

LILIANA BARON, ANNA KOZŁOWSKA*, STEFAN S. KUREK**

DEHALOGENATION OF HEXABROMOCYCLODODECANE – A COMMONLY USED FLAME RETARDANT

DEHALOGENACJA HEKSABROMOCYKLODODEKANU – POWSZECHNIE STOSOWANEGO UNIEPALNIACZA

Abstract

Hexabromocyclododecane, a commonly used flame retardant and possible persistent pollutant undergoes reductive debromination at very cathodic potentials in the absence of a catalyst. The process starts at much less cathodic potentials but is extremely slow. Cobalt tetraphenylporphyrin catalyses very efficiently the process at potentials shifted by 1.2 V and at much higher rates. 1,2-dibromocyclododecane was also debrominated electrochemically, but showed higher energy barrier than observed for HBCD.

Keywords: hexabromocyclododecane, HBCD, reductive dehalogenation, cobalt porphyrin

Streszczenie

Heksabromocyklododekan, powszechnie stosowany uniepalniacz i potencjalny uporczywy środek zanieczyszczający środowisko, ulega redukcyjnej debrominacji przy silnie katodowych potencjałach w nieobecności katalizatora. Proces rozpoczyna się przy potencjałach znacznie mniej katodowych, ale jest nadzwyczaj powolny. Tetrafenylporfiryne kobaltowa katalizuje bardzo wydajnie proces przy potencjałach przesuniętych o 1,2 V i przy znacznie większych szybkościach. 1,2-dibromocyklododekan był także debromowany elektrochemicznie, ale wykazywał wyższą barierę energetyczną niż HBCD.

Słowa kluczowe: heksabromocyklododekan, HBCD, dehalogenacja redukcyjna, porfiryne kobaltowa

* Liliana Baron, Anna Kozłowska, Final course student at Faculty of Chemical Engineering and Technology, Cracow University of Technology.

** PhD. Stefan S. Kurek, Lecturer at Physical Chemistry Group, Faculty of Chemical Engineering and Technology, Cracow University of Technology.

1. Introduction

Flame retardants are chemicals that raise the flash point and inhibit or hinder the spread of fire. Various materials may be used for this purpose such as inorganic chemicals like aluminium hydroxide, magnesium hydroxide, hydromagnesite and the like. Such materials decompose endothermically at high temperatures, which hinders the spreading of fire by cooling the material. Other retardants may act by diluting either the fuel or the air, which slows or even stops the reaction.

Brominated fire retardants (BFR) work by breaking down and producing Br[•] radicals that quench free radicals in the gas phase or directly in the burning material. They have been used since the 1960s in a variety of polymers. On the one hand they save lives on the other they raise issues over health safety and the role they play in the environmental pollution [1–3]. The demand for those materials rises steadily owing to the introduction of new fire safety regulations. Most often they are applied in electronics, for fire protection of textiles, insulation materials in construction industry and the like.

Bromine Science Environmental Forum (BSEF), an international organization gathering the producers of bromine, issued a statement on the status of BFRs in connection with REACH legislation [4]. It reads that the main BFRs in use (Deca-BDE, TBBP-A, HBCD) have already been tested within EU risk assessments. Despite that new analysis methods are needed [5].

1, 2, 5, 6, 9, 10-hexabromocyclododecane (HBCD) is an additive flame retardant commonly used in expanded polystyrene foam employed for thermal insulation of buildings. It is generally applied on the outside and very often scraps of it are blown about by the wind during insulation works. HBCD is not chemically bound to the polymer and thus may leach to the environment. As the compound is highly lipophilic it causes serious environmental concerns.

It has already been shown that HBCD is degraded in the environment, but the process is very slow [6]. Halogenated compounds are difficult to oxidise, but much easier to reduce. Once the electron is transferred onto such a molecule, the carbon-halogen bond instantly breaks yielding a halide anion and leaving a carbon radical [7]. High energy level of the radical creates thermodynamic problems. The radicals are highly reactive species and undergo further reactions, but the process has to pass through a very high energy barrier, which results in a very slow rate of the overall reaction. The process can be, however, catalysed.

Halogenated compounds undergo anaerobic degradation either as a result of anaerobic co-metabolism, accidentally as it were, taking advantage of processes the real substrate of which is another compound without benefitting the organism or in dehalorespiration that provides energy for the organism. The former processes are more common, they occur in sulphate-reducing bacteria, methanogens, acetogens and the like. Methyl coenzyme M reductase in Factor F-430, with a nickel isobacteriochlorin in its centre, is active in these processes. Dehalorespiration processes occur most often on cobalamin (Vitamin B12). Generally, a transient alkyl-metal complex is formed in the catalytic process. Its energy is lower than that of a carbon radical mentioned above and thus the energy barrier is much lower. In electrochemistry, overpotential is related to the energy barrier. In the presence of a catalyst, the reduction occurs at a much less cathodic potential. The redox potential for cob(I)alamin is about -0.61 V [8], and for methyl

coenzyme M reductase between -0.6 and -0.7 V [9]. Rarely, haem cofactor, an iron porphyrin, may also be active in dehalogenation [10].

Literature data on biodegradation of these compounds are not consistent, particularly with respect to the time needed for this process to occur. They range from a couple of hours to several months. One of the problems encountered in the literature is that titanium (III) citrate is used as a reducing agent in slightly basic solutions. Its redox potential at basic pH values ensures the reductive dehalogenation to occur but it is not possible to study in detail the potentials needed for this process to proceed. The activity of some enzymes is also pH dependent and that precludes the use of titanium (III) citrate in those cases.

Dehalogenation often proceeds sequentially, successive halogen atoms are removed one-by-one, which is characteristic and fully proven for polyhalogenated aromatic compounds or, in general, compounds with conjugated bonds. Successive halogen atoms are removed at more and more cathodic potentials. In some cases this is the reason for the failure to totally dehalogenate such a compound, if it was not possible to attain a sufficiently cathodic potential under given conditions. On the other hand, the less halogen atoms in a molecule, the lower the oxidation potential, and consequently the molecule becomes more prone to oxidative biodegradation. The knowledge of potentials of the successive dehalogenation steps may be important for the process planning. A knowledge of redox potentials at which the successive dehalogenation steps occur might be important for process planning and prediction of expected products, as some partial dehalogenation products may be even more hazardous both for the environment and health safety.

Dehalogenation of vicinal dihalogen compounds may proceed differently [11]. The reaction gives rather alkenes as products as a result of elimination of both halogen atoms than sequential abstraction.

The technical product obtained by bromination of a butadiene trimer, (1*Z*, 5*E*, 9*E*)-cyclododeca-1, 5, 9-triene, contains predominantly γ -HBCD (>70%), with a minor amount of α - and traces of β -isomers [12]. Interconversion proceeds rather easily and regardless of the initial isomeric composition, heating to temperatures above 160°C results in a mixture at equilibrium at that temperature. Schematic representation of all possible isomers is shown below [13]. Three pairs of enantiomers (α , β and γ) and two further meso forms (δ and ϵ) were identified from NMR spectra.

The aim of this work was to determine the potentials needed for reductive debromination of HBCD and to test in this reaction the catalytic activity of cobalt tetraphenylporphyrin, a cobalt complex with a tetrapyrrole macrocyclic ligand, like cobalamin, active in the anaerobic microbial dehalogenation.

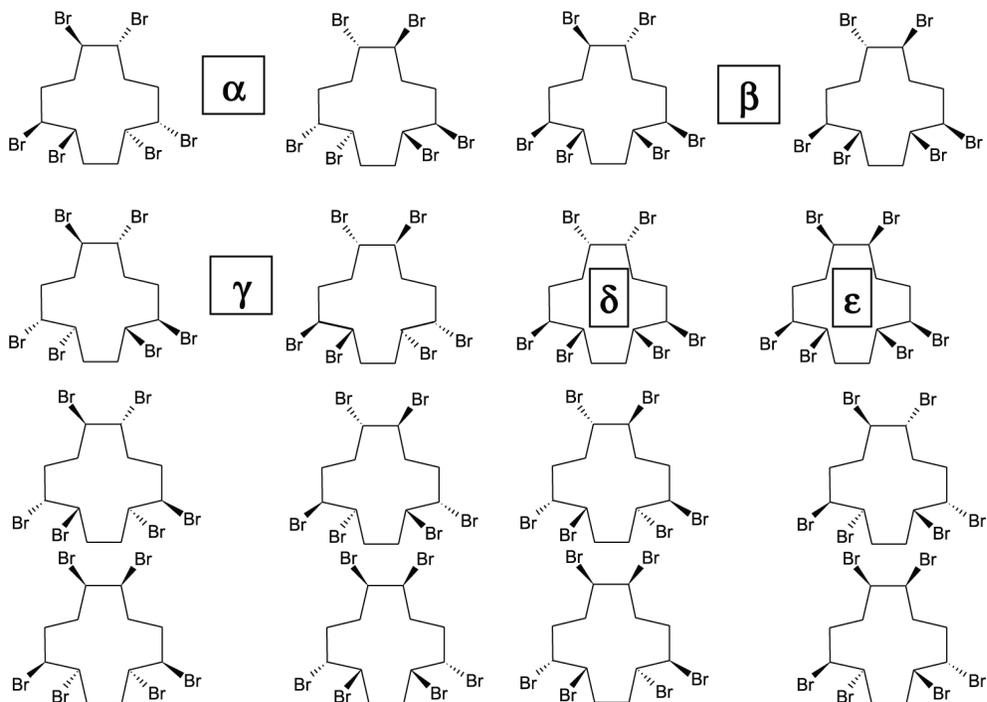


Fig. 1. Schematic representation of all possible isomers of HBCD

Rys. 1. Schematyczne przedstawienie wszystkich możliwych izomerów HBCD

2. Experimental

Cyclic voltammetry measurements were done using a BAS 100B/W Electrochemical Workstation with a C3 Cell Stand (Bioanalytical Systems) with a standard three-electrode cell. The working electrode was a 1.6 mm diameter glassy carbon electrode (Mineral) and platinum wire was the auxiliary electrode. All potential were measured and quoted against an Ag/AgCl (3 M NaCl) electrode that was put into a double bridge filled in the upper part with 3 M NaCl solution and in the lower part with supporting electrolyte solution, both solutions being separated by a cotton wool plug, and separated from the test solution by a dense ceramic frit. 0.1 M tetra-*n*-butylammonium tetrafluoroborate (Fluka) was employed as the supporting electrolyte solution. The ready solution was additionally dried with 4A molecular sieves. All measurements were done under dry argon atmosphere (Ar-N 5.0, Linde). Voltammograms were registered at 100 mV s⁻¹ scan rate unless otherwise noted.

Ferrocene was used as an internal standard and the $E_{1/2}$ potential for Fc⁺/Fc was 0.544 V vs. employed reference electrode in the cell used.

Dimethylformamide (for analysis, POCh) was purified in two steps. First, toluene was added and toluene-water-DMF azeotrope was distilled off. Then, DMF was distilled fractionally under vacuum at temperatures not exceeding 90°C. Purified DMF was kept under 4 A molecular sieves dried under vacuum at 180°C.

3. Results and discussion

HBCD is practically insoluble in water. Initial attempts to use carbon paste electrodes demonstrated that it undergoes reduction, but the waves were very broad and practically no peak could be spotted. It was decided to continue measurements in dimethylformamide (DMF). HBCD gives very distinct reduction wave with a peak at -1.6 to -2.0 V vs. Ag/AgCl electrode, as shown in Fig. 2. When scanning first towards anodic potentials starting at 0 V no anodic process can be observed. Yet if scanning first towards cathodic potentials and next towards anodic on the reverse scan, then a wave appears at $+0.77$ V. Its intensity depends above all on the time that had gone since the reduction of HBCD, the wave might even disappear after longer time, as seen in hold-ramp-step experiments. Adding a bromide salt has proven that the wave was due to bromide anion oxidation and even a small reduction wave observed at about 0 V is due to the reduction of the formed bromine or its chemisorbed form on the carbon electrode. It is thus a direct proof of debromination occurring.

The presence of a wave due to the oxidation of bromide anion was applied to measure the potentials at which debromination might proceed. It was demonstrated that this occurs even at potentials as high as -1.0 V, i.e., 1.0 V more anodic than the peak potential. It means that the reductive debromination is associated with a high energy barrier. Experiments with high or low scanning rates did not show any new waves. Characteristically, at high scan rates the intensity of bromide oxidation was higher due to a shorter time that had passed since the reduction of HBCD. The opposite was observed at low scan rates. It is rather improbable that bromide anion undergoes any further reaction. Its disappearance is most probably associated with its dispersion by diffusion. Even scan rates as high as 2 V s^{-1} did not show any trace of the anodic wave corresponding to the reduction of HBCD, which proves that breaking off the bromide is a very fast process, as known from the literature.

Cobalt tetraphenylporphyrin (CoTPP) shifts the reduction of HBCD by more than 1 V, as can be seen from Fig. 4. The bromide wave also appears, which proves the catalytic activity

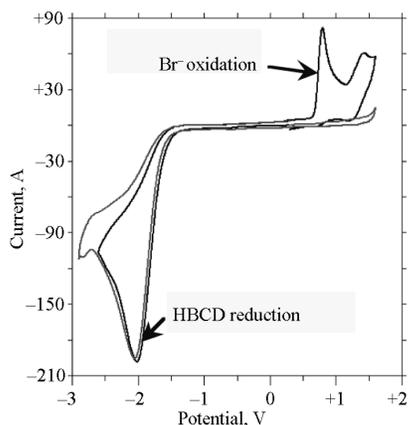


Fig. 2. Cyclic voltammetry of HBCD reduction in DMF. Seen are HBCD reduction and Br^- oxidation. When the scanning was started towards positive potentials, no Br^- wave appeared

Rys. 2. Woltamperogram cykliczny dla redukcji HBCD w DMF. Widać redukcję HBCD i utlenianie Br^- . Gdy skanowanie rozpoczęto w kierunku potencjałów dodatnich, nie pojawiła się fala Br^-

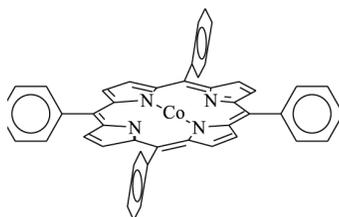


Fig. 3. Cobalt tetraphenylporphyrin

Rys. 3. Tetrafenyloporfiryra kobaltowa

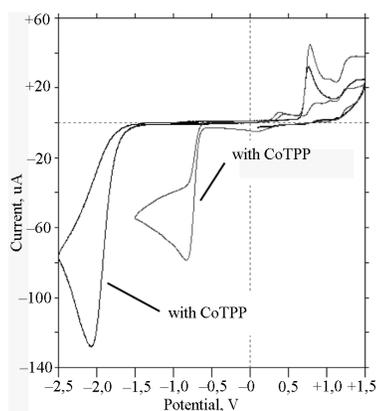


Fig. 4. Comparison of HBCD reduction in the presence and without CoTPP. The reduction potential is shifted by more than 1 V. The presence of Br^- oxidation is a proof that debromination occurs in both uncatalysed and catalysed processes

Rys. 4. Porównanie redukcji HBCD w obecności i bez CoTPP. Potencjał redukcji został przesunięty o więcej niż 1 V. Obecność utleniania Br^- stanowi dowód, że debrominacja zachodzi zarówno w procesie katalizowanym jak i niekatalizowanym

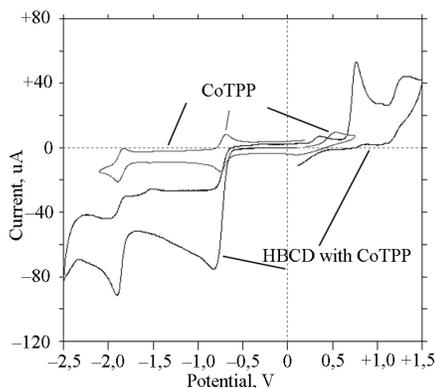


Fig. 5. Comparison of HBCD catalytic reduction with CoTPP voltammogram

Rys. 5. Porównanie katalitycznej redukcji HBCD z voltamperogramem CoTPP

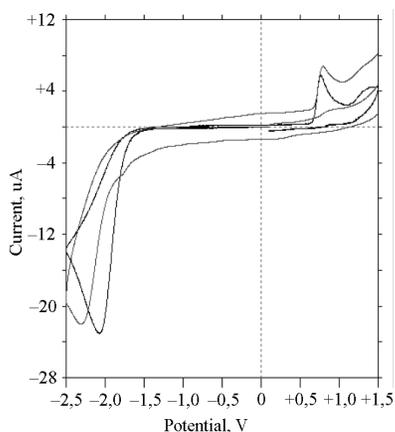


Fig. 6. Comparison of HBCD reduction with 1,2-dibromocyclododecane

Rys. 6. Porównanie redukcji HBCD z redukcją 1,2-dibromocyklododekanu

of CoTPP. A steeper curve of the reduction indicates also an increase in the rate. Apart from bromide anion oxidation a small wave is seen at +0.36 V.

It was also interesting to compare the voltammograms of pure CoTPP without HBCD added with that of the catalysed process. As can be seen from Fig. 5, the catalytic process is associated with the Co(II)/Co(I) and the further reduction of Co(I)TPP. The height of the catalytic wave, several times greater than for CoTPP alone indicates also high turnover numbers.

It might be expected that the catalytic reaction proceeds by transient formation of an alkyl-cobalt complex, as in other cobalt porphyrin catalysed reductive dehalogenations.

It is known that halogen atoms are removed sequentially, which means at more and more cathodic potentials in conjugated systems. Thus it could be expected that bromide anions might be removed upon reductive dehalogenation in two steps, at two different potentials. To verify this hypothesis, 1,2-dibromocyclododecane was synthesised. With respect to this hypothesis there should be no difference between HBCD reduction and 1,2-dibromocyclododecane reduction. However, the results proved otherwise. As can be seen in Fig. 6, the reduction wave for 1,2-dibromocyclododecane is shifted towards more cathodic potentials with respect to HBCD reduction. On the other hand, it was also checked in hold-ramp-step experiments, that 1,2-dibromocyclododecane can be reduced even at -1.0 V. That means that the process is associated with a high energy barrier, as in the case of HBCD. But in the case of 1,2-dibromocyclododecane, there are even bigger kinetic obstacles that shift the peak further towards negative potentials.

4. Conclusions

Hexabromocyclododecane undergoes reductive debromination at the cathode at highly cathodic potentials in the absence of a catalyst. The presence of bromide anions as reaction products is a direct proof of debromination occurring. The process starts at potentials more positive by about 1 V, but is very sluggish. Cobalt tetraphenylporphyrin catalyses the process

very efficiently. The potential is shifted by 1.2 V and the steepness of the voltammetric wave indicates high rate. 1,2-dibromocyclododecane is also debrominated electrochemically. The process is associated however with higher energy barriers than that for HBCD. This means that debromination is favoured by the presence of more bromine atoms in the saturated molecule, not necessarily placed at very close positions.

References

- [1] Yogui G.T., Sericano J.L., *Environ. Int.*, 2009, 35, 655-666.
- [2] Jiao L., Zheng G.J. et al., *Environ. Pollut.*, 2009, 157, 1342-1351.
- [3] Wang Z., Ma X., Lin Z., Na G., Yao Z., *Chemosphere*, 2009, 74, 896-901.
- [4] BSEF, *Brominated Flame Retardants and the new EU chemical policy (REACH)*, 2006 (www.ebfrp.org/publications.html).
- [5] Kemmlein S., Herzke D., Law R.J., *J. Chromatogr. A*, 2009, 1216, 320-333.
- [6] Gerecke A.C., Giger W. et al., *Chemosphere*, 2006, 64, 311-317.
- [7] Costentin C., Robert M., Savéant J.-M., *J. Am. Chem. Soc.*, 2004, 126, 16834-16840.
- [8] Lexa D., Savéant J.-M., *Acc. Chem. Res.*, 1983, 16, 235-243.
- [9] Thauer R. K., *Microbiology*, 1998, 144, 2377-2406.
- [10] Holliger C., Wohlfarth G., Diekert G., *FEMS Microbiol. Rev.*, 1999, 22, 383-398.
- [11] Lexa D., Savéant J.-M., Binh Su K., Li Wang D., *J. Am. Chem. Soc.*, 1987, 109, 6464-6470.
- [12] Hu X., Hu D., Song Q., Li J., Wang P., *Chemosphere*, 2011, 82, 698-707.
- [13] Heeb N.V., W. Schweizer W.B., Mattrel P., Haag R., Gerecke A.C., Schmid P., Zennegg M., Vonmont H., *Chemosphere*, 2008, 73, 1201-1210.