HOST–GUEST INTERACTION OF PESTICIDE BIFENOX WITH CYCLODEXTRIN MOLECULES. AN ELECTROCHEMICAL STUDY

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This work is dedicated to the late Professor Jaroslav Heyrovský for his numerous scientific achievements in the fields of analytical and physical chemistry. We want to commemorate the 50th anniversary of the Nobel Prize awarded to him for his discovery and development of the polarographic methods of analysis.

The reduction of nitroaromatic compound bifenox (methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate) was studied in aprotic solvents in the absence or presence of cyclodextrin (CD) molecules of different cavity sizes. βCD and γCD form complexes with bifenox in DMSO with the complex formation constants $(5 \pm 2) \times 10^2$ M^{-1} [βCD–bifenox] and $(3 \pm 1) \times 10^2$ M^{-1} [γCD–bifenox], respectively. Bifenox yields a relatively stable anion radical in dimethyl sulfoxide, which is further reduced at more negative potentials by an overall addition of three electrons and four protons to the corresponding phenylhydroxylamine. In the presence of βCD the first reduction wave of bifenox becomes irreversible, it is shifted towards more positive potentials and the uptake of more than one electron is observed (up to four electrons during the exhaustive electrolysis). The first reduction wave of bifenox is not affected by the addition of glucose confirming that a simple availability of protons from the OH groups is not the main factor in further transformation of anion radical in the presence of βCD. The complex formation with βCD facilitates the protonation and additionally protects the molecule from disintegration into 2,4-dichlorophenol. A yield of 2,4-dichlorophenol decreases in the order βCD, γCD and αCD, respectively.

Keywords: Reductions; Electroreduction; Nitro anion radical; Diphenyl ether herbicide; Bifenox; Cyclodextrins; Pesticides; Electrochemistry; Polarography.

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Bifenox (methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate), trade name Modown, belongs to a group of nitro pesticides (Fig. 1) acting on the foliar tissue of broad-leaved weeds and grasses. Its herbicidal action is directly linked to the production of reactive free radicals, which inhibit the photosynthetic process and cause the cell damage.

Electrochemical properties of bifenox are primarily given by the presence of a nitro group. The reduction of aromatic nitro compounds was investigated for decades and reduction products in different reaction media are well-known[1,2]. In the aprotic media, it starts with an uptake of one electron leading to the formation of a nitro anion radical

$$\mathrm{Ar{-}NO_2} + \mathrm{e} \rightleftarrows \mathrm{Ar{-}NO_2^{\bullet -}} . \qquad (1)$$

The reactivity and stability of the electrochemically-generated anion radical depend strongly on the presence of proton donors in the system. The second reduction step leading to a dianion of nitro compounds is not observed at ordinary experimental conditions and was detected only in liquid ammonia[3]

$$\mathrm{Ar{-}NO_2^{\bullet -}} + \mathrm{e} \rightleftarrows \mathrm{Ar{-}NO_2^{2-}} . \qquad (2)$$

In the non-aqueous aprotic solvents the anion radical is further reduced by an overall addition of three electrons and four protons yielding phenylhydroxylamine[3–5]

$$\mathrm{Ar{-}NO_2^{\bullet -}} + 3\ \mathrm{e} + 4\ \mathrm{H^+} \rightarrow \mathrm{Ar{-}NHOH} + \mathrm{H_2O} . \qquad (3)$$

Many researchers studied different aspects of the formation and reactivity of aromatic nitro anion radicals[6–13]. This included the effect of ion-pairing[6], the reactant size[11] and solvent effect[12], the effect of adsorption on the electron transfer rates[7,9,14], and the double-layer effect resulting from the different planes of the closest approach for different electrolyte cations[15].

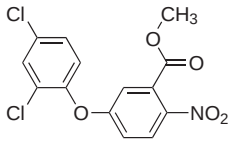

FIG. 1
Chemical structure of bifenox

Squella et al.[16–18] studied the coupled chemical reactions of the electrochemically-generated nitro radical anion by cyclic voltammetry and concluded that the electrode process follows an EC_2 mechanism. In buffered mixed media the second-order kinetics lead to disproportionation of the nitro anion radical

$$2\ Ar–NO_2^{\bullet -} + 2\ H^+ \rightarrow Ar–NO_2 + Ar–NO + H_2O \qquad (4)$$

whereas the dimerization reaction is the primary mode of the radical anion decay in the aprotic medium. Kastening[19,20] followed the disappearance of $Ar–NO_2^{\bullet -}$ anion radical with EPR and UV-Vis spectroscopy techniques. He concluded that the decrease in anion radical concentration occurs in two competitive processes, one of which is the first order in H^+ and $Ar–NO_2^{\bullet -}$ concentration. The other one is the second order in $Ar–NO_2^{\bullet -}$ concentration and its rate is pH independent.

The reduction of bifenox in aprotic solvents proceeds in a sequence of redox steps common to nitroaromatic compounds. The reduction is characterized by a reversible monoelectronic formation of a reactive anion radical at –1.45 V against ferrocene/ferrocenium couple (Fc) according to Eq. (*1*). The anion radical is characterized by an EPR spectrum with the hyperfine coupling constants a_N = 9.358 G, a_H = 3.31 G and $2a_H$ = 21.07 G. The EPR spectrum is consistent with spectra of radicals of aromatic nitro compounds. The anion radical is further reduced at more negative potentials (–1.9 V or more against Fc) in an irreversible three-electron process described by Eq. (*3*). Details concerning the reaction mechanism, EPR spectra and product identification were thoroughly described in our previous communication[21]. Further reduction of the electrochemically-generated bifenox anion radical is strongly influenced by the concentration and nature of the cation of the indifferent electrolyte[22]. In this work we focused our attention on the reactivity of electrochemically-generated bifenox anion radical in dimethyl sulfoxide in the absence or presence of cyclodextrin (CD) molecules.

Cyclodextrins are macrocyclic glucose oligomers capable of binding a variety of guest molecules inside their torus-shaped cavities[23] altering the immediate environment of the reacting species. In this communication we studied bifenox reduction in the presence of three cyclodextrin molecules of different cavity size, namely, α-cyclodextrin (αCD), β-cyclodextrin (βCD), and γ-cyclodextrin (γCD). The internal diameter of their cavities is in the range of 0.42–0.53 nm for αCD, 0.56–0.65 nm for βCD and 0.68–0.83 nm for γCD, respectively.

Electrochemical behavior of nitrobenzene and substituted nitrobenzenes in the presence of CD molecules has been studied only in the aqueous environment[24–29]. The electrochemical measurements confirmed the complex formation of αCD with *p*-chloronitrobenzene and *p*-nitrophenolate. Kano et al.[31] proved the stabilization of nitrophenolate anion radical by αCD in aqueous solutions, since the anodic reoxidation was barely visible in the absence and clearly recognizable in the presence of CD. EPR spectra provided further evidence for the incorporation of anion radical into the CD cavity. It was suggested that the observed stabilization of the anion radical could have resulted from suppression of the protonation of the nitro group inside the CD cavity.

We did not find any reports dealing with transformation of the nitro anion radicals in aprotic solvents in the presence of CD molecules. Although the stability of complexes in aprotic solvents is lower than in water, it is still high enough to permit the complex formation. Main goal of this work is to investigate the effect of CD molecules of different cavity size on the redox properties of pesticide bifenox with particular focus on the fate of bifenox anion radical.

EXPERIMENTAL

Materials

Bifenox was purchased as a pesticide reference material (with the 99.0% purity certificate) from Dr. Ehrenstorfer, GmbH (Augsburg, Germany). Nitrofen, pestanal grade, was obtained from Riedel-de-Haën. All three cyclodextrins, glucose (Fluka) and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) from Sigma were dried before use. 2,4-Dichlorophenol (Aldrich) was used as received. Dimethyl sulfoxide (DMSO; Sigma) as received contained 1200 ppm of water, whereas the treatment with activated molecular sieves 3 Å (Lachema, Brno) decreased the water content to 60 ppm based on the Karl Fischer titration.

Techniques

Electrochemical measurements were done using an electrochemical system for cyclic voltammetry, phase-sensitive AC polarography and DC polarography. It consisted of a fast rise-time potentiostat and a lock-in amplifier (Stanford Research, model SR830). The instruments were interfaced to a personal computer via an IEEE-interface card (PC-Lab, AdvanTech Model PCL-848) and a data acquisition card (PCL-818) using 12-bit precision. A three-electrode electrochemical cell was used. The reference electrode (Ag|AgCl|1 M LiCl) was separated from the test solution by a salt bridge with double fritted junction. After the measurement, ferrocene was added as an internal standard, voltammogram on the gold electrode was recorded and all potentials are reported against the potential of the ferrocene/ferrocenium couple (Fc). The working electrode was either a valve-operated static mercury electrode (SMDE2, Laboratorní přístroje, Prague) with an area of 1.03×10^{-2} cm^2 or a dropping

mercury electrode with a flow rate of 1.01 mg s^{-1}, reservoir height equal to 43 cm and a computer-controlled drop time of 2 s. The auxiliary electrode was cylindrical platinum net. Oxygen was removed from the solution by passing a stream of argon.

UV spectra were obtained in DMSO using a diode-array UV-Vis spectrometer Agilent 8453.

Since CDs are well soluble in DMSO, this solvent was used exclusively in the experiments that compare the behavior of bifenox radical anion in the absence and presence of cyclodextrin cavities. After exhaustive electrolysis of bifenox the supporting electrolyte was precipitated from the sample by an addition of 4 ml of water to 1 ml of the sample (80% water v/v). In this ratio, DMSO and water form an immiscible phase with dichloromethane, which was used for the extraction of the reduction products. We repeated the extraction three times, each time with a volume of 1 ml. The total volume was adjusted to 5 ml, whereas 1 μl of the resulting solution was injected into the GC/MS spectrometer. The chromatographic separation was performed on a 5% phenyl–95% methylpolysiloxane HP-5MS chemical-bonded fused silica capillary column (Hewlett–Packard) of 30 m length, 0.25 mm internal diameter and 0.25 μm film thickness. A 6890 gas chromatograph (Agilent Technologies) equipped with a quadrupole mass spectrometric detector (at 150 °C), model 5973N (electron impact 70 eV, ion source 230 °C, interface temperature 280 °C), was used for GC/MS analysis of the reduction products. Helium of 99.995% purity was used as a carrier gas. The temperature profile consisted of an isothermal period of 1 min, at an initial temperature of 35 °C, a temperature increase of 10 °C min^{-1} up to 300 °C, followed by an isothermal period of 2.5 min. The sample was also injected without any previous treatment, in which case the initial temperature was 80 °C, with a temperature increase of 10 °C min^{-1} up to 300 °C, followed by an isothermal period of 20 min. The injector (splitless mode) was kept at 250 °C.

RESULTS AND DISCUSSION

Complex Formation Equilibria

The complex formation ability of bifenox with cyclodextrin molecules of different cavity size was studied in dimethyl sulfoxide by UV-Vis spectroscopy. The UV-Vis spectra of bifenox obtained in the presence of different concentrations of βCD are shown in Fig. 2. The absorbance values *A* decrease with the increasing concentration of βCD. The Benesi–Hildebrand analysis[32] of the absorbance spectra at the maximum decrease of *A* (λ = 300 nm) is shown in the inset. Linearity of the plot points to the formation of a 1:1 complex between βCD and bifenox. The Benesi–Hildebrand equation for a 1:1 inclusion complex formation assuming the excess of βCD concentration with respect to bifenox can be expressed as

$$\frac{1}{\Delta A} = \frac{1}{\Delta\varepsilon[\mathrm{G}]} + \frac{1}{\Delta\varepsilon[\mathrm{G}]K_{\mathrm{a}}}\frac{1}{[\mathrm{H}]} \qquad (5)$$

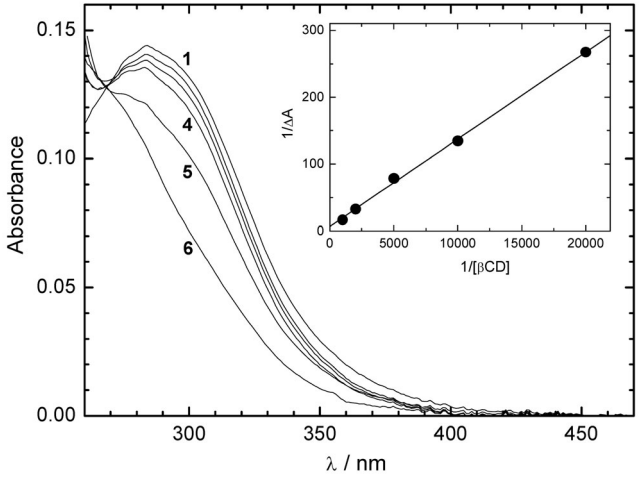

FIG. 2
Absorption spectra of 1×10^{-6} M bifenox in DMSO in the presence of 0 (1), 5×10^{-5} (2), 1×10^{-4} (3), 2×10^{-4} (4), 5×10^{-4} (5) and 1×10^{-3} M (6) βCD. Benesi–Hildebrand analysis of the absorption spectra is shown in the inset

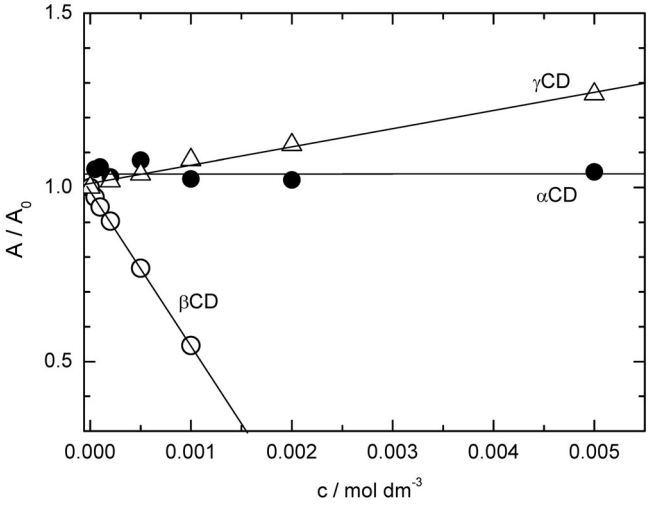

FIG. 3
Graph of the relative absorbance changes A/A_0 of 1×10^{-6} M bifenox as a function of the αCD (●), βCD (○) and γCD (△) concentration in DMSO at λ = 300 nm

where [G] and [H] are the concentrations of the guest and host molecules, ΔA is the change in the absorbance of the guest before and after βCD addition and $\Delta\varepsilon$ is the difference in molar absorptivities between the complexed and free guest. The complex formation constant K_a is obtained from the intercept/slope ratio.

Changes of the bifenox absorbance expressed as A/A_0 at λ = 300 nm as a function of the increasing concentration of αCD (full circles), βCD (○) and γCD (△) are shown in Fig. 3. The absorbance of bifenox in the absence of the cyclodextrin molecules is labeled A_0. Data demonstrate that the absorbance signal of bifenox was not affected by the presence of αCD, whereas the most pronounced changes were observed for βCD followed by γCD. Based on the Benesi–Hildebrand equation (*5*), the following values of the complex formation constants were obtained: $(5 \pm 2) \times 10^2$ M^{-1} for the [βCD–bifenox] complex and $(3 \pm 1) \times 10^2$ M^{-1} for the [γCD–bifenox] complex, respectively. αCD does not form the inclusion complex with bifenox in DMSO.

Electrochemical Behavior

Our electrochemical studies focused on the effect of CD molecules of different cavity size on the reduction behavior of bifenox in DMSO. These cyclodextrins can be divided into two groups: complexing (βCD and γCD) and non-complexing (αCD) species. The redox behavior of bifenox was also investigated in the presence of D-glucose, which is the closest analog to cyclodextrins lacking their ability to form the inclusion complexes. Figures 4 and 5 compare the polarographic behavior of bifenox in the presence of all four compounds.

In the presence of non-complexing species, the first polarographic wave remains unchanged (data are shown for D-glucose in Fig. 4a and for αCD in Fig. 4b) and the first reduction wave is a one-electron reversible process corresponding to reaction (*1*). Only the second polarographic wave shifts towards more positive potentials. A slight decrease of the first polarographic wave in the presence of D-glucose is due to the increased solution viscosity since the concentration of D-glucose was purposely higher in order to achieve the concentration of hydroxyl groups similar to those of the CD molecules. The reversibility of the first reduction process is retained as it is demonstrated in Fig. 6a (●) by the cyclic voltammetry of bifenox in the presence of D-glucose.

Changes in the polarographic behavior of bifenox in the presence of the complexing species are shown in Fig. 5a (βCD) and 5b (γCD). In the pres-

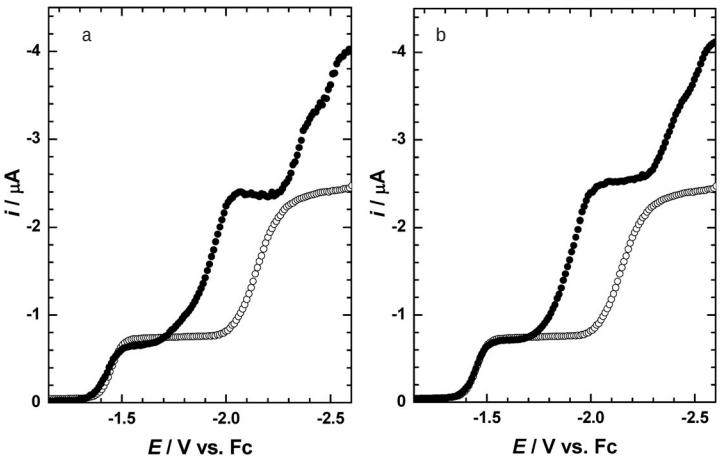

FIG. 4
DC polarograms of 5×10^{-4} M bifenox in 0.1 M tetrabutylammonium hexafluorophosphate in DMSO in the absence (○) or presence (●) of 0.35 M glucose (a) and 8×10^{-3} M αCD (b)

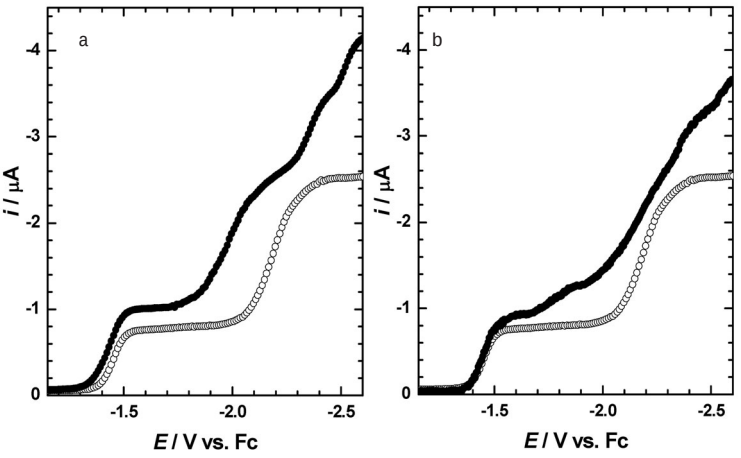

FIG. 5
DC polarograms of 5×10^{-4} M bifenox in 0.1 M tetrabutylammonium hexafluorophosphate in dry DMSO in the absence (○) or presence (●) of 8×10^{-3} M βCD (a) and 8×10^{-3} M γCD (b)

ence of these cyclodextrins, both polarographic waves (first and second) shift towards more positive potentials. The height of the first polarographic wave increases. The log-plot analysis of the first polarographic wave of bifenox (Fig. 5a, ○) gives the slope 60 mV/decade, whereas the higher slopes are obtained for data in the presence of the complexing cyclodextrins. The chemical irreversibility of the electron transfer process is clearly visible in the cyclic voltammogram of bifenox in the presence of βCD (Fig. 6b, ●).

The effect of βCD additions on the reduction of 5.1×10^{-4} M bifenox is shown in Fig. 7. The first reduction wave of bifenox shifts towards more positive potentials and is accompanied by an increase of the limiting current. The second wave is shifted in the same direction as the first one and its height decreases at the expense of the first one. The sum of the currents of both waves remains constant. Two more reduction waves are observed at more negative potentials. The inset in Fig. 7 shows the graph of the half-wave potential shift $\Delta E_{1/2} = E_{1/2} - E_{1/2}^{\text{bif}}$ as a function of the logarithm of the βCD concentration. $E_{1/2}^{\text{bif}}$ is the half-wave potential of the first polarographic wave of bifenox. From the linear segment of the dependence $\Delta E_{1/2}$ against log *c*, the value of 64 ± 2 mV/decade was obtained. Assuming a simple preceding protonation step, one estimates the value of the protonation rate constant as 3×10^6 M^{-1} s^{-1} from the limiting currents of the first reduction wave[33]. The complex formation constant K_a was used instead of the

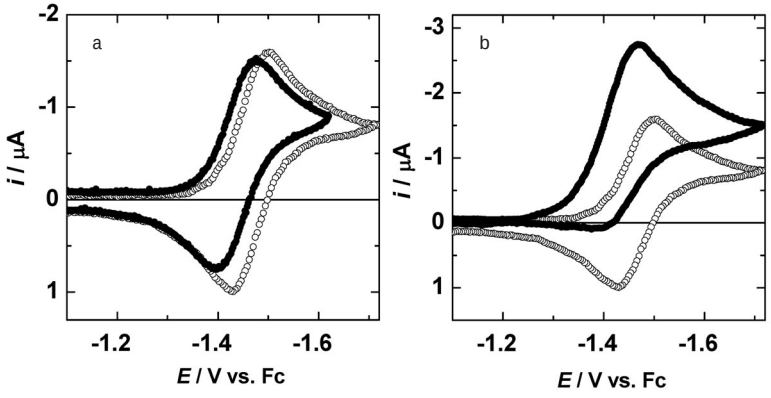

FIG. 6
Cyclic voltammograms of 5.3×10^{-4} M bifenox in 0.1 M tetrabutylammonium hexafluorophosphate in dry DMSO in the absence (○) or presence (●) of 0.354 M glucose (a) and 0.056 M βCD (b). Scan rate was 0.5 V s^{-1}

acid–base equilibrium and the apparent K' was taken from the intersection of the limiting currents of the first and second reduction wave as a function of βCD concentration (data not shown). The determination of the individual steps of the overall mechanism is more complicated, since the complex formation between βCD and the electrochemically-generated bifenox anion radical cannot be excluded[34–36].

It is well known that the nitro group is reduced in two or more separated one-electron transfer steps only in the absence of proton donors[1,2]. At sufficiently low pH and in protic environment only a single four-electron reduction wave to the corresponding hydroxylamine is observed. Therefore, data in Fig. 7 give a strong indication that βCD molecule serves as a proton donor during the bifenox reduction. More importantly, the data in Figs 4–7 show that the presence of the glycosidic OH groups (see data in the presence of D-glucose) is not sufficient for the anion radical protonation and the non-complexing αCD is not a sufficient proton donor either. There is a clear indication that the proton is transferred within the [CD–bifenox] complex.

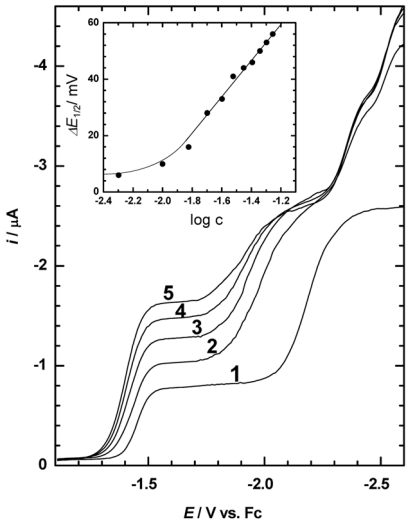

FIG. 7
DC polarograms of 5.1×10^{-4} M bifenox in 0.1 M tetrabutylammonium hexafluorophosphate in dry DMSO in the presence of 0 (1), 0.01 (2), 0.02 (3), 0.03 (4) and 0.039 M (5) βCD. Inset shows the shift of the half-wave potential as a function of βCD concentration

An addition of water to DMSO (up to 12% v/v) does not affect the reversibility of the first reduction wave of bifenox, only the second wave moves slightly towards more positive potentials (data not shown). Therefore, an increase in the current and change of the reduction process to an irreversible one, as can be seen in Fig. 6b in the presence of βCD cannot be caused by any accidental water impurities in the system. It is a direct consequence of the addition of the complexing cyclodextrin. Based on the Bordwell acidity tables[37], water is not a good source of protons in DMSO. Substituted phenols should have this ability. In order to prove the proton-donating abilities of the complex-forming cyclodextrins, 2,4-dichlorophenol was selected as a suitable proton donor. DC polarograms for reduction of bifenox in the presence of increasing amounts of 2,4-dichlorophenol are shown in Fig. 8. They closely resemble those in Fig. 7 and the effect is qualitatively the same. With an increasing amount of the proton donor both the first and second wave shift towards more positive potentials and the first wave increases in height at the expense of the second one. This observation confirms our assumption that the complex-forming CD molecules can serve as proton donors in the overall process of bifenox reduction in the aprotic solvents.

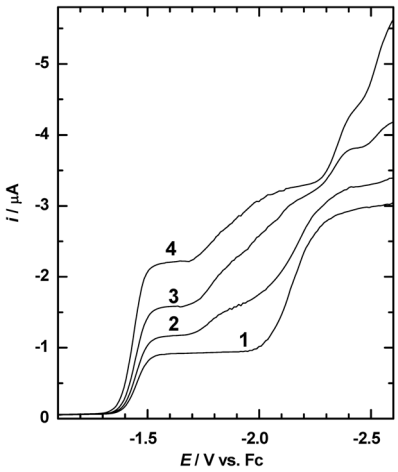

FIG. 8
DC polarograms of 6.2×10^{-4} M bifenox in 0.1 M tetrabutylammonium hexafluorophosphate in dry DMSO in the absence (1) or presence of 1.2×10^{-3} (2), 4.7×10^{-3} (3) and 16×10^{-3} M (4) 2,4-dichlorophenol

Constant Potential Electrolysis

Further insight into the transformation of nitro anion radical in the absence and presence of CD molecules was obtained by a constant potential electrolysis at the limiting current of the first wave (–1.62 V against Fc). The samples were analyzed at different bifenox concentrations from 0.0001 to 0.005 mol l^{-1}, whereas the cyclodextrin concentration varied from 0 to 0.05 mol l^{-1}. The concentration ratio of bifenox and CD was optimized for the GC/MS analysis.

If the anion radical was chemically stable, one should recover the original compound after the exposure of the electrolyzed solution to air due to a so-called "futile cycle" process

$$Ar–NO_2^{\bullet -} + O_2 \rightarrow Ar–NO_2 + O_2^{\bullet -} . \qquad (6)$$

A complete recovery of the aromatic nitro compounds was not observed in the literature due to the follow-up chemical processes[17]. In this work DC polarograms are shown two hours after the exposure of the electrolyzed samples to the air. They remained identical after a prolonged exposure time.

Figure 9 shows a comparison of the DC polarograms of two systems: bifenox in the absence (Fig. 9a) and in the presence (Fig. 9b) of a hundredfold excess of βCD before (●) and after (○) the electrolysis at –1.62 V. The corresponding cyclic voltammograms for the electrolyzed samples are shown in the insets of Fig. 9. Up to 1.3 electrons were consumed during the exhaustive electrolysis of bifenox in the absence of CD, whereas in the presence of βCD the total number of electrons varied from 3 to 4 depending on the βCD concentration (data not shown).

Cyclic voltammograms of the reduction products of bifenox (inset in Fig. 9a) show three peaks labeled *I*, *II* and *III*. Peaks *I* and *III* correspond to the reduction of a nitro group, whereas a new redox couple *II* is observed at –1.87 V at the potential values coinciding with those reported for the reduction of aromatic azoxy compounds[21,38,39]. Cyclic voltammogram of the reduction products of bifenox in the presence of βCD (inset in Fig. 9b) yields also three redox systems. Peaks *I* and *III* correspond to the same nitro product as in the absence of βCD. A new anodic wave *IV* is located at the potential corresponding to oxidation of the arylhydroxylamine derivative[18,40].

The electrolyzed solutions were subjected to GC/MS analysis. Gas chromatogram of the dichloromethane extract of 5×10^{-3} M bifenox is shown in Fig. 10a. The sample contained bifenox and four reduction prod-

ucts labeled A to D. Their mass spectra are shown in Fig. 11. Based on the analysis of the MS fragmentation patterns the main reduction products are: 2,4-dichlorophenol (A), nitrofen, i.e. 2,4-dichlorophenyl-4-nitrophenyl ether (B), and butyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate (D). The identification of compounds A and B was confirmed also by the addition of 2,4-dichlorophenol and nitrofen standards to the analyte. Nitrofen is electroactive and produces similar polarogram to bifenox with two polarographic waves. The electrochemically detected azoxy product (see Fig. 9) was not detected in the extract.

The gas chromatogram of the electrolyzed solutions of bifenox in the presence of βCD is shown in Fig. 10b. These data were obtained at less than a two-fold excess of βCD and three electrons were consumed during the exhaustive electrolysis at –1.62 V. Four products (labeled A, C, E and F) were detected in the dichloromethane extract of this sample. From the analysis of the fragmentation pattern of their mass spectra (see Fig. 11), the products are identified as 2,4-dichlorophenol (A), methyl 5-(2,4-dichlorophenoxy)-2-aminobenzoate (C), 5-(2,4-dichlorophenoxy)-2-nitrosobenzoic acid (E) and methyl 5-(2,4-dichlorophenoxy)-2-nitrosobenzoate (F). Nitroso prod-

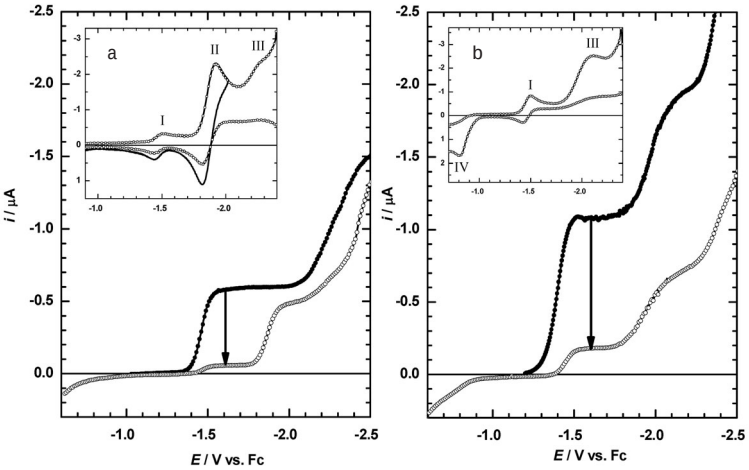

FIG. 9

DC polarograms of 5.1×10^{-4} M bifenox in 0.1 M tetrabutylammonium hexafluorophosphate in dry DMSO in the absence (a) or presence of 5×10^{-2} M βCD (b) before (●) and after (○) exhaustive electrolysis at –1.62 V. Drop time was 1.5 s. Inset shows the corresponding cyclic voltammogram of electrolyzed solutions at scan rate 0.5 V s^{-1}. Electrolyzed samples were exposed to air before the measurements

ucts E and F were not detected at higher ratios of βCD and the corresponding DC polarograms of the electrolyzed solutions showed an increase of the anodic polarographic wave around –0.8 V (see Fig. 9). The GC/MS detection of the hydroxylamine derivative was not possible owing to the instability of this species during the analytical manipulation, which renders its isolation difficult.

The effect of CD on the reduction of bifenox was also studied by the exhaustive electrolysis at the constant potential of the second reduction wave (–2.0 V against Fc). In these experiments 1×10^{-3} M solution of bifenox and 1.6×10^{-2} M αCD, βCD and γCD in 0.1 M $TBAPF_6$ in DMSO were used. Total number of electrons consumed during the exhaustive electrolysis was four for all three CDs and the originally colorless solution changed color to yellow. Only a small continuous increase with respect to the baseline current was observed in DC polarography in the potential range from –1.1 to –2.6 V. No well-defined cathodic wave was discernible, but two anodic waves were observed at $E_{1/2}$ = –0.88 V and $E_{1/2}$ = –0.59 V (data not shown). The first wave corresponds to the oxidation of the hydroxylamine product, the second wave to the oxidation of an amino group[18,40]. The GC/MS analysis of 2 μl of the electrolyzed solutions was performed without any previous

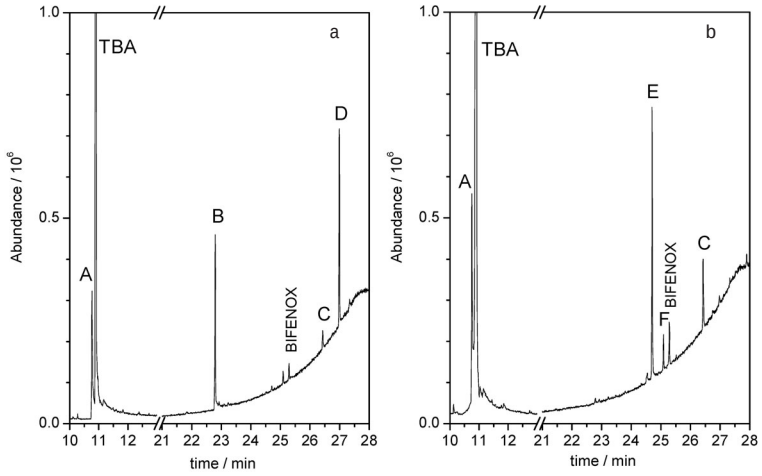

FIG. 10

Gas chromatogram of 5×10^{-3} M bifenox solution in 0.1 M tetrabutylammonium hexafluorophosphate in dry DMSO in the absence (a) or presence (b) of 8.4×10^{-3} M βCD after an exhaustive electrolysis at –1.62 V vs Fc. Products are labeled by capital letters A to F

sample treatment and yielded up to four chromatographic peaks in the gas chromatograms with the retention times 7.3 (A), 10.8 (A′), 18.4 (B) and 22.3 min (C), respectively. The identification of the products as 2,4-dichlorophenol (A), butyl 2,4-dichlorophenolate (A′), nitrofen (B) and methyl 5-(2,4-dichlorophenoxy)-2-aminobenzoate (C) was based on the analysis of

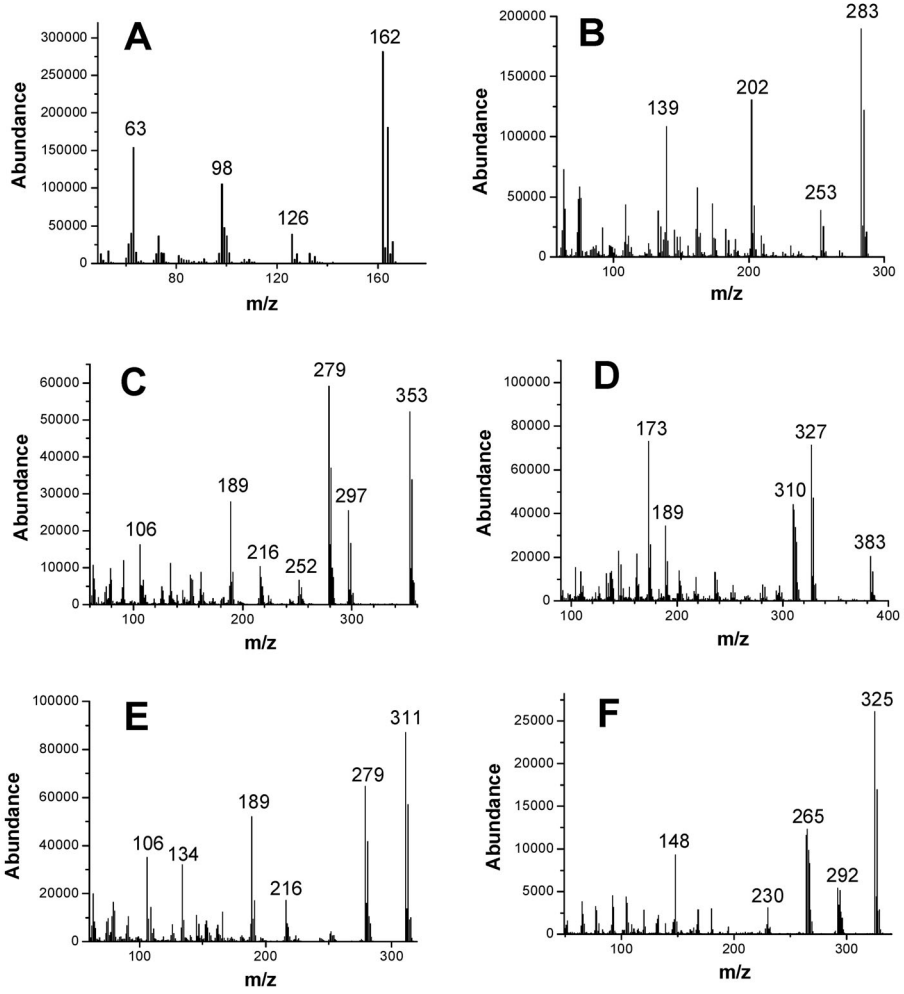

FIG. 11

Mass spectra of the main reduction products A to F obtained after the gas chromatographic separation shown in Fig. 10

their mass spectra. Table I summarizes the yield of each compound in per cent of the peak area to the total peak area of all compounds detected in the chromatogram.

The total percentage of products originating from the cleavage of bifenox at the bridging ether bond (A and A′) correlates with the ability of CDs to form inclusion complexes with bifenox. Such correlation is obvious from Fig. 12, which shows the comparison of the actual peak area of 2,4-dichlorophenol in the GC chromatograms in the presence of different CD molecules. The smallest amount of 2,4-dichlorophenol was observed after electrolysis in the presence of βCD, for which the largest complex formation constant was obtained in DMSO by UV-Vis analysis.

TABLE I
Summary of the electrolytic product yields in per cent of the peak area to the total peak area in the GC chromatogram for bifenox reduction in the presence of CDs

Compound	A, %	A′, %	B, %	C, %
αCD	23.4	62.8	6.6	7.2
βCD	37.3	–	37.7	25
γCD	76.1	–	23.9	–

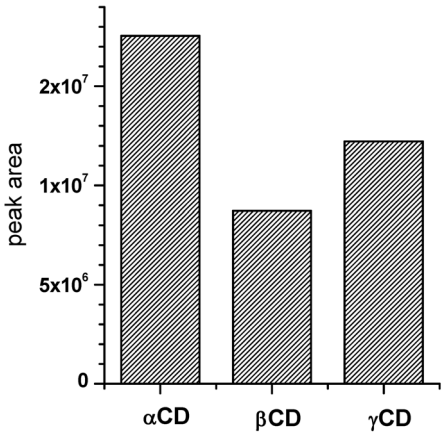

FIG. 12
Histogram of the peak area of 2,4-dichlorophenol product obtained from GC analysis of 1×10^{-3} M bifenox and 1.6×10^{-2} M CD molecules in 0.1 M tetrabutylammonium hexafluorophosphate in DMSO after exhaustive electrolysis at –2.0 V vs Fc

Cyclodextrin molecules have been known to mimic activities of the hydrolytic enzymes and promote the ester hydrolysis through the involvement of the OH groups at the rim of the CD ring[41]. The ability of CD molecules to serve as proton donors in the electrochemical reaction schemes has been demonstrated in our previous work on the reduction of atrazine pesticide in the neutral aqueous environment. Cyclodextrins promote the formation of a protonated form of atrazine leading to the electrochemically-active form of pesticide[42]. We demonstrated in this contribution that the CD molecules provide the necessary protons to complete the reduction of bifenox according to the reaction (*3*) in the aprotic solvent. The complex formation not only facilitates the proton transfer to a bifenox moiety, but also protects the molecule from disintegration.

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