The Cation-radical Salts of *p*-Phenylenediamine. A Modified Method of Preparation and the Electrical Resistivity of the Salts

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A method of oxidation using Fe(III) salts was developed for preparing various types of cation radical salts of *p*-phenylenediamine (*p*PD) and its analogue in place of the familiar Br_2-oxidation method.[1,2] As an example, we will briefly describe below the method of preparing $p\mathrm{PD}^+\mathrm{Cl}^-\cdot H_2O$ and some physico-chemical properties of the salt.

In a cooled methanol solution of *p*PD, a methanol solution containing an equivalent amount of $FeCl_3\cdot 6H_2O$ was added in small portions, while the reacting system was flushed with nitrogen (or helium) during the mixing. The precipitate formed in the deep green solution was collected, washed repeatedly with a methanol-ether mixture, dried, and stored in an evacuated desiccator. The product thus obtained was a lustrous brownish green powder; it was stable in air, at least at room temperature. Iron was not detected in the product by a colorimetric test. The results of the elemental analysis were as follows:

Found: C, 44.42; H, 6.25; N, 17.14; Cl, 22.03%. Calcd for $C_6H_{10}N_2OCl$: C, 44.59; H, 6.24; N, 17.34; Cl, 21.82%.

Among the observed IR absorption bands of this salt in a KBr disk, the one at 1395 cm^{-1} was characteristic and was common to all the $p\mathrm{PD}^+$ salts prepared. The absorption band can probably be attributed to the C–N stretching in the *p*PD cation radical.

The aqueous solution of this salt ($\sim 10^{-3}$ M) was initially green, but it turned a dark violet within several minutes. The green solution exhibited an esr signal exactly identical to that reported for the cation radical of *p*PD,[3] although the signal soon disappeared as the color changed. The *p*PD cation radical was fairly stable in an ethanolic solution (yellow, $\sim 10^{-4}$ M) and gave rise to an esr signal significantly different in linewidth from that in an aqueous solution, suggesting that the ion-pair was formed between $p\mathrm{PD}^+$ and Cl^-. The UV and visible absorption spectra of this salt in the ethanolic solution almost coincided with those reported by Iida and Matsunaga.[4] Judging from this information, it seems almost certain that the salt of the *p*PD cation radical was formed.

Electrical resistivity measurements were made with a disk of the salt (prepared under 500 kg/cm^2) in an atmosphere of nitrogen. Accordingly, the specific resistivity was $3\times 10^8\ \Omega$ cm at 20°C, with a negative temperature coefficient of *ca.* 0.7 eV. Other salts, with different cations and counter anions, prepared by this method are listed in Table 1, together with their approximate electrical resistivity data.

TABLE 1. CATION-RADICAL SALTS AND THEIR PROPERTIES

Salts*1	Color of powder	Electrical resistivity at 20°C (Ω cm)
$p\mathrm{PD}^+\mathrm{Br}^-\cdot H_2O$*2	lustrous brown	10^9
$p\mathrm{PD}^+\mathrm{NO_3}^-\cdot H_2O$	black	10^6
$p\mathrm{PD}^+p\text{-}\mathrm{CH_3}\text{-}\phi\text{-}\mathrm{SO_3}^-\cdot \frac{1}{2}H_2O$	violet	10^{13}
$\mathrm{Benzidine}^+\mathrm{Cl}^-\cdot \frac{1}{4}H_2O$	grey	10^{10}
$\mathrm{Benzidine}^+\mathrm{Br}^-\cdot \frac{1}{4}H_2O$	deep blue	10^6
$(p\mathrm{PD}^+)_2[\mathrm{Fe_2(SO_4)_3}]^{2-}$	greenish grey	10^{10}
$p\mathrm{PD}^+[\mathrm{K_3Fe(CN)_6}]^-\cdot nH_2O$*3	deep blue	10^7
$p\mathrm{PD}^+p\text{-}\mathrm{Chloranil}^-$	deep purple	10^7

*1 The chemical compositions were estimated from elemental analyses of C, H and N.
*2 The X-ray analysis of the salt is now in progress.
*3 $n=1$—3.

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