Chapter Four

Photodegradation of Butyltin Compounds

4.1 Experimetal

4.2 Materials

The chemicals such as tributyltin chloride (TBTCl), hexane, ethylmagnesium bromide, tetrapropyltin, tropolone, nano anatase, nano rutile, $P_{25}TiO_2$, and polyoxometallate, $H_3[PMo_{12}O_{40}]_X.H_2O$ were commercial chemicals and were used without any purification. Medium pressure mercury lamp (125 W, SAIC India) with emission at UV region of 365, 313, 303, 297 and 265 nm was used for the photo-reaction. The chromatographic analysis of degraded organotin compounds were performed on a Shimadzu Gas chromatograph Model GC-14A, equipped with flame ionization detector and a SGE HT-5 capillary column. A JAC 1505 (JEIO Tech Korea) sonicator was used in the preparation and spiking of the organotin samples in water.

4.3 Photodegradation of tributyltin chloride (TBTCl) :

The photodegradation of TBTCl involved the following steps.

1- Preparation of the stock solution of TBTCl in methanol.
2- Spiking of TBTCl in water
3- Photo-reaction
4- Extraction of the degraded products with hexane and tropolone
5- Addition of Grignard reagent to derivatize the degraded products.
6- Decomposition and hydrolysis of the excess Grignard reagent
7- Extraction of the degraded products by hexane and adjusting the volume with hexane in volumetric flask
8- Addition of internal standard and analysis by GC-FID technique.

4.3.1 Preparation of TBTCl stock solution (1000 ppm)

The photo-degradation of TBTCl is usually carried out in aqueous medium. In order to prepare the TBTCl stock solution, 1 g of TBTCl was first dissolved in methanol, and transferred to a volumetric flask followed by adjusting the volume to 1 liter with methanol.

4.3.2 Spiking of TBTCl in water (100 ppm)

10 ml of the 1000 ppm stock solution was mixed with water and sonicated with a sonicator, and then it was transferred to a 100 ml volumetric flask and the volume was adjusted to 100 ml with distilled water.

4.4 Photo-reaction

100 ml of the spiked solution was transferred to a photo- reactor and irradiated with UV at different length of times (0 - 40 hours).

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4.4.1 Extraction of compounds with hexane and tropolone

The solution after the photo-reaction was extracted with 25 ml hexane containing 0.05% (w/v) of tropolone. The solution was then dried by molecular sieve and the organic layer was collected for subsequent Grignard reaction.

4.4.2 Grignard reaction

5 ml of C_2H_5MgBr (3 M) was added dropwise to the dried extracts from 4.4.1 under nitrogen atmosphere during 2 minutes, and stirred for 30 minutes.

4.4.3 Hydrolysis of excess Grignard reagent

After the Grignard reaction, the product was hydrolysed by using HCl (2 M) to destroy the excess Grignard reagent.

4.4.4 Extraction of the ethylated products

The solution after removing of the excess Grignard reagent was then transferred to a separating funnel and the ethylated compound was extracted with 25 ml hexane and dried over molecular sieves.

4.4.5 Addition of internal standard and analysis by GC-FID

To the sample containing ethylated compound, 0.5 µl tetrapropyltin (internal standard) was added and the sample was injected into the GC instrument. The analytical condition of temperature programming used is summarized in Table 4.1.

The peak of TBTCl, and tetrapropyltin was identified, the peak areas were recorded and the ratio of the peak area for TBTCl to that of the standard (tetrapropyltin) was calculated.

Table 4.1 Temperature programming of gas chromatographic condition for analyzing tributyltin chloride

Initial temperature	80^{o}C
Final temperature	150^{o}C
Initial time	3 min
Program rate	10^{o}C/min
Final time	15 min
Injection port temperature	200^{o}C
Detector temperature	280^{o}C

The flow diagram showing the different steps used in the GC analysis of TBTCl as shown in diagram 4.1.

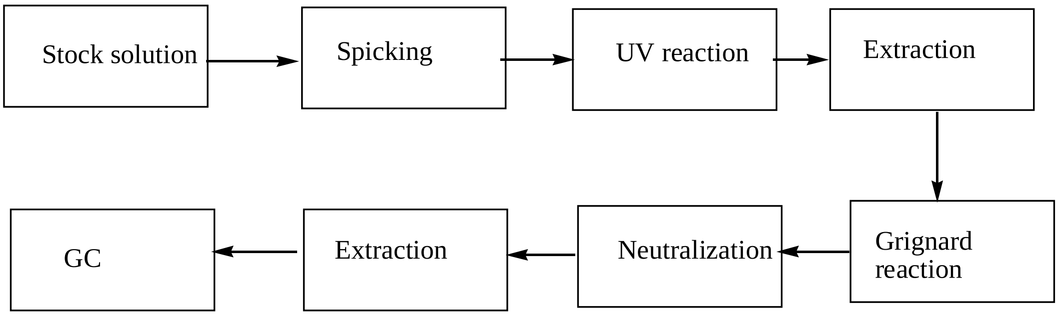

Diagram 4.1: Flow diagram for the analyzing of photo-degradation products of TBTCl

4.5 Photo-catalytic degradation of TBTCl

In order to investigate the effect of catalyst and photosensitizer, polyoxometallate (POM) on the rate of photo-degradation of TBTCl and also the effect of types of TiO_2 (Degussa P_{25}, nano anatase , and nano rutile), the following procedures were carried out.

Photo-catalytic degradation of TBTCl with TiO_2 (Degussa P_{25})

0.1 g of TiO_2 (Degussa P_{25}) was mixed with 100 ml of TBTCl solution (100 ppm) in water and was irradiated with UV at different length of times. The subsequent steps for GLC analysis were similar to that mentioned in sections 4.4.1 to 4.4.5.

Photo-catalytic degradation of TBTCl with mixture of TiO_2 and POM

0.1 g of TiO_2 Degussa P_{25} with 0.25 g POM were mixed with 100 ml TBTCl solution (100 ppm) in water and was irradiated with UV at different length of times. The subsequent steps for the analysis were similar to that mentioned in sections 4.4.1 to 4.4.5.

Photo-catalytic degradation of TBTCl with TiO_2 (anatase)

0.1 g of TiO_2 anatase was mixed with 100 ml TBTCl solution (100 ppm) in water and was irradiated with UV at different length of times. The subsequent steps for the analysis were similar to that mentioned in sections 4.4.1 to 4.4.5.

Photocatalytic degradation of TBTCl with TiO_2 (rutile)

0.1 g of TiO_2 rutile, mixed with 100 ml TBTCl solution (100 ppm) in water and was irradiated with UV lamp at different length of times. The subsequent steps for the analysis were similar to that mentioned in sections 4.4.1 to 4.4.5.

4.6 Determination of concentration of tributyltin chloride:

There are various methods used for the quantitative analysis of organotin compounds (OTCs). These include photometric, spectrometric, and chromatographic methods. However, the products formed after photo-reaction usually contain a mixture of organotins such as tri- , di- and monoorganotins. Hence , in order to separate the various types of organotins before quantitative analysis, chromatographic technique namely GLC is recommended (Belikov, et al., 1990).

4.6.1 Internal standard:

The determination of the quantity of analyte by GC technique required the use of an internal standard. The choice of internal standard is important so that no side reaction occurred between the internal standard and the organotin products.

Tetrabutyltin (TeBT) has been used as internal standard. However, problem arises when this compound was used as internal standard. This is because side reaction between TeBT and DBT ocuurs and produces TBT during the photo-reaction. Such comproportionation reaction is shown as below.

TeBT + DBT $\longrightarrow$ 2 TBT (comproportionation reaction)

Hence, tetrapropyltin was used as internal standard in this work.

The other problem encountered in the analysis of a mixture of organotin compounds is the difficulty in dissolving these compounds in water. Since the photo-reaction usually carried out in aqueous medium, the organotin compounds were dissolved in a solvent such as methanol and then introduced to the water by spiking method.

4.6.2 Derivatization:

Due to the high polarity of triorganotin compounds and their high boiling points, the organotins should be derivatized to non polar and volatile species before injecting into the G.C column. Three methods of derivatization of organotin compounds have been used, there are:

1- Grignard method
2- Ethylation by sodium tetraethyl borate.
3- Hydride generation by sodium borohydride.

Although the Grignard method is a relatively long process with several steps, this derivativation method is widely used due to its ease of handling and it’s easily availability. The use of sodium borohydride has also been attempted but was found to be not suitable as the result obtained was observed to be not repeatable, probably due to the highly volatile hydride compounds and required accessory such as purge and trap attached to the GC chromatograph. On the other hand, sodium tetraethyl borate was not attempted because of the restriction in importing this compound due to its high flammability.

4.7 Photo-reaction Data

Degradation data of TBTCl for UV, UV in the presence of P_{25}, and UV in the presence of a mixture of P_{25} and POM are summarized in Tables 4.2 to 4.6.

Table4.2: Photodegradation of TBTCl by UV radiation

t (hours)	area ratio	$\ln[C/C_0]$	%TBT
0	6.9	1.93	100
4	6.2	1.85	90
8	5.6	1.72	81
10	5.4	1.64	78
16	4.9	1.58	71
20	4.2	1.48	60
30	3.2	1.17	47
40	2.5	0.83	36

Table4.3: Photodegradation of TBTCl by UV radiation in the presence of TiO_2 (P_{25})

t (hours)	area ratio	$\ln[C/C_0]$	%TBT
0	6.9	1.93	100
4	5.3	1.66	77
8	4.1	1.41	60
10	3.6	1.28	52
16	2.4	0.87	34
20	1.9	0.64	27
24	1.4	0.33	21
30	1	0	14.5
40	0.5	-0.69	7

Table4.4: Photodegradation of TBTCl by UV radiation in the presence of a mixture of TiO2 (P_{25}) and POM

t (hours)	area ratio	$\ln[C/C_0]$	%TBT
0	6.9	1.93	100
2	4.8	1.60	70
4	3.4	1.22	49
6	2.4	0.78	33
8	1.7	0.53	25
10	1.2	0.33	17.3
16	0.4	-1.2	5.7
20	0.23	-1.46	3.3

Table4.5: Relative area ratio of TBTCl to internal standard with irradiation time

t (hours)	UV	UV with $TiO_2(P_{25})$	UV with mixture of $TiO_2(P_{25})$ and POM
0	6.9	6.9	6.9
2	-	-	4.8
4	6.2	5.3	3.4
6	-	-	2.4
8	5.6	4.1	1.7
10	5.4	3.6	1.2
16	4.9	2.4	0.4
20	4.2	1.9	0.23
30	3.2	1	-
40	2.5	0.5	-
Rate constant (K) h^{-1}	2.5×10^{-2}	6.5×10^{-2}	1.8×10^{-1}

Table4.6: Degradation data for UV, UV in the presence of TiO_2 (P_{25}), and UV in the presence of a mixture of TiO_2 (P_{25}) and POM

t (hours)	UV			UV with TiO_2($_{P25}$)			UV with mixture of TiO_2 (P_{25}) and POM		
	area ratio	ln[C/C_0]	%TBT	area ratio	ln[C/C_0]	%TBT	area ratio	ln[C/C_0]	%TBT
0	6.9	1.93	100	6.9	1.93	100	6.9	1.93	100
2	-	-	-	-	-	-	4.8	1.60	70
4	6.2	1.85	90	5.3	1.66	77	3.4	1.22	49
6	-	-	-	-	-	-	2.4	0.78	33
8	5.6	1.72	81	4.1	1.41	60	1.7	0.53	25
10	5.4	1.64	78	3.6	1.28	52	1.2	0.33	17.3
16	4.9	1.58	71	2.4	0.87	34	0.4	-1.2	5.7
20	4.2	1.48	60	1.9	0.64	27	0.23	-1.46	3.3
24	-	-	-	1.4	0.33	21	-	-	-
30	3.2	1.17	47	1	0	14.5	-	-	-
40	2.5	0.83	36	0.5	-0.69	7	-	-	-

The kinetic curve for the photo-degradation of TBTCl is shown in Figure4.1, while the effect of irradiation time on the degradation of TBTCl is given in Figure4.2.

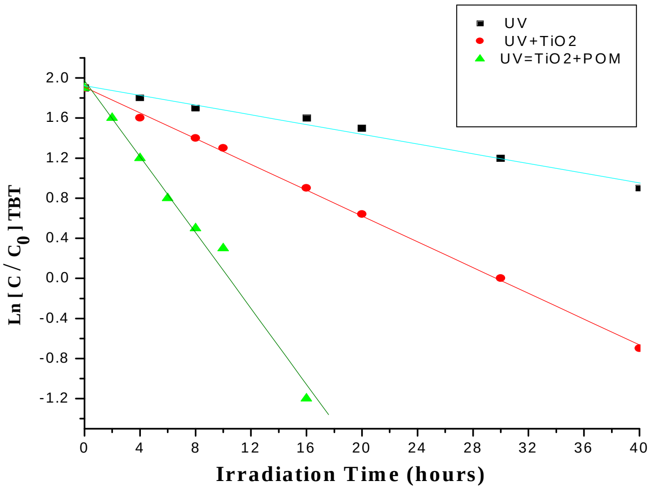

Figure4.1 Kinetic plot of TBT photo-degradation

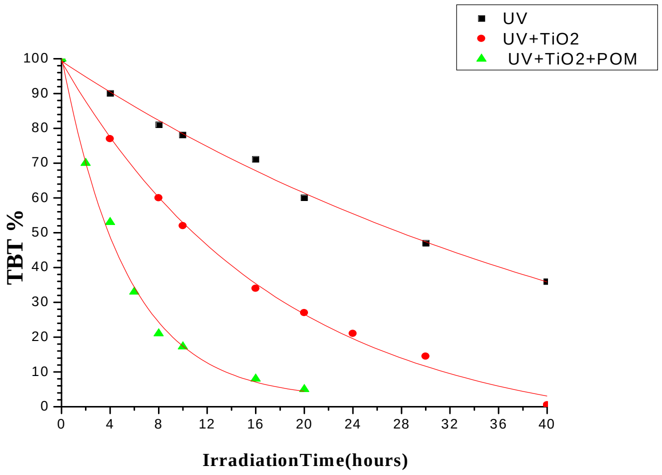

Figure4.2 Variation of the concentration of TBT with irradiation time

4.7.1 Degradation data using different types of TiO_2 (Nano anatase, Nano rutile and Degussa P_{25})

The photo-degradation of TBTCl by using different types of TiO_2 was investigated and the results obtained from this investigation are summarized in Tables 4.7–4.10.

Table 4.7 Photo-degradation of TBTCl by UV radiation in the presence of $TiO_2(P_{25})$

t (hours)	area ratio	$\ln[C/C_0]$	%TBT
0	6.9	1.93	100
4	5.3	1.66	77
8	4.1	1.41	60
10	3.6	1.28	52
16	2.4	0.87	34
20	1.9	0.64	27
24	1.4	0.33	21
30	1	0	14.5
40	0.5	-0.69	7

Table4.8: Photodegradation of TBTCl by UV radiation in the presence of TiO2 (anatase)

t (hours)	area ratio	$\ln[C/C_0]$	%TBT
0	6.9	1.93	100
2	4.8	1.60	70
4	3.4	1.22	49
6	2.4	0.78	33
8	1.7	0.53	25
10	1.2	0.33	17.3
16	0.4	-1.2	5.7
20	0.23	-1.46	3.3
30	-	-	-
40	-	-	-

Table4.9: Photodegradation of TBTCl by UV radiation in the presence of TiO_2 (rutile)

t (hours)	area ratio	$\ln[C/C_0]$	%TBT
0	6.9	1.93	100
2	5.75	1.70	83.3
4	4.79	1.59	69.4
6	3.99	1.38	57.8
8	3.33	1.20	48.2
10	2.77	1.02	40
16	1.6	0.47	23.2
20	1.12	0.11	17.3
30	0.45	-0.79	6.5
40	0.18	-1.7	2.6

Table4.10: Relative area ratio of TBTCl to internal standard with UV irradiation time for different phase of TiO_2

Time (hours)	UV with TiO_2 rutile	UV with (P_{25}) TiO_2	UV with TiO_2 (anatase)
0	6.9	6.9	6.9
2	5.75	-	4.8
4	4.79	5.3	3.4
6	3.99	-	2.4
8	3.33	4.1	1.7
10	2.77	3.6	1.2
16	1.6	2.4	0.4
20	1.12	1.9	0.23
30	0.45	1	-
40	0.18	0.5	-
Rate constant (K) h^{-1}	9.1×10^{-2}	6.5×10^{-2}	18×10^{-2}

The above data showed that photocatalytic activity for the order , anatase > rutile > P_{25} Degussa. The trend of activity will be discussed in detail in section4.8.3. The effect of irradiation time on the degradation of TBTCl with using different types of TiO_2 is shown in Figure 4.3.

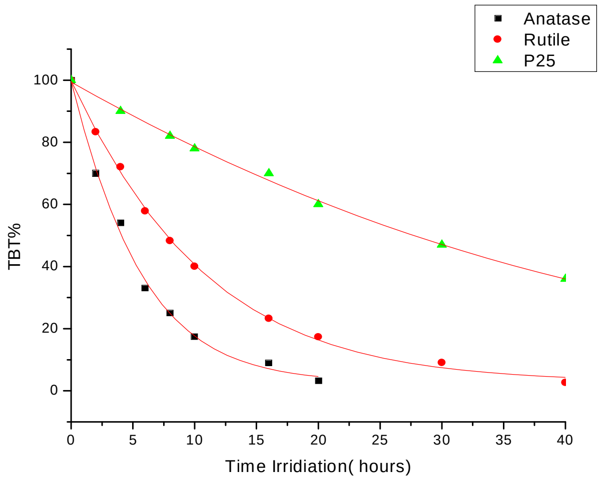

Figure4.3 Variation of TBTCl concentration with UV irradiation time for different types of TiO_2

The kinetic curves for the photo-degradation of TBTCl when using different types of TiO_2 are shown in Figure 4.4.

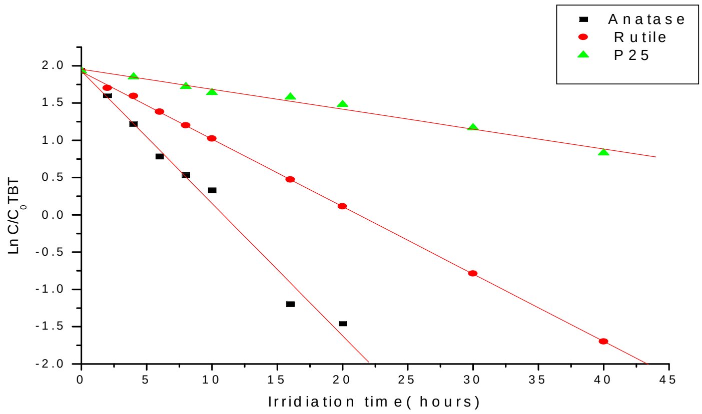

Figure4.4 Kinetic plot of TBT photo-degradation by UV with different types of TiO_2

4.8 Photo-reaction:

Photo-reaction of organotin compounds requires the use of UV radiation as the source of energy to cleave the Sn-C bond. Due to the low UV radiation in solar light, solar light cannot be used to degrade TBTCl. The UV lamp used for the photo-reactions has the range of wavelengths that was suitable for providing the energy for the reaction.

The results obtained from the degradation of TBTCl by UV radiation showed that the rate of reaction is very low. Hence in this work, the use of photocatalyst has also been carried out. Various types of TiO_2 catalysts were used in the study , this include nano anatase, nano rutile, and Degussa P_{25} (80% anatase, 20% rutile).

Langmuir equation:

The Langmuir isotherm equation relates the coverage or adsorption of molecules on a solid surface to gas pressure or concentration of a medium above the solid surface at a fixed temperature. The equation was developed by Irving Langmuir in 1916 where he used this equation for the study of reaction that occurred on surface between solid–gas interfaces. The equation states that:

$$\theta = \frac{\alpha \times P}{1 + \alpha \times P} \qquad (1)$$

where θ is the percentage coverage of the surface, P is the gas pressure or concentration and , α is Langmuir adsorption constant and increases with an increase in the strength of adsorption and with a decrease in temperature.

This equation can be rewritten as:

$$\theta = \frac{KC_o}{1 + KC_o} \qquad (2)$$

where K is the equilibrium constant of adsorption and desorption and C_o is the initial concentration of adsorbent (reactant).

Since the rate equation is proportional to θ, thus

$$R = -\frac{dc}{dt} = K_r\theta = K_r \times \frac{KC_o}{1 + KC_0} \qquad (3)$$

where K_r is rate constant

If there is a competition between different reactants occupying the active surface, the equation is:

$$R = K_r \frac{KC_o}{1 + KC_o + \Sigma KiCi} \qquad (4)$$

Modified Langmuir-Hinshelwood equation:

In order to use the Langmuir-Hinshelwood equation (L-H equation) for solid-liquid interface such as photo-catalytic reaction by TiO_2, six assumptions should be considered.

1- The number of the sites of adsorption on the surface of catalyst is limited.

2- One site can adsorb only one molecule and the catalyst surface can be covered by maximum one layer.

3- The reaction of adsorption is reversible

4- The surface of catalyst is vigorously homogenous

5- There isn't any interaction between adsorbed molecules.

6- The rate of surface adsorption is higher than any secondary chemical reaction.

With attention to these assumptions and considering equation 2, the following equation is used.

$$\theta = \frac{KC_o}{1 + KC_o + K_sC_s} \qquad (5)$$

K_s is adsorption coefficient of solvent

C_s is Solvent concentration

Thus for solid-liquid interface reaction , L-H equation is:

$$R = -\frac{dc}{dt} = K_r\theta = K_r\frac{KC_o}{1 + KC_o + K_sC_s} \qquad (6)$$

Because C_s (solvent concentration) is approximately constant, thus

$$Ka = \frac{K}{1 + K_sC_s} \qquad (7)$$

Here Ka is proportion to equilibrium constant of adsorption (K).

by substituting equation 7 to equation 6 , the equation becomes

$$R= -\frac{dc}{dt} = k_r\,\theta = K_r\,\frac{KaC_o}{1+KaC_o} \tag{8}$$

$$\frac{1}{R} = \frac{1}{K_r\,KaC_0} + \frac{1}{K_r} \tag{9}$$

By plotting $\frac{1}{R}\,versus\,\frac{1}{C_o}$, a linear plot will be obtained.

Because the rate of unimolecular surface reaction is proportion to θ when the rate of adsorption of reactants is higher than adsorption rate of products, the eqaution obtained is

$$R= -\ \frac{dc}{dt} = K_r\theta = K_r\frac{KC_o}{1+KC_o+K_sC_s} \tag{10}$$

$$R= -\frac{dc}{dt} = K_r\theta = K_r\frac{KC_o}{1+KC_o} \tag{11}$$

K_r = rate of reaction θ = percentage of surface coverage

K= Adsorption coefficient of reactant

K_s= adsorption coefficient of solvent

C_s concentration of solvent

Since $Cs > C_o$ and C_s (Solvent concentration) is approximately constant,

Integration of equation 11 gives

$$\ln\frac{C_o}{C} + \frac{K}{1+K_sC_s}(C_o - C) = \frac{K_rK}{1+K_sC_s}t \tag{12}$$

$$\ln\frac{C_o}{C} = K(C_o - C) = K_r\mathrm{K}\times t \tag{13}$$

The equations 12 and 13 are sum of the first order and zero order reactions, because C_o is very small, thus the final equation for solid–liquid interface reaction is:

$$\ln \frac{C_o}{C} = K \times t \tag{14}$$

By plotting $\ln \frac{C_o}{C}$ versus time of irradiation, a linear plot will be achieved (Langmuir, 1916; Guettai and Ait Amar, 2005; Joes et al., 2006). As a result the L-H equation for solid–liquid interface reaction follows first order reaction.

4.8.1 Photoreaction mechanism and rate equation:

Since the rate determining step of photo-catalytic degradation of tributyltin chloride is the initial step, that is, the conversion of tributyltin chloride to dibutyltin chloride, thus the rate of reaction can be determined by measuring the rate of this step. The ratio of peak areas for tributyltin chloride and internal standard in the GC analysis can be obtained as in Table4.2 to 4.6. This area ratios are related to $[C]/[C_o]$. A plot of $\ln[C]/[C_o]$ versus times showed a linear relationship (Figure4.1), indicating the photo-degradation of tributyltin chloride is a first order reaction that follows modified Langmuir–Hinshelwood equation which is usually adopted by the heterogeneous catalyst system (Sobczyński and Dobosz, 2001; Pellizzeletti and Minreo, 1993).

The percentage of TBT at different times can be calculated by dividing the relative area ratio of TBTCl to relative area ratio of TBT at t = 0 (6.9). The amount of TBTCl irradiated with UV versus the irradiation time is given in Figure 4.2. The results showed that in the presence of photosensitized catalyst, the time taken for 95% of tributyltin chloride to be degraded was 20 hours. On the other hand, it takes 40 hours for the degradation of the same percentage of tributyltin chloride if

TiO_2 was used. In the absence of any TiO_2 or catalyst, only 65% of tributyltin chloride will be degraded after 40 hours. With comparison of rate constant of reactions, it was found that rate of the photo-reaction of TBTCl with mixed TiO_2 and polyoxometallate increases seven times relative to the rate of reaction when only UV was used (Table4.6). This is probably due to the presence of polyoxometalate, which acts as a scavenger of electrons and prevents the recombination of holes (h^+) and electrons (e). When the titanium dioxide (TiO_2) absorbed ultraviolet radiation, it will produce pairs of electrons and holes. The electrons of the valence band of titanium dioxide becomes excited by light to the conduction band, therefore creating the negative-electron (e^-) and positive-hole (h^+) pair.

$$\begin{array}{lll}
TiO_2 + h\nu & \longrightarrow & h^+(VB) + e^-(CB) \\
POM + e^- & \longrightarrow & POM^- \\
H_2O + h^+ & \longrightarrow & OH^\bullet + H^+ \\
O_2 + e^- & \longrightarrow & O_2^{\bullet -} \\
O_2 + H^+ & \longrightarrow & HO_2^\bullet
\end{array}$$

◌̇◌̇ Hydroxyl radicals and hydroperoxide radicals have important impact on pollutant oxidation and degradation.

$$\text{Organic pollutant} + OH^\bullet \text{ or } HO_2^\bullet \rightarrow CO_2 + H_2O$$

If there is no scavenger, the electron and hole recombine has no affect on the photo-degradation but in presence of scavenger such as polyoxometallate (POM) the reaction was proceeded and the rate of reaction increased.

Photocatalytic cycle of TiO_2 and polyoxometallateon organotin compounds resemble for organic compounds as shown in Figure 4.5.

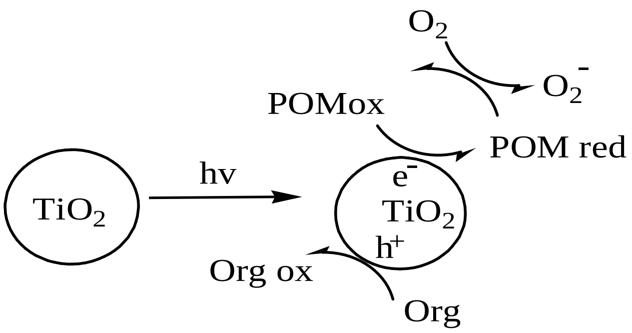

Figure 4.5 Photo-catalytic cycle of degradation of organic compounds

The reduced form of polyoxometallate was blue in color and should be easily monitored by visible spectra (Ozer and Ferry, 2001). Polyoxometallate has been reported and used in some green applications and for the decontamination of water (Hiskia et al., 2006).

4.8.2 Effect of different parameters on photocatalytic activity

Particle size, surface area, phase, morphology, synergetic effect of mixed phases is the parameters affecting the photochemical activity. When the size of particles decreases, the surface area increase and thus photochemical activity increases and facilitates the diffusion of excited electrons and holes toward a reaction surface before recombination. The experiments also showed that the existence of amorphous particles has detrimental effects on photo-catalytic activity (Lian Gao Shanghai, L., 2004). It is mentionable that, all parameters such as particle size, surface area, phase, morphology, and synergetic effect of mixed phases have affects on photochemical activity , but our results showed that, surface area is the most important factor in the photodegradation of tributyltin chloride with the order of anatas > rutile > P_{25}. This order is similar to the order of decreasing surface area of these catalysts that were reported by the suppliers (Table4.11).

Among the various semiconductors materials, TiO_2 is the most widely used photo-catalyst because of its high efficiency, non toxic, chemical and biological stability and low cost. TiO_2 exists in three different crystalline forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). In general it is believed that anatase has greater photo-catalytic activity than rutile. This is because the anatase phase has a higher Fermi level than the rutile phase by about 0.1 eV, hence the anatase phase will have lower capacity to absorb oxygen and higher degree of hydroxylation, this gives a higher number of hydroxyl group on the surface and thus should have greater photocatalytic activity than the rutile phase. Another substantial difference is that the anatase phase has a wider optical absorbtion gap and may have smaller electron effective mass and hence higher mobility. It has also been reported that the anatase has an indirect band gap whereas rutile has a direct band gap, the indirect band gap will causes further decrease in the recombination of e-h pair. If the mobility of e^- and h^+ are different then the recombination will also decrease (Banerjee et al., 2006).

Among three structures of TiO_2, anatase, rutile and brookite, anatase and rutile are commonly used as photo-catalysts. There is little report about photo-catalytic activity of brookite, but pure brookite has been used for photo-degradation of 2-propanol and was shown to have the best photo-activity (Maurazio et al., 2006).

Photo-catalytic degradation of phenol was also investigated by different kinds of TiO_2 (Lian Gao Shanghai, L., 2004).

Anatase TiO_2 nanorods with predominately (101) surface exhibited low activity for Congo red degradation. This means that in addition to phase, morphology is also important in photo-catalytic activity. It was shown for first time that the shape of TiO_2 nanocrystals will significantly affect their photo-catalytic activity (Rajeev et al., 2005). Because of there is no dissociation bond of H_2O-TiO_2, this surface (nanorods) retarded the generation of $OH^{\cdot}$ band radicals that was requires for photo-catalytic oxidation.

Enhanced activity in mixed phase catalysts results from a synergetic effect involving prolonged separation of photo generated electrons and holes through interfacial electron transfer from conduction band of rutile phase to the trapping states of anatase phase (Rajeev et al., 2005).

Degussa P_{25} contains 80% anatase and 20% rutile has a remarkable photo-catalytic activity than pure anatase. The enhanced activity in Degussa P_{25} has been attributed to the efficient electron transfer from rutile to anatase which increase the charge separation needed for efficient photo-catalytic reactions at the particle surfaces.

It has been showed photo-catalytic activity of 40/60 and 70/30 (anatase/rutile) are less than pure anatase for photo-degradation of Congo Red. This trend also was seen in my research for degradation of TBTCl [Rajeev K.Wahi et al. ,2005].

Photo-catalytic activity of TiO_2 for TBTCl degradation showed that the order of pure anatase > pure rutile > P_{25}. This order indicates mixed phase does not have any synergetic effect on photo-catalytic activity for photo-degradation of TBTCl.

Heterogeneous photo-catalysis is an attractive approach for the destruction of inorganic and organic pollutants present in air and water. Among the three polymorph TiO_2 phases, i.e. anatase, rutile and brookite, only the first two have been widely studied and their photo-activity analysed and compared with either in powders or as thin films. On the contrary, only a few recent papers dealing with the preparation of pure brookite powders or films have been found in the literature, and to the best of our knowledge, no studies on the photo-catalytic activity of brookite thin films have ever been published either in liquid–solid or in gas–solid systems. The scarcity of results is due to various reasons among which the most relevant is the difficulty of synthesizing pure brookite, as it is usually formed as a secondary minority phase along with rutile and/or anatase, depending on the experimental conditions used.

Table 4.11 Surface area (m^2/g) of different types of TiO_2

TiO_2	particle size (nm)	surface area (m^2/g)	density(gcm^{-3})
P_{25}	20	50	-
Anatase	<25	200-220	3.9
Rutile	10× 40	130-190	4.17

The target of photodegradation of OTCs is the breaking of Sn-C bond to form non- toxic inorganic tin compounds based on reaction sequence below:

$R_4Sn \rightarrow R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4$ (Inorganic tin compound)

The products that are formed after photodegradation usually are a mixture of TBT, DBT, MBT and inorganic tin compounds. These compounds should be separated before GC analysis.

The results from the photodegradation of TBT indicated that only TBT was detected and other species such as DBT and MBT were absent according to GC analysis. This is due to the degraded products DBT and MBT have decomposed to carbonaceous and tin oxide residue which deposited in the column (Polar et al, 1964).

In general this method for analyzing of OTCs does not allow the identification of the degraded products because of their tendency to fragmentate in the GC column in the presence of the reactive stationary phase.

Evidence of the decomposition of DBT and MBT in GC column comes from the attempted GC analysis of pure DBT and MBT which didn’t reveal any GC signals in their GC chromatograms.

Attempt to carry out the photodegradation of the dibutyltin carboxylate and dibutyltin saltris Schiff base complexes was met with difficulty. This is due to the fact that in both of these dibutyltin compounds, the presence of -OH functional groups tends to undergo esterification with the acid sites on the column solid support materials (Crompton, 1982).

As a result the GC analysis of these complexes failed to produce any useful information. In addition di-n-butyl bis(2-hydroxybenzoate)tin(IV) distanoxane and Schiff base complexes exist as macromolecules which rendered them difficult to dissolve in any organic solvent. Hence it was found that suitable concentration of the complex used for photodegradation study was difficult to obtain.

In view of these problems, the use of LC-ICP-MS technique is recommended as this technique can be used due to its sensitivity in the ppb level.

Conclusion:

TiO_2 as photocatalyst increases the rate of photodegradation of tributyltin chloride by 2.5 times. Polyoxometallate modifies photocatalytic activity. The rate of the photodegradation with mixed TiO_2 and polyoxometallate increases seven times relative to rate of reaction when only UV is used, and the surface area is a more important factor than the structure for photodegradation of tributytin chloride by TiO_2.

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