Mechanism of Pyrrolyl Oxidation in Star-Shaped Compounds

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The oxidation products in acetonitrile of hexapyrrolylbenzene (HPyB) and hexakis(3-octylpyrrolyl)benzene (HOPyB), two star-shaped compounds consisting of 6-fold *N*-pyrrolyl-substituted benzenes, were characterized by MALDI-TOF. These products result from intramolecular coupling of pyrrolyl residues without dimer or polymer products. Transient electrochemical and flash photolysis experiments on HPyB indicate that this intramolecular coupling occurs via a radical cation/substrate mechanism and not by a radical cation/radical cation mechanism, as usually observed in intermolecular coupling that occurs during the polymerization of pyrrole derivatives.

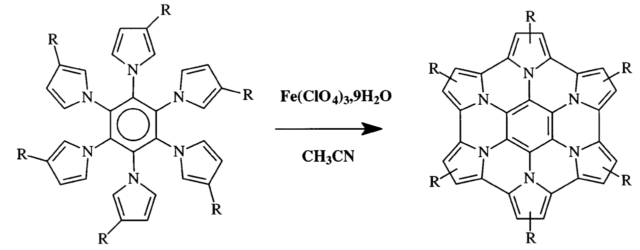
Introduction

Organic conducting materials are now extensively investigated because of their potential in the design of a new generation of organic or hybrid mineral−organic computers.[1−3] The electrooxidation of aromatic organic molecules leads to the growth of organic conducting polymer[4] or salt[5] films on a metallic anode. The growth of such a material on the electrode in organic solvents generally proceeds through the coupling of two radical cations.[6] This is a multistep process that involves the formation of carbon−carbon bonds between the two radical cations and then the release of two protons to rearomatize the dihydrodimer dication, which thereby recovers electroneutrality. The intermediate dication is a reactive species that can lead to the formation of defects if the rearomatization reaction is not fast enough.[7,8]

In the present work, the star-shaped compound hexapyrrolylbenzene (HPyB), a 6-fold *N*-pyrrolyl-substituted benzene (Scheme 1), has been investigated by chemical, photochemical[9] (homogeneous), and electrochemical[6a,10] (heterogeneous) oxidation in acetonitrile. The main difference between HPyB and other pyrrole derivatives is the proximity of pyrrolyl residues that could have an effect on the nature of the material and the condensation mechanism.

Vegh[11] et al. reported that when HPyB is oxidized chemically or electrochemically it leads to a polymeric material. In 1,4-dipyrrolylbenzene, where the pyrrolyl residues are linked by a rigid spacer, intermolecular coupling leads to a polymer.[12] Nevertheless, when the link between two pyrrolyl residues is a flexible spacer, inter- and intramolecular coupling reactions occur.[13] In HPyB, where the benzene is substituted by several pyrrolyl groups, steric considerations suggest that both coupling reactions are possible, and the question arises as to whether one reaction is favored: information on the reaction type has direct implications concerning the structure of the material. If the coupling is intermolecular, then the material will be a polymer, whereas if it is intramolecular, the material will be discotic. Disc-shaped materials such as hexabenzocoronene and other polycyclic aromatic hydrocarbons (PAH) and their supramolecular motifs are the object of intensive research.[14]

SCHEME 1: Hexapyrrolylbenzene Chemical Oxidation Reaction



R = H: Hexapyrrolylbenzene
R = octyl: Hexaoctypyrrolylbenzene

R= H: HPyB6σ
R = octyl: HOPyB6σ

Moreover, a fundamental issue arises: in HPyB, if intermolecular coupling is involved, then a radical cation/radical cation mechanism is expected, as classically encountered in the formation of conducting polymers based on pyrrole derivatives. However, if intramolecular coupling occurs, then both mechanisms—radical cation/radical cation and radical cation/substrate—can be expected. The question is, Which one?

Experimental Section

MALDI-TOF mass spectrometry was performed using a Perspective Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in the reflectance mode. The spectra were averaged over 256 laser shots.

Voltammetric and potentiostatic experiments were performed in a one-compartment three-electrode cell. The working elec-

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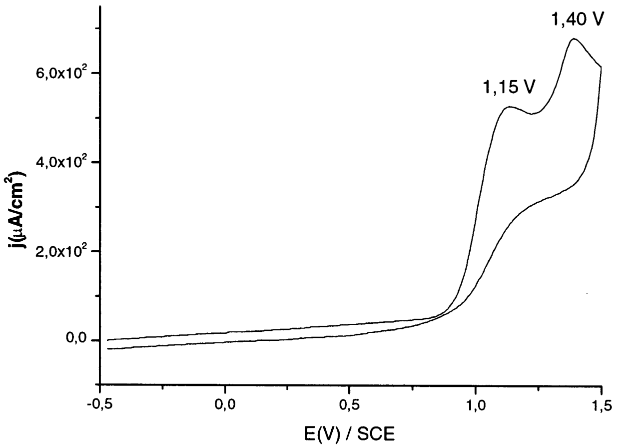


Figure 1. Cyclic voltammogram of 10^{-3} M HPyB and 0.1 M $LiClO_4$ in acetonitrile at 50 mV/s obtained on 3-mm-diameter glassy carbon electrode.

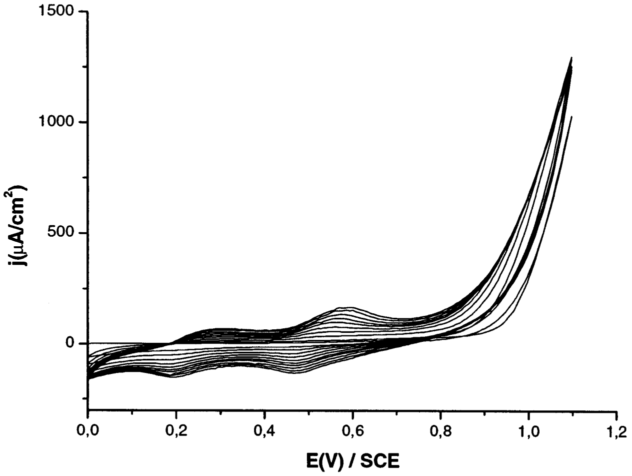


Figure 2. Cyclic voltammograms of film growth on a platinum electrode (1 cm^2 surface) for 10^{-3}M HPyB and 0.1 M $LiClO_4$ in acetonitrile.

trode was a carbon disk (either a 1-mm- or a 3-mm-diameter disk electrode) polished with 1-μm diamond paste before use. Electrochemical instrumentation consisted of a Tacussel GSTP4 programmer and a home-built potentiostat equipped with a positive feedback compensation device.[15] The data were acquired with a 310 Nicolet oscilloscope. Under our experimental conditions (solvent, scan rates, concentrations, etc.), the error due to the uncompensated resistance was lower than 1 mV. The counterelectrode was a stainless steel grid, and the reference electrode was an aqueous saturated calomel electrode with a salt bridge containing the supporting electrolyte. For large-scale electrolysis (or electrodeposition), the potentiostat was an EG&G PAR model 362 potentiostat/galvanostat, and the working electrode was a 1-cm^2 platinum plate. Experiments were performed at room temperature (20 ± 2°C).

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (200 MHz) spectrometer in $CDCl_3$. Chemical shifts (□) are given in ppm with respect to the solvent ($\delta^1H = 7.27$, $\delta^{13}C = 77.0$).

Hexafluorobenzene (HFB) (Aldrich), pyrrole (Acros), CCl_4, and $CHBr_3$ were freshly distilled; $LiClO_4$ (Acros), $Fe(ClO_4)_3\cdot 9H_2O$ (Fluka), and CH_3CN (Merck, spectroscopic grade) were used as received.

Hexapyrrolylbenzene (HPyB). HPyB (Scheme 1) was prepared in 37% yield according to a previously described procedure.[16] Hexafluorobenzene was reacted with the sodium pyrrolyl salt. The product was purified by silica gel column chromatography.

$C_{30}H_{24}N_6$, M = 468.57; chemical analysis: C 76.7 (76.92); H, 5.4 (5.13); N, 17.9 (17.94); MALDI-TOF mass spectrometry (*m*/*z*): 468.57 ($M^{\bullet+}$); ^1H NMR ($CDCl_3$): δ 6.08 (12H), 6.18 (12H); ^{13}C NMR ($CDCl_3$): δ 110.6, 120.8, 134.2.

Hexakis(3-octylpyrrolyl)benzene (HOPyB). HOPyB (Scheme 1) was prepared in 51% yield by the same procedure used for HPyB. Hexafluorobenzene reacted with the sodium 3-octylpyrrolyl salt.[17−19]

$C_{78}N_6H_{120}$, M = 1140.96; chemical analysis: C, 82.0 (82.05); H, 10.7 (10.59); N, 7.4 (7.36); MALDI-TOF mass spectrometry (*m*/*z*): 1140.98 ($M^{\bullet+}$); ^1H NMR ($CDCl_3$): δ 0.89 (30H), 1.25 (60H), 2.24 (12H), 5.84 (12H), 6.00 (6H); ^{13}C NMR ($CDCl_3$): δ 14.2, 22.7, 26.7, 29.2, 29.4, 29.6, 30.9, 32.0, 110.8, 117.8, 120.4, 126.4, 133.5.

For flash photolysis experiments, fresh solutions of HPyB (10^{-3} M) in CH_3CN containing 1% CH_3Br or CCl_4 were prepared. The irradiations were performed with a Questek Laser 2048 (100−130 mJ, 20−50 ns) using a XeCl mixture (λ = 308 nm). The kinetic spectrophotometric detection system consisted of a 150-W xenon lamp, a 1.5-cm optical path length homemade irradiation cell, a Jobin-Yvon high-intensity monochromator, and a Hamamatsu photomultiplier.[20] The signals were digitized with a Nicolet 450 digital oscilloscope and analyzed on a PC.

Results and Discussion

Electrochemical and Chemical Oxidation of HPyB. The cyclic voltammogram of a 10^{-3} M HPyB solution in acetonitrile (Figure 1) shows two irreversible waves indicating two irreversible oxidation processes. During repeated voltammetric scans, the increase of a double reversible wave was observed (Figure 2), indicating the growth of a conducting and electroactive material (peaks around 0.25 and 0.55 V in Figure 2 that are not visible on the first scan). Similarly, the homogeneous chemical oxidation of HPyB by $Fe(ClO_4)_3$ in acetonitrile leads to a black powder, which is also a conducting material. (Measurements performed on the powder using the four-points contact method give $10^{-5}\ \Omega^{-1}\ cm^{-1}$.) During the electropolymerization process, a coloration of the solution is observed near the electrode surface, which indicates the formation of soluble oxidized compounds. The MALDI-TOF characterization of these soluble oxidized products shows the presence of doubly deprotonated HPyB molecules (Figure 3, *m*/*z* = 466). This suggests that even if the electropolymerization of HPyB occurs the main soluble products at the electrode surface are the intramolecularly coupled and deprotonated HPyB molecules (Scheme 2).

The successive reaction intermediates were produced by chemical oxidation using 1 to 14 equiv of $Fe(ClO_4)_3$ per HPyB (cyclization yield = 30% at 14 equiv $Fe(ClO_4)_3$, calculated as the ratio of the initial number of moles of HPyB to the number of moles of solid HPyB6σ obtained after treatment with excess 0.1 M KOH then water and drying at 100 °C). They were identified by MALDI-TOF mass spectrometry. Starting from the smallest amount of oxidant, we observe first HPyB1σ (Figure 3, *m*/*z* = 466 and Scheme 2), the product obtained by the coupling of two adjacent pyrrolyl residues on the same HPyB molecule. Further additions of the oxidant increase the proton loss by pairs. HPyB2σ (Figure 3, *m*/*z* = 464) appears in the sample, indicating two coupling reactions between two adjacent pyrrolyl residues. The major part of the intermediates is detected

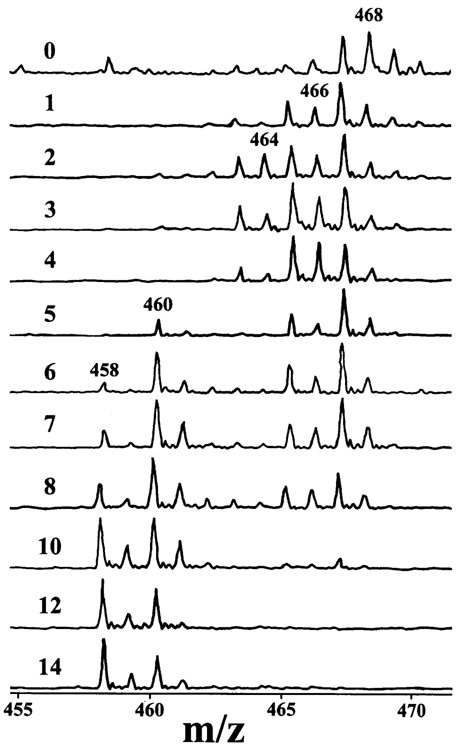


Figure 3. MALDI-TOF spectra of HPyB oxidation products obtained using various amounts of $Fe(ClO_4)_3$. The ratio $[Fe(ClO_4)_3]/[HPyB]$ is indicated on the spectra.

up to HPyB5σ (Figure 3, $m/z = 458$ and Scheme 2) unless HPyB3σ is not detected ($m/z = 462$).

When the amount of oxidant is 6 equiv of $Fe(ClO_4)_3$ per 1 HPyB molecule, a black powder starts to precipitate. This powder is insoluble in all common solvents. In the MALDI-TOF spectra of the soluble products, the fully coupled molecule HPyB6σ that corresponds to the loss of 12 protons is not observed even for large amounts of oxidant (Scheme 2). To explain this, two hypotheses were considered: (i) The intramolecularly coupled HPyB6σ product is completely insoluble and cannot be observed by MALDI-TOF. (ii) HPyB6σ does not form, and HPyB5σ oxidation produces a dimer and not the intramolecularly coupled molecule HPyB6σ. To elucidate this point and to improve the solubilities of the different intermediates, we investigated the oxidation of a similar molecule where long alkyl side-chains are introduced: hexakis(3-octylpyrrolyl)benzene (HOPyB) (Scheme 1).[21] The MALDI-TOF spectrum (Figure 4) of the $^{1}/_{14}$ mol/mol products of hexakis-(β-octylpyrrolyl)benzene oxidation by $Fe(ClO_4)_3$ shows the presence of the fully intramolecularly α,α'-pyrrolyl coupled compound ($m/z = 1129$), which is present with all of the other soluble intramolecularly coupled products. This indicates that the coupling in this alkylated star-shaped compound proceeds through an intramolecular mechanism. By structural analogy, we can say that during the chemical and electrochemical oxidation of HPyB the reaction between pyrrolyl moieties is intramolecular.

Evolution of the HPyB Oxidation Product. Flash Photolysis. As stated in the Introduction, in the case of pyrrole derivatives the electrochemical oxidation involves the coupling of two radical cations to produce a dihydrodimer dication. The kinetic decay of this species has been studied in organic and in aqueous media by flash photolysis[9] and pulse radiolysis.[20] Photoinduced electron transfer produces oligopyrrole radical cations; the oligopyrrole is irradiated to give an excited state that is quenched by an irreversible electron acceptor.[9b] The decays of the several oligopyrrole radical cations were found to follow a second-order rate law,[9b,c] demonstrating that C−C bond formation occurs through the coupling of two radical cations. We used a similar procedure to investigate the oxidation of HPyB in organic solvents. When a 10^{-3} M HPyB acetonitrile solution is irradiated at 308 nm in the presence of an irreversible electron acceptor (CHBr3 or CCl4), the species observed after the shortest delay possible (300 ns) absorbs at 400 nm (Figure 5). This absorption wavelength is similar to that for oligopyrrole derivatives (e.g., the bipyrrole radical cation is observed at 360−370 nm) when they are irradiated under the same conditions.[20] However, this appears to be too high to correspond to the radical cation of a simple pyrrole head, taking into account that conjugation through a nitrogen atom is generally weak. This result suggests that the coupling reaction has already taken place at our observation time and that the first radical cation produced has a lifetime much lower than 300 ns. As for the coupling reaction, the question is, Does it involve the reaction of the first oxidation product with another neutral pyrrole moiety (addition of a radical to a double bond) or intramolecular coupling in a bis(radical cation)? Given that the concentration of intermediates produced in flash photolysis experiments is in the range of 10^{-6} M, this observation time is too short for a second-order reaction involving two radical cations to occur. Even for a diffusion-limited reaction, the shortest possible lifetime for such second-order decay is in the range of some 10^{-4} s (i.e., several orders of magnitude greater than the observed limit ($\tau \approx 1/(10^{10} \times 10^{-6}) = 10^{-4}$ s with kdiff $\approx 10^{10}$ M^{-1} s^{-1} in acetonitrile).[22] At this point, we should recall that the initial photochemical oxidation gave only a one-electron oxidation product. The production of a bis(radical cation) may occur only through a disproportionation reaction between two radical cations, which is incompatible with the short experimental time. In conclusion, we suggest that the observed signal can be ascribed to the radical cation of an already-coupled pyrrole produced by the intramolecular coupling reaction (radical addition to a double bond). Later, this intermediate slowly decays with first-order kinetics (Figure 6, rate constant 10 s^{-1}). This reaction may be a slow deprotonation (or reaction with impurities). The photooxidation of HPyB (in the presence of 10^{-1} M $CHBr_3$) at pH 10 obtained by adding a nonnucleophilic base (diisopropylamine) does not change the decay constant obtained previously in neutral acetonitrile. This result indicates that the species observed by absorption measurements is not the acidic dication HPyB1σ^{2+} but the radical cation HPyB1$\sigma^{\bullet +}$ (Scheme 3).[23,24]

We conclude the following from this experiment:

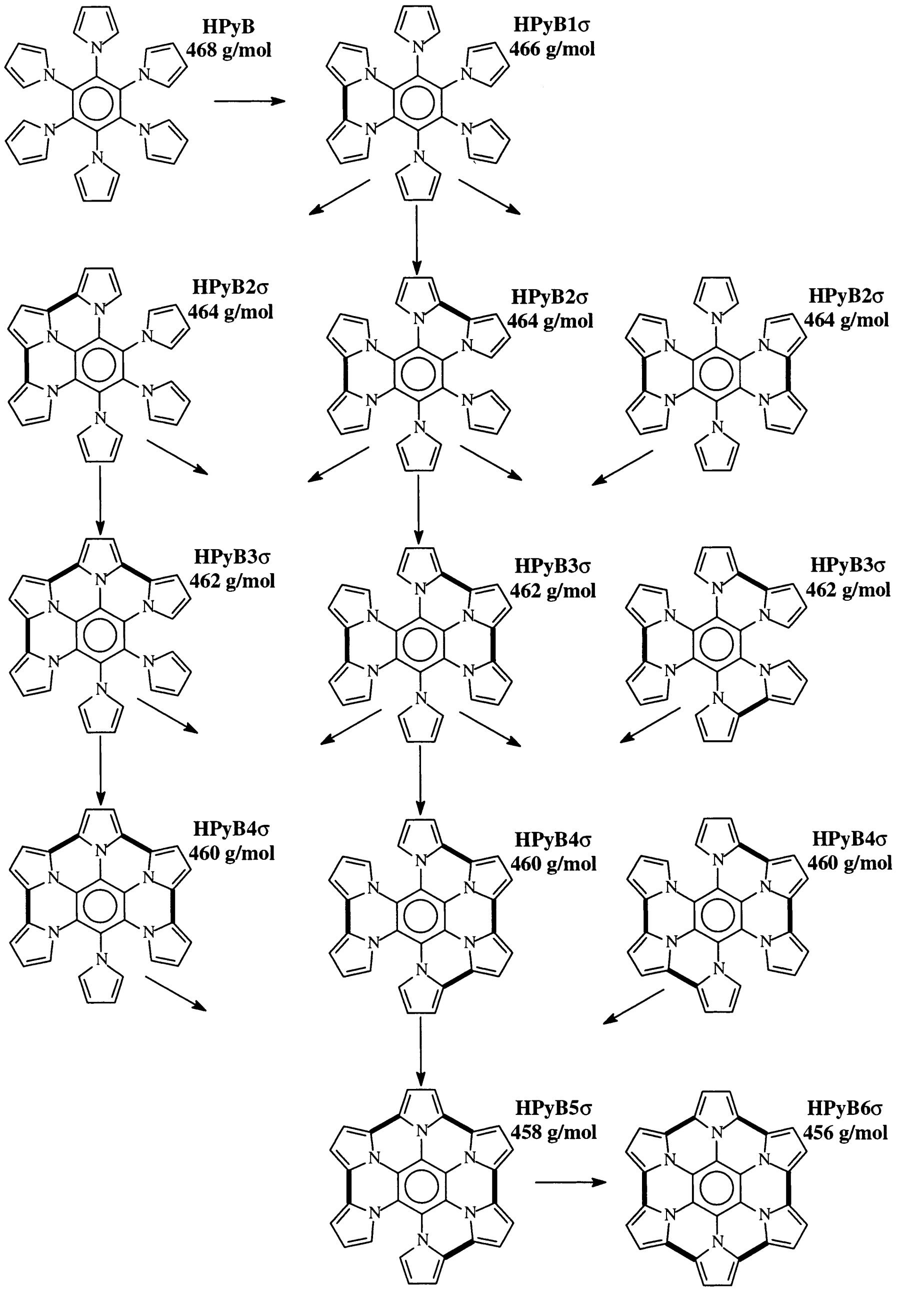
(i) The absence of a radical cation coupling (or disproportionation) reaction that could enhance its decay. This result is expected because we have demonstrated that there is no dimerization reaction, as discussed before.

(ii) The absence of a radical cation disproportionation mechanism ($2\ R^{\bullet +} \rightarrow R^{2+} + R$), which also could enhance the decay of the radical cation.

(iii) The existence of fast intramolecular coupling due to the proximity of the two pyrrole moieties.

Cyclic Voltammetry. The rapid cyclic voltammetry of HPyB oxidation in acetonitrile does not attain electron-transfer reversibility even at 1000 V s^{-1} on a glassy carbon microelectrode. This observation indicates that the chemical reaction that follows the first electron transfer is so fast that it is complete in less than our observation time (on the order of 10^{-4} s), in agreement with the flash photolysis experiments. Comparing the first

SCHEME 2 : Possible Pathways for the HPyB Oxidation Reaction.



oxidation peak current with the one-electron reversible oxidation of ferrocene (used as an internal reference) shows that this first process was multielectronic with 10.1 electrons, a value that was uncorrected for the difference between the diffusion coefficients of the two redox couples. A rough correction assuming that the diffusion coefficients decrease with the cubic root of the molecular weight gives a value of around 12 electrons per mole of HPyB that is close to the expected value for the oxidation of HPyB to HPyB6σ.[25] Another interesting result can be obtained from the variation of the peak potential with the scan rate.[26]

The peak potential E_{peak} varies linearly with the logarithm of the scan rate, v, with a slope of

$$\frac{\partial E_{\text{peak}}}{\partial \log(v)} = 79 \text{ mV}$$

per decade of v (Figure 7). This large gradient indicates that the electrochemical oxidation is an irreversible reaction, with the electron transfer being the rate-determining step corresponding to an anodic transfer coefficient $\alpha_a = 0.38$ (assuming that the Butler−Volmer law describes the electron-transfer kinetics).[26] This kinetic situation impedes the direct observation of the chemical step following the electron transfer because the shift of the peak potential depends only on the first electron transfer (even if more than one electron is transferred). However, electron-transfer reactions for pyrrole/pyrrole radical cation pairs (pyrrole, substituted pyrroles, or oligopyrroles) were previously found to be fast (standard heterogeneous electron-transfer rate, k_s, in the range of 1−2 cm s^{-1}),[27] and it is likely that HPyB presents a similar k_s value. In this case, the observed electrochemical behavior (irreversible voltammogram, highest value of the slope) can be understood if electron transfer is followed by a very fast chemical reaction.[26] The theory of this kinetic situation was drawn up at the beginning of the 1970s.[28] The nature of the kinetic control of the process (by the chemical

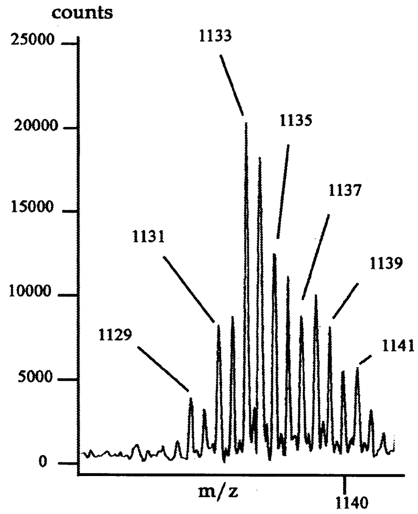


Figure 4. MALDI-TOF spectrum for HOPyB products from chemical oxidation by $Fe(ClO_4)_3$.

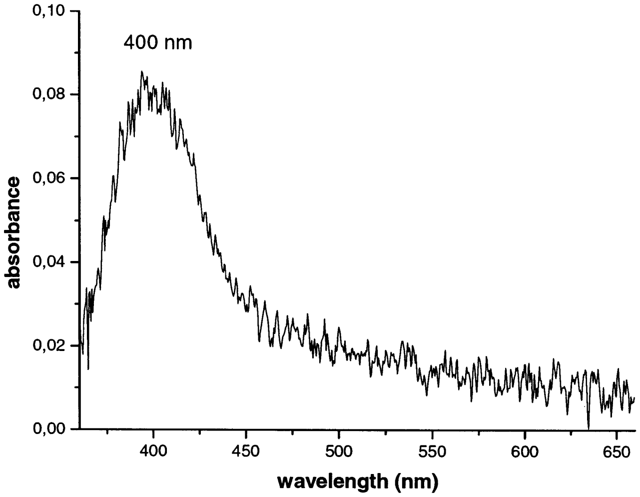


Figure 5. Flash photolysis of HPyB (10^{-3} M) in acetonitrile solution containing 10^{-1} M $CHBr_3$ monitored 5 μs after the laser pulse, showing the differential absorption spectra of the species produced.

step or the electron transfer) depends on a single kinetic parameter

$$p = \left(\frac{\alpha_a F v}{RT}\right)^{(\alpha_a - 1)/2\alpha_a} k_s^{1/\alpha_a} k^{-1/2} D^{-1/2\alpha_a}$$

D is the diffusion coefficient, k_s is the standard heterogeneous rate constant, and *k* is the rate constant of the chemical reaction that is considered to be first order. For kinetic behavior corresponding to rate-determining electron transfer, *p* should be less than 1,[28] which leads roughly to the condition that *k* should be greater than 10^{10} s^{-1} (taking values for k_s, *D*, and *v* of 1 cm s^{-1}, 10^{-5} cm^2 s^{-1}, and 0.1−1 V s^{-1}, respectively). Another point is that the α_a coefficient is much less than 0.5. In the framework of Marcus theory,[26,29] this indicates that the oxidation peak potential is much more negative than the standard potential of the couple involved in the electrochemical process. Such a situation is classically encountered when the chemical reaction is concerted with the electron transfer.[30] However, a clear-cut answer to this question would require a knowledge of the standard potential $E°$ for the oxidation of HPyB to the radical cation before and after coupling.[30] For the purpose of our investigations, suffice it to say that the chemical reaction following the electron transfer is very fast, in agreement with the conclusions from the flash photolysis and electrochemical experiments. Thus, we conclude that the formation of the product occurs through fast intramolecular coupling. (This

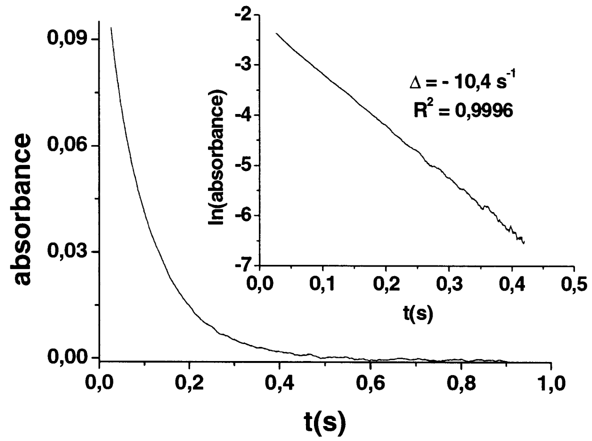


Figure 6. Absorbance decay of $HPyB^{\bullet +}$ monitored after the laser pulse at 400 nm in acetonitrile containing 10^{-1} M $CHBr_3$ and 10^{-3} M HPyB. The inset represents the first-order fit.

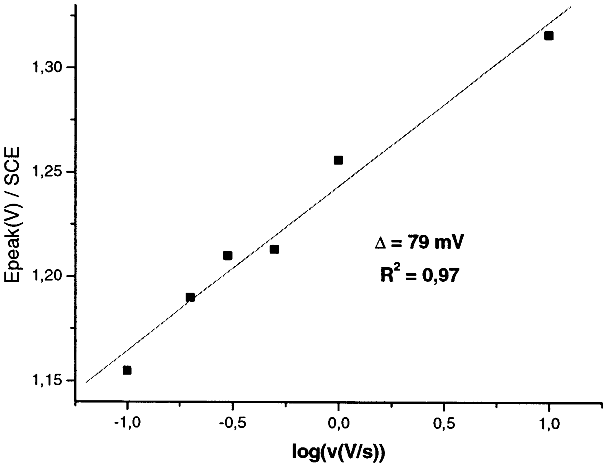
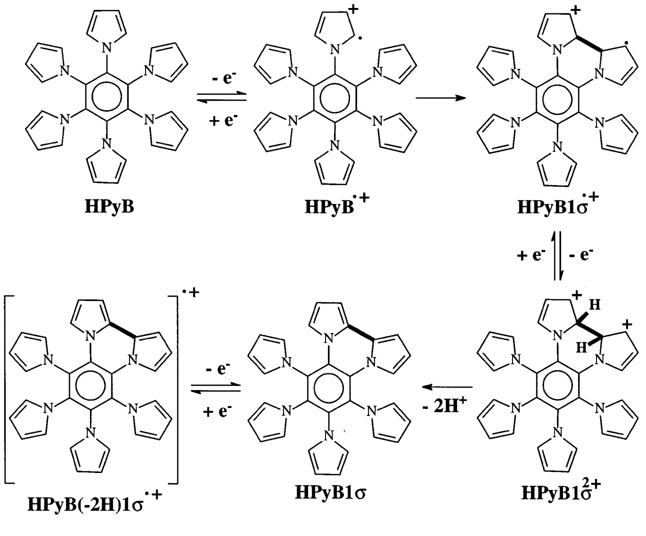


Figure 7. Cyclic voltammetry of 10^{-3} M HPyB and 10^{-1} M $LiClO_4$ in acetonitrile. Variation of the peak potential E_{peak} with the logarithm of the scan rate (*v*).

SCHEME 3 : First Intramolecular Coupling Reaction of HPyB Involving the Radical Cation/Substrate Mechanism



coupling reaction may be concerted with the electron transfer.) As far as HPyB is concerned, the radical cation produced by flash photolysis does not react with another radical cation either by coupling or by disproportionation. Transient cyclic voltammetry indicates that a rapid chemical reaction (EC mechanism) occurs just after the heterogeneous electron transfer, and this occurs even after the homogeneous electron transfer in flash photolysis. Moreover, the chemical steps following the C−C bond formation have been investigated by chronoamperometry of 10^{-3} M HPyB in acetonitrile (in the presence of 0.1 M $LiClO_4$) at a low potential value (0.7 V/SCE). Under similar conditions, the electrooxidation of pyrrole leads to short-chain oligomers, and the formation of long chains is hindered by the generation of defects.[8] We observed the formation of an insoluble organic film. This indicates that the coupling reaction proceeds up to the formation of solid HPyB6σ (Scheme 2) even at this low potential.

From all of these results, we can describe the overall reaction of formation of the insoluble product as follows:

(i) After the first one-electron transfer (HPyB$^{\bullet+}$, Scheme 3), the very fast formation of mono-oxidized HPyB1$\sigma^{\bullet+}$ (Scheme 3) occurs by intramolecular coupling between a radical cation of a pyrrolyl residue and a neutral pyrrolyl residue located at an adjacent position on the benzene ring (very fast chemical reaction following electron transfer).

(ii) The mono-oxidized HPyB1$\sigma^{\bullet+}$ that is produced is a new radical cation species that seems to be stable and to decrease very slowly in flash photolysis (where only one electron is transferred), but it is too reactive to be reduced and detected in rapid cyclic voltammetry. In electrochemical experiments, this species loses another electron (HPyB1σ^{2+}) and two protons to rearomatize and to lead to the neutral HPyB1σ (Scheme 3), which is more easily oxidized than the neutral parent HPyB.

(iii) Despite the delocalization of the charge of the radical cation produced by the oxidation of HPyB1σ, this compound reacts to give HPyB2σ because the subsequent chemical reactions remain fast because of the vicinity of the substrate that belongs to the same molecule.

(iv) The reaction undergoes the same processes (mono-oxidation followed by fast radical cation/substrate reaction) more and more easily up to the formation of solid HPyB6σ.

Conclusions

The star-shaped compound HPyB undergoes an irreversible first electron transfer in oxidation (electrochemical and photochemical) followed by a fast chemical reaction (EC mechanism). This EC mechanism is a radical cation/substrate type. After photooxidation, a radical cation species that has a very long lifetime and does not undergo any change in its basic medium is formed, indicating that no dimerization or deprotonation reaction occurs consecutively with the fast intramolecular coupling reaction. This species, HPyB1$\sigma^{\bullet+}$, is an intramolecularly coupled radical cation. The major HPyB oxidation intermediates have been characterized as products obtained by successive intramolecular coupling reactions between the pyrrolyl residues of the same monomer. The all-intramolecularly coupled HPyB6σ compound is completely insoluble and has been characterized by analogy with the oxidation product of a more soluble derivative, HOPyB.

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