Effects of Alkyl Chain Length on Molecular Interactions. II.[1] Complex Isomerism in the Alkyl *p*-Aminobenzoate-Picric Acid Systems

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Synopsis. While a combination of *p*-aminobenzoic acid and picric acid gives a yellow-colored salt by proton transfer, the esterification of the former component compound with methyl to octadecyl groups results in the formation of not only stable salts but also metastable charge-transfer complexes.

We earlier studied the charge-transfer complex formation in pyrene-*N*-alkyl-2,4,6-trinitroaniline systems.[1] The thermal stability of the orange-colored 1:1 complex between the hydrocarbon and unsubstituted 2,4,6-trinitroaniline is drastically decreased by *N*-alkylation. The *N*-octyl derivative and most of the higher homologs produce a single peritectic or a eutectic in the phase diagrams with pyrene, whereas red solids formed on rapid cooling of the melts are progressively stabilized with an increase of the alkyl chain length. Even a stable existence of the red-colored 1:1 complex can be achieved with the *N*-pentadecyl and *N*-heptadecyl derivatives. In the present paper, we compare the effects of alkyl chain length on charge-transfer and proton-transfer interactions operating in solid addition compounds between alkyl *p*-aminobenzoate and picric acid.

Experimental

Materials. Alkyl *p*-aminobenzoates were prepared by reactions between *p*-nitrobenzoyl chloride and appropriate alcohols and then by reduction with iron powder and dilute hydrochloric acid as described by Adams et al.[2] The alkyl groups employed and the melting points of the esters were as follows: methyl, 110.5 °C; ethyl, 89.5 °C; propyl, 76.5 °C; butyl, 59 °C; pentyl, 54.5 °C; hexyl, 62.5 °C; heptyl, 80.5 °C; octyl, 71.5 °C; nonyl, 73 °C; decyl, 79 °C; undecyl, 81 °C; dodecyl, 84.5 °C; tridecyl, 87.5 °C; tetradecyl, 89 °C; pentadecyl, 91 °C; hexadecyl, 89.5 °C; heptadecyl, 95 °C; octadecyl, 96 °C.

Measurements. The phase diagrams were determined using calorimetric curves recorded on a Rigaku Thermoflex differential scanning calorimeter during the process of heating and also by visual examination.[1]

Results and Discussion

The yellow-colored addition compound between *p*-aminobenzoic acid and picric acid has been characterized to be a salt on the basis of its vibrational spectrum according to Issa and El-Essawey.[3] The methyl ester forms only a 1:1 salt when it is combined with picric acid. As is shown in Fig. 1a, the phase diagram is dominated by the freezing point curve of the salt. The melting point is as high as 159 °C. The color changes from yellow to red upon fusion, indicating isomerization into a charge-transfer complex.[4] By rapid cooling solidification occurs without a color change. The melting point of this metastable phase is measurable (see a shaded circle in Fig. 1a). However, it is not clear whether the fusion is congruent or incongruent because the endothermic peak due to the fusion of this charge-transfer complex is followed by an exothermic peak due to the solidification to the stable salt. This temperature is close to the melting point of the corresponding 1,3,5-trinitrobenzene complex, 114—114.5 °C, reported by Sudborough and Beard.[5]

Figure 1b presents the phase diagram of the ethyl ester–picric acid system. This ester forms a congruently melting 1:1 salt and an incongruently melting 2:1 salt. The melting point is located at 128 °C and the peritectic point at 120 °C. The metastable red complex is obtainable by quenching of the melt at 50 mol%. The melting point of this complex is found at 104.5 °C and is significantly higher than that of the corresponding trinitrobenzene complex, 88 °C.[5] The vibrational spectrum of the 2:1 salt shows clearly the presence of both NH_2 and NH_3^+ groups. The color of specimens having the composition of about 2:1 mole ratio is deeper than

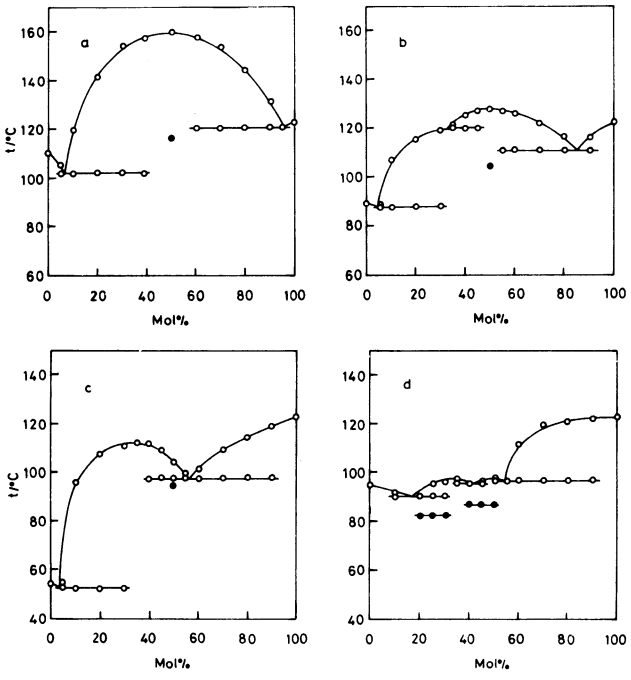

Fig. 1. Phase diagrams of the systems of picric acid with (a) methyl *p*-aminobenzoate, (b) the ethyl ester, (c) the pentyl ester, and (d) the heptadecyl ester. The shaded circles are the melting points of the metastable phase.

that of the 1:1 salt, suggesting a charge-transfer interaction between the donor molecule and the picrate anion.[6] The phase diagram of the propyl ester–picric acid system is of a type similar to that described above. The 1:1 salt melts at 114 °C and the 2:1 salt decomposes at 105.5 °C. The latter temperature is lower by 2 °C than the eutectic on the picric acid-rich side. Molten mixtures in the composition range from 50 to 80 mol% can form red solids on rapid cooling. The metastable phase melts at 89 °C regardless of the composition. The flatness over such a range may be the indication of incongruent melting of the charge-transfer complex. When the butyl ester is employed as a base, the thermal stabilities of the 1:1 and 2:1 salts are reversed. The former salt melts incongruently at 109.5 °C and the latter melts congruently at 112 °C. The charge-transfer complex melting at 97 °C is observed at 45 and 50 mol%.

The phase diagrams obtained empolying the pentyl and hexyl esters show only 2:1 salts. The red complex of the pentyl ester is found only at 50 mol% and melts at 94.5 °C (see Fig. 1c). In the case of the hexyl ester, the 2:1 salt melts at 101.5 °C and the red complex observed in the range from 40 to 50 mol% melts at 90.5 °C. These charge-transfer complexes are possibly of the 1:1 mole ratio.

Simple salts appear again in the systems with the heptyl ester and with the higher homologous members. The octyl, undecyl, and pentadecyl esters are exceptions. The diagrams given by the heptyl, nonyl, decyl, dodecyl, tridecyl, and tetradecyl esters are of the same type as that shown in Fig. 1b. However, the eutectic on the picric acid-rich side is located near 55 mol% because of the low thermal stability of the 1:1 salt. The heptyl ester is unique in the sense that two metastable complexes with distinctly different melting points are formed with picric acid. The one appearing in the range from 10 to 20 mol% melts at 71 °C and the other in the range from 40 to 50 mol% melts at 91 °C. The metastable picric acid complex of the tetradecyl ester is found in an exceptionally wide composition range, namely, from 40 to 80 mol%. The 1:1 salt melts congruently at 99 °C and the charge-transfer complex melts at 90.5 °C. In this combination, the difference in the melting point is the smallest among the similar examined combinations.

The octyl, undecyl, and pentadecyl esters produce phase diagrams which bear a certain similarity to that given in Fig. 1c. The thermal stability of the congruently melting 2:1 salts is lower than that of the salt derived from the pentyl ester. It must be noted that the stability is enhanced by an increase in the alkyl chain length; that is, 92 °C with the octyl ester salt, 95 °C with the undecyl ester salt, and 97.5 °C with the pentadecyl ester salt. The metastable charge-transfer complex is also stabilized in the same order; namely, 67.5 °C in the octyl ester complex, 82.5 °C in the undecyl ester complex, and 88 °C in the pentadecyl ester complex.

The phase diagrams given by the hexadecyl, heptadecyl, and octadecyl esters are exemplified by

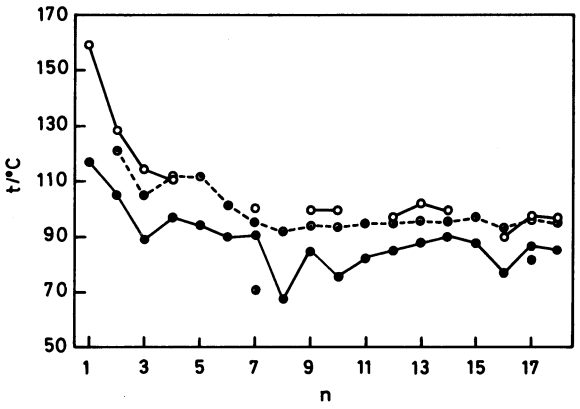

Fig. 2. Congruent or incongruent melting points of the 1 : 1 salt (○), of the 2 : 1 salt (⊙), of the 1 : 1 charge-transfer complex (●), and of the 2 : 1 complex (◐) plotted against the ester alkyl chain length (n).

that of the second member shown in Fig. 1d. Both the 1:1 and 2:1 salts melt congruently. The relative thermal stability of the 1:1 salt is increased by an increase in the alkyl chain length. While the 1:1 salt of the hexadecyl ester melts at 90.5 and the 2:1 salt at 93 °C, the former salt of the octadecyl ester melts at 97 °C and the latter at 95 °C. Note that the two salts in Fig. 1d have approximately the same melting points. Although two metastable charge-transfer complexes melting at 82.5 and 87 °C, respectively, are formed with the heptadecyl ester, the other two esters give only one kind. The hexadecyl ester complex melts at 77.5 °C and the octadecyl ester complex at 85.5 °C. They appear in the composition range covering 50 mol%.

The congruent or incongruent melting points of the 1:1 and 2:1 picrates and also of the 1:1 charge-transfer complex are plotted against the ester alkyl chain length in Fig. 2. The thermal stability of the 1:1 salt represented by open circle diminishes drastically in the first four members. The salt appears intermittently among the higher members. The charge-transfer complex shown by shaded circle is formed with all the esters examined. Contrary to the case of pyrene-*N*-alkyl-2,4,6-trinitroaniline reported earlier,[1] the complexes are similarly colored. Therefore, it is difficult to determine whether the complexes of the lower homologous members are different in the nature from those of the higher members or not. When the 1:1 salt and the 1:1 complex are obtainable with a given ester, the two products may be called isomorphs. The charge-transfer complexes found in the present series are metastable without exception. Nevertheless, one can see that the longer the alkyl group, the thermal stability of the complex comes closer to that of the salt.

The ethyl to octadecyl esters produce 2:1 salts with picric acid. The melting point is least dependent upon the ester alkyl group and is almost constant from the octyl ester to the octadecyl ester. It may be emphasized that complex isomerism is observed even in the 2:1 composition range when the heptyl and heptadecyl esters are the donor compounds.

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