TC NES SUBGROUP ON IDENTIFICATION OF PBT AND VPVB SUBSTANCES

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

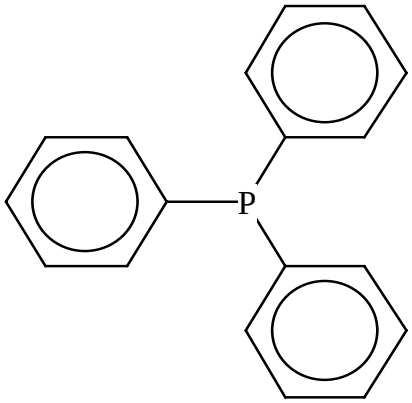
Substance name: triphenylphosphine

EC number: 210-036-0

CAS number: 603-35-0

Molecular formula: C18H15P

Structural formula:



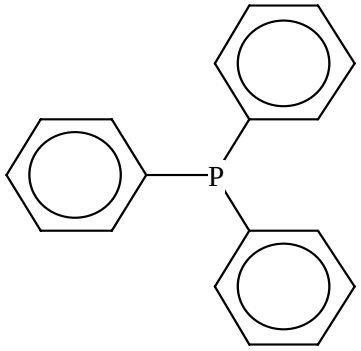
Summary of the evaluation:

Triphenylphosphine is not considered to be a PBT substance. It does not meet the P criterion due to a fast oxidation. Relevant bioaccumulation of the substance is not likely to occur due to the fast oxidation (although screening B criterion is fulfilled). The substance may meet the T criterion based on screening data. Its oxidation product triphenylphosphine oxide (CAS 791-28-6) does not meet the screening B and T criteria. The screening P/vP criterion is considered fulfilled for this substance.

JUSTIFICATION

1 IDENTIFICATION OF THE SUBSTANCE AND PHYSICAL AND CHEMICAL PROPERTIES

Name: Triphenylphosphine
EC Number: 210-036-0
CAS Number: 603-35-0
IUPAC Name:
Molecular Formula: C18H15P
Structural Formula:



Molecular Weight: 262.29
Synonyms: Phosphine, triphenyl; triphenylphosphorus

1.1 PURITY/IMPURITIES/ADDITIVES

No data available.

1.2 PHYSICO-CHEMICAL PROPERTIES

Table 1 Summary of physico-chemical properties

REACH ref Annex, §	Property	Value	Comments
V, 5.1	Physical state at 20 C and 101.3 Kpa	solid	
V, 5.2	Melting/freezing point		
V, 5.3	Boiling point		
V, 5.5	Vapour pressure		
V, 5.7	Water solubility	0.09 mg l^{-1} (at 25ºC)	BASF AG (1992 as cited in European Commission, 2000a) (data not evaluated)
		0.28 mg l^{-1} (at 25ºC)	WSKOW v1.41
V, 5.8	Partition coefficient n-octanol/water (log value)	> 2.59 (at 25ºC)	BASF AG (1988a as cited in European Commission, 2000a) (the used method OECD 107 not applicable)
		5.02	KOWWIN v1.67
		5.69	KOWWIN v1.67 exper. database (data not evaluated)
VII, 5.19	Dissociation constant	-	

2 MANUFACTURE AND USES

Five companies have provided information on the substance under Regulation 937793/EEC. According to European Commission (2000a), a quantity of 5,000-10,000 tonnes/annum is produced and/or imported in Europe. Newer information gathered in the framework of OSPAR (2003) indicates that the production volume in Europe is 3,000 to 5,000 tonnes/annum. Three major producers are providing the substance to the European market and half of the production volume is exported from the EU. According to industry, the substance is used as basic chemicals and intermediate. It is used for production of complexing agents, reducing agents, process regulators and pharmaceuticals. The three major producers have confirmed to use the substance in closed systems only and that emissions to the environment are expected to be very limited.

3 CLASSIFICATION AND LABELLING

The substance is not classified in the Annex I of Directive 67/548/EEC.

4 ENVIRONMENTAL FATE PROPERTIES

4.1 DEGRADATION (P)

4.1.1 Abiotic degradation

BASF AG (2003) tested in accordance with GLP the stability of triphenylphosphine in the frame of an octanol-water partitioning test according to (draft) OECD 123. For the determination of the stability, a stock solution (test substance diluted in acetonitrile in concentration of 554.9 mg l^{-1}) was introduced to deionised water saturated with octanol to produce in the aqueous phase a test concentration of 0.0554 mg l^{-1}. Sampling from this solution took place at 0, 3 and 5 hours. During the stability test all the samples were purged with argon and covered with aluminium foil (=dark incubation). Analysis of the test substance was carried out with HPLC/UV.

Concentration of 0.024 mg l^{-1} (mean of two) was detected from the sample at the start of the test. No test substance was detected at the two later sampling occasions. Retention time of a new peak observed was compared with a peak produced by a triphenylphosphine oxide (CAS 791-28-6) solution and with a blank solution (octanol saturated water). The identity of the new peak was checked by LC/MS/MS spectra additionally (spectra not showed in the report). The results confirmed that triphenylphosphine had oxidised to triphenylphosphine oxide (see Figure 1). The test is considered well documented and reliable for confirming a rapid oxidation despite the unfavourable for oxidation.

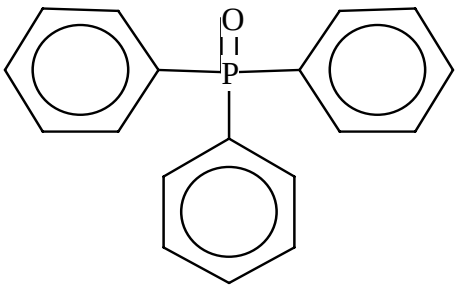


Figure 1. Triphenylphosphine oxide (CAS 791-28-6).

Industry had conducted before the test reported above abiotic degradation tests at screening level, where no oxidation was observed. According to BASF AG (2004), the reason industry observed no oxidation in water is that triphenylphosphine was added into water in pellet form in these tests. It can be assumed that in the screening tests the persistence was caused by an inactive layer of triphenylphosphine oxide which is formed at the surface of the pellets thus preventing further oxidation of triphenylphosphine. In addition, the kinetics for dissolving the substance from the solid pellets are also slowed down by the very low water solubility of the substance so that its oxidation could not be observed within screening test timeframe.

Indirect photochemical degradation in the atmosphere is considered to be slow based on the estimated half-life of 2.7 days for the reaction with OH-radicals using AOP v1.91 (24 h day^{-1}; $5 \cdot 10^5$ OH^- cm^{-3}).

4.1.2 Biotic degradation

A respirometry test was conducted by BASF AG (1988b; as cited in European Commission, 2000a) under similar conditions with OECD 301F. Domestic sludge was used. The test resulted in less than 20% oxygen consumption in 28 days. The test report was not available to the Rapporteur for evaluation. It is noted, that based on the result of the stability test, it is not sure whether the test measured biodegradation of triphenylphosphine or its oxidation product.

A respirometry test similar as above was reported by BASF AG (1980) with a test concentration of 100-2,000 mg l^{-1}. Industrial sludge was used in concentration of 0.2 g l^{-1}. Mean biodegradation of < 0.2 O_2/C was observed in seven days indicating that the substance was not readily biodegradable. A respiration inhibition control was included. The test is documented in a very limited manner but provide an indication of that the substance is not readily biodegradable. It is not possible to clarify, whether the test has actually measured the biodegradation of triphenylphosphine oxide.

BIOWIN v4.02 predicts for BIOWIN2 model a value of 0.99, for BIOWIN3 model a value of 2.69 (weeks-months) and that the substance is not readily biodegradable.

For the oxidation product triphenylphosphine oxide, a test according to OECD 301F was conducted by BASF AG (1987a) using domestic sludge (30 mg TSS l^{-1}) and a test substance concentration of approximately 12, 26 and 51 mg l^{-1}. No degradation (0% as BOD/ThOD) was observed in 28 days. The test is considered valid with restrictions. The substance is concluded to be not readily biodegradable.

For triphenylphosphine oxide, BIOWIN2 model predicts a value of 0.99 and BIOWIN3 model a value of 2.65. The substance is not readily biodegradable according to BIOWIN v4.02. CATABOL predicts for the substance a low probability of biodegradation (p = 5%). The first biodegradation step would be according to CATABOL hydroxylation causing a loss of the phenylring in para - position to phosphorus.

4.1.3 Other information[1]

No data available.

4.1.4 Summary and discussion of persistence

On the basis of the stability test, which was conducted under worst case conditions for oxidation, it is concluded that triphenylphosphine oxidises rapidly (in a matter of hours) in water. The oxidation product is confirmed to be triphenylphosphine oxide (CAS 791-28-6). Two screening biodegradation tests are available indicating that triphenylphosphine is not readily biodegradable. However, it is not sure, whether the tests have measured biodegradation of triphenylphosphine or its oxide. BIOWIN 2 and BIOWIN 3 models predict that the substance is not persistent.

For triphenylphosphine oxide no information on abiotic stability in water is available. The available biodegradation test (OECD 301F) indicates that the substance is not readily biodegradable. The result is supported by a CATABOL –prediction. BIOWIN2 and BIOWIN 3 models, in turn, indicate, that the substance would not be persistent.

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

4.2 ENVIRONMENTAL DISTRIBUTION

Data not reviewed for this report.

4.2.1 Adsorption

4.2.2 Volatilisation

4.2.3 Long-range environmental transport

4.3 BIOACCUMULATION (B)

4.3.1 Screening data[2]

Using the logKow of 5.69, a BCF of 4,801 was derived by BCFWIN v2.15.

For the oxidation product triphenylphosphine oxide KOWWIN v1.67 predicts a logKow of 3.10 and the experimental database of the program contains a logKow of 2.83 (data not evaluated by the Rapporteur) A BCF of 30 was predicted by BCFWIN v2.15 using the experimental logKow.

4.3.2 Measured bioaccumulation data[3]

No experimental data on bioaccumulation are available for triphenylphosphine or its oxide.

4.3.3 Other supporting information[4]

No data available.

4.3.4 Summary and discussion of bioaccumulation

No experimental data on bioccumulation are available for triphenylphosphine and its oxide. The high logKow (5.69) and the predicted BCF (4,801) indicate a high to very high potential for bioaccumulation for triphenylphosphine. Further testing would be necessary to determine the actual accumulation potential. However, due to the rapid oxidation, relevant bioaccumulation of triphenylphosphine is not expected to occur in the environment. The oxidation product triphenylphosphine oxide has a low bioaccumulation potential based on its logKow (2.83) and the predicted BCF (30).

2 For example, log K_{ow} values, predicted BCFs

3 For example, fish bioconcentration factor

4For example, measured concentrations in biota

5 HUMAN HEALTH HAZARD ASSESSMENT

Data not reviewed for this report.

6 ENVIRONMENTAL HAZARD ASSESSMENT

6.1 AQUATIC COMPARTMENT (INCLUDING SEDIMENT)

The substance may degrade in test conditions typical for testing ecotoxic effects. Therefore only flow through tests and semi-static tests with test concentration monitoring are capable to produce reliable information on the effects of the test substance whereas results of static tests may underestimate the ecotoxicity.

6.1.1 Toxicity test results

6.1.1.1 Fish

Acute toxicity

A static test with *Leuciscus idus* according to a DIN standard showed an LC_{50} (96 hours) > 10,000 mg l^{-1}. (BASF AG, 1989; as cited in European Commission, 2000a). Monitoring of test concentration occurred according to the author. The study report was not available to the Rapporteur for evaluation. The result may underestimate the ecotoxicity of triphenylphosphine as fast oxidation is expected under the test conditions. It is noted that the result is far above the expected water solubility of the substance.

ECOSAR v0.99h predicts a LC_{50} (96 hours) of 0.2 mg l^{-1} for fish (logKow 5.69 used).

For triphenylphosphine oxide two ecotoxicity tests on fish are available and show LC_{50} (96 hours) -values > 0.1 mg l^{-1} (BASF AG, 1988c and Geiger et al., 1986; as cited in European Commission, 2000b). The study reports were not available to the Rapporteur for evaluation. It is noted that the water solubility of triphenylphosphine oxide is predicted at 62.8 mg l^{-1} by WSKOW v1.41.

ECOSAR v0.99h predicts a LC_{50} (96 hours) of 19.1 mg l^{-1} for fish (logKow 3.1 used).

Long-term toxicity

No experimental data are available.

6.1.1.2 Aquatic invertebrates

Acute toxicity

Daphnia magna was used in a test carried out by BASF AG (1988; as cited in European Commission, 2000a) according to Directive 84/449/EEC C.2 (static test). Tween 80 solvent was employed. No monitoring of the test substance concentrations occurred. An EC_{50} (48 hours) of 0.6 mg l^{-1} was obtained. The study report was not available to the Rapporteur for evaluation. The result may underestimate the ecotoxicity of triphenylphosphine as fast oxidation is expected under the test conditions. It is noted that the result is above the expected water solubility of the substance.

ECOSAR v0.99h predicts an EC_{50} (48 hours) of 0.09 mg l^{-1} for Daphnia (logKow 5.69 used).

For triphenylphosphine oxide a test according to Directive 79/831/EEC C.2 using *Daphnia magna* showed an EC_{50} (48 hours) of 42.7 mg l^{-1} (BASF AG, 1987b; as cited in European Commission, 2000). The study report was not available to the Rapporteur for evaluation.

ECOSAR v0.99h predicts a LC_{50} (48 hours) of 22.1 mg l^{-1} for Daphnia (logKow 3.1 used).

Long-term toxicity

No data available.

6.1.1.3 Algae and aquatic plants

No experimental data are available. ECOSAR v0.99h predicts an EC_{50} (96 hours) of 0.07 mg l^{-1} for green algae (logKow 5.69 used).

For triphenylphosphine oxide a test according to DIN 38412/9 was conducted using *Scenedesmus subspicatus*. A EC_{50} (96 hours) of 20.6 mg l^{-1} was observed (BASF AG, 1987c; as cited in European Commission, 2000b). The study report was not available to the Rapporteur for evaluation.

ECOSAR v0.99h predicts an EC_{50} (96 hours) of 14.7 mg l^{-1} for green algae (logKow 3.1 used).

6.1.2 Sediment organisms

No data available.

6.1.3 Other aquatic organisms

Data not reviewed.

6.2 TERRESTRIAL COMPARTMENT

No data available.

6.3 ATMOSPHERIC COMPARTMENT

No data available.

7 PBT AND VPVB

7.1 PBT, VPVB ASSESSMENT

Persistence: Triphenylphosphine does not meet the P/vP criteria. The substance is rapidly oxidised in aquatic solution. The oxidation product triphenylphosphine oxide (CAS 791-25-6) is according to a OECD 310F –test not readily biodegradable. CATABOL predicts a very low probability (p = 0.5%) for biodegradation of triphenylphosphine oxide. Although the screening P/vP criterion would not be fulfilled according to BIOWIN2 and BIOWIN3 predictions, it is considered that the available ready biodegradability test supported by CATABOL result override the BIOWIN

predictions in the absence of further experimental data. It is concluded that triphenylphosphine oxide fulfils the screening P/vP criteria.

Bioaccumulation: Triphenylphosphine is not likely to be subject to relevant bioaccumulation due to its fast oxidation. However, the screening B/vB criterion is fulfilled for the substance based on its logKow (5.69). The oxidation product triphenylphosphine oxide does not meet the screening B criterion based on its logKow (3.1).

Toxicity: It is concluded that triphenylphosphine may meet the T criterion based on screening data. Experimental ecotoxicity data are not reliable and ECOSAR predicts acute values < 0.1 mg l^{-1}. Due to the fast oxidation it is unlikely, that the substance would elicit effects in the environment. Hence, testing is not considered necessary in the frame of this assessment. The oxidation product triphenylphosphine oxide does not meet the screening T criterion based on the ECOSAR predictions and the available data (data not evaluated by the Rapporteur).

Summary: Triphenylphosphine oxide does not meet the P/vP criteria due to a fast oxidation. Relevant bioaccumulation of the substance is not likely to occur due to the fast oxidation, although screening B criterion is fulfilled. The substance may meet the T criterion based on screening data. The oxidation product triphenylphosphine oxide (CAS 791-28-6) does not meet the screening B and T criteria. The screening P/vP criteria are considered fulfilled for triphenylphosphine oxide. It is concluded that triphenylphosphine is not considered to be a PBT substance.

INFORMATION ON USE AND EXPOSURE

Not relevant as the substance is not identified as a PBT.

OTHER INFORMATION

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

European Commission, 2000a. IUCLID Dataset, triphenylphosphine, CAS 603-35-0, 18.2.2000.

Other sources:

BASF AG (2004) Email of H. Winterling on 8.4.2004 referring to a personal communication on 1.3.2004.

BASF AG (2003) Determination of the Octanol Water Partition Coefficient of Triphenylphosphin (RegNo 31628) -slow stirring method. Studv Code 71995_2, BASF DoclD 2003/1021971, December 16, 2003.

BASF AG (1980) Determination of the Biodegradation of Triphenylphosphine in a Respirometric Test. Reprint of the test report. Date of the test report: 1 February 1980. Date of the reprint: 15 April 2002.

BASF AG (1987a) Determination of the Biodegradation of Triphenylphosphine oxide in a Respirometric Test. Reprint of the test report. Date of the test report: 9 January 1987. Date of the reprint: 15 April 2002. Original registration number: 187186.

European Commission (2000b) IUCLID Dataset, triphenylphosphine oxide, CAS 791-28-6, 19.2.2000.

OSPAR (2003) Draft OSPAR Background Document on Hazardous Substances Identified for Priority Action, Triphenylphosphine. Presented by Germany. Meeting of the Hazardous Substances Committe (HSC), The Hague: 7-11 April 2003. HSC 03/4/11-E.