BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(12), 3747—3748 (1975)

Complex Cation-radical Salts Derived from Phenothiazine and Related Compounds

Susumu Doi* and Yoshio Matsunaga**
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received May 29, 1975)

Synopsis A new class of complex cation-radical salts is formed by the reaction of phenothiazine bromide with phenoxazine, phenothiazine, its benzo derivatives, and phenoselenazine.

Phenothiazine has been known to form a number of cation-radical salts.[1,2] However, the incorporation of formally neutral molecules has been established in no case. We have now discovered the formation of complex phenothiazine and phenoselenazine cation-radical bromides and also of some mixed complex bromides.

Simple phenothiazine cation-radical bromide was prepared by the oxidation of the parent organic compound dissolved in ether with bromine, as has been described by Kehrmann and Diserens.[2] The bromine content was a little higher than that corresponding to the 1 : 1 salt. Found: C, 48.82; H, 3.07; N, 4.71; Br, 31.54%. Calcd for $C_{12}H_9NS \cdot Br_{1.18}$: C, 49.10; H, 3.09; N, 4.77; Br, 32.12%. We earlier noted that the vibrational spectra exhibited by the bromide samples thus prepared are often superpositions of the spectra of the A and B types in various ratios.[3] The present sample showed the spectrum of the B type. When the salt was ground with an equimolar amount of phenothiazine wetted with benzene, drastic changes in both the vibrational and electronic spectra were observed. In Fig. 1, the electronic spectrum of the product is compared with that of the starting bromide. The former salt retains the spectral pattern of the latter. In addition, a broad band appears at 5.2×10^3 cm^{-1}. The resulting electronic spectrum and also the vibrational spectrum coincide with those of the A type in the previous work. It must be realized that the spectrum of the A type is not of the polymorphic form of the simple cation-radical salt suggested earlier, but of the complex salt, $(C_{12}H_{19}NS)^+(C_{12}H_9NS)^0 \cdot X^-$, in which the positive charge may be equally shared by the two molecules of phenothiazine. The low-energy absorption band newly appearing in the complex salt may be a manifestation of such a delocalization of the positive charge.

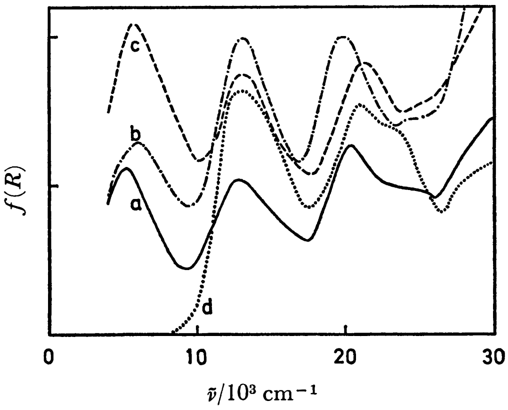

Fig. 1. Diffuse reflection spectra of the combinations of the phenothiazine bromide and a) phenothiazine, b) phenoxazine, and c) phenoselenazine, and d) the phenothiazine bromide alone.

The frequent superposition of the vibrational spectra of the A and B types in the bromide samples with an apparent composition of 1 : 1 implies that the simple cation-radical bromide, the complex cation-radical bromide, and polybromide (possibly tribromide) are all formed under similar conditions. Such complexity was further demonstrated by the transformation of the spectrum of the B type to that of the A type by storage. When the samples prepared over six years before were reexamined, only the spectrum of the A type could be detected. The following analytical results indicate a loss of bromine during the storage; nevertheless, the contents are still appreciably higher than that of the complex (2 : 1) bromide. Found: C, 53.16, 53.06; H, 3.25, 3.32; N, 4.98, 5.15; Br, 25.58, 25.54% for two independent samples. Calcd for $C_{12}H_9NS \cdot Br_{0.88}$: C, 53.46; H, 3.36; N, 5.20; Br, 26.08%. The rearrangement of the simple cation-radical bromide to a mixture of the complex cation-radical bromide and tribromide may account for the constitution of the product.

Additional evidence for the formation of the complex cation-radical salt was provided by the examination of the electrical resistivity and the Seebeck coefficient. Mixtures of the bromide and phenothiazine in five different mole ratios were heated to 80 °C in a short time to complete the reaction and also to remove all traces of the solvent. The vibrational spectra of the mixtures after the treatment were essentially the same as those made at room temperature except at a ratio of 4 : 1. Thus, the complex cation-radical bromide appeared to be more stable than the simple bromide.

The measurements were carried out on pressed pellets in the range from -90 to $+50$ °C by procedures described elsewhere.[4] The plot of the logarithm of resistivity against the reciprocal temperature gives a straight line. The resistivity values at 20 °C and the activation energies for semiconduction calculated on the basis of $\rho = \rho_0 \exp(\Delta E/kT)$ are presented in Table 1. The sharp maximum of the resistivity located at the 1 : 1 mole ratio supports the complex (2 : 1) salt formation. The Seebeck coefficient at 20 °C

---

* Present address: Central Research Laboratory, Showa Denko K. K., Tamagawa, Tokyo.

** To whom inquiries may be addressed.

is negative for all the samples, but the temperature-dependence is sensitive to the composition. As is shown in Fig. 2, the value is nearly constant at the 4 : 1 mole ratio. On the further addition of phenothiazine, the slope against the reciprocal temperature becomes negative and is exceptionally steep at the composition of the complex salt. In the presence of an excess of phenothiazine, the slope changes its sign.

TABLE 1. ELECTRICAL PROPERTIES OF THE MIXTURES OF THE PHENOTHIAZINE BROMIDE AND PHENOTHIAZINE

Mole ratio	Resistivity at 20°C (ohm cm)	Activation energy (eV)	Seebeck coeff. at 20°C (μV°C^{-1})
4 : 1	1600	0.27	−24
3 : 2	90	0.19	− 5
1 : 1	770	0.23	− 6
2 : 3	100	0.23	− 9
1 : 4	370	0.17	−15

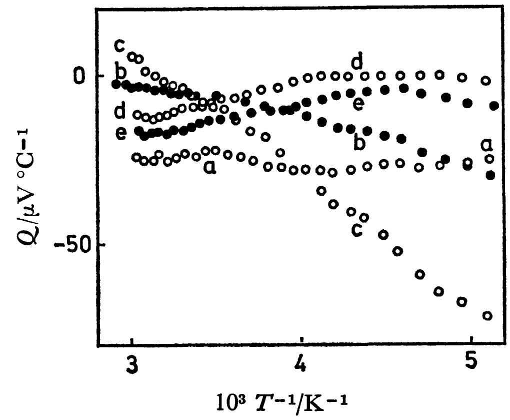

Fig. 2. Seebeck coefficients (Q) of the mixtures of the phenothiazine bromide and phenothiazine, a) 4 : 1, b) 3 : 2, c) 1 : 1, d) 2 : 3, and e) 1 : 4 (mole ratio).

On the basis of the close similarity between the vibrational spectrum of the A type and that of the phenothiazine-iodine complex, we were previously led to conclude that every phenothiazine molecule in the iodine complex bears an approximate unit-positive charge.[3] This conclusion must be revised in the light of the new findings presented above. It is now apparent that the iodine complex is a kind of complex cation-radical salt. The complex phenoselenazine cation-radical bromide was also prepared. The vibrational spectrum of this salt resembles that of the corresponding iodine complex reported previously.[5] The maximum of the low-energy electronic band appears at 6.4×10^3 cm^{-1}.

Figure 1 shows also the electronic spectra produced by the reaction of the phenothiazine bromide with phenoxazine and phenoselenazine in a mole ratio of 1 : 1. The maxima of the low-energy bands in these products are at 6.0 and 5.7×10^3 cm^{-1} respectively. The disagreement between the latter spectrum and the superposition of those of the two complex cation-radical salts suggests the formation of a complex salt containing both the thiazine and the selenazine. Similar spectral changes were observed in the combinations of the phenothiazine bromide and benzo[*a*]- and benzo[*c*]-phenothiazines. As the absorption bands in the phenothiazine bromide are overlapped by those of the benzophenothiazine bromides, the spectra of the products are dominated by the latter. The low-energy bands are located at about 4.5×10^3 cm^{-1}.

Although *p*-phenylenediamine and benzidine may be expected to have ionization potentials a little higher than the thiazines,[6] the reaction with the phenothiazine bromide resulted in the electron-transfer from the diamine to the thiazine. The dark blue products showed the spectra of the diamine cation-radical bromides.[7]

References

1) R. Pummerer and S. Gassner, *Ber.*, **46**, 2310 (1913).
2) F. Kehrmann and L. Diserens, *ibid.*, **48**, 318 (1915).
3) Y. Matsunaga and K. Shono, This Bulletin, **43**, 2007 (1970).
4) K. Kan and Y. Matsunaga, *ibid.*, **45**, 2096 (1972).
5) Y. Matsunaga and Y. Suzuki, *ibid.*, **45**, 3375 (1972).
6) G. Saito and Y. Matsunaga, *ibid.*, **44**, 1788 (1971).
7) Y. Iida and Y. Matsunaga, *ibid.*, **41**, 2615 (1968).