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Dicyclopentadiene
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THE ECETOC PROGRAMME FOR THE

JOINT ASSESSMENT OF COMMODITY CHEMICALS (JACC)

This report has been prepared as part of the ECETOC programme for preparing critical reviews of the toxicology and ecotoxicology of selected existing existing industrial chemicals.

In the programme, commodity chemicals, that is those produced in large tonnage by several companies and having widespread and multiple uses, are jointly reviewed by experts from a number of companies with knowledge of the chemical. It should be noted that in a JACC review only the chemical itself is considered; products in which it appears as an impurity are not normally taken into account.

ECETOC is not alone in producing such reviews. There are a number of organisations that have produced and are continuing to write reviews with the aim of ensuring that toxicological knowledge and other information are evaluated. Thus a Producer, Government Official or Consumer can be informed on the up-to-date position with regard to safety, information and standards. Within ECETOC we do not aim to duplicate the activities of others. When it is considered that a review is needed every effort is made to discover whether an adequate review exists already; if this is the case the review is checked, its conclusions summarised and the literature published subsequent to the review assessed. To assist ourselves and others working in this field we publish annually a summary of international activities incorporating work planned, in hand, or completed on the review of safety data for commodity chemicals. Interested readers should refer to our Technical Report No 30 entitled "Existing Chemicals; Literature Reviews and Evaluations".

This document presents a critical assessment of the toxicology and ecotoxicology of dicyclopentadiene (CAS No 77-73-6).

CONTENTS

1. SUMMARY AND CONCLUSIONS

Dicyclopentadiene (DCPD) is a chemical intermediate, used in the manufacture of a wide range of organic chemicals.

The results of biodegradation studies suggest dicyclopentadiene is poorly degraded in soil and water, with estimated half-lives of 1-2 years and 4-7 years respectively. The rate of photolysis in water is slow. In the event of release into top soil or water, concentrations will decrease largely as a result of volatilisation into the atmosphere; the rate of degradation of dicyclopentadiene in air is rapid, the estimated half-life being one day.

Acute and subacute studies indicate that dicyclopentadiene is slightly toxic to fish, algae and a variety of other aquatic species. Although detected in the tissues of fish immediately following exposure, concentrations declined during the period of exposure and rapid decontamination occurred following transfer to clean water. No significant bioaccumulation was seen in duck, quail or plants and a low potential to accumulate was supported by the results of absorption/ excretion studies in mice, rats, dogs and cows.

Distribution studies using ^{14}C-dicyclopentadiene in mice, rats and dogs have shown that up to 85% of orally administered radioactivity appears in the urine or faeces within 24 hours. Tissues containing the highest concentration 1-2 hours after administration were the urinary bladder, gall bladder and body fat; metabolites were found in the urine. In the lactating cow, most dicyclopentadiene was eliminated within 24 hours as glucuronide conjugates in urine; only trace amounts were detected in milk.

Animal studies indicate that the predominant acute systemic effect is on the central nervous system; stimulation is followed by prolonged depression. There is some inter-species variation in susceptibility to the lethal effect of dicyclopentadiene. Percutaneous LD_{50} values indicate that dicyclopentadiene is poorly absorbed through the skin. Prolonged skin exposure under occlusion caused slight redness, a 4-hour exposure under semi-occluded conditions

resulted in well-defined irritation and swelling, whilst non-occluded application to bare skin caused moderate irritation. Direct application of the liquid to the eye caused only slight irritation. Studies in guinea pigs revealed no potential to induce allergic skin reactions.

Studies on the effects of repeated dietary exposure to dicyclopentadiene for up to 90 days in mice and rats revealed no treatment-related effects at nominal concentrations up to 273 ppm or 750 ppm respectively. In a study of similar duration in dogs there was some evidence of gastro-intestinal disturbance at the highest dietary concentration (1,000 ppm nominal). Repeated exposure of mice, rats and dogs to dicyclopentadiene vapour produced reversible kidney lesions in male rats only; the lesions were similar to those of hyaline droplet degeneration produced by certain hydrocarbon solvents. The role of alpha-2μ-globulin accumulation in the aetiology of such lesions and the fact that they are of no relevance to man is widely accepted. The reason for the absence of renal effects in the diet studies has not been investigated.

Dicyclopentadiene does not induce gene mutation in bacterial or yeast assays. Studies in animals indicated there is no selective toxicity to the embryo or foetus or any teratogenic potential. No long-term or carcinogenicity studies have been reported.

The odour of dicyclopentadiene has been reported to be detectable at concentrations as low as 0.003 ppm. Headache was reported in workers following prolonged exposure to low vapour concentrations.

2. IDENTITY, PHYSICAL AND CHEMICAL PROPERTIES, ANALYTICAL METHODS

2.1 Identity

Common Name : Dicyclopentadiene

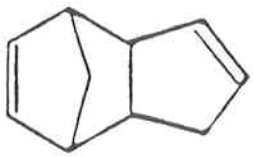
Synonyms: 4,7-Methano-1H-indene, 3a,4,7,7a-tetrahydro-
Bicyclopentadiene
Biscyclopentadiene
3a,4,7,7a-Tetrahydro-4,7-methanoindene
4,7-Methanoindene, 3a,4,7,7a-tetrahydro-
Cyclopentadiene dimer
Tricyclo[5.2.1.02,6]deca-3,8-diene

CAS No: 77-73-6

EINECS No: 201-052-9

Molecular formula: $C_{10}H_{12}$

Structural formula:



Molecular weight: 132.21

2.2 Physical and Chemical Properties

Dicyclopentadiene (DCPD) is a colourless, waxy, flammable solid with a camphor-like odour. Generally, the endo-configuration is present at higher concentrations than the exo-configuration under normal conditions. It is soluble in ethyl alcohol, diethyl ether and acetic acid and sparingly soluble in water. Its physical and chemical data are summarised in Table 1.

2.3 Conversion Factors

1 ppm = 5.40 mg/m^3
1 mg/l = 185 ppm

2.4 Analytical Methods

Methods to determine DCPD are generally based on gas chromatography. Typical conditions for the gas chromatographic analysis of hydrocarbon mixtures like DCPD are given in Table 2.

DCPD has been assayed in air at concentrations in the range of 0.1 - 10 mg/m^3 after absorption on active charcoal and desorption with carbon disulfide. The conditions for gas chromatographic determination were similar to those described in Table 2 (Shell, 1990).

DCPD has been analysed in ground water by gas chromatography/mass spectroscopy following extraction with methylene chloride (Van Breemen et al, 1987) or by gas chromatography, following extraction with carbon disulfide. The latter method is capable of determining DCPD at concentrations of 10 µg/l (Shell, 1990).

2.5 Purity of Commercial DCPD

Commercial samples of DCPD are of different degrees of purity. Typical commercial specifications are:

DCPD 94% - Impurities :

- Acylic dienes <2%
- Cyclopentadiene monomer <3%
- Methylcyclopentadienes <1%
- Inhibitor 100-200ppm

DCPD 92% -	Impurities:	Codimers of cyclopentadiene with isoprene, piperylene, butadiene - total approximately 8% Benzene <0.1% Inhibitor - approx. 100ppm
DCPD 75% -	Impurities:	Codimers of cyclopentadiene with isoprene, piperylene, butadiene - total approximately 23% Benzene approximately 0.05% Inhibitor - approx. 100ppm

More than 50% of DCPD produced is of the 92% and 94% purity grades. Unless otherwise stated in the text, data presented refers to the higher purity grades.

3. PRODUCTION, STORAGE, TRANSPORT AND USE

DCPD is produced commercially by recovery from hydrocarbon streams originating from high temperature cracking of petroleum fractions and as a by-product of the coke-oven industry. It is formed by the spontaneous dimerization of cyclopentadiene in a Diels-Alder addition reaction. Cyclopentadiene and its dimer may be readily inter-converted and the proportion of each present depends on the physical conditions: cyclopentadiene is favoured in the vapour state, particularly at elevated temperatures (above 130^{o}C) and DCPD in the liquid or solid phases. World production in 1989 was estimated to be of the order of 185,000 tonnes (Exxon, 1990a).

DCDP is unstable when stored at temperatures above 50^{o}C at atmospheric pressure; partial polymerisation can occur (Exxon, 1990b). Commercial grades contain small quantities of anti-oxidant inhibitor to prevent peroxide formation.

DCDP is produced as a chemical intermediate for use in the manufacture of alkyd resins, synthetic rubbers, perfume ingredients, plasticizers, flame retardants

pharmaceuticals, paints, lubricants, antioxidants, pesticides and a variety of other organic chemicals (Griesbaum and Hoenicke, 1987; OECD, 1977).

4. ENVIRONMENTAL DISTRIBUTION, BIOTRANSFORMATION AND ENVIRONMENTAL FATE

4.1 Environmental Distribution

The environmental distribution of DCPD at equilibrium has been estimated using the computer programme QSAR, developed and maintained by the Institute for Process Analysis, Montana State University on behalf of the EPA (1989). Taking the solubility in water to be 300 mg/l, the distribution was estimated as 72% in water, 15% in air and 12% in soil and sediment. When taking the solubility in water as 100 mg/l, the distribution was estimated as 55% in water, 35% in air and 10% in soil and sediment.

These results suggest that in the environment a major part of DCPD will be present in water, but also a substantial amount in air. However, uncertainty exists concerning the solubility of DCPD in water (Table 1) which is reported as less than 300 mg/l and probably less than 100 mg/l. If the solubility in water was much below the latter value, then DCPD is expected to partition mainly in air.

Smith et al (1980) calculated the rate of volatilisation of DCPD from water. From the experimentally determined volatilisation rate constant and reported values for oxygen reaeration rate constants in representative water bodies (lake, pond, river), a range of volatilisation rate constants for DCPD in the environment could be estimated. The half-life in water was estimated to range from 1.3-9.9 days. Spanggord et al (1979) estimated a half-life of DCPD in still surface water (marshland) of 5.3 days using a similar experimental method and calculations. Dow (1989) showed 77% removal of DCPD from water with aeration in a 4-hour laboratory test.

Volatilisation thus appears to be rapid when taking the concentration in air to be zero.

4.2 Biotransformation and Environmental Fate

4.2.1 Atmospheric Fate

DCPD will be transformed in air by reaction with hydroxyl radicals and ozone. Its half-life in the troposphere is estimated as less than 0.1 day (Hendry and Kenly, 1979; Atkinson, 1985; OECD, 1990).

4.2.2 Aquatic Fate

Spanggord et al (1979) studied the rate of phototransformation of DCPD in water. The results suggested that DCPD was transformed indirectly, by reaction with reactive species such as hydroxyl radicals and singlet oxygen. Spanggord concluded that the half-life of DCPD through indirect phototransformation in natural water would be about 76 days.

4.2.3 Terrestrial Fate

DCPD is expected to degrade slowly in soil. While the absorption coefficient of 2.9 suggests that only moderate soil adsorption would occur (EPA, 1989), a ^{14}C-DCPD tracer study (O'Donovan and Woodward, 1977) showed that the major portions of the 20 ppm DCPD test samples remained fixed in the soil under experimental conditions. The experiment was designed to observe the stability of DCPD in soil under a moving airstream. After 250 hours, moist soil samples had retained 62% and dry soil samples 95% of their activity.

4.2.4 Biodegradation

DCPD appears not to be readily biodegraded in water or in soil. Spanggord et al (1979) studied the biodegradation of DCPD by micro-organisms. The half-life for microbial decomposition in water was estimated to be 1 to 2 years. Decomposition by micro-organisms in the

soil takes place still more slowly than in water. At a soil temperature of 25°C, the estimated half-life was 4 to 7 years. The growth of water and soil micro-organisms in culture medium was not inhibited when DCPD was added at 10 mg/l or less; higher concentrations slowed growth.

In a 5 day biological oxygen demand test (BOD5) oxygen consumption of less than 4% of the theoretical oxygen demand (ThOD) was observed (Kaczmarek and Palis, 1981). On the basis of these results DCPD can be classified as not readily biodegradable.

4.2.5 Bioaccumulation

Bluegill sunfish (Lepomis macrochirus) were exposed to ^{14}C-DCPD at a concentration in water of approximately 1 mg/l for 14 days. During the first 96 hours the concentration of DCPD in fish muscle tissue increased to 51 mg/kg. Subsequently this concentration decreased rapidly to a constant level of 11 mg/kg during the next 10 days. When placed in pure water the concentration in fish muscle tissue declined to a level of less than 5 mg/kg within 24 hours (Bentley et al, 1976). These results suggest that, after a short adaptation period, DCPD may be metabolised by fish. On the basis of the experimental results during the first 96 hours, the bioaccumulation factor is calculated to be 53. This is in close agreement with calculated values of 37 (Mackay, 1982) and 76 (EPA, 1989). However, the bioaccumulation factor subsequently fell to around 11, possibly due to metabolism.

DCPD did not bioaccumulate in the plasma, liver, adipose tissue, skin, red blood cells, kidney, brain or muscle of Mallard duck (Anas platyrhynchos) or Bobwhite quail (Colinus virginianus) fed diet containing 100 mg DCPD/kg for 3 or 5 days, or dosed once by gavage at 100 mg DCPD in corn oil/kg body weight. In the dietary studies the average DCPD tissue residues were less than 1 ppm, and declined to less than the detection limit (average 0.04 ppm) in most tissues by the 3rd day following withdrawal. All tissues, except quail skin and duck kidney, were clear of DCPD residues by day 5 after withdrawal from radiolabelled diet. In the dosing experiments, the maximum residue of

50 ppm was in quail adipose tissue two hours after dosing. As was seen in the feeding study, DCPD tissue residues decreased rapidly, with a biological half-life of 12.7 hours, so that concentrations in most tissues were near the detection limit after 48 hours (Aulerich et al, 1979). Taking into consideration the rapid elimination of DCPD (see Section 7.2), it is probable that this compound will not significantly bioaccumulate despite its low or negligible water solubility.

O'Donovan and Woodward (1977) observed no uptake of DCPD above a level of 100 ppm in 10 plant species after treatment with DCPD in a water culture system (hydroponic) at concentrations up to level of 1,000 ppm.

On the basis of the above result it is concluded that DCPD has a low potential for bioaccumulation.

5. ENVIRONMENTAL LEVELS AND HUMAN EXPOSURE

DCPD does not occur naturally and few data on environmental concentration are available. It has been detected in ground water near chemical disposal sites and identified in river water contaminated by industrial and agricultural activities. Drinking water standards and occupational exposure limits have been established.

5.1 Environmental Levels

5.1.1 Air

No data on environmental concentrations could be found, possibly because of short atmospheric half-life (see Section 4.2.1).

5.1.2 Water

DCPD was detected in certain groundwater supplies in Colorado, USA (Burrows, 1977). It arose from the disposal of pesticide wastes in unlined ponds or from deep-well injection at the Rocky Mountain Arsenal.

Although the disposal of these wastes ended no later than 1966, DCPD continued to be detectable in the sub- to low- ppm range in some well-water supplies (quantities not specified). Van Breemen et al (1987) reported that extensive transformation of DCPD occurs in the environment, as evidenced by the many derivatives of the compound still detected in ground water extracts near the Rocky Mountain Arsenal.

DCPD was also detected in drinking water in a survey of water from 13 U.S. cities (Keith et al, 1976). In particular, three drinking water sources on the Mississippi River at New Orleans were investigated because of consumer complaints of "oily" and "chemical" flavours; DCPD was identified (not quantified) in these three samples. It was not found in the water supplies of the other cities studied.

During an evaluation of water treatment methods, DCPD was also identified, at a low concentration, in a sample of water from the River Rhine in the Netherlands (Zoeteman et al, 1982).

In a study of water samples from an aquifer beneath an alkyd resin plant in Italy (Mantica et al, 1986) DCPD and its oxidation products were detected but not quantified.

5.1.3 Soil and Plants

No data on environmental concentrations could be found.

5.2 Hygiene Standards

5.2.1 Occupational Exposure Levels

In the USA (ACGIH, 1989-1990) and The Netherlands (Arbeidsinspectie, 1989), an occupational exposure limit (8 hour TWA) of 5 ppm (27 mg/m^3) has been adopted for DCPD, based largely on the data from animal and human studies published by Kinkead et al (1971). An occupational exposure limit of 0.185 ppm (1 mg/m^3) is reported in the USSR (Shashikina, 1965).