Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. XI.[1] Phase Transitions in Hertel's Picric Acid Complexes

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(Received May 9, 1974)

The isomerization from true phenolates to charge-transfer complexes by phase transitions in Hertel's five amine–picric acid complexes was confirmed by spectroscopic examinations. The amines and the estimated heats of transition were as follows: *o*-bromoaniline, 6.7; *o*-iodoaniline, 6.2; 1-chloro-2-naphthylamine, 8.0; 1-bromo-2-naphthylamine, 8.2; 1,6-dibromo-2-naphthylamine, 3.3 kcal/mol. The transition temperatures and/or the heats in the naphthylamine complexes were shown to be markedly reduced by crushing the crystals. The charge-transfer complexes have electrical resistivities lower by a factor of many decades than the isomeric phenolates. Phase transitions without isomerization were found in the metastable 1-halo-2-naphthylamine complexes of the charge-transfer type.

In connection with our work on new complex isomers,[1-3] a physicochemical study of the isomeric pairs of Hertel's five picric acid complexes has been undertaken. Phase transitions accompanied by a color change from yellow to red in the solid phase were found by Hertel in the complexes with *o*-bromo- and *o*-iodoanilines and 1-chloro-, 1-bromo-, and 1,6-dibromo-2-naphthylamines.[4] Some years ago, Briegleb and Delle carried out spectroscopic studies of the isomeric pairs in the complexes of the last two amines.[5,6] Their conclusions that the yellow low-temperature forms are true phenolates and that the red high-temperature forms are charge-transfer (CT) complexes are in accordance with ours for some new complex isomers. However, the vibrational spectra of the low-temperature forms presented by Briegleb and Delle show patterns due to the NH_2 groups which one would not expect in true phenolates. Consequently, spectroscopic examinations of all the above-mentioned pairs were performed in the present work. Then, changes in the enthalpy and in the electrical resistivity by the transitions were studied in order to find additional manifestations of the complex isomerization. Anomalous changes in the electrical resistivity have been found at the transition temperatures of a number of organic materials—*e.g.*, hexamethylbenzene,[7,8] phenanthrene,[9,10] phenanthrene–picric acid,[11] and some tetracyanoquinodimethane anion-radical salts.[12-14] As it has been recognized that a lowering of resistivity is generally associated with complex formation,[15] the change at the transition accompanied by the isomerization from a true phenolate to a CT complex might be quite drastic.

Experimental

Materials. The picric acid and the *o*-haloanilines were commercially obtained. The derivatives of 2-naphthylamine were prepared as has been described in a previous paper of ours.[3] The complexes were precipitated by mixing component compounds which had been separately dissolved in chloroform or methanol. The 1,6-dibromo-2-naphthylamine complex was obtained as yellow fine crystals, but it slowly turned reddish brown upon filtration, as has been reported by Hertel.[4] The complex was redissolved in methanol, and then the solution was slowly evaporated to dryness by letting it stand at room temperature. In this way, the yellow form could be isolated.

Measurements. The spectroscopic, calorimetric, and X-ray measurements were made as has been reported in previous papers of the present series.[2,3] The procedure used for recording the electrical resistivity curve has been described in a paper by Koizumi and Matsunaga.[11]

Results and Discussion

Vibrational Spectra. As an example, Fig. 1 presents the spectra of two forms of the *o*-bromoaniline complex. The red form was obtained by the solidification of the fused sample between rocksalt plates. The presence of the NH_3^+ group in the yellow form is clearly indicated by broad bands appearing at 2575 and 2825 cm^{-1}. Upon transition, they are replaced by rather sharp bands located at 3375 and 3475 cm^{-1}. The latter pattern arises from the stretching vibration of the NH_2 group.

The spectra of the 1-bromo-2-naphthylamine complex are shown in Fig. 2. Unlike the spectrum of the yellow form reported by Briegleb and Delle, our spectrum

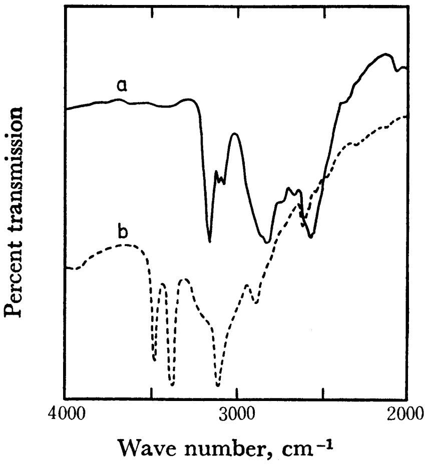

Fig. 1. Vibrational spectra of a) the yellow form and b) the red form of the *o*-bromoaniline–picric acid complex.

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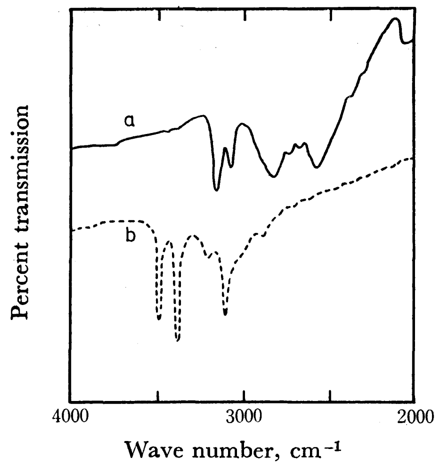

Fig. 2. Vibrational spectra of a) the yellow form and b) the reddish brown form of the 1-bromo-2-naphthylamine–picric acid complex.

shows no band assignable to the NH_2 group. This disagreement may be attributed to the extent of dissociation of the complex on the surface of the alkali halides. One may suppose that the complex in a potassium bromide disc employed by the German workers was well dispersed; therefore, an appreciable amount of the free amine might exist in equilibrium. On the other hand, the complex examined by our technique may be essentially free from such a complication because of its small surface area. It must be added that no color change could be observed upon heating above the transition temperatures when we examined the *o*-haloaniline complexes by the KBr disc technique. The presence of the proton-transfer from picric acid to the amine molecule in the low-temperature form and its absence in the high-temperature form were similarly confirmed for the other combinations.

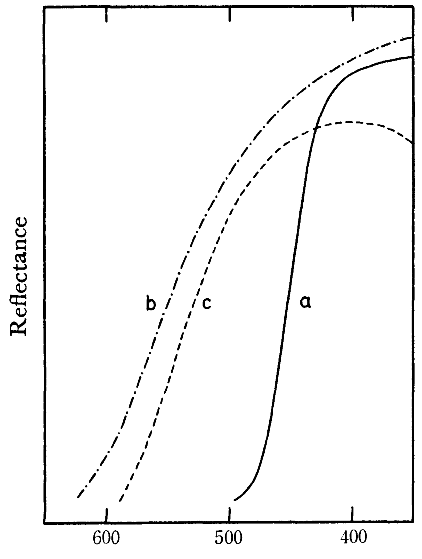

Fig. 3. Reflectance spectra of a) the yellow form and b) the red form of the *o*-bromoaniline–picric acid complex and c) the corresponding *s*-trinitrobenzene complex.

Electronic Spectra. Briegleb and Delle have shown that the absorption bands characteristic of the high-temperature forms of the bromo- and dibromo-naphthylamine complexes are similar to the CT absorption bands in the corresponding *s*-trinitrobenzene complexes. As the electron-acceptor strength of picric acid is nearly the same as that of *s*-trinitrobenzene, the similarity in the spectrum has been considered as evidence that the high-temperature forms of the picric acid complexes are of the CT type. In Fig. 3, the spectra of the yellow and red forms of the bromoaniline-picric acid are compared with that of the trinitrobenzene complex. Here again, the absorption band which appears when the complex is heated above the transition temperature is located close to that of the CT absorption band in the trinitrobenzene complex. In the same way, the appearance of CT absorption in the high-temperature forms was firmly established for all the complexes.

TABLE 1. TRANSITION TEMPERATURES AND ENTHALPY CHANGES IN THE PICRIC ACID COMPLEXES

Amine	Temp. (°C)		ΔH (kcal/mol)
	This work	Hertel	
o-Bromoaniline	103—110	95	6.7
o-Iodoaniline	100—107	90	6.2
1-Chloro-2-naphthylamine	128—138	130	8.0
	74—76[a]	—	1.4[a]
1-Bromo-2-naphthylamine	118—125	114	8.2
	76—79[a]	—	0.8[a]
1,6-Dibromo-2-naphthylamine	99—108	96	3.4

a) Transitions in the charge-transfer complexes.

Calorimetric Data. The transition temperatures and enthalpy changes are listed in Table 1. These values were for polycrystalline samples as deposited from solutions. It must be noted that the endothermic peaks recorded at a heating rate of 3 °C/min are anomalously broad. The temperature intervals defined by the points of departure from and return to the baseline of the calorimetric curves in Table 1 are several times broader than those of the ordinary transitions—*e.g.*, that in hexamethylbenzene used for the calibration. Moreover, our temperatures tend to be higher than those reported by Hertel.[4] Especially in

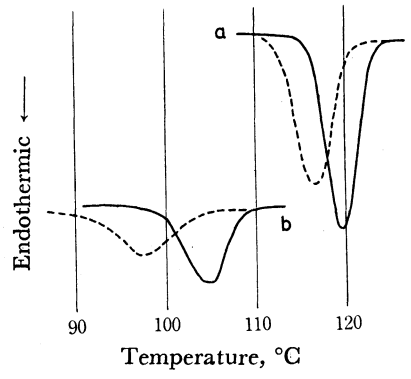

Fig. 4. DSC thermograms of the picric acid complexes of a) 1-bromo-2-naphthylamine and b) 1,6-dibromo-2-naphthylamine before grinding (——) and after grinding (------).

the case of the haloaniline complexes, even the lower limit of the interval is as much as 10 °C higher. When the polycrystalline samples of the bromo- and dibromonaphthylamine complexes were crushed, all the peaks were found to shift significantly to lower temperatures (see Fig. 4). Only a few minutes were enough to produce these changes by grinding. The points of departure from the baseline in the calorimetric curves of the ground samples are located below the transition temperatures reported by Hertel. In addition, the endothermic peaks become a little broader and the amounts of heat of the transition become as much as 20% less than the values given in Table 1. In the case of the chloronaphthylamine complex, the peak was found at almost the same temperature interval before and after grinding; however, the decrease in the heat was comparable with those in the other two naphthylamine complexes. On the other hand, grinding for a short time does not seem to affect much the transitions in the haloaniline complexes. Although small shifts in the transition to lower temperatures were observed, grinding did not result in any observable change in the amount of the heat. These observations suggest that the behavior in complex isomerization is more or less modified by the imperfections incorporated into the crystals by grinding.

The high-temperature forms of the naphthylamine complexes can be cooled to room temperature without any color change. Nevertheless, X-ray examinations revealed that the 1-halonaphthylamine complexes of the CT type at room temperature are different from those obtained by heating the salts above the transition temperature. The existence of phase transitions without complex isomerization between these two forms could be established by the calorimetric method, as is indicated in Table 1. It may be added that the corresponding trinitrobenzene complexes also exhibit phase transitions a little below the transition temperatures in the picric acid complexes of the CT type; that is, they are at 0.9 kcal/mol at 65 °C in the chloronaphthylamine complex and at 1.4 kcal/mol at 60 °C in the bromonaphthylamine complex. All the heats of transition accompanied by complex isomerization listed in Table 1 are appreciably larger than those without isomerization. Such a relation may be recognized as a general tendency, but it is not always true. The heat of transition with isomerization can be as small as 2.2 kcal/mol, as has been found in *o*-chloroaniline–trinitrobenzoic acid,[3] while that without isomerization can be as large as 3.5 kcal/mol, as has been reported for anthracene–picric acid.[11]

Electrical Resistivity. The logarithm of the resistivity of the *o*-haloaniline complexes recorded at ascending temperatures is plotted against the reciprocal temperature in Fig. 5. In the first run, the slope becomes progressively steeper. The activation energy for semiconduction (E), defined by $\rho=\rho_0\exp(E/kT)$, is about 2.25 eV at 60 °C and 4.0 eV at 95 °C in the case of the bromoaniline complex, while the values for the iodoaniline complex are 2.55 and 7.2 eV. At the end of the run, the samples were found to be dark red. Therefore, no anomaly locating the lower limit of transition temperature interval in these complexes was found by our resistivity measurements. On the other hand, the upper limit in the bromoaniline complex may be located in the vicinity of 100 °C. This marked lowering of the upper limit compared to the value in Table 1 may be attributed to the effect of imperfections incorporated by compression to as much as 3 ton/cm^2 employed in the preparation of the sample rod. After the first run, the samples were quickly cooled and the second run was immediately recorded. The slopes in the range from 60 to 80 °C are nearly constant—that is, 1.6 and 2.0 eV. The resistivity values at room temperature may be estimated as 10^{13}—10^{14} ohm cm by extrapolation; they are in good agreement with that of a closely-related CT complex, the 5×10^{13} ohm cm value of the *p*-chloroaniline–*s*-trinitrobenzene.[16] Nevertheless, the activation energies in this temperature range can hardly be considered those

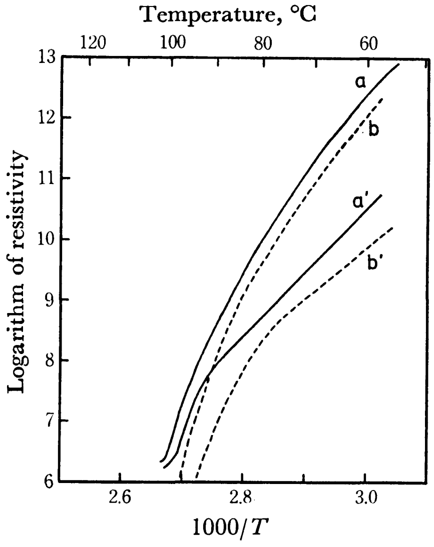

Fig. 5. Electrical resistivities of the picric acid complexes of a) *o*-bromoaniline and b) *o*-iodoaniline. a' and b' are the second runs.

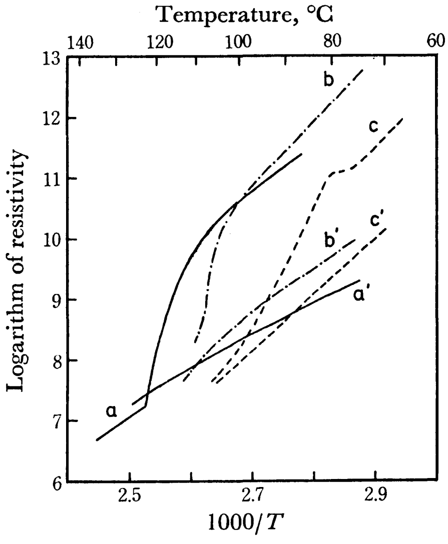

Fig. 6. Electrical resistivities of the picric acid complexes of a) 1-chloro-2-naphthylamine, b) 1-bromo-2-naphthylamine, and c) 1.6-dibromo-2-naphthylamine. a', b', and c' are the second runs.

of the CT complexes. At room temperature, standing overnight is enough for the red form of the *o*-haloaniline complex to return to the stable yellow form. The rate can, of course, be expected to be very much faster in the measured temperature range. Moreover, the slope becomes as steep as that in the first run at high temperatures. Such behavior may suggest that a part of the sample changes into the yellow form during the process of reheating. The transition in the reverse direction in the naphthylamine complexes is slower than those in the aniline complexes. Therefore, the electrical behavior shown in Fig. 6 seems easily explainable. The yellow form of the chloronaphthylamine complex shows an activation energy of 1.5 eV below 100 °C. Then, the slope becomes gradually steeper. The completion of the isomerization may account for the constancy of activation energy above 123 °C. In the second run, the average of the activation energy is about 1.1 eV and the extrapolation to higher temperature almost coincides with the linear part of the first run. As might be expected, the CT complex is more conducting by two orders of magnitude at the beginning of the transition, which may be located around 100 °C. The resistivity extrapolated to room temperature is 10^{16} ohm cm in the yellow form and 10^{12} ohm cm in the red form. Similar anomalous behavior in the transition-temperature interval and a large difference in the electrical resistivity between the complex isomers can also be noted in the other two complexes (see Fig. 6). The activation energy for semiconduction in the yellow form of the bromonaphthylamine complex is 2.2 eV, and that in the red form, 1.4—1.9 eV. The corresponding values in the dibromonaphthylamine complex are 2.1 and 1.8 eV respectively. According to the resistivity measurements, the transformation in the latter complex occurs in the interval from 85 to 100 °C. The large shift to the lower-temperature side and the great breadth in the compressed sample compared to the values given in Table 1 seem to be in accord with the observation of the grinding effects made by the calorimetric method; however, the general tendency here is more pronounced than that demonstrated by the calorimetric curve.

The authors wish to express their thanks to Professor Toshio Yokokawa for letting them use the X-ray diffractometer.

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