## CHAPTER II

## THEORETICAL AND PRACTICAL ASPECTS

### 2.1  Theory of Knock in Internal-Combustion Engines(3)

Of the various kinds of irregular or abnormal combustion which may occur in an engine, the most importance from both the theoretical and practical points of view is the type variously known as knock, pink or detonation. Knock may be defined as an abnormally rapid explosion of a certain portion of the charge which is the last to burn in an internal combustion engine, resulting in the formation of pressure-waves in the gas.

The occurrence of knock was known as early as about 1882 (8), but detailed investigations of the phenomenon did not begin until much later. In 1918 Ricardo stated that knock resulted not from mechanical defects in the engines, but from a simultaneous and spontaneous ignition of the last part of the charge to burn. Migley and Boyd (9) announced in 1920 and 1922, the discovery of the antiknock effect of very small amounts of different compounds. The ideas of

theory of knock were based upon experimental facts which, in large part, had been obtained under conditions more or less different from those found in an engine, and a considerable degree of confusion and several distinctly erroneous conclusions resulted therefrom.

The series of fact which brought out by the experiments conducted directly with engines or in closely related apparatus indicated that the development of the chain-reaction theory of the slow oxidation and explosion of gases provided a reasonable basis for the explanation of the phenomena observed. Consequently, it is now possible to advance a general outline of the nature of engine combustion, knock and antiknock action, which is accord with the known facts and appears to be theoretically sound.

## Normal combustion

In non-knocking combustion the flame starting from one or more points of ignition, travels through the charge with a moderately fast velocity but shows no indication of pulsations or vibration. The flame speeds relative to the cylinder-head walls, usually range from 25 to about 250 ft.per sec. in a conventional types of engine with a maximum value at the point where some 50 % of the charge has been

burned. They are determined principally by the turbulence in the charge, which is a function of combustion-chamber design, engine speed, temperature of the combustion-chamber walls, chemical composition of the fuel, the air to fuel ratio and dilution by exhaust gas.

Combustion of the fuel is practically complete within the narrow flame front, yielding carbon monoxide, carbon dioxide, and water(10). The traces of hydrocarbons found in exhaust gases result from the thermal decomposition of unvaporized fuel and oil on the cylinder walls. When the gases behind the flame front begin to cool down, readjustments occur in the equilibria, $2 CO + O_2 \longrightarrow 2 CO_2$,

$$CO + H_2O \longrightarrow CO_2 + H_2$$
$$\text{and } H_2 + 2 OH\cdot \longrightarrow 2 H_2O \ .$$
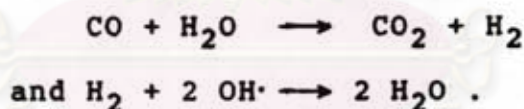
The spectrum of the flame front in an engine similar to that of a Bunsen burner, comprising a number of well-known bands (e.g. C-H and C-C) superimposed on a background of continuous emission; its ultra-violet spectrum shows CO and OH bands(1); its infrared emission indicates the presence of carbon dioxide and water.

In normal combustion the pressure increases to its maximum value in a smooth, continuous manner without pulsations or vibration.

## Characteristics of knock

The occurrence of knock in the engine is marked by flame and pressure characteristics distinctly different from those of normal combustion. These characteristics are confined to a portion of the charge, which is the last to burn; so called " end gas ". The flame of knockihg combustion seems to sweep through the charge practically instantaneously. Its actual velocity is not accurately known but appears to be in the neighbourhood of 1,000 ft.per sec. This value is much greater than the rate of normal flame travel.

The spectral emission of the knocking flame in general resembles that of the normal flame, but extends farther into the ultra-violet and infrared; the intensity is much greater than in the normal case and the C-H and C-C bands are weak or disappear in the knocking flame.

## Factors influencing the tendency to knock

Any change in operating conditions which tends to increase the temperature of the charge or to lengthen its time of heating prior to ignition increases the tendency to knock. The effect of engine speed is of great importance whereas the influence of an increase in compression ratio is particularly marked in increasing

the tendency to knock and the tendency to knock depends not only on the physical factors of time and temperature, but also on the chemical composition of the charge which influences oxidation reactions in the end gas and affects to a certain degree the temperature and speed of the normal flame wave.

From the practical point of view the most important chemical variable apart from the action of antiknock agents is the chemical structure of the different compounds of which the fuel is composed. Generally, it appears that the oxidizability of the fuel is the basic factor in determining its knocking tendency.

Preflame reactions in the engine and preflame oxidation

In non-knocking operation no indication is found of any extensive chemical change in the end gas. When the fuel or operating conditions are changed in the direction to produce knock, absorption spectra show the presence of formaldehyde in the non-inflamed end gas, in amounts which increase as the threshold of knock is approached. Concurrently, the flame spectra show a decrease in the emission of C-C and C-H bands, suggesting that the original fuel molecules have been partially oxidized or dissociated before the arrival of the flame front.
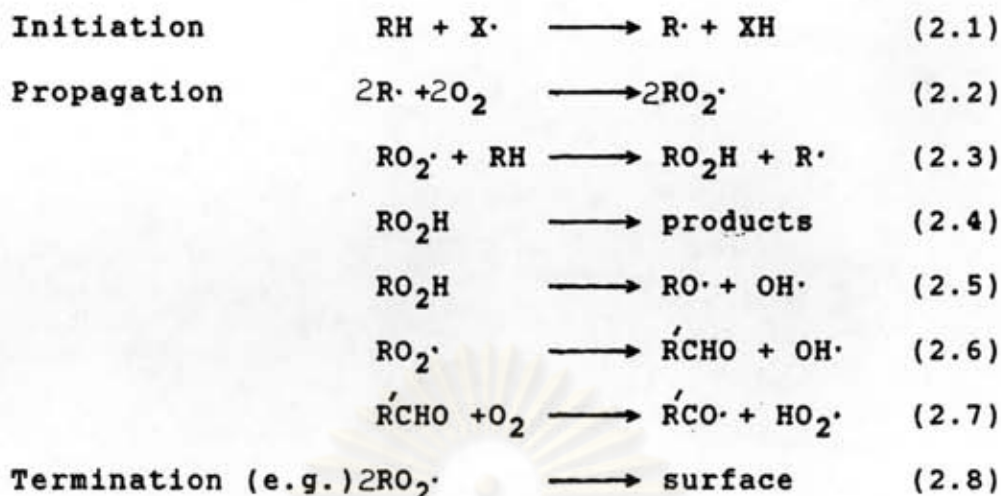
In knocking combustion, absorption spectra of the end gas begin to show the presence of formaldehyde about 0.001 sec. before the knock in an engine running at 600 rpm. The concentration of formaldehyde increases up to the point of inflammation. The chemical analysis of the end gas show the presence of aldehydes and substances of the peroxide type when operating under knocking conditions. In non-knocking operation no peroxides are detected; aldehydes may or may not be found.

It seems probable that the original fuel molecules are partially oxidized, giving active or energy-rich products. These may subsequently, on a favourable collision with other reactants, bring about further oxidation and the formation of additional active products, thus continuing a reaction chain. On the other hand , an unfavourable type of collision will cause a deactivation of these chain carriers and a termination of the chain, the energy of the carriers being distributed throughout the gas in the form of heat. In the absence of knock, this condition prevails in the end gas until the arrival of the flame front and the subsequent inflammation of the gas at about the normal rate.

## Chain-reaction theory

The investigations about the actual mechanisms indicate that the reaction products which can be isolated and, in part, identified, such as aldehydes, alcohols, peroxides, etc. are no more than the end products of the reaction chain; they are chemically too stable to play an active role in the reaction mechanism. The chain carriers and the chemically active products which are responsible for such phenomena as autocatalysis and induced oxidation appear to exist as such for no more than a fraction of a second, and are probably best described by the general designation of free radicals.

Semenov suggested the most widely accepted explanation of gas-phase oxidation of hydrocarbons behavior(11). This mechanism proposed that, during reaction, a product was formed which reacted after a time ( very long compared with the normal life of a chain carrier), to initiate two new chains carriers, except at very high temperatures, were taken to be free radicals or atoms. Thus the reaction may be represented by the following general scheme for the oxidation of an alkane ( where RH represents an alkane and X. represents an initiating species):

| Initiation | $RH + X\cdot \longrightarrow R\cdot + XH$ | (2.1) |
|---|---|---|
| Propagation | $2R\cdot + 2O_2 \longrightarrow 2RO_2\cdot$ | (2.2) |
| | $RO_2\cdot + RH \longrightarrow RO_2H + R\cdot$ | (2.3) |
| | $RO_2H \longrightarrow products$ | (2.4) |
| | $RO_2H \longrightarrow RO\cdot + OH\cdot$ | (2.5) |
| | $RO_2\cdot \longrightarrow \acute{R}CHO + OH\cdot$ | (2.6) |
| | $\acute{R}CHO + O_2 \longrightarrow \acute{R}CO\cdot + HO_2\cdot$ | (2.7) |
| Termination (e.g.) | $2RO_2\cdot \longrightarrow surface$ | (2.8) |

In this scheme, reaction (2.4) is the normal fate of, for example, the hydroperoxide formed during propagation. Occasionally, however, decomposition occurs which yields two chains centers (reaction (2.5)) and brings about chain branching. Reaction (2.5) is not the only step by which branching occurs; thus in reaction (2.6) an aldehyde is formed which reacts further to effect chain branching. The radicals are terminated by surface destruction.

Elbe and Lewis(10) presented the theory of hydrocarbon combustion reactions in the internal combustion engine. The combustion process is pictured to involved a race between combustion by a moving flame and the spontaneous ignition of the unburnt charge ahead of the flame.

## 2.2   Antiknock Compounds and Their Actions(3),(10)-(15)

The theory of the mechanism of the normal and knocking flames outlined above indicates a relation between these phenomena and the chemical composition of the fuel charge. It receives its strongest support from the fact that the only mechanism yet found satisfactory to explain the effect of antiknock agents is the inhibition of chain reactions in the end gas.

Antiknock agents fall into two distinct classes: metallic elements and non-metallic organic compounds. They exhibit a difference in relative effectiveness so marked as to suggest a fundamental distinction between their respective modes of action. Egerton(12) attributes the antiknock effect of the metallic agents to the fact that the metals in question are capable of forming two or more oxides in equilibrium at the end gas in an engine, and that the oxide is the active agent which breaks the reaction chains. Other evidence suggests that the free metal atom is involved. On the other hand, the relatively unstable organic antiknock compounds probably cannot undergo such reactions in an engine. They usually are, in act of chain-breaking, oxidized, decomposed or otherwise rendered ineffective for further inhibitory action.
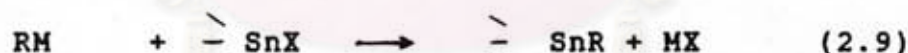
In the case of organometallic compounds, it is

stated by Egerton (12) that the molecule must be dissociated before the metal atom can be effective; correspondingly, metals in the form of compounds which are chemically stable under the conditions existing in an engine are inactive as antiknock agents. Sims & Hardless( 3) established that the metal rather than the organic radical is the active constituent of antiknock compound.

The causes of knock and the mode of action of antiknock agents are not yet fully understood. Many experiments have been performed to show that the two-stage ignition occurring in an engine parallels that at low pressures. All the evidence indicates that if particles of metal oxide with adequate surface were to be formed in an engine, such surfaces could then inhibit the reaction in the end gas zone to prevent knock. Recent experiments performed by V.K.Rao and C.R.Prasad (13) has been shown that the total extent of effectiveness of TEL can be completely accounted for if some of the TEL decomposes forming PbO particles before the reactions leading to knock occur in the end gas. The experiments concluded that PbO, in the solid phase, does inhibit engine knock and the total surface area of the inhibiting compound in the end gas zone is the chief criterion that decides its effectiveness.

## 2.3  Organotin Compounds and Their Preparations[16]-[21]

Most known organotin compounds are derivatives of tin (IV).  The alkyl groups are usually introduced onto tin by complete alkylation of tin tetrachloride with an organometallic reagent, then the various alkyltin chlorides, $R_nSnCl_{4-n}$ are prepared.

The three principle ways in which the carbon-tin bond can be formed involve the reaction between an organometallic compound and a tin derivative (equation 2.9) (X = Cl, etc) or between a tin-metal compound and an alkyl halide (equation 2.10) (M = Li, etc) or between a tin hydride and an alkene (equation 2.11).  The acidolysis reaction (equation 2.12) is of more limited scope.

$$RM \quad + \quad {>}SnX \quad \longrightarrow \quad {>}SnR + MX \qquad (2.9)$$

$$RX \quad + \quad {>}SnM \quad \longrightarrow \quad {>}SnR + MX \qquad (2.10)$$

$${>}C = C{<} \quad + \quad {>}SnH \quad \longrightarrow \quad {>}Sn-C-C-H \qquad (2.11)$$

$$RH \quad + \quad {>}SnNR_2 \quad \longrightarrow \quad {>}SnR + HNR_2 \qquad (2.12)$$

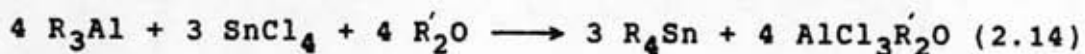### 2.3.1 Reactions of tin tetrahalide and some organometallic compounds[22]-[29]

The first reaction is the most important and the only one which is at present used industrially [19]. The alkylation of tin tetrachloride with a Grignard

reagent is difficult to stop cleanly at the stage of partial alkylation and the tetraalkyltins(22) are first prepared and then used as a source of the alkyltin chlorides (17).

$$4 \text{ RMgX} + \text{SnCl}_4 \longrightarrow \text{R}_4\text{Sn} + 4 \text{ MgXCl} \qquad (2.13)$$

Mixed tetraalkyltins can similarly be prepared from the reaction between a Grignard reagent and an alkyltin halide and the reaction is easier to carry out as these halides, unlike tin tetrachloride, do not form a solid complex with ether vapors.

Alkylation of tin tetrachloride with organoaluminium compounds has the advantage that it can be carried out in the absence of solvent but the aluminium chloride which is formed during the reaction forms a complex with the dialkyltindichloride and trialkyltinchloride which inhibits further alkylation ; this can be avoided by carrying out the reaction in the presence of a strong complexing agent such as ether or amine.

$$4 \text{ R}_3\text{Al} + 3 \text{ SnCl}_4 + 4 \text{ R}_2'\text{O} \longrightarrow 3 \text{ R}_4\text{Sn} + 4 \text{ AlCl}_3\text{R}_2'\text{O} \quad (2.14)$$

Alkylation of tin halides with organolithium compounds proceeds in good yield and is used particularly when the corresponding Grignard reagents

are not readily available .

The Wurtz process in which probably intermediate alkylsodium compound is formed from alkylchloride, and then reacts with tin chloride <u>in situ</u>, does not appear to have been readily used due to disadvantages, of large volume of solvent used to suppress the conversion of the alkylchloride,RCl to the hydrocarbon, RR. This is less of a problem when the reaction is carried out with alkyltin chlorides rather than tin tetrachloride.

A very important route to the organotin halides, discovered by Kocheskov called the Kocheskov Comproportionation reaction involves the redistribution reactions of tetraorganotin compounds with anhydrous tin (IV) chloride which the three basic reactions are represented by equations (2.15)-(2.17) and are used industrially for the manufacture of the triorganotin and diorganotin compounds.

$$3 \; R_4Sn + SnCl_4 \longrightarrow 4 \; R_3SnCl \qquad (2.15)$$
$$R_4Sn + SnCl_4 \longrightarrow 2 \; R_2SnCl_2 \qquad (2.16)$$
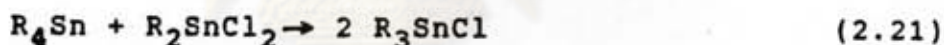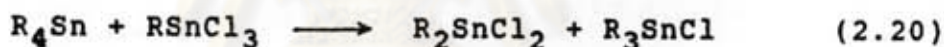$$R_4Sn + 3SnCl_4 \longrightarrow 4 \; RSnCl_3 \qquad (2.17)$$

The initial reaction (equation 2.18) proceeds very rapidly at room temperature and, at higher temperatures, if equimolar quantities of $R_4Sn$ and $SnCl_4$
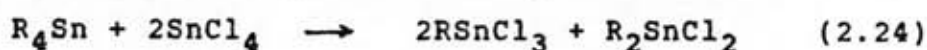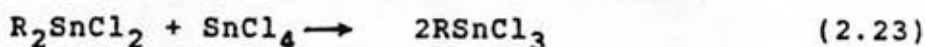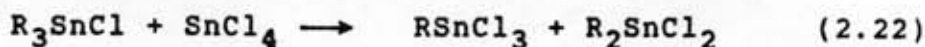
are used (equation 2.16), this is followed by a second reaction (equation 2.19) which furnishes the diorganotin dichloride.

$$R_4Sn + SnCl_4 \longrightarrow RSnCl_3 + R_3SnCl \qquad (2.18)$$
$$RSnCl_3 + R_3SnCl \longrightarrow 2\ R_2SnCl_2 \qquad (2.19)$$

If the tetraorganotin compound is in excess (equation 2.15). This reacts with diorganotin dichloride formed in the two intermediate steps (equation 2.19, 2.20) to yield the triorganotin chloride (equation 2.21).

$$R_4Sn + RSnCl_3 \longrightarrow R_2SnCl_2 + R_3SnCl \qquad (2.20)$$
$$R_4Sn + R_2SnCl_2 \longrightarrow 2\ R_3SnCl \qquad (2.21)$$

If the tin (IV) chloride is present in excess (equation 2.17), this reacts with the initially formed triorganotin chloride (equation 2.18) to give a mixture of the di-and mono-organotin chlorides (equation 2.22), but its reaction with the resulting diorganotin dichloride (equation 2.23) is extremely slow. This reaction requires prolonged heating in the presence of coordinating solvents such as DMSO, $POCl_3$, $P_2O_5$

$$R_3SnCl + SnCl_4 \longrightarrow RSnCl_3 + R_2SnCl_2 \qquad (2.22)$$
$$R_2SnCl_2 + SnCl_4 \longrightarrow 2RSnCl_3 \qquad (2.23)$$
$$R_4Sn + 2SnCl_4 \longrightarrow 2RSnCl_3 + R_2SnCl_2 \qquad (2.24)$$

Tetraorganotin compounds react with one mole of halogen to form the triorganotin halide (equation 2.25) and most commonly ; bromine and iodine are employed. The relative ease of cleavage of the various organic groups from tin is phenyl > benzyl > vinyl > methyl > ethyl > butyl and this property may be used in the synthesis of asymmetric triorganotin halides by varying the conditions ; temperature and solvents used.
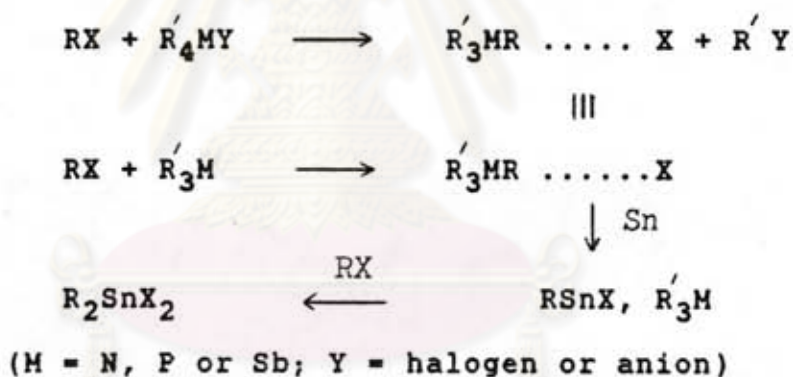
$$R_4Sn + X_2 \longrightarrow R_3SnX + RX \qquad (2.25)$$
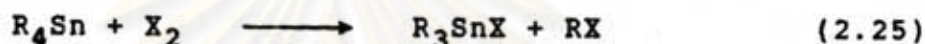
2.3.2 <u>Direct synthesis of organotin compounds</u> (30)-(39)

The organotins may be synthesized directly from tin metal, tin alloys or tin (II) and tin (IV) halides and this method was first used by Frankland in 1849. The direct synthesis of organotin halides has been reviewed by Murphy and Poller (22).

The reaction of the tin metal with an alkylhalide has obvious attractions as an industrial process, but in practice is rather limited, since the dominant product is most commonly the diorganotin dihalide. The order of reactivity of the alkylhalide is RI>RBr>RCl. A catalyst is also required and this is typically a quarternary halide or trialkylderivative of the Group V. elements, $R_4MX$ or $R_3M$ (M = N,P or Sb). The

direct synthesis is employed for the industrial manufacture of dimethyltin dichloride.

The mechanism of the direct reaction (16) may involve an initial activation by the catalyst of the carbon-halogen bond in the alkyl halide, thereby facilitating its reaction with the metal to form an organotin (II) intermediate, RSnX, this can then undergo a carbenoid-like insertion into the carbon-halogen bond of a second mole of alkylhalide, to form the dialkyltin dihalide .

$$RX + R'_4MY \longrightarrow R'_3MR \ldots\ldots X + R'Y$$

$$|||$$

$$RX + R'_3M \longrightarrow R'_3MR \ldots\ldots X$$

$$\downarrow Sn$$

$$R_2SnX_2 \xleftarrow{\quad RX \quad} RSnX, R'_3M$$
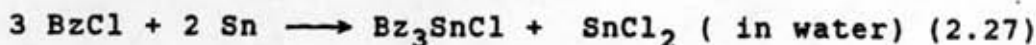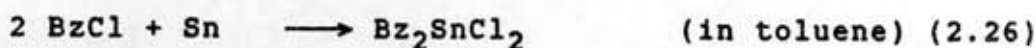
(M = N, P or Sb; Y = halogen or anion)

The direct synthesis may also be promoted by a second metal, usually alloyed with tin, e.g. Na, Zn, Cu or Mg or by the use of $\gamma$-irradiation.

Under certain circumstances, the direct reaction may occur without the addition of a catalyst. The reaction of benzyl chloride with tin powder is one such sample with the use of toluene and of water or n-butanol as the solvent at its reflux temperature gives good

yields of dibenzyltin dichloride or tribenzyltin chloride respectively (37)-(38).

$$2 \; BzCl + Sn \longrightarrow Bz_2SnCl_2 \qquad \text{(in toluene) (2.26)}$$
$$3 \; BzCl + 2 \; Sn \longrightarrow Bz_3SnCl + \; SnCl_2 \; (\text{ in water) (2.27)}$$

In the aqueous synthesis, the tribenzyltin chloride is known to result from the reaction of dibenzyltin dichloride, which is formed initially, with tin powder.

$$3 \; Bz_2SnCl_2 \longrightarrow 2 \; Bz_3SnCl + 2 \; SnCl_2 (\text{in water)(2.28)}$$
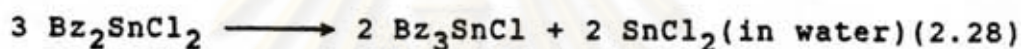
The synthesis of triorganotin halides directly from tin is described by F.S. Holland (39) and in U.S. patent No.4,510,095(1985). The addition of an alkyl halide to tin metal dispersed in a molten quaternary halide rapidly and selectively produces the trialkyltin halide and a by-product containing the quaternary halide as a tin halide complex. The quaternary halide, tin, and the halide ion are all recovered from the by-product by electrolysis which is described in U.S. Patent No. 4,437,949 (1984) and reused. This is the potential process which is operating in a pilot scale.

A route for preparing tetraorganotin compounds by direct synthesis is described by J.W. Nicholson et al (31)-(32). The dropwise addition of straight chain

alkyl halides to tin in a manner similar to that of triorganotin synthesis but zinc is used as the secondary metal in this reaction and iodide ion has to be used in order to stabilize the stannylene formed at the early stage of the reaction.

Van der Kerk et al (33) described the conversion of dialkyltin dichloride into trialkyltin chloride and tetraalkyltin and suggested that the metal having strong affinity for halogen or stronger ionization tendency than tin gave tetraalkyltin. When zinc was used in the reaction, the yield of tetraorganotin increased rapidly in the suitable medium and an organic base.

### 2.3.3 Organotin coordination complexes (40)-(50)

Many compounds are known in which the coordination number of tin is higher than four. In general, the acceptor strength of an organometallic compound is determined mainly by the nature of the metal atom and of its ligands. For tin tetrahalides it was found that complexes were formed with decreasing strength as the halide change, in the sequence F>Cl>Br>I and it is clear that the acceptor strength of tin in the compound is proportional to the electronegativity of the substituents bonded on tin. The presence of an organic group in a molecule usually diminishes its tendency to

form complexes, and hence the observed stability of the
complexes should decreases as follows :

$$SnX_4 > RSnX_3 > R_2SnX_2 > R_3SnX > R_4Sn$$
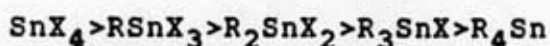
The studies by spectroscopic techniques
mainly X-ray, IR, Raman, NMR, and Mossbauer Spectroscopy
result in the data relating to the coordination number
and configuration which may be concisely summarized that
most $RSnX_3$ compounds form six-coordinate octahedral
complexes whereas $R_2SnX_2$ complexes are sometimes
octahedral and sometimes trigonal bipyramidal ; $R_3SnX$
compounds form only trigonal bipyramidal complexes while
$R_4Sn$ form no complexes whatsoever and always exists in a
tetrahedral configuration.

The organotin compounds can form complexes with
either monodentate ligands and bidentate ligands depend
on the vacancies of the molecular orbitals of tin in the
compounds and O - or N - donors ligands form complexes
with organotin compounds more efficiently than S - and
P- donors.