

TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

RESULTS OF THE EVALUATION OF THE PBT/VPVB PROPERTIES OF:

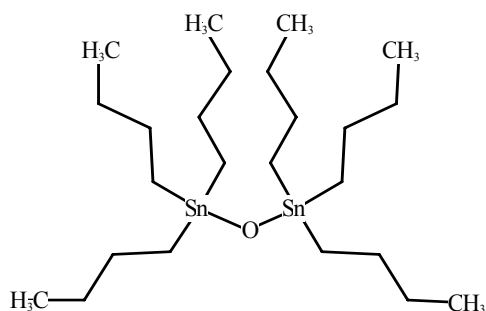
Substance name: Bis(tributyltin) oxide

EC number: 200-268-0

CAS number: 56-35-9

Molecular formula: C₂₄H₅₄O₂Sn₂

Structural formula:



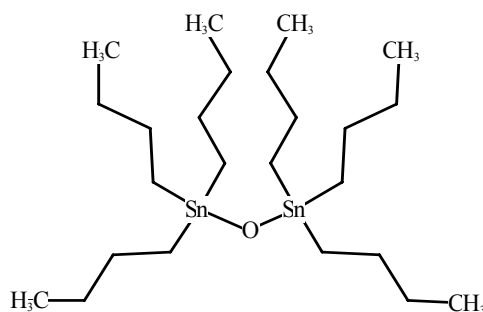
Summary of the evaluation:

Bis(tributyltin) oxide is considered as a PBT substance. Tributyltin, to which the substance transforms in the aqueous environment, fulfils the P, B and T criteria. Furthermore, bis(tributyltin) oxide fulfils the T criterion for human health due to the hazard classification of tributyltin compounds.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: Bis(tributyltin) oxide
EC Number: 200-268-0
CAS Number: 56-35-9
IUPAC Name:
Molecular Formula: C₂₄H₅₄OSn₂
Structural Formula:



Molecular Weight: 596.12
Synonyms: TBTO; Hexa-n-butylstannoxan; Bis(tri-n-butylzinn)oxid; Tri-n-butylzinnoxid

1.1 PURITY/IMPURITIES/ADDITIVES

Impurities as reported by CDCh (2003) are:

Di-n-butyltin oxide approximately 0.5% w/w

Tetra-n-butyltin approximately 1.2% w/w

Tetra-n-butyl-1,3-di-(2-ethyl-hexyl)-di-stannoxane approximately 1.3% w/w

1.2 PHYSICO-CHEMICAL PROPERTIES

Table 1 Summary of physico-chemical properties

REACH ref Annex, §	Property	Value	Comments
VII, 7.1	Physical state at 20 C and 101.3 Kpa	liquid, metallic, organometallic	European Commission (2000)
VII, 7.2	Melting / freezing point	< - 45°C	Chapman and Hall (1984) as cited in GDCh (2003)
VII, 7.3	Boiling point	220-230°C at 13 hPa	Chapman and Hall (1984) as cited in GDCh (2003)
VII, 7.5	Vapour pressure	0.00000085 – 0.00016 hPa at 20°C	Blunden et al. (1984) as cited in GDCh (2003)
VII, 7.7	Water solubility	0.090 mg l ⁻¹ at 25°C 100 mg l ⁻¹ 0.73 mg l ⁻¹ (at pH 6.0-6.6; distilled water) 4.0 mg l ⁻¹ (at pH 7.0; 20°C; distilled water) 18-71.2 mg l ⁻¹ 3-10 mg l ⁻¹ (artificial seawater)	WSKOW v1.41 WSKOW v1.41, exper. database (data not evaluated) Maguire et al. (1983) as cited in GDCh (2003) Maguire et al. (1983) as cited in GDCh (2003) The range of several sources as cited in GDCh (2003) Blunden et al. (1984) as cited in GDCh (2003)
VII, 7.8	Partition coefficient n-octanol/water (log value)	4.05 (estimated) 3.84 3.31 3.2 (pH 6.0, at 20°C) 3.8	KOWWIN v1.67 KOWWIN v1.67, exper. database (data not evaluated) CITI (1992) as cited in GDCh (2003) Maquire et al. (1982) as cited in GDCh (2003) Laughlin et al. (1986) as cited in GDCh (2003)
	Dissociation constant	6.25 6.51	GDCh (2003); for tributyltin cation OECD (2007); for unspecified tributyltin compound

It is noted, that the results of water solubility and logKow –tests are significantly dependent on the pH where the tests have been conducted.

2 MANUFACTURE AND USES

Two producers/importers have provided data under Regulation 93/793/EEC. TBTO among other triorganostannic compounds have been formerly used as biocides in antifouling paints and coatings and for other biocidal uses. In the frame of Directive 76/769/EEC (amended by Regulation 782/2003/EC), the use of organostannic compounds (no CAS or EINECS entry) is forbidden in following uses:

1. as substances and constituents of preparations when acting as biocides in free association paint.
2. as substances and constituents of preparations which act as biocides to prevent the fouling by micro-organisms, plants or animals of:
 - (a) all craft irrespective of their length intended for use in marine, coastal, estuarine and inland waterways and lakes;
 - (b) cages, floats, nets and any other appliances or equipment used for fish or shellfish farming;
 - (c) any totally or partly submerged appliance or equipment.
3. as substances and constituents of preparations intended for use in the treatment of industrial waters.

TBTO will not be evaluated under the Biocides Directive (98/8/EEC), as no data submissions were provided within the deadlines set under the Review Programme of the Directive. Hence, any potential biocidal use of TBTO under Annex I of Biocides Directive is not in sight.

Furthermore, tributyltin compounds (CAS 688-73-3) are identified as “hazardous priority substances” under the Water Framework Directive (2000/60/EU). The objectives of this regulatory instrument apply in principle to any use of these compounds.

According to ESPA (2005), tributyltin compounds are not used as stabilisers in plastics, as they are not technically applicable for this use. However, tributyltins can be present in mono- and dibutyltin stabilisers for plastics, but their content is voluntarily controlled by industry to $\leq 0.67\%$ (as tin) (OECD, 2007). This impurity presumably originates from tributyltin compounds used as intermediates for the stabiliser production, not from TBTO.

3 CLASSIFICATION AND LABELLING

The classification of tributyltin compounds (no CAS entry) in Directive 67/548/EEC applies for TBTO:

T; R25	Toxic if swallowed
T; 48/23/25	Toxic; danger of serious damage to health by prolonged exposure through inhalation and if swallowed
Xn; R21	Harmful in contact with skin
Xi; R36/R38	Irritating to eyes and skin
N; R50-53	Very toxic to aquatic organisms. May cause long-term adverse effects in the aquatic environment

4 ENVIRONMENTAL FATE PROPERTIES

4.1 DEGRADATION (P)

4.1.1 Abiotic degradation

Maguire et al. (1984 as cited in GDCh, 2003) and Laughlin et al. (1986 as cited in GDCh, 2003) expect that TBTO dissociates in aqueous solution forming a hydrated tributyltin (TBT) cation. According to data compiled by GDCh (1988), TBTO forms in seawater mainly TBTCl, TBTOH, an aqueous complex (TBTOH₂⁺) and calcareous compounds ((TBT)₂CO₃). Also WHO (1990) reports, that tributyltins are present in seawater and normal conditions as three species (hydroxide, chloride and carbonate). The speciation of tributyltin cation is dependent on the pH, anion content and temperature (WHO, 1990).

The C-Sn bonds of TBTO are stable against hydrolysis under environmental conditions (GDCh, 2003) but this bond can be cleaved under UV-radiation at 290 nm according to Navio et al. (1993 as cited in GDCh, 2003). WHO (1990) reviews similar study results on photodegradation in water under various conditions. Photodegradation of TBT can be expected to be a relevant removal pathway in the environment only in very shallow clear waters and in the first few centimeters layer of the water column. Aquatic photodegradation is not considered to have relevant impact on the overall persistency of TBT in the environment.

Indirect photochemical degradation in the atmosphere is considered to be fast based on the estimated half-life of 4.5 hours for the reaction with OH-radicals using AOP v1.91 (24-hour day⁻¹; 5*10⁵ OH⁻ cm⁻³). It is noted, however, that due to the very low volatility of TBTO, atmospheric degradation is not a relevant route of degradation for this substance.

4.1.2 Biotic degradation

Degradation half-lives from experiments with natural micro-organism populations under aerobic conditions in aquatic systems are between 4 and 225 days and describe mainly primary degradation and not complete mineralisation (GDCh, 1988). In the studies reviewed by WHO (1990), half-lives from several days to several months in water have been determined for different test temperatures and including both pre-adapted (polluted) and non-adapted water samples.

Only few studies are available on sediment; the degradation half-life in these studies is > 1-15 years. Studies in highly polluted areas show, that after a certain concentration has been reached, no further TBT degradation occurs (GDCh, 2003).

Springborn Laboratories (1995b, as cited in GDCh, 2003) has reported on an aerobic degradation test with ¹⁴C-TBTO and sandy loam soil. A nominal test concentration of 1.15 mg TBTO kg⁻¹ dw and a test temperature of 25°C were employed. Half-life for primary degradation was estimated to be 114 days (323 days corrected to 12°C according to the TGD), whereas the main degradation product was identified as dibutyltin and monobutyltin as a minor product. The recovery at day 365 of the experiment was still 80% (at the start 100%). Springborn Laboratories (1994 as cited in GDCh, 2003) determined a half-life of 130 days (368 days corrected to 12°C according to the TGD) for primary degradation of ¹⁴C-TBTO in anaerobic conditions in a test similar to the aerobic soil test.

4.1.3 Other information ¹

4.1.4 Summary and discussion of persistence

TBTO is subject to transformation when dissolved to aqueous solution. Different tributyltin (TBT) species form as dissolution products, whereas the species formed depend mainly on the pH but also on other abiotic conditions. TBT is expected to be stable to abiotic degradation in the normal environmental conditions.

Experimental half-lives of tributyltin compounds in water between 4 and 225 days have been reported by GDCh (1988) and between several days to several months by WHO (1990). According to GDCh (2003), the few studies available on degradation in sediment showed degradation half-lives of > 1-15 years.

In a soil degradation study an aerobic half-life of 114 days at 25°C was estimated corresponding to 323 days at 12°C.

4.2 ENVIRONMENTAL DISTRIBUTION

4.2.1 Adsorption

Sorption behaviour of TBTO was investigated by Springorn laboratories (1995a as cited in GDCh, 2003) in a system consisting of seawater and sandy sediment (OC of 1.8%) in volume ratio of 10:1. The partitioning coefficient between water and sediment was determined to be 28 after the establishment of the equilibrium within 48 hours. A Koc was estimated to be 2,650. As the test was conducted in seawater (pH > 7 assumed), TBTO has been mainly present in non-dissociated form of tributyltin (e.g. TBTOH). The Koc at pH < approximately 6.5 can be assumed to be lower than at pH around 7 to 8 due to the predominance of the cationic, more hydrophilic form of tributyltin at pH approximately < 6.5.

The partitioning coefficient can be expected to vary along the whole range of environmentally relevant pH due to the speciation behaviour of TBT. Ma et al. (2000 as cited in GDCh, 2003) observed partitioning in water-sediment sorption tests using tributyltin chloride as test substance and adjusting individual test systems to a pH between 1.5 and 11.5. Partitioning between porewater and water was highest within pH of 7.5 – 8 decreasing below and beyond this range.

For the comparison, Koc for predominantly hydrophobics is predicted at 2400 based on the logKow of 4.05 according to the TGD. PCKOWIN v1.66 predicts a Koc of 3.7×10^7 for TBTO, but it is likely, that this program does not take into account the transformation of TBTO to TBT in water. PCKOWIN v1.66 predicts for tributyltin (CAS 20763-88-6) a Koc of 9950 and for tributyltin chloride (CAS 56573-85-4) and tributyltin hydroxide (CAS 1067-97-6) a Koc of 15,010.

Based on the information described above, TBTO (more precisely its aqueous transformation product TBT) is expected to be very slightly mobile in sediment and soil in the pH-range of approximately 6.5 to 8 based on the experimental and estimated adsorption coefficients and its dissociation behaviour. The adsorption potential to sediment and soil can be expected to be significantly lower at pH < 6.5 and pH > 8.

¹ For example, half life from field studies or monitoring data

4.2.2 Volatilisation

Based on the vapour pressure provided in Table 1, TBTO has a very low volatility. An estimated Henry's Law coefficient has been reported to be 2×10^{-5} kPa mol⁻¹ (GDCh, 1988) indicating that the substance is only slightly volatile from aqueous surfaces. Volatilisation to air is therefore assumed to be not a relevant route of distribution for TBTO.

4.2.3 Long-range environmental transport

Due to the fast estimated atmospheric degradation and the very low volatility, TBTO is not expected to be susceptible to long-range transport via air in vapour phase.

4.3 BIOACCUMULATION (B)

It is noted, that due to the transformation of TBTO in aqueous solution to TBT species, and as TBTO cannot be analysed in aqueous solution (GDCh, 2003; WHO, 1990), the experimental results presented generally refer to TBT.

4.3.1 Screening data

Due to the dissociation behaviour of tributyltin cation, it can be expected, that its bioaccumulation potential is lower at pH –range below its pKa (approximately 6.5), whereas its undissociated, more hydrophobic forms (TBTOH and TBTCl) predominate at a pH-range above this value up to the point where an anionic species is formed.

4.3.2 Measured bioaccumulation data

Experimental bioaccumulation data of various aquatic species have been reviewed by, e.g. WHO (1990) and GDCh (2003 and 1988).

BCFs for whole fish in experiments using TBTO as test substance at levels below its water solubility and an appropriately long exposure time (8 weeks) have been reported by Yamada and Takayanagi (1992, as cited in GDCh, 2003) for *Pargus major* (11 000), *Mugil cephalus* (3,000) and *Rudarius ercodes* (3,600) and by Ward et al. (1981 as cited in WHO, 1990) for *Cyprinodon variegatus* (2,600). Metabolism seems to take place in fish according to several studies, where additional butyltin compounds have been analysed (e.g. Ward et al., 1981 as cited in WHO, 1990). Depuration half-lives in the study of Yamada and Takayanagi (1992, as cited in GDCh, 2003) were between 7 and 29 days.

Among invertebrates, annelids and crustaceans exhibit bioaccumulation factors around 1,000, while molluscs and particularly predatory prosobranchs have had concentration factors of 10,000 to 100,000 in a variety of laboratory and field studies (GDCh, 2003).

4.3.3 Other supporting information²

Data not reviewed for this report.

²For example, measured concentrations in biota

4.3.4 Summary and discussion of bioaccumulation

Based on the reviews of WHO (1990) and GDCh (2003), experimental BCFs in whole fish > 2,000 were determined in studies with appropriately low test concentrations and long exposure periods. Bioaccumulation potential of molluscs and prosobranchs seems to be even higher based on various field and laboratory studies. Due to the dissociation behaviour, high bioaccumulation potential is generally expected at pH > 6.5, whereas in the acidic range a lower bioaccumulation potential can be anticipated due to the predominance of the ionised, more hydrophilic form of tributyltin. Similarly, in the basic pH –range, the accumulation potential is expected to decrease from the point, where anionic species of TBT start to dominate.

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

6 ENVIRONMENTAL HAZARD ASSESSMENT

6.1 AQUATIC COMPARTMENT (INCLUDING SEDIMENT)

Endocrine effects have been observed amongst various aquatic species, the review of which has been provided, e.g. in GDCh (2003), RPA (2003) and Vos et al. (2000).

A large dataset exists for TBT with standard acute and chronic studies at three trophic levels. The lowest reliable chronic NOEC for TBT was identified in the risk assessment of organotin compounds (RPA, 2003 and 2005) to be $0.06 \mu\text{g Sn l}^{-1}$ for *Daphnia magna* (Kühn et al., 1989 as cited in RPA, 2003). This corresponds to approximately $0.15 \mu\text{g TBT l}^{-1}$.

Based on the review of European Commission (2005), the mollusc species *Nucella lapillus* (dog whelk) is the most sensitive species to tributyltin compounds. A NOEC of $0.001 \mu\text{g l}^{-1}$ was obtained in a 360-day study looking at imposex. European Commission (2005) derived a SSD curve using 24 NOECs in total from several species of fish, crustaceans, molluscs, insects and echinoderms. A 5th percentile of the SSD was calculated to be $0.00083 \mu\text{g TBT l}^{-1}$. The highest NOEC-value of the data used for the SSD was $18 \mu\text{g TBT l}^{-1}$ from a 4-day test with *Chlorella pyrenoidosa*.

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

Long-term toxicity

6.1.1.2 Aquatic invertebrates

Acute toxicity

Long-term toxicity

6.1.1.3 Algae and aquatic plants

6.1.2 Sediment organisms

Data not evaluated for this report.

6.1.3 Other aquatic organisms

Data not evaluated for this report.

6.2 TERRESTRIAL COMPARTMENT

Data not evaluated for this report.

6.3 ATMOSPHERIC COMPARTMENT

Data not evaluated for this report.

7 PBT AND VPVB

7.1 PBT, VPVB ASSESSMENT

Persistence: Bis(tributyltin) oxide (TBTO) transforms in aqueous solution to tributyltin (TBT). The form in which TBT is present in the environment, depends much on pH, but also on other abiotic conditions. Various degradation studies in water show half-lives between few days to several months. Half-lives of > 1- 15 years have been observed in sediment degradation experiments. It is considered that TBT fulfils the P criterion.

Bioaccumulation: Experimental reliable BCFs are available for four fish species and they all are > 2,000. The bioaccumulation potential is expected to be dependent on the pH of the exposure medium. At pH of approximately < 6.5 bioaccumulation potential is based on the speciation of TBT lower than around pH 7. In the basic pH –range, bioaccumulation potential decreases when the anionic species of TBT start to predominate. Accumulation of TBT compounds to invertebrates has been observed in various studies. The accumulation/concentration factors in certain molluscs have been observed in a range of 10,000 to 100,000. It is considered that TBT fulfils the B criterion.

Toxicity: A large data set on standard and non-standard long-term effect studies is available for TBT compounds. NOECs are generally in the range of < 1 to several ten $\mu\text{g TBT l}^{-1}$. In addition to the very high toxicity in relation to conventional toxicity end-points, TBT compounds elicit effects in the endocrine systems of aquatic organisms at the ng to $\mu\text{g TBT l}^{-1}$ –level. TBT compounds are considered to fulfil the T criterion for ecotoxicity. Furthermore, TBTO fulfils the T criterion for human health through the hazard classification of tributyltin compounds (T; R48/R23/R25).

Summary: Tributyltin, the aqueous transformation product of bis(tributyltin) oxide, fulfils the P, B and T criteria. Furthermore, bis(tributyltin) oxide fulfils the T criterion for human health due to the hazard classification of tributyltin compounds. Bis(tributyltin) oxide is considered to be a PBT substance.

INFORMATION ON USE AND EXPOSURE

A risk assessment according to EU guidance has been conducted for TBT in the frame of the work of RPA (2005 and 2003). These reports contain the relevant information on uses and exposure in the EU.

OTHER INFORMATION

The information and references used in this report were taken from the following sources:

Other sources:

European Commission (2005) Common Implementation Strategy of the Water framework Directive, Environmental Quality Standards (EQS), Substance Data Sheet, Priority Substance No. 30, Tributyltin compounds. Final version, Brussels, 15 January 2005.

European Commission (2000) IUCLID Dataset, Bis(tributyltin)oxide, CAS 56-35-9, 18.2.2000.

ESPA (2005) European Stabiliser Producers Association, Email of J.P.Donnely to the Norwegian Rapporteur, 31.01.2005.

GDCh (2003) BUA Report 238 (Supplementary Reports IX), Tributyltin oxide (Bis-[tri-n-butyltin]oxide) (No. 36), CDCh-Advisory Committee on Existing Chemicals (BUA).

GDCh (1988) BUA Report 36, Tributyltin oxide (Bis-[tri-n-butyltin]oxide), GDCh-Advisory Committee on Existing Chemicals (BUA).

OECD (2007) SIDS Initial Assessment Profile for SIAM 24, 19-20 April, 2007. Tributyltin chloride, CAS No. 1461-22-9.

RPA (2005) Risk assessment studies on targeted consumer applications of certain organotin compounds. Final Report – September 2005. Prepared for the European Commission by Risk & Policy Analysts Limited (RPA).

RPA (2003) Revised assessment of risks to health and the environment associated with the use of organostannic compounds (excluding use in antifouling paints). Final Report (Draft) – December 2003. Prepared for the European Commission by Risk & Policy Analysts Limited (RPA).

WHO (1990) Environmental Health Criteria 116, Tributyltin compounds. International Programme on Chemicals Safety, World Health Organisation, Geneva, 1990.