X-ray photoelectron spectroscopy studies of deprotonated polypyrrole and its complexes

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Oxidized polypyrrole (PPY) was subjected to deprotonation by 0.5 M NaOH. The interactions of the deprotonated pyrrolylium nitrogens with various protonic acids and organic electron acceptors were studied by X-ray photoelectron spectroscopy (XPS) and were found to be similar to those observed for the imine nitrogens in the emeraldine oxidation state of polyaniline. However, the cyclic acid/base treatments of the deprotonated PPY were not completely reversible. The interactions with the halobenzoquinones, such as *o*-chloranil, *p*-chloranil and *o*-bromanil, resulted in the formation of positively charged nitrogens and the halogen and benzoquinone anions. In the case of interaction with TCNE, cyano anions were involved while interaction with DDQ involved all three types of anions. The charge transfer (CT) behaviour of the deprotonated pyrrolylium nitrogens towards acid protonation, and 'doping' by the organic acceptors, together with the charge neutrality considerations, suggested the presence of localized units positive charge on the pyrrolylium nitrogens.

(Keywords: XPS; polypyrrole; deprotonation; reprotonation; organic acceptors; charge transfer)

INTRODUCTION

The synthesis and characterization of electroactive conjugated polymers have become one of the most important areas of research in polymer science in recent years[1]. Among the electroactive polymers reported, 'doped' polyaniline (PAN) and polypyrrole (PPY) have received a great deal of attention because of their high electrical conductivity, environmental stability and interesting redox properties involving the chain nitrogens[2–5]. The reversibility of the doping process, after subjecting to 'chemical compensation' or 'undoping', has also been widely studied[4–9]. The physicochemical nature of the doping and undoping processes perhaps is best understood in the case of aniline polymers. In PAN, the compensation and redoping involve simple deprotonation and subsequent reprotonation[4,5]. However, in the case of chemical compensation of oxidized PPY in certain alkaline environments, the mechanism and structural changes associated with the process have not been resolved unambiguously[7].

An earlier study[8] has suggested that the oxidized pyrrolylium nitrogen ($-N^+H-$ structure) can undergo deprotonation in alkaline solution to give rise to an imine-like ($=N-$) structure. Furthermore, this effect is readily reversed in protonic acid media. Accordingly, it would be of great interest to compare the charge transfer (CT) behaviour of the deprotonated pyrrolylium nitrogen with that of the imine nitrogen in the emeraldine base of PAN. Thus, this study deals with a detailed investigation of the CT interactions between the deprotonated PPY and various protonic acids and proton free organic electron acceptors, using X-ray photoelectron spectroscopy (XPS) as a primary tool. The organic electron acceptors used consisted of tetrachloro-*o*-benzoquinone (*o*-chloranil), tetrachloro-*p*-benzoquinone (*p*-chloranil), tetrabromo-*o*-benzoquinone (*o*-bromanil), tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). Most of the XPS studies on PPY have been devoted to its chemically and electrochemically oxidized complexes[10–17]. In comparison, the XPS of deprotonated PPY has only been studied briefly[7,8].

EXPERIMENTAL

In order to have an oxidized pyrrolylium nitrogen structure similar to that of the acid protonated imine structure of PAN, chemically synthesized PPY-halogen complex was used as the starting material. The PPY/I_2 complex was synthesized via the simultaneous chemical polymerization and oxidation of pyrrole by iodine in an aqueous medium at 4°C according to the method reported earlier[18]. The PPY/I_2 complex used in the present study had a bulk composition of $C_{4.1}H_{3.1}\cdot N_{1.0}O_{0.60}(I_2)_{0.22}$ and an electrical conductivity (σ) of about $5\,S\,cm^{-1}$. Most of the iodine existed as ionic iodide. The infrared (i.r.) absorption spectrum of the complex suggested the presence of a linear chain of α,α'-disubstituted pyrrole rings. The PPY/Br_2 and PPY/Cl_2 complexes were avoided since a substantial proportion of bromine and chlorine could become covalently bonded to the polymer during synthesis[19]. Deprotonation of the PPY/I_2 complex was carried out by dispersing the complex in excess of 0.5 M NaOH with vigorous agitation. The compensated or deprotonated polymer was then treated with various protonic acids, such as

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HCl, H_2SO_4 and HBr, of unit molarity. Complex formation with the organic acceptors was carried out by dispersing the deprotonated polymer in the acetonitrile solution of the acceptor containing the same number of moles of the acceptor as the monomer units.

The uncomplexed acceptor was removed by washing the complex with copious amounts of acetonitrile. The organic acceptors used were tetrachloro-*o*-benzoquinone (*o*-chloranil), tetrachloro-*p*-benzoquinone (*p*-chloranil), tetrabromo-*o*-benzoquinone (*o*-bromanil), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). All acceptors were obtained from the Aldrich Chemical Co. and were recrystallized from appropriate organic solvents before use. In all cases, the polymer and the complexes were dried by pumping under reduced pressure.

Electrical conductivities of the various PPY samples were measured using either the standard collinear four-probe or the two-probe techniques on compressed pellets. The infrared (i.r.) absorption spectra were measured on a Perkin–Elmer Model 682 spectrophotometer with the polymer samples dispersed in KBr. Bulk elemental analyses were carried out on a Perkin–Elmer 2400 Elemental Analyzer. X-ray photoelectron spectroscopy (XPS) measurements were made on a VG ESCALAB MkII spectrometer with a MgKα X-ray source (1253.6 eV photons). The X-ray power supply was run at 12 kV and 10 mA. The PPY samples in powder form were mounted on the standard sample studs by means of double-side adhesive tapes. All core-level spectra were referenced to the C1s neutral carbon peak at 284.6 eV. All spectra were curve-fitted with Gaussian component peaks. The peak width (full width at half maximum, FWHM) was maintained constant for all components in a particular spectrum. The peak area ratios for the various elements were corrected by the experimentally determined instrumental sensitivity factors and might be liable to not more than ±10% error.

RESULTS AND DISCUSSION

Oxidized polypyrrole, such as the PPY/I_2 complex, exhibits a single major N1s component at about 399.7 eV, characteristic of the pyrrolylium nitrogen (–NH– structure), and a high B.E. tail, comprising about 1/4 of the total N1s area and attributable to the positively charged nitrogen. The localization of positive charges on the nitrogens has been favoured in a number of XPS studies[14,16], while other studies suggested partially charged nitrogens or delocalized charges[10–12]. *Figure 1* shows the N1s and I3d$_{5/2}$ XPS core-level spectra for the PPY/I_2 complex used in the present study. The I3d$_{5/2}$ core-level spectrum can be curve-fitted with two major components at B.E. positions of 618.8 and 620.5 eV, attributable to the formation of various iodide anions[16].

Reprotonation of deprotonated PPY by acids

Upon 'compensation' of the PPY/I_2 complex with excess 0.5 M NaOH, most of the iodide has been removed, as suggested by an almost complete loss of the I3d$_{5/2}$ core-level signal. Furthermore, the electrical conductivity of the complex decreases by more than five orders of magnitude. Subtle changes in the N1s line-shape are also observed, as revealed by *Figure 2a*. The high B.E. tail that is characteristic of the positively charged nitrogen has diminished. The remaining trace amount of this component is probably attributable to the surface oxidation products, such as the CT complexing with oxygen, as PPY has a relatively low oxidation potential[3,20,21]. A new low B.E. shoulder which is shifted by about −2 eV from that of the pyrrolylium nitrogen can also be discerned. Earlier XPS studies have associated this low B.E. structure with dehydrogenation of a certain fraction of the pyrrolylium nitrogen, followed by rearrangement of the pyrrole bonds to satisfy the three nitrogen valences, resulting in a =N– type structure[8,15]. Similar B.E. shifts have also been observed recently for the imine and amine nitrogens in PAN[22].

Furthermore, similar to the imine structure of the emeraldine base in PAN[4,5], this dehydrogenated pyrrolylium nitrogen is preferentially protonated by acids. *Figure 2b* shows the N1s core-level spectrum of the structure after protonation by H_2SO_4. The disappearance of the low B.E. shoulder and the appearance of the high B.E. tail after acid treatment are consistent with the proposed mechanism. The use of other protonic acids, such as HCl and HBr can result in a substantial covalent bonding of the halogens to the polymer (see below).

Finally, as in the case of protonated imine nitrogen of PAN, the protonated structure of *Figure 2b* can in turn be deprotonated by NaOH to give rise to the structure

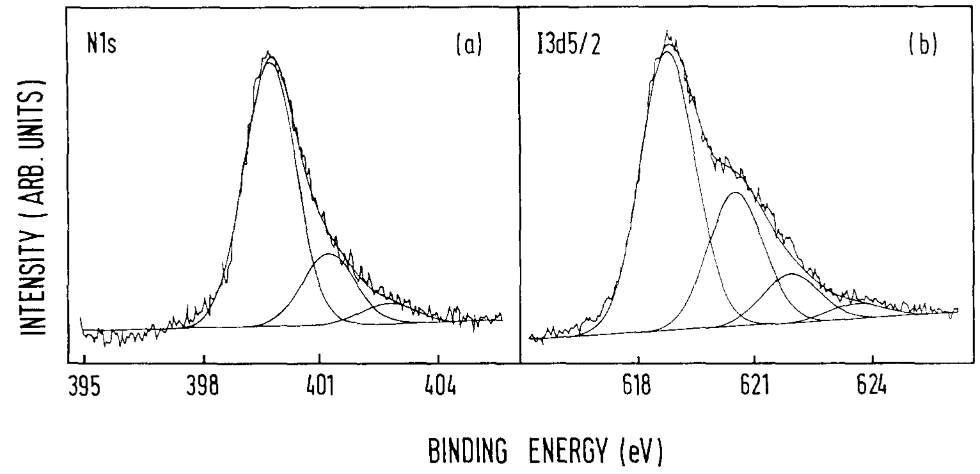

Figure 1 N1s and I3d$_{5/2}$ XPS core-level spectra of a chemically synthesized PPY/I_2 complex

shown in *Figure 2c*, which is similar to that of *Figure 2a*. Similar changes in the N1s line shapes are observed in the subsequent cycles of acid/base treatment. However, bulk elemental analysis results suggest a slight increase in the C/N ratio upon each cycle of acid/base treatment. An increase in the C/N ratio above the theoretical value of 4 readily suggests that a small degree of ring opening and hydrolysis must have occurred[23]. This may help to account, at least partially, for a gradual decrease in the electrical conductivity of the protonated sample after each acid/base cycle which has been observed in the present and earlier[8] studies.

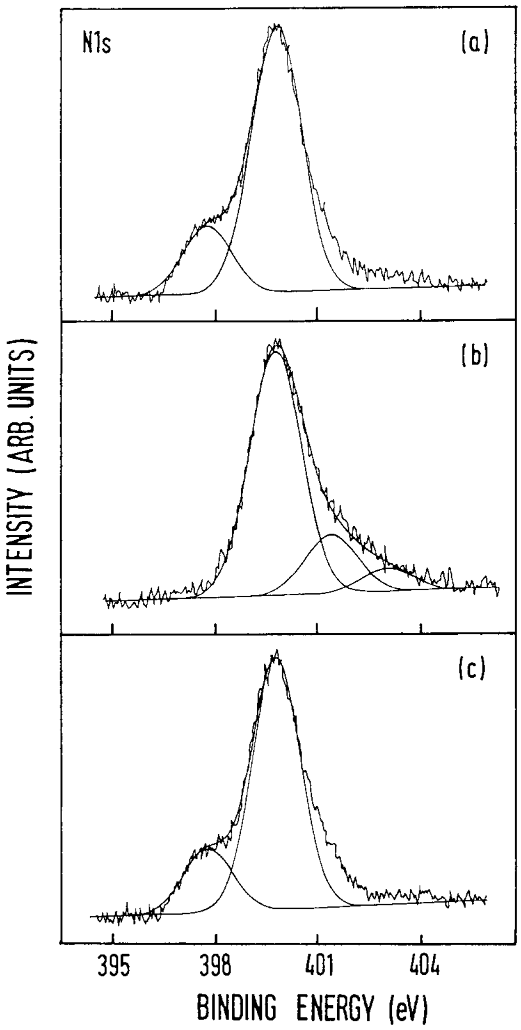

Figure 2 N1s XPS core-level spectra of (a) 0.5 M NaOH deprotonated PPY/I_2 complex, (b) deprotonated PPY after treatment with 1 M H_2SO_4, and (c) H_2SO_4 reprotonated complex further treated with 0.5 M NaOH

The electrical conductivities, stoichiometries and structural compositions for the deprotonated PPY and its H_2SO_4, HBr and HCl reprotonated complexes are summarized in *Table 1*. The S2p XPS core-level spectrum of the H_2SO_4 complex shows the presence of a single component with a $S2p_{3/2}$ B.E. of 168.5 eV, consistent with a sulphate environment[24]. Comparison of the spectral component area ratios suggests that the proportion of positively charged nitrogens is close to the S/N ratio. Thus, if these nitrogens carry a unit positive charge (see below), charge neutrality consideration suggests that the sulphate species probably exists as monovalent anion, such as HSO_4^-.

Monovalent sulphate anion species has also been observed in the H_2SO_4 protonated PAN[25]. The data in *Table 1* indicate the presence of a close balance between the proportion of positively charged nitrogen and the anion/N ratio for the HCl and HBr protonated complexes, as well as for the organic acceptor complexes (see below). This is consistent with the concept of localized unit positive charge on the pyrrolylium nitrogen. Furthermore, the presence of unit positively charged nitrogens in the present complexes would be analogous to the formation of the nitrogenonium ion structure in PAN as a result of acid protonation at the imine units[4,5]. Finally, the fact that the positive charge on the nitrogen is removed simultaneously during deprotonation suggests that the positive charge in oxidized PPY is not delocalized over the pyrrole units. Thus, the polarons and bi-polarons in PPY[26] are likely to be associated with the nitrogen atoms, as in the case of PAN[4].

The electrical conductivity of the H_2SO_4 reprotonated complex is similar to that of the starting PPY–I_2 complex. However, the conductivities are somewhat lower in the HCl or HBr reprotonated samples. In these latter complexes, substantial halogen addition to the polymer has also been observed. *Figure 3* shows the N1s and Cl2p XPS core-level spectra for a deprotonated PPY sample after treatment with 1 M HCl. The Cl2p core-level spectrum can be curve-fitted with $Cl2p_{1/2}$ and $Cl2p_{3/2}$ components at B.E. positions corresponding to those for covalent and ionic chlorine species. The $Cl2p_{3/2}$

Table 1 XPS results and stoichiometries of the various complexes arising from deprotonated PPY

Sample	Dopant	Dopant/ monomer[a] ratio	Proportion[b] of -N=[c]	-NH-	N^+	Anion/N ratio S or halogen[d]/N	O/N	Conductivity σ (S cm^{-1})
Pristine (deprotonated)	–	–	0.21	0.75	0.04	–	–	$\sim 10^{-5}$
1	1 M H_2SO_4	0.20	0.0	0.75	0.25	0.20	–	4
2	1 M HCl	0.31	0.03	0.74	0.23	0.21	–	0.5
3	1 M HBr	0.28	0.02	0.74	0.24	0.21	–	0.8
4	*o*-chloranil	0.26	0.05	0.73	0.22	0.16	0.10	0.3
5	*o*-bromanil	0.18	0.12	0.72	0.16	0.09	0.10	2×10^{-2}
6	*p*-chloranil	0.16	0.13	0.71	0.16	0.03	0.12	8×10^{-3}

[a] Final complex stoichiometry determined from XPS
[b] Determined from the deconvoluted N1s core-level spectrum
[c] Neutral imine structure
[d] The covalent component has been excluded

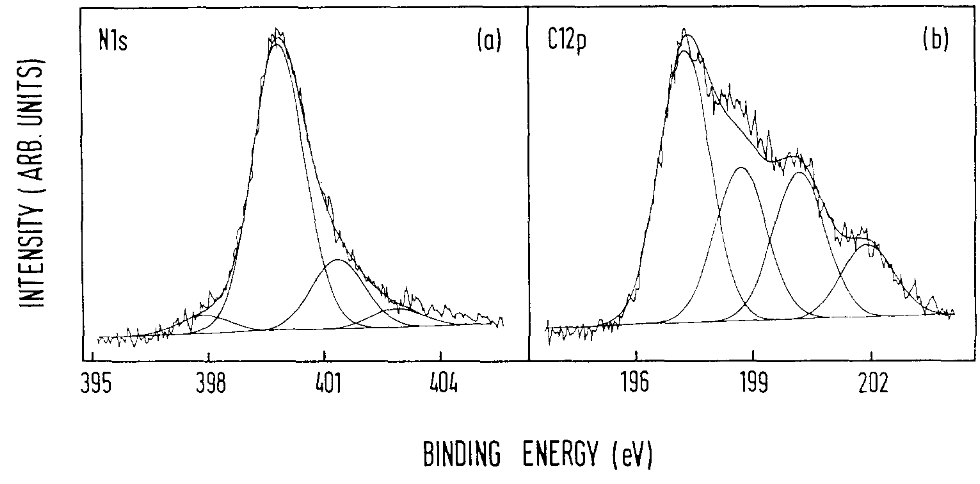

Figure 3 N1s and Cl2p XPS core-level spectra of a deprotonated PPY after treatment with 1 M HCl

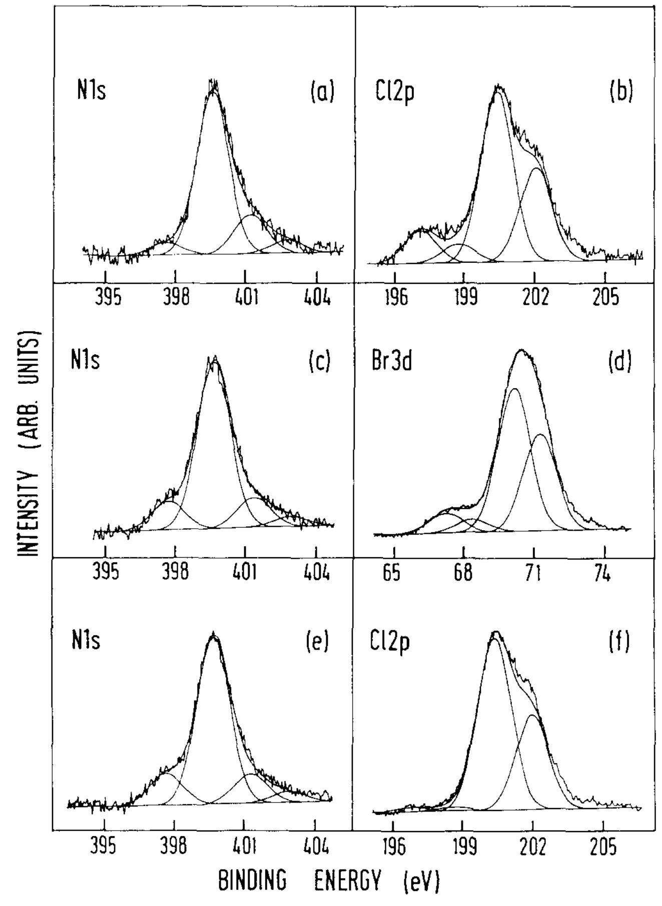

Figure 4 (a) N1s and (b) Cl2p XPS core-level spectra of the deprotonated PPY/*o*-chloranil complex; (c) N1s and (d) Br3d XPS core-level spectra of the deprotonated PPY/*o*-bromanil complex; (e) N1s and (f) Cl2p XPS core-level spectra of the deprotonated PPY/*p*-chloranil complex

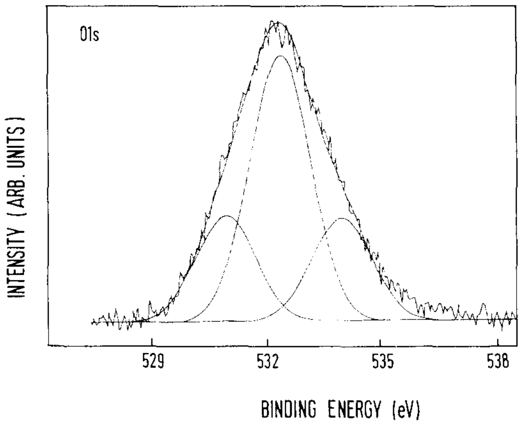

Figure 5 O1s XPS core-level spectrum of the deprotonated PPY/*o*-chloranil complex

B.E. corresponding to these two species are at about 200.3 eV and 197.1 eV, respectively. The formation of a large proportion of covalently bonded halogen will undoubtedly cause substantial changes in the intrinsic structure of the polymer and render the base/acid treatment irreversible.

Interaction of deprotonated PPY with organic acceptors

Our earlier study has shown that the imine nitrogens of the emeraldine oxidation state of PAN also interact with some organic electron acceptors[27]. *Figures 4a* and *b* show the respective N1s and Cl2p XPS core-level spectra for the present deprotonated PPY after treatment with *o*-chloranil. The Cl2p core-level spectrum reveals the presence of both covalent and ionic environments. The $Cl2p_{3/2}$ binding energies for the respective species are at about 200.4 eV and 196.8 eV. Thus, the interactions between *o*-chloranil and the deprotonated PPY must have proceeded further than the formation of pure molecular CT complex.

To account for the formation of chloride anions, cleavage of some of the C–Cl bonds of the acceptor, accompanied by the formation of linkages between the acceptor and the pyrrolylium nitrogen of the polymer through the cleavage sites, must have occurred. Furthermore, the O1s core-level spectrum reveals the presence of a low and a high B.E. component of about equal size located at about 1.5 eV on either side of the carbonyl peak at about 532.4 eV[28]. The low B.E. component can probably be associated with the formation of negatively charged oxygen, such as the benzoquinone or semibenzoquinone anions, while the high B.E. component is probably attributable to oxygen bonded to an electron withdrawing group, such as the positively charged pyrrolylium nitrogen[29]. *Figure 5* shows the O1s core-level spectrum for the present *o*-chloranil complex. The formation of the benzoquinone anion is consistent with a substantial reduction in the C=O stretching vibration[30] at about 1700 cm^{-1} in the i.r. absorption spectra of all the present complexes involving benzoquinone acceptors. The formation of chloride and benzoquinone anions through interaction with the deprotonated pyrrolylium nitrogens is consistent with the disappearance of the low B.E. =N– component and a substantial enhancement of the high B.E. N$^+$ component in the N1s core-level spectrum of the complex.

Similar CT interactions with the formation of halogen and benzoquinone anions and nitrogen cations are observed between the deprotonated PPY and *o*-bromanil. In this case, the Br3d$_{5/2}$ B.E. for the covalent and ionic bromine are at about 70.1 eV and 67.2 eV, respectively. *Figures 4c* and *d* show the respective N1s and Br3d XPS core-level spectra for the complex. Again, fairly strong CT interactions are observed between the polymer and the acceptor, as suggested by a substantial reduction in the =N– units. The similarity in the CT behaviour of the two halobenzoquinone acceptors towards the polymer is consistent with the similarity in chemical structure and reduction potential[31] of the two acceptors. However, in the case of CT interaction between the deprotonated PPY and *p*-chloranil, relatively little chloride anions were detected although a reduction in the =N– component and the formation of benzoquinone anions were observed. *Figures 4e* and *f* show the respective N1s and Cl2p XPS core-level spectra for the *p*-chloranil complex.

Thus, the XPS results for the three halobenzoquinone complexes readily suggest that the formation of halogen anions and the extent of CT is facilitated in the *ortho*-halobenzoquinones, probably as a result of substantially less steric hindrance at the C_4 position of these acceptors. *Figure 6* shows the plausible structures of the complexes, using *o*-chloranil complex as an example. These structures suggest that CT interaction between deprotonated PPY and the halobenzoquinone resembles that of protonation by acids, with the hydrogen atoms in the latter replaced by the bulky acceptor rings. The proposed mechanism of interaction between the deprotonated PPY and *o*-chloranil is similar to that observed between the imine nitrogens of PAN and the halobenzoquinones[27] and between the nitrogen atoms of molecular pyridine (=N– structure) and *p*-chloranil[29].

The electrical conductivities and the amounts of the anion and cation species for the various halobenzoquinone complexes are summarized in *Table 1*. Thus, the XPS data reveal a relatively good balance between the number of nitrogen cations and the sum of the chloride and benzoquinone anions in all of the complexes. This gives further support to the presence of localized unit positive charges on the pyrrolylium nitrogens. Furthermore, the electrical conductivity of the *o*-chloranil complex is significantly higher than those of the *p*-chloranil and *o*-bromanil complexes. This is consistent with a greater reduction in the =N– structure and the presence of a more enhanced N$^+$ high B.E. tail in the N1s core-level spectrum of the *o*-chloranil complex. The degree of CT and the electrical conductivity of the present *p*-chloranil complex appears to be somewhat lower than the corresponding complex obtained from bulk polymerization of pyrrole by *p*-chloranil[32]. This is probably associated with the fact that in the latter mechanism, the monomer forms a CT complex with the acceptor prior to polymerization and is less susceptible to steric effects.

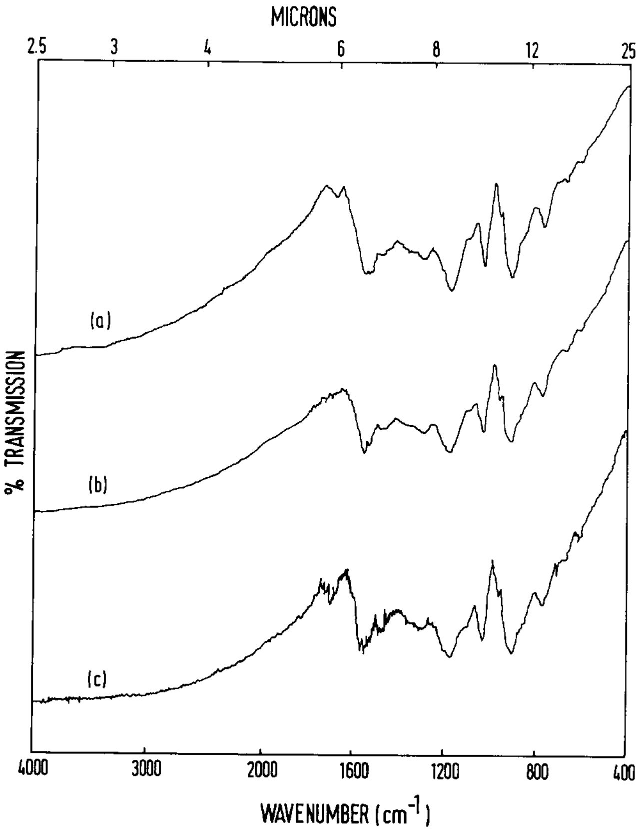

Figure 7 I.r. absorption spectra of the complexes formed between deprotonated PPY and curve a, *o*-chloranil; curve b, *o*-bromanil and curve c, *p*-chloranil

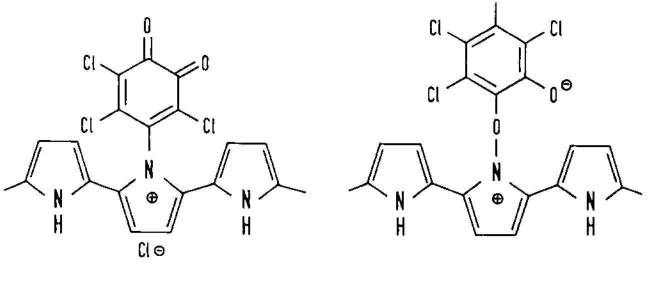

Figure 6 Plausible structures resulting from the CT interaction between deprotonated PPY and *o*-chloranil

With the exception of a weak absorption band at about 1700 cm^{-1} and attributable to the C=O group, the i.r. absorption bands due to the acceptors are not clearly visible in the present halobenzoquinone complexes. On the other hand, the absorption tail between 4000 and 1800 cm^{-1} and the absorption bands at about 1540, 1480, 1300, 1180, 1040 and 900 cm^{-1} are all characteristic of oxidized PPY[3,33]. *Figure 7* shows the i.r. absorption spectra of the complexes formed between deprotonated PPY and the three halobenzoquinones. The presence of a strong C_β–H in-plane vibration band[33] at about 1040 cm^{-1} in all of the present complexes indicates that the acceptors do not interact to a significant extent with the β-carbon of the pyrrole unit. Thus, the i.r. results are consistent with the proposed CT interaction involving the deprotonated pyrrolylium nitrogen.

The studies of CT interactions are further extended to the use of acceptors containing the cyano functional groups, such as TCNQ, TCNE and DDQ. The deprotonated PPY does not interact with TCNQ to a significant extent, as suggested by the persistence of the =N– component and the lack of N^+ component in the N1s core-level spectrum of the complex. However, strong CT interactions were observed between deprotonated PPY and TCNE. *Figure 8* shows the N1s core-level spectrum of the complex. Careful deconvolution of the N1s spectrum reveals the appearance of the N^+ high B.E. tail and that the =N– peak component of the polymer at 397.7 eV has been replaced by a new component at 398.2 eV. The latter, which is shifted by about −1.5 eV from the neutral nitrogen species at 399.7 eV, must be attributable to the formation of cyano anions. In other CT complexes involving organic cyano groups, such as the mixed valence salt complex of TCNQ anion $(TCNQ)^-$ and tetrathiafulvalene and tetramethyltetraselenafulvalene cations[34,35], a N1s peak component with a negative chemical shift of about 1.1 to 1.2 eV from the neutral nitrogen peak has been observed.

The composition of the present TCNE complex cannot be determined unambiguously from the elemental or XPS analysis. The N1s components of the neutral nitrogen species for the polymer and the acceptor overlap one another. In addition, although the presence of cyano anions is required to balance the formation of positively charged nitrogen, the structure of the present TCNE complex cannot be resolved from the XPS results alone. The presence of about equal amounts of the negatively and positively charged nitrogens and the similarity in B.E. of the present nitrogen anion with that of nitrogen in KCN[36] suggests the presence of the cyano anions of the type $(CN)^-$.

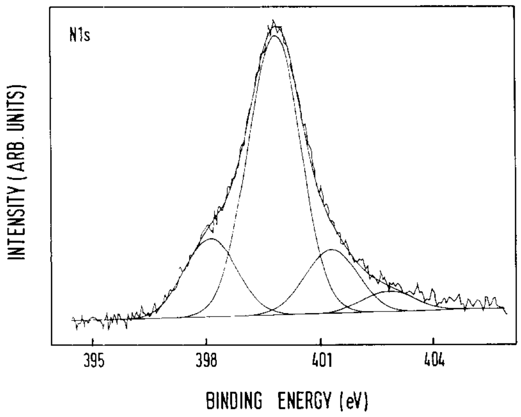

Figure 8 N1s core-level spectrum of the complex formed between deprotonated PPY and TCNE

An earlier study involving neutral PPY (–NH– structure) and TCNE has suggested the formation of $(CN)^-$ anion and covalently bonded TCNE at the β-carbon of the pyrrole ring, as a result of cleavage of the C–CN band of the acceptor[37]. The formation of linkage at the β-carbon would be accompanied by a significant change in the i.r. absorption bands at about 1040 cm^{-1} and 1480 cm^{-1}, attributable to the C_β–H in-plane vibration and pyrrole ring vibration[33], respectively. However, these have not been observed in the i.r. spectrum of the present TCNE complex. In fact, the i.r. absorption spectrum of the TCNE complex resembles those of the halobenzoquinone complexes shown in *Figure 7*. Thus, the CT interaction of the deprotonated PPY with TCNE probably proceeds through the pyrrolylium nitrogens, as in the case of interaction with the halobenzoquinones.

Significant CT interactions are also observed between deprotonated PPY and DDQ, which contains the carbonyl, halogen and cyano functional groups. *Figure 9* shows the N1s and Cl2p core-level spectra of the complex with an acceptor/monomer ratio of about 0.20, as determined from chlorine balance. The N1s core-level spectrum indicates the replacement of the =N– component of the polymer by the cyano anions, as in the case of TCNE complex. However, only a small fraction of the chlorine exists as chloride anion. The O1s core-level spectrum suggests the presence of a low B.E. semibenzoquinone anion component similar to that observed earlier in the halobenzoquinone complexes. Thus, the CT interaction between the deprotonated PPY and DDQ occurs preferentially through the cyano and oxygen functional groups of the acceptor. The limited involvement of the chlorine functional group in the DDQ complex can probably be attributed to the same steric effect that hinders the CT interaction in the *p*-chloranil complex. Finally, the electrical conductivities of the present TCNE and DDQ complexes are in the order of 10^{-2} S cm^{-1}.

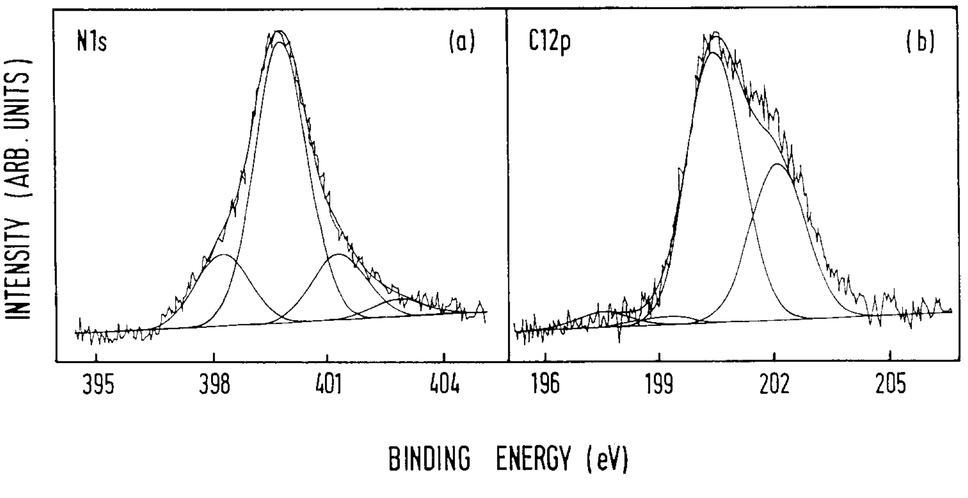

Figure 9 (a) N1s and (b) Cl2p XPS core-level spectra of the complex formed between deprotonated PPY and DDQ

CONCLUSIONS

The CT interactions between deprotonated PPY and various protonic acids and organic electron acceptors were studied by XPS. The protonic acids used were HCl, HBr and H_2SO_4 while the organic acceptors consisted of *o*-chloranil, *p*-chloranil, *o*-bromanil, TCNQ, TCNE and DDQ. The deprotonated pyrrolylium nitrogens can be subjected to cyclic protonation and deprotonation although the process is not completely reversible. With the exception of TCNQ which failed to interact, the CT interactions with the organic acceptors were found to be similar to protonation, with the hydrogen atoms replaced by the bulky acceptor molecules. XPS data suggested cleavage or modification of the functional groups of the complexed organic acceptors. The CT behaviour of the deprotonated pyrrolylium nitrogens towards protonation and organic acceptor complexing was found to be similar to that observed for the imine nitrogens in the emeraldine oxidation state of polyaniline. The CT behaviour also supports the presence of localized unit positive charge on the pyrrolylium nitrogen.

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