BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2007—2011 (1970)

Effects of Iodine Addition on the Electrical and Optical Properties of the Semiquinoid Phenothiazine Bromide

Yoshio MATSUNAGA and Kosuke SHONO

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received January 29, 1970)

The electrical resistivity and the electronic and vibrational spectra of the semiquinoid phenothiazine bromide have been found to be drastically modified by the addition of iodine. The resistivity minimum lies around the mole ratios of 0.25 to 0.30, while the value in this composition range is from 4 to 5 ohm cm. The combined spectroscopic data indicate three different stages in the intermolecular interactions in this system; the first around a mole ratio of 0.25, the second near 0.5, and the third above 1.00. The higher the iodine content, the less conductive the adducts appear to be. Iodine addition was attempted also to the *p*-phenylenediamine bromide; however, no pronounced effect on the physical properties could be found in this system.

Earlier one of the present authors reported that the vibrational spectrum of the phenothiazine-iodine complex, which exhibits a resistivity of 20 ohm cm at room temperature, is quite different from that of the parent organic compounds, but identical with that of semiquinoid phenothiazine bromide.[1] On the basis of these observations, it was concluded that every phenothiazine molecule in the solid iodine complex bears an approximately unit-positive charge. The hypothesis that the highly-conducting iodine complexes of phenothiazine and its derivatives have essentially dative ground states seemed to receive strong support from the additional observations that the iodine adducts of semiquinoid phenothiazine chloride and bromide have resistivities of the order of 10 ohm cm. Thus far, though, no attempt has been made to determine the exact composition of such mixed halogen complexes. Now we wish to report the results of our measurements of the electrical and optical properties of the semiquinoid phenothiazine bromide-iodine system.

Experimental

Materials. Semiquinoid phenothiazine bromide was prepared by the oxidation of the parent organic compound with bromine, as has been described by Kehrmann and Diserens.[2] For example, 0.4 g of bromine, dissolved in 30 m*l* of ethyl ether, was slowly added to 1.0 g of the thiazine in 30 m*l* of the same solvent cooled with an ice-salt mixture. The greenish-black precipitate was filtered and washed with the solvent. As the bromide is not stable above 50°C, the sample was dried at room temperature over silica gel and under a vacuum.

The addition of iodine to the bromide was carried out by the careful grinding of the weighed components in the presence of a small amount of benzene. The solvent was evaporated at room temperature; then the mixture was heated to 80°C for a short time to complete the reaction and also to remove all traces of the solvent. Samples with the following mole ratios were prepared: 0.10, 0.20, 0.25, 0.30, 0.40, 0.50, 0.75. 1.00, 1.25, and 1.50.

The phenothiazine-iodine complex was precipitated by mixing 1.5 g of the thiazine in 25 m*l* of hot benzene with 3 g of iodine in 75 m*l* of the same solvent. The mole ratio of the complex is known to be 2 : 3.[1]

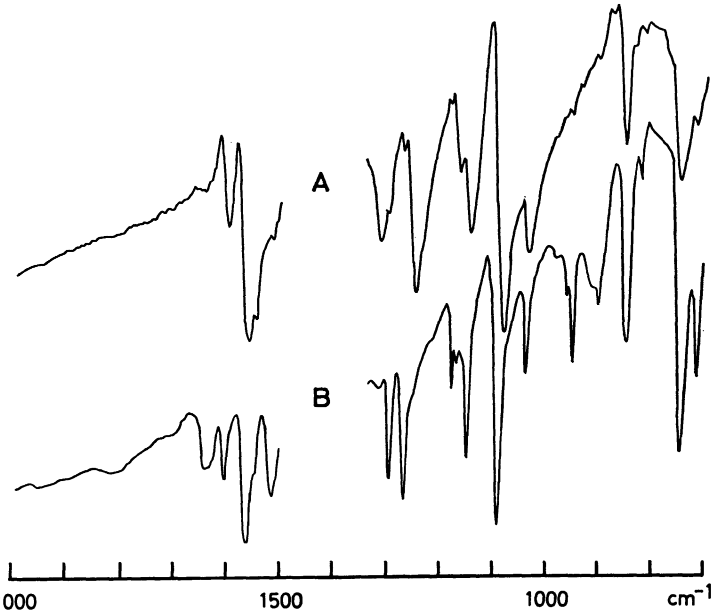
The *p*-phenylenediamine bromide was prepared by the oxidation of the diamine with bromine.[3] The addition of iodine to the bromide was made by the same method as has been described above.

Measurements. The electrical resistivities of the phenothiazine bromide-iodine system and the phenothiazine-iodine complex were examined on pressed pellets by a potential-probe method. The temperature de-

---

[1] Y. Matsunaga, *Helv. Phys. Acta*, **36**, 800 (1963).

[2] F. Kehrmann and L. Diserens, *Ber.*, **48**, 318 (1915).



Wave number

Fig. 1. Two extremes in the vibrational spectrum of semiquinoid phenothiazine bromide. The spectrum is often a superposition of these two.

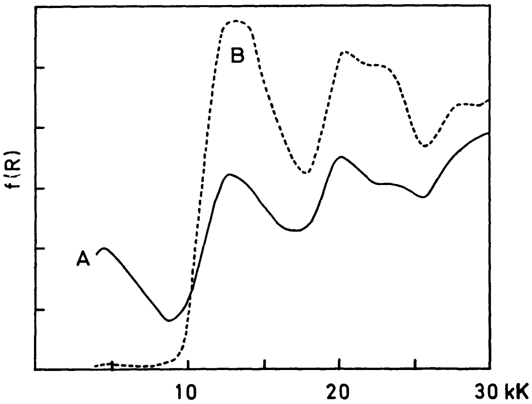
pendence was measured in the range from 20 to 70°C unless otherwise stated. The resistivities observed in the *p*-phenylenediamine bromide-iodine system are in the order of 10^6 ohm cm or higher; therefore, only the values at room temperature were examined by a two-probe method employing a cell similar to that reported by LaFlamme[4] and a TOA Electronics DC microvolt ammeter, Model PM-18C.

The diffuse reflection spectra were measured with a Beckman DK-2A spectroreflectometer in the range from 4 to 30 kK. The pulverized sample was diluted with potassium bromide in concentrations of the order of 0.1 weight percent. The spectra were recorded as the difference in reflectance between the mixture and pure potassium bromide and were plotted using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance.

The vibrational spectra in the rock salt region were measured as Nujol mineral oil mulls by means of a Jasco IR-G infrared spectrophotometer. Because of the presence of an electronic absorption in this region, the reference light had to be highly attenuated in many cases in order to obtain a reasonable transmittance.

Results

Phenothiazine Bromide. We found that the vibrational spectra exhibited by the samples are often superpositions of two patterns in various ratios. The two extremes are presented in Fig. 1 as the spectra A and B. The transformation of the spectrum B to A by storage was observed on one occasion only. Although there is essentially no difference in the electronic spectrum in the region from 10 to 30 kK between the samples showing the vibrational spectra A and B, a considerable change may be noted in the region below 10 kK. As is shown in Fig. 2, the sample showing the vibrational spectrum A exhibits an electronic absorption extending into the rock salt region, but the one showing the vibrational spectrum B does not.



Wave number

Fig. 2. Two extremes in the electronic spectrum of semiquinoid phenothiazine bromide.

The bromide samples had resistivities in the order of 10^4—10^5 ohm cm, *e.g.*, a resistivity of 1.5×10^5 ohm cm at 20°C, and an activation energy of 0.30 eV defined by $\rho=\rho_0\exp(E/kT)$ in the temperature range from 4 to 35°C was obtained by one of the

---

3) L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, **65**, 1747 (1943).

4) P. M. LaFlamme, *Rev. Sci. Instr.*, **35**, 1193 (1964).

preparations. Above 50°C, a rapid irreversible decrease in the resistivity was observed. The vibrational spectrum of such a heat-treated sample was found to be different from either the spectrum A or B.

Phenothiazine Bromide-iodine System. The electrical resistivity value at 20°C is plotted against the mole ratio (iodine/bromide) in Fig. 3. A deep minimum is located around mole ratios from 0.25 to 0.30, the value in this composition range being from 4 to 5 ohm cm. When the mole ratio is below these values, the vibrational spectrum of the iodine adduct consists of very broad lines as is represented by the spectrum a in Fig. 4, measured at a mole ratio of 0.25. Nevertheless, it may be noted that the whole pattern is rather close to the spectrum A of the bromide. The electronic spectrum bears also some resemblance to that of the bromide, especially the one showing the vibrational spectrum A. However, the low-energy absorption is shifted further into the rock salt region and its maximum is located below 4 kK. In addition, an extra absorption appears at about 9 kK as a shoulder. The absorption in the region above 20 kK becomes high and almost flat, as is shown in Fig. 5. The activation energies for semiconduction in the four samples in this composition range were found to be 0.10±0.01 eV.

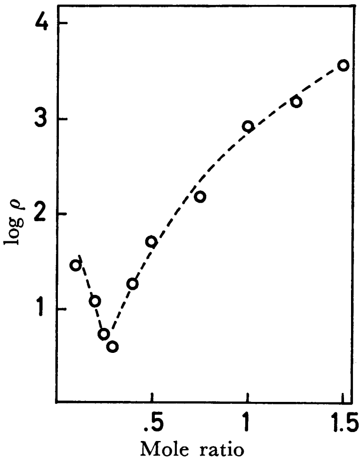


Fig. 3. Electrical resistivity plotted against the mole ratio (iodine/bromide) in the phenothiazine bromide-iodine system.

As the iodine content rises above 0.30, the resistivity increases monotonously. At a mole ratio of 0.40, a new electronic absorption is observed at 5.5 kK in addition to the one found in the low-energy region of the spectrum a in Fig. 5. By the further addition of iodine, the absorption having a maximum in the region below 4 kK is completely replaced by the one at 5.5 kK. The spectrum b in Fig. 5, recorded at a mole ratio of 0.50, represents such a stage. At this composition the resistivity at room temperature is about 50 ohm cm and the activation energy is 0.20 eV. It must be pointed out that the absorption lines in the vibrational spectrum b in Fig. 4 are a little bit sharper

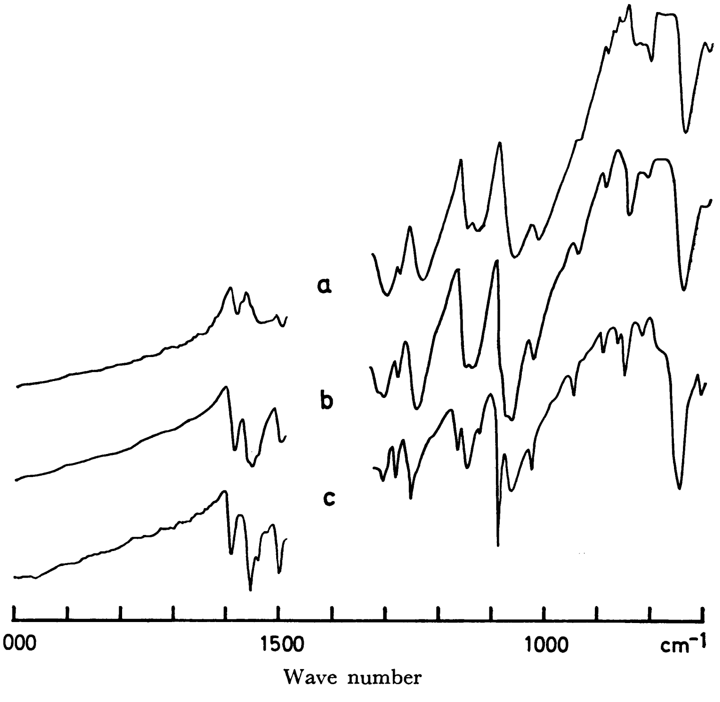


Fig. 4. Vibrational spectra in the phenothiazine bromide-iodine system; a) mole ratio 0.25, b) 0.50, c) 1.00.

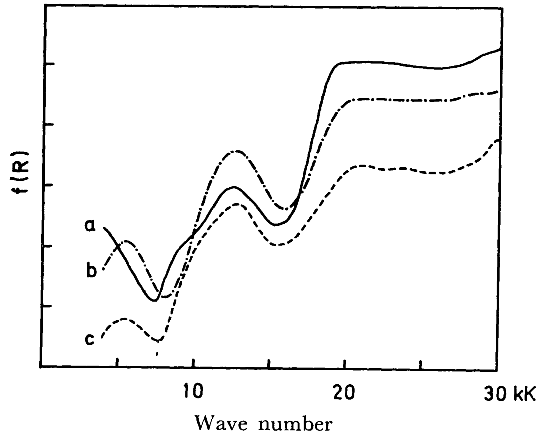


Fig. 5. Electronic spectra in the phenothiazine bromide-iodine system;
a) mole ratio 0.25, b) 0.50, c) 1.00.

than those in the spectrum a.

Then, at a mole ratio of 1.00 the intensity of the electronic absorption at 5.5 kK is markedly diminished. Moreover, the vibrational spectrum is characterized by a superposition of a pattern consisting of lines as sharp as those in the spectrum B of the bromide. The resistivity is about 8.4×10^2 ohm cm at this composition. If more iodine is added, the electronic absorption in the low-energy region disappears completely and the intensities of the sharp vibrational absorption lines belonging to the newly-appeared pattern are much enhanced. At the maximum iodine content of 1.50 the electrical resistivity is almost one thousand times as high as the minimum value.

The iodine adducts exhibiting low electrical resistivities are more stable than the semiquinoid bromide. Neither a change in the vibrational spectrum nor the vaporization of the iodine is observed by heating to 80°C. However, the coloration of polyethylene stoppers by iodine after a short storage of the samples in vials can be noticed even at room temperature if the mole ratios are higher than 0.75.

Phenothiazine-iodine Complex. An electrical resistivity of 13 ohm cm and an activation energy of 0.19 eV were obtained in the present work. These values are in good agreement with those found earlier by one of the present authors,[1] however, our resistivity is approximately two orders of magnitude lower than that reported by Gutmann and Keyzer.[5] In Fig. 6 the vibrational spectrum is compared with the spectrum of the parent organic compound. They are much better resolved than those cited in an earlier paper and are still in accordance with our previous argument.

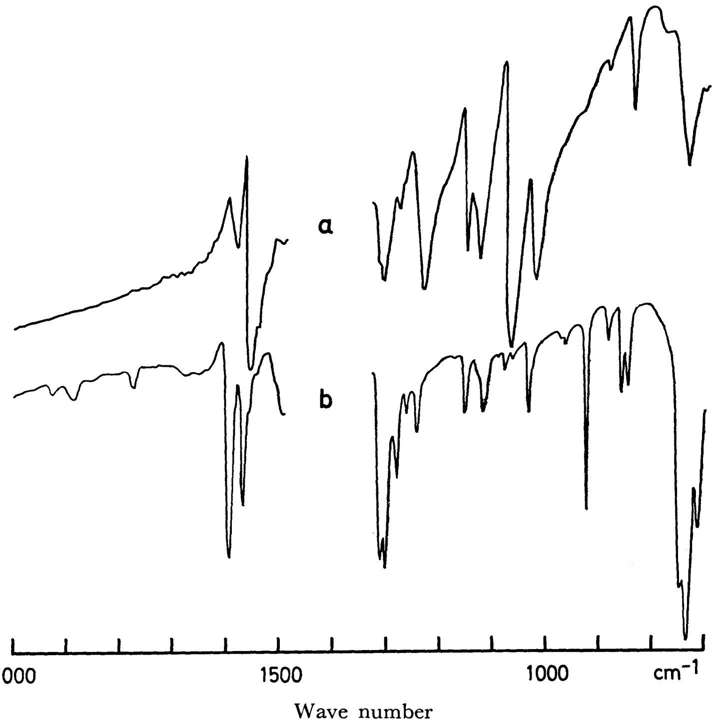


Fig. 6. Vibrational spectra of the phenothiazine-iodine complex (a) and phenothiazine itself (b).

---

[5] F. Gutmann and H. Keyzer, *J. Chem. Phys.*, **46**, 1969 (1967).

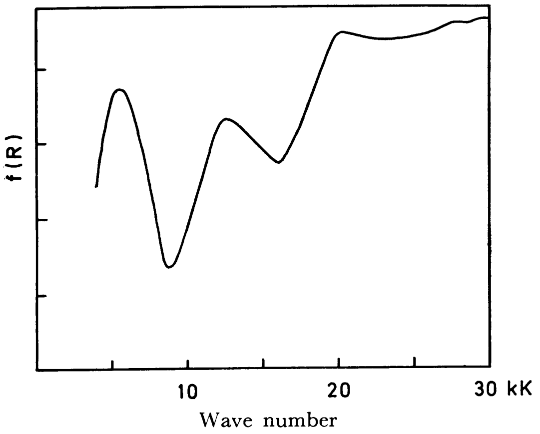


Fig. 7. Electronic spectrum of the phenothiazine-iodine complex.

It is easy to see that the spectrum of the iodine complex is quite similar to the spectrum A of the bromide, but very different from the spectrum of phenothiazine itself. The electronic spectrum was also examined. As is shown in Fig. 7, the maximum of low-energy absorption is located at 5.5 kK.

***p*-Phenylenediamine Bromide-iodine System.** The bromide has a resistivity of 5×10^7 ohm cm at room temperature. The compound becomes ten times more conductive by the addition of 0.25 to 0.75 mol of iodine. The further addition results in an increase in the resistivity again to the order of 10^7 ohm cm. Thus, this system was found to be less conductive than the iodine complex, for which Nishizaki and Kusakawa reported the minimum resistivity of 1.7×10^5 ohm cm at a mole ratio of 0.82.6) No significant change could be observed in the electronic and vibrational spectra.

Discussion

The molecule of phenothiazine is known to have a folded configuration.7) The large difference in the vibrational spectrum between phenothiazine and its semiquinoid bromide should be attributed to the change in the electronic and geometrical structures caused by the loss of one electron. Although the cation radical has often been assumed to be planar,8) Pullman favored a bent form to the planar one because of its better agreement with the ESR data.9) The barrier to the flattening the molecule is probably of about the same energy as that of a rather strong intermolecular interaction;10) it is likely that the balance of these two forces is achieved at two different configurations, depending upon the mode of intermolecular interaction. By analogy with the electronic spectra of Würster cations,11,12) we may assume that the cation radicals in the bromide sample showing the electronic spectrum A in Fig. 2 are in an interaction more extended than those in the sample showing the spectrum B.

In the phenothiazine bromide-iodine system the three different stages in the intermolecular interactions can be pointed out on the basis of the electrical and optical data. The first stage is represented by the adduct at mole ratios from 0.25 to 0.30. As the composition corresponds approximately to (phenothiazine)$_2$Br$_2$I, and as the mixed halide ion, Br_2I^-, is a known species, we may suggest the formation of a complex cation radical salt, (phenothiazine)$^+$(phenothiazine)^{0}Br$_2$I$^-$, which is a cationic analogue of the TCNQ complex anion radical salts, well known for their low electrical resistivities.13) The composition range from 0.50 to 0.75 may be considered to be the second stage, which is characterized by an electronic absorption having a maximum at 5.5 kK. This location is the same as that of the low-energy absorption appearing in the iodine complex; however, these adducts are less conductive than the complex. The shift of the low-energy absorption by the transition from the first to the second stage is parallel with an increase in the activation energy for semiconduction. It should be noted that the vibrational spectra of the iodine adducts in these two stages and also that of the iodine complex resemble the spectrum A of the semiquinoid bromide. In these adducts and the complex the intermolecular interaction is supposed to be more-than-by-pairs; otherwise, we would not observe such low electrical resistivities. These observations are in good accordance with the assumption made at the end of the last paragraph. The third stage appears in the composition range above 1.00. Not only the vibrational but also the electronic spectra are similar to the spectra B of the bromide. The high resistivities observed in this stage are consistent with such optical behavior.

The absence of a low-resistivity phase in the *p*-phenylenediamine bromide-iodine system indicates that the formation of a mixed halide complex such as the one found in the present work may be rather specific.

---

6) S. Nishizaki and H. Kusakawa, This Bulletin, **36**, 1681 (1963).

7) J. D. Bell, J. F. Blount, O. V. Briscoe and H. C. Freeman, *Chem. Commun.*, **1968**, 1656.

8) J. M. Lhoste and F. Tonnard, *J. Chim. Phys.*, **63**, 678 (1966).

9) J. P. Malrieu and B. Pullman, *Theoret. Chim. Acta*, **2**, 293 (1964).

10) C. J. Fritchie, Jr., *J. Chem. Soc.*, *A*, **1969**, 1328.

11) Y. Iida and Y. Matsunaga, This Bulletin, **41**, 2615 (1968).

12) A. Hakusui, Y. Matsunaga and K. Umehara, *ibid.*, **43**, 709 (1970).

13) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).