X.p.s. studies of charge transfer interactions in some polyaniline complexes

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The imine, amine and positively charged nitrogen in polyaniline at various oxidation states can be quantitatively differentiated in the properly deconvoluted N1s X-ray photoelectron spectroscopy (X.p.s.) core-level spectrum. The structural changes of polyemeraldine base during 'doping' by protonic acid and by proton-free organic acceptors, such as the halobenzoquinones, were compared. X.p.s. results suggest the presence of halogen and benzoquinone anions in the latter complexes. The mechanism of interactions with the organic acceptors was found to be analogous to that of protonation, with the charge transfer interactions occurring preferentially at the imine repeating units.

INTRODUCTION

Recent interest in the conducting polymers[1] has resulted in extensive renewed work[2-6] on the century-old[7] aniline family of polymers. The electronic structure of polyaniline can be varied either by varying the number of electrons per repeat unit through electrochemical doping or by the addition of protons associated with individual nitrogen sites. It has been proposed[2,6] that polymer of the 'emeraldine base' form consists of equal numbers of benzoid amine and quinoid imine repeating units and the latter is preferentially protonated, for example, by HCl. The redox state of the polymer can vary from the fully reduced poly(paraphenyleneamine) or 'leucoemeraldine' to the fully oxidized poly(paraphenyleneimine) or 'pernigraniline'. The chemical structures of polyaniline have been investigated extensively by infrared (i.r.) spectroscopy[8-11], X-ray photoelectron spectroscopy (X.p.s.)[12-15] and nuclear magnetic resonance (n.m.r.)[16,17], as well as by studying model compounds[13,18,19]. Most of the X.p.s. studies have been centred on protonated and electrochemically oxidized polyaniline. This report, however, focuses on the charge transfer (c.t.) interactions between polyemeraldine base and some organic electron acceptors, as revealed by X.p.s. It is also demonstrated that the structural changes associated with polyaniline oxidation and reduction can be quantitatively and unambiguously determined by using the X.p.s. technique.

EXPERIMENTAL

Polymer samples

Polyemeraldine hydrochloride was prepared at 0–5°C from aniline and $(NH_4)_2S_2O_8$ in 1.0 M aqueous HCl according to the method in the literature[2,6]. It was converted to the emeraldine base by treatment with excess 0.5 M aqueous NH_4OH. The polyemeraldine–acceptor complexes were then prepared by suspending the finely ground polymer base in the acetonitrile solution of the acceptor at various acceptor concentrations. Each complex mixture was vigorously agitated under a nitrogen atmosphere. The solvent was allowed to evaporate slowly. The trace amount of solvent in the final complex was removed by pumping under reduced pressure. The organic acceptors used consist of the following halobenzoquinones: tetrachloro-*o*-benzoquinone (*o*-chloranil), tetrachloro-*p*-benzoquinone (*p*-chloranil), tetrabromo-*o*-benzoquinone (*o*-bromanil) and tetrafluoro-*p*-benzoquinone (*p*-fluoranil). The acceptors were recrystallized from appropriate organic solvents before use. The electrocial conductivities of the complexes were measured using both the standard collinear four-probe and the two-probe technique on compressed pellets.

X.p.s. measurements

X.p.s. measurements were made for the polyemeraldine base, polyemeraldine hydrochloride at various protonation levels, polyleucoemeraldine and the various polyemeraldine–organic acceptor complexes. Sample measurements were made on a VG ESCALAB MkII spectrometer with a $MgK\alpha$ X-ray source (1253.6 eV photons) in powder form. All core-level spectra were referenced to the C1s neutral carbon peak at 284.6 eV. The X-ray power supply was run at 12 kV and 10 mA. Pressure in the analysis chamber during the scans was $\leqslant 10^{-8}$ mbar. In spectral deconvolution, the peak width (f.w.h.m.) was maintained constant for all components in a particular spectrum. The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors and may be subject to $\pm 10\%$ error. The sensitivity factors were determined by comparison of the core-level peak area ratios in standard sample of well defined stoichiometry.

RESULTS AND DISCUSSION

Protonation of polyaniline by HCl

Previous X.p.s. studies revealed that the N1s core-level

spectrum of the polyemeraldine base comprised a broad peak with a line width of about 2.4 eV[12,13]. The line width is substantially reduced[13] in the polyemeraldine hydrochloride and a high binding energy (b.e.) shoulder or tail also becomes prominent[12,14]. However, the structure of polyaniline at a particular redox state, such as the proportions of benzoid amine, quinoid imine and protonated nitrogens, has yet to be determined quantitatively and unambiguously.

Figure 1a shows the N1s X.p.s. core-level spectrum of the polyemeraldine base. The broadness of the main component peak allows two inequivalent nitrogens to be discerned. The two main peak components at b.e. = 399.3 ± 0.1 eV and 398.1 ± 0.1 eV with a line width of 1.65 eV can be assigned to the benzoid amine and quinoid imine structure, respectively. The peak area ratio of the two components indicates that approximately equal amounts of amine and imine structure are present in the polyemeraldine base, consistent with the structure
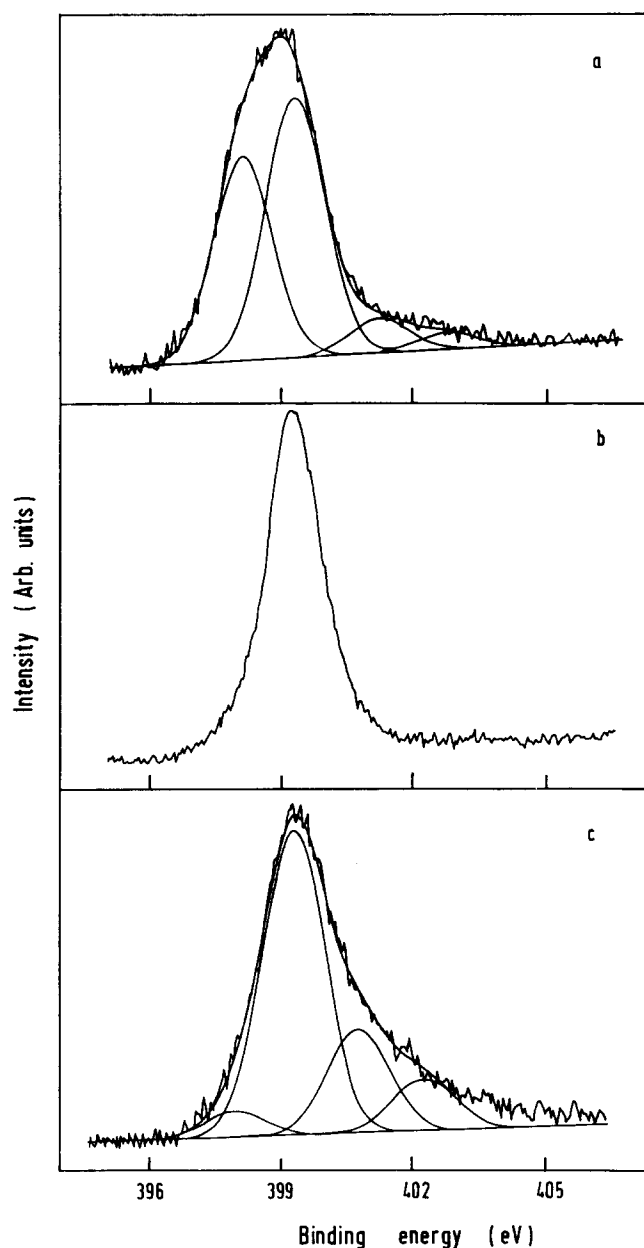
proposed by MacDiarmid *et al.*[2,4]. The slightly reduced imine structure is compensated by the presence of a small high b.e. tail, attributable to the positively charged nitrogen[12,14].

The present peak assignment is further supported by the fact that the fully reduced polyleucoemeraldine (all amine structure)[17] exhibits only a single N1s component at a b.e. of 399.3 eV with a line width of ≈1.45 eV, as shown in *Figure 1b*. Furthermore, comparative studies reveal that the b.e. of imine-like pyridinium nitrogen in poly-2-vinylpyridine is shifted by about −1.1 eV from that of the amine-like pyrrolylium nitrogen in polypyrrole[20] (398.4 eV *versus* 399.5 eV). Dehydrogenation of polypyrrole nitrogen can give rise to an imine-like structure and a corresponding negative shift in the N1s b.e. by ≈1.3 eV[21,22].

Figure 1c shows the N1s core-level spectrum of a polyemeraldine hydrochloride sample with an X.p.s. determined Cl/N ratio of 0.42. The imine peak component has decreased to only ≈5% of the total N1s area and a high b.e. tail (32%) attributable to positively charged nitrogen[12,14] becomes apparent. This is entirely consistent with the reports that the imine units of the polyemeraldine base are preferentially protonated by HCl[2,4] and also gives further confirmation to the present peak assignments. The smaller amount of positively charged nitrogen and higher amount of amine structure than expected from the total chlorine balance can be attributed to the fact that a substantial fraction of the chlorine can become covalently bonded to the quinoid units[10,15], resulting in an increase in the benzoid/quinoid ratio[10]. The Cl2p core-level spectrum of the present sample suggests that as much as 20% of the chlorine can exhibit a covalent character. Thus good charge balance can indeed be observed based on the actual amount of Cl⁻ anion present and not on the total chlorine balance. The presence of unit positively charged nitrogen has also been suggested by Munro *et al.*[14] and is consistent with the concept of nitrogenonium ion polymer proposed by MacDiarmid *et al.*[23,24], although other studies suggest the presence of delocalized radical cations in aniline oligomers[19] and electrochemically prepared polyaniline[13].

Charge transfer interactions in polyaniline–organic acceptor complexes

Since the imine units of the polyemeraldine base are preferentially protonated by HCl[2,6], it would be of great interest to trace the structural changes of polyemeraldine base associated with the various degrees of c.t. interaction with the proton-free organic acceptors.

Figure 2 shows the structural changes of four polyemeraldine samples, as revealed by the N1s core-level spectra, upon progressive 'doping' by *o*-chloranil. The corresponding area ratios for the three nitrogen species in each complex are given in *Table 1*. Upon further increase of the acceptor loading, the chemical structure and electrical conductivity of the complex do not show any appreciable changes. Both *Figure 2* and *Table 1* readily indicate that *o*-chloranil interacts preferentially with the imine nitrogen of polyemeraldine base to give rise to the nitrogenonium cation, as in the case of protonation by HCl. The proportion of the amine nitrogen remains relatively constant at low acceptor level. It increases, however, above 50% at high acceptor levels. This suggests some addition of the acceptor to the
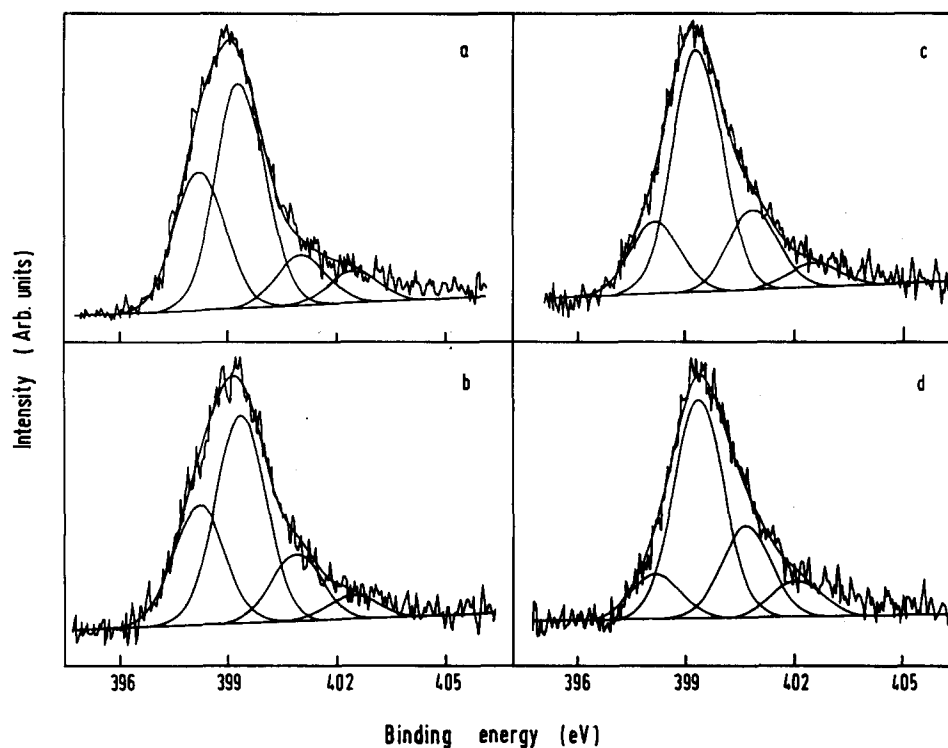

Figure 1 N1s X.p.s. core-level spectra of (a) polyemeraldine base, (b) polyleucoemeraldine and (c) polyemeraldine hydrochloride

Figure 2 N1s X.p.s. core-level spectra of polyemeraldine/o-chloranil complexes at monomer:acceptor ratios of (a) 1:0.12, (b) 1:0.34, (c) 1:0.45 and (d) 1:0.71

Table 1 X.p.s. results and stoichiometries[a] of the polyemeraldine/o-chloranil complexes

o-Chloranil/N ratio[b]	Proportion of			Ratio[c] of		Conductivity
	–N=	–NH–	N[+]	Cl^{-}/N	–O[-]/N	σ (S cm^{-1})
0.12	0.32	0.50	0.18	0.08	0.09	1×10^{-5}
0.34	0.29	0.49	0.22	0.10	0.11	5×10^{-3}
0.45	0.17	0.57	0.26	0.20	0.10	3×10^{-2}
0.55	0.11	0.56	0.33	0.23	0.09	1×10^{-1}
0.71	0.12	0.57	0.31	0.20	0.13	1×10^{-1}

[a] All core-level peak areas were corrected with the experimentally determined sensitivity factors
[b] Based on the corrected total halogen to nitrogen area ratios
[c] Based on the anion peak component to total nitrogen area ratio

quinoid units at high acceptor level and a subsequent increase in the benzoid/quinoid ratio[10].

A strong correlation between the amount of positively charged nitrogen in each complex and electrical conductivity is observed. The conductivity exhibits the strongest dependence on the amount of positively charged nitrogen at low acceptor levels. Both *Table 1* and *Figure 2* suggest that not all of the imine repeating units are involved in the c.t. interactions even at an *o*-chloranil/N ratio >0.5. This differs from the oxidation by protonic acids, and is probably associated with steric hindrance to c.t. interactions arising from the bulky organic acceptor molecules.

Of particular interest is the distribution of the negative charges on the organic acceptor. *Figure 3a* shows the Cl2p core-level spectrum for a typical polyemeraldine/*o*-chloranil complex. The spectrum can be 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$_{3/2}$ b.e. corresponding to these two species are at ≈ 200.2 eV and ≈ 196.6 eV, respectively. The presence of chloride anions, as well as other halogen anions (see below), in the present polyemeraldine/halobenzoquinone

complexes readily indicates that the c.t. interactions must have proceeded further than the formation of pure molecular complexes. Thus, some of the halogen atoms of the halobenzoquinone acceptor may have been replaced by the formation of linkage between the polymer and the acceptor. *Figure 4* shows the O1s X.p.s. core-level spectrum for a polyemeraldine/*o*-chloranil complex. The O1s envelope suggests the presence of three different environments for the oxygen of the acceptor. The centre peak component at ≈ 531.5 eV is attributable to the carbonyl oxygen of the acceptor. The lower b.e. peak, which is chemically shifted by about -1.5 eV from the carbonyl peak, can probably be associated with the formation of negatively charged oxygen, such as the benzoquinone or semi-benzoquinone anions[20,25]. The formation of benzoquinone anion structure resulting from donor–acceptor interactions has been widely observed[26]. Furthermore, a substantial reduction in the C=O stretching vibration at about 1700 cm^{-1} in the infrared absorption spectra of the present complexes, especially at low acceptor level, is consistent with the formation of the benzoquinone or semi-benzoquinone anion[27]. On the other hand, however, a positive b.e. shift
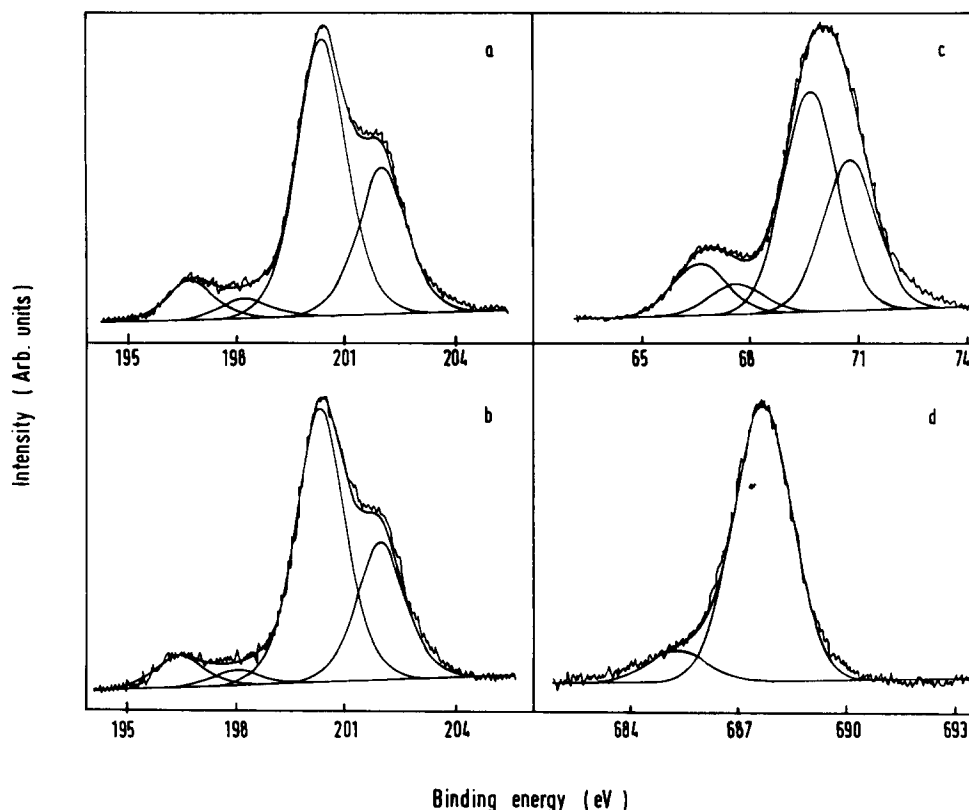
Figure 3 Halogen core-level spectra of (a) *o*-chloranil, (b) *p*-chloranil, (c) *o*-bromanil and (d) *p*-fluoranil complexes of polyemeraldine with monomer:acceptor ratios of 1:0.45, 1:0.29, 1:0.27 and 1:0.46, respectively
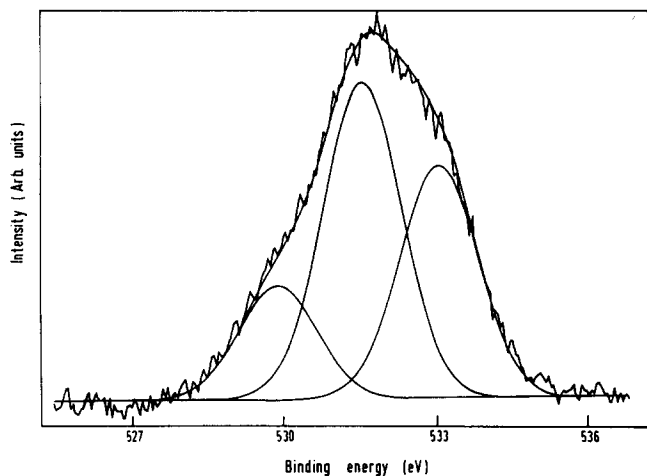

Figure 4 O1s X.p.s. core-level spectrum of polyemeraldine/*o*-chloranil complex at a monomer:acceptor ratio of 1:0.12

of 1.5 eV strongly suggests that some of the carbonyl

oxygens are involved in the formation of $-\text{C-O}-$

structure, such as the formation of linkage between carbonyl oxygen and positively charged nitrogen of the polymer[25]. Finally, the presence of surface oxidation products and contaminants may also have contributed to some extent to the present O1s spectrum, as suggested by the presence of a slight excess of oxygen in most of the complexes. The presence of excess oxygen at the surface has also been observed for the electrochemically prepared polyanilines[28]. The amounts of the chlorine and oxygen anion species in the present *o*-chloranil complexes are summarized in *Table 1*.

The respective halogen core-level spectra for the other three halobenzoquinone complexes are given in *Figure 3b–d*. The nature of the c.t. interactions in these complexes closely resembles that of the *o*-chloranil complex mentioned above. This includes the preferential interactions of the acceptors with the imine nitrogen and the formation of halogen and benzoquinone anions. The X.p.s. results for the *p*-chloranil, *o*-bromanil and *p*-fluoranil complexes are summarized in *Table 2*. The data in *Tables 1* and *2* reveal a relatively good balance between the number of nitrogenonium cations and the sum of the chloride and benzoquinone anions in most of the complexes. The presence of localized unit positive charge on the nitrogen in the present polyemeraldine–organic acceptor complexes is similar to that of the protonation by HCl. It is again consistent with the concept of nitrogenonium ion polymer proposed for the polyaniline complexes[23,24].

The data in *Tables 1* and *2* further suggest that, for complexes at moderate to high acceptor levels, the number of nitrogenonium cations is substantially lower than the number of the acceptor molecules incorporated. Thus, the halobenzoquinone acceptors in most of the present complexes probably exist only as monovalent anions, in spite of the fact that the presence of multivalent anions has been suggested for the pyridine/*p*-chloranil complexes[25] and other complexes involving chloranil[26]. Comparison of the degree of c.t. interaction observed in the present *o*-chloranil and *p*-chloranil complexes at various acceptor levels suggests the presence of substantially less chloride anion formation and electrical conductivity in the latter complex. More extensive halogen anion formation is also observed in the *o*-bromanil complex than in the *p*-fluoranil and *p*-chloranil

Table 2 X.p.s. results and stoichiometries[a] of the various polyemeraldine/halobenzoquinone complexes

Acceptor	Acceptor/N ratio[b]	Proportion of			Ratio[c] of		Conductivity
		–N=	–NH–	N$^+$	Cl$^-$, Br$^-$ or F$^-$/N	–O$^-$/N	σ(S cm^{-1})
p-chloranil	0.14	0.36	0.49	0.15	0.10	0.07	1×10^{-5}
	0.29	0.34	0.47	0.19	0.13	0.06	6×10^{-5}
	0.34	0.29	0.51	0.20	0.08	0.07	6×10^{-5}
	0.56	0.36	0.48	0.16	0.04	0.09	1×10^{-5}
o-bromanil	0.09	0.31	0.51	0.18	0.06	0.10	5×10^{-5}
	0.21	0.27	0.51	0.22	0.14	0.11	1×10^{-3}
	0.27	0.14	0.56	0.30	0.20	0.13	4×10^{-3}
	0.30	0.27	0.50	0.23	0.16	0.12	4×10^{-3}
p-fluoranil	0.08	0.42	0.47	0.11	0.02	0.07	2×10^{-6}
	0.17	0.38	0.50	0.12	0.05	0.11	3×10^{-5}
	0.46	0.29	0.58	0.13	0.12	0.05	5×10^{-4}
	0.48	0.29	0.57	0.14	0.10	0.07	6×10^{-4}

[a,b,c] See footnotes to *Table 1*
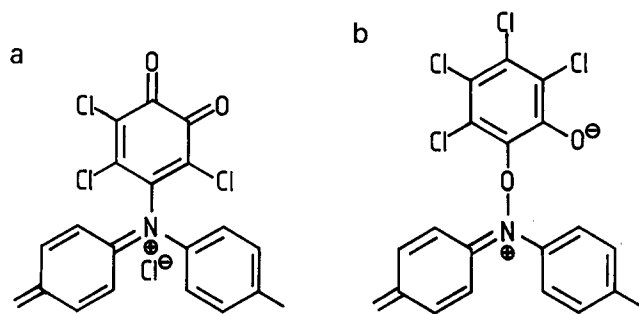
Figure 5 Possible structures associated with the charge transfer interactions between polyemeraldine and *o*-chloranil

complexes. Thus, the formation of halogen anions is facilitated in the *ortho*-halobenzoquinones, probably as a result of substantially less steric hindrance at the C$_4$ position. Based on the present experimental evidence, the c.t. interactions between polyemeraldine and halobenzoquinones would probably involve the chemical structures shown in *Figure 5*, using *o*-chloranil complex as an example. Similar mechanisms have been proposed for the c.t. interactions between *p*-chloranil and the nitrogen atom of molecular pyridine[25] to account for the presence of positively charged pyridinium nitrogen and the chloride and benzoquinone anion. Close examination of the structure in *Figure 5a* reveals that the c.t. interaction between polyemeraldine base and halobenzoquinone is analogous to protonation by HCl, with the hydrogen atoms in the latter replaced by the bulky halobenzoquinone rings. Furthermore, most of the halobenzoquinones in the complexes can be removed by treatment with a base, such as ammonium hydroxide, after which the polymer returns to its insulating state, as in the case of deprotonation of polyemeraldine hydrochloride.

Finally, based on the present X.p.s. results, the reactivity of the halobenzoquinones towards c.t. complex formation with polyemeraldine base is in the following order: *o*-chloranil > *o*-bromanil > *p*-fluoranil, *p*-chloranil.

CONCLUSIONS

It was shown that the proportion of amine, imine and positively charged nitrogen in polyaniline complexes could be quantitatively differentiated in the properly

deconvoluted N1s X.p.s. core-level spectrum. The structural changes associated with the interaction of polyemeraldine base with a protonic acid and with some proton-free organic electron acceptors were compared. The interaction between polyemeraldine base and the halobenzoquinone acceptors resulted in the formation of halogen and benzoquinone anions. X.p.s. results suggest that the mechanism of c.t. interactions and the associated structural changes appear to be analogous in both cases.

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