Reactivity of Main-group–Transition-metal Bonds. Part II.[1] The Kinetics of Reaction between Tricarbonyl(η-cyclopentadienyl)(trimethylstannyl)-chromium and Iodine

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The kinetics of reaction between [$Me_3SnCr(CO)_3(cp)$] (cp = η-cyclopentadienyl) and iodine in carbon tetrachloride solution have been studied, and can be explained by a reaction mechanism that involves formation of an intermediate complex that subsequently gives products by iodine cleavage of the tin–chromium bond. A charge-transfer complex is probably formed prior to the intermediate. The kinetics are analysed by a minimisation procedure. The reaction is analogous to that of related Mo, W, Mn, and Fe compounds.

In the preceding paper[1] we reported the kinetics of reaction between [$Me_3SnMo(CO)_3(cp)$], [$Me_3SnW(CO)_3(cp)$], [$Me_3SnMn(CO)_5$], and [$Me_3SnFe(CO)_2(cp)$] with iodine (cp = η-cyclopentadienyl). The reactions, although superficially simple, show features that we explain with a complex reaction scheme involving both a charge-transfer complex and a chemical intermediate. An obvious omission from the set of compounds was [$Me_3SnCr(CO)_3(cp)$]. The reaction of this compound with iodine in chloroform has been reported by Bichler *et al.*[2] and is as given by equation (1). We have now

$$[Me_3SnCr(CO)_3(cp)] + I_2 \longrightarrow Me_3SnI + [ICr(CO)_3(cp)] \quad (1)$$

studied the kinetics of this reaction which show major differences from the four compounds listed above.

RESULTS

The compound [$Me_3SnCr(CO)_3(cp)$] decomposes rapidly at room temperature in the presence of air and moisture, slowly under an atmosphere of nitrogen at 0 °C, but is stable for several weeks under an atmosphere of high-purity argon particularly if kept in the dark. **CAUTION.** It should be handled with care in a fume-cupboard as the compound, or its decomposition products, readily cause headaches and nausea, even at very low concentrations. In this respect it is far worse than any of the related compounds.

The u.v. absorption spectra of [$Me_3SnCr(CO)_3(cp)$], I_2, and the reaction products are given in Figure 1. When iodine was added to an excess of the chromium compound in carbon tetrachloride solution the optical density of the solution changed with time as shown in Figure 2. At 540 nm, near the maximum absorbance of iodine, the optical density first decreased rapidly and then increased. This behaviour strongly suggests a two-stage process; in the first step the iodine is used up and in the second an absorbing product is formed. The measurements made at 620 nm, where iodine has a low absorbance, showed an initiation period followed by an increase in the optical density. Equation (2) gives a likely reaction sequence. The complex (A) may react to form products either spontaneously or by reaction with the solvent.

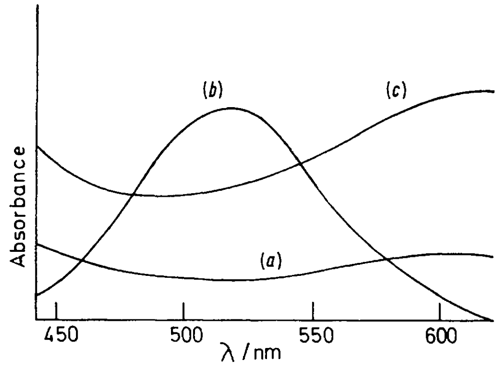

FIGURE 1 Visible spectra in CCl_4 at 20 °C: (*a*) [$Me_3SnCr(CO)_3(cp)$]; (*b*) I_2; (*c*) reaction products

$$I_2 + [Me_3SnCr(CO)_3(cp)] \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{(A)}{\text{Intermediate complex}} \xrightarrow{k_3} \underbrace{Me_3SnI + [ICr(CO)_3(cp)]} \quad (2)$$

Concentration			(A)	
Initial	a	b	0	0
After time t	$(a - p - c)$	b	c	p
At end	0	b	0	a
Absorption coefficient	ε_{I_2}		ε_A	ε_P

The results may be treated as follows. Let the concentrations of reactants and products initially, during, and at the end of the reaction, and the absorption coefficients, be as given below equation (2). In all experiments the concentration of the chromium compound, b, was in large excess over the concentration of iodine, a, and b can be assumed to remain constant. Let $k_1' = k_1b$. The differential equation for reaction scheme (2) is given by (3). The solution for

$$(d^2p/dt^2) + (dp/dt)(k_1' + k_2 + k_3) + k_1'k_3p = k_1'k_3a \quad (3)$$

equation (3) is given by (4), where λ_1 and λ_2 are the roots of (5).[3] As $dp/dt = k_3c$ we can obtain (6). There is always

$$p = a - \{a[\lambda_2e^{-\lambda_1t} - \lambda_1e^{-\lambda_2t}]/(\lambda_2 - \lambda_1)\} \quad (4)$$

$$\lambda^2 - \lambda(k'_1 + k_2 + k_3) + k_1'k_3 = 0 \quad (5)$$

$$c = ak_1'[e^{-\lambda_1t} - e^{-\lambda_2t}]/(\lambda_2 - \lambda_1) \quad (6)$$

an excess of the chromium compound and this will contribute a constant optical density, D_{Cr}, to all optical-

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[1] Part I, J. R. Chipperfield, J. Ford, and D. E. Webster, preceding paper.

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

[3] N. M. Rodiguin and E. N. Rodiguina, ' Consecutive Chemical Reactions,' Van Nostrand, Princeton, New Jersey, **1964**, p. **42**.

density readings. The calculated optical density is given by equation (7). Initially $D_0 = a\varepsilon_{I_2} + D_{Cr}$, and after

$$D_t^{calc.} = \varepsilon_{I_2}(a - p - c) + \varepsilon_A c + \varepsilon_P p + D_{Cr} \quad (7)$$

reaction $D_\infty = \varepsilon_P a + D_{Cr}$. Substituting these into equation (7) gives (8).

$$\begin{aligned} D_t^{calc.} = D_\infty + \{&[(D_0 - D_{Cr})(\lambda_2 - k_1') \\ &+ ak_1'\varepsilon_A - (D_\infty - D_{Cr})\lambda_2]e^{-\lambda_1 t} \\ &+ [(D_0 - D_{Cr})(k_1' - \lambda_1) - ak_1'\varepsilon_A \\ &\qquad + (D_\infty - D_{Cr})\lambda_1]e^{-\lambda_2 t}\}(\lambda_2 - \lambda_1)^{-1} \quad (8) \end{aligned}$$

To calculate values of k_1', k_2, k_3, ε_A, and D_{Cr} from measured optical densities, $D^{obs.}$, recorded at various times it is necessary to choose values for these constants that make F in equation (9) a minimum. In equation (9) W_t is a

$$F = \sum_{t=0}^{t=\infty} W_t\,(D_t^{obs.} - D_t^{calc.})^2 \quad (9)$$

factor $(D_t^{obs.} - D_\infty)^2$ introduced to give low weightings to measurements that are close to D_∞. The simplex minimisation procedure [4] was used in a suitable computer program, and estimates of the parameters were thus obtained. For all sets of data k_2 was a factor of 100 less than k_3. This shows that the complex (A) reacts almost completely to give products, and the back reaction, measured by k_2, can be ignored. Also at 540 nm, ε_A was at least 100 times smaller than ε_{I_2} and the absorbance of (A) can be neglected.

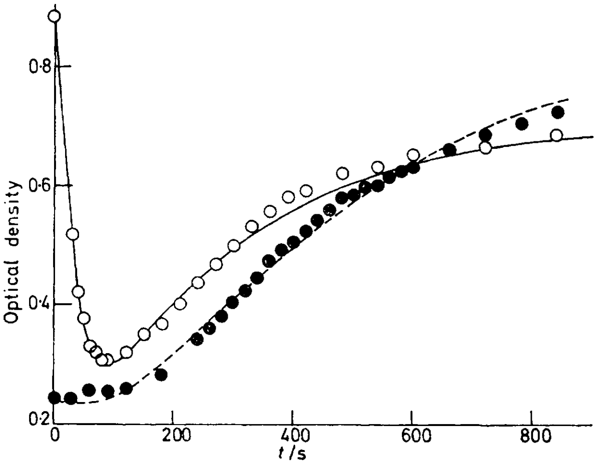

FIGURE 2 Plots of optical density against time for the reaction of [$Me_3SnCr(CO)_3(cp)$] with I_2 in CCl_4 at 30 °C. (○) and (—), Observed and calculated values for run (3) at 540 nm; (●) and (— — —), similar values for run (2) at 620 nm

Reaction of [$Me_3SnCr(CO)_3(cp)$] with I_2 in CCl_4 at 30.0 °C

Run	(1)	(2)	(3)	(4)	(5)	(6)	(7)
λ/nm	620	620	540	540	540	540	540
$10^3[I_2]$/mol l^{-1}	1.39	0.63	0.87	0.391	0.391	0.87	0.74
$10^3[Me_3SnCr(CO)_3(cp)]$/mol l^{-1}	9.6	9.6	11.9	11.9	37.0	9.9	19.2
k_1/l mol^{-1} s^{-1}	0.41	0.43	3.05	5.59	3.01	1.2	1.36
10^3k_3/s^{-1}	3.15	3.97	3.54	4.36	17.3	6.3	12.9
D_{Cr}	0.097	0.111	0.173	0.248	0.077	0.077	0.085
ε_A	87	86	*ca.* 0.01	*ca.* 0.01	*ca.* 0.01	*ca.* 0.01	*ca.* 0.01
Number of data points	34	34	25	30	14	42	34
10^3k_2/s^{-1}	0.01	0.009	0.01	0.008	0.008	0.01	0.03

Averages: $\varepsilon_A^{620} = 86$ l mol^{-1} cm^{-1}, $\varepsilon_A^{540} = 0.01$ l mol^{-1} cm^{-1}, $k_1 = 2.8$ l mol^{-1} s^{-1}, and $k_3 = 7.3 \times 10^{-3}$ s^{-1} [excluding run (5), 5.7×10^{-3} s^{-1}]

The Table gives details of the conditions used for studying the kinetics, and the values of the parameters, k_1, k_3, D_{Cr}, and ε_A, obtained from the minimisation procedure. In Figure 2 are plotted the experimental values (as points) and the lines are computer calculated for the reaction using the method just described. The agreement between the observed and calculated values is excellent, *i.e.* values of $D_t^{calc.}$ agree with $D_t^{obs.}$ within experimental error. Values of k_1 obtained for runs (1) and (2), measured at 620 nm, were lower than the average from runs (3)—(7), measured at 540 nm (Table). This is probably because accurate estimation of k_1 requires that the optical density should change during the first stage, rather than remaining almost constant. The value of F in equation (9) for runs (1) and (2) with k_1 fixed at 2.8 l mol^{-1} s^{-1} was calculated and is only slightly greater than the minimum that gives $k_1 = 0.4$ l mol^{-1} s^{-1}. The high value of k_3 for run (5) probably arises from the smaller number of optical densities measured compared with the other runs; this reaction was the fastest studied because of the high concentration of [$Me_3SnCr(CO)_3$-(cp)] used. This high concentration also resulted in the first step being too fast to be observed. The rate coefficient k_2 for the reverse reaction is very small. If it is zero then equation (2) represents two consecutive first-order reactions. As a check we used the appropriate equations [1] to calculate $D^{calc.}$, and the minimisation gave the same values for k_1, k_3, ε_A, and D_{Cr} as those shown in the Table.

DISCUSSION

The second-order rate coefficient, k_1, for the reaction of [$Me_3SnCr(CO)_3(cp)$] with I_2 measured here is 100 times less than that found for the analogous reaction of [$Me_3SnMo(CO)_3(cp)$].[1] This could be caused by steric factors. The chromium atom is somewhat smaller than molybdenum, the Bragg–Slater atomic radii being 140 and 145 pm respectively, and the chromium is less exposed to incoming reagents. This feature gives us no information about the reaction mechanism, and it is of interest that the rate order Cr < Mo is found both for reactions where dissociation of a CO group is the rate-limiting step, *i.e.* CO exchange in $M(CO)_6$,[5] and for reactions which are at least partly bimolecular, *i.e.* PR_3 + [$M(CO)_4$(bipy)] (bipy = 2,2′-bipyridyl).[5]

The i.r., u.v., and mass spectra from which the reaction products were identified were all recorded after completion of the second stage of the reaction. Complex (A) [equation (2)] must have a structure which is consistent with the reactants that formed it and the products that

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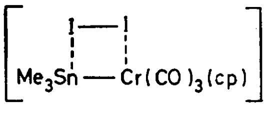
[4] J. A. Nelder and R. Mead, *Computer J.*, 1965, **7**, 308.

[5] D. A. Brown, *Inorg. Chim. Acta Rev.*, 1967, **1**, 35.

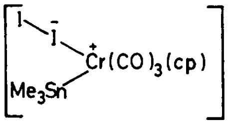
it forms. The formation of a conventional charge-transfer complex of I_2 with the chromium compound to give structure (B) (which is similar to the complexes formed between I_2 and benzene or ethanol [6]) should be rapid. The rate coefficient, k_1, for formation of (A) is far too small to refer to such a process. We have had hints of such complexes being formed prior to (A) in related systems.[1] A structure such as (C) for the intermediate (A), where Sn–I and Cr–I bonds have formed before the I–I bond has broken, would seem unlikely if the reaction of I_2 with [$Me_3SnCr(CO)_3(cp)$] is at all similar to that with [$Me_3SnMo(CO)_3(cp)$].[1]



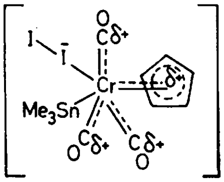
(B)

$$[Me_3Sn{-}I{-}I{-}Cr(CO)_3(cp)]$$

(C)



(D)



(E)

The absorption coefficient ε_A for the intermediate (A) at 540 nm is very small (Table). In (A) the iodine must be in a completely different environment to I_2 in CCl_4. We suggest that the intermediate may have a structure (D), where the iodine has carried out an electrophilic attack on the t_{2g} orbitals of the chromium. The positive charge on the chromium will be delocalised on to the co-ordinated CO and cp ligands as shown by (E). The general scheme for this type of reaction is given by equation (10), where, we suggest, the charge-transfer complex and intermediate resemble structures (B) and (E) respectively. Any of the three stages could cause absorbance changes of reaction solutions, and either the second or third stage could be rate limiting. These features can lead to difficulties in interpreting the observed kinetics and can make it impossible to compare results from reactions with different reactants. The reaction may be more complicated than described above. Inspection of the rate coefficient for the formation of products (k_3) in the Table shows that it is not constant, but appears to be dependent on the concentration of the organometallic compound which is present in large excess during these reactions. This feature will be discussed further in a later paper of this series.

$$\text{Reactants} \rightleftharpoons \text{Charge-transfer complex} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Intermediate complex} \xrightarrow{k_3} \text{Products} \qquad (10)$$

We attempted to record the i.r. spectrum of a reacting mixture of [$Me_3SnCr(CO)_3(cp)$] with I_2 in CCl_4 using an i.r. cell made of germanium metal. In addition to the bands in the carbonyl region due to [$Me_3SnCr(CO)_3(cp)$] and [$Cr(CO)_3(cp)I$], we hoped to see bands for the carbonyls of an intermediate. Unfortunately we could not use dilute solutions as they do not absorb enough to show CO bands, and with more concentrated solutions by the time the spectrum was recorded reaction was complete. Practical problems associated with the measurement of the kinetics of this reaction are formidable; [$Me_3SnCr(CO)_3(cp)$] reacts readily with constituents of the atmosphere and during the preparation of pure solutions of known concentration it is easy for impurities to be formed. [This is shown by the range of D_{Cr} values obtained (Table).]

Conclusion.—The reactions of iodine with [$Me_3SnCr(CO)_3(cp)$], [$Me_3SnMo(CO)_3(cp)$],[1] [$Me_3SnW(CO)_3(cp)$],[1] [$Me_3SnMn(CO)_5$],[1] and [$Me_3SnFe(CO)_2(cp)$] [1] are all of the same form and involve formation of a charge-transfer complex and a chemical intermediate, as illustrated by equation (10), before the products. The reaction is electrophilic cleavage of the metal–metal bond.

EXPERIMENTAL

The compound [$Me_3SnCr(CO)_3(cp)$] was prepared by the method of Keppie and Lappert.[7] It was purified by vacuum sublimation at 80 °C onto a water-cooled probe, and resublimed shortly before use.

Solutions of weighed amounts of the chromium compound and of I_2 were made with argon-saturated spectroscopic grade CCl_4, and those of the compound were stored at *ca.* 0 °C in the dark under an atmosphere of argon. Optical densities were measured in a 10 mm cell at 30 °C with a Unicam SP 500 spectrophotometer fitted with a constant-temperature cell block. Absorbance readings were started *ca.* 20 s after rapidly mixing the prewarmed reactants. The i.r. spectrum of a solution after reaction was complete had bands in the carbonyl region corresponding to [$Me_3SnCr(CO)_3(cp)$] present initially in large excess over I_2, and [$Cr(CO)_3(cp)I$]. The mass spectrum of the residue left after evaporation of CCl_4 from the reacted solution had molecular ions corresponding to [$Me_3SnCr(CO)_3(cp)$], [$Cr(CO)_3(cp)I$], and Me_3SnI, thus confirming the reaction products. The reaction product, [$Cr(CO)_3(cp)I$], is not very stable in solution,[8] and absorbance values increased slowly after completion of the second stage of the reaction. D_∞ Values used were the optical density after 10 times the apparent half-life of the second stage. D_0 Values were calculated from measured absorbance values of iodine solutions.

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

[7] S. A. Keppie and M. F. Lappert, *J. Organometallic Chem.*, 1969, **19**, P5.

[8] A. R. Manning and D. J. Thornhill, *J. Chem. Soc. (A)*, **1971**, 637.