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Short communication

Reductive debromination of decabromodiphenyl ether yields brominated dibenzofurans in a Pschorr-type cyclisation

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Grzegorz Rotko, Piotr P. Romańczyk *, Stefan S. Kurek *

Faculty of Chemical Engineering and Technology, Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, Poland

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ABSTRACT

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1. Introduction

Calculations

Dibenzofurans have not been expected as products of the reductive debromination of polybrominated diphenyl ethers (PBDEs). Based on literature data, this process, occurring in nature under anoxic conditions, would give less-brominated diphenyl ethers [1] that are hazardous environmental pollutants but not as notorious as polyhalogenated dioxins or dibenzofurans. These may be formed from PBDEs in free-radical thermolysis [2] or photochemical degradation [3]. The occurrence of dibenzofurans in aquatic sediments polluted by PBDEs has never been reported. However, they have been occasionally found in GC–MS analyses of environmental samples, but it was suspected that they were products of thermal decomposition of PBDEs in the chromatograph inlet system. On the other hand, mass balances of the reductive dehalogenation products indicated that the identified substances constitute only a fraction of all products [4]. In some cases most compounds remained unidentified.

Intramolecular substitution of aromatic compounds by aryl radicals leading to cyclisation, called Pschorr reaction, proceeds easily, particularly in systems that are activated by the character of the bridge linking the two reacting aryl rings, like ether or carbonyl groups [5,6], and electron-withdrawing substituents in the aryl ring [7]. Using typical conditions, dibenzofurans may be synthesised from diazotised *o*-(aryloxy)anilines [8]. Cathodic generation of aryl-centred radicals may also serve as a convenient route to the Pschorr-type cyclisation

* Corresponding authors. Tel.: +48 126282770.

E-mail addresses: piotrom@chemia.pk.edu.pl (P.P. Romańczyk), skurek@chemia.pk.edu.pl (S.S. Kurek).

Brominated dibenzofurans are readily produced from decabromodiphenyl ether by a Pschorr-type cyclisation upon reductive debromination in the absence of good H-donors. DFT-D calculations confirmed that, for polybrominated diphenyl ethers, the reaction is strongly favoured both kinetically and thermodynamically. © 2013 Elsevier B.V. All rights reserved.

[9,10]. Recently, the presence of non-brominated dibenzofuran was reported in the electrolysis products of decabromodiphenyl ether in DMF [11]. The electrolysis was carried out at a highly cathodic potential, under conditions, where degradation of diphenyl ether occurred with even benzene and phenol as products. In the same paper, as well as in earlier works [12,13], it was shown that the use of a better H-atom donor, as a solvent, leads to a simpler cyclic voltammetry pattern and no detectable amounts of dibenzofuran in the products.

Here, we report that heptabromodibenzofuran (HeptaBDF) is readily formed from decabromodiphenyl ether (DecaBDE) under reducing conditions in aprotic media with no easily available H-atom donor.

2. Electrochemical and analytical methods

Electrochemical measurements were performed on a BAS 100B/W Electrochemical Workstation in $0.1 \, M \, n$ -Bu₄NBF₄ N,N-dimethylformamide (SeccoSolv, Merck) (DMF) solution under argon at RT. A glassy carbon electrode (2.3 mm²) was used as the working electrode, platinum as the auxiliary and Ag/AgCl (3 M NaCl) as the reference. The transfer coefficient was calculated using the published method [14]. Spectroelectrochemistry measurements were carried out with a HP 8453 spectrophotometer in 0.2 cm quartz cuvette equipped with Pt band working electrode. DecaBDE (Sigma-Aldrich, 98%) was recrystallised from CH₂Cl₂. 1,2,3,4,6,7,8-Heptabromodibenzofuran (HeptaBDF) was synthesised according to [15], and its identity was checked spectroscopically. GC–MS analyses were carried out on Trace GC Ultra/ITQ 1100 instrument with an Rtx-1614 column (30 m, 0.25 mm ID, 0.10 µm df). Calibration standard: BFR-CS5 Wellington Laboratory.

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3. Quantum chemical calculations

All calculations were carried out with Gaussian program package [16] using density functional theory (DFT). The B3LYP [17,18] hybrid functional with 6-31+G(d,p) basis set was employed for geometry optimisations and calculation of harmonic frequencies followed by single-point energy calculations with a larger triple- ζ basis 6-311+G(d,p). Open-shell species were treated within the spin-unrestricted scheme. The polarisable continuum solvation model (IEF-PCM) [19] was used to account for the effect of DMF solvent. The reported energies and barriers include dispersion corrections obtained from a single-point DFT-D2 [20] calculation on top of the DFT-optimised structures. We found that this computational protocol satisfactorily takes into account van der Waals interactions [21]. The standard Gibbs energies are given for 1 mol·L⁻¹ at 298.15 K. Reduction potentials were calculated from the total free energy of an electron attachment in solution.

4. Results and discussion

Cyclic voltammetry (CV) of DecaBDE in dry DMF showed unexpectedly a quasi-reversible wave at the end of the reduction (Fig. 1). This wave was found to be due to non-brominated dibenzofuran by comparison with an authentic sample. It also appeared that the voltammogram of HeptaBDF is virtually identical with that of DecaBDE in the range of the last six waves, as shown in Fig. 1a. This would indicate that the cyclisation to dibenzofurans occurs in the early stage of the reduction. To prove it, we analysed the reaction mixture taken from under the electrode after electrolysis at -1.8 V vs. Fc^{+/0}. GC–MS showed the presence of mainly 2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether (o-NonaBDE) as the principal constituent, but also the presence of HeptaBDF. We also recorded UV-vis spectra of the mixture adjacent to a Pt band electrode during electrolysis at -1.8 V vs. Fc^{+/0}. At the beginning, the spectrum pointed to DecaBDE decay and NonaBDEs formation mixed with some unidentified compounds. At the later stage, the differences between subsequent spectra became clearer, as demonstrated in Fig. 2. Eventually, the spectrum of HeptaBDF emerged, but blurred by a spectrum of another product(s). It can be due to oligomeric substances usually observed at the electrode.

The addition of alcohols brings about a change in the voltammetric pattern. As shown in Fig. 1b, a 200-fold excess of 1-propanol totally inhibits the formation of dibenzofuran. The reduction waves are shifted, which proves that we are dealing with a different mechanism. Moreover, beginning with a potential of -1.7 V, the number of waves decreased to four, which corresponds to the number expected for the reduction of OctaBDEs. This is in agreement with a typical pattern observed for polyhalogenated arene reduction, where the number of waves matches the number of halogen atoms in the ring [22,23]. We



Fig. 2. Difference between the consecutive spectra during electrolysis of DecaBDE at -1.8 V (solid lines) and the comparison spectrum of HeptaBDF (dotted line).

also found that lesser quantities of 2-propanol (50-fold excess), a better H[•] donor, suffice to block the cyclisation. This indicates that the cyclisation is suppressed rather by H-transfer than by H⁺ transfer. In the presence of effective H-donors, the reaction proceeds in consecutive steps of debromination, and the final product is non-brominated diphenyl ether.

To gain a deeper insight into the mechanism of the cyclisation, DFT-D calculations were performed at the PCM-B3LYP-D2/6-311+G(d,p)// PCM-B3LYP/6-31+G(d,p) level. Fig. 3a demonstrates the contour plot of the lowest unoccupied molecular orbital (LUMO) for DecaBDE. This orbital has an antibonding σ^*_{C-Br} character; thus, the electron transfer onto DecaBDE in DMF should follow a concerted dissociative electrontransfer (DET) pathway. In fact, an optimisation of DecaBDE^{*-} in solution leads to its spontaneous breaking into the radical-anion pair (Ar^{*}, Br⁻)_{solv} (Fig. 3b), which corresponds well with the obtained values of the transfer coefficient, α , as low as 0.25, characteristic of the concerted DET [24]. This result is in sharp contrast to the dominant view that ET to aromatic halides gives stable transient radical anions (stepwise mechanism) [24–26], which indeed is true in the case of molecules with π^* -type LUMO.

The cleaved C-Br bond is that in the *ortho* position and the adduct 1^{-} Br⁻ thus formed readily dissociates in DMF, yielding free Br⁻ (detected in CV) and radical 1^{+} that is more stable in energy than the *p*- and *m*-isomer by 1.0 and 2.0 kcal·mol⁻¹, respectively.

Next, the radical **1**[•] undergoes outer-sphere reduction to an anion $(E^{0}_{calcd} = 0.03 \text{ V vs. Fc}^{+/0})$ that abstracts a proton, most probably from residual water, yielding *o*-NonaBDE. The results of GC–MS analysis (vide supra) fully confirm that the main product of the first step of debromination is *o*-NonaBDE.



Fig. 1. Semi-differential CVs of (a) DecaBDE (2 mM) and HeptaBDF (satd., ca. 1 mM) (please note the wave at -2.9 V ascribed to non-brominated dibenzofuran quasi-reversible reduction), (b) DecaBDE prior to and after addition of a 200-fold excess of 1-propanol. Conditions: DMF/0.1 M *n*-Bu₄NBF₄ at GCE, v = 0.1 V s⁻¹.



Fig. 3. (a) LUMO of DecaBDE (contour plots for isovalue of 0.04 bohr^{-3/2}) and (b) radical-anion pair ($1^{-}Br^{-}$), the direct product of DecaBDE one-electron "sticky" dissociative reduction; d = 2.60 Å.



Fig. 4. (a) Gibbs energy diagram (kcal·mol⁻¹) for (a) the cyclisation of the radical **3**[•] formed upon *o*-NonaBDE one-electron dissociative reduction, and (b) plausible H-atom migration following Br⁻ dissociation in **3**⁻ eventually to yield 1,2,3,4,6,7,8-heptabromodibenzofuran (HeptaBDF).

Calculations have shown that o-NonaBDE also possesses the σ^*_{C-Br} -based LUMO, but located only on the phenyl ring containing more Br atoms, in agreement with recently published data [27]. Therefore, it undergoes concerted DET leading to the radical 2' (Fig. 4a), which may next be easily converted to radical 3' (the Pschorr-type cyclisation). Our DFT-D results clearly demonstrate that the energy barrier for thermodynamically favourable ring closure in radical 2' is only 4.4 kcal·mol⁻¹ (rate constant, k, of the order of 10^9 s^{-1} at 298 K), which corresponds well to the electrochemical results showing this to be a very fast process. Moreover, we found that the bromine substituents in the rings play an important role since the TS for a similar cyclisation of non-brominated diphenyl ether radical lies 7 kcal·mol⁻¹ higher than **TS1** (i.e., $\Delta G^{\ddagger} = 11.4 \text{ kcal} \cdot \text{mol}^{-1})^1$. Radical **3** thus formed may be rapidly reduced by outer-sphere ET to anion $\mathbf{3}^{-}$ ($E^{0}_{\text{calcd}} = -0.56 \text{ V vs. Fc}^{+/0}$, and a very low estimated reorganisation energy of $4.3 \text{ kcal} \cdot \text{mol}^{-1}$), in which in turn occurs a loss of bromide to give a carbene followed by 1,2hydrogen atom shift (TS2) eventually leading to HeptaBDF (Fig. 4b). This step is predicted to be a moderately fast $(k \sim 10^2 \text{ s}^{-1})$ and strongly exergonic process ($\Delta G^0 = -73.5 \text{ kcal} \cdot \text{mol}^{-1}$). The occurrence of HeptaBDF in the reaction mixture after reduction at a potential -1.8 V was proven by CV and spectroelectrochemistry (see Figs. 1a and 2); the reversible wave of dibenzofuran reduction diminishes significantly only for scan rates exceeding 10 V s⁻¹. Experimental results indicate that the cyclisation may be blocked by the addition of excess alcohol, which is corroborated by DFT-D modelling showing that 2-propanol is an effective H[•] donor for radical **2'** leading to the formation of stable OctaBDE ($\Delta G^0 = -23.1 \text{ kcal} \cdot \text{mol}^{-1}$).

5. Conclusions

Joint experimental and quantum chemical studies clearly showed that environmentally hazardous polybrominated dibenzofurans are formed at the early stage of the reductive dehalogenation of PBDEs. The presence of a good H-atom donor suppresses the reaction. The cyclisation is strongly favoured, both thermodynamically and kinetically, for diphenyl ethers containing many Br atoms.

 $^{^1}$ This result agrees well with the previous prediction for non-brominated or monobrominated BDE radicals (ca. $10\,kcal\cdot mol^{-1})$ [2,6].

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