Catalytic and Electrocatalytic Hydrogenation of Brominated Diphenyl Ethers

Pascale M.L. Bonin[a], Patrick Edwards[a], Dorin Bejan[a], Chun Chi Lo[a], Alexandre D. Konstantinov[b] and Nigel J. Bunce[a]

[a]Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1

[b]Wellington Laboratories, 345 Southgate Drive, Guelph, Ontario, Canada, N1G 3M5

Introduction

Polybrominated diphenyl ethers (PBDEs) are part of the family of brominated flame retardants [1]. Commercial PBDEs are mixtures of congeners; the commercial mixtures presently in use are nominally penta-, octa-, and deca-BDEs [2]. The pentaBDE mixture, for example, typically comprises 37% of 2,2',4,4'-tetraBDE (congener 47) and 35% of 2,2',4,4',5-pentaBDE (congener 99), which are the most prevalent congeners found in the environment [3], along with decreasing amounts of congeners 100, 153, 154, and 85 [4].

Hydrogenolysis offers a possible method to degrade PBDEs by replacing the bromine atoms with hydrogen atoms, leaving diphenyl ether. Although this compound is potentially bioaccumulable and toxic to fish, it is biodegradable [5], suggesting that hydrogenolysis might be useful as a front-end technology for dehalogenating the PBDE molecules prior to biodegradation [6]. In this study we have examined conventional and electrocatalytic hydrogenolysis (ECH) as methods for the debromination of PBDEs.

Materials and Methods

Chemicals. Phenyl ether and 4-MBDE (congener 3) were obtained from Aldrich (Oakville, Ontario) as were palladium (5% by weight on alumina) and 1-naphthol, which served as an HPLC internal standard. 4,4'-DBDE (congener 15) was obtained from Alfa Aesar (Wardhill, Massachussetts). PBDE congeners 17, 28, 47, 66, 85, 99, 100, 153 and 154 were available from a previous study [7]; while 2-MBDE (congener 1) and 3-MBDE (congener 2) were prepared by the method of Marsh et al. [8]. A commercial pentaBDE mixture (Great Lakes DE-71) was provided by Great Lakes Chemical Co. (West Lafayette, Indiana).

Analytical procedures. The samples were analyzed by HPLC, using a Waters model 600 pump (flow rate 1.0 mL min^{-1}), a Rheodyne injector containing a 20 mL sample loop, and a Waters model 486 tunable absorbance detector operated at 220 nm (except for congeners 153 and 154, which were monitored at 210 nm). Separation was achieved on a Waters Spherisorb ODS1 (5μm X 4.6mm X 25 cm) column. The mobile phase was 90:10 v/v methanol:water, which was degassed before use. Some samples were also analyzed by API-MS in the positive atmospheric pressure chemical ionization (APCI) mode, using

a Waters single quadrupole ZQ-LC/MS 2000 system equipped with an APCI probe and a Z-spray source.

Catalytic hydrogenolysis. Catalytic hydrogenolysis was carried out in 10 mL round-bottom flasks, using stirred solutions of BDE congeners and 1-naphthol (internal standard) in methanol, and amounts of catalyst powder representing 15 to 40% by mass of the congeners. Solutions were protected from the light by covering the flask with aluminum foil. The flask was sealed by a rubber septum through which three syringe needles were inserted, one to bubble hydrogen gas into the solution, the others to allow excess gas to escape.

Electrocatalytic hydrogenolysis. ECH was carried out under galvanostatic conditions using a PAR Model 363 potentiostat /galvanostat and a flow-through batch cell with a glass tube attached to the side to allow recirculation of the cathodic solution. The anode and cathode compartments were separated with a Dupont Nafion® 424 cation exchange membrane (CEM). The cathode was a circular piece of Duocel® reticulated vitreous carbon (RVC) (100 ppi, 6 mm thick and 35 mm in diameter) with a copper wire lead. The anode was a rectangular piece of ELTECH IrO_2/Ti dimensionally stable anode (DSA®) (55 mm x 13 mm x 1.5 mm) with a stainless steel wire lead. The anolyte (5 mL) was 0.02 M aq. sulphuric acid, and the catholyte was the BDE in methanol - water (80:20 or 70:30), containing 0.02 M sodium sulphate as supporting electrolyte.

Results and Discussion

Catalytic Hydrogenolysis. A 1.25 mM solution of 4-MBDE (1.25 mg) in methanol (4 mL) was hydrogenolyzed in the presence of 0.5 mg of catalyst; after 90 min, 97% of the 4-MBDE was converted to diphenyl ether (Figure 1). With 0.2 mg of catalyst, the reaction was slower (66% conversion after the same time). 4,4'-DBDE underwent sequential debromination to 4-MBDE and diphenyl ether: with 17.5 mg of catalyst, 98% of a 3.32 mM solution of 4,4'-DBDE (109 mg) in methanol (100 mL) had degraded after 45 minutes, affording 0.18 mM of 4-MBDE and 2.85 mM of diphenyl ether.

A mixture of *o*-, *m*-, and *p*-MBDE was hydrogenated to determine their relative rates of debromination. The solution contained 0.95 mM 2-MBDE, 1.34 mM 3-MBDE and 1.15 mM 4-MBDE (total mass 3.43 mg) in methanol (4 mL) with 1.4 mg of catalyst. The reaction rates were 3-MBDE > 4-MBDE > 2-MBDE, with apparent first order rate constants 0.012, 0.008, and 0.002 min^{-1}.

Catalytic hydrogenolysis of a 10 mM solution of commercial penta-BDE (33.8 mg) in methanol (6 mL) was carried out using 5.1 mg of catalyst (Figure 2). These experiments were analyzed by LC-MS in positive ion mode, to show overall congener group patterns, and by HPLC to obtain congener-specific information. Sequential debromination was observed, and after 80 min, the reaction mixture comprised diphenyl ether (49%), MBDE isomers (38%) and DBDE isomers (12%). The monobrominated compounds were 4-MBDE > 2-MBDE > 3-MBDE, the preponderance of *o*- and *p*-isomers being consistent with the initial composition of the pentaBDE mixture

(principally congeners 47 and 99). Faster debromination was observed when more catalyst was used.

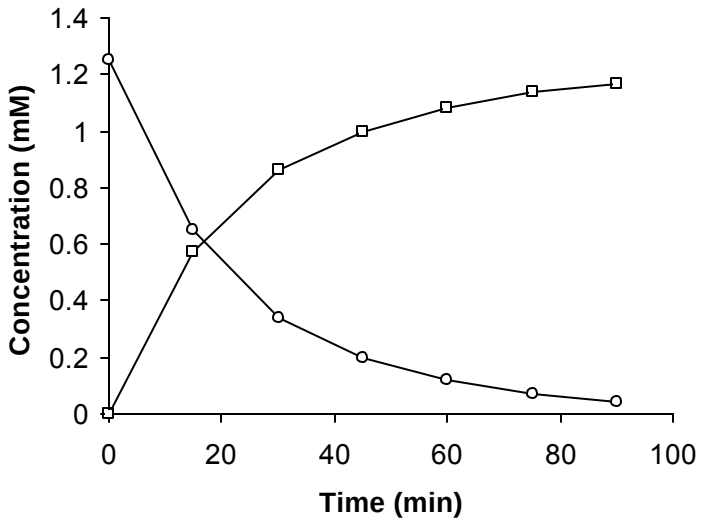

Figure 1. Catalytic hydrogenation of 4-MBDE. Concentration versus time for 4-MBDE (empty circle) and phenyl ether (empty square).

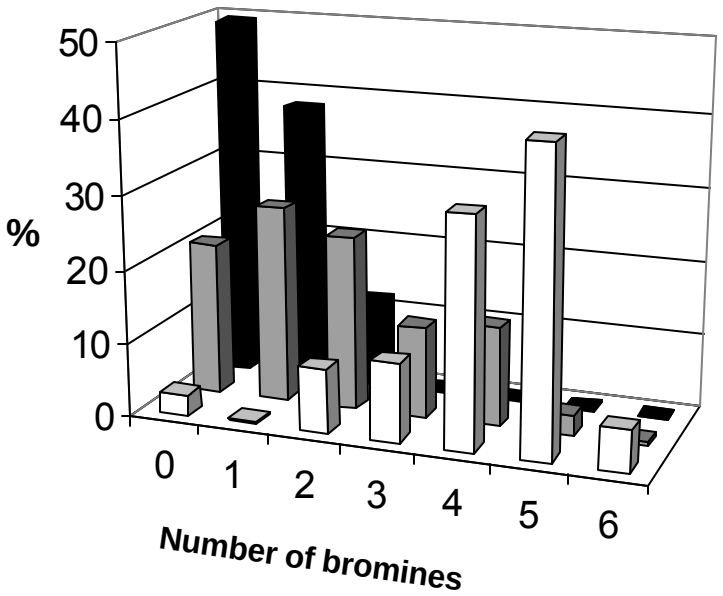

Figure 2. Catalytic hydrogenation of a commercial penta-mixture. Mixture composition (%) versus time for phenyl ether and for the mono- to the hexa-brominated compounds. Initial mixture composition (white pillars), after 40 min (textured pillars) and after 80 min (black pillars).

Electrocatalytic hydrogenation. The limited solubility of PBDE congeners in aq. MeOH required a high proportion of methanol in the solvent mixture: 80:20 v/v MeOH: H_2O for experiments with 4-MBDE and 70:30 for 4,4'-DBDE. This necessitated a trade-off, because hydrogenolysis was slower when there was less water in the mixture, probably because of a slower rate of forming nascent hydrogen atoms. A problem was encountered in that bubbles of hydrogen gas formed an isolating layer around the electrode; this led to an increased ohmic drop, and hence to current overload. The hydrogen gas bubbles were dispersed by physically tapping the electrode.

At a current of 0.06 A, a 44 mM solution of 4-MBDE (1 g) in methanol (100 mL) was hydrogenolysed in the presence of 150 mg of catalyst. After 90 min, 48% of the 4-MBDE was converted to diphenyl ether. ECH of a 2.4 mM solution of 4,4'-DBDE (70.8 mg in 100 mL methanol, with 10.3 mg catalysts) at a current of 0.065 A gave 75% consumption of the reactant after 90 min, with the formation of 0.95 mM of 4-MBDE and 0.83 mM of diphenyl ether.

Conclusions

Both catalytic and electrocatalytic hydrogenolysis could be used to debrominate PBDEs. In this application, the conventional method was preferable, because it employs simpler equipment, and there appears to be no need for the "extra" reactivity of ECH. Moreover, the poor solubility of PBDEs, even in aqueous methanol solutions, made study of the commercial pentaBDE by ECH impractical.

References

1. International Program on Chemical Safety (IPCS), 1994, vol. 162. World Health Organization, Geneva.
2. Wenning, R.J., *Chemosphere* 2002, 46, 779-796.
3. Lindstrom, G.; Wingfors, H.; Dam, M., vanBavel, B., *Arch. Environ. Contam. Toxicol.* 1999, 36, 355-363.
4. Chen, G.; Bunce, N.J., *Toxicol. Sci.* 2003, 76, 310-320.
5. Schmidt, S., Wittich, R.-M., Erdmann, D.; Wilkes, H.; Francke, W., Fortnagel, P., *Applied Environ. Microbiol.* 1992, 58, 2744-2750.
6. Rodgers, J.D., Jedral, W., Bunce, N.J., *Environ. Sci. Technol.* 1999, 33, 1453-1457.
7. Chen, G; Konstantinov, A.D.; Chittim, B.G.; Joyce, E. M., Bols, N.C., Bunce, N.J., *Environ. Sci. Technol.* 2001, 35, 3749-3756.
8. Marsh, G.; Hu, J.; Jacobson, E.; Rahm, S., Bergman, A., *Environ. Sci. Technol.* 1999, 33, 3033-3037.