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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

VII. BOND POLARISABILITY INDEX AND REACTIVITY OF ORGANOTIN COMPOUNDS

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SUMMARY

Using the Del Re method a simple reactivity index, defined as the bond polarisability index, has been derived. The observed reactivity sequence for the cleavage of the alkyl groups from metalalkyls both in the polar and in the non-polar solvents have been interpreted, and the relative rates of these reactions correlated with this index. The relative rates of the exchange reactions between trialkylaluminium and trialkyltin hydrides have also been satisfactorily interpreted.

INTRODUCTION

The reactivity index Z_μ developed in our earlier papers[1,2] is a true quantum mechanical reactivity index in as much as it reflects the variation in the transition energy of the reactant molecule. However, many simple parameters, though not apparently related to the transition energy, often provide satisfactory explanations for the relative reactivity of a group of compounds under similar conditions. One such parameter is the polarisability of the metal–carbon bond in organometallic compounds, and it has been already suggested[3] that the $C \leftarrow Sn$ polarisation governs the reactivity of the alkyl groups in alkyltin compounds. This could readily be understood, since the greater the polarisability of the metal–carbon bond, *i.e.*, the greater the increase in the polarity of the metal–carbon bond due to the approach of the reagent molecule, the easier will be the cleavage of the metal–carbon bond. Based on this argument, a simple reactivity index, termed the "bond polarisability index" is developed in the present communication using the Del Re approximations. Though qualitative in nature, the bond polarisability index can explain almost all the important features of tin–carbon bond cleavage reactions, and offers a simple explanation for the existence of two solvent-dependent reactivity sequences for the demetallation reactions in metal alkyls, as proposed by Abraham and Hill[4]. The relative rates of hydride exchange reaction between trialkylaluminium and trialkyltin hydrides can also be satisfactorily interpreted.

RESULTS AND DISCUSSION

In the Del Re approximation, the bond polarity, Q_{MC}, of the metal–carbon bond is given by eqn. (1) where all the quantities have their usual significance.

$$Q_{MC} = (\delta_C - \delta_M)/2\varepsilon_{MC} \tag{1}$$

As discussed in our earlier paper[1] the Coulomb integral parameters δ_C and δ_M will be changed during the course of a reaction due to the approach of the attacking reagent. This will result in a change in the metal–carbon bond polarity, the change being given by eqn. (2), where $\Delta(\delta_C)$ and $\Delta(\delta_M)$ represent the changes in δ_C

$$\Delta Q_{MC} = \frac{\partial Q_{MC}}{\partial(\delta_C)} \cdot \Delta(\delta_C) + \frac{\partial Q_{MC}}{\partial(\delta_M)} \cdot \Delta(\delta_M) \tag{2}$$

and δ_M. Expressing δ_C as a function of δ_M as in eqn. (3) where A_C and K_{CM} are independent of δ_M and using eqn. (1) it is easy to derive eqns. (4) and (5).

Combining eqns. (4), (5) and (2) gives eqn. (6)

$$\delta_C = A_C + K_{CM} \cdot \delta_M \tag{3}$$

$$\frac{\partial Q_{MC}}{\partial(\delta_C)} = (1 - 1/K_{CM})/2\varepsilon_{MC} \tag{4}$$

$$\frac{\partial Q_{MC}}{\partial(\delta_M)} = (K_{CM} - 1)/2\varepsilon_{MC} \tag{5}$$

$$\Delta Q_{MC} = [(1 - 1/K_{CM}) \cdot \Delta(\delta_C) + (K_{CM} - 1) \cdot \Delta(\delta_M)]/2\varepsilon_{MC} \tag{6}$$

In order to use eqn. (6) directly for the discussion of metal–carbon bond cleavage reactions, it is necessary to evaluate the actual changes in the Coulomb integrals of the metal atom and the carbon atom bonded to it brought about by the attacking reagent. Drastic simplification is possible, however, if we consider the electrophilic attack at the carbon atom of the alkyl group and the nucleophilic attack at the metal atom (mechanisms S_E2 and S_EC of ref. 4) separately.

In an electrophilic attack at the carbon atom by the reagent, the Coulomb integral, δ_C, of the attacked carbon atom will be primarily altered, so that ΔQ_{MC} will be given by eqn. (7). For a given metal, ε_{MC}, the metal–carbon bond resonance integral, is a constant, and $\Delta(\delta_C)$ may also be treated as constant[1] for a particular reagent in a given solvent, so that only the parameter K_{CM} governs the change in the metal–carbon bond polarity under such circumstances. Qualitatively, the increase in the metal–carbon bond polarity due to the approach of the reagent may be related to greater reactivity towards metal–carbon bond cleavage, and thus the parameter K_{CM} may be expected to correlate the reactivity of a group of similar compounds. In an electrophilic attack $\Delta(\delta_C)$ is positive due to electron withdrawal from the attacked carbon atom by the reagent[1], and an increase in K_{CM} will thus lead to greater polarisation of the bond and hence greater reactivity towards cleavage.

$$\Delta Q_{MC} = (1 - 1/K_{CM}) \cdot \Delta(\delta_C)/2\varepsilon_{MC} \tag{7}$$

For a nucleophilic attack at the metal atom similar considerations show that ΔQ_{MC} will be given by eqn. (8) and that the parameter K_{CM} determines the polarisation

$$\Delta Q_{MC} = (K_{CM} - 1) \cdot \Delta(\delta_M)/2\varepsilon_{MC} \tag{8}$$

of the metal–carbon bond in this case as well. In a nucleophilic attack, the Coulomb integral of the metal atom will be decreased because of electron donation to the metal atom through coordination by the attacking reagent so that $\Delta(\delta_{Sn})$ will be negative in sign. Therefore, an increase in K_{CM} will decrease the metal–carbon bond polarisation resulting in lower reactivity, and *vice versa*. Thus the parameter K_{CM} may be used as a reactivity index both for the nucleophilic attack and the electrophilic attack. As K_{CM} is a measure of the bond polarisation induced by the reagent, the parameter K_{CM} will be referred to hereafter as the bond polarisability index.

Demetallation reactions in metal alkyls reveal the existence of two solvent-dependent reactivity sequences[3-6]. In polar media such as methanol or acetic acid, in which the reaction is believed to proceed via electrophilic attack at the carbon atom, the relative rates of the cleavage of the group R from metal alkyls of the type RMX_n (where X may be R) follow the order Me > Et > Pr > i-Pr > t-Bu. This sequence was believed to be a steric series due to the non availability of any reactivity index for its correlation. By using the reactivity index Z_{μ}, we have already shown that, at least for the organotin compounds, the sequence is primarily determined by the variation in electronic effects, the steric factors being relatively unimportant. A comparison of the reported rate constants or relative rates $(k_R)^{3-6}$ of cleavage of the alkyl groups in a number of tetraalkyltins by different reagent in various solvents with the polarisability

TABLE 1

THE BOND POLARISABILITY INDEX K_{CSn} AND THE RELATIVE RATES OF HALODEMETALLATION OF SOME TETRALKYLTINS IN DIFFERENT SOLVENTS

Compounds	K_{CSn}	k_R *(relative)* *(Br_2 in AcOH)*	k_R *(relative)* *(I_2 in AcOH)*	k_R *(relative)* *(Br_2 in CCl_4)*
$(CH_3)_4Sn$	0.1563	100	100	100
$(C_2H_5)_4Sn$	0.1344	83	41	9300
$(C_3H_7)_4Sn$	0.1340	12	4.4	4500
$(C_4H_9)_4Sn$	0.1340	10.4	3.7	5300
$(i\text{-}C_3H_7)_4Sn$	0.1179	2.6	0.04	80000

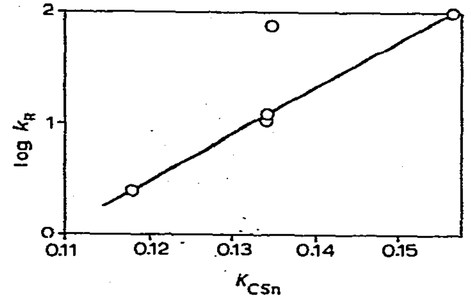
TABLE 2

THE BOND POLARISABILITY INDEX K_{CSn} AND THE EXPERIMENTAL RATES OF CLEAVAGE OF THE GROUP R IN Me_3SnR TYPE COMPOUNDS BY BROMINE AND IODINE IN SOME POLAR SOLVENTS

R	K_{CSn}	k_R *(I_2 in MeOH)*	k_R *(I_2 in AcOH)*	k_R *(Br_2 in AcOH)*
Methyl	0.1563	1.77	0.061	2.92
Ethyl	0.1344	0.256	0.0095	1.21
Propyl	0.1340	0.056	0.00166	0.36
Butyl	0.1340	0.132	0.00317	0.55
Isopropyl	0.1179	0.01	0.00046	0.03
tert-Butyl	0.1049		0.00005	

index, given in Tables 1 and 2, supports this view. Figs. 1–3 show the correlation between the polarisability index and logarithm of the rate constants, or relative rates. In agreement with the preceding discussion, the rate constant increases with the increase in the polarisability index for reactions in polar solvents, while the trend is reversed for reactions in non-polar solvents such as carbon tetrachloride. The linear correlation between the polarisability index and log k_R clearly shows that the steric factors are relatively unimportant in determining the reactivity sequence. Positive slopes of the correlation curve for reactions in polar solvents (Figs. 1 and 2) indicate electrophilic attack at the carbon atom by the reagent, while the negative slope for reactions in non-polar solvent (Fig. 3) indicates nucleophilic attack at the tin atom. The signs of the slopes are consistent with the proposed mechanisms (S_E2 and S_EC)[4].

It will now be shown that the same reactivity sequences will also be valid for the metal–alkyl bond cleavage reactions in other metal alkyls. Application of the Del Re method to a metal alkyl of the type RMX_n, shows that the bond polarisability index, K_{CM}, can be written as in eqn. (9), where the subscript v stands for the atoms



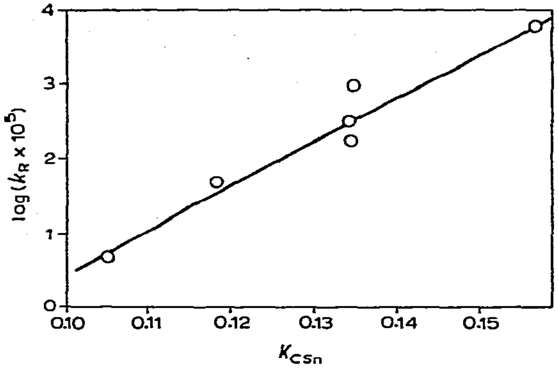


Fig. 1. Correlation between the polarisability index K_{CSn} and the logarithm of the relative rates of bromodemetallation of R_4Sn compounds in acetic acid.

Fig. 2. Correlation between the polarisability index K_{CSn} and the logarithm of the rate of iododemetallation of Me_3SnR compounds in acetic acid.

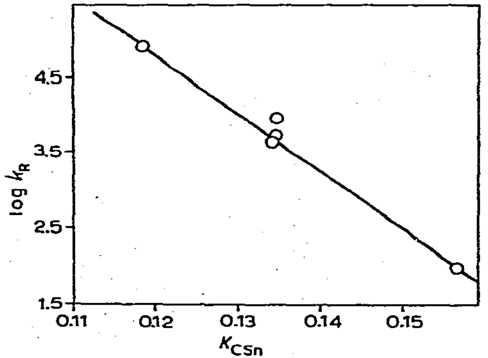


Fig. 3. Correlation between the polarisability index K_{CSn} and the logarithm of the relative rates of bromodemetallation in CCl_4.

(other than the metal atom) bound to the carbon atom of the C–M bond, the γ's are the inductive parameters, and the K_{vC}'s are given by eqn. (10). For a given metal, the inductive parameter $\gamma_{C(M)}$ is constant, so that the bond polarisability index will be pro-

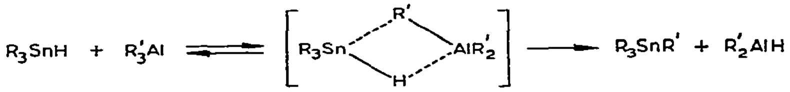
$$\begin{aligned} K_{CM} &= \gamma_{CM}/[1-\Sigma\gamma_{C(v)}\cdot K_{vC}] \\ &= f\cdot\gamma_{C(M)} \end{aligned} \tag{9}$$

(where $f=1/[1-\Sigma\gamma_{C(v)}\cdot K_{vC}]$)

$$\delta_v = A_v + K_{vC}\cdot\delta_C \tag{10}$$

portional to the factor f which is a function of the alkyl group R only. The values of this factor for some of the alkyl groups are: Methyl, 1.563; Ethyl, 1.344; Propyl, 1.340; Butyl, 1.340; Isopropyl, 1.179; and tert-Butyl, 1.049. Provided the signs of the inductive parameter, $\gamma_{C(M)}$ for other metal–carbon bonds are the same as that for the tin–carbon bond, the reactivity sequence will be the same for all the metal alkyls. The bond polarisability index thus provides a satisfactory explanation for almost all the important features of metal–carbon bond cleavage reactions in metal alkyls.

To demonstrate the possibility of extending the bond polarisability index to the discussion of other types of reactions, we will now consider the exchange reactions between trialkyltin hydride and trialkylaluminium. These reactions are of second order and are believed to proceed through a four-centred transition state shown below[7]:



For a given trialkylaluminium, the rate of exchange can be expected to increase with increasing polarisability of the tin–hydrogen bond, because of the increase in the negativity of the hydride hydrogen. This will lead to a stronger coordination between the hydride hydrogen and the aluminium atom, which is a crucial step as shown by the fact that complexing agents, such as ethers and amines, which are capable of saturating the coordination sphere of aluminium, inhibit the exchange reaction completely[7].

Using eqns. (11) and (12), the change in the tin–hydrogen bond polarity, ΔQ_{SnH}, due to the formation of an alkyl bridge by the tin atom is given by eqn. (13). For R_3SnH type compounds K_{SnH} is given by eqn. (14). Combining eqns. (13) and (14)

$$Q_{SnH} = (\delta_H - \delta_{Sn})/2\varepsilon_{SnH} \tag{11}$$

$$\delta_{Sn} = A_{Sn} + K_{SnH}\cdot\delta_H \tag{12}$$

$$\begin{aligned} \Delta Q_{SnH} &= \frac{\partial Q_{SnH}}{\partial(\delta_{Sn})}\cdot\Delta(\delta_{Sn}) \\ &= (1/K_{SnH}-1)\cdot\Delta(\delta_{Sn})/2\varepsilon_{SnH} \end{aligned} \tag{13}$$

and substituting the values of $\gamma_{Sn(C)}$ and $\gamma_{Sn(H)}$[8,9] gives the final eqn. (15) which shows that $Sn^{\delta+}-H^{\delta-}$ polarity will increase with increase in K_{CSn} because $\Delta(\delta_{Sn})$

$$K_{SnH} = \gamma_{Sn(H)}/[1-3\gamma_{Sn(C)}\cdot K_{CSn}] \tag{14}$$

$$\Delta Q_{SnH} = (1-0.6\,K_{CSn})\cdot\Delta(\delta_{Sn})/2\varepsilon_{SnH} \tag{15}$$

TABLE 3

HALF-TIMES OF EXCHANGE REACTION BETWEEN TRI-n-BUTYL-ALUMINIUM AND R_3SnH TYPE COMPOUNDS AND THE POLARISABILITY INDEX K_{CSn}

R	K_{CSn}	$t_{\frac{1}{2}}$ (*min*)	*Ref.*
Ethyl	0.1344	6.2	
Propyl	0.1340	14.8	
Butyl	0.1340	14.0	7
Isobutyl	0.1337	120	
sec-Butyl	0.1175	420	
tert-Butyl	0.1049	>10000	

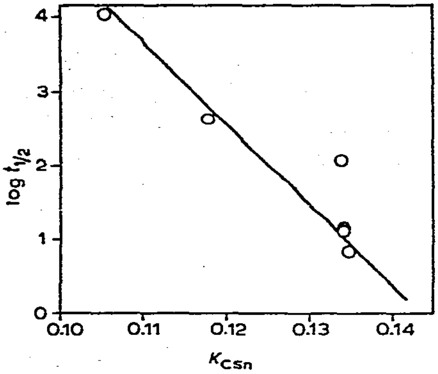


Fig. 4. Correlation between the polarisability index K_{CSn} and the logarithm of the half-times ($t_{\frac{1}{2}}$) of the exchange reaction between tri-n-butylaluminium and some trialkyltin hydrides.

is negative. For a given trialkylaluminium the rate of hydride exchange reaction will therefore be expected to increase with the increase in K_{CSn}. The data given in Table 3, and the plot in Fig. 4, in which logarithms of the half-times of the exchange reaction between tri-n-butylaluminium with some trialkyltin hydrides are used, justify this conclusion.

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