Reactivity of Main-group–Transition-metal Bonds. Part I. Kinetics of Iodination of Tricarbonyl(η-cyclopentadienyl)(trimethylstannyl)-molybdenum and -tungsten, Dicarbonyl(η-cyclopentadienyl)(trimethylstannyl)iron, and Pentacarbonyl(trimethylstannyl)manganese

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

The kinetics of cleavage of the tin–transition-metal bond in [$Me_3SnMo(CO)_3(cp)$], [$Me_3SnW(CO)_3(cp)$], [$Me_3SnMn(CO)_5$], and [$Me_3SnFe(CO)_2(cp)$] by iodine in carbon tetrachloride have been studied (cp = η-cyclopentadienyl). The reaction is an electrophilic substitution at the metal–metal bond. The relative rates for the above four compounds are M = Fe > Mo ≈ W ≫ Mn. The simplicity of the kinetics for the iodination of these compounds probably masks the complexity of the reaction, and schemes involving charge-transfer complexes and chemical intermediates are proposed.

MANY compounds containing a main-group 4 element bonded to a transition metal have been prepared during the last decade,[1] the structures of some of them have been determined by *X*-ray crystallography,[1] and spectroscopic studies have been carried out. The chemical reactions of this class of compounds are of interest because there are several possible reaction sites. Consider, for example, [$Ph_3SnFe(CO)_2(cp)$] (cp = η-cyclopentadienyl). It may undergo reaction with cleavage of a Ph–Sn bond, the Sn–Fe bond, or an Fe–CO bond, as well as possible substitution in the Ph or cp rings, and even ' insertion ' of a small molecule between the two metal atoms. A number of reactions of this type of compound have been studied in an attempt to define the features that determine where chemical reaction occurs in a particular molecule.[2-5]

We have begun a programme of work to study quantitatively these reactions with a variety of reagents. Some of the reactions that we have studied have recently been reported in the literature,[2-5] but so far there are no quantitative data from which detailed reaction mechanisms can be deduced. Most of our work has been concerned with reactions with halogens and mercury(II) compounds. We have been particularly interested in reactions where cleavage of the metal–metal bond occurs (see Discussion section). The reactions are often quite complex, unstable intermediate species being involved, and kinetic analysis of the experimental results can be far from simple.[6] The stoicheiometric equation (1)

$$[R_3MM'L_n] + XY \longrightarrow R_3MY + [XM'L_n] \quad (1)$$

(R = alkyl or aryl; M = Si, Ge, Sn, or Pb; M' = Cr, Mo, W, Mn, Fe, or Co; L = CO or cp; X = I, Br, or Cl; Y = I, Br, Cl, HgBr, or HgCl) for the reaction masks these complexities. Here we report some of the, apparently, simplest reactions that we have studied (R = Me; M = Sn; M' = Mo, W, Mn, or Fe; L = CO or cp; and X = Y = I).

RESULTS

For each of the four reactions investigated we carried out the following experiments. (*a*) The compound containing the metal–metal bond was prepared and purified until spectroscopic analysis showed it to be pure. (*b*) The compound was allowed to react with a halogen in a 1 : 1 molar ratio at room temperature in carbon tetrachloride solution under an atmosphere of nitrogen. (*c*) The products from (*b*) were characterised by spectroscopic methods, and g.l.c. and elemental analysis. Frequently it was necessary to synthesise the expected reaction products by another route for comparison. (*d*) If a quantitative reaction of the type (1) occurred, *i.e* the metal–metal bond had been cleaved (as it had in these four reactions), the reaction rate was measured, usually under first-order conditions with the organometallic compound in ten-fold excess over iodine, and the rate equation was established. (*e*) The dependence of rate coefficients on temperature and solvent was measured for some reactions.

Before carrying out a kinetic study it is, of course, essential that the reaction products be carefully characterised to ensure that the reaction is quantitative with no side reactions. The characterisation of the products and details of the kinetic study are given in full for [$Me_3SnMo(CO)_3(cp)$] and briefly for the other three compounds.

The Reaction of [$Me_3SnMo(CO)_3(cp)$] *with* I_2 *in* CCl_4.—(a) *Product analysis*. The compound (0.228 g, 0.56 mmol) was dissolved in CCl_4 (20 cm^3) in one limb of a Schlenk tube under an atmosphere of nitrogen. Iodine (0.147 g, 0.56 mmol) dissolved in CCl_4 (20 cm^3) was added, and the resulting solution was stirred rapidly at room temperature. When reaction was complete (judged by the disappearance of the iodine colour) a portion of the solution was transferred to an i.r. cell with a path length of 0.195 mm and the i.r. spectrum was recorded. Further portions of the solution were diluted with CCl_4 and used to obtain n.m.r. and u.v. spectra of the reaction products. Finally the solvent was distilled from the remaining solution and the mass spectrum of the residue was obtained.

The i.r. spectrum had bands in the carbonyl region at 2 044, 1 975, and 1 961 cm^{-1}. A sample of [$(cp)(OC)_3MoI$] dissolved in CCl_4 had bands at 2 045, 1 975, and 1 960 cm^{-1}. The n.m.r. spectrum of the solution of the reaction products had peaks at δ 5.59 and 0.87 p.p.m.; Me_3SnI and [$(cp)(OC)_3MoI$] have peaks at δ 0.88 [7] and 5.60 p.p.m. respect-

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[1] F. G. A. Stone in ' New Pathways in Inorganic Chemistry,' eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968, p. 283.

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

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

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

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

[6] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, following paper.

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

ively. The mass spectrum of the residue showed a series of peaks identical to those found in the mass spectrum of [(cp)(OC)$_3$MoI]. A portion of the residue was placed in a sublimator at 0 °C (0.5 mmHg) * and a white compound collected on the probe at −70 °C. This compound is a liquid at room temperature and its mass spectrum was consistent with it being Me$_3$SnI. The u.v. spectrum of the solution of reaction products was similar to that of [(cp)(OC)$_3$MoI].

These experiments showed no evidence for any other reaction products and the reaction is quantitatively described by equation (2).

$$[\mathrm{Me_3SnMo(CO)_3(cp)}] + \mathrm{I_2} \longrightarrow \mathrm{Me_3SnI} + [\mathrm{(cp)(OC)_3MoI}] \quad (2)$$

(b) *Kinetics.* The kinetics of reaction were studied under pseudo-first-order conditions with an excess of the organometallic compound. All solutions were degassed by shaking *in vacuo* prior to mixing, and as the reactions were rapid their progress was studied in a stopped-flow spectrophotometer. The change in absorbance due to I$_2$ at 540 nm was measured and used to calculate the first-order rate coefficients, $k_1^{\mathrm{obs.}}$. The second-order rate coefficients $k_2^{\mathrm{obs.}}$ were then calculated and are given in Table 1. The results are consistent with the iodination being a second-order process, described by (3). The coefficient $k_2^{\mathrm{obs.}}$ was

$$\text{Rate} = k_2^{\mathrm{obs.}}[\mathrm{Me_3SnMo(CO)_3(cp)}][\mathrm{I_2}] \quad (3)$$

measured over the temperature range 30—45 °C and activation parameters were calculated (see Table 2).

TABLE 1

Second-order rate coefficients for the reaction of metal–metal bonded compounds with I$_2$ at 30.0 °C in CCl$_4$

Complex	10^3[Complex]/mol l^{-1}	10^3[I$_2$]/mol l^{-1}	$k_2^{\mathrm{obs.}}$/l mol^{-1} s^{-1}	
[Me$_3$SnMo(CO)$_3$(cp)]	12.17	0.60	230 ± 8	226
	12.17	1.20	222 ± 8	
	12.17	2.40	237 ± 9	
	16.56	1.08	217 ± 7	
[Me$_3$SnW(CO)$_3$(cp)]	11.08	0.539	198 ± 2	210
	11.08	1.078	205 ± 2	
	5.54	0.539	227 ± 0	
[Me$_3$SnFe(CO)$_2$(cp)]	4.27	2.61	2 760 ± 140	2 780
	1.87	0.33	2 870 ± 90	
	0.94	0.33	2 720 ± 100	
	2.68	0.23	2 760 ± 120	
[Me$_3$SnMn(CO)$_5$]	15.27	0.835	0.005 02	0.005 10
	12.30	0.418	0.005 28	
	23.00	0.439	0.005 58	
	23.00	0.439	0.004 51	

TABLE 2

Activation parameters for reactions of complexes with I$_2$ in CCl$_4$

Complex	θ$_c$/°C	$k_2^{\mathrm{obs.}}$/l mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
[Me$_3$SnMo(CO)$_3$(cp)]	30.0	217 *	18.6 ± 2	−139 ± 5
	35.0	249		
	40.0	263		
	45.0	331		
[Me$_3$SnFe(CO)$_2$(cp)]	30.0	2 780	−1.0 ± 2	−187 ± 5
	45.0	2 780		
[Me$_3$SnMn(CO)$_5$]	30.0	0.005 02 *	50.5 ± 4	−122 ± 10
	35.0	0.009 12		
	40.0	0.010 14		
	45.0	0.014 55		

* Obtained using the same solutions used to measure $k_2^{\mathrm{obs.}}$ at the other temperatures. The value in Table 1 is the average of all runs at 30.0 °C.

The Reaction of [Me$_3$SnW(CO)$_3$(cp)] *with* I$_2$ *in* CCl$_4$.—(a) *Product analysis.* A solution of [Me$_3$SnW(CO)$_3$(cp)] (0.060 g, 0.12 mmol) in CCl$_4$ (10 cm^3) was allowed to react with an equimolar solution of I$_2$ in CCl$_4$. The i.r. spectrum of the resulting solution had bands in the carbonyl region at 2 038 and 1 961 with a shoulder at 1 949 cm^{-1}; [(cp)(OC)$_3$WI] has bands at 2 040 and 1 961 cm^{-1}.[8] The n.m.r. spectrum of the product solution had peaks at δ 5.70 and 0.87 p.p.m.; [(cp)(OC)$_3$WI] and Me$_3$SnI have peaks at δ 5.70 [8] and 0.88 p.p.m.[7] respectively.

The reaction can be quantitatively described by equation (4).

$$[\mathrm{Me_3SnW(CO)_3(cp)}] + \mathrm{I_2} \longrightarrow \mathrm{Me_3SnI} + [\mathrm{(cp)(OC)_3WI}] \quad (4)$$

(b) *Kinetics.* The kinetics of reaction were studied under pseudo-first-order conditions, as for the molybdenum compound described above, and the rate equation was similar to (3); rate coefficients are given in Table 1.

The Reaction of [Me$_3$SnFe(CO)$_2$(cp)] *with* I$_2$ *in* CCl$_4$.—(a) *Product analysis.* A solution of [Me$_3$SnFe(CO)$_2$(cp)] (0.0500 g, 0.146 mmol) in CCl$_4$ (10 cm^3) was allowed to react with a solution of I$_2$ (0.0372 g, 0.146 mmol) in CCl$_4$(10 cm^3). The i.r. spectrum of the resulting solution had bands in the carbonyl region at 2 045 and 2 002 cm^{-1}. A sample of [(cp)(OC)$_2$FeI] dissolved in CCl$_4$ had bands at 2 043 and 1 999 cm^{-1}. The n.m.r. spectrum of the solution of the reaction products had peaks at δ 5.04 and 0.89 p.p.m; samples of [(cp)(OC)$_2$FeI] and Me$_3$SnI have peaks at δ 5.03 and 0.88 p.p.m.[7] respectively. The u.v. spectrum of the products was the same as that of [(cp)(OC)$_2$FeI]. The mass spectrum

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[8] T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, 1968, **7**, 1268.

of the residue obtained by removal of CCl_4 had peaks at the same *m/e* values as $[(cp)(OC)_2FeI]$.

The reaction can, therefore, be quantitatively described by equation (5).

$$[Me_3SnFe(CO)_2(cp)] + I_2 \longrightarrow Me_3SnI + [(cp)(OC)_2FeI] \quad (5)$$

(b) *Kinetics.* The kinetics of reaction were studied under pseudo-first-order conditions, as for the molybdenum compound described above, and the rate equation was similar to (3); rate coefficients are given in Table 1. The rate of this reaction was independent of temperature over the range 30—45 °C (see Table 2).

The Reaction of $[Me_3SnMn(CO)_5]$ *with* I_2 *in* CCl_4.—(a) *Product analysis.* A solution of $[Me_3SnMn(CO)_5]$ (0.450 g, 0.125 mmol) in CCl_4 (10 cm^3) was allowed to react with a solution of I_2 (0.031 g, 0.128 mmol) in CCl_4 (10 cm^3). The i.r. spectrum of the solution, when reaction appeared complete, had bands in the carbonyl region at 2 124, 2 086, 2 042, 2 032, 2 007, 2 002, and 1 977 cm^{-1}; $[Mn(CO)_5I]$ has bands at 2 125, 2 044, and 2 003 cm^{-1}.[9] The latter compound is known to readily react to form $[\{Mn(CO)_4I\}_2]$ as in equation (6). The carbonyl bands in $[\{Mn(CO)_4I\}_2]$ are at

$$2[Mn(CO)_5I] \longrightarrow [\{Mn(CO)_4I\}_2] + 2CO \quad (6)$$

2 087, 2 033, 2 009, and 1 976 cm^{-1}.[9] Hence the i.r. spectrum of the reaction products is consistent with a mixture of $[Mn(CO)_5I]$ and $[\{Mn(CO)_4I\}_2]$. The n.m.r. spectrum of the solution of the reaction products had a peak at δ 0.92 p.p.m; Me_3SnI has a peak at δ 0.88 p.p.m.[7] The mass spectrum of the residue after removal of the solvent showed the presence of a molecular ion of $[Mn(CO)_5I]$ at *m/e* 322, and also the molecular ion from Me_3SnI at *m/e* 292. The reaction can be quantitatively described by equation (7) followed by (6).

$$[Me_3SnMn(CO)_5] + I_2 \longrightarrow Me_3SnI + [Mn(CO)_5I] \quad (7)$$

(b) *Kinetics.* The kinetics of reaction were studied under pseudo-first-order conditions, with an excess of the organometallic compound. The change in optical density at 540 nm of a reacting solution when placed in the thermostatted cell compartment of a Unicam SP 500 spectrophotometer was recorded. The i.r. spectrum of solutions at the end of kinetic runs showed no peaks arising from $[\{Mn(CO)_4I\}_2]$. This means that when I_2 reacts with a tenfold excess of $[Me_3SnMn(CO)_5]$ only reaction (7) takes place. The results (Table 1) are consistent with a second-order reaction analogous to (3). The observed rate coefficients, $k_2^{obs.}$, increased with temperature and activation parameters are given in Table 2.

We therefore confirm the reports [2-5] that the reaction of iodine with these four compounds is quantitative with the transition metal–tin bond being cleaved. There are no side reactions, and the kinetics of the reactions are, therefore, amenable to study.*

DISCUSSION

The cleavage of the bond between a main-group 4 element and an aromatic ring by a variety of reagents has been extensively studied,[10] and these reactions have done much to extend our understanding of electrophilic, and to a lesser degree, nucleophilic substitutions. The kinetics of electrophilic substitution by iodine at an Sn–alkyl bond in tetra-alkyltin compounds,[11] and at the Sn–Sn bond in hexa-alkylditin compounds,[12,13] have also been reported. Relative reactivities with different alkyl groups have been obtained and reaction mechanisms proposed. It should be noted that in non-aqueous solvents such as CCl_4 iodination proceeds by molecular attack by I_2, and not by a reaction involving I^+ as found in aqueous solutions.

The iodine cleavage of the transition metal–tin bond is another example of electrophilic substitution at an atom adjacent to a tin atom. The four compounds studied contain bonds from tin to molybdenum, tungsten, manganese, and iron. These are the lower members of Group 6 of the transition elements and the first members of Groups 7 and 8. An obvious omission from this set of compounds is that containing the first element in Group 6, $[Me_3SnCr(CO)_3(cp)]$. We have studied the iodination of this compound in considerable detail, but its kinetics are apparently much more complicated and a complete analysis of them is given in the following paper.[6] It is sufficient for our present purposes to note that this chromium compound is *ca.* 100 times less reactive than the molybdenum or tungsten analogues, although it is difficult to compare rate coefficients with those reported here.[6]

The rate coefficients in Table 1 show the reaction to be very close to second order. This may be contrasted with iodine cleavage of the aryl–tin bond, also in carbon tetrachloride, where the reaction is third order.[14] The reaction appears, therefore, to be simple and to fit the equation $M{-}M' + I_2 \xrightarrow{k_2^{obs.}} MI + IM'$. A complex formed between I_2 and R_3SnI (R = alkyl) has been reported[15] in several solvents (MeCN, MeOH, and dimethyl sulphoxide), and this complex, $R_3SnI{:}I_2$, can also act as an electrophile that is 15 times less reactive than I_2. However, like other workers, we find no evidence for the formation of such a complex. Our reactions were first order in both iodine and the organometallic compound, and addition of a second portion of iodine to a reacted solution gave the expected $k_2^{obs.}$ This latter evidence also shows that there are no fast-reacting impurities in the system.

As one of our aims is to study the effect on the kinetics of changing the transition element, we would like, ideally, to keep all the other groups in the molecules constant. Unfortunately, of course, this is not possible. On chang-

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* The i.r. spectra of solutions from kinetic runs showed carbonyl bands of starting material and the expected product. These solutions were too dilute for characterisation of Me_3SnI.

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

[10] See R. Taylor in 'Comprehensive Chemical Kinetics,' eds. C. H. Bamford and C. F. H. Tipper, Elsevier, London, 1972, vol. 13, pp. 278—387 and refs. therein.

[11] M. Gielen and J. Nasielski, *J. Organometallic Chem.*, 1967, **7**, 273.

[12] G. Tagliavini, S. Faleschini, G. Pilloni, and G. Plazzogna, *J. Organometallic Chem.*, 1966, **5**, 136.

[13] M. Gielen, J. Nasielski, and G. Vandendunghen, *Bull. Soc. chim. belges*, 1971, **80**, 165.

[14] R. W. Bott, C. Eaborn, and J. A. Waters, *J. Chem. Soc.*, 1963, 681.

[15] R. M. G. Roberts, *J. Organometallic Chem.*, 1971, **32**, 323.

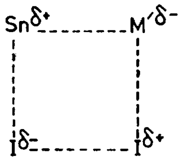
ing from a Group 6 to a Group 7 to a Group 8 element the number of electrons increases and hence a decreasing number of electrons must be supplied by the ligands to give the stable 18 electrons around the transition metal. Consequently the compounds of Groups 6 and 8 require the five-electron cp ligand in addition to carbon monoxide; Group 7 elements can form stable compounds with carbon monoxide ligands alone.

There is a large difference between the rate of reaction of [$Me_3SnMn(CO)_5$] and the other compounds studied, all of which contain a cp ring. This difference in reactivity is most probably a consequence of the different electronic effects of the cp and carbonyl ligands. The cp group is electron donating compared with CO,[16] and because of this there will be an enhancement in the electron density around the transition metal in the cp compounds. This will aid attack by an electrophile at the metal atom. Also it is known that iodine forms charge-transfer complexes with benzene,[17] and the presence of an aromatic cp group in the molecule may help bring the iodine towards the reaction site.

The rates of reaction of analogous compounds of molybdenum and tungsten are almost equal (Table 1). This is surprising and it is tempting to suggest that this is an example of the similarity of the chemistry of these two elements that has been brought about by the lanthanoid contraction, but it should be remembered that these are fast reactions and are probably of low selectivity. Only small differences in rate are to be expected when different compounds react with an electrophile of low selectivity.

The reactivity of [$Me_3SnFe(CO)_2(cp)$] is 10 times that of [$Me_3SnM(CO)_3$ (cp)] (M = Mo or W) (Table 1). Iron has only two CO groups attached to it, and the iron *d* electrons will tend to remain more on the metal atom than those in molybdenum and tungsten where there are three CO groups with π^* orbitals into which the electrons can delocalise. Also the extra outer electrons on iron, compared with molybdenum and tungsten, make it a better site for attack by the electrophilic iodine molecule. These results are in accord with those of Jolly *et al.*[18] who found that [$Fe(CO)_2(cp)$]$^-$ was a better electrophile than [$Mn(CO)_5$]$^-$. Also Dessy *et al.*[19] compared the relative nucleophilicities of carbonyl anions towards MeI in dimethoxymethane, and finds the order [$Mo(CO)_3$-(cp)]$^-$: [$Mn(CO)_5$]$^-$: [$W(CO)_3(cp)$]$^-$: [$Fe(CO)_2(cp)$]$^-$ to be $1 : 1.1 : 7 : 10^6$.

The activation parameters (Table 2) further illuminate these reactions. The enthalpies of activation are low; indeed, for the iron compound it is almost zero. Low activation enthalpies often mean that the reaction is complex, and made up of several stages, the activation enthalpies for the different stages compensating each other to give a small resulting value. The entropies of activation are large and negative, and in the range expected for a bimolecular reaction in solution whether the transition state is cyclic [as in (A)] or not. We think that a cyclic transition state is most likely, (A), with the second iodine atom attacking the tin atom. This has also been suggested by Roberts[15] and Clark[5] and is reasonable in a solvent of low polarity such as carbon tetrachloride.



(A)

An alternative mechanism that we can discount for this reaction is reductive elimination [equation (8)].

$$[Me_3SnMn(CO)_5] + I_2 \longrightarrow [Me_3SnMn(CO)_5I]^+ + I^- \longrightarrow [Me_3SnI{\cdot}Mn(CO)_5]^+ + I^- \longrightarrow MeSnI + [Mn(CO)_5I] \quad (8)$$

This mechanism would predict the products of the reaction of [$Me_3SnMn(CO)_5$] with ICl to be Me_3SnI and [$Mn(CO)_5Cl$], whereas they are Me_3SnCl and [$Mn(CO)_5I$].[5,20] We strongly suspect that the reactions are more complex than outlined above. The principal evidence for this is the low activation enthalpies and the change in $k_2^{obs.}$ with wavelength. These features are discussed below.

In a later paper we shall show that IBr and ICl form 1 : 1 charge-transfer complexes with [$Me_3SnMo(CO)_3$-(cp)]. This was revealed as the absorbance at 540 nm of a solution of either of the interhalogens mixed with the molybdenum compound, recorded before any chemical reaction occurred, was greater than that expected from the absorption coefficients of the interhalogen and [$Me_3SnMo(CO)_3(cp)$]. Using a stopped-flow spectrophotometer we examined the initial (*ca.* 0.002 s after mixing) optical densities, $D_0^{obs.}$, of solutions of I_2 mixed with excess of [$Me_3SnMo(CO)_3(cp)$]. Both at 520 and 540 nm the optical densities of mixtures of I_2 and [Me_3-$SnMo(CO)_3(cp)$] do not differ significantly from those of I_2 alone (Table 3); [$Me_3SnMo(CO)_3(cp)$] does not absorb appreciably at these wavelengths.

Using a treatment similar to that used by Ketelaar[21] we can show that failure to detect any significant change in $D_0^{obs.}$ with increase in concentration of [Me_3SnMo-$(CO)_3(cp)$] places an upper limit of *ca.* 10 l mol^{-1} on K, the equilibrium constant for formation of a charge-transfer complex, $I_2 + [Me_3SnMo(CO)_3(cp)] \overset{K}{\rightleftharpoons} I_2 \cdots [Me_3SnMo(CO)_3(cp)]$, unless by chance the absorption

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[16] M. L. H. Green in G. H. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' Methuen, London, 1960, vol. 2, p. 115.

[17] L. J. Andrews and R. M. Keefer, *Adv. Inorg. Chem. Radiochem.*, 1961, **3**, 91.

[18] P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 5830.

[19] R. E. Dessy, R. L. Pohl, and R. B. King, *J. Amer. Chem. Soc.*, 1966, **88**, 5121.

[20] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, unpublished work.

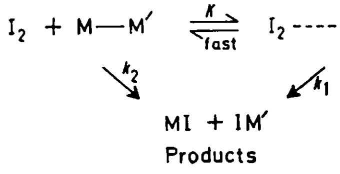
[21] J. A. A. Ketelaar, C. van de Stolpe, A. Goudsmit, and W. Dzcubas, *Rec. Trav. chim.*, 1952, **71**, 1104.

coefficients of I_2 and the charge-transfer complex are identical. We obtained similar results for $D_0^{obs.}$ measurements on the reaction of I_2 with $[Me_3SnMn(CO)_5]$; $D_0^{obs.}$ was that expected from the I_2 concentration.* Charge-transfer complexes of iodine with similar compounds, *viz.* organosilicon compounds, are known [22] with K values *ca.* 1 l mol^{-1}. Hence for I_2 we have not been able to detect any charge-transfer complexes. They can be observed with the interhalogens studied, and the reasoning just given shows that under certain conditions they cannot be detected. It seems most likely that I_2 will react in an analogous manner to the interhalogens and formation of such a complex is allowed for in the Scheme.

TABLE 3

Optical densities, $D_0^{obs.}$, of solutions of I_2 and $[Me_3SnMo(CO)_3(cp)]$ in CCl_4 measured 0.002 s after mixing. Concentrations are those after mixing

		$10^2[Me_3SnMo(CO)_3(cp)]$/mol l^{-1}			
	$10^4[I_2]$/mol l^{-1}	0	0.5	1.0	2.0
520 nm	1.25	0.16		0.18	0.16
	2.50	0.28	0.26	0.28	0.28
	5.0	0.49	0.48	0.53	0.52
540 nm	1.25	0.16	0.14	0.16	0.22
	2.50	0.225	0.225	0.235	0.29
	5.0	0.385	0.385	0.40	0.49
	10.0	0.71	0.66	0.67	0.71



SCHEME

The rate equation for the Scheme is given by equation (9), where i, m, p, and c are the concentrations of I_2, $[Me_3SnMo(CO)_3(cp)]$, products, and charge-transfer complex at time t, respectively. Let the initial concentration of I_2 and $[Me_3SnMo(CO)_3(cp)]$ be a and b respectively where $b \gg a$ so that $m \approx b$. Using equation (10) to substitute for c in (9) gives (11). Now $i = a - c - p$, and substitution for c leads to equation (12) and thence to (13). Substituting in the observed second-order rate coefficient [equation (14)] leads to (15) and (16). Equation (16) is simplified to (17) if it is assumed that the products are formed only by reaction of the charge-transfer complex (*i.e.* $k_2 = 0$). From equation (17) a plot of $1/k_2^{obs.}$ against b should be a straight line cutting the abscissa at $-1/K$. Inspection of the data in Table 1 shows that for the molybdenum and tungsten compounds $k_2^{obs.}$ is independent of the concentration of the organometallic compound (b) within the experimental error. This indicates that K must be small, <1 l mol^{-1}. If K is ≈ 1 l mol^{-1} and under the experimental conditions m is $\approx 10^{-2}$ mol l^{-1}, we can neglect the Kb term in the denominator of equation (15), hence $k_2^{obs.} = k_2 + k_1K$. Further analysis of this data to give individual values of k_1 and k_2 is not possible.

$$dp/dt = k_2im + k_1c \tag{9}$$

$$c/im = K \tag{10}$$

$$dp/dt = (k_2 + k_1K)im \tag{11}$$

$$i = (a - p)/(1 + Km) \tag{12}$$

$$dp/dt = (k_2 + k_1K)(a - p)b/(1 + Kb) \tag{13}$$

$$dp/dt = k_2^{obs.}\ (a - p)b \tag{14}$$

$$k_2^{obs.} = (k_2 + k_1K)/(1 + Kb) \tag{15}$$

$$1/k_2^{obs.} = [1/(k_2 + k_1K)] + [Kb/(k_2 + k_1K)] \tag{16}$$

$$1/k_2^{obs.} = (1/k_1K) + (b/k_1) \tag{17}$$

A further significant clue to the complex nature of the iodination of $[Me_3SnMo(CO)_3(cp)]$ is provided by studies at different wavelengths. All the rate coefficients in Table 1 were obtained from measurements of the decrease in absorbance at 540 nm. This is close to the maximum absorbance for I_2; $[Me_3SnMo(CO)_3(cp)]$ and the iodination products, Me_3SnI and $[Mo(CO)_3(cp)I]$, do not absorb in this region. The product $[Mo(CO)_3(cp)I]$ absorbs at 450 nm, whereas $[Me_3SnMo(CO)_3(cp)]$ and I_2 do not, and during a reaction the optical density of the solution at this wavelength increases. At 30 °C the value found for $k_2^{obs.}$ at 450 nm was 302 l mol^{-1} s^{-1}, and not 226 l mol^{-1} s^{-1} as found at 540 nm (Table 1). It is, of course, to be expected that the rate of formation of products ($k_2^{obs.}$ at 450 nm) will be the same as the rate of loss of reactant iodine ($k_2^{obs.}$ at 540 nm), and not as we find *ca.* 1.5 times as large. At first we thought that the reaction might be light catalysed, but experiments using different amounts of light passing through reacting solutions (by variation of the slit width on the monochromator) showed that photocatalysis was negligible under these conditions.

An explanation can be given to this anomaly if a more complicated reaction mechanism is proposed. This is as given by equation (18). Iodine and $[Me_3SnMo(CO)_3(cp)]$ form a chemical intermediate (B) (not to be confused with the charge-transfer complex discussed earlier) instead of directly giving products. If, like the products, (B) does not absorb at 540 nm then $k_2^{obs.}$ at 540 nm will refer to the formation of (B), *i.e.* $k_2^{obs.\,540} = k_3$. We also assume that at 450 nm, (B) and products absorb whereas reactants do not. Let the intermediate, (B), have an absorption coefficient at 450 nm equal to a multiple ϕ of that of the products, *i.e.*

$$I_2 + [Me_3SnMo(CO)_3(cp)] \xrightarrow{k_3} \underset{(B)}{I_2 \cdots [Me_3SnMo(CO)_3(cp)]} \xrightarrow{k_4} \text{Products} \tag{18}$$

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* These experiments also show that the organometallic compounds contain no impurities that react rapidly with iodine.

[22] I. Vêle, V. Vaisarová, and V. Chvalovský, *Coll. Czech. Chem. Comm.*, 1972, **37**, 1396.

$\varepsilon_i = \phi\varepsilon_p$. If i and p are the concentrations of intermediate and products then by the equations for con-

$$i = a\,k_3'[\exp(-k_3't) - \exp(-k_4t)]/(k_4 - k_3') \qquad (19)$$

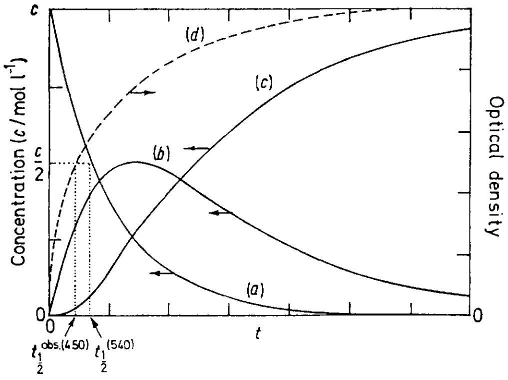
$$p = a[k_3' - k_4 + k_4\exp(-k_3't) - k_3'\exp(-k_4t)]/(k_3' - k_4) \qquad (20)$$

secutive reactions[23] we obtain (19) and (20) where $k_3' = k_3b$ (a and b as defined above).

The observed absorbance of the solution, $D^{\text{obs.}}$, will be given by equation (21). A plot of $D^{\text{obs.(450)}}$ against time

$$D^{\text{obs.}} = i\varepsilon_i + p\varepsilon_p = (p + \phi i)\,\varepsilon_p = a\varepsilon_p[(k_4 - k_3') + (\phi k_3' - k_4)\exp(-k_3't) + k_3'(1 - \phi)\exp(-k_4t)]/(k_4 - k_3') \qquad (21)$$

will appear roughly exponential (Figure) and if $D^{\text{obs.(450)}}$ measurements are made during the first two apparent half-lives the usual first-order treatment gives an observed rate coefficient, $k_1^{\text{obs.(450)}}$, and an observed half-life, $t_{\frac{1}{2}}^{\text{obs.(450)}}$, with acceptable values for the correlation coefficient. The observed rate coefficient at 450 nm, $k_2^{\text{obs.(450)}}$ is then equal to $k_1^{\text{obs.(450)}}/b$. When the value for $k_2^{\text{obs.(540)}}$ is substituted for k_3, we find that there is a range of pairs of values of k_4 and ϕ that give $D^{\text{obs.}}$ against time curves with half-lives equal to $t_{\frac{1}{2}}^{\text{obs.(450)}}$. The absorbance of the solution at 450 nm increases in the beginning more rapidly than expected as the strongly absorbing intermediate, (B), is produced, and over the latter part of the reaction as strongly absorbing (B) changes to less strongly absorbing products the change in optical density is less than expected for a simple exponential (see Figure).



Plots of $[I_2]$ (*a*), [Intermediate] (*b*), [Products] (*c*), and $D^{\text{obs.(450)}}$ (*d*) against time for the reaction of $[\text{Me}_3\text{SnMo(CO)}_3\text{(cp)}]$ with I_2

$D^{\text{obs.}}$ Values in the early part of the reaction increase as if (B) were to be the product with a final optical density of D_∞^{B}. However the observed final optical density $D_\infty^{\text{obs.}} < D_\infty^{\text{B}}$ because $\phi > 1$. Hence $k_1^{\text{obs.(450)}}$ values calculated using $D_\infty^{\text{obs.}}$ and data from the early part of reaction will be larger than k_3' (which would result from using D_∞^{B} in the calculation). This approach does not rule out the fast formation of a charge-transfer complex which rearranges to give the intermediate (B). For (B) we tentatively propose a structure similar to that illustrated in (A).

EXPERIMENTAL

The compounds $[\text{Me}_3\text{SnMo(CO)}_3\text{(cp)}]$,[24] $[\text{Me}_3\text{SnW(CO)}_3\text{(cp)}]$,[24] $[\text{Me}_3\text{SnFe(CO)}_2\text{(cp)}]$,[25] and $[\text{Me}_3\text{SnMn(CO)}_5]$[26] were prepared by the usual route of treating the sodium salt of the appropriate substituted transition-metal anion with trimethyltin chloride in tetrahydrofuran solution under a nitrogen atmosphere; $[\text{Me}_3\text{SnMo(CO)}_3\text{(cp)}]$ was recrystallised from light petroleum (b.p. 40—60%)–dichloromethane (1 : 1) and $[\text{Me}_3\text{SnW(CO)}_3\text{(cp)}]$ from pentane–dichloromethane. The compound $[\text{Me}_3\text{SnFe(CO)}_2\text{(cp)}]$ was purified by distillation at reduced pressure (0.2 mmHg) on to a probe cooled to −78 °C, and $[\text{Me}_3\text{SnMn(CO)}_5]$ was first recrystallised from pentane at −78 °C followed by vacuum sublimation at 0 °C (0.2 mmHg) on to a probe cooled to −78 °C. The identity and purity of each compound was checked by comparing its i.r. and n.m.r. spectra with those in the literature. Mass spectra confirmed the structures and showed the absence of impurities. Carbon and hydrogen elemental analyses for the compounds were all satisfactory.

The kinetic runs were carried out using either a Unicam SP 500 spectrophotometer fitted with a thermostatically controlled cell housing or in a stopped-flow spectrophotometer made to the design of Gibson and Milnes.[27] The stopped-flow technique gives a record of the transmittance (T) of a solution with time and this is commonly recorded photographically from an oscilloscope screen. Our spectrophotometer is linked to a small data-gathering computer that gives a printed numerical record of T against time.[28] The concentration of an absorbing species in solution is proportional to the optical density (D) of the solution. This is related to transmittance by the well known equation $D = \log_{10}(1/T)$. A computer program was written to analyse the data of T against time. As well as carrying out a simple calculation of the first-order rate coefficient, $k_1^{\text{obs.}}$, in the usual way, the program allows for weighting of data points, formula weighting,[29] and can also calculate rate coefficients by an optimisation procedure when an 'infinity' value was not obtained. All the rate coefficients in Table 1 that were measured by the stopped-flow technique are the mean of between six and ten independent kinetic runs.

I.r. spectra were measured on a Perkin-Elmer 457 grating spectrophotometer, and carbonyl peaks in high-resolution scans were bracketted with the spectra of gaseous CO and water vapour and are estimated to be accurate to ±1 cm^{-1}.

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