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Charge Transfer and Proton Transfer in the Formation of Molecular Complexes. XII.[1]

o-Aminobenzoic Acid–Picric Acid and Related Complexes

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The combination of *o*-aminobenzoic acid and picric acid was found to yield four kinds of adducts. These were a stable yellow (1:1) salt, formed by the proton transfer from the picric acid to the *o*-aminobenzoic acid molecule, two red (1:1) molecular complexes of markedly different stability, and a red (2:1) complex consisting of the *o*-aminobenzoic acid molecule, its protonated ion, and the picrate ion. The enthalpy change and the activation energy for the isomerization from the salt to the charge-transfer complex by a solid-solid transformation were shown to decrease during storage. The 1,3,5-trinitrobenzene complexes with *o*-(methylamino)benzoic acid, *o*-, *m*-, and *p*-(dimethylamino)benzoic acids, and their sodium and potassium salts were prepared. Their electronic spectra were measured, along with those of the complexes with *o*- and *p*-aminobenzoic acids and their salts presented in the work of Sudborough and Beard. The displacement of the charge-transfer absorption maxima to the lower wavenumber side by the salt formation is 2×10^3 cm^{-1} on the average and seems to be consistent with our proposition that the picrate ion acts as an electron acceptor in aromatic amine-picric acid (2:1) complexes.

One of the most striking properties of *o*-aminobenzoic acid is the formation of both a yellow salt and a red molecular complex with picric acid;[2] and another is the formation of the 1,3,5-trinitrobenzene complexes of the potassium salt as well as of the acid itself.[3] They have received no further attention, however. When picric acid is combined with an aromatic amine, the acid-base interaction generally predominates in the solid state. With this acid, only three other anilines and three naphthylamines are known to exhibit the phenomenon of complex isomerism: that is, the formation of both a salt and a charge-transfer complex.[4,5] In some cases, the two forms are enantiotropically related to each other, while in the others, the molecular complex is metastable with respect to the salt at every temperature. One of the aims of the present work was to clarify the relation between the two forms of the *o*-aminobenzoic acid–picric acid reported by Issa and El-Essawey.[2]

1-Naphthylamine was shown by Kofler to form the yellow 1:1 and red 2:1 adducts with picric acid.[6] The former is a simple salt, while the latter consists of naphthylamine molecule, naphthylammonium cation, and picrate anion.[7] The red color presumably arises from the charge-transfer interaction between the amine molecule and the picrate ion. We assumed that the electron acceptor in this 2:1 adduct is the picrate ion. Our proposition that the acceptor strength of picric acid is not much affected by the salt formation seems to be consistent with numerous examples subsequently accumulated by us; however, this is in serious conflict with Tanaka's recent theoretical view.[8] On the basis of his molecular orbital calculations, he suggested that the picrate anion is a donor and the indole moiety an acceptor in the tryptophan picrate. If so, the change in the electronic structure of picric acid by salt formation must be substantial, because indole is known to act as a donor in the complex formation with picric acid.[9] The second aim of the present work was to find out experimentally how large the change in the donor strength of aminobenzoic acid by salt formation is. The spectral measurements of the trinitrobenzene complexes of *o*- and *p*-aminobenzoic acids and their potassium salts originally prepared by Sudborough and Beard will provide the means of giving a certain answer to this question. Both the acids and the salts undoubtedly function as electron donors in forming the complexes. If the energy differences in the charge-transfer absorption maxima observed with them are significantly smaller than the magnitude predicted by Tanaka for picric acid, our proposition becomes more likely than his.

Experimental

Materials. The *o*- and *p*-aminobenzoic acids, *m*- and *p*-(dimethylamino)benzoic acids, and picric acid were obtained from commercial sources. The methylation of *o*-aminobenzoic acid with a calculated amount of dimethyl sulfate yields the *N*-methyl derivative, while that with an excess of methyl iodide yields the *N*,*N*-dimethyl derivative.[10] The latter was isolated as the polyiodide. After removing iodine by steam distillation, the acid was freed from hydrogen iodide by the treatment with silver oxide. The *o*-(dimethylamino)benzoic acid thus separated was purified by the precipitation from a methanol solution by the addition of diethyl ether. The synthesis of 1,3,5-trinitrobenzene was carried out starting from 2,4,6-trinitrotoluene, Eastman yellow label, through 2,4,6-trinitrobenzoic acid.[11] The alkali-metal salts of the aminobenzoic acids were obtained by dissolving equimolar amounts of the acid and the hydroxide in water and then evaporating to dryness. The use of an excess of the latter reagent must be carefully avoided; otherwise, a small amount of Meisenheimer complex is formed in the step of the trinitrobenzene-complex preparation and interferes with the measurements of the electronic spectra. The complexes were isolated by concentration or by evaporation of a solution containing equimolar amounts of the components in an appropriate solvent.

Measurements. The spectroscopic, calorimetric, and X-ray measurements were made using the procedures reported in a previous paper of this series.[12] As the red form of *o*-aminobenzoic acid–picric acid is too unstable to be ground, the thin layers of the complex were prepared by evaporating the warm solution on sodium chloride or quartz plates for the spectroscopic measurements.

Results and Discussion

When a hot methanol solution of equimolar amounts of *o*-aminobenzoic acid and picric acid is concentrated, red crystals appear. They are not stable at room temperature and are gradually transformed into yellow crystals. Found: C, 43.13; H, 2.78; N, 15.00%. Calcd for $C_7H_7NO_2$–$C_6H_3N_3O_7$: C, 42.63; H, 2.75; N, 15.30%. In agreement with the observation made by Issa and El-Essawey, the former form exhibits an asymmetric N–H stretching band and a symmetric one at 3485 and 3375 cm^{-1} respectively, while the latter shows broad bands covering the region from 2925 to 2625 cm^{-1}, to be assigned to the NH_3^+ group. The red form deposited on a quartz plate shows an electronic absorption band which is not present in either of the components. The maximum is hidden under a strong higher-energy band, but is possibly at about 22×10^3 cm^{-1}. This wavenumber is not far from that of the charge-transfer absorption band in the orange-yellow *o*-aminobenzoic acid–trinitrobenzene complex, about 24×10^3 cm^{-1}. As the acceptor strength of picric acid is known to be comparable with that of 1,3,5-trinitrobenzene, the band may be ascribed to the charge-transfer transition from the *o*-aminobenzoic acid molecule to the picric acid molecule.

Upon heating the yellow crystals at a scanning rate of 2.5 °C min^{-1}, an endothermic peak extending from 156 to 171 °C is observed on the calorimetric curve. Above this temperature range, the red form produced by the phase transition starts to decompose exothermally. The enthalpy change of the transition from the yellow salt to the red molecular complex decreases during storage. The fresh samples give a value of 10.2 kJ mol^{-1}. On the other hand, the value obtained after one-month storage at room temperature is 6.6 kJ mol^{-1}. These enthalpy changes are rather small compared to those so far examined. The values recorded earlier range from 9.2 kJ mol^{-1} of *o*-chloroaniline-2,4,6-trinitrobenzoic acid to 34 kJ mol^{-1} of 1-bromo-2-naphthylamine-picric acid.[1,12] It is apparent that these isomeric forms are enantiotropically related to each other. Previously we showed that the picrates of all the anilines with pK_a values of less than 3 isomerize into charge-transfer complexes upon melting, if they do not isomerize by an enantiotropic solid-solid transition.[13] The pK_a value reported by Schwarzenbach *et al.* for *o*-aminobenzoic acid is 2.09,[14] and nicely fits into the range where complex isomerization is expected to occur.

The endothermic peak due to the transformation covers a temperature range as wide as 15 °C and is asymmetric, in contrast to those of Hertel's picric acid complexes described earlier.[1] The slope changes very gently on the lower-temperature side and sharply on the other side. Up to near the maximum, the curve is characteristic of a transition whose extent increases linearly with time under isothermal conditions. In other words, the rate constant, *k*, is given by

$$k=B(\mathrm{d}H/\mathrm{d}t),$$

where *B* is a constant and where $(\mathrm{d}H/\mathrm{d}t)$ is the rate of change of enthalpy with time and is proportional to the departure of the peak from the baseline at the associated temperature.[15] The activation energy of such a transition can be estimated by a plot of log $(\mathrm{d}H/\mathrm{d}t)$ *versus* $1/T$. The energy given by the fresh samples is relatively large and is scattered in a wide range. At the heating rate of 2.5 °C min^{-1}, six independently-prepared samples gave 449, 600, 640, 719, 879, and 931 kJ mol^{-1} (see Plots a and b in Fig. 1). This energy decreases during storage at room temperature and becomes more reproducible. After one month, the six runs performed at the scanning rates of 2.5, 5, 10, and 20 °C min^{-1} yielded the mean value of 306±15 kJ mol^{-1} (see Plots c and d in Fig. 1). The over-all activation energy of a solid-solid transformation depends mostly upon the kinetics of the nucleation, which takes place heterogeneously and preferentially at grain boundaries.[16] When the red charge-transfer complex is transformed into the yellow salt below the transition temperature, the initially-formed crystals are supposed to be highly strained because of the change of molecular arrangement. Upon storage, such a stress may be largely reduced by the spontaneous growth of the grain boundaries. The relatively large and markedly scattered activation energies observed with the fresh samples suggest that the growth of the grain boundaries proceeds rather slowly and irregularly. This postulate seems to be in accordance with the observations made earlier with some Hertel's picric acid complexes that the endothermic peak due to the transformation from the salt to the charge-transfer complex is appreciably broadened and weakened by the grinding of the crystals.[1]

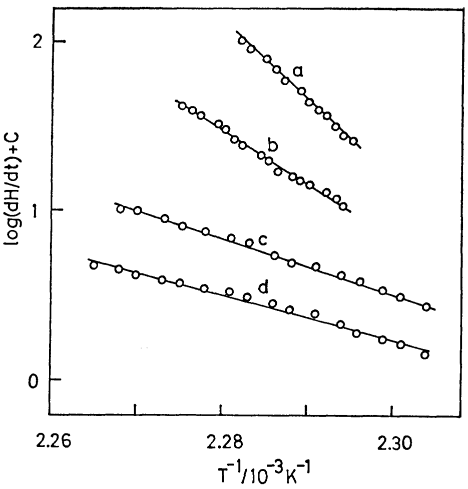

Fig. 1. Arrhenius plots constructed from the endothermic peak due to the isomerization from the yellow salt to the red molecular complex of the *o*-aminobenzoic acid–picric acid (1:1). a) and b), fresh samples at a heating rate of 2.5 °C min^{-1}. The estimated activation energies are 931 and 600 kJ mol^{-1} respectively. c) and d), samples stored for one month at room temperature. The heating rates are 10 and 5 °C min^{-1}, and the activation energies are 275 and 271 kJ mol^{-1} respectively.

The vermillion crystals deposited from a chloroform solution are also of the 1:1 mole ratio. Found: C,

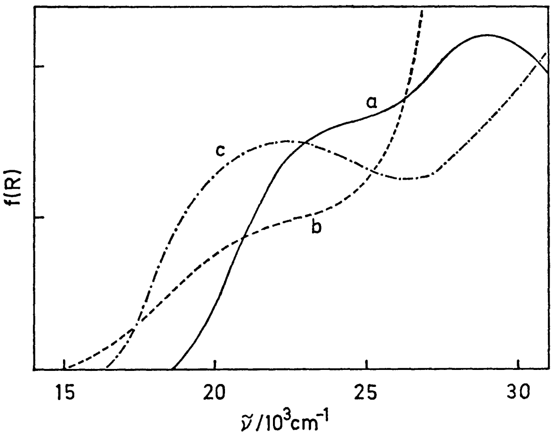

Fig. 2. Kubelka-Munk plots of diffuse reflectance of the 1,3,5-trinitrobenzene complexes with a) *o*-aminobenzoic acid, b) the sodium salt, and c) the potassium salt.

42.62, 42.49; H, 2.71, 2.70; N, 15.25, 15.32%. Contrary to the red-colored form from a methanol solution, the crystals could be kept at room temperature over several months without the transformation to the yellow salt. However, they are easily transformed into yellow powder by crushing. A comparison of the X-ray diffraction patterns revealed that the molecular complex is polymorphic. The N–H stretching bands are found at 3500 and 3380 cm^{-1}. The maximum of the charge-transfer absorption band in the second form of the molecular complex is not separable from a strong higher-energy band, but is possibly located around $21\times10^3\ \mathrm{cm}^{-1}$.

Stable scarlet crystals can also be obtained from a methanol solution if *o*-aminobenzoic acid is dissolved in excess. The compound is of the 2:1 mole ratio. Found: C, 47.61; H, 3.41; N, 13.99%. Calcd for $(C_7H_7NO_2)_2$–$C_6H_3N_3O_7$: C, 47.72; H, 3.40; N, 13.91%. The vibrational bands due to the NH_2 group, 3475 and 3375 cm^{-1}, and also the pattern characteristic of the NH_3^+ group in the range from 2875 to 2625 cm^{-1} are found in the infrared spectrum. Without doubt, the proton-transfer and charge-transfer interactions operate simultaneously in this solid. The electronic absorption band appearing as a shoulder at about $20\times10^3\ \mathrm{cm}^{-1}$ is assigned to the charge-transfer transition between the *o*-aminobenzoic acid molecule and the picrate ion. Following our earlier view,[7] we tentatively suppose that the latter species acts as an electron acceptor in this complex. This point will be discussed in detail later.

Sudborough and Beard noted that the trinitrobenzene complex of *o*-aminobenzoic acid is orange yellow and that of its potassium salt is deep red.[3] Their electronic spectra are presented in Fig. 2, which includes the spectrum of the complex formed with the sodium salt. The charge-transfer absorption maximum of the potassium-salt complex is seen at $22.3\times10^3\ \mathrm{cm}^{-1}$. In the other two, the absorption maximum is not explicit because of overlapping with a stronger absorption band; nevertheless, it is very likely that the sodium-salt complex gives a maximum at the same wavenumber as that of the potassium-salt complex. The maximum in the *o*-aminobenzoic acid complex is probably at about $24\times10^3\ \mathrm{cm}^{-1}$. Thus, the difference which should reflect the relative ionization potentials of the acid and its salts is only about $2\times10^3\ \mathrm{cm}^{-1}$ or 0.2 eV. Some additional spectral measurements were made in which the *N*-methyl and *N*,*N*-dimethyl derivatives were employed as donors. Here again, no large shift due to salt formation can be found. The observed wavenumbers are listed in Table 1.

TABLE 1. THE WAVENUMBERS OF THE CHARGE-TRANSFER ABSORPTION MAXIMA IN THE SOLID TRINITROBENZENE COMPLEXES

Donor	Wavenumber $/10^3\ \mathrm{cm}^{-1}$	Color
o-Aminobenzoic acid	24	yellowish orange
Sodium *o*-aminobenzoate	22	dull red brown
Potassium *o*-aminobenzoate	22.3	scarlet
o-(Methylamino)benzoic acid	23	orange
Sodium *o*-(methylamino)benzoate	21.2	brown carmine
Potassium *o*-(methylamino)benzoate	21.2	brown carmine
o-(Dimethylamino)benzoic acid	23.5	orange brown
Potassium *o*-(dimethylamino)benzoate	23	violet black
m-(Dimethylamino)benzoic acid	21.5	violet black
Sodium *m*-(dimethylamino)benzoate	19.5	blackish violet
Potassium *m*-(dimethylamino)benzoate	20.5	violet black
p-Aminobenzoic acid	25	orange
Sodium *p*-aminobenzoate	22.0	violet brown
Potassium *p*-aminobenzoate	24	brown orange
p-(Dimethylamino)benzoic acid	21.5	deep carmine
Sodium *p*-(dimethylamino)benzoate	21.3	dark violet red
Potassium *p*-(dimethylamino)benzoate	21.0	violet black

Although *m*-aminobenzoic acid does not form a molecular complex with trinitrobenzene, the potassium salt is known to give a dark reddish brown complex.[3] With the *N*,*N*-dimethyl derivative, however, both the acid and the salts yield the complexes. Sudborough and Beard have isolated the trinitrobenzene complexes of *p*-aminobenzoic acid and its potassium salt. The former is red and the latter dark red. The *N*,*N*-dimethyl derivative and its salts form more deeply colored complexes. Their spectral data are also given in Table 1. In all cases, the charge-transfer absorption maxima of the salt complexes are consistently displaced to the lower wavenumber side, but only by $2\times10^3\ \mathrm{cm}^{-1}$ on the average, compared to those of the corresponding acid complexes. The results may be understood from the fact that the ionization potentials of the salts are lower than those of the acids by the same magnitude.

Tanaka has presented the location of the highest occupied molecular orbital (HOMO) of picrate anion and that of the lowest unoccupied molecular orbital (LUMO) of the indole moiety of tryptophan as the criteria of electron donor and acceptor strength.[8] His conjecture of the donor character of the picrate anion comes from the calculations that its HOMO is located 3.78 eV above the HOMO of the indole moiety and its LUMO is 2.30 eV above the LUMO of the latter. However, the charge-transfer absorption in the tryptophan picrate appears in the same region as that of the indole–picric acid.[9] Furthermore, indole is well-known to behave as an electron donor in forming molecular complexes with a number of compounds including picric acid.[9,17] If it is assumed that picric acid is an acceptor but its anion is a donor with respect to essentially the same species, then the relative locations between the HOMO of indole and the LUMO of picric acid must resemble those between the HOMO of picrate ion and the LUMO of indole moiety calculated by Tanaka. As a consequence, the LUMO of picrate ion should be located at an energy higher by about 6 eV than the LUMO of the acid. If so, the HOMO of picrate ion should be also higher to a similar extent than the HOMO of picric acid. Analogously, one may expect a considerable difference, presumably of the order of 1 eV, in the location of the HOMO between an aminobenzoic acid and its anion. The experimental results summarized in Table 1 are definitely not in accord with the assumption made above. Thus, an alternative explanation that the picrate anion is not an electron donor but an electron acceptor in the tryptophan picrate and also in the *o*-aminobenzoic acid–picric acid (2:1) complex appears to be more likely. In this regard, it should be noted that the picrate anion in the solid complex is under the strong influence of the counter ion.[18] The charge on the anion in such solids may be largely localized by the polarizing power of the cation. The resultant situation would be more or less similar to the electronic structure of a picric acid molecule. Therefore, we feel that Tanaka's theoretical work on either an isolated picrate anion or a composite molecule does not reflect the situation in the solid salt complexes.

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