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# REACTIVITY OF MAIN-GROUP—TRANSITION-METAL BONDS

## VI *. THE KINETICS OF IODINATION OF TETRACARBONYL(TRIMETHYLSTANNYL)COBALT AND PENTACARBONYL(TRIMETHYLSTANNYL)RHENIUM

JOHN R. CHIPPERFIELD *, ANDY C. HAYTER and DAVID E. WEBSTER
*Department of Chemistry, The University, Hull, HU6 7RX (Great Britain)*
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## Summary

The kinetics of the iodine cleavage of the Sn—Co bond in $[Me_3SnCo(CO)_4]$ and of the Sn—Re bond in $[Me_3SnRe(CO)_5]$ have been measured. The order of rates of cleavage of the Sn—M bond in the compounds $[Me_3SnM(CO)_x(cp)_y]$ (M = Mn, Re, $x = 5$, $y = 0$; M = Co, $x = 4$, $y = 0$; M = Cr, Mo, W, $x = 3$, $y = 1$; M = Fe, $x = 2$, $y = 1$; cp = $\eta$-cyclopentadienyl) indicates that the main factors determining reactivity towards iodine are the size of the metal atom (M) and the shielding of it by the other ligands.

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## Introduction

We are carrying out a systematic study of the kinetics of the bond cleavage reactions of tin—transition metal bonds, and have already reported on the iodine cleavage of tin—chromium [2], —molybdenum, —tungsten, —manganese, and —iron [3] bonds. On the evidence then available it was suggested that electronic effects were determining the relative reactivities of the compounds studied. We have now been able to extend this work to cover compounds containing tin bonded to cobalt and to rhenium, and their reactions indicate that steric factors are of more importance than electronic.

The products of iodination of $[Me_3SnCo(CO)_4]$ in hexane at —10° C have been identified by Abel and Hutson [4] as those formed by cleavage of the Sn—Co bond (eq. 1). However, $[Co(CO)_4I]$ is unstable and decomposes rapidly

$$[Me_3SnCo(CO)_4] + I_2 \rightarrow [Co(CO)_4I] + Me_3SnI \quad (1)$$

at room temperature [5]. The iodination of $[Me_3SnRe(CO)_5]$ has not been previously investigated.

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* For Part V see ref. 1.

## Results

### *The reaction of [$Me_3SnRe(CO)_5$] with iodine in tetrachloromethane*

A solution of [$Me_3SnRe(CO)_5$] (20 mg, 41 μmol) in tetrachloromethane (1 ml) was allowed to react with iodine (4 mg, 16 μmol) in the same solvent (0.5 ml). After reaction was complete (no iodine colour remaining) an IR spectrum of the solution showed peaks at 2043, 2013, and 1985 $cm^{-1}$ in addition to those from starting material (cf. [$Re(CO)_5I$] with peaks at 2145, 2042, 2013, and 1987 $cm^{-1}$ [6]). A NMR spectrum of the same solution showed peaks at $\delta$ 0.42 ppm (cf. [$Me_3SnRe(CO)_5$] with a peak at $\delta$ 0.42 ppm [7]) and $\delta$ 0.89 ppm (cf. $Me_3SnI$ with a peak at $\delta$ 0.88 ppm [8]). This product analysis confirms that reaction takes place according to eq. 2.

$$[Me_3SnRe(CO)_5] + I_2 \xrightarrow{k_2(obs)} Me_3SnI + [Re(CO)_5I] \tag{2}$$

The kinetics of the reaction were studied in tetrachloromethane under pseudo-first-order conditions (excess of [$Me_3SnRe(CO)_5$]) by monitoring the disappearance of iodine at 540 nm. The results (Table 1) support rate eq. 3.

$$-d[I_2]/dt = k_2(obs)[I_2][complex] \tag{3}$$

### *The reaction of [$Me_3SnCo(CO)_4$] with iodine in cyclohexane*

A solution of [$Me_3SnCo(CO)_4$] (13 mg, 39 μmol) in cyclohexane (1 ml) was added to a solution of iodine (10 mg, 39 μmol) in the same solvent (1 ml) at room temperature. An IR spectrum was recorded as quickly as possible after mixing (ca. 1 min). This showed that the [$Me_3SnCo(CO)_4$] had reacted, but there were no carbonyl-containing products. This is consistent with the work of Abel and Hutson. The [$Co(CO)_4I$] which is formed had decomposed before the IR spectrum was recorded.

The kinetics of reaction 1 were studied in a similar way to [$Me_3SnRe(CO)_5$] above and the results (Table 1) support rate eq. 3. For this reaction cyclohexane was used as the solvent as the reaction was too fast to measure in tetra-

TABLE 1

THE REACTION OF IODINE WITH [$Me_3SnRe(CO)_5$] AND [$Me_3SnCo(CO)_4$] [a]

| Complex | $10^3$ [complex] (mol $l^{-1}$) | $10^3$ [$I_2$] (mol $l^{-1}$) | $k_2$(obs) (l $mol^{-1}$ $s^{-1}$) | |
|---|---|---|---|---|
| [$Me_3SnRe(CO)_5$] [b] | 8.1 | 0.704 | 1.02 | 1.01 |
| | 8.7 | 0.488 | 1.05 | |
| | 7.9 | 0.396 | 0.99 | |
| [$Me_3SnCo(CO)_4$] [c] | 9.77 | 0.51 | 770 | 777 [d] |
| | 9.77 | 0.89 | 786 | |
| | 5.43 | 0.51 | 776 | |

[a] Wavelength used = 540 nm. [b] $CCl_4$ as solvent, 30.0°C. [c] Cyclohexane as solvent, 28.5°C. [d] 811 l $mol^{-1}$ $s^{-1}$ at 30.0°C from activation parameters.

chloromethane. These iodinations take place between three and ten times faster in tetrachloromethane [1], and the rate of iodination of $[Me_3SnCo(CO)_4]$ would be comparable with or faster than that of $[Me_3SnFe(CO)_2(cp)]$ * $k_2(obs) = 2780\ l\ mol^{-1}\ s^{-1}$ [3]).

If the decomposition of $[Co(CO)_4I]$ involved a fast reaction with further molecules of iodine, the kinetics would show an order of greater than one with respect to iodine concentration, and in the product analysis above there would be some unreacted $[Me_3SnCo(CO)_4]$.

The iodination of $[Me_3SnCo(CO)_4]$ in cyclohexane was also studied over the temperature range 28.5 to 43.6°C and the activation parameters found are $\Delta H^{\ddagger} = 20.8 \pm 2.2$ kJ $mol^{-1}$, $\Delta S^{\ddagger} = 120.8 \pm 7.3$ J $K^{-1}$ $mol^{-1}$. The calculated value of $k_2(obs)$ at 30°C is 811 l $mol^{-1}$ $s^{-1}$. The low activation enthalpy is in accord with iodination being a multi-step process as discussed previously [3].

## Discussion

We have already found the following reactivity order for iodination as measured by $k_2(obs)$ (eq. 3, 30°C, solvent $CCl_4$): ($k_2(obs)/l\ mol^{-1}\ s^{-1}$) $[Me_3SnFe(CO)_2(cp)]$ 2780; $[Me_3SnMo(CO)_3(cp)]$ 226; $[Me_3SnW(CO)_3(cp)]$ 210; $[Me_3SnCr(CO)_3(cp)]$ ca. 1 **; $[Me_3SnMn(CO)_5]$ 0.005. These results were interpreted to indicate that $[Me_3SnMn(CO)_5]$ was less reactive than the other compounds because it did not contain an electron-donating cyclopentadienyl ligand. Compared with carbonyl, the cyclopentadienyl ligand is a better electron donor, and the transition metal will be a good site for electrophilic attack in compounds containing it. However this hypothesis cannot be correct since, contrary to expectation, both $[Me_3SnCo(CO)_4]$ and $[Me_3SnRe(CO)_5]$ (with no cp ligands), react rapidly with iodine. $[Me_3SnRe(CO)_5]$ is about 200 times more reactive than $[Me_3SnMn(CO)_5]$, and $[Me_3SnCo(CO)_4]$ is of comparable reactivity with $[Me_3SnFe(CO)_2(cp)]$ the most reactive of our compounds.

Dessy et al. [9] have measured the relative nucleophilicities of anions derived from transition-metal carbonyls by measuring reactivities towards alkyl halides. They found the order $[Co(CO)_4]^- < [Cr(CO)_3(cp)]^- < [Mo(CO)_3(cp)]^- < [Mn(CO)_5]^- < [W(CO)_3(cp)]^- << [Re(CO)_5]^- < [Fe(CO)_2(cp)]^-$. There is clearly no correlation between this series and that found for iodination.

This recent work indicates that it is steric factors which are important in determining relative rates of iodination of these compounds. The later members of any group in the periodic table are larger than the earlier members and, because they can increase their co-ordination number more easily, they are more readily attacked by an electrophile. Thus we get the reactivity orders for $[Me_3SnM(CO)_5]$ (M =) Re > Mn, and for $[Me_3SnM(CO)_3(cp)]$ (M =) W ≈ Mo > Cr. Tungsten and molybdenum are of equal size and their complexes have similar reactivity.

The order of reactivities of compounds of the first-row transition metals is $[Me_3SnCo(CO)_4] \geqslant [Me_3SnFe(CO)_2(cp)] > [Me_3SnCr(CO)_3(cp)] > [Me_3SnMn-$

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* cp = η-cyclopentadienyl.

** The reaction of $[Me_3SnCr(CO)_3(cp)]$ with iodine is complex, there being two observable stages [2]. However, its position in the reactivity series is clearly between $[Me_3SnMo(CO)_3(cp)]$ and $[Me_3SnMn(CO)_5]$.

$(CO)_5$]. In [$Me_3SnMn(CO)_5$] manganese is surrounded by six ligands and low reactivity is found. The relative reactivity of five-coordinated complexes is [$Me_3SnCo(CO)_4$] > [$Me_3SnCr(CO)_3(cp)$]. The activating electron donation of the cp group is not sufficient to counter the steric retardation from its larger size. Four-coordinated [$Me_3SnFe(CO)_2(cp)$] is of a similar reactivity to [$Me_3SnCo(CO)_4$], which suggests that the combined electronic and steric effects of one cp ligand are roughly equal to two CO ligands.

When the kinetics of the iodination of [$Me_3SnRe(CO)_5$] were studied by measuring optical densities at 380 nm (where the product [$Re(CO)_5I$] absorbs, but iodine does not) the usual first-order plots of log $(D_t - D_\infty)$ against $t$ were curved giving an approximate value for $k_2$(obs) of $1.4\ l\ mol^{-1}\ s^{-1}$. Iodinations where $k_2$(obs) (from formation of products) is greater than $k_2$(obs) (from disappearance of iodine) have been encountered before [3], and can be explained by assuming that the reaction proceeds in two stages (eq. 4), where $k_1$ is the observed $k_2$(obs)

$$I_2 + [Me_3SnRe(CO)_5] \xrightarrow{k_1} \text{intermediate} \xrightarrow{k_2} Me_3SnI + [Re(CO)_5I]$$

from the disappearance of iodine. Using the method previously described [2] with $k_1 = 1.0\ mol^{-1}\ s^{-1}$ (Table 1), the optical density measurements at 380 nm can be used to calculate values of $k_2$. It is ca. $0.06\ s^{-1}$ and the extinction coef- of the intermediate is ca. $350\ l\ mol^{-1}\ cm^{-1}$.

## Experimental

*Preparations.* [$Me_3SnCo(CO)_4$] was prepared by the reaction of $NaCo(CO)_4$ with $Me_3SnCl$ [10], and [$Me_3SnRe(CO)_5$] was prepared in a similar manner to [$Me_3SnMn(CO)_5$] [3]. Their IR spectra agreed with those in the literature [7,11].

*Kinetics.* The kinetics of iodination of [$Me_3SnCo(CO)_4$] and [$Me_3SnRe(CO)_5$] were measured with a stopped-flow spectrophotometer and a Unicam SP500 spectrophotometer, respectively, as previously described [3].

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