# CHAPTER 4

## DISCUSSION AND CONCLUSION

One of the organotin compounds used in this experiment was tetrahexyltin. Tetrahexyltin was synthesized by Grignard process.

Although the Grignard synthesis, consisting of many steps, required careful operation and the reactants were more expensive than the direct synthesis, the Grignard synthesis had good selectivity and provides higher yield. In this study, the reaction gave 88.55% yield based on stannic chloride.

By use of Grignard reagent for organotin synthesis,the reactants and the solvents must be absolutely dried, therefore, the humidity must be totally excluded from the reaction medium which could be achieved by using equipments and procedure in this study.

This synthesis was modified by replacing the solvent, THF, with toluene after the Grignard reagent had been generated and allowed the Grignard reagent to react with stannic chloride in toluene. This increased the yield of the product and prevent the formation of a solid stannic chloride-THF complex, which would clog the dropping funnel. It was believed that the product yield increased due to the higher solubility of stannic chloride in dried toluene than in THF, otherwise, toluene had much higher boiling point than THF which was advantageously for this exothermic reaction and toluene did not form the solid complex with stannic chloride.
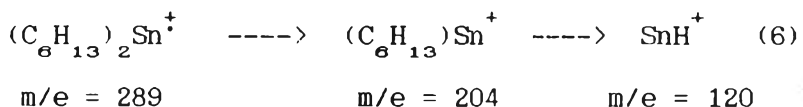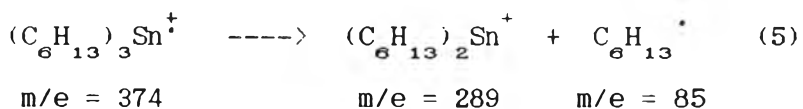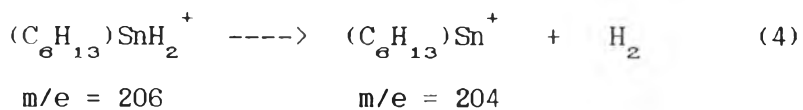
Characterization of the product with FTIR spectroscopy showed the characteristic peaks of general alkyl group at 2957, 2923, 2852 $cm^{-1}$.

Characteristics of tetrahexyltin could be confirmed by using $^{13}$C-NMR and Mass Spectrometer. $^{13}$C-NMR showed the peak of $CH_3$- at 14.193 ppm and $-CH_2$- at 22.861, 27.141, 31.592, 34.146 ppm, respectively. The peak of $CH_2$-Sn appeared at 9.263 ppm. The value of $^1J(Sn{-\!-}^{13}C)$ coupling constant was 149.2 Hz.

Mass Spectrum showed base peak at 375 and the other peaks at 291, 207, 123 due to the lost of $C_6H_{12}$ group as the following mechanism (40-41).
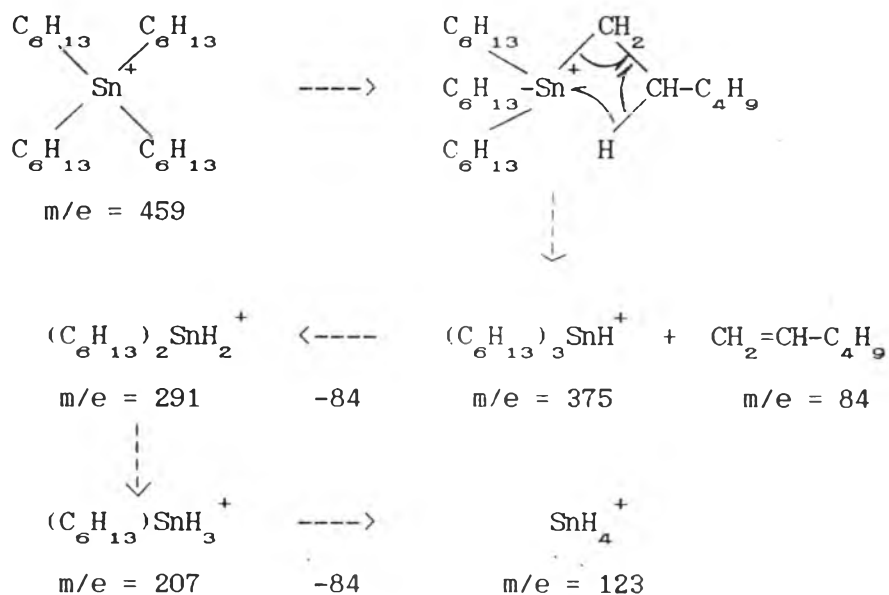


and other equations that could be occurred such as (40-41):

$$(C_6H_{13})_4Sn^{\cdot+} \quad ----> \quad (C_6H_{13})_3Sn^+ + C_6H_{13}^{\cdot} \qquad (1)$$

m/e = 459 \qquad\qquad m/e = 374 \qquad m/e = 85

$$(C_6H_{13})_3Sn^{\cdot+} \quad ----> \quad (C_6H_{13})_2SnH^{\cdot+} + C_6H_{12} \qquad (2)$$

m/e = 374 \qquad\qquad m/e = 290 \qquad m/e = 84

$$(C_6H_{13})_2SnH^+ \quad ----> \quad (C_6H_{13})SnH_2^+ + C_6H_{12} \qquad (3)$$

m/e = 290 \qquad\qquad m/e = 206 \qquad m/e = 84

$$(C_6H_{13})SnH_2^+ \quad ----> \quad (C_6H_{13})Sn^+ + H_2 \qquad (4)$$

m/e = 206 \qquad\qquad m/e = 204

$$(C_6H_{13})_3Sn^{\cdot+} \quad ----> \quad (C_6H_{13})_2Sn^+ + C_6H_{13}^{\cdot} \qquad (5)$$

m/e = 374 \qquad\qquad m/e = 289 \qquad m/e = 85

$$(C_6H_{13})_2Sn^{\cdot+} \quad ----> \quad (C_6H_{13})Sn^+ \quad ----> \quad SnH^+ \qquad (6)$$

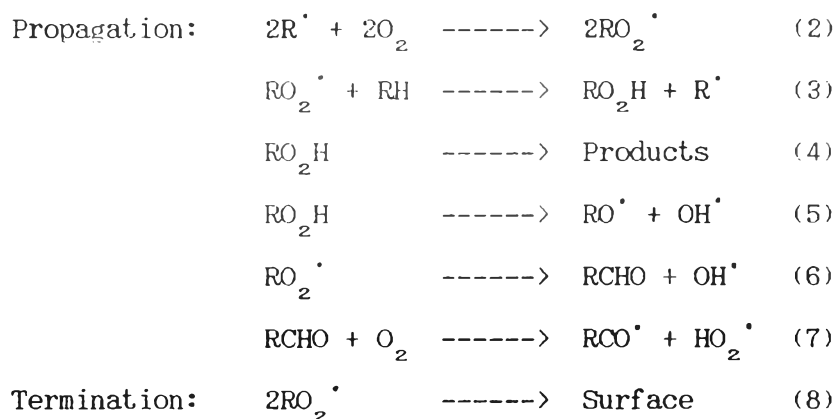m/e = 289 \qquad\qquad m/e = 204 \qquad m/e = 120
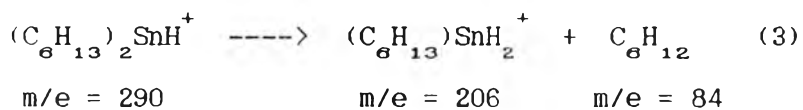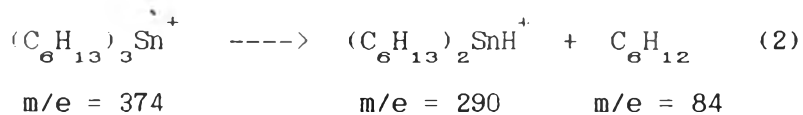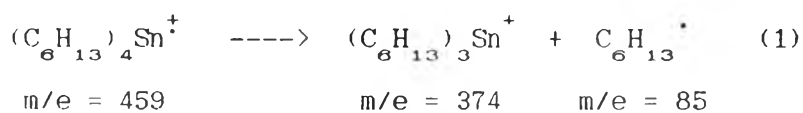
etc.

From the theoretical part in chapter two, it was reported that MTBE could act as an anti-knock agent by introducing two chemical species with high blending octane rating, isobutene and methanol. Both of them were the oxidative products of MTBE (28).

In the case of tetraalkyltins, the same as MTBE, it should be able to proof their anti-knock performance by using Semenov's explanation of gas-phase hydrocarbons oxidation (23).

Initiation: \quad RH + Sn$^{\cdot}$ \quad ------> \quad R$^{\cdot}$ + SnH \qquad (1)

$$\text{Propagation:} \quad 2R^{\cdot} + 2O_2 \quad \text{------>} \quad 2RO_2^{\cdot} \quad \quad (2)$$

$$RO_2^{\cdot} + RH \quad \text{------>} \quad RO_2H + R^{\cdot} \quad (3)$$

$$RO_2H \quad \text{------>} \quad \text{Products} \quad (4)$$

$$RO_2H \quad \text{------>} \quad RO^{\cdot} + OH^{\cdot} \quad (5)$$

$$RO_2^{\cdot} \quad \text{------>} \quad RCHO + OH^{\cdot} \quad (6)$$

$$RCHO + O_2 \quad \text{------>} \quad RCO^{\cdot} + HO_2^{\cdot} \quad (7)$$

$$\text{Termination:} \quad 2RO_2^{\cdot} \quad \text{------>} \quad \text{Surface} \quad (8)$$

This chain reaction was initiated by tin radicals, $Sn^{\cdot}$, which were the product due to the combustion of tetraalkyltins, shown as reaction (1). These radicals all reacted with hydrocarbons or oils, and then alkyl radicals would be formed. The propagation took place after that, however, alkyl radicals in this step not only were formed by reaction (1) but also were formed by the combustion of tetraalkyltins. Products from this chain reaction might be able to identified as aldehydes, alcohols, peroxides, alkenes, etc., and some of these products were the high octane numnber species (12). In addition, the final product, due to the combustion of tetraalkyltins, tin oxide ($SnO_2$), was a nontoxic compound. Moreover, $SnO_2$ gave catalytic activities by changing carbonmonoxide to carbondioxide, so it was believed that it might be able to decrease toxicity of gasoline emissions. For the reasons above, tetraalkyltins could be used as octane number improver instead of tetraalkylleads which resulted in exhaust gases that endanger health.

To determine antiknock properties, synthesized tetrahexyltin was blended with clear unleaded gasoline base and various compositions of unleaded gasoline bases, which were mixed with MTBE or IPA, in order to determine octane number by using CFR Standard

engine. To compare with tetrahexyltin, commercial tetrabutyltin was tested by the same procedure. All of the data in this study was taken from the samples with organotin content of 1g/l and 2g/l. Results from octane number determinations of gasoline composition bases which blended with tetrahexyltin, tetrabutyltin, MTBE and IPA showed that octane number of these compositions were improved.

Figure 3.5 and 3.6 (Table 3.1) indicated that RON of unleaded gasoline bases which were blended with both tetrahexyltin-MTBE mixtures and tetrabutyltin-MTBE mixtures increased by the addition of MTBE content. The increase of percentage from 5% to 10%, MTBE made higher octane number than pure unleaded gasoline base, which gave octane number 83.2, by 1.8-3.8 units. Similar to MTBE, increasing in tin content from 1g/l to 2g/l gave RON in the same direction. Tetrahexyltin added 1.2-1.8 units to unleaded base but tetrabutyltin was the better octane improver and increased RON by 1.7-2.5 units. Because of its better properties, it has been commercially produced by several chemical industries, tetrabutyltin would be interested in this studies. In addition, results from Figure 3.5 and 3.6 showed that when 10% MTBE and 2g/l tetrabutyltin were used as blending components, they improved antiknock properties to give the highest octane number of 89.2 whereas gasoline composition containing 7% MTBE and 1.5g/l tetrabutyltin was the optimum system in order to meet the commercial regular grade gasolines with octane number 87.0.

Although the solubility, stability and other properties of MTBE were favored to use as an antiknock additive, its cost was more expensive than some additives such as commercial alcohols. Fortunately, it had been studied that the gasoline composition containing 5%, 7% and 10% isopropyl alcohol (IPA) increased octane

number by 1.4, 2.3 and 3.9 units respectively comparing with pure unleaded gasoline base which gave octane number 86.2 (12). Otherwise, both MTBE and IPA were oxygenated compounds, they should showed complete combustion and no gum occured. For these reasons, the following tests aimed at 5% MTBE blended base comparing with 5% IPA and 5% MTBE-IPA mixtures. The observed data from Figure 3.7 and 3.8 (Table 3.2) showed that the best proportion of MTBE to IPA in those mixtures was unleaded gasoline base containing 3% MTBE and 2% IPA.

Results from Figure 3.9 (Table 3.3) illustrated the tendency to improve octane number of 5% oxygenated bases comparing with clear gasoline base. The observed data showed that IPA was a better octane booster than mixed MTBE-IPA and MTBE, respectively. For example, adding 2g/l tetrabutyltin to 5% IPA, 3% MTBE-2% IPA and 5% MTBE blended base made higher octane number than clear base by 4.2, 4.0 and 3.6 units, respectively. When the test (called 5% oxygenated test 1) was repeated, the data was reported in Table 3.4, 3.5, 3.6 which were plotted in the Figure 3.10, 3.11, 3.12. Figure 3.10 showing the direction to improve octane number was similar to Figure 3.9. On the other hand, Figure 3.11 showed the opposite direction when used another IPA sample. It was believed that effect of humidity which was appeared by having a trace of water in non-distilled IPA reduced the antiknock properties of IPA and gave this different results. After distillation of the same IPA sample which was used in Figure 3.11, the results from Figure 3.12 indicated that tendency to improve octane number was similar to those of Figure 3.9 and 3.10. One serious disadvantage by using IPA was the possibility of humid absorption when gasoline samples were left in atmosphere for a long period of time. The quantity of IPA that used to blend with gasoline base was limited by the water solubility of IPA for the reason above.

Nevertheless, all of the data observed from testing each of 5% oxygenated bases indicated that the best proportion which gave highest octane number was the sample containing 5% IPA and 2g/l tetrabutyltin. Although gasoline samples containing high percentage of IPA would be able to decrease gasoline cost and gave higher octane number than using of MTBE at the same quantities but humid absorption of IPA might be occured. This effect would separate gasoline into two layers. Moreover, some additives could be dissolved by water. That was the reason why MTBE-IPA mixtures were able to solve this problem. Like oxygenated compounds, using of 2g/l tetrabutyltin gave higher octane number than using of 1g/l. However, tendency to increase octane number by using tetrabutyltin from none to 1g/l was greater than from 1g/l to 2g/l. Cost from tetrabutyltin usage increased twice but it gave a lower tendency to improve octane number. So unleaded gasoline which was blended with 3% MTBE, 2% IPA and 1.5g/l tetrabutyltin should be the optimum proportion. Though gasoline containing 5% IPA and 1g/l tetrabutyltin was the cheapest one.

The observed data from Figure 3.13 showed that gasoline composition containing 3% MTBE, 4% IPA, 1.5g/l tetrabutyltin was the optimum condition which gave octane number up to 88.2, 5.3 units higher than clear base and the best mixed gasoline which gave the highest octane number, 89.9, was the sample containing 3% MTBE, 7% IPA and 2g/l tetrabutyltin. However, results from Figure 3.14 could not differentiate for octane number of 2% MTBE-5% IPA mixture, 3.5% MTBE-3.5% IPA mixture and 5% MTBE-2% IPA mixture.

Finally, in order to decrease gasoline price from MTBE usage and to decrease the effect of humidity from IPA usage, MTBE-IPA mixtures may be the better choice for using as the antiknock

improvers to meet octane number in commercial than using each of them. In this study, the best proportion was unleaded gasoline base containing 3% MTBE, 2% IPA and 1.5g/l tetrabutyltin. However, the tendency to decrease exhaust emission should be investigated further.