Chemosphere 79 (2010) 476–481

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Chemical degradation of 2,2-bis(bromomethyl)propan-1,3-diol (DBNPG) in alkaline conditions

Shai Ezra [a], Itzhak Bilkis [b], Shimon Feinstein [c,*], Eilon Adar [c,d], Jiwchar Ganor [c]

[a] Water Quality Division, Mekorot, Israel National Water Co., P.O.B 2012, 9 Lincoln St., Tel Aviv 61201, Israel
[b] Institute of Biochemistry, Food Science, and Nutrition, Faculty of Agricultural, Food and Environmental Quality Sciences, The Hebrew University of Jerusalem, P.O.B. 12, Rehovot 76100, Israel
[c] Department of Geological and Environmental Sciences, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel
[d] Department of Environmental Hydrology and Microbiology, Zuckerberg Institute for Water Research at the Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev, Sede Boqer Campus 84990, Israel

ARTICLE INFO

Article history:
Received 16 April 2009
Received in revised form 11 January 2010
Accepted 12 January 2010
Available online 26 February 2010

Keywords:
2,2-bis(bromomethyl)propan-1,3-diol
DBNPG
Half-life
Decomposition

ABSTRACT

The mechanism and kinetics of the spontaneous decomposition of 2,2-bis(bromomethyl)propan-1,3-diol (DBNPG) and its decomposition daughter products were determined in aqueous solution at a temperatures range between 30 and 70 °C and pH from 7.0 to 9.5. DBNPG decomposition in basic aqueous solutions involves release of bromide ions through a sequential formation of 3-bromomethyl-3-hydroxymethyloxetane (BMHMO) and 2,6-dioxaspiro[3.3]heptane (DOH). DBNPG decomposition into BMHMO is a two-stage reaction. The first stage is an acid/base equilibrium, in which an alkoxide is formed. In the second stage, DBNPG predominantly undergoes an intramolecular nucleophilic substitution to form the BMHMO. The transformation rate increases with the pH and the energy barrier for the degradation is 98 kJ mol^{-1}. Good agreement was found between the rate coefficients derived from variations in the organic molecules concentrations and those determined from the changes in the Br^- concentration. DBNPG is one of the most abundant pollutants in a studied polluted aquitard underneath industrial park in the northern Negev, Israel, and together with its by-products pose an environmental hazard. DBNPG half-life is estimated to be about 65 years. This implies that high concentrations of DBNPG will persist in the aquifer long after the elimination of all its sources.

1. Introduction

2,2-bis(bromomethyl)propan-1,3-diol, or as it is known commercially dibromoneopentyl-glycol (DBNPG), is regulated by the US environmental protection agency (EPA) under the toxic substances control act (TSCA). This compound has been defined as carcinogenic and has been shown to be mutagenic in bacteria (Zeiger et al., 1992). DBNPG is used mainly as flame retardant in plastics where its high solubility in organic solvent (825 g L^{-1} in acetone and 70 g L^{-1} in benzene) makes it especially useful (Material safety data sheet; MSDS, 1999).

The EPA included DBNPG in its 1990 list of high-production-volume chemicals, indicating that in the US, at least 4×10^9 tons of this chemical had been used. The EPA's report (EPA, 1983) refers to it as a compound that is anticipated to last in water for long periods of time. The Japanese Ministry of International Trade and Industry (MITI) test has shown that DBNPG is not readily biodegradable [3–33% by Biochemical Oxygen Demand (BOD) after 28 d] (Chemicals and Testing Institute, 1992). Recent study that used contaminated soil from the studied aquitard showed the biodegradation of DBNPG under aerobic conditions (Segev et al., 2007). Under enhanced aerobic conditions DBNPG demonstrated complete mineralization after 58 d. The relatively good resistance to biodegradation along with its relatively high solubility in water (20 g L^{-1}) are probably the main reason for DBNPG's wide distribution in aqueous environments (Chemicals and Testing Institute, 1992; Ezra, 2005).

The groundwater in the fractured Eocene chalk aquitard underlying an industrial complex in the Negev desert, Israel, is contaminated by numerous volatile and non-volatile organic compounds and heavy metals. Among the enormous variety of organic contaminants found, DBNPG is one of the dominant semi-volatile contaminants.

In the last three decades extensive efforts have been devoted in order to determine the pathways and rates of decomposition of halogenated alkanes and alkenes in aqueous solutions (Burlinson et al., 1982; Bouwer and McCarty, 1983; Schwarzenbach et al., 1985, 2003; Vogel and Reinhard, 1986; Cooper et al.,

* Corresponding author. Tel.: +972 8 6472622; fax: +972 8 6472997.
E-mail addresses: sezra@mekorot.co.il (S. Ezra), shimon@bgu.ac.il (S. Feinstein).

0045-6535/$ - see front matter © 2010 Published by Elsevier Ltd.
doi:10.1016/j.chemosphere.2010.01.016

1987; Ellenrieder and Reinhard, 1988; Barbash and Reinhard, 1989; Jeffers et al., 1989, 1996; Jeffers and Wolfe, 1996; Pagan et al., 1998; Ezra et al., 2005; Furey et al., 2008). Nucleophilic substitution and 1,2-elimination are usually considered the major chemical degradation pathways for these compounds. DBNPG cannot undergo 1,2-elimination due to its lack of β-hydrogen atoms. Its transformation in basic solutions involves intramolecular nucleophilic substitution and the so-called 1,4-elimination (Searles and Gortatowsky, 1953; Searles et al., 1960; Abdun-Nur and Issidorides, 1962). The ratio between these two pathways depends on the nature of the solvents. The kinetics of these transformations has not been studied, and the available data in the literature do not allow an estimation of DBNPG half-life under environmental conditions. Considering the alkaline pHs that characterize the Eocene aquitard, the chemical transformation processes should be even more pertinent in our case than in less alkaline environments.

The present study describes the hydrolysis pathways and the kinetics of DBNPG and its daughter product, BMHMO, in aqueous alkaline solution, and estimates their half lives in the studied contaminated groundwater in chalk aquitard.

2. Methods

2.1. Experimental setup

Batch experiments were carried out in 500 mL glass bottles, at constant temperature of 30, 50 or 70 ± 0.2 °C, and a pH between 6.8 and 9.9 (Table 1). Experimental mixtures were prepared using 1000 mg L^{-1} DBNPG, 98% purity (Sigma), KH_2PO_4/Borax or NaOH/Borax buffer solution (reagent grade, BDH) (Dean, 1985) and double-distilled water (DDW). In the experiments held at 30 °C and pH 8.07, the estimation of the kinetics constant was based on four batches with different initial concentrations of DBNPG, 1000, 750, 500 and 250 mg L^{-1}. The pH values measured in these experiments were 8.05, 8.06, 8.07 and 8.07, respectively.

2.2. Analytical methods

2.2.1. Extraction preparation

For the Gas Chromatograph Flame Ionization Detector (GC–FID) a 10 mL of filtered experimental solution was passed by vacuum through an Envi™-18 Tube (Supelco) that had been previously washed with dichloromethane (DCM) and conditioned with 2 mL methanol followed by 2 mL DDW. The tubes were dried for 20 min under vacuum. The dried tubes were extracted with 2 mL DCM; 5 μL of an internal standard solution of biphenyl and diphenyl ether, 25 g L^{-1}, was added to the extract. The extract solution was concentrated to 0.5 mL under a weak flow of dry nitrogen.

In the case of preparation for the Gas Chromatograph Electron Capture Detector (GC–ECD) Analysis 1 mL of nitric acid (15%) was added to 5 mL of the filtered solution. As in the extraction for the GC–FID, the mixed solution was passed by vacuum through an Envi™-18 Tube that had been previously conditioned with 2 mL methanol followed by 2 mL DDW. The tubes were dried for 20 min under vacuum and extracted with 2 mL methanol. Internal standards 2,4,6-trichlorophenol and 1-bromooctane were added, and the extract solution was concentrated to 0.5 mL under a weak flow of dry nitrogen.

The preparation for the Nuclear Magnetic Resonance (NMR) included: 300 mL of each sample were mixed with 15% D-chloroform and shaken for 5 min. After reaching fluid separation, the solvent was removed using a separation funnel. This process was repeated three times to ensure sufficient extraction. The extracted fluid was dehydrated with anhydrous magnesium sulfate and the organic solvent was initially concentrated by evaporator and subsequently by a weak flow of dry nitrogen, to a volume of 1 mL.

2.2.2. Analysis of organic compounds

A 1 μL sample of the extract was injected into a Hewlett Packard (HP) 5890 equipped with an FID and ECD detector and an HP-5 fused silica column (30 m, 0.32 mm i.d., 0.25 μm film) and HP-5 MS (30 m, 0.32 mm i.d., 0.25 μm film) connected to the FID and ECD, respectively. The injector and the detector were held at

Table 1
The conditions and the kinetic coefficients calculated from the experiments.

Temperature (°C)	Buffer concentration	pH	$k_{DB(obs)}/s^{-1}$ (Eq. (7))	$R^2_{(Eq.\ (7))}$	$k_{DB(obs)}/s^{-1}$ (Eq. (5))	$k_{BM(obs)}/s^{-1}$	$R^2_{(Br)}$
70	0.025M[a]	9.46	1.72×10^{-5}	0.9994	1.57×10^{-5}	3.51×10^{-6}	0.9978
	0.031M[c]						
	0.051M[a]	8.86	6.87×10^{-6}	0.9885	6.07×10^{-6}	3.43×10^{-6}	0.9988
	0.036M[a]	8.41	3.94×10^{-6}	0.9939	3.67×10^{-6}	2.21×10^{-6}	0.9991
	0.030M[b]						
	0.025M[a]	7.60	1.43×10^{-6}	0.9950		9.64×10^{-7}	0.9928
	0.065M[b]						
	0.018M[a]	6.82	5.03×10^{-7}	0.9939	4.37×10^{-7}	6.14×10^{-7}	0.9961
	0.065M[b]						
50	0.025M[a]	9.62	7.45×10^{-7}	0.9987		2.35×10^{-7}	0.9983
	0.031M[c]						
	0.051M[a]	9.06	3.17×10^{-7}	0.9973		2.17×10^{-7}	0.9992
	0.036M[a]	9.04	3.12×10^{-7}	0.9945		2.01×10^{-7}	0.9988
	0.030M[b]						
	0.025M[a]	8.54	2.13×10^{-7}	0.9988		1.7 × 10–7	0.9987
	0.065M[b]						
	0.018M[a]	7.70	7.33×10^{-8}	0.9917		1.02×10^{-7}	0.9984
	0.065M[b]						
30	0.025M[a]	9.86	2.13×10^{-8}	0.9970			
	0.031M[c]						
	0.051M[a]	9.26	1.10×10^{-8}	0.9979			
	0.025M[a]	8.07	4.83×10^{-9d}	0.9520			
	0.065M[b]						

[a] Borax.
[b] KH_2PO_4.
[c] NaOH.