CAS RN 38051-10-4

Substance Name

Phosphoric acid, P,P'-[2,2-bis(chloromethyl)-1,3-propanediyl] P,P,P',P'tetrakis(2-chloroethyl) ester (V6)



Uses

V6 has been used as an additive flame retardant in polyurethane foam and has been identified in a number of consumer and children's products including in children's products sold in Washington State[1]. Items positive for V6 in U.S. product testing include foam carpet pads, children's foam furniture, tent fabric, the fabric of a baby carrier, and a number of foam baby products [1-4]. Average concentration in foam baby products that tested positive was 4.6% by weight of the

foam [3]. It is reportedly used in interior foam for automotive and furniture foam at typical loadings of ~6% w/w [5]. The low volatility of V6 is an important property for automobile foam where interior temperatures can reach high levels. High temperatures can cause more volatile flame retardants to form a fog across the inside of the windshield. A domestic producer of V6 reported industrial use in "Processing—incorporation into formulation, mixture, or reaction product" and for unspecified commercial use. The manufacture reported no known use in "products intended for children" [6].

Manufacturing

Only one U.S. manufacturing site, located in another state, reported to the U.S. Environmental Protection Agency (EPA) in 2016 that it manufactures or imports V6¹. All Information about production volume was withheld as confidential business information [6]. In 2002, U.S. national production volume of V6 was reported as between 500,000 and 1 million pounds [8].

Toxicity

EPA classified V6 a moderate hazard for carcinogenicity based on cancer-testing results of a similar chemical (2-Propanol, 1,3-dichloro-, phosphate (CASRN 13674-87-8) [7]. V6 is a dimer of tris(2-chloroethyl)phosphate (TCEP) and also contains TCEP as an impurity. TCEP is of concern because it is classified as a carcinogen by the State of California [8] and 1B mutagen by the European Union [9]. Based on information from EPA and from product testing efforts, it appears that commercial V6 contains

¹ Manufacturers of chemicals listed on the Toxic Substances Control Act (TSCA) Inventory were required to report to EPA in 2016 if they produced or imported the chemical in volumes ≥25,000 pounds at a US site during any of the calendar years 2012, 2013, 2014, or 2015. <u>https://www.epa.gov/chemical-data-reporting/2016-chemical-datareporting-results#overview</u>

from 4.5 – 13.5% TCEP as an impurity [2, 7]. According to a 2016 Danish government report, industries providing V6 to the European market have significantly reduced the TCEP concentration in commercial formulations. A product called "V66", with TCEP levels below 1000 ppm, is apparently replacing V6 on the European market [4].

EPA considered V6 to have high hazard for developmental toxicity and moderate hazard for reproductive toxicity [7]. In a two-generation oral rat study, doses of 86 mg/kg-day caused thyroid effects (follicular hypertrophy and increased organ weight) in the parental generation and caused retarded fetal and pup growth in offspring [5]. Increased absolute and relative liver weight and hepatocyte hypertrophy were observed in both generations at the lowest observed adverse effect level (LOAEL). The no observed adverse effect level (NOAEL) was 29 mg/kg-day [7]. TCEP is considered a 1B reproductive hazard by the European Union [9].

Exposure

We did not identify migration data for V6 from consumer products. In product exposure testing by the Danish Environmental Protection Agency, it was shown that TCEP readily migrated from textile and foam materials in children's cars seats and baby slings into a test substance designed to mimic sweat. Over a three hour test period, TCEP migration into the artificial sweat was measured up to 620 mg/m². This study did not test for V6 [4].

V6 has not been widely studied in U.S. house dust or the environment. A study of flame retardants in U.S. college dorms detected V6 in 8% of samples with a maximum detection of 450 ng/g dust [10]. V6 was detected in 95% of 20 car dust samples and 75% of 20 house dust samples in a Boston area study [2]. The concentration of V6 ranged from <5 ng/g to 1110 ng/g in house dust and <5 ng/g to 6160 ng/g in car dust. Median levels in dust were 12.5 ng/g and 103.0 ng/g in houses and cars, respectively. The higher concentrations observed in car dust are consistent with higher use in automobile foam.

In Europe, V6 was measured in house dust of a small number of Norwegian homes (n=10), United Kingdom (UK) homes (n=10) and UK stores and offices (n=12) [11]. Median levels in dust were 4 ng/g, 17 ng/g, and 40 ng/g respectively. The higher levels observed in the UK may be a result of UK fire standards that drive increased flame retardant use in consumer products. The authors estimated exposure scenarios for "stay at home" adults and toddlers living in the UK homes using standard assumptions. High ingestion rate scenarios using median dust values yielded estimated daily intake of 0.27 ng/kg-day for toddlers and 0.012 ng/kg-day. Normal dust ingestion scenarios using maximum dust values yielded daily intake estimates of 3.073 ng/kg-d toddlers and 0.216 ng/kg-d for adults [11]. In a study of car dust in Greece, V6 was detected in 80% of car dust samples. Median V6 in car dust was 13 ng/g and the range of concentrations detected was 1 – 8535 ng/g. Authors estimated median daily ingestion of V6 in car dust for adults (0.00076 ng/kg-day) and toddlers (0.00532 ng/kg-day) assuming they spend 1 hour/day in a car [12].

We did not identify any biomonitoring studies for V6. In rodents, the compound is readily absorbed across the gut and less readily across skin. It is metabolized and excreted in feces, and urine. Half-life for

September 12, 2018 - draft for stakeholder comment. No not cite or quote.

elimination from the body was 99-113 hours in orally exposed rats [7]. *In vitro* absorption of V6 across human skin membranes was low (0.51% and 6% for undiluted V6 or in an ethanol vehicle, respectively).

Environmental Fate and Transport

EPA rated the persistence hazard for V6 as high based on observational studies and modelling [7].

Summary of information in EPA, 2015 [7]

| If released to air | V6 expected to exist in both vapor and particulate phase in the air based on estimated vapor pressure. Vapor phase V6 is expected to be broken down by photochemically produced hydroxyl radicals (estimated half-life = 0.14 days in sunlight). V6 associated with particulate will be removed from air by wet or dry deposition and may undergo atmospheric transport. |
|--------------------------------------|--|
| If released to soil | V6 is only slowly biodegraded and is relatively stable to hydrolysis and photolysis. Predicted half-life in soil was >1 year in EPA models. Under aerobic conditions in domestic activated sludge (OECD test 301B), 5% biodegradation occurred after 28 days. V6 is expected to have negligible mobility in soil, based on K_{oc} values. |
| If released into water | V6 is expected to partition to sediments and soils with limited biodegradation. Limited hydrolysis is expected to occur (experimental half-lives were >1 year at pH 4, pH 7, and pH 9). V6 is not expected to volatilize from surface water based on Henry's constant. |
| Bioconcentration and bioaccumulation | Estimated BCF and BAF values (using EPI v4.11) were 11 and 31 indicating that V6 may have a low potential to bioaccumulate in fish |

Physical-Chemical Properties for V6 from EPA Chemistry Dashboard

September 12, 2018 - draft for stakeholder comment. No not cite or quote.

| | Predicted | Predicted | | |
|---------------------|--------------|-----------|----------------------|--------------------------|
| Property | Average | Median | Predicted Range | Unit |
| LogP: Octanol-Water | 3.36 (5) | 3.31 | 1.92 to 4.57 | - |
| Water Solubility | 1.18e-03 (4) | 5.23e-05 | 5.35e-07 to 4.61e-03 | mol/L |
| Density | 1.52 (2) | 1.52 | 1.47 to 1.58 | g/cm ³ |
| Flash Point | 444 (2) | 444 | 299 to 588 | °C |
| Melting Point | 49.1 (4) | 43.4 | 19.4 to 90.3 | °C |
| Boiling Point | 473 (5) | 433 | 407 to 620 | °C |
| Surface Tension | 46.2 (1) | - | - | dyn/cm |
| Vapor Pressure | 3.45e-06 (4) | 2.39e-06 | 1.21e-14 to 9.03e-06 | mmHg |
| LogKoa: Octanol-Air | 11.7 (1) | - | - | - |
| Henry's Law | 3.06e-07 (1) | - | - | atm-m ³ /mole |
| Index of Refraction | 1.49 (1) | - | - | - |
| Molar Refractivity | 116 (1) | - | - | cm ³ |
| Molar Volume | 398 (1) | - | - | cm ³ |
| Polarizability | 45.8 (1) | - | - | Å ³ |

Numbers in parentheses indicate the number of measurements or model predictions identified by EPA.

Regulatory (related to TCEP impurity)

In 2016, Washington was the fifth state to pass a state restriction on TCEP in children's products (NY 2011; MD 2014; VT 2013; MN 2015). Washington also restricted TCEP in residential upholstered furniture. The limit of TCEP in both categories of products is 1,000 ppm. The ban became effective July 1, 2017.

In Europe, TCEP is a "Substance of very high concern" requiring authorization before it is used (Annex XIV of Registration, Evaluation, Authorization and Restriction of Chemicals) [9].

The European Commission (EC) adopted Directive 2014/79/EU, which limits TCEP concentration to 5 mg/kg in toys for children up to the age of 3 years and in any toys intended to be placed in the mouth, regardless of intended age. TCEP alternatives, namely tris(2-chloro-1-methylethyl) phosphate (TCPP), CAS No 13674-84-5, and tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDCP), CAS No 13674-87-8, are also subject to the same limit adopted for TCEP. The restriction became effective on December 21, 2015.

References

- 1. Ecology, Flame Retardants in General Consumer and Children's Products. 2014.
- 2. Fang, M., et al., *Investigating a novel flame retardant known as V6: measurements in baby products, house dust, and car dust.* Environ Sci Technol, 2013. **47**(9): p. 4449-54.
- 3. Stapleton, H.M., et al., *Identification of flame retardants in polyurethane foam collected from baby products.* Environ Sci Technol, 2011. **45**(12): p. 5323-31.
- 4. Agency, D.E.P., Chlorinated phosphorous-based flame retardants in children's articles containing foam: Background for content and possibilities for prevention in the EU Environmental Project No. 1855. 2016, Ministry of Environment and Food Denmark.

September 12, 2018 - draft for stakeholder comment. No not cite or quote.

- 5. ECHA, 2,2-bis(chloromethyl) trimethylene bis[bis(2-chloroethyl) phosphate] (V6) Summary Risk Assessment Report. 2008, European Union: Ireland and United Kingdom.
- 6. EPA, 2016 Chemical Data Reporting (CDR) online database initial information reported under TSCA. May 2017, US Environmental Protection Agency.
- 7. EPA, *Flame Retardants Used in Flexible Polyurethane Foam: An Alternatives Assessment Update.* 2015, Environmental Protection Agency.
- 8. California, S.o. *Chemicals Known to the State to Cause Cancer or Reproductive Toxicity*. 2016 [cited 2016 August]; Available from: <u>http://oehha.ca.gov/proposition-65/proposition-65-list</u>.
- 9. ECHA, Brief Profiles: Tris(2-chloroethyl) phosphate. 2016.
- 10. Dodson, R.E., et al., *Flame Retardant Chemicals in College Dormitories: Flammability Standards Influence Dust Concentrations.* Environ Sci Technol, 2017. **51**(9): p. 4860-4869.
- 11. Kademoglou, K., et al., *Legacy and alternative flame retardants in Norwegian and UK indoor environment: Implications of human exposure via dust ingestion.* Environ Int, 2017. **102**: p. 48-56.
- 12. Christia, C., et al., *Legacy and emerging organophosphomicronrus flame retardants in car dust from Greece: Implications for human exposure.* Chemosphere, 2018. **196**: p. 231-239.