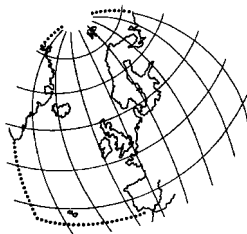


# **Triphenylphosphine**



## **OSPAR Commission 2003 (2005 Update)**

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\* OSPAR 2005 agreed to deselect triphenylphosphine from the List of Chemicals for Priority Action (OSPAR 05/21/1, § 7.5a).

The Convention for the Protection of the Marine Environment of the North-East Atlantic (the “OSPAR Convention”) was opened for signature at the Ministerial Meeting of the former Oslo and Paris Commissions in Paris on 22 September 1992. The Convention entered into force on 25 March 1998. It has been ratified by Belgium, Denmark, Finland, France, Germany, Iceland, Ireland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland and the United Kingdom and approved by the European Community and Spain.

*La Convention pour la protection du milieu marin de l'Atlantique du nord-est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par la Communauté européenne et l'Espagne.*

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ISBN 1-904426-18-2  
Publication Number: 2005/169

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## EXECUTIVE SUMMARY

Triphenylphosphine is a neutral organic chemical. It is used as basic chemical in synthesis and as intermediate for production of complexing agents, reducing agents, process regulators, and pharmaceuticals. The three producers in Europe have confirmed that triphenylphosphine is produced and used in closed systems only. On the basis of the product registers of the Nordic countries, Sweden and Norway reported similar uses of triphenylphosphine. Norway reported some minor open uses in "paint" with a triphenylphosphine content of  $\leq 1\%$ .

The production volume of triphenylphosphine is 3 000 to 5 000 tonnes per year in Europe, about half the amount of which is used in industrial processes in other continents. There are no monitoring data available. Given the intended uses of triphenylphosphine as an intermediate or catalysing agent, the substance is supplied to the processors of the pharmaceutical, agro and chemical industry. According to industry, almost all deliveries of triphenylphosphine are made as pellets and flakes, as the handling and properties of the solid version are favoured. Transport is in sealed containers in accordance with the legal regulations applying and with the high standard of safety precautions and measures required.

Triphenylphosphine is "not readily biodegradable" and is therefore considered to be potentially persistent. It further shows a low acute aquatic toxicity within a wide range of species. Triphenylphosphine has a high estimated octanol – water-partitioning coefficient (log  $P_{OW}$  value), indicating a high potential for bioaccumulation. The data presented in the background document show that triphenylphosphine has a hazard potential, resulting from its intrinsic properties, but since this substance is practically not expected to occur in the environment in significant amounts, the risk for the marine environment is considered low.

At present, there is no need for OSPAR to propose measures for the reduction of emissions of triphenylphosphine. The action recommended is: to avoid any new open/and or widely dispersive uses of triphenylphosphine in order to prevent future risks resulting from changes in use of triphenylphosphine; to invite industry to report any new information on existing open and/or widely dispersive uses of triphenylphosphine and any changes in the use of triphenylphosphine, especially if the changes in use result in an open and/or wide dispersive use; OSPAR to communicate this background document to the European Commission and to other appropriate international organisations which deal with hazardous substances to take account of this background document in a consistent manner.

A monitoring strategy for triphenylphosphine is annexed to this background document.

## RECAPITULATIF

La triphénylphosphine est un produit chimique organique neutre. Il est utilisé comme produit chimique de base dans les synthèses et comme intermédiaire pour fabriquer des agents complexants, des réducteurs, des régulateurs de procédé et des produits pharmaceutiques. Les trois fabricants implantés en Europe ont confirmé que la triphénylphosphine n'était fabriquée et utilisée qu'en circuit fermé. En se fondant sur les nomenclatures de produits des pays nordiques, la Suède et la Norvège ont signalé les mêmes applications pour la triphénylphosphine. La Norvège a fait part de quelques petites applications de la triphénylphosphine dans la peinture, à une teneur  $\leq 1\%$ .

En Europe, le volume de la production de triphénylphosphine se situe entre 3 000 et 5 000 tonnes par an, dont la moitié environ est utilisée dans des procédés industriels sur d'autres continents. Il n'existe aucune donnée qui serait issue de la surveillance continue. Vu les applications prévues pour la triphénylphosphine comme intermédiaire ou comme catalyseur, cette substance est fournie à des transformateurs dans l'industrie pharmaceutique, dans l'agro-industrie et dans l'industrie de la chimie. Selon l'industrie, la presque totalité de la triphénylphosphine est livrée sous forme de granulés et de flocons, en raison des caractéristiques de manipulation de sa version solide et de ses autres propriétés. Le transport se fait dans des récipients scellés conformément aux règles légales applicables, un haut niveau de précautions et de mesures de sécurité étant exigé.

La triphénylphosphine n'est « pas directement biodégradable » et est donc considérée comme potentiellement persistante. Elle possède de plus une faible toxicité aiguë en milieu aquatique pour un large éventail d'espèces. Selon les estimations, la triphénylphosphine possède un haut coefficient de partage octanol-eau (valeur  $\log P_{OW}$ ), indice d'un haut potentiel de bioaccumulation. Les données présentées dans le document de fond prouvent que la triphénylphosphine est potentiellement dangereuse, en raison de ses propriétés intrinsèques ; toutefois, du fait que cette substance n'a pratiquement aucune chance d'être présente dans l'environnement en quantités significatives, le risque pour le milieu marin est considéré comme faible.

Pour l'heure, il n'est pas nécessaire qu'OSPAR propose des mesures visant à réduire les émissions de triphénylphosphine. L'action recommandée consiste à : éviter toute nouvelle application en circuit ouvert et/ou toute utilisation très dispersive de la triphénylphosphine de manière à prévenir les risques qui découleraient dans l'avenir des modifications de son utilisation ; inviter l'industrie à communiquer tout nouvel élément d'information sur les applications actuelles en circuit ouvert et/ou très dispersives de la triphénylphosphine ainsi que tout changement intervenant dans son utilisation, surtout si ces modifications aboutissent à une utilisation en circuit ouvert et/ou très dispersive ; ce qu'OSPAR communique le présent document de fond à la Commission européenne et aux autres organisations internationales compétentes chargées des substances dangereuses, afin qu'elles tiennent compte du présent document de fond dans des conditions cohérentes.

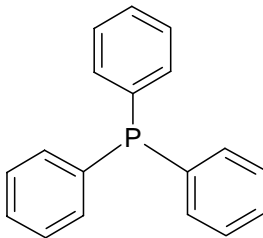
Une stratégie de surveillance sur la triphénylphosphine est annexée à ce document de fond.

## 1. INTRODUCTION

Triphenylphosphine is a neutral (pH) organic chemical. It is a white, odourless, solid compound.

The chemical identity of triphenylphosphine is presented in Table 1; further physico-chemical data are given in Annex 1.

**Table 1: Chemical identity of triphenylphosphine**

CAS-No. 603-35-0 EINECS-No. 210-036-0		triphenylphosphine Synonyms: triphenylphosphorus; triphenylphosphane triphenylphosphide
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For the use in polymers, triphenylphosphine can be functionalised with divinylbenzene that has been lightly (1-2%) cross-linked with a polystyrene backbone (see Material Safety Data Sheet of ARGONAUT TECHNOLOGIES, CA USA). This polystyrene-triphenylphosphine resin seems to be identical with a polymer-supported triphenylphosphine that has been registered under the CAS No. 39319-11-4 (MSDS Aldrich Chemical Co., WI USA; Catalogue No. 366455).

## 2. IDENTIFICATION OF SOURCES OF TRIPHENYLPHOSPHINE AND ITS PATHWAYS TO THE MARINE ENVIRONMENT

### 2.1 Production of triphenylphosphine and main uses

The major producers in Europe have provided information on the production volumes, uses and emissions. Producers are BASF AG (Ludwigshafen, Germany), ROCHE Vitamins Ltd. (Basel, Switzerland), and ATOFINA (Vlissingen, Netherlands). The three producers form a consortium to provide basic data on triphenylphosphine within the framework of the International Council for Chemicals Associations (ICCA)-Programme ([www.ICCA-chem.org](http://www.ICCA-chem.org)).

The production volume of triphenylphosphine is 3 000 to 5 000 tonnes per year in Europe, about half the amount of which is used in industrial processes in other continents (see also IUCLID Dataset 18-FEB-2000).

Triphenylphosphine is used as basic chemical in synthesis and as intermediate in closed systems (non dispersive use; MC I; IUCLID Dataset 18-FEB-2000). It is used for production of complexing agents, reducing agents, process regulators, and pharmaceuticals. All three producers have confirmed that triphenylphosphine is produced and used in closed systems only.

Norway reported (as of 30 October 2002) minor uses of triphenylphosphine in the range of altogether 35 kg. The applications were most frequently related to the "manufacture of basic metals" and the "manufacture of chemicals". The most frequent national use category is reported as "paint" (imported to Norway) with a triphenylphosphine content of  $\leq 1\%$ . Further communication (February 2003) established that the declaration to the Register indicates that such paints are mainly used in ship repairs. The paint appears to be used in professional applications only and is generally not available to consumers. Therefore, there is a potential of triphenylphosphine exposure from these applications, but the significance appears to be low.

Sweden reported a use of 36 tonnes of triphenylphosphine per year. The bulk of the 36 tonnes is used as intermediate, similar as in the rest of Europe. Further, the Swedish Product Register lists two low volume products with a low content of triphenylphosphine. These products are imported and for professional use only. Due to these information releases into the environment can be considered negligible.

Besides the information on uses by the companies and the information from Norway and Sweden, no further information on production or uses was provided.

The use of triphenylphosphine as starting material for Wittig reactions (primarily for the synthesis of vitamins and pharmaceuticals) and the use of triphenylphosphine as catalyst ligand in hydroformylation reaction of olefins (oxosynthesis) are playing a key role in those markets which are supplied by BASF (see Annex 2 with further information on these processes). Furthermore, that means that according to internal BASF guidelines the waste flow (waste disposal, recycling procedures or reuses) is strictly controlled (information provided by BASF, Germany).

Other industrial intermediate uses of triphenylphosphine such as uses as reduction agent, as process additive for the synthesis of polyurethanes (PURs) or as catalysing agent for the hardening and curing reactions of epoxy resins are rounding off the picture of the overall triphenylphosphine uses (*ibid*; see Ullmann's Encyclopaedia of Industrial Chemistry).

Information on the distribution of triphenylphosphine and its transport between environmental compartments is lacking in the IUCLID Dataset (18-FEB-2000). The distribution in a Mackay Level 1 model is calculated according to HANSEN ET AL. (1999) for a log  $P_{OW}$  of 5,02 (Table 2). This gives an impression of the affinity of the substance to different compartments and can be a basis for hazard assessment. The model calculation suggests that the substance enters the environment in a large amount. This, however, is not the case, due to the actual production and use conditions as outlined above.

**Table 2: Distribution of triphenylphosphine to different compartments in a Mackay Level I model (according to HANSEN ET AL. 1999) with a log  $P_{OW}$  of 5,02 (cf. Annex 1)**

Compartment	Percentage of substance distributed (Level I); log $P_{OW}$ 5,02
Air	0,45 %
Water	1,04 %
Sediment	2,14 %
Soil	96,3 %
Biota	0,011 %

According to the fugacity model in equilibrium (Mackay Level I), triphenylphosphine will preferentially distribute to soil (log  $P_{OW}$  5,02; see section 3.2.3). A minimal distribution to air can be attributed to the semi-volatile characteristic of triphenylphosphine.

### 3. MONITORING DATA, QUANTIFICATION OF SOURCES AND ASSESSMENT OF THE EXTENT OF PROBLEMS

#### 3.1 Monitoring and quantification of sources

The IUCLID Dataset (18-FEB-2000) indicates that there are no monitoring data available for triphenylphosphine.

Given the intended uses of triphenylphosphine as an intermediate or catalysing agent, the substance is supplied to the processors of the pharmaceutical, agro and chemical industry. According to industry, almost all deliveries of triphenylphosphine are made as pellets and flakes, as the handling and properties of the solid version are favoured (confirmed by all three producers in Europe). All transportations are made in sealed containers in accordance with the legal regulations applying and with the high standard of safety precautions and measures required. Within the BASF plant in Ludwigshafen, triphenylphosphine is transported by pipeline.

### ***3.1.1 Emissions to the atmosphere***

According to the information provided by industry, emissions into the atmosphere are lower than 25 kg/year and therefore have not to be reported to the German authorities. Emission from pellets and flakes does practically not occur because containers are sealed during transport.

As triphenylphosphine has no emission threshold limit or any other air threshold limit within the EU, triphenylphosphine is not monitored in air. However, an actual emission to air is not expected.

### ***3.1.2 Riverine inputs to the North Sea***

At the production sites in Europe triphenylphosphine is actually not monitored in effluents discharged.

## **3.2 Assessment of the extent of the problem**

### ***3.2.1 Physico-chemical properties***

Representative physico-chemical data of triphenylphosphine are presented in Annex 1.

### ***3.2.2 Biotic and abiotic degradation***

#### **Aerobic biodegradation**

A respirometry test (1980; non-GLP (non-Good Laboratory Practice)) was conducted under similar conditions as prescribed in the later OECD-Guideline 301 F (Manometric Respirometry Test). Test substance concentration was 200 mg/l, industrial sludge was used and peptone as co-substrate. No inhibition of bacterial growth by triphenylphosphine was observed in a pre-test. The test resulted in less than 20% oxygen consumption in 28 days. A substance can only be considered to be readily biodegradable if the endpoint value (in this case O<sub>2</sub>-consumption) is higher than a certain pass level (in this case 60% of the theoretically expected O<sub>2</sub>-consumption). Since O<sub>2</sub>-consumption for triphenylphosphine was far lower than the pass level, triphenylphosphine is characterised as "not readily biodegradable" (IUCLID Dataset 18-Feb-2000).

Even though this test was not performed according to current guidelines, test conditions are described sufficiently to show that even under these favourable degradation conditions, triphenylphosphine will not degrade to a high degree. Therefore, the test result can be considered as valid.

This type of screening tests does not allow the estimation of half-lives. However, according to the revised Technical Guidance Document (TGD)<sup>1</sup>, when results from biodegradation tests simulating the conditions

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<sup>1</sup> The Technical Guidance Document (TGD) was revised and has been published in April 2003. It contains a new chapter on marine risk assessment and criteria for the assessment of persistence, bioaccumulation potential and toxicity (PBT) of substances, which may pose a risk for the marine environment. Risk assessment in this background document follows the PBT assessment scheme in the revised TGD, a draft of which has already been available in the 2<sup>nd</sup> half of 2002. This risk assessment methodology has been formally agreed by the EC in April 2003 and has been adopted by the OSPAR Commission in June 2003 as the common EU/OSPAR risk assessment methodology for the marine environment.



in surface waters are not available, the use of results from various screening tests may be considered, and mineralisation half-lives (days) are recommended according to the outcome of degradation screening tests. A substance, which is "not readily biodegradable", is to be considered to have an indefinite half-life. According to the marine PBT assessment (revised TGD, 2003; Chapter 3, Sections 4.2.3.4, 4.4.2 and 4.4.3.5) it is suggested that, in the absence of other biodegradation tests, in particular simulation tests in freshwater and/or saltwater, a characterisation as "persistent" or "very persistent" may be derived from the screening test result.

Triphenylphosphine has a low water solubility (see Annex 1). By means of mechanical precipitation it can be eliminated in sewage treatment plants (IUCLID Dataset 18-Feb-2000).

### Atmospheric degradation

The specific degradation rate constant of triphenylphosphine with hydroxyl radicals in the atmosphere was calculated to  $5,85 \cdot 10^{-12} \text{ cm}^3/\text{molecule} \cdot \text{sec}$  from the structure of the molecule. From this, the pseudo-first-order rate constant for degradation in air can be calculated according to the TGD (24 h day,  $5 \cdot 10^5 \text{ OH}/\text{cm}^3$ ) to 0,25. The resulting half-life of 2,74 days corresponds to 65,8 hours.

### Combustion

When triphenylphosphine is heated to decomposition, e.g. in case of accidents, carbon dioxide, carbon monoxide, phosphorous oxides, and phosphine are formed, which are irritating or toxic (see also ILO ICSC).

### 3.2.3 Bioaccumulation

The  $\log P_{OW}$  has been estimated according to the method laid down in Council Directive 92/69/EEC (No. A.8). However, the concentration of the test substance in the water phase was so low that only a limit of 0,005 mg/l could be determined in the UV-spectroscopy. From this, the  $\log P_{OW}$  was calculated to  $> 2,59$  (information provided by BASF). Later measurements of the water solubility (0,165 mg/l) indicate, that a higher concentration should have been detected in the water phase, which would result in a lower  $\log P_{OW}$ . Considering the uncertainty in the performance of the test, the  $\log P_{OW}$  of 2,59 should be disregarded. However, an experimental determination of the  $\log P_{OW}$  is presently ongoing, which, in future, can replace the estimates in Table 3.

Information on bioaccumulation (in terms of bioconcentration, BCF) for triphenylphosphine can be derived from the  $\log P_{OW}$ . In Table 3, BCF calculations are summarised:

**Table 3: BCF values for triphenylphosphine, calculated from estimated  $\log P_{OW}$  values**

<b><math>\log P_{OW}</math></b>	<b>Source of <math>\log P_{OW}</math></b>	<b>Calculated BCF</b>	<b>Calculation method for BCF</b>	<b>Remarks</b>
5,02	KOWWIN v1.66	1 464	MEYLAN ET AL. 1999	$\log P_{OW}$ calculation is independent of water solubility
5,5	OSPAR Fact sheet	4 786	?	
5,69	HANSCH ET AL. (1995) data base	4 801	MEYLAN ET AL. 1999	

With the method of MEYLAN ET AL. (1999) BCFs can be calculated as follows:

$$\log \text{BCF} = 0,77 * \log P_{\text{OW}} - 0,70;$$

no correction factors applied.

The method of MEYLAN ET AL. (1999) is improved against the method of VEITH ET AL. (1979) which is:

$$\log \text{BCF}_{\text{fish}} = 0,85 * \log P_{\text{OW}} - 0,70.$$

However, VEITH ET AL. (1979) is mentioned in the TGD (rev. 2003; Chapter 3, Section 3.8.3.2 and Chapter 4 on the use of QSARs). The method of VEITH ET AL. (1979) generally results in higher BCF values.

Calculated BCF values in Table 3 vary according to the variation of the log  $P_{\text{OW}}$  values, all being higher than 5. Therefore, a potential for bioaccumulation has to be assumed. According to the marine PBT-assessment, the trigger for the B-criterion is  $\text{BCF} > 2\,000$ . Two of the BCF estimates exceed this trigger (i.e. 4 786 and 4 801). Therefore, the B-criterion is potentially met for triphenylphosphine based on QSAR calculations. The criterion for "very bioaccumulative" (vB;  $\text{BCF} > 5\,000$ ) is fulfilled, when the BCF is calculated with the method of VEITH ET AL. (1979; i.e.  $\text{BCF} = 13\,693$ ).

Further, the estimated log  $P_{\text{OW}}$  values in Table 3 (log  $P_{\text{OW}}$ : 5,02-5,69) exceed the trigger of 4,5. According to the marine PBT assessment, a substance is considered to potentially fulfil the B-criterion, when the log  $P_{\text{OW}}$  exceeds a value of 4,5.

### 3.2.4 Acute and chronic ecotoxicity effects

Some data on ecotoxicity of triphenylphosphine are given in the following Table 4.

**Table 4: Data on the ecotoxicity of triphenylphosphine**

Triphenylphosphine CAS No. 603-35-0					
Test organism	Trophic level / Habitat	Endpoint / Effect	Test conditions	Endpoint concentration	Source Year
<i>Photobacterium phosphoreum</i>	Micro-organism FW	EC <sub>50</sub>	Microtox-Test 30 min.	1,54 mg/l	[1] 1991
<i>Desmosdesmus subspicatus</i>	pProd FW	EC <sub>50</sub> GRO	3d; STA; eluate OECD 201	> 5 mg/l nominal	[2] 1999
<i>Daphnia magna</i>	pCons FW	EC <sub>50</sub> IMM	2 d; STA; aux. EEC C.2	0,6 mg/l	[3] 1988
<i>Daphnia magna</i>	pCons FW	EC <sub>50</sub> IMM	2 d; STA; eluate EEC C.2	> 5 mg/l nominal	[2] 1999
<i>Leuciscus idus</i>	sCons FW	LC <sub>50</sub> MOR	4 d; STA; DIN 38 412	> 10 000 mg/l	[4] 1982

[1] IUCLID Data Set 17-Feb-2000 (KAISER ET AL. 1991; non-GLP).

[2] IUCLID Data Set 2002 (internal report from BASF 99/0479)

[3] IUCLID Data Set 17-Feb-2000 (internal Report from BASF 88/1165; non-GLP).

[4] IUCLID Data Set 17-Feb-2000 (internal Report from BASF 88/654; non-GLP).

Complete references may be obtained from the IUCLID Dataset.

pProd: primary producer; pCons: primary consumer; sCons: secondary consumer; FW: freshwater species; GRO: Growth; MOR: Mortality; IMM: Immobilisation; STA: static test; aux: an auxiliary substance for solving the chemical (solubilising agent) was used in the test.

The 1988 *Daphnia* study [3] with triphenylphosphine was performed above the water solubility of the substance and in presence of a dispersant (solubilising agent). This was possibly responsible for a higher toxicity caused by an enhanced bioavailability or by physical effects. Since some years, it is therefore recommended by the respective guidelines to run studies in the range of the water solubility and if possible without dispersant (information provided by industry).

In the new *Daphnia* study [2] a saturated solution of triphenylphosphine was prepared by using 2 to 5 times the amount of the water solubility concentration (0,165 mg/l at 20 °C; therefore, stock solution is 5 mg/l) in order to increase the speed of the dissolving process. After an appropriate mixing time (e.g. 24 h), substance, which is not dissolved, is separated. With the eluate, the test with *Daphnia* was performed<sup>2</sup>. The EC<sub>50</sub> was not reached after 48 h, the result therefore being "EC<sub>50</sub> (48h) > 5 mg/l nominal (no relevant effect at the range of water solubility)". Triphenylphosphine and its possible oxidation product, triphenylphosphineoxide, cannot be distinguished technically at very low concentrations in the test medium. Therefore, concentration control analyses and the stability of the test item in the test medium have not been determined<sup>3</sup>. Nevertheless, the test result is considered valid if it is referred to the water solubility (EC<sub>50</sub> > 0,165 mg/l).

According to current classification criteria, a substance with a low water solubility, if tested as an eluate with the respective low substance concentration, has not to be classified according to the aquatic toxicity ranges (R50 to R52; "very toxic/toxic/harmful to aquatic organisms") if no toxicity occurs at the range of water solubility. Nevertheless, the criteria for R53 have been met, which means that, if the substance has a water solubility below 1 mg/l and is not biodegradable, the R53 ("may cause long-term adverse effects in the aquatic environment") has to be given (*ibid.*).

From the EPIWIN 3.20 QSAR programme estimated ecotoxicity concentrations are reported for triphenylphosphine as a neutral organic substance, which are below 1 mg/l. However, the cut-off for such calculations is a log P<sub>ow</sub> of 5,0, which is exceeded in the case of triphenylphosphine (log P<sub>ow</sub> 5,02-5,69).

The information available on the ecotoxicity of triphenylphosphine and in particular the results from the newer *Daphnia* study are considered in the light of the marine PBT assessment. In the absence of accurate chronic aquatic toxicity data, a decision is based on the available acute test, which shows that no toxicity is observed at the limit of water solubility (0,165 mg/l). Acute toxicity to *Daphnia* is therefore above the trigger of 0,1 mg/l (for acute toxicity test results). Therefore, it is concluded that the T-criterion is not met for triphenylphosphine.

### **3.2.5 Carcinogenicity, mutagenicity or harmful reproductive effects**

Several tests on genetic toxicity in vitro showed to be negative (Ames, DNA damage and repair assay, *E. coli* and *Salmonella typhimurium* reverse mutation assay, micronucleus and SOS induction test; IUCLID Dataset 18-Feb-2000). A micronucleus assay in vivo conducted in mouse was negative (information provided by BASF).

Tests on carcinogenicity are not reported. In a 90 days repeated dose study on male and female rats (substance administration by oral gavage at 6, 60 and 120 mg/kg body weight (bw) the NOAEL was determined as 6 mg/kg bw. Apart from a slight decrease in testicular spermatid count in the highest dose group, which was not paralleled by a decrease of total sperm count, no statistically significant effects were seen on the male nor on the female reproductive organs. No signs of neurotoxicity were observed.

<sup>2</sup> The testing strategy has been described in the "VCI-strategy for testing the acute toxicity of sparingly soluble substances and mixtures" (1996; VCI: Verband der chemischen Industrie in Deutschland) and has consent from the authorities. The criteria for classification of sparingly soluble substances, e.g. eluates, were also accepted in the international process of harmonisation of classification and labelling.

<sup>3</sup> In another experiment, using air and helium as atmosphere above the solution, it was demonstrated that oxidation to triphenylphosphineoxide is insignificant and triphenylphosphine is stable also in the presence of oxygen.

There was a statistically significant increase in liver weights both in the male and female animals at the highest dose group and in female animals only in the intermediate dose group. The females also showed an increase in kidney weight at the highest dose (*ibid.*).

This leads to the conclusion that CMR properties do not seem significant.

### **3.2.6 Toxicological effects**

Several acute oral toxicity studies on rats show LD<sub>50</sub> values of 700 to more than 6 400 mg/kg bw (IUCLID Dataset 18-Feb-2000). LD<sub>50</sub> for mouse is in the range of 800-1 600 mg/kg bw. Rabbits show lethality above 2 000 mg/kg bw. 300 to 600 mg/kg bw may well affect cats and dogs, while hens react only slightly at concentrations above 5 000 mg/kg bw (*ibid.*).

Acute inhalation toxicity is reported for male rats with a LC<sub>50</sub> of 12,5 mg/l during a 4 hours exposure interval. The atmospheric concentrations of triphenylphosphine were generated by nebulising triphenylphosphine molten under dry nitrogen atmosphere and dilution of the enriched nitrogen stream to 20 % oxygen prior to entering the exposure chamber. Clinical signs were typical of respiratory irritation. No triphenylphosphine-related histopathological findings were reported (information provided by BASF).

Triphenylphosphine was not irritating on skin of rabbits and guinea pigs. Also eye irritation was not observed in rabbits. In a guinea pig maximisation test (Council Directive 84/449/EEC, B.6) skin sensitisation was observed (IUCLID Dataset 18-Feb-2000).

Sub-acute neurotoxicological tests on dogs, cats, rabbits and ferrets (100 – 500 mg/kg p.o., i.m. and s.c.) showed neurotoxicological effects and signs such as convulsions and paralysis. Experiments in chicken, however, did not show a peripheral neurotoxicity as it is commonly observed with organic phosphates. A 90-day study in rats with oral administration did not reveal neurotoxicological effects (IUCLID Dataset 18-Feb-2000 and information provided by BASF).

This leads to the conclusion that triphenylphosphine must be considered as "harmful" when incorporated but neurotoxicological effects are not pronounced.

## **3.3 Risk to the environment**

Triphenylphosphine was selected as priority substance according to the DYNAMEC criteria partly based on QSAR data. Revision of data and application of the risk assessment based on the criteria as outlined in the Technical Guidance Document have led to the following assessment of the substance.

Triphenylphosphine showed to be "not readily biodegradable". Since no other biodegradation tests were available, this screening test result may be used to evaluate the P-criterion according to the marine P assessment. Therefore, triphenylphosphine is considered to be potentially persistent (P- or vP criterion is met).

Triphenylphosphine is to be considered as semi-volatile, but the partition model on Mackay Level I indicates only a minimal distribution into air (for log P<sub>OW</sub> 5,02), if a release would actually occur. In principle, the calculated half-life of 2,74 days would allow a considerable long-range air transport.

Triphenylphosphine shows a low acute aquatic toxicity within a wide range of species. In recent experiments with eluates, it was demonstrated that triphenylphosphine does not show toxicity to *Daphnia* in the range of water solubility. In the absence of accurate chronic aquatic toxicity data, a decision is based on the available acute toxicity test to *Daphnia*, which is above the trigger of 0,1 mg/l (for acute toxicity test results; cf. marine PBT assessment). Therefore, the T-criterion is not met.

With regard to human health, triphenylphosphine is considered as "harmful" when incorporated but neurotoxicological effects are not pronounced. Further, CMR properties do not seem to be significant.

Triphenylphosphine has an estimated log  $P_{OW}$  value of more than 4,5 (i.e. 5,02-5,69). According to the marine PBT assessment, triphenylphosphine is therefore considered to potentially meet the B-criterion.

The bioaccumulation, expressed as BCF calculated from log  $P_{OW}$  values, ranges from about 1 460 to 4 800. Thus, a BCF > 2 000 exists and the B-criterion can be considered fulfilled. Considering further that the BCF calculated according to MEYLAN ET AL., 1999, nearly reaches 5 000 (i.e. 4 801) and another calculation method (VEITH ET AL., 1979) achieves a far higher calculated BCF (13 693) triphenylphosphine may be considered as a vB substance. It should be borne in mind, that this decision is based on estimated log  $P_{OW}$  and BCF values. An experimental determination of the log  $P_{OW}$  is presently ongoing.

The use of triphenylphosphine in open applications, was reported by Norway with a total consumption of 35 kg per year, resulting in a very low potential exposure to the marine environment. Also from Sweden two low volume products for professional use were reported to contain triphenylphosphine in low amounts (< 1%). A considerable amount of triphenylphosphine (36 t) is used in Sweden as intermediate.

All other presently available information on uses, as provided by industry and from the Nordic Product Registers, indicates that triphenylphosphine is generally used as intermediate and basic chemical in closed processing systems. Transport is either in pipelines within factories or as pellets and flakes in sealed containers. Under normal handling conditions, there is no contact with the environment of triphenylphosphine in production, transport, use waste-disposal, recycling or reuse. Except in the case of an accident, it is very unlikely that triphenylphosphine will enter the environment and lead to a marine exposure.

The data presented here show that there is a hazard potential by triphenylphosphine, resulting from its PBT properties according to DYNAMEC criteria, but since this substance is practically not expected to occur in the environment in significant amounts, the risk for the marine environment is lower than anticipated.

Triphenylphosphine cannot be considered to be a PBT-substance according to the TGD marine PBT assessment since the T-criterion is not met, but it may be considered a vPvB substance. Regardless of that, a performance of a quantitative marine risk assessment (PEC/PNEC-risk quotients) does not seem appropriate, since this substance is practically not expected to occur in the environment in significant amounts due to its almost exclusive use in closed applications.

## 4. DESIRED REDUCTION

According to its intrinsic properties, triphenylphosphine is a "harmful" substance, and its deliberate release to the marine environment should be avoided.

However, since it is used virtually entirely as an intermediate or basic chemical in closed production, as far as has become known, there is presently no indication of a marine exposure.

Therefore, no reduction objective is presently provided. If, in future, triphenylphosphine should be used in significant amounts in an open application or in a matrix, appropriate measures should be taken to avoid entry into the marine environment.

## **5. REVIEW OF AGREED MEASURES AND POSSIBLE SUBSTITUTES**

### **5.1 Review of agreed national and international measures for the regulation of triphenylphosphine**

#### **OSPAR Strategy with regard to Hazardous Substances**

Triphenylphosphine was selected in the DYNAMEC process early in 2000. At the OSPAR Commission meeting in 2001 triphenylphosphine was selected as a priority substance and Germany volunteered in the preparation of the background document. Under the assumption that triphenylphosphine is used exclusively as an intermediate in closed production systems, OSPAR's Working Group on Priority Substances agreed in 2001 that the background document should be prepared in an abbreviated manner ("tailored approach"). The working group provided evidence to underpin that assumption.

#### **Water Framework Directive 2000/60/EC**

Triphenylphosphine is not included in the priority list of the Water Framework Directive 2000/60/EC.

#### **Council Regulation (EEC) No. 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances**

Under the Regulation (EEC) 793/93, triphenylphosphine has been included in the EINECS list of existing substances produced or imported within the Community in quantities exceeding 1 000 tonnes per year and an appropriate data reporting has been established.

#### **The new EU Chemicals legislation**

Triphenylphosphine, considered as a vPvB substance, and regarded as an intermediate with a certain distribution, may be recognised as a substance for authorisation in the future EU Chemicals legislation.

#### **Administrative rules concerning substances hazardous to water**

Triphenylphosphine is officially classified as "weakly water polluting" (Water Hazard Class 1/ Wassergefährdungsklasse 1, WGK) according to the German Administrative Regulation relating to Substances Hazardous to Water (Verwaltungsvorschrift wassergefährdende Stoffe; Bundesanzeiger Nr. 51, 98a, 1 (1999)). The purpose of the classification is to identify the technical requirements of industrial plants, which handle substances hazardous to water. Presently, a reclassification is discussed relating to the available neurotoxicological studies.

#### **Other administrative rules**

The present German list of occupational exposure limits TRGS 900 (Technische Regeln für Gefahrstoffe - Grenzwerte in der Luft am Arbeitsplatz) does not give a value for triphenylphosphine. The IUCLID data set (18-Feb-2000), as the older source, states a value of 6 mg/m<sup>3</sup>.

### **5.2 Choice of substitutes**

For the intended uses of triphenylphosphine (see Section 2.1), substitutes are not known.

## **6. CHOICE FOR ACTION/MEASURES**

According to the information available, it has become clear that triphenylphosphine is nearly entirely produced and used in closed systems, and transportation of this substance in solid form is normally not a

source of environmental contamination. The data presented in this background document show that there is a hazard potential by triphenylphosphine, resulting from its PBT properties, but since this substance is practically not expected to occur in the environment in relevant amounts, the risk for the marine environment from exposure to this substance does not justify specific measures.

### **The conclusion on the avoidance of future risks**

According to the TGD PBT assessment, triphenylphosphine only meets the thresholds for P- and B-criteria. However, according to the criteria related to the OSPAR Hazardous Substances Strategy, triphenylphosphine still has to be regarded as hazardous substance according to the DYNAMEC PBT-criteria. Accordingly, in accordance with the strategy,

- OSPAR confirms that triphenylphosphine requires to be treated as a hazardous substance for the purpose of the Hazardous Substances Strategy.

Nevertheless, at present, there is no need for OSPAR to propose measures for the reduction of emissions of triphenylphosphine.

In order to avoid future risks resulting from changes in use of triphenylphosphine,

- Contracting Parties should avoid any new open/and or widely dispersive uses of triphenylphosphine;
- OSPAR should invite Contracting Parties to report
  - (i) any new information on existing open and/or widely dispersive uses of triphenylphosphine,
  - (ii) any changes in the use of triphenylphosphine, especially if the changes in use result in an open and/or wide dispersive use.
- OSPAR should invite industry to report significant changes in the production volume and in the use of triphenylphosphine to OSPAR, so that an evaluation of the risk to the marine environment can be reviewed, if necessary.

In order to avoid future risks resulting from the use of triphenylphosphine as intermediate,

- OSPAR should invite Contracting Parties to check that the operation of the plants using triphenylphosphine is controlled according to the principles of BAT (Best Available Techniques) and that any releases are eliminated or minimised to the greatest extent possible.

### **The need for consistency in actions by other bodies**

To ensure that the information in this background document and the conclusions reached by OSPAR are taken into account in the approach of the European Community,

- OSPAR should communicate this background document to the European Commission for information.

To ensure that the information in this background document can be considered in the context of other international agreements which deal with hazardous substances, and with which Contracting Parties are associated,

- OSPAR should send copies of this background document to the appropriate bodies dealing with those agreements and invite Contracting Parties who are parties both to OSPAR and those other agreements to promote action to take account of this background document by those other international bodies in a consistent manner.

## 7. REFERENCES

European Commission (2003): Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) 1488/94 on Risk Assessment for existing substances, Directive 98/8/EC of the European Parliament and the Council concerning the placing of biocidal products on the market. Part II, 2<sup>nd</sup> edition, 328 p., No. EUR 20418 EN/2.

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ILO (International Labour Organization) ICSC (International Chemical Safety Cards) (1994): Triphenylphosphine, ICSC 0700 (April 1994).

IUCLID (2000): Dataset for triphenylphosphine. CAS No. 603-35-0; created 18-FEB-2000 (European Commission, European Chemicals Bureau); 47 p.

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Meylan, W.M.; Howard, P.H.; Boethling, R.S.; Aronson, SD.; Printup, H.; Gouchie, S. (1999): Improved method for estimating bioconcentration/bioaccumulation factor from octanol/water partition coefficient. *Environm. Toxicol. Chem.* 18 (4): 664-672.

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Veith, G.D.; DeFoe, D.L.; Bergstedt, B.V. (1979): Measuring and estimating the bioconcentration factor of chemicals in fish. *J. Fish Res. Board Can.* 36:1040-1048.

### EU-DIRECTIVES QUOTED

**2000/60/EC:** Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. Official Journal No. L 327 of 22/12/2000, p. 1-73.

**EEC 793/93:** Council Regulation (EEC) No. 793/93 of 23 March 1993 on the evaluation and control of the risks of existing substances. Official Journal No. L 84 of 5/4/1993, p. 1.



## ANNEX 1: PHYSICO-CHEMICAL PROPERTIES OF TRIPHENYLPHOSPHINE

Property	Value	Source
Chemical name	triphenylphosphine	IUCLID Dataset (18-Feb-2000)
CAS-No.	603-35-0	IUCLID Dataset (18-Feb-2000)
EEC No. (EINECS)	210-036-0	IUCLID Dataset (18-Feb-2000)
Molecular formula	C <sub>18</sub> H <sub>15</sub> P	
Molecular Mass M [g/mol]	262,29	EPIWIN 3.20
Physical state of matter at 20 °C	solid	IUCLID Dataset (18-Feb-2000)
Colour / odour	white / none	
Density [g/cm <sup>3</sup> ]	1,194 at 20 °C	IUCLID Dataset (18-Feb-2000)
Melting point T <sub>m</sub> [°C]	78,5 – 81,5 109	IUCLID Dataset (18-Feb-2000) EPIWIN 3.20 (mean or weighted)
Boiling point T <sub>b</sub> [°C]	195 – 205 at 7 hPa 375	IUCLID Dataset (18-Feb-2000) EPIWIN 3.20 (adap. Stein & Brown method)
Solubility in water S [g/l]	3,4*10 <sup>-7</sup> 9*10 <sup>-5</sup> at 25 °C (meas.) 1,65*10 <sup>-4</sup> at 20 °C (meas.) 2,8*10 <sup>-4</sup> at 25 °C (calc.)	OSPAR fact sheet <sup>4</sup> IUCLID Dataset (BASF 1988) BASF (1992) EPIWIN 3.20 <sup>5</sup>
log P <sub>ow</sub>	(> 2,587 at 25 °C) 5,02 at 25 °C (calc.) 5,69 (estimated)	IUCLID Dataset (18-Feb-2000) <sup>6</sup> EPIWIN 3.20 HANSCH ET AL. (1995; ref. in EPIWIN 3.20)
Adsorption coefficient log K <sub>oc</sub> [l/kg]	5,65 (calc.)	EPIWIN 3.20 <sup>7</sup>
Vapour pressure P [Pa]	1 at 88 °C 1,33 * 10 <sup>-3</sup> (at 25 °C) 1,36 * 10 <sup>-3</sup> at 25 °C	IUCLID Dataset (18-Feb-2000) OSPAR fact sheet (DK-QSAR) EPIWIN 3.20 (mod. Grain meth.)
Henry's Law constant [-]	9,24*10 <sup>-7</sup> (calc. at 25 °C) 5,15*10 <sup>-4</sup> (calc. at 25 °C)	EPIWIN 3.20 (Bond method) <sup>8</sup> EPIWIN 3.20 (Vp/Wsol*RT) <sup>9</sup>

<sup>4</sup> This value on water solubility can not be confirmed by the producer (BASF).

<sup>5</sup> The water solubility of 2,8 \* 10<sup>-4</sup> g/l from EPIWIN 3.20 is based on a log P<sub>ow</sub> of 5,69. Using a lower log P<sub>ow</sub> of 2,56 (IUCLID data set) results in a water solubility of 0,132 g/l which appears completely unrealistic.

<sup>6</sup> The log P<sub>ow</sub> is given in the IUCLID data set with "more than" 2,59. The test substance could not be determined in the water phase over a limit of 0,005 mg/l. This test result is considered invalid.

<sup>7</sup> The log K<sub>oc</sub> value of 5,65 is probably based on a log P<sub>ow</sub> of 5,17 (own calculations according to KARICKHOFF or SABLJIC result in slightly lower log K<sub>oc</sub> values (resp. 5,28 or 5,15)).

<sup>8</sup> This value for the Henry's Law constant is also stated by BASF. When considering a lower log P<sub>ow</sub> (2,56) and re-running EPIWIN 3.20, the method from KLÖPFFER (1996; Vp/Wsol\*RT) results in a similar value of 1,1\*10<sup>-6</sup>.

<sup>9</sup> This calculation method for the Henry's Law constant is described in KLÖPFFER (1996).

Property	Value	Source
Volatilisation from water: Half-life from river model [h] Half-life from lake model [h]	4,2*10 <sup>4</sup> (1748 d) 4,6*10 <sup>5</sup> (19 079 d)	EPIWIN 3.20 (using Henry LC 9,24 * 10 <sup>-7</sup> )
Reactivity with OH-radicals atmospheric half-life [d]	no data available 1,83 (eq. 22 h) 2,74 (eq. 66 h)	IUCLID Dataset (18-Feb-2000) EPIWIN 3.2 (OSPAR fact sh.) <sup>10</sup> Calculation acc. TGD
Hydrolysis half-life [d]	no data available -	IUCLID Dataset (18-Feb-2000) EPIWIN 3.20 <sup>11</sup>
Toxicological classif. (EU)	Xn (harmful)	MSDS BASF (2002) <sup>12</sup>
R-Phrases	R22, R43, R53	MSDS BASF (2002)
S-Phrases	S22, S24, S61	MSDS BASF (2002)

<sup>10</sup> The atmospheric half-life is calculated on a basis of a 12-hour day and 1,5 \* 10<sup>6</sup> OH-radicals/cm<sup>3</sup>.

<sup>11</sup> EPIWIN 3.20 could not estimate a hydrolysis rate constant for the structure of triphenylphosphine.

<sup>12</sup> According to new test results, the R50 is no longer appointed to triphenylphosphine (see § 30; BASF MSDS 2002). As only the R53 is left, triphenylphosphine must no longer be classified with the N-symbol ("environmentally dangerous"). Presently a reclassification with respect to R-phrases is discussed relating to the available neurotoxicological studies.

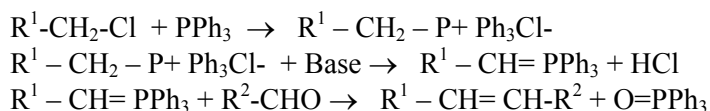
## ANNEX 2: INFORMATION PROVIDED BY THE BASF AKTIENGESELLSCHAFT (LUDWIGSHAFEN, GERMANY) ON 20 AUGUST 2002

### Triphenylphosphine is used:

#### *As starting material for Wittig reactions*

The Wittig reaction is widely used in the production of vitamins, carotenoids, pharmaceuticals, antibiotics, crop protection agents and cosmetics.

It proceeds according to the following scheme:



e.g. the Vitamin A synthesis is using the Wittig reaction for achieving the C<sub>20</sub>-skeleton.

The Wittig reaction is characterised by mild reaction conditions and high yields. Its more widespread use is hindered by the fact that equimolar amounts of TPP must be used. Since TPPO is not easily degraded and phosphorous must not be present in wastewater, the TPPO containing residues are incinerated to form P<sub>2</sub>O<sub>5</sub>, which is removed in a scrubber with the aid of dilute sodium hydroxide solution. Phosphorus is then precipitated as calcium phosphate and filtered off and the filter cake is disposed of on a hazardous waste dump.

As this disposal method has several disadvantages attempts were made to convert inactive TPPO back to active TPP, which could then be used again in the Wittig reaction. A route along the following lines was ultimately found by BASF to be successful:

The TPPO-containing residues are dissolved in chlorobenzene and reacted with phosgene gas to form triphenylphosphine chloride, with liberation of CO<sub>2</sub>. In the second step, finely divided aluminium powder is added with mixing. The TPP · AlCl<sub>3</sub> complex formed is then decomposed hydrolytically in a third reaction step, giving the desired TPP.

Process at BASF: The TPPO-containing residues from various operations are collected. Pure TPPO is recovered by distillation and dissolved in chlorobenzene.

Chlorination is carried out in a stirred-tank reactor inside a gastight chamber. Phosgene is also generated in this chamber and fed immediately to the reactor.

Dehalogenation with aluminium powder is carried out in the next stirred-tank reactor.

The TPP · AlCl<sub>3</sub> complex is then hydrolytically decomposed with water in another stirred tank in which the pH is adjusted with HCl so that water-soluble Al(OH)Cl<sub>2</sub> is formed. The TPP is dissolved in the chlorobenzene layer. Traces of TPP are recovered from the aqueous phase by extraction with chlorobenzene. In a subsequent distillation stage, chlorobenzene is distilled off and recycled. The TPP is then purified by distillation. The aqueous phase from the extraction stage is fed to a sewage treatment plant, which operates in the weakly alkaline range, so that aluminium is precipitated as Al(OH)<sub>3</sub> and acts as a flocculation agent in the desired manner.

The ecological advantages of the new process can be seen from a comparison of the ecological balances:

The new process results in the complete absence of phosphorus emissions, a reduction of the chloride load of the wastewater to one-third of its former value, and a reduction of CO<sub>2</sub> emission to only ca. 5% of its former value.

### ***As catalyst ligand in hydroformulation reactions of olefins***

Homogeneous catalysis by platinum group metals, especially rhodium, has made a major impact in industrial chemistry. Important characteristics of these catalysts include high activity and, therefore, low concentration; high selectivity leading to absence of side products; and mild reaction conditions, enabling the use of low temperature and pressure and facilitating the control of reaction conditions.

The discovery of chlorotris(triphenylphosphine)rhodium(I),  $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ , a highly effective hydrogenation catalyst opened a new chapter in homogeneous catalysis and in the complex chemistry of rhodium. Today, a number of modified complexes of this and similar types are known.

Homogeneous catalysis by rhodium complexes in *oxo synthesis (hydroformylation)* has attained great importance and made possible the synthesis of industrially important aldehydes from alkenes, the so-called Oxo Synthesis. This process was formerly carried out with homogeneous cobalt catalysts. Initially,  $[\text{RhCl}\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$  was used as catalyst; subsequently, halogen-free catalysts were introduced. Some of these can be used at room temperature, whereas cobalt complexes require temperatures up to 200 °C, necessitating the use of high-pressure reactors. Generally, the catalytically active compound is not manufactured. Instead, other compounds are used as precursors from which the actual catalyst is formed during the reaction. These include  $[\text{Rh}(\text{CO})_2 \text{acac}]$ ,  $[\text{Rh}\{\text{P}(\text{C}_6\text{H}_5)_3\}(\text{CO}) \text{acac}]$ , and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ , which form the catalyst  $[\text{RhH}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$ .

*Carbonylhydrido-tris(triphenylphosphine)rhodium(I)*, carbonyl-tris(triphenylphosphine)rhodium(I) hydride, forms yellow crystals that are stable in air, and melt at 172 – 174 °C in a closed nitrogen-filled capillary. It is readily soluble in benzene, chloroform, and dichloromethane. In solution, one phosphine ligand is readily lost by dissociation to give a 16-electron complex that is an active catalyst for the hydrogenation of alkenes and for hydroformylation.

This complex is obtained by the reaction of a solution of  $\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$  in alcoholic alkali with aqueous formaldehyde (the carbon monoxide source) and an excess of triphenylphosphine. The commercial product is a microcrystalline powder with a purity of 97 % (Degussa).

Carbonylhydrido-tris(triphenylphosphine)rhodium(I) is used in industry for the hydroformulation reaction. The reaction takes place rapidly at 25 °C giving a product in which the ratio of n- to iso-aldehydes is very favourable (ca. 20 : 1), a much higher ratio than can be obtained with cobalt catalysts.

#### ***Low-Pressure Oxo (LPO) process:***

In the mid-1970s Union Carbide and Celanese succeeded in using rhodium – triphenylphosphine catalysts for the hydroformylation of olefins on an industrial scale. Since then some other companies have developed modifications of this process. The most important of these, however, is the low-pressure oxo (LPO) process jointly developed by Union Carbide, Davy McKee, and Johnson Matthey.

A detailed description of this specific low-pressure route follows with the conversion of propene to butyraldehyde as an example:

The reaction takes place in a stirred-tank reactor made of stainless steel. The reactants and supplementary catalyst to make up for catalyst lost in production are fed in from below. Due to the sensitivity of the rhodium catalyst system toward catalyst poisons, the olefin and synthesis gas or hydrogen used as makeup gas must first be carefully purified. The reactor contains the catalyst dissolved in high-boiling reaction by-products. In order to maintain catalyst activity a portion of the solution must be continuously removed and reprocessed separately, and the noble metal and the phosphine returned to the process. From time to time, all of the catalyst must be removed and reprocessed externally. The hydroformylation reaction takes place at < 20 bar and 85 – 115 °C. The reactor jacket is cooled to remove the heat of reaction. The reaction products and unreacted gaseous

reactants (conversion of about 30 % per pass) are forced out of the reactor by the recycled gas and pass through the demister and the condenser into the separator.

Unreacted starting materials and part of the propane formed as by-product are recycled to the reactor by means of the compressor. The level of propane in the circulating gas is adjusted by means of the outlet. The liquid reaction products are freed from residual olefin in a stripping column and are worked up by multistage distillation. Residual olefin from the stripping column is recycled. To limit the build-up of inerts in the recycled gas stream and to reduce losses by venting, other treatment steps may be applied. These include extraction of propene with the aldehyde products, stripping the olefin from the aldehydes with synthesis gas and recycling both to the reactor, and washing the off-gas with stripped catalyst solution.

The LPO gas-recycle process has been partly replaced by a liquid-recycle variant, in which the catalyst solution and the aldehyde products leave the reactor as a liquid. The catalyst solution is separated from the aldehydes in several distillation steps and recycled. Combinations of gas and liquid recycle have also been described and are claimed to give increased propene conversion.

#### ***As catalyst and catalyst ligand for other reactions***

Aliphatic and cycloaliphatic polyisocyanates are used to obtain PURs that do not become discoloured on exposure to light or heat. This is particularly important for coating materials (paints, varnishes, textile coatings, and glass-fibre sizes). Triphenylphosphine is facilitating the dimerization step of the chemical NCO group in the synthesis of PURs.

Other examples of the catalysing activity of TPP involved are polymerisation reactions of olefins, isomerisation reactions of olefins, hardening and curing reactions of epoxy resins.

### ANNEX 3: MONITORING STRATEGY FOR TRIPHENYLPHOSPHINE

As part of the Joint Assessment and Monitoring Programme (*reference number 2003-22*), OSPAR 2004 adopted an Agreement on monitoring strategies for OSPAR Chemicals for Priority Chemicals (*reference number 2004-15*) to implement the following monitoring for tracking progress towards the objectives of the OSPAR Hazardous Substances Strategy (*reference number 2003-21*) with regard to triphenylphosphine. The Monitoring Strategy for triphenylphosphine will be updated as and when necessary, and redirected in the light of subsequent experience.

Triphenylphosphine is produced as intermediate and used in closed systems only and transported in solid form in sealed containers. The only reported open use is 35kg by Norway and small amounts in two imported products in Sweden.

OSPAR will seek to estimate quantities of triphenylphosphine imported to, and exported from, the OSPAR region. No other monitoring is necessary, neither for sources, nor for the marine environment, since no releases to the environment are expected except in the case of accidents only.

Contracting Parties should, however, report any change to use pattern of triphenylphosphine to uses outside closed systems. In which case the approach in this monitoring strategy will need to be reconsidered, bearing in mind that the T-criterion is not met for triphenylphosphine.

TRIPHENYLPHOSPHINE MONITORING STRATEGY	
<b><i>Implementation of actions and measures</i></b>	<ul style="list-style-type: none"><li>• Examination of progress in the implementation of regulations on marketing and/or use or emission and/or discharge which have been agreed, or are endorsed, by the Background Document</li></ul>
<b><i>Production/use/sales/figures</i></b>	<ul style="list-style-type: none"><li>• Contracting Parties should report any use of triphenylphosphine outside closed systems. Following any such report the need for revision of this monitoring strategy should be considered</li><li>• Estimate quantities imported to, and exported from, the OSPAR Convention Area</li></ul>