April, 1987] © *1987 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *60*, *1519—1520 (1987)* 1519

Electrocrystallization of Phenothiazine

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(Received October 1, 1986)

Synopsis. New cation radical salts of phenothiazine with (1:1), (3:2), and (2:1) compositions were prepared by the method of electrochemical oxidation. The electrical resistivities measured on the compaction of crystalline powder were 10^3—10^5 Ω cm at room temperature in the case of the complex salts. The powder absorption spectra in IR and Visible regions were also studied.

Phenothiazine (PTZ) is an electron donor with relatively low oxidation potentials, 0.58 volt vs. SCE, in acetonitrile solution.[1] The electron donor-acceptor compounds and the cation radical salts of PTZ have been studied by several groups,[2–9] but little is known about the behaviors of the complex salts: Only the bromine and iodine complexes prepared by the solid state reaction[10–13] are the complex salts of PTZ which have been studied so far. In addition to the property as an electron donor, PTZ is expected to behave as a proton donor as well as proton acceptor. This could provide a possibility to prepare a new type electronic conductor in which the coupling between the conduction electrons and proton plays an important role. From this point of view, we synthesized several complex salts of PTZ by means of the electrochemical method.

Experimental

The PTZ were recrystallized twice from its benzene solution. As the solvent of elctrochemical reaction, we used 1,2-dichloroethane which were purified by distillation with CaH_2 in nitrogen atmosphere. The materials for the counter anions, $(n\text{-Bu})_4NX$, ($X=BF_4$, ClO_4, ReO_4, $FeCl_4$, PF_6, AsF_6) were recrystallized for 2 or 3 times from methanol or ethanol. The electrochemical preparation of PTZ salts were carried out by using a U-shape electrochemical cell, in which the anode and the cathod compartments are separated by glass filters. Platinum plates were used as the electrodes. The concentrations of PTZ and supporting electrolyte were 2×10^{-2} mol dm^{-3} and 3×10^{-2} mol dm^{-3}, respectively. The electrochemical preparation were conducted in the galvanostatic mode with a current of 100 μA for 2 d. Since the solubility of PTZ salt is very high, the electrochemical cell were cooled down to −35 °C. The salt crystals deposited on the anode were washed by cooled 1,2-dichloroethane. The results of the chemical analysis are as follows; $(PTZ)FeCl_4$, Found/Calcd: C, 36.50/36.31; H, 2.75/2.29; N, 3.65/3.53; S, 7.80/8.08; Cl, 32.78/35.73.[14] $(PTZ)_2BF_4$, Found/Calcd: C, 57.87/59.39; H, 3.79/3.74; N, 5.62/5.77; S, 12.92/13.21. $(PTZ)_2ClO_4$, Found/Calcd: C, 57.76/57.88; H, 3.65/3.64; N, 5.70/5.63; S, 13.21/12.88; Cl, 7.39/7.12. $(PTZ)_2PF_6$,[15] C, 52.07/53.04; H, 3.30/3.34; N, 5.08/5.15. $(PTZ)_2AsF_6$, C, 48.91/49.07; H, 3.06/3.09; N, 4.79/4.77; S, 11.37/10.91. $(PTZ)_3(ReO_4)_2$, C, 39.42/39.37; H, 2.70/2.48; N, 3.76/3.83; S, 8.56/8.76.

The powder absorption spectra of PTZ salts were measured with HITACHI 260-30 for the infrared region and HITACHI 340 for the Near IR and visible region by use of the KBr disk method.

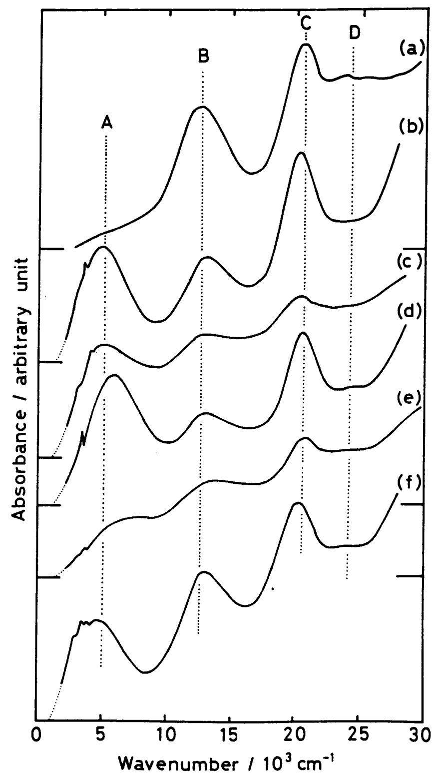

Fig. 1. Absorption spectra of phenothiazine (PTZ) radical salts. (a) $(PTZ)FeCl_4$, (b) $(PTZ)_2BF_4$, (c) $(PTZ)_2ClO_4$, (d) $(PTZ)_2PF_6$, (e) $(PTZ)_2AsF_6$. (f) $(PTZ)_3(ReO_4)_2$.

Results and Discussion

All PTZ complexes were obtained as black crystalline powders. Hexagonal prism were sometimes obtained in the case of $(PTZ)_2ClO_4$ when acetonitrile was used as a solvent, but they were found to be not a single crystal but polycrystalline by X-ray diffraction. PTZ is known to have many oxidation stages in solution including the transfer of hydrogen atom.[16] In this electrochemical cell, the solution always had an orange color at low temperature, which is the typical color of a PTZ radical cation. However, the color of the solution rapidly changed to deep green on mixing of the solutions in the anode and the cathod compartments. The UV-Visible absorption spectrum of the 1,2-dichloroethane solution of each PTZ salt exhibited the spectrum characteristic of PTZ cation radical, which has a weak absorption band around 13.5×10^3 cm^{-1} accompanied by several vibrational structures, a strong band at 19.3×10^3 cm^{-1} with vibrational progressions and a band at 22.5×10^3 cm^{-1}.[7] The absorption bands, B, C, and D of the solid PTZ complexes shown in Fig. 1 correspond to each of these characteristic absorption bands of PTZ cation radical, providing an evidence for the formation of the PTZ cation radical salt.

The absorption spectrum of solid $(PTZ)FeCl_4$ is quite similar to the polarized absorption spectrum of the single crystal of the PTZ simple salt, $(PTZ)SbCl_6$,[8] in which the PTZ cation is isolated without charge-transfer interaction. Therefore, solid $(PTZ)FeCl_4$ is likely to be composed of an isolated PTZ cation radical. The spectra of $(PTZ)_2BF_4$, $(PTZ)_2ClO_4$, $(PTZ)_2PF_6$, and $(PTZ)_2AsF_6$ are quite similar to each other. They exhibit an absorption band, A, around 5×10^3 cm^{-1}, in addition to bands associated with the intramolecular transitions of PTZ cation radical, B, C, and D. These salts involve formally PTZ^+ and PTZ^0 according to their chemical composition. We can assign the new absorption band, A, to the charge-transfer(CT) transition from PTZ^0 to PTZ^+, since this type of CT band usually appears in the near infrared or infrared region in the case of the organic charge-transfer salts with a mixed valence molecular column. The CT transition of the same type were observed at about 4×10^3 cm^{-1} in TCNQ complex salt[17] and around 2×10^3 cm^{-1} in (2 : 1) TMTTF salt.[18] Very similar spectra were observed by Doi and Matsunaga in $(PTZ)_2Br$, which were synthesized by the solid state reaction between (PTZ)Br and PTZ.[10] The absorption band corresponding to A was also observed in (PTZ)Br by Iida who attributed it $(PTZ^0)(PTZ^+)(Br_3^-)$ contained by a small amount in the sample of (PTZ)Br.[7] Matsunaga and Shono found that the intensity of the above-mentioned band significantly increased by the addition of iodine to (PTZ)-Br,[11] and suggested the formation of a complex cation salt, $(PTZ^0)(PTZ^+)(IBr_2^-)$. All these PTZ complex salts hitherto investigated were prepared by means of the solid state reaction, and are not stoichiometric compounds. In contrast, the PTZ complex salts obtained in the present study were prepared by the electrochemical oxidation and have a definite composition. To the best of our knowledge, these are the first stoichiometric complex salts of PTZ ever made. Among the complex salts prepared here, $(PTZ)_3(ReO_4)_2$ has a stoichiometry different from other salts, but the absorption spectrum of this material was almost the same as the (2 : 1) complex salts except that the CT band is slightly shifted to the low-wavenumber side.

Table 1. Electrical Resistivity and the Position of the CT Band of PTZ Cation Radical Salts

Salts	ρ/Ωcm	$\nu_{max}/10^3$ cm^{-1}
$(PTZ)FeCl_4$	2×10^7	—
$(PTZ)_2BF_4$	4×10^4	4.8
$(PTZ)_2ClO_4$	1×10^5	5.0
$(PTZ)_2PF_6$	7×10^5	5.9
$(PTZ)_2AsF_6$	2×10^5	7.6
$(PTZ)_3(ReO_4)_2$	4×10^3	4.5

Finally we listed in Table 1 the electrical resistivities measured on the compaction of powder sample. Unfortunately, none of them exhibits a metallic low resistivity, although the resistivities of the complex salts are found to be smaller by a factor of 10^2—10^3 than that of the simple salt, $(PTZ)FeCl_4$.

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