Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

V. THE CHEMICAL REACTIVITY OF ORGANOTIN COMPOUNDS

R. GUPTA and B. MAJEE
Department of Chemistry, North Bengal University, Dt. Darjeeling, West Bengal (India)

(Received February 4th, 1972)

SUMMARY

A simple reactivity index has been developed in terms of the Del Re approximations. The relative case of halodemetallation of organotin compounds in polar and non-polar solvents has been successfully explained by application of this reactivity index, it being shown that the relative rates of cleavage of the R–Sn bond in Me_3SnR, Et_3SnR and R_4Sn compounds can be correlated with the appropriate reactivity index.

INTRODUCTION

Theoretical interpretation of the reactivity of molecules is one of the principal aims of any quantum chemical model, and thus simple reactivity indices such as localization energy, frontier electron density, free valency etc. have been derived within the framework of LCAO MO theory[1–8]. However, the application of quantum mechanical reactivity theory is at present limited mainly to organic molecules, and no calculations have been carried out on organometallic compounds. Although it is possible, in principle, to extend the quantum mechanical reactivity theory of the organic compounds to organometallic compounds, such an extension is not feasible at present for several reasons, the most important being the non-availability of reliable empirical parameters needed for such calculations. However, the Del Re method, because of its extreme mathematical simplicity and its remarkable success in correlating a large number of physical properties of organotin compounds, offers an excellent means for developing simple reactivity indices for the interpretation and correlation of the chemical reactivities of organometallic compounds. In the present communication a simple reactivity index has been developed within the framework of the Del Re approximations, and has been successfully applied to the tin–carbon bond cleavage reactions in saturated organotin compounds, for which reliable Del Re parameters have been already obtained by us[9].

PROCEDURE

The quantum mechanical reactivity theory aims to predict or explain the relative ease of a given reaction, and for this purpose a simple quantum mechanical quantity, often called the "reactivity index", is employed, which is related to the activation energy of the reaction. Although the ideal reactivity index is the activation energy, the calculation of this quantity is by no means simple and drastic simplifications are usually employed. One such approach is the "isolated molecule approximation" in which the reactivity indices relate only to the property of the isolated reactant molecule. Several examples belonging to this category are total π-electron density, free valency, polarizability of the atom itself, localization energy and frontier electron density, developed for the discussion of aromatic reactions[1-7].

For a complete theoretical interpretation of reaction rates, a knowledge of the entropy term is also needed in addition to the activation energy. However, in a discussion of a group of similar reactions, the entropy term need not be considered explicitly. (The approximations involved in neglecting the entropy term have been discussed in several standard treatments on aromatic reactivity theory[10,11].) The treatment that follows is based on similar approximations, and uses the "isolated molecule approximation" in as much as only the change in the energy of the isolated reactant molecule brought about by the reagent is considered.

In the Del Re approximation, the total bond energy, E, of a saturated molecule is given[9] by eqn. (1) where all the quantities have their usual significance. Because

$$E = \sum_{\text{all bonds}} [(\delta_\mu + \delta_\nu) + \{4\varepsilon_{\mu\nu}^2 + (\delta_\mu - \delta_\nu)^2\}^{\frac{1}{2}} - (\delta_\mu^0 + \delta_\nu^0)] \cdot \beta \tag{1}$$

the bond polarity, $Q_{\mu\nu}$, is given by eqn. (2), eqn. (1) may be rewritten as in eqn. (3).

$$Q_{\mu\nu} = (\delta_\nu - \delta_\mu)/(2\varepsilon_{\mu\nu}) \tag{2}$$

$$E = \sum_{\text{all bonds}} [(\delta_\mu + \delta_\nu) + 2\varepsilon_{\mu\nu}\{1 + Q_{\mu\nu}^2\}^{\frac{1}{2}} - (\delta_\mu^0 + \delta_\nu^0)] \cdot \beta \tag{3}$$

Since $Q_{\mu\nu}$ is generally found to be small, the term, $(1 + Q_{\mu\nu}^2)^{\frac{1}{2}}$, may be taken as approximately equal to $(1 + \frac{1}{2}Q_{\mu\nu}^2)$, leading to the following expression:

$$E = \sum_{\text{all bonds}} [(\delta_\mu + \delta_\nu) + 2\varepsilon_{\mu\nu} + \varepsilon_{\mu\nu} \cdot Q_{\mu\nu}^2 - (\delta_\mu^0 + \delta_\nu^0)] \cdot \beta \tag{4}$$

To calculate the change in the total energy of the molecule on attack by a reagent at the μth atom, it is necessary to consider the various changes brought about in the system by this attack. Firstly, the Coulomb integral, δ_μ, of the μth atom will change from its original value because of the additional bond formed by the reagent in the transition state. This change in δ_μ will be relayed to the other atoms through the inductive parameters $\gamma_{\mu(\nu)}$. Secondly, the inductive parameters $\gamma_{\mu(\nu)}$, may themselves undergo some change from the original value. However, the changes in the inductive parameters, $\gamma_{\mu(\nu)}$, may be neglected since it is found that the same set of inductive parameters is applicable to both sp^2 and sp^3 hybridized carbon atoms[9,12], although the number of σ bonds formed by the carbon atom changes from three in the former to four in the latter. Thus the changes in energy, ΔE, may be considered in terms of a single variable δ_μ only, and may be represented approximately as in eqn. (5), where

$$\Delta E = \frac{\partial E}{\partial(\delta_\mu)} \cdot \Delta(\delta_\mu) \tag{5}$$

$\Delta(\delta_\mu)$ is the change in the Coulomb integral, δ_μ, of the μth atom. Eqn. (4), on differentiation with respect to δ_μ, gives eqn. (6). Since the Coulomb integral δ_ν is given by

$$\frac{\partial E}{\partial(\delta_\mu)} = \sum_{\text{all bonds}} \left[1 + \frac{\partial(\delta_\nu)}{\partial(\delta_\mu)} + 2\varepsilon_{\mu\nu}\cdot Q_{\mu\nu}\cdot\frac{\partial Q_{\mu\nu}}{\partial(\delta_\mu)}\right]\cdot\beta \tag{6}$$

eqn. (7)[13], any change in δ_μ will produce a first order change in δ_ν only if ν is directly attached to μ; for all other atoms the change in Coulomb integral will be insignificant

$$\delta_\nu = \delta_\nu^0 + \sum_{\text{all bonds to}\,\nu} (\gamma_{\nu(\mu)}\cdot\delta_\mu) \tag{7}$$

and may be neglected. With this approximation eqn. (6) may be rewritten as in eqn. (8),

$$\frac{\partial E}{\partial(\delta_\mu)} = \sum_\nu \left[1 + \frac{\partial(\delta_\nu)}{\partial(\delta_\mu)} + 2\varepsilon_{\mu\nu}\cdot Q_{\mu\nu}\cdot\frac{\partial Q_{\mu\nu}}{\partial(\delta_\mu)}\right]\cdot\beta \tag{8}$$

where ν signifies atoms directly bonded to the atom μ.

In the Del Re method it is always possible to express the Coulomb integral of the νth atom in terms of the Coulomb integral of the μth atom by simple algebraic manipulations, so that δ_ν may be expressed as in eqn. (9), where A_ν and $K_{\nu,\mu}$ will be

$$\delta_\nu = A_\nu + K_{\nu,\mu}\cdot\delta_\mu \tag{9}$$

independent of δ_μ, and may be found by actual Del Re calculation on the molecule. From eqn. (2) and eqn. (9) it is easy to derive eqns. (10) and (11). Combining eqns. (10),

$$\frac{\partial(\delta_\nu)}{\partial(\delta_\mu)} = K_{\nu,\mu} \tag{10}$$

$$\frac{\partial Q_{\mu\nu}}{\partial(\delta_\mu)} = (K_{\nu,\mu}-1)/(2\varepsilon_{\mu\nu}) \tag{11}$$

(11) and (8) gives eqn. (12), in which n_μ is the total number of bonds formed by the

$$\frac{\partial E}{\partial(\delta_\mu)} = \sum_\nu\left[1+K_{\nu,\mu}+Q_{\mu\nu}\cdot(K_{\nu,\mu}-1)\right]\cdot\beta = \{n_\mu - q_\mu + \sum_\nu[K_{\nu,\mu}\cdot(1+Q_{\mu\nu})]\}\cdot\beta \tag{12}$$

atom μ, and $q_\mu(=\sum_\nu Q_{\mu\nu})$ is the partial charge on the atom μ. Defining a new parameter, Z_μ, as in eqn. (13) eqns. (5), (12) and (13) taken together give the final eqn. (14).

$$Z_\mu = n_\mu - q_\mu + \sum_\nu [K_{\nu,\mu}\cdot(1+Q_{\mu\nu})] \tag{13}$$

$$\Delta E = Z_\mu\cdot\beta\cdot\Delta(\delta_\mu) \tag{14}$$

In the reactions of a group of similar compounds with a particular reagent in a given solvent, $\Delta(\delta_\mu)$ may be regarded as remaining constant throughout the series. In such cases, Z_μ will serve as a relative measure of the activation energy and hence may be regarded as a reactivity index.

RESULTS AND DISCUSSION

Although eqn. (14) is quite general, the present applications will be limited to organotin compounds only, as all the necessary Del Re parameters are available for organotin compounds[9].

The bromo- and iodo-demetallation reactions of a number of tetraalkyltins have been studied in a range of solvents[14-16]. In polar nucleophilic solvents such as methanol or acetic acid, the cleavage of the tin–carbon bond is thought to occur by an S_E2 mechanism[17]. The observed reactivity sequence for cleavage of R group in Me_3SnR is R = Me > Et > Bu > Pr > i-Pr > t-Bu. This steric rather than inductive sequence was unexpected, and no entirely satisfactory explanation could be offered for it. It will now be shown that this sequence can be satisfactorily explained by the newly developed reactivity index, Z_μ, both qualitatively and quantitatively.

TABLE 1

THE CALCULATED REACTIVITY INDEX $Z_{C(R)}$ AND THE EXPERIMENTAL RATE OF CLEAVAGE OF THE GROUP R IN $(CH_3)_3SnR$ TYPE COMPOUNDS BY BROMINE AND IODINE IN SOME POLAR SOLVENTS

R	$Z_{C(R)}$	k_R I_2 *in methanol*	k_R I_2 *in acetic acid*	k_R Br_2 *in acetic acid*
Methyl	5.5021	1.77	0.061	2.92
Ethyl	5.2251	0.256	0.0095	1.21
Propyl	5.2093	0.056	0.00166	0.36
Butyl	5.2092	0.132	0.00317	0.55
iso-Propyl	4.9596	0.01	0.00046	0.03
tert-Butyl	4.6880		0.00005	

TABLE 2

THE CALCULATED REACTIVITY INDEX $Z_{C(R)}$ AND THE EXPERIMENTAL RATE OF CLEAVAGE OF THE GROUP R IN $(C_2H_5)_3SnR$ TYPE COMPOUNDS BY IODINE IN METHANOL

R	$Z_{C(R)}$	k_R I_2 *in methanol*
Methyl	5.5013	3.58
Ethyl	5.2301	0.22
Propyl	5.2085	0.065
Butyl	5.2084	0.060
iso-Propyl	4.9590	0.004

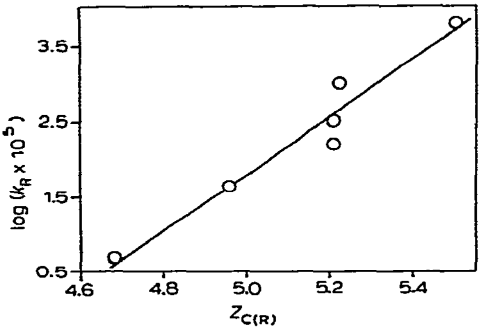
TABLE 3

THE CALCULATED REACTIVITY INDEX $Z_{C(R)}$ AND THE RELATIVE RATE OF HALODEMETALLATION OF TETRAALKYLTIN COMPOUNDS IN ACETIC ACID

Compound	$Z_{C(R)}$	k_R *(relative)* *(Br_2 in acetic acid)*	k_R *(relative)* *(I_2 in acetic acid)*
$(CH_3)_4Sn$	5.5021	100	100
$(C_2H_5)_4Sn$	5.2301	83	41
$(C_3H_7)_4Sn$	5.2087	12	4.4
$(C_4H_9)_4Sn$	5.2085	10.4	3.7
$(i\text{-}C_3H_7)_4Sn$	4.9582	2.6	0.04

If the cleavage of the group R in R'_3SnR type compounds occurs by an S_E2 process, then the appropriate reactivity index for correlating this reaction will be $Z_{C(R)}$ where C(R) signifies the carbon atom of the group R directly bonded to the tin atom. The calculated values of $Z_{C(R)}$ along with reported rate constants or relative rates $(k_R)^{14-17}$ of bromo- and iodo-demetallation in some polar solvents are given in Tables 1–3 for a number of organotin compounds. The data reveal a striking parallel between $Z_{C(R)}$ and the relative rates except for some minor perturbations with the butyl compounds.

In Figs. 1–4, the calculated values of $Z_{C(R)}$ for compounds of the type $(CH_3)_3SnR$, $(C_2H_5)_3SnR$, and R_4Sn are plotted against log k_R. As pointed out earlier, Z values can be used to correlate the reactivities of a given series of compounds towards a particular reagent under comparable conditions only. Within these restrictions which apply to all the quantum mechanical reactivity indices, Figs. 1–4 show that there is a



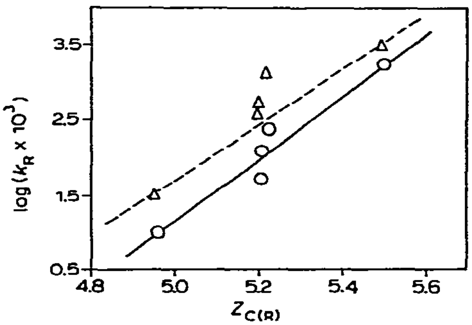
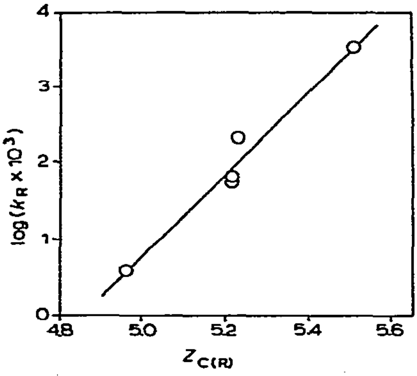


Fig. 1. Correlation between the reactivity index $Z_{C(R)}$ and the logarithm of rate of iodo-demetallation of $(CH_3)_3SnR$ compounds in acetic acid.

Fig. 2. Correlation between the reactivity index $Z_{C(R)}$ and the logarithm of the rate of halodemetallation of Me_3SnR compounds (○, iodo-demetallation in CH_3OH, △, bromo-demetallation in acetic acid.)



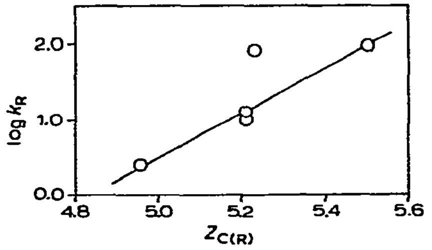


Fig. 3. Correlation between the reactivity index $Z_{C(R)}$ and the logarithm of the rate of iodo-demetallation of $(C_2H_5)_3SnR$ compounds in methanol.

Fig. 4. Correlation between the reactivity index $Z_{C(R)}$ and the logarithm of the relative rates of bromo-demetallation of R_4Sn compounds in acetic acid.

remarkably good correlation between $Z_{C(R)}$ and log k_R. The existence of such linear correlation confirms the validity of the approximations involved in the derivation of the reactivity index, and also justifies the earlier suggestion that the tin–carbon bond cleavage occurs by an S_E2 process in polar solvents.

The halodemetallation reaction in less polar solvents cannot, however, be so easily correlated, since in such solvents the reagent may attack simultaneously at the carbon and tin atoms, giving rise to a cyclic S_Ei mechanism[17]. In this case the change in the energy will be given by eqn. (15). Thus no correlation is possible without the

$$\Delta E = \beta \cdot [Z_C \cdot \Delta\delta(C) + Z_{Sn} \cdot \Delta\delta(Sn)] \tag{15}$$

evaluation of actual changes in the Coulomb integrals of the carbon and the tin atoms. Further, an electrophilic attack at the carbon atom will increase $\delta(C)$ by lowering the electron density at the carbon atom, while the nucleophilic attack at the tin atom will lower $\delta(Sn)$ by increasing the electron density at the tin atom by donation. Thus $\Delta\delta(C)$ and $\Delta\delta(Sn)$ will be of opposite signs. However, some generalizations can be made by considering the extreme case in which the reaction proceeds through nucleophilic attack at the tin atom only (mechanism S_EC of ref. 17). Since the order of Z_{Sn} in R'_3SnR and R_4Sn series is R = Me > Et > Pr = Bu > i-Pr > t-Bu (Tables 4 and 5) and since $\Delta\delta(Sn)$ is negative, the expected reactivity sequence is t-Bu > i-Pr > Bu = Pr > Et > Me, in full agreement with the earlier suggestions[17].

TABLE 4

THE VALUES OF THE REACTIVITY INDEX Z_{Sn} FOR S_EC ATTACK AT THE TIN ATOM IN $(CH_3)_3SnR$ AND $(C_2H_5)_3SnR$ TYPE COMPOUNDS

$(CH_3)_3SnR$		*$(C_2H_5)_3SnR$*	
R	*Z_{Sn}*	*R*	*Z_{Sn}*
Methyl	4.0852	Methyl	4.0081
Ethyl	4.0838	Ethyl	3.9821
Propyl	4.0594	Propyl	3.9819
Butyl	4.0594	Butyl	3.9819
iso-Propyl	4.0404	iso-Propyl	3.9628
tert-Butyl	4.0253	tert-Butyl	3.9478

TABLE 5

THE CALCULATED REACTIVITY INDEX Z_{Sn} AND THE RELATIVE RATES OF BROMODEMETALLATION OF SOME TETRAALKYLTINS IN CCl_4

Compound	*Z_{Sn}*	*k_R (relative) Br_2 in CCl_4*
$(CH_3)_4Sn$	4.0852	100
$(C_2H_5)_4Sn$	3.9821	9300
$(C_3H_7)_4Sn$	3.9815	4500
$(C_4H_9)_4Sn$	3.9815	5300
$(i\text{-}C_3H_7)_4Sn$	3.9047	80000

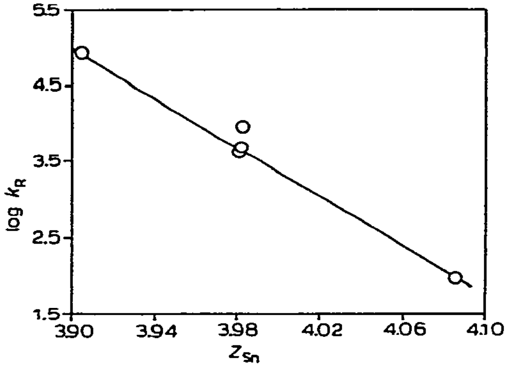


Fig. 5. Correlation between the reactivity indez Z_{Sn} and logarithm of the relative rates of bromo-demetallation in CCl_4.

Although tin–carbon bond cleavage by pure S_EC mechanism is unlikely to occur, the bromo-demetallation of R_4Sn compounds in carbon tetrachloride can be regarded as being very close to an S_EC process. This is confirmed by the linear relation between Z_{Sn} and log k_R as shown in Fig. 5. In general, however, no fixed reactivity sequence can be expected in the less polar solvents such as benzene or chlorobenzene because of the opposing effects due to the simultaneous electrophilic attack at the carbon atom and nucleophilic attack at the tin atom, and the observed sequence will be influenced by the relative magnitudes of $\Delta\delta(C)$ and $\Delta\delta(Sn)$ (eqn. 15), which are clearly influenced by the solvent polarity and the nature of the attacking reagent. This is again supported by experimental observations.

It is thus seen that the newly developed reactivity index provides a very satisfactory theoretical interpretation of the ease of tin–carbon bond cleavage in alkyltin compounds. In a future communication the method will be extended to unsaturated organotin compounds as well as some other organometallic molecules.

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