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Oxidative Coupling of Small Oligothiophenes and Oligopyrroles in Water in the Presence of Cyclodextrin. Pulse Radiolysis Investigations

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The oxidation of small oligothiophenes and oligopyrroles (bipyrroles) has been investigated by pulse radiolysis in aqueous solutions containing hydroxypropyl-β-cyclodextrin. Oxidation by the $N_3^\bullet$, $Cl_2^{\bullet-}$, or $Br_2^{\bullet-}$ radicals produces the corresponding radical cations, which are identical to those observed in organic solvent. Detailed kinetic studies with methylbipyrrole show that the homogeneous oxidation occurs after dissociation of the complex but also with the complex itself, contrarily to what is commonly described for electrochemical reduction or oxidation. The produced cation radical is not associated with the cylodextrin and is rapidly expelled from the host after its formation. On the contrary, if the cation radical is deprotonated to form the neutral radical, the neutral radical is associated with the cyclodextrin. Dissociation kinetics rate constants were found to be fast for both cation radical and neutral radical.

Introduction

In organic solvents, the oxidation of small oligothiophenes or oligopyrroles leads to the formation of longer oligomers or polymers.[2] This process involves the formation of the corresponding cation radical[3] which reacts with another cation radical to form a new carbon−carbon bond. This mechanism has been demonstrated in several cases for electrochemical[4−6] and photochemical[7,8] oxidations of these compounds. Water may be an ideal solvent for industrial applications, but it is more difficult to achieve electropolymerization of thiophenes in water. This is mainly due to the low water solubility of the monomers (for example, thiophene) and of their oligomers and also because of the possible high reactivity of the cation radical with water molecules. Such nucleophilic attack reactions lead generally to the formation of defects in the polymer and thus to a decrease of the conducting properties and may even impede the electropolymerization itself. However, a new strategy has been recently proposed for the electropolymerization of oligothiophene based on host−guest complexation by cyclodextrin.[9] It was shown that polythiophene can be generated by this process and that this polymer presents an electroactivity in water and an enhanced solubility in common solvents and processability.[9] Besides the interest in industrial applications, complexation of oligothiophenes (or oligopyrroles) by cyclodextrins permits assessment of the properties of these oligomers and of their oxidation intermediates in aqueous media. More generally, there are numerous studies in the literature concerning the electrochemical or homogeneous oxidations of molecules included in cyclodextrin.[10] It is generally accepted that the inclusion complex cannot be directly oxidized (or reduced) on an electrode and has to dissociate before the electron transfer.[11,12] The complexation equilibrium between cyclodextrin and a series of electroactive molecules (see, for example, ferrocenes,[13] viologens,[14] or cobaltocenes[15]) have been investigated in detail and found to be fast, with dissociation rate constants of the order of 10^4 s^{-1}. It was found that neutral intermediates of appropriate size are strongly bound by the CD host while corresponding charged species were not[16] because of the hydrophobic nature of the cavity.[17] No such studies have been carried out on electropolymerizable monomers such as thiophene or pyrrole. In the pyrrole series, the water solubility of the bipyrrole is sufficiently high to allow us to study its oxidation by pulse radiolysis in aqueous solutions. The results can serve as the basis for examining the influence of the cyclodextrin on the various chemical steps. In water (without cyclodextrin), it was found that the cation radical decays by bimolecular reactions (coupling between two cation radicals).[8] Less is known about the reactivity of oligothiophene cation radicals in water. Concerning homogeneous electron transfer and oligothiophenes, electron transfer reactions have been studied in the case of the quenching of terthiophene triplet state encapsulated in β-cyclodextrin by methyl-viologen in water.[10]

In the present paper, we report on the homogeneous oxidation of bithiophenes, terthiophene, and bipyrroles by pulse radiolysis in water in the presence of hydroxypropyl-β-cyclodextrin. These studies are aimed at investigating whether the same type of cation radical can be produced in aqueous solution as in organic solvent and to examine the effect of cyclodextrin on the kinetics of cation radical production (whether oxidation occurs inside or outside the cavity). In addition, we wish to compare the reactivity of the cation radical in water and in organic media. Such information can be used in the design of encapsulated wires.[9,18] For the current studies, we used pulse radiolysis in aqueous solutions under conditions which allow the formation of the cation radical by homogeneous oxidation and its detection by UV−visible spectroscopy. This method has been used previously to study the oxidation of small oligopyrroles and the decay of the produced cation radicals in water.[8] For

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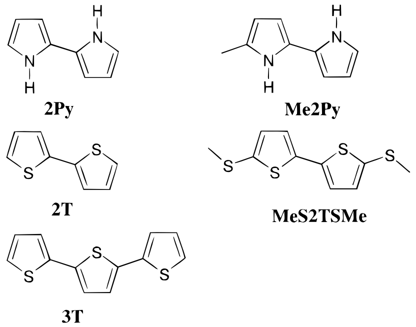
SCHEME 1



oligothiophenes, the spectra of several cation radicals produced in CH_2Cl_2 by pulse radiolysis have been described recently, but no kinetic studies of their decay have been reported.[19]

Experimental Section[20]

2,2′-bipyrrole[21] (2Py), 5-methyl-2,2′-bipyrrole[21] (Me-2Py), and 5,5′-dithiomethyl-2,2′-bithiophene[22] (MeS-2T-SMe) were prepared according to previously described procedures. Bithiophene (2T), terthiophene (3T), and hydroxypropyl-β-cyclodextrin (HP-β-CD) are commercially available and were purchased from Acros and Aldrich. See Scheme 1 for structures.

Determination of the Association Constants. The determination of the association constants of 2,2′-bipyrrole (2Py) and 5-methyl-2,2′-bipyrrole (Me-2Py) complexes were carried out by measuring the variation of absorbance of the oligomer (ΔA) as a function of the HP-β-CD concentration in pH 5 acetic buffer. The association equilibrium constant K has been determined by a nonlinear fit using the following expression

$$\Delta A = \frac{K\Delta\epsilon[\mathrm{S}]_{\mathrm{T}}[\text{HP-}\beta\text{-CD}]}{1 + K[\text{HP-}\beta\text{-CD}]}$$

where $\Delta\epsilon$ is the difference in molar absorption coefficient for the complexed and uncomplexed compound and $[\mathrm{S}]_{\mathrm{T}}$ is the 2Py or Me-2Py total concentrations. The classical approach[23] (i.e., the Benesi−Hildebrand plots) gives estimates of the equilibrium constants but does not weigh the data properly, especially the data points at low HP-β-CD concentrations.

Determinations of the association constants for 2T and MeS-2T-SMe were performed from fluorescence measurements as previously done for other oligothiophenes.[10,18]

Radiolytic Experiments. Solutions of the oligothiophene/HP-β-CD complexes in water (purified with a Millipore Super-Q system) were prepared by heating the solution under strong agitation until complete dissolution (in 10^{-2} mol L^{-1} of HP-β-CD). All solutions were prepared under argon atmosphere to avoid oxidation of the oligomer. For 2T, the solubilization at a temperature of 60−80 °C of 10^{-3} mol L^{-1} was almost complete after 30 min. For MeS-2T-SMe and 3T, higher temperatures were used (90−95 °C) for 12 h. The solutions were cooled by 10 °C temperature steps down to room temperature. Solutions were checked by UV−visible absorption, and indicate maximum concentrations around 10^{-4} and 5×10^{-4} mol L^{-1}, respectively, for 3T and MeS-2T-SMe with 10^{-2} mol L^{-1} of HP-β-CD. Fresh solutions of the bipyrroles in the mmol L^{-1} range were prepared at room temperature by sonication just prior to the experiments. Final solutions were prepared by bubbling N_2O and adding 0.1 mol L^{-1} of NaN_3, NaCl, or KBr. The pH was adjusted by using KOH or phosphate buffer. The pulse radiolysis apparatus has been described before.[24] It utilizes 50 ns pulses of 2 MeV electrons from a Febetron 705 accelerator. The dose per pulse was varied between 8 and 80 Gy, to produce between 5×10^{-6} and 5×10^{-5} mol L^{-1} of oxidizing radicals, as determined by SCN^- dosimetry.[25] All experiments were carried out at room temperature 20 ± 1 °C. The produced cation radicals were observed through their UV−visible spectra recorded at different times after the pulse.

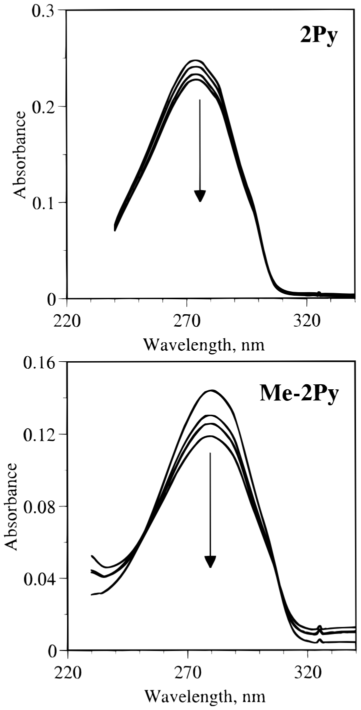


Figure 1. UV−visible spectra of 2Py and Me-2Py in water ($C° = 1 \times 10^{-5}$ mol L^{-1}) with different concentrations of HP-β-CD, $C = 0$, 5×10^{-4}, 1×10^{-3}, 4×10^{-3} mol L^{-1} (pH 5 buffer). Optical path = 1 cm. The arrows indicate the change upon increasing HP-β-CD concentration.

Results

Inclusion Complexes of the Neutral Oligomers with Cyclodextrin. The unsubstituted terthiophene has been shown to form 1:1 or 2:1 complexes with cyclodextrins depending on the size of the host cavity and of the concentration of the cyclodextrin.[10,26] β-Cyclodextrins have been shown to have a suitable cavity size for incorporation of small oligothiophenes.[18] In the present study, we used hydroxypropyl-β-cyclodextrin, which is more soluble in water than simple β-cyclodextrin. Oligothiophenes are insoluble in water (solubility in the range of 10^{-7} to 10^{-6} mol L^{-1}) but quite soluble in the presence of HP-β-CD (up to several mmol L^{-1}). The stoichiometry of all these complexes were found to be 1:1 for concentrations of HP-β-CD in the 10^{-2} molar range and the oligomers concentrations used in this work. The existence of the inclusion complexes with bipyrroles was checked through their UV−visible behavior in the presence of HP-β-CD. Figure 1 shows the UV−visible spectra of 2Py and Me-2Py recorded at different HP-β-CD concentrations between 0 and 4×10^{-3} mol L^{-1}.

When adding HP-β-CD, a decrease of the intensity is observed, confirming the existence of the complexes.[27] The different association constants at 25 °C for the studied oligomers/HP-β-CD complexes are gathered in Table 1. The association constant of bipyrrole with HP-β-CD is lower than that for the corresponding bithiophene which can be related to a higher hydrophobicity of bithiophene compared to bipyrrole and also to the steric hindrance of the N−H bonds.

TABLE 1: Association Constant at 25 °C of Oligomers with HP-β-CD

compounds	K (L mol^{-1})
2T	3400 ± 300[a,b]
MeS-2T-SMe	1400 ± 300[a,b]
3T	5800 ± 300[a,c]
2Py	1300 ± 300[b,d]
Me-2Py	2000 ± 200[b,d]

[a] From fluorescence measurements. [b] This work. [c] From ref 10 and for β-CD. [d] From absorbance measurements.

Oxidation of Bipyrroles or Oligothiophenes in Water by Pulse Radiolysis. The pulse radiolysis of water solution leads to production of e^-_{aq}, $H^\bullet$, and $OH^\bullet$. The e^-_{aq} and $OH^\bullet$ radical can be converted into purely oxidant species, such as $N_3^\bullet$, $Cl_2^{\bullet-}$, or $Br_2^{\bullet-}$ radicals, in N_2O saturated solutions containing NaN_3, NaCl, or KBr, respectively. Homogeneous oxidation of the oligomer then occurs via reaction with $N_3^\bullet$, $Cl_2^{\bullet-}$, or $Br_2^{\bullet-}$ which can be exemplified by the following reactions:

$$H_2O \rightarrow e^-_{aq}, H^\bullet, OH^\bullet, H^+, H_2, H_2O_2$$

$$e^-_{aq} + N_2O \rightarrow N_2 + OH^- + OH^\bullet$$

$$OH^\bullet + N_3^- \rightarrow OH^- + N_3^\bullet$$

$$N_3^\bullet + \text{oligomer} \xrightarrow{k_f} N_3^- + \text{oligomer}^{+\bullet}$$

or

$$OH^\bullet + Br^- \rightarrow OH^- + Br^\bullet$$

$$Br^\bullet + Br^- \rightarrow Br_2^{\bullet-}$$

$$Br_2^{\bullet-} + \text{oligomer} \xrightarrow{k_f} 2\,Br^- + \text{oligomer}^{+\bullet}$$

In experiments containing HP-β-CD, $OH^\bullet$ radicals may also react with the cyclodextrin. For example, the rate constant for the reaction of $OH^\bullet$ with the β-cyclodextrin has been reported as 4.2×10^9 L mol^{-1}s^{-1}.[28] The second-order reaction rates of $OH^\bullet$ with the precursor anions are in the same range or only slightly higher (1.2×10^{10}, 3.0×10^9, 1.1×10^{10} L mol^{-1} s^{-1} with N_3^-, Cl^-, and Br^-, respectively).[29] To minimize the reaction of $OH^\bullet$ with HP-β-CD, in most of the experiments, we used concentrations of cyclodextrin 10 times lower than those of the salts NaCl, KBr, or NaN_3 (typically 0.01 and 0.1 mol L^{-1}, respectively, for the cyclodextrin and the salt). Under these experimental conditions, it was noticed that most of the starting oligomers were included inside the cyclodextrin.

Spectroscopic and kinetic data are available from previous pulse radiolysis experiments[8] with bipyrrole to allow direct comparison between the intermediates produced in water with and without cyclodextrin. At pH 5.7 in the presence of 10^{-2} mol L^{-1} HP-β-CD, the transient absorption spectra corresponding to the intermediates produced by pulse radiolysis of bipyrrole (2Py) and methylbipyrrole (Me-2Py), monitored several microseconds after the pulse (Figure 2), exhibit a sharp peak around 360 nm and a broad band centered at 560−600 nm. The spectra were practically identical whether $Br_2^{\bullet-}$ or $N_3^\bullet$ was used as the oxidant. These spectra are the same as those obtained in water without cyclodextrin[8] at the same pH, indicating that the same cation radicals are produced.

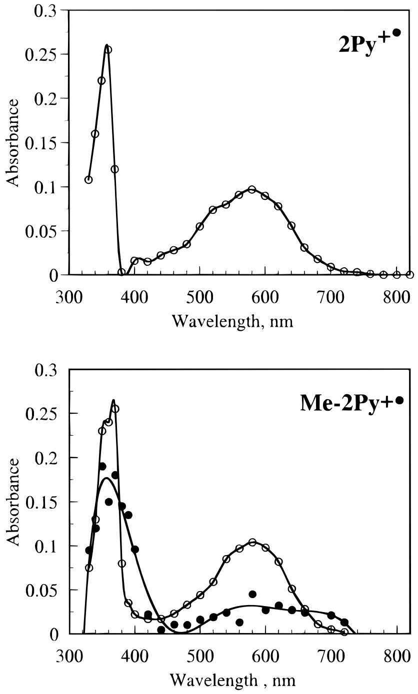


Figure 2. Pulse radiolysis of bipyrroles in water in the presence of 10^{-2} mol L^{-1} HP-β-CD. Differential absorption spectra of $2Py^{\bullet+}$ and $Me\text{-}2Py^{\bullet+}$ in N_2O saturated aqueous solutions (pH 5.7) containing 0.1 mol L^{-1} NaN_3 and 1×10^{-3} mol L^{-1} 2Py or Me-2Py recorded 1 μs (○) and 500 μs (●) after the pulse.

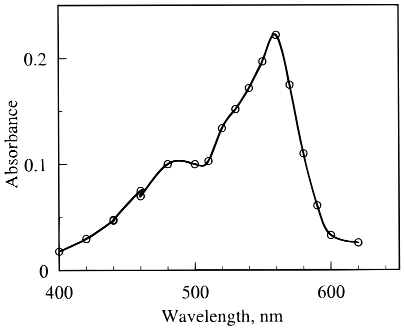


Figure 3. Pulse radiolysis of 2,2′-dithiomethylbithiophene (MeS-2T-SMe) in N_2O saturated aqueous solutions containing 10^{-2} mol L^{-1} HP-β-CD and 0.1 mol L^{-1} KBr at pH 4.3. The differential absorption spectrum was recorded 10 μs after the pulse.

Similar experiments were performed with α,α′-dithiomethylbithiophene (MeS-2T-SMe), bithiophene (2T), and terthiophene (3T). The solubilities of these oligothiophenes in water in the presence of 10^{-2} mol L^{-1} HP-β-CD are lower than those of the bipyrroles and are limited to concentrations in the range of 10^{-4}−10^{-3} mol L^{-1}. Contrarily to oligopyrroles, no spectral data were available on the cation radicals of oligothiophenes in water. MeS-2T-SMe was the first studied oligothiophene because the cation radicals of α,α′-dithioaryloligothiophenes have long lifetimes in many organic solvents and can be oxidized at lower potentials than the unsubstituted oligothiophenes.[22] This makes them a good choice to first examine the possibility of producing the radical cation in water under our experimental conditions. MeS-2T-SMe was oxidized by $Br_2^{\bullet-}$, and the radical cation exhibits a peak with $\lambda_{max} = 560$ nm (Figure 3). We observed the same spectrum when MeS-2T-SMe was oxidized in a mixture of water/2-propanol containing 2% CCl_4 under air. Under these conditions, irradiation of the solution leads to the formation of the peroxyl radical $CCl_3OO^\bullet$,[30] which is able to oxidize the oligomers. These spectra are similar to that recorded upon electrochemical oxidation of MeS-2T-SMe in acetonitrile in a spectroelectrochemical cell.[22]

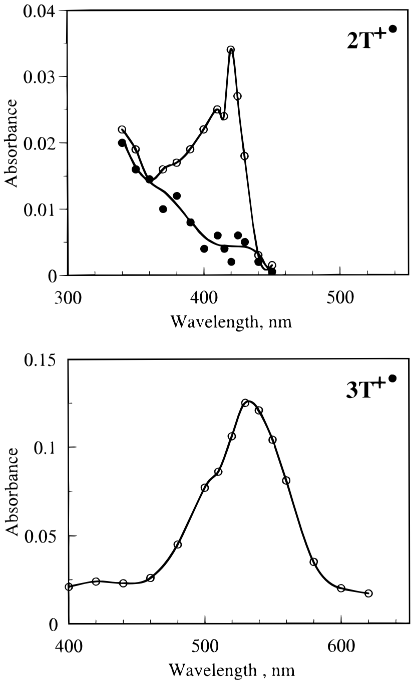


Figure 4. Pulse radiolysis of unsusbtituted bithiophene (2T) and terthiophene (3T) in N$_2$0 saturated aqueous solutions containing 1 × 10^{-2} mol L^{-1} HP-β-CD. 2T was oxidized by $Cl_2^{\bullet-}$ (0.1 mol L^{-1} NaCl) at pH 2.8 and 3T was oxidized by $Br_2^{\bullet-}$ (0.1 mol L^{-1} KBr) at pH 4.3. The differential absorption spectra were recorded 10 μs (○) after the pulse. For oxidation of 2T, the spectrum recorded at 1ms (●) is also shown (see text).

Thus, both spectra obtained in the pulse radiolysis experiments can be ascribed to the cation radical MeS-2T-SMe$^{\bullet+}$. A small fraction of these radicals decayed at short times (around 10 μs) while the remaining absorbance was very long-lived. The amplitude of the first decay increases with the quantity of cyclodextrin and the dose, suggesting that the decay is due to a reaction of the radical cations with the radicals produced by reaction of cyclodextrin with OH$^\bullet$. The slow decay of MeS-2T-SMe$^{\bullet+}$ is in agreement with the stability of the same radical cation produced by electrochemical oxidation in water + HP-β-CD and observed by cyclic voltammetry (the oxidation wave remains reversible for scan rates down to 1 V s^{-1}).[31]

The oxidation potentials of unsubstituted oligothiophenes are more positive than those of the corresponding analogues substituted by electron donor groups, and their solubilities are lower than those of the bipyrroles. For these reasons, it is more difficult to achieve rapid oxidation of oligothiophenes and to avoid overlap of the formation and decay kinetics of the cation radicals. Several oxidants were examined: $N_3^\bullet$, $Cl_2^{\bullet-}$, and $Br_2^{\bullet-}$. Although the redox potentials of the two last oxidants are higher than that of $N_3^\bullet$,[29] they generally react more slowly than $N_3^\bullet$. In this case, the transient spectra recorded after irradiation were not the same with all the oxidants. Oxidation of terthiophene 3T by $Br_2^{\bullet-}$ produced a species which exhibits absorption at 540 nm (Figure 4). By comparison with literature data,[7,10,32] this peak can be ascribed to the terthiophene cation radical 3T$^{\bullet+}$.

On the other hand, oxidation by $N_3^\bullet$ produced some absorbance at 540 nm 1 μs after the pulse, but within several microseconds, the major absorbance was around 450 nm (Figure 5). This change in absorbance is probably due to a subsequent reaction involving 3T$^{\bullet+}$. Since the 450 nm absorption was not observed when $Br_2^{\bullet-}$ was used to oxidize 3T, we suggest that this absorbance results from a rapid reaction between 3T$^{\bullet+}$ and N_3^- which can lead either to a deprotonation of the radical cation or more likely to a new adduct species. The same general behavior was observed upon oxidation of bithiophene. Oxidation by $Cl_2^{\bullet-}$ produced a species absorbing at 420 nm (Figure 4) whereas oxidation by $N_3^\bullet$ produced only a small absorbance at 420 nm and a larger absorbance below 350 nm (Figure 5).

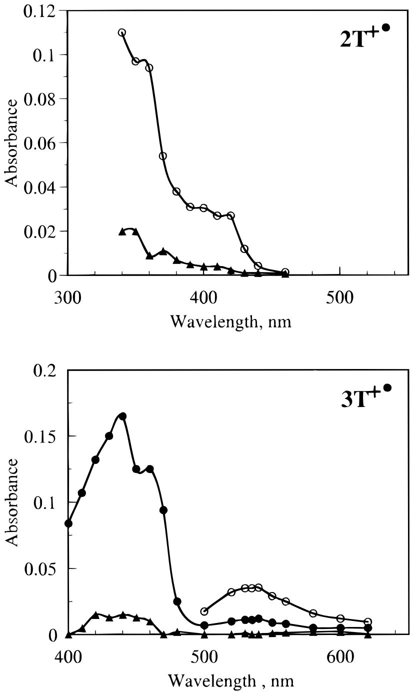


Figure 5. Pulse radiolysis of oligothiophenes in N_2O saturated aqueous solutions containing 1 × 10^{-2} mol L^{-1} HP-β-CD and 0.1 mol L^{-1} N_3^- at pH 5.7. The differential absorption spectra were recorded 1 μs (○), 500 μs (●), and 20 ms (▲) after the pulse.

The peak at 420 nm is similar to that reported in the literature for the cation radical of the bithiophene 2T$^{\bullet+}$ produced by flash photolysis[32] or by pulse radiolysis[19] in CH_2Cl_2. The absorbance at lower wavelengths observed in azide solutions must be due to reaction of the radical cation with azide ions. We were not able to determine the kinetics for this process because the reaction between N_3^- and 2T$^{\bullet+}$ is much more rapid than the reaction with 3T$^{\bullet+}$. It should be noted that the large absorbances at low wavelengths, due to the reaction of the oligothiophene cation radicals with N_3^-, were not observed with the bipyrroles, showing the stronger electrophilic character of the unsubstituted oligothiophene cation radicals. Nevertheless, all these experiments show that similar oligothiophene cation radicals are formed in water in the presence of cyclodextrin and in organic solvents.

Kinetics of Formation and Decay of the Oligomer Cation Radicals. The formation and decay of the cation radicals were followed at the absorption peaks of these species (Table 2). Measurements with oligothiophenes were done only with $Cl_2^{\bullet-}$ or $Br_2^{\bullet-}$ as the oxidant, to avoid the subsequent nucleophilic attack of azide on the radical cation. Under our experimental conditions, we found that the formation of the cation radical was not sufficiently rapid to avoid interference by the subsequent decay. Moreover, the oxidation was not always quantitative, i.e., not all of the oxidizing radicals were scavenged by the oligothiophene. This prevents us from knowing the initial concentration of the cation radical produced or determining the ϵ from the dosimetry. However, if we just consider the decay at long times, second-order decays of the oligothiophenes cation radicals were observed with rate constants of $2k/\epsilon = 1.6 \times 10^6$ cm s^{-1} ($\lambda = 420$ nm) and 5.6×10^4 cm s^{-1} ($\lambda = 530$ nm) for

TABLE 2: Absorption Spectra and Decay Kinetics of the Oligomer Radical Cations

	water containing 10^{-2} mol L^{-1} HP-β-CD			without cyclodextrin			
compound	λ_{max} (nm)	ϵ	$2k_{dim}$ (L mol^{-1} s^{-1})	λ_{max} (nm)	ϵ	$2k_{dim}$ (L mol^{-1} s^{-1})	method[b]/solvent
2T	420		$\sim 2.5 \times 10^{10}$ [a]	425			PR in CH_2Cl_2[19]
				420	15900		FP in acetonitrile[32]
MeS-2T-SMe	560	15000		560			PR in water/2-propanol 50/50
3T	530		$\sim 1.5 \times 10^{9}$ [a]	540	29000	$2-3 \times 10^{8}$	FP in acetonitrile[7,32]
							CV in acetonitrile[33]
2Py	360			360			PR in water[8]
	580	6500		580	6200	7.8×10^{8}	
Me-2Py	370			370		8×10^{8} [c]	PR in water[8]
	580	7000	1.0×10^{9} [c]	600	7900		

[a] Estimations based on ϵ in acetonitrile. [b] PR: pulse radiolysis, FP: flash photolysis, CV: cyclic voltammetry. [c] Standard uncertainties on $2k_{dim}$ measured by pulse radiolysis are estimated to be ±20%.

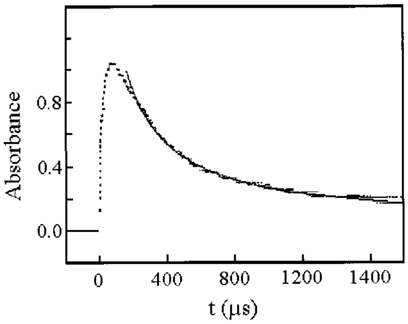


Figure 6. Second-order decay of $3T^{\bullet+}$ observed at $\lambda = 540$ nm in water containing 1×10^{-2} mol L^{-1} HP-β-CD and 1×10^{-1} mol L^{-1} KBr at pH 4.3. The line is the second-order fit.

the bithiophene and the terthiophene cation radicals, respectively. These measured values were found to be almost independent of the dose (except for the lowest doses), i.e., independent of the initial concentration of the cation radical, confirming the second-order nature of the process (Figure 6). It should be noted that first-order reactions should be observed if the cation radical reacted with water or with the neutral oligomer. Our results show that these processes do not occur in our systems or have only minor contributions.

For terthiophene cation radical, the observed second-order kinetics suggests that the nature of the cation radical decay is the same as that observed in organic media, i.e., coupling between two cation radicals.[7,33] Values of 15 900 and 29 000 L mol^{-1} cm^{-1} were reported from flash photolysis experiments in acetonitrile for the absorption coefficients ϵ of $2T^{\bullet+}$ and $3T^{\bullet+}$, respectively.[32] If we assume that these values are in the same range in water and in acetonitrile, we deduced a value of 1.4×10^{9} L mol^{-1} s^{-1} for the second-order decay rate constant of $3T^{\bullet+}$. This rate constant is 3−5 times larger than the values previously measured in acetonitrile by electrochemical[33] or photochemical technique.[7] Direct comparison is difficult because the dimerization rate constant of $3T^{\bullet+}$ cannot be measured in water without cyclodextrin due to the low solubility of the terthiophene in this solvent.

However, an increase in the rates of the coupling reactions is expected upon increasing solvent polarity, as suggested by recent theoretical calculations.[34] Similarly, for the cation radical of bithiophene and using the value of ϵ estimated in acetonitrile, we derived a second-order rate constant of 2.5 10^{10} L mol^{-1} s^{-1}, a value close to the diffusion-controlled limit. However, because of the low yield for the formation of the cation radical (15% and 30% for $2T^{\bullet+}$ and $3T^{\bullet+}$, respectively, based on the ϵ values measured in acetonitrile), the decay rate constant estimated in this system may be affected by reactions with other radicals produced in the solutions, e.g., from the cyclodextrin.

Variations in the Rate Constants with Cyclodextrin Concentration. Because of the faster formation of the cation radical in the bipyrrole series compared to that in the oligothiophene, we have focused our attention on bipyrroles to study the influence of the cyclodextrin on the kinetics. When $N_3^{\bullet}$ was used as the oxidant, the formation of the cation radical was sufficiently rapid to allow a study of the subsequent reactions of the radical without interference by its formation process. The evolution of the spectrum was studied in detail for Me-2Py, which upon oxidation only leads to a dimer because one of the α-terminal positions is sterically hindered.[8] At long time, the absorbance in the 560 nm range disappears and only an absorbance in the 350 nm range remains, in agreement with formation of a coupling product (see Figure 2).[8] The decay kinetics of the cation radical was monitored at 560 nm and found to fit a second-order law with $2k/\epsilon = 1.4 \times 10^{5}$ cm s^{-1} ($\lambda = 580$ nm). Using the absorption coefficient value, ϵ, determined from thiocyanate dosimetry, the second-order rate constant was found to be 1×10^{9} L mol^{-1} s^{-1} which is similar to that found in water without cyclodextrin.[8] Under these experimental conditions, most of the radicals (e^{-}_{aq}, $OH^{\bullet}$) produced after the pulse are efficiently converted into bipyrrole cation radical, allowing an accurate measurement of the dimerization rate constants of the cation radicals. Thus, it is clear that the reactivity of the cation radical of bipyrrole is completely unchanged by the addition of HP-β-CD. Oxidation of bipyrrole leads to the formation of the corresponding cation radical which reacts with another cation radical to form a dimer $(\text{Me-2Py})_2^{2+}$. In the case of the bipyrrole, the oxidation rate constants, k_f, were measured for the oxidation of Me-2Py by $Br_2^{\bullet-}$ for increasing concentrations of HP-β-CD (in this scheme Me2Py represents the total amount of methylbipyrrole, whether or not complexed by the cyclodextrin):

$$Br_2^{\bullet-} + \text{Me-2Py} \xrightarrow{k_f} \text{Me-2Py}^{\bullet+}$$

$$\text{Me-2Py}^{\bullet+} + \text{Me-2Py}^{\bullet+} \xrightarrow{2k_{dim}} (\text{Me-2Py})_2^{2+}$$

We have previously shown that the cation radical of bipyrrole $\text{Me-2Py}^{\bullet+}$ is rapidly deprotonated at basic pH to form a neutral radical $\text{Me-2Py}^{\bullet}$. (Cation radicals of bipyrrole are weak acids in water with a pK_a of 8.7 for methylbypyrrole.[8]) Both cation radical and neutral radical decay by second-order processes (Figure 7). The second-order decay of the cation radical of bipyrrole leads to the formation of quaterpyrrole and longer oligomers, but the decay of the neutral radical does not lead to such dimeric products.[8] The second-order rate constants for their decays ($2k_{dim}$) were measured at two pH values, corresponding

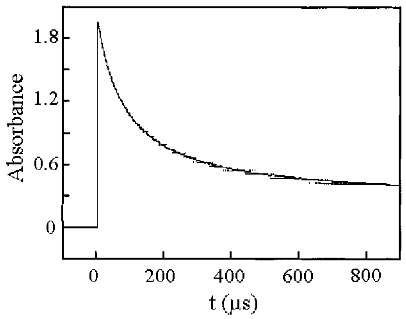


Figure 7. Second-order decay of Me-2Py$^{\bullet+}$ monitored at 560 nm in aqueous solutions containing 1 × 10^{-2} mol L^{-1} HP-β-CD and 1 × 10^{-1} mol L^{-1} NaN_3 at pH 5.7. The line is the second-order fit.

TABLE 3: Effect of Cyclodextrin Concentration on the Kinetic Parameters during Oxidation of Me-2Py

cyclodextrin (HPβCD) concn (mol L^{-1})	k_f (L mol^{-1} s^{-1})[a]	cation radical pH 5.7 $2k_{dim}$ (L mol^{-1} s^{-1})[a]	radical pH 11.3 $2k_{dim}$ (L mol^{-1} s^{-1})[a]
0	6.0×10^9	1.0×10^9	1.4×10^9
10^{-2}	1.6×10^9	1.0×10^9	4.6×10^8
6×10^{-2}	5.5×10^8	9×10^8	2.5×10^8

[a] Errors are estimated to be ±20%.

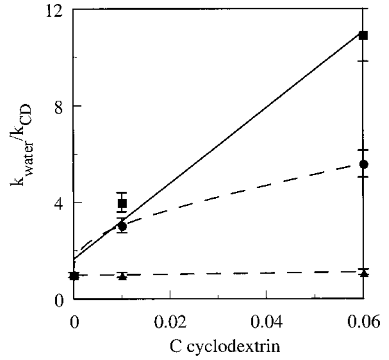


Figure 8. Variation in the relative rate constants k_{water}/k_{CD} as a function of the concentration of cyclodextrin: (■) for $k_{f,water}/k_{f,CD}$, oxidation of Me-2Py by $Br_2^{\bullet-}$; (●) for $k_{dim,water}/k_{dim,CD}$, second-order decay of the neutral radical of Me-2Py; (▲) for $k_{dim,water}/k_{dim,CD}$, dimerization of Me-2Py$^{\bullet+}$.

to the formation of the cation radical and the neutral radical arising from the deprotonation of the initially produced cation radical. The values for the different kinetic rate constants are gathered in Table 3.

It is interesting to consider the relative variations in the rate constants k_{water}/k_{CD} for the different types of reaction as a function of HP-β-CD concentration (k_{water} is the rate constant in the absence of cyclodextrin ($k_{f,water}$ or $2k_{dim,water}$) and k_{CD} is the rate constant in the presence of HP-β-CD) as displayed in Figure 8. The rate constant k_f for the oxidation of Me-2Py by $Br_2^{\bullet-}$ was measured by following the formation of the absorbance of the cation radical at pH 4.8, where the cation radical does not deprotonate.[8] A decrease of the oxidation rate by at least a factor of 10 is observed upon adding 0.1 mol L^{-1} cyclodextrin. A decrease in reactivity is expected when the oligomers are included inside the cyclodextrin due to shielding of this species from reacting with another molecule. Such effects have been observed in several instances in the protection of excited states from reacting with quenchers,[10,35] and more precisely similar variations were described for the quenching of terthiophene triplet by methylviologene or Cu(II)SO_4 in the presence and absence of β-cyclodextrin. The next question is whether the oxidation takes place between the oxidant and the Me-2Py−HP-β-CD complex or whether the bipyrrole has to leave the host before oxidation. For electrochemical heterogeneous electron transfers (with an electrode), it is generally accepted that the oxidation (or reduction) does not involve the complex directly and takes place only after dissociation.[12−14] If we assume a similar situation in our case and assume that the complexation equilibrium is fast, the apparent oxidation rate $k_{f,CD}$ is related to the value in water without cyclodextrin $k_{f,water}$ by the following relation: $k_{f,water}/k_{f,CD} = 1 + K[\text{HP-}\beta\text{-CD}]$ (where K is the association equilibrium constant for Me-2Py and the cyclodextrin). It should be noted that this limiting kinetic case will give the smallest decrease of $k_{f,CD}$ for a given value of K (or the largest value of K for a given decrease of $k_{f,CD}$). In a situation where the kinetic of dissociation becomes involved in the process (slow dissociation), a larger decrease in K would be expected. Estimating the maximum value of K from our data points, we derive a value of ~150 mol^{-1} L. This estimate is more than 10 times lower than the value measured for the association constant (K = 2000 mol^{-1} L, Table 1), showing that another oxidation pathway exits, i.e., direct oxidation of the complex, characterized by another rate constant $k_{f,direct}$:

$$(\text{Me-2Py}-\text{HP-}\beta\text{-CD}) \overset{K}{\rightleftarrows} \text{Me-2Py} + \text{HP-}\beta\text{-CD}$$

$$Br_2^{\bullet-} + \text{Me-2Py} \xrightarrow{k_{f,water}} \text{Me-2Py}^{\bullet+}$$

$$Br_2^{\bullet-} + (\text{Me-2Py}-\text{HP-}\beta\text{-CD}) \xrightarrow{k_{f,direct}} \text{Me-2Py}^{\bullet+} + \text{HP-}\beta\text{-CD}$$

$$\text{Me-2Py}^{\bullet+} + \text{Me-2Py}^{\bullet+} \xrightarrow{k_{dim}} (\text{Me-2Py})_2^{\ 2+}$$

In our experimental conditions, bipyrroles form 1:1 complexes with HP-β-CD. This can explain the difference in behavior between electrochemical and homogeneous oxidation because $Br_2^{\bullet-}$ is relatively small and thus has little difficulties to access the oligomer. Thus, direct oxidation of the complex can occur.

The reactivity of the neutral radical was studied in the presence of HP-β-CD by investigating its second-order decay, $2k_{dim}$. This rate constant decreases considerably as the concentration of cyclodextrin increases ($2k_{dim}$ is decreased by a factor of 3 for 1 × 10^{-2} mol L^{-1}). This is contrary to the measured dimerization rate of the cation radical, which was not sensitive to the concentration of cyclodextrin. The difference in behavior observed for the decay of the cation radical and the neutral radical strongly suggests that the cation radical is not included in the cyclodextrin host and that its dimerization occurs outside the cavity. On the contrary, the variation of $2k_{dim}$ for the neutral radical in the presence of HP-β-CD demonstrates that the neutral radical is included inside the cyclodextrin. However, it is difficult to conclude at this time whether the coupling reaction occurs between two complexed radicals or if one or both radicals have to leave the host to react because the association constant between the neutral radical and the cyclodextrin is unknown. However, one should notice that the neutral radical is produced by the deprotonation of the cation radical which is outside the cyclodextrin and that the neutral radical has to enter into the host. This observation confirms that the inclusion reaction between the neutral radical and HP-β-CD is faster than the second-order decay and thus that encapsulation equilibrium should also be fast as generally found. From the good second-order fits found for the decay of the neutral radical and the radical cation in the presence of large concentrations of HP-β-CD, we can deduce that the dissociation or association reactions (k_{diss} or k_{ass} in the scheme below) take place during the first

100 μs, indicating that the dissociation rate constant should be higher than 10^4 s^{-1}. Values in this range have been reported for complexes with cyclodextrin (see, for examples, refs 11 and 15). The reactions in basic media can be summarized by the following scheme where (1) is the association of the starting methylbipyrrole by the cyclodextrin, (2) and (2′) the formations of the cation radical, (3) the deprotonation of the cation radical to form the neutral radical, (4) the complexation of the neutral radical by the cyclodextrin, and (5) and (5′) the second-order decays of the neutral radical:

$$\text{(Me-2Py}-\text{HP-}\beta\text{-CD)} \overset{K}{\rightleftharpoons} \text{Me-2Py} + \text{HP-}\beta\text{-CD} \qquad (1)$$

$$\text{Br}_2^{\bullet-} + \text{Me-2Py} \xrightarrow{k_{\text{f,water}}} \text{Me-2Py}^{\bullet+} \qquad (2)$$

$$\text{Br}_2^{\bullet-} + \text{(Me-2Py}-\text{HP-}\beta\text{-CD)} \xrightarrow{k_{\text{f,direct}}} \text{Me-2Py}^{\bullet+} + \text{HP-}\beta\text{-CD} \qquad (2')$$

$$\text{Me-2Py}^{\bullet+} \rightarrow \text{Me-2Py}^{\bullet} + \text{H}^{+} \qquad (3)$$

$$\text{(Me-2Py}^{\bullet}-\text{HP-}\beta\text{-CD)} \underset{k_{\text{ass}}}{\overset{k_{\text{diss}}}{\rightleftharpoons}} \text{Me-2Py}^{\bullet} + \text{HP-}\beta\text{-CD} \qquad (4)$$

$$\text{Me-2Py}^{\bullet} + \text{Me-2Py}^{\bullet} \xrightarrow{2k_{\text{dim,water}}} \text{products} \qquad (5)$$

$$\text{(Me-2Py}^{\bullet}-\text{HP-}\beta\text{-CD)} + \text{(Me-2Py}^{\bullet}-\text{HP-}\beta\text{-CD)} \xrightarrow{2k_{\text{dim}}} \text{products} \qquad (5')$$

Conclusion

All the studied oligomers (bipyrroles, bithiophenes, and terthiophene) are complexed into β-cyclodextrin with association constants in the range of 1×10^3 to 5×10^3 L mol^{-1}. From the pulse radiolysis results, we conclude that the cation radicals of small oligopyrroles and oligothiophenes can be produced in water by homogeneous oxidation and that their reactions are similar to those observed in organic solvents (second-order decays). The spectral features are also the same as those described in organic solvents. Detailed kinetic studies with methylbipyrrole show that the homogeneous oxidation occurs after dissociation of the complex but also with the complex itself, contrarily to what is commonly described for electrochemical reduction or oxidation. The produced cation radical is not associated with the cylodextrin and is rapidly expelled from the host after its formation. On the contrary, if the cation radical is deprotonated to form the neutral radical, the neutral radical is associated with the cyclodextrin. Dissociation kinetics rate constants were found to be fast both for cation radical and neutral radical.

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