Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. IX.[1] Polynitrobenzoic Acid Complexes with Aromatic Monoamines

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When 2,4,6-trinitrobenzoic acid is combined with aromatic monoamines, true benzoates are mostly formed. However, not only a white true benzoate, but also a red 2: 1 complex of the CPT type, in which charge-transfer and proton-transfer interactions operate simultaneously between the component molecules, were obtained with aniline. In addition, the brown 2,4,5-trimethylaniline complex reported by Noelting and Sommerhoff was found to be of a similar nature. The phenomenon of complex isomerism was observed upon combination with *o*-chloroaniline; that is, the colorless salt isomerizes into an orange-colored charge-transfer complex at about 133 °C. Only the complexes with *p*-dimethylaminobenzaldehyde and *o*-nitroaniline, which have the lowest pK_a values among the amines examined, and those with the halogenated 2-naphthylamines are of the charge-transfer type. The 3,5-dinitrobenzoic acid complexes were also examined. Complexes of the CPT type with a 3: 2 composition were isolated with aniline and *p*-toluidine.

The combination of an aromatic amine and a polynitrophenol is known to form a true phenolate by acid-base interaction or a charge-transfer (CT) complex by electron donor-acceptor interaction. In addition, some interesting phenomena have been noted with the complexes of such bifunctional component molecules. Many years ago, Hertel demonstrated that the same components, if appropriately chosen, can form either phenolates or CT complexes, depending upon the ambient conditions.[2] This phenomenon was named "complex isomerism" by this author. Further pairs of complex isomers have been presented in a previous paper of the present series.[3] Secondly, our study of the vibrational and electronic spectra of the orange-colored 1-naphthylamine-picric acid (2: 1) complex revealed that a proton is transferred from the acid to the amine, and that the interaction between the picrate ion and the second amine molecule is capable of producing a CT absorption band.[4] For brevity, such a complex was denoted as a complex of the CPT type because of the simultaneous operation of CT and proton-transfer (PT) interactions between the component molecules. Many complexes of a similar nature, including the brick red *o*-toluidine–picric acid (1: 1), the reddish orange tryptophan picrate, and the orange-red *o*-toluidine-tetranitrobiphenyldiol (2: 1), have been prepared by us.[1,5–7]

Bifunctional component molecules are not limited to aromatic amines and polynitrophenol. The present work will be concerned with the behavior of polynitrobenzoic acids when subjected to complexation with aromatic monoamines. 2,4,6-Trinitrobenzoic acid, hereafter abbreviated as TNBA, was selected for this purpose, because not only its strength as an acid but also that as an electron acceptor are well comparable with those of picric acid.[8,9] The salts of TNBA with fourteen aromatic amines, including aniline, 2,4,5-trimethylaniline, *m*-nitroaniline, and naphthylamines, were prepared by Sudborough and his collaborators as early as the turn of the century.[10,11] They noted that all the salts become dark when heated and then melt, evolving a considerable quantity of gas and yielding a dark red oil. The melting points were observed to depend on the rate of heating. The red product was identified by Sudborough to be the corresponding *s*-trinitrobenzene (TNB) complex formed by the decarboxylation of TNBA.[12] Moreover, Noelting and Sommerhoff isolated a colorless salt by combining TNBA and 2,4,5 trimethylaniline in cold ethanol and a brown complex in warm methanol.[13] The nature of the latter was left unclarified. In addition, we studied the complexes of 3,5-dinitrobenzoic acid (DNBA) in the present investigation.

Experimental

Materials. The polynitrobenzoic acids, all the derivatives of aniline, and 1-naphthylamine used in this work were commercially obtained. The 1-chloro-2-naphthylamine was prepared by the procedure of Cleve,[14] and the 1-bromo- and 1,6-dibromo-2-naphthylamines, by those of Franzen and Eidis.[15] The complexes were precipitated by mixing the component compounds separately dissolved in ethanol.

Measurements. The vibrational spectra of the solid complexes were measured as hexachloro-1,3-butadiene mulls in the region from 2000 to 4000 cm^{-1} and as Nujol mineral oil mulls in the region from 1500 to 1800 cm^{-1} with a Jasco IR-G infrared spectrophotometer, and the electronic spectra of the powdered complexes sandwiched between two quartz plates in the visible region, with a Beckman DK-2A spectroreflectometer. The calorimetric curves were recorded on a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, at a heating rate of 3 °C/min. The heats of transition were estimated by comparing the peak areas with that for the transition in hexamethylbenzene, which is known to take place at 110.6 °C with $\Delta H = 0.422$ kcal/mol.[16]

Results and Discussion

TNBA Complexes. The solid complexes with the following twenty-three amines (arranged in the order of decreasing pK_a values) were found to be colorless or pale yellow, in accordance with the work by Lloyd and Sudborough:[10] *N,N*-diethyl-*m*-toluidine (pK_a= 7.12), *N,N*-diethylaniline (6.61), *p*-anisidine (5.31),

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p-phenetidine (5.20), *N*-butylaniline (5.12), *N*-ethylaniline (5.12), *p*-toluidine (5.10), 2,4,5-trimethylaniline (4.96), *m*-xylidine (4.89), *N*-methylaniline (4.84), *m*-toluidine (4.69), aniline (4.60), *o*-anisidine (4.52), *o*-toluidine (4.39), *m*-aminophenol (4.3), *m*-anisidine (4.20), *p*-chloroaniline (4.15), 1-naphthylamine (3.96), *m*-chloroaniline (3.46), *o*-chloroaniline (2.65), *o*-iodoaniline (2.60), *o*-bromoaniline (2.53), and *m*-nitroaniline (2.46). As no experimental pK_a value is available for 2,4,5-trimethylaniline,[17] the value predicted by the equation of Clark and Perrin is used above.[18] The large shift of the carbonyl-stretching vibrational band clearly indicates that the expected PT from TNBA to the amines is taking place in these complexes. While TNBA exhibits a band at about 1730 cm^{-1}, the salts have a band around 1630 cm^{-1} attributable to the COO^- group. Additional evidence for the PT is provided by the replacement of an NH_2 pattern by a NH_3^+ pattern when the amines are primary. Furthermore, an examination of the vibrational spectrum revealed that the red decomposition product is essentially the corresponding TNB complex, as was noted by Sudborough and also by Noelting and Sommerhoff.[12,13] As has been demonstrated with picrates and 2,4-dinitrophenolates,[19] the phenomenon of complex isomerization by melting may be expected to be observed with the complexes with some amines with relatively low pK_a values if there is no decarboxylation.

In addition to the colorless trinitrobenzoate, a red complex with a 2: 1 mole ratio was isolated with aniline by employing an excess of the donor component. Calcd for $2C_6H_7N \cdot C_7H_3N_3O_8$: C, 51.46; H, 3.83; N, 15.79%. Found: C, 51.39; H, 3.84; N, 15.86%. The vibrational spectrum has a carbonyl-stretching band at about 1630 cm^{-1}, indicating the PT from the acid to the amine and both the NH_2 and NH_3^+ patterns in the region from 2300 to 3500 cm^{-1}. Consequently, it is certain that this complex consists of anilinium trinitrobenzoate and aniline. The diffuse reflectance spectrum given in Fig. 1 is almost identical with that of the aniline-TNB complex. The absorption appearing upon the incorporation of the second aniline molecule is undoubtedly, to be ascribed to a CT interaction between the amine molecule and the trinitrobenzoate ion. Therefore, this is a complex of the CPT type as defined in our previous paper.[5] As the acceptor-strength of TNBA is comparable with that of TNB,[9] the effect of the dissociation of the carboxyl group appears to be negligible. This conclusion is in accordance with that for the case of picric acid.[4,20] The brown 2,4,5-trimethylaniline complex reported by Noelting and Sommerhoff was found to be of a 3: 2 composition. Calcd for $3C_9H_{13}N \cdot 2C_7H_3N_3O_8$: C, 53.54; H, 4.93; N, 13.70%. Found: C, 54.08; H, 5.15; N, 14.22%. Here again, a close similarity in the diffuse reflectance spectrum was observed between this complex and the corresponding TNB complex (see Fig. 1). It is evident that this deeply colored complex is also of the CPT type. This conclusion is supported by the presence of the NH_2, NH_3^+, and COO^- patterns in the vibrational spectrum.

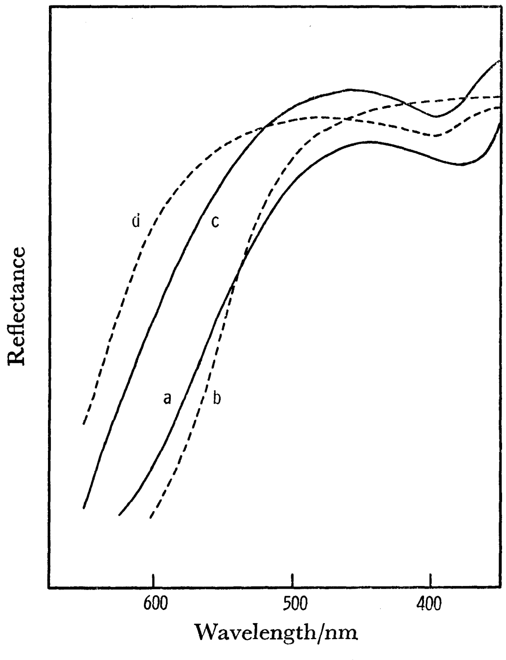

Fig. 1. Reflectance spectra of a) the aniline–TNBA (2: 1) complex, b) the corresponding TNB complex, c) the 2,4,5-trimethylaniline–TNBA (3: 2) complex, and d) the corresponding TNB complex.

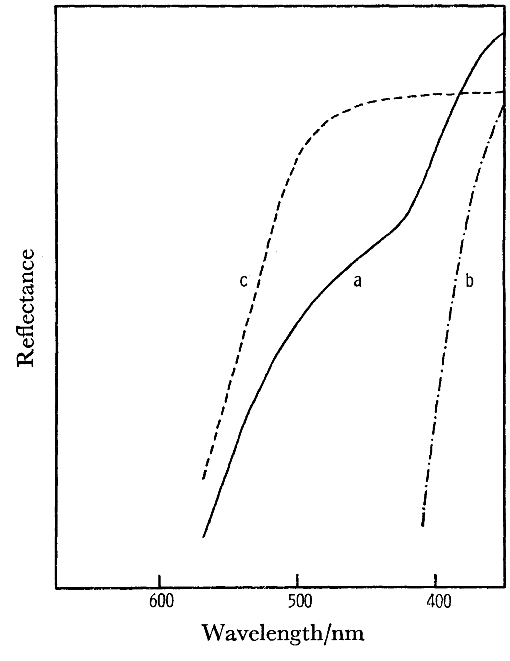

Fig. 2. Reflectance spectra of a) the orange form and b) the colorless form of the *o*-chloroaniline-TNBA complex and c) the corresponding TNB complex.

The most interesting result of the present work is the complex isomerism observed with the *o*-chloroanilinium salt. The colorless benzoate was found to turn orange at about 133 °C. Calcd for $C_6H_6NCl \cdot C_7H_3N_3O_8$: C, 40.57; H, 2.34; N, 14.56; Cl, 9.23%. Found: C, 40.41; H, 2.21; N, 14.58; Cl, 8.96%. The color change is due to the appearance of an absorption in the region from 410 to 600 nm; see Fig. 2. This location is in good agreement with that of the CT absorption in the corresponding TNB complex. The transition is accompanied by a drastic change in the

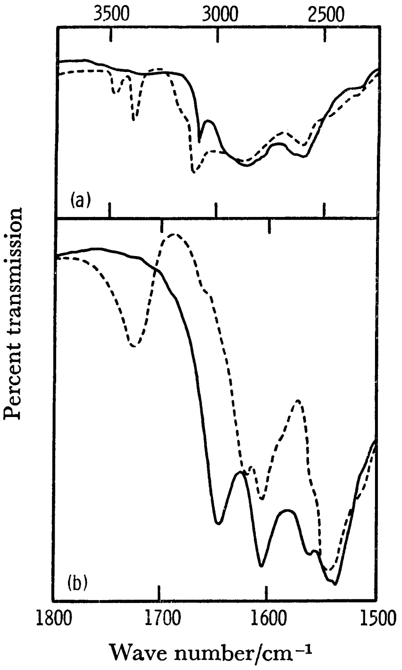

Fig. 3. Vibrational spectra of the colorless form (——) and the orange form (------) of the *o*-chloroaniline–TNBA complex.

vibrational spectrum. As is shown in Fig. 3, the appearance of an NH_2 pattern is noted above the transition temperature. Moreover, the carbonyl-stretching band located at 1650 cm^{-1} in the colorless form is replaced by the one located at 1730 cm^{-1} in the orange form. The X-ray diffraction patterns of these two forms are distinctly different from each other. The complex melts at about 145 °C. The narrow temperature difference between the transition point and the melting point did not allow us to carry out the above-mentioned measurements at high temperatures. Therefore, samples heated a little above the transition point with the differential scanning calorimeter and then cooled as quickly as possible were employed for the spectroscopic and X-ray examinations. These observations lead to the conclusion that the benzoate isomerizes into a CT complex at about 133 °C. The heat of this enantiotropic transition was estimated to be about 2.2 kcal/mol. It must be added that this value is markedly smaller than those observed with the transitions in Hertel's picric acid complexes; that is, 6—8 kcal/mol.[21] Previously it was noted that the chance of finding complex isomers is high in the salts derived from halogenated amines, especially *o*-haloanilines.[3] The newly-found pair fits into this group. As to the electron-acceptor components, it may be said that all the component compounds so far found have two nitro groups at the *ortho* positions related to the proton-donating group; namely, 2,6-dinitrophenol, picric acid and its alkyl derivatives, 3,3′,5,5′-tetranitrobiphenyl-4,4′-diol, and the present acid.[2,3,7]

The complexes with *p*-dimethylaminobenzaldehyde and *o*-nitroaniline, which have the lowest pK_a values among the amines examined (1.62 and −0.26 respectively) are deeply colored. Their vibrational spectra indicate the lack of PT; therefore, these two complexes may be supposed to be of the CT type. The pK_a value of the former amine is significantly higher than that of the acid, 0.65, suggesting that pK_a is not a good measure of the acid strength in these molecular solids or that the pK_a value of TNBA is a little too small. It must be noted that, in contrast to the case studied here, we have seen a good coincidence between the pK_a value of the acceptor component and the lower limit of the pK_a range when PT occurs in the complex formation of 2,4-dinitrophenol.[19] 1-Chloro-, 1-bromo- and 1,6-dibromo-2-naphthylamines are known to form true phenolates with picric acid which isomerize into CT complexes at the transition points.[2,22] Their TNBA complexes are as red as the TNB complexes are. Because of the deep coloration and the presence of the NH_2 and COOH patterns in the vibrational spectra, these three complexes are also considered to be of the CT type.

DNBA Complexes. Solid complexes were obtained with all the above-mentioned anilines except *m*- and *o*-nitroanilines. The fifteen anilines among the seventeen with pK_a values higher than 4.15 give colorless or pale yellow benzoates. The pK_a value of the last aniline in this group is, again, markedly higher than that of DNBA, that is, 2.82.[8] They easily lose the electron-donor component upon heating; therefore, we did not attempt to examine the possible complex isomerization by melting. However, the observation made by Ley and Grau of the diethylanilinium salt might be related to this phenomenon. This salt, with a melting point of 93 °C, was reported to turn a brownish red at 70 °C when heated under water.[23] The calorimetric measurements indicated that a transition without complex isomerization takes place at 108 °C in the pale-yellow *m*-hydroxyanilinium salt. Calcd for $C_6H_7NO \cdot C_7H_4N_2O_6$: C, 48.61; H, 3.45; N, 13.08%. Found: C, 49.75; H, 3.60; N, 13.03%. The enthalpy change is as small as 1.3 kcal/mol, reflecting the absence of complex isomerization.

p-Toluidine and aniline give deep orange-colored complexes of a 3:2 composition. Calcd for $3C_7H_9N \cdot 2C_7H_4N_2O_6$: C, 56.39; H, 4.73; N, 13.15%. Found: C, 55.93; H, 4.72; N, 13.11%. Calcd for $3C_6H_7N \cdot 2C_7H_4N_2O_6$: C, 54.62; H, 4.15; N, 13.93%. Found: C, 54.49; H, 4.12; N, 13.98%. As may be expected from the high pK_a values of these amines, the spectroscopic examinations revealed that these two complexes are of the CPT type. Since we made no effort to prepare such complexes, their isolation may have been rather accidental and the formation of this type of complexes may not be limited to these two amines. The CT complex-forming ability of the 3,5-dinitrobenzoate ion has been known by the work of Menger and Bender on complexes in an aqueous solution with *N*-(indole-3-acryloyl)-imidazole and two more compounds, and also by the work of Colter and Grunwald on a complex in an aqueous solution with 1-naphthol.[24,25] However, no solid complex containing the anion as an electron-acceptor has been isolated. The five anilines the pK_a values of which are in the range from 3.46 to 1.62 form complexes of the CT type.

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