(CO)$_2$(SnMe$_3$)], and [Mn(CO)$_5$(SnMe$_3$)] (cp = η-cyclopentadienyl) with iodine in tetrachloromethane, and have shown that they are electrophilic substitutions that can be described by a reaction scheme of the form (i). Here we extend the study of this

$$\begin{aligned}I_2 + \text{organometallic compound} &\rightleftharpoons \text{charge-transfer}\\ \text{compound} &\longrightarrow \text{intermediate} \longrightarrow \text{products} \quad \text{(i)}\end{aligned}$$

rather complicated reaction into three independent but related areas. These are (*a*) the use of bromine as the electrophile, (*b*) the use of interhalogen compounds as electrophiles, and (*c*) the effect of the solvent on the iodination.

EXPERIMENTAL

Preparations.—The compounds [Mn(CO)$_5$(SnMe$_3$)], [Mo(cp)(CO)$_3$(SnMe$_3$)], and [Fe(cp)(CO)$_2$(SnMe$_3$)] were prepared as described previously.[2] Solutions of halogens and interhalogens were standardised by titration with Na$_2$[S$_2$O$_3$] prior to use.

Spectra.—I.r., n.m.r., and mass spectra were recorded using the instruments already described.[2]

Kinetics.—Reactions were studied by measuring changes in the optical density with time at a wavelength where the halogen or interhalogen absorbs (I_2, ICl, and IBr, 540 nm; Br_2 480 nm). Halogenations of [Mo(cp)(CO)$_3$(SnMe$_3$)] and [Fe(cp)(CO)$_2$(SnMe$_3$)] were followed in a stopped-flow spectrophotometer; a Unicam SP 500 spectrophotometer fitted with a constant-temperature cell holder was used for the other reactions. For the reaction of bromine with [Mn(CO)$_5$(SnMe$_3$)] the SP 500 was used in the 'direct read-out mode' and connected to a chart recorder.

Reaction kinetics were usually studied under first-order conditions with an excess of the organometallic compound. The observed first-order rate coefficient, $k_1^{\text{obs.}}$, was measured and the appropriate second-order rate coefficient, $k_2^{\text{obs.}}$, was calculated. Second-order conditions (still with an excess of the metal compound) were used for bromination of [Mn(CO)$_5$(SnMe$_3$)] and the appropriate second-order rate expression was used to calculate $k_2^{\text{obs.}}$.

RESULTS

As only a few of the reactions have been reported previously, it was necessary to characterise the products carefully to ensure that the kinetic measurements were valid. The results of the product analysis show that reactions can

---

[1] Part IV, J. R. Chipperfield, J. Ford, A. C. Hayter, and D. E. Webster, *J.C.S. Dalton*, 1976, 360.

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

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

be described by equation (1) (X, Y = Cl, Br, or I; M′ = Mn, Mo, or Fe) with no evidence for any side reactions.

$$\mathrm{XY} + [\mathrm{M'(cp)}_m\mathrm{(CO)}_n\mathrm{(SnMe_3)}] \longrightarrow \mathrm{SnMe_3X} + [\mathrm{M'(cp)}_m\mathrm{(CO)}_n\mathrm{Y}] \quad (1)$$

Reactions.—$[\mathrm{Mn(CO)_5(SnMe_3)}]$ *with* ICl. The compound $[\mathrm{Mn(CO)_5(SnMe_3)}]$ (0.063 mol $\mathrm{dm^{-3}}$) in tetrachloromethane was mixed with an equal volume of ICl solution (0.0053 mol $\mathrm{dm^{-3}}$) in the same solvent. When the reaction was complete (3 h), an i.r. spectrum was recorded which showed (in addition to bands due to the reactant) peaks at 2 127, 2 045, 2 022, and 1 994 $\mathrm{cm^{-1}}$ * {*cf.* $[\mathrm{Mn(CO)_5I}]$, peaks[4] at 2 125, 2 044, 2 016, and 2 003 $\mathrm{cm^{-1}}$}. The n.m.r. spectrum of a similar solution showed a peak at δ 0.62 p.p.m.† (*cf.* $\mathrm{SnMe_3Cl}$,[5] δ 0.63 p.p.m.), as well as that of $[\mathrm{Mn(CO)_5(SnMe_3)}]$. Reaction proceeds according to equation (1) (X = Cl, Y = I, M′ = Mn, $n = 5$, $m = 0$).

$[\mathrm{Mn(CO)_5(SnMe_3)}]$ *with* IBr. The compound $[\mathrm{Mn(CO)_5(SnMe_3)}]$ (0.190 mol $\mathrm{dm^{-3}}$) in tetrachloromethane was mixed with an equal volume of IBr (0.002 57 mol $\mathrm{dm^{-3}}$) in the same solvent. When the reaction was complete (3 h), an i.r. spectrum was recorded which showed (in addition to bands from the reactants) peaks due to $[\mathrm{Mn(CO)_5I}]$. The n.m.r. spectrum of a similar solution showed a peak at δ 0.71 p.p.m. (*cf.* $\mathrm{SnBrMe_3}$,[5] δ 0.74 p.p.m.). After 24 h in daylight a band at δ 0.62 p.p.m. appeared. This was probably due to $\mathrm{SnMe_3Cl}$ formed by reaction with the solvent ($\mathrm{SnMe_3Cl}$,[5] δ 0.62 p.p.m.), and at the same time the band due to $\mathrm{SnBrMe_3}$ vanished. Reaction proceeds according to equation (1) (X = Br, Y = I, M′ = Mn, $n = 5$, $m = 0$).

$[\mathrm{Mo(cp)(CO)_3(SnMe_3)}]$ *with* ICl. The compound $[\mathrm{Mo(cp)(CO)_3(SnMe_3)}]$ (0.500 8 g, 1.22 mmol) in tetrachloromethane (10 $\mathrm{cm^3}$) was mixed with ICl (0.201 g, 1.24 mmol) in the same solvent (10 $\mathrm{cm^3}$) at 20 °C. Reaction was rapid and the i.r. spectrum of the solution showed peaks at 2 044, 1 975, and 1 960 $\mathrm{cm^{-1}}$ {*cf.* $[\mathrm{Mo(cp)(CO)_3I}]$, peaks[2] at 2 045, 1 975, and 1 960 $\mathrm{cm^{-1}}$}. The n.m.r. spectrum showed peaks at δ 5.60 p.p.m. {*cf.* $[\mathrm{Mo(cp)(CO)_3I}]$,[2] δ 5.60 p.p.m.} and 0.63 p.p.m. (*cf.* $\mathrm{SnMe_3Cl}$,[5] δ 0.62 p.p.m.). After the removal of the solvent the mass spectrum of the residue showed the presence of $[\mathrm{Mo(cp)(CO)_3I}]$ with a breakdown pattern similar to that of a prepared sample of $[\mathrm{Mo(cp)(CO)_3I}]$. Reaction proceeds according to equation (1) (X = Cl, Y = I, M′ = Mo, $n = 3$, $m = 1$).

$[\mathrm{Mo(cp)(CO)_3(SnMe_3)}]$ *with* IBr. The compound $[\mathrm{Mo(cp)(CO)_3(SnMe_3)}]$ (0.216 3 g, 0.527 mmol) in tetrachloromethane (10 $\mathrm{cm^3}$) was mixed with IBr (0.175 2 g, 0.84 mmol) in the same solvent (10 $\mathrm{cm^3}$) at 20 °C. Reaction was rapid and the i.r. spectrum of the solution showed peaks at 2 044, 1 975, and 1 960 $\mathrm{cm^{-1}}$ {*cf.* $[\mathrm{Mo(cp)(CO)_3I}]$ [2]}. The n.m.r. spectrum showed peaks at δ 5.59 and 0.73 p.p.m. {*cf.* $[\mathrm{Mo(cp)(CO)_3I}]$; and $\mathrm{SnBrMe_3}$,[5] δ 0.74 p.p.m.}. The mass spectrum of the residue, recorded after removal of the solvent, showed the presence of $[\mathrm{Mo(cp)(CO)_3I}]$. Reaction proceeds according to equation (1) (X = Br, Y = I, M′ = Mo, $n = 3$, $m = 1$).

$[\mathrm{Mn(CO)_5(SnMe_3)}]$ *with* $\mathrm{Br_2}$. The compound $[\mathrm{Mn(CO)_5(SnMe_3)}]$ (*ca.* 1.7 mmol) in tetrachloromethane (10 $\mathrm{cm^3}$) was mixed with a solution of $\mathrm{Br_2}$ (1.7 mmol) in the same solvent at 20 °C. An orange precipitate formed at once, and was filtered off. Its i.r. spectrum in tetrachloromethane showed peaks at 2 134, 2 050, and 2 000 $\mathrm{cm^{-1}}$, consistent with $[\mathrm{MnBr(CO)_5}]$ (peaks[4] at 2 133, 2 050, and 2 001 $\mathrm{cm^{-1}}$). The remaining solution showed i.r. peaks at 2 134, 2 050, 2 044, 2 010, 2 000, and 1 974 $\mathrm{cm^{-1}}$ {*cf.* $[\mathrm{MnBr(CO)_5}]$ and $[\{\mathrm{MnBr(CO)_4}\}_2]$,[4] peaks at 2 099, 2 042, 2 011, and 1 974 $\mathrm{cm^{-1}}$}. An n.m.r. spectrum of this solution showed a peak at δ 0.73 p.p.m. (*cf.* $\mathrm{SnBrMe_3}$,[5] δ 0.74 p.p.m.). After removal of the solvent the mass spectrum of the residue was recorded and showed the presence of $[\mathrm{Mn^{81}Br(CO)_5}]$ (*m/e* 276), with a breakdown pattern similar to that of a prepared sample of $[\mathrm{MnBr(CO)_5}]$. However, in dilute solutions when $\mathrm{Br_2}$ (0.001 mol $\mathrm{dm^{-3}}$) in tetrachloromethane was added to $[\mathrm{Mn(CO)_5(SnMe_3)}]$ (0.01 mol $\mathrm{dm^{-3}}$) in the same solvent, no precipitate was formed and the i.r. spectrum of the solution showed peaks corresponding to $[\mathrm{MnBr(CO)_5}]$ with no evidence for $[\{\mathrm{MnBr(CO)_4}\}_2]$ which is formed at the higher concentration of reactants above. Under the conditions used for kinetic measurements therefore, reaction proceeds according to equation (1) (X = Y = Br, M′ = Mn, $n = 5$, $m = 0$).

In all reactions kinetic measurements were consistent with equation (2).

$$-\mathrm{d[XY]}/\mathrm{d}t = k_2^{\mathrm{obs.}}[\mathrm{XY}][\mathrm{organometallic}] \quad (2)$$

DISCUSSION

Bromination of $[\mathrm{Mn(CO)_5(SnMe_3)}]$.—The rate coefficients for the reaction of bromine with $[\mathrm{Mn(CO)_5(SnMe_3)}]$ in tetrachloromethane at several temperatures are given in Table 1. A hint that the reaction mechanism may be more complicated than a simple bimolecular process is given by the Arrhenius plot of log $k_2^{\mathrm{obs.}}$ against $1/T$. This is linear for the first four data points, from 23.5 to 39.4 °C, giving the activation parameters in Table 2. Above 39.4 °C the plot begins to curve towards the abscissa. Non-linear Arrhenius plots usually indicate that a reaction proceeds by more than one step, and $[\mathrm{Mn(CO)_5(SnMe_3)}]$ may react with bromine by a similar mechanism to that by which it reacts with iodine, where an intermediate compound is probably formed.[2]

TABLE 1

Reaction of $[\mathrm{Mn(CO)_5(SnMe_3)}]$ with bromine in tetrachloromethane

θ_c / °C	$10^3[\mathrm{Mn(CO)_5(SnMe_3)}]$ / mol $\mathrm{dm^{-3}}$	$10^3[\mathrm{Br_2}]$ / mol $\mathrm{dm^{-3}}$	k_2 / $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
23.5	4.95	3.24	10.0
	4.95	3.24	9.9
29.9	4.95	3.24	16.1
	4.95	3.24	20.5
	4.95	3.24	22.4
30.0	2.47	1.62	22.7
30.1	4.95	1.62	19.8
30.6	4.95	3.24	18.5
37.1	4.95	3.24	30.7
	4.95	1.62	25.8
	4.95	1.62	23.6
39.4	4.95	1.62	29.2
	4.95	3.24	29.5
50.0	4.95	3.24	43.0
53.0	4.95	3.24	37.2
53.5	4.95	3.24	39.1

Bromine reacts with $[\mathrm{Mn(CO)_5(SnMe_3)}]$ 4 000 times

---

* Difficult to measure in the presence of excess of $[\mathrm{Mn(CO)_5(SnMe_3)}]$ which has a band at 1 992 $\mathrm{cm^{-1}}$.

† Proton shifts are relative to $\mathrm{SiMe_4}$.

[4] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1962, **1**, 933.

[5] H. Schmidbaur and I. Ruidisch, *Inorg. Chem.*, 1964, **3**, 599.

faster than does iodine. Qualitatively, reactions of bromine are always considered faster than those of iodine, although direct comparisons of reactivity are difficult as in aqueous media rate equations for bromination become complicated to allow for species such as HOBr and $[Br_3]^-$,[6] while in aprotic solvents iodinations are often greater than first order in the concentration of iodine.[7] A relative rate of 4 000 is very similar to that for bromination and iodination of SnR_4 in the non-polar solvent chlorobenzene[8,9] (R = Me, 670; Et, 1 400; Pr^i, 370; Pr^n, 4 100; Bu^n, 5 100). In the polar solvent acetic acid, lower relative rates are found[9,10] (R = Me, 50; Pr^i, 2 500; Pr^n, 120; Bu^n, 130).

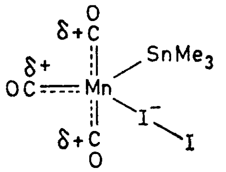
Table 2

Activation parameters for the reaction of $[Mn(CO)_5(SnMe_3)]$ with halogens and interhalogens (XY) in tetrachloromethane

X	Y	$\Delta H^‡$ / kJ mol^{-1}	$\Delta S^‡$ / J K^{-1} mol^{-1}
I	I	50.5 ± 4 [a]	−122 ± 10 [a]
Br	Br	48 ± 10 [b]	−61 ± 30 [b]
I	Br	55 ± 5	−108 ± 15
I	Cl	61 ± 5	−87 ± 15

[a] From ref. 2. [b] 23.5—39.4 °C.

The greater reactivity of bromine compared with iodine indicates that bromine is a less selective electrophile than iodine. We suggest that iodination proceeds through a transition state that is similar to the intermediate (I),[1] possibly with some interaction of the terminal iodine atom with the tin atom, whereas bromination takes place rapidly through a less ordered transition state.



(I)

Only representative CO groups have been included

Reaction of Interhalogen Compounds with $[Mn(CO)_5(SnMe_3)]$ *and* $[Mo(cp)(CO)_3(SnMe_3)]$.—The products of reaction of an interhalogen IX (X = Cl or Br) with $[Mn(CO)_5(SnMe_3)]$ or $[Mo(cp)(CO)_3(SnMe_3)]$ are quite specific. The iodine atom is attached to the transition metal and the other halogen atom (X) is joined to the trimethyltin group [equation (3)]. Clark and his co-workers reported that $SnMe_3I$ is an additional product from the reactions of ICl with $[Mn(CO)_5(SnMe_3)]$ in pentane,[11] and $[Fe(cp)(CO)_2(MMe_3)]$ in cyclohexane[12] (M = Si, Ge, or Sn), but we found no $SnMe_3I$ from reactions carried out in tetrachloromethane. It is possible that Clark was observing a side reaction as he allowed at least 12 h before isolating the products (the reaction is complete in <3 h).

$$IX + [Me_3Sn\text{-}M'L_n] \longrightarrow SnMe_3X + [M'L_nI] \quad (3)$$

Both ICl and IBr are polar molecules with a positive iodine atom. In both $[Mn(CO)_5(SnMe_3)]$ and $[Mo(cp)(CO)_3(SnMe_3)]$ there are 18 electrons on the transition metal and it has filled *d* orbitals that can attract an electrophile. In contrast there are no unshared pairs of electrons on tin. The nature of the products suggests that an important feature of the reaction is electrophilic attack of the iodine on the transition metal.

Specificity of the products is found for other reactions of interhalogen compounds. In the reactions of ICl with aromatic hydrocarbons (RH) the products are RI and HCl[13] and with organosilicon compounds ($SiMe_3R$) the products are RI and $SiMe_3Cl$,[14] while in the reaction of IBr with tetra-alkyltin compounds (SnR'_4) the products are R'I and $SnBrR'_3$.[15] These three reactions are all electrophilic substitutions by the iodine of the interhalogen on the aryl or alkyl group.

The rate coefficient, $k_2^{obs.}$, obtained for the reactions of $[Mn(CO)_5(SnMe_3)]$ are given in Table 3 and activation parameters derived therefrom are given in Table 2. Similar rate data for $[Mo(cp)(CO)_3(SnMe_3)]$ are given in Table 4. We found no evidence for multiple order in interhalogen as found in the reaction of ICl with aromatic compounds,[13] nor did we find any positive evidence for a two-stage process such as we have reported for the reaction of $[Cr(cp)(CO)_3(SnMe_3)]$ with iodine,[3] although the reactions probably take place by a similar mechanism.

Table 3

Reaction of $[Mn(CO)_5(SnMe_3)]$ with halogens and interhalogens (XY) in tetrachloromethane

$10^3[Mn(CO)_5(SnMe_3)]$ / mol dm^{-3}	X	Y	$10^3[IX]$ / mol dm^{-3}	θ_c / °C	$10^3k_2^{obs.}$ / dm^3 mol^{-1} s^{-1}
	I	I		30.0	5.0 *
63.2	I	Cl	5.3	30.0	3.78
128.5	I	Cl	5.3	30.0	3.94
168.1	I	Cl	5.3	34.9	7.00
179.9	I	Cl	5.3	40.2	10.75
179.9	I	Cl	5.3	45.0	13.90
168.1	I	Cl	5.3	49.9	18.04
128.5	I	Br	0.9	30.0	4.76
190.4	I	Br	2.57	30.0	4.93
186.0	I	Br	2.57	34.9	7.67
186.0	I	Br	2.57	40.1	10.13
189.5	I	Br	2.57	44.9	14.60
189.5	I	Br	2.57	50.0	19.96

* From ref. 2.

---

[6] R. O. C. Norman and R. Taylor, ' Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, p. 131.

[7] G. Martino and J-C. Jungers, *Bull. Soc. chim. France*, 1970, 3392.

[8] M. Gielen and J. Nasielski, *J. Organometallic Chem.*, 1963, **1**, 173.

[9] S. Boué, M. Gielen, and J. Nasielski, *J. Organometallic Chem.*, 1967, **9**, 443.

[10] M. Gielen and J. Nasielski, *Bull. Soc. chim. belges*, 1962, **71**, 601.

[11] M. R. Booth, D. J. Cardin, N. A. D. Carey, H. C. Clark, and B. R. Sreenathan, *J. Organometallic Chem.*, 1970, **21**, 171.

[12] R. E. J. Bichler, H. C. Clark, B. K. Hunter, and A. T. Rake, *J. Organometallic Chem.*, 1974, **69**, 367.

[13] L. J. Lambourne and P. W. Robertson, *J. Chem. Soc.*, 1947, 1167.

[14] L. M. Stock and A. R. Spector, *J. Org. Chem.*, 1963, **28**, 3272.

[15] G. Redl, B. Altner, D. Anker, and M. Minot, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 861.

Iodine monochloride is usually regarded as a more reactive electrophile than iodine,[16] but the evidence for this is not clear. There does not appear to be any quantitative study of their comparative reactivity with the same substrate. In the light of current beliefs, we were somewhat surprised to find that the rates of reaction of ICl and IBr with our compounds were very similar to those of I_2 (Tables 3 and 4). The activation enthalpies and entropies (Table 2) for $[Mn(CO)_5(SnMe_3)]$ with the interhalogen are close to those found when iodine or bromine is the electrophile. This is good evidence that there is no dramatic change in the mechanism on changing from one interhalogen to another. Iodine monobromide is known to dissociate: $2IBr \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_2 + I_2$. In tetrachloromethane at 25 °C, 8% dissociation is observed.[17] When solutions of bromine (0.002 mol dm^{-3}) and iodine (0.002 mol dm^{-3}) in tetrachloromethane are mixed to form IBr, the colour change is rapid with a reaction half-life of <1 s. If the reaction is second order, k_{-1} must be $>1\,000$ dm^3 mol^{-1} s^{-1}. Using the reported value [17] of 1/495 for the dissociation constant ($= k_1/k_{-1}$) of IBr, we can calculate $k_1 > 2$ dm^3 mol^{-1} s^{-1}. This estimate indicates that the dissociation rate of IBr is considerably faster than the observed rate of reaction of IBr with $[Mn(CO)_5(SnMe_3)]$. It is difficult to see how this can be so, since when IBr is mixed with an excess of $[Mn(CO)_5(SnMe_3)]$ the free bromine should react rapidly, as bromine is 4 000 times more reactive than iodine, to give $SnBrMe_3$ and $[MnBr(CO)_5]$. As bromine is used up more IBr should dissociate. When all the bromine has reacted a slow reaction of iodine with $[Mn(CO)_5(SnMe_3)]$ should be observed giving $SnMe_3I$ and $[Mn(CO)_5I]$ as products. However, only $SnBrMe_3$ and $[Mn(CO)_5I]$ were found, which suggests that reaction with bromine is not taking place and IBr is the only reactant. Why the dissociation of IBr appears to be suppressed during a reaction is not clear. Further studies, currently being undertaken, are needed to resolve this problem. The dissociation rate may not be as large as the observed rate of reaction of IBr with $[Mo(cp)(CO)_3(SnMe_3)]$ or $[Fe(cp)(CO)_2(SnMe_3)]$, and the reaction with these two compounds is possibly uncomplicated by the dissociation.

TABLE 4

Reaction of $[Mo(cp)(CO)_3(SnMe_3)]$ with iodine and interhalogens (IX) in tetrachloromethane at 30.0 °C

$10^3[Mo(cp)(CO)_3(SnMe_3)]$ / mol dm^{-3}	X	$10^3[IX]$ / mol dm^{-3}	$k_2^{obs.}$ / dm^3 mol^{-1} s^{-1}	
	I		226 *	
16.56	Br	0.735	182	174
8.28	Br	0.735	171	
8.28	Br	0.368	169	
8.28	Cl	0.52	173	

* From ref. 2.

Earlier we reported that when $[Mo(cp)(CO)_3(SnMe_3)]$ or $[Mn(CO)_5(SnMe_3)]$ react with iodine the initial optical density ($D_0^{obs.}$) of the solution at 540 nm is independent of the concentration of the organometallic compound (which does not absorb at 540 nm). We concluded that either the equilibrium constant K for formation of a charge-transfer complex (D) was small (<10 dm^3 mol^{-1}),

$$IX + M{-}M \overset{K}{\rightleftharpoons} \underset{(D)}{IX \cdots M{-}M} \qquad (4)$$

or that the difference between the absorption coefficients of the charge-transfer complex (D) and iodine, ε_D and ε_{I_2} respectively, was small. The initial optical densities, $D_0^{obs.}$ (recorded after *ca.* 0.002 s), of mixtures of interhalogen and $[Mo(cp)(CO)_3(SnMe_3)]$ are greater than those expected from the concentration of interhalogen (Table 5). If a and b are the concentrations of interhalogen and $[Mo(cp)(CO)_3(SnMe_3)]$ respectively we can calculate an observed absorption coefficient, $\varepsilon^{obs.}$, which is the gradient of a graph of $D_0^{obs.}$ against a at constant b. Using the equation derived by Keteelar *et al.*[18] where

$$1/(\varepsilon^{obs.} - \varepsilon_{IX}) = [1/(\varepsilon_D - \varepsilon_{IX})bK] + [1/(\varepsilon_D - \varepsilon_{IX})] \qquad (5)$$

ε_{IX} is the absorption coefficient of the interhalogen (*i.e.* $\varepsilon^{obs.}$ for $b = 0$), we see that a plot of $1/(\varepsilon^{obs.} - \varepsilon_{IX})$ against $1/b$ should be a straight line, cutting the abscissa at $1/b = -K$. The plots are shown in the Figure and lead to K values of 70 and 290 dm^3 mol^{-1} for ICl and IBr respectively. At the concentrations used for kinetic runs, say $a \approx 8 \times 10^{-4}$ and $b \approx 8 \times 10^{-3}$ mol dm^{-3}, *ca.* 40 and 70% of the ICl and IBr respectively are present as charge-transfer complex (D).

TABLE 5

Initial optical densities, $D_0^{obs.}$, at 540 nm for mixtures of $[Mo(cp)(CO)_3(SnMe_3)]$ and IBr or ICl in tetrachloromethane at 30 °C. Values of $\varepsilon^{obs.}$ (in dm^3 mol^{-1} cm^{-1}) are given in parentheses

	$10^2[Mo(cp)(CO)_3(SnMe_3)]$/mol dm^{-3}			
$10^4[IBr]$ / mol dm^{-3}	0	0.5	1	2
1.25	0.047	0.11	0.088	0.13
2.5	0.088	0.14	0.135	0.175
5.0	0.157	0.23	0.23	0.285
10.0	0.303	0.44	0.445	0.50
	(290)	(384)	(409)	(426)
$10^4[ICl]$ / mol dm^{-3}				
1.25	0.01	0.064	0.044	0.078
2.5	0.025	0.086	0.066	0.113
5.0	0.048	0.131	0.123	0.182
10.0	0.082	0.211	0.238	0.32
	(80)	(167)	(244)	(277)

We found no evidence of formation of charge-transfer complexes between $[Mn(CO)_5(SnMe_3)]$ and ICl, IBr, or Br_2. Initial optical densities were those expected for the halogen.

Rôle of the Solvent in the Iodination of Tin–Transition-metal Compounds.—The rates of reaction of iodine with

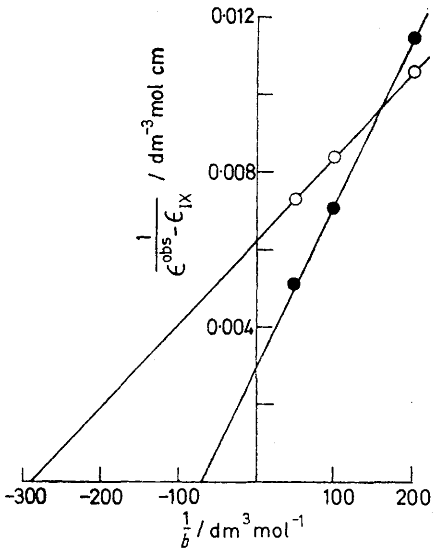
---

[16] Ref. 6, p. 133.

[17] J. D. Childs, L-N. Lin, and S. D. Christian, *J. Inorg. Nuclear Chem.*, 1975, **37**, 757.

[18] J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. chim.*, 1952, **71**, 1104.

$[Mn(CO)_5(SnMe_3)]$, $[Mo(cp)(CO)_3(SnMe_3)]$, and $[Fe(cp)(CO)_2(SnMe_3)]$ in various solvents are shown in Table 6. For all three compounds there is a decrease in rate when cyclohexane is used as solvent instead of tetrachloromethane. Two important solvent parameters are the polarity, Q [measured by $(\varepsilon - 1)/(2\varepsilon + 1)$ where ε is the dielectric constant of the solvent], and the polarisability, P [measured by $(n^2 - 1)/(n^2 + 2)$ where n is the refractive index of the solvent].[19] Values of Q and P for the solvents used are also given in Table 6, and these show that tetrachloromethane is a little more polar and less polarisable than cyclohexane. For $[Mn(CO)_5(SnMe_3)]$, further increase in solvent polarity (using benzene and diethyl ether) caused the reaction rate to increase, and a plot of log $k_2^{obs.}$ against Q is a fair straight line with a gradient of *ca.* 12 (a reasonable value compared to organic reactions).[19] Reactions in the more polar solvents tetrahydrofuran and nitrobenzene were very fast. Increase in the polarity of a solvent causes reaction rates to accelerate where there is a greater charge separation in the transition state than in the ground state. Iodine and $[Mn(CO)_5(SnMe_3)]$ are both neutral molecules and in the transition state considerable charge separation will have taken place, as shown in structure (I).



Charge-transfer complex formation between iodine halides, IX, and $[Mo(cp)(CO)_3(SnMe_3)]$. Plots of $1/(\varepsilon^{obs.} - \varepsilon_{IX})$ against $1/b$ for X = Cl (●) and Br (○)

TABLE 6

Reactions of compounds containing metal–metal bonds with iodine in various solvents at 30 °C

Compound	Solvent	$k_2^{obs.}$ $dm^3 mol^{-1} s^{-1}$	Q	P
$[Mo(cp)(CO)_3(SnMe_3)]$	Cyclohexane	24.9	0.203	0.256
	CCl_4	226 [a]	0.226	0.274
$[Fe(cp)(CO)_2(SnMe_3)]$	Cyclohexane	216	0.203	0.256
	CCl_4	2 780 [a]	0.226	0.274
$[Mn(CO)_5(SnMe_3)]$	Cyclohexane	0.0021	0.203	0.256
	CCl_4	0.0050 [a]	0.226	0.274
	Benzene	0.0076	0.231	0.295
	OEt_2	0.133	0.345	0.217
	Tetrahydrofuran	*ca.* 20 [b]	0.405	0.246
	$PhNO_2$	*ca.* 150 [b]	0.479	0.321

[a] From ref. 2. [b] Rough estimate from half-life of reaction.

Conclusions.—Reactions of compounds containing Group 4 elements bonded to transition metals that react with halogens or interhalogen compounds with cleavage of the metal–metal bond do so by a reaction mechanism that involves initial formation of a charge-transfer complex, followed by an intermediate complex [the structure of which we suggest is as in (I)] that decomposes to give the products. Studies with halogens and interhalogens in various solvents, and with a variety of substituents on the tin and transition metal, all support the general mechanism proposed. In favourable cases the charge-transfer complex can be detected, and in others formation and decomposition of the intermediate complex can be studied. The intermediate for the reaction, (I), is stabilised by vertical hyperconjugation.[20] The reaction differs from other halogenations in non-polar solvents in that it is first order in halogen concentration, others being of higher order. The general form of the reaction is very reminiscent of aromatic halogenation and we have called the reaction a 'pseudo-aromatic' substitution.[20]

[5/1763 *Received*, 15*th September*, 1975]

---

[19] I. A. Koppel and V. A. Palm, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum, London, 1972, ch. 5.

[20] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Chem. Comm.*, 1975, 625.