BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (11), 2873—2874 (1974)

Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. X.[1] Picric Acid Complexes with 2,5-Dichloroaniline

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(Received April 13, 1974)

Synopsis. Yellow 2,5-dichloroanilinium picrate was found to isomerize into a red complex of the charge-transfer type at 74 °C with a heat of transition of 4.2 kcal/mol. In addition, a charge-transfer complex with a 1:3 mole ratio was isolated.

Previously we demonstrated that the picrates of all the anilines with pK_a values of less than 3 isomerize into charge-transfer complexes upon melting if not by an enantiotropic transition.[2] Moreover, the chance of finding complex isomers was recognized to be high in the salts derived from *o*-haloanilines.[1,3] The combinations reported to date include picric acid with *o*-bromo- and *o*-iodo-anilines found by Hertel,[4] and methylpicric acid with *o*-chloro- and *o*-bromo-anilines and trinitrobenzoic acid with *o*-chloroaniline, both found by us.[1,3] As 2,5-dichloroaniline has a pK_a value in the above-mentioned range (that is, 1.57),[5] and as its structure fits into the group of *o*-haloanilines, there is a possibility that its picrate exhibits the phenomenon of complex isomerism. However, it must be added that an isomeric amine, 2,4-dichloroaniline, has been known to form only a salt with picric acid.[4]

When equimolar amounts of the component compounds separately dissolved in hot methanol were mixed, yellow fine crystals were precipitated. The composition appeared to be 1:1. Calcd for $C_6H_5NCl_2 \cdot C_6H_3N_3O_7$: C, 36.85; H, 2.06; N, 14.32; Cl, 18.13%. Found: C, 36.68; H, 1.99; N, 14.38; Cl, 17.40%. The product is a true phenolate, as is indicated by the presence of the vibrational pattern characteristic of the anilinium ion extending from 2400 to 3000 cm^{-1}. A color change to red was observed at 74 °C. The isomerization into a complex of the charge-transfer type was confirmed by the replacement of the above-mentioned NH_3^+ pattern by the NH_2 bands appearing at 3375 and 3475 cm^{-1}, and also by the change in the electronic spectrum (see Fig. 1). The maximum of the newly-appeared absorption is located close to that of the charge-transfer absorption in the corresponding *s*-trinitrobenzene complex. Nevertheless, the picric acid complex is more deeply colored than the *s*-trinitrobenzene complex, mainly because of the difference in breadth. The heat of transition was estimated to be about 4.2 kcal/mol by use of a differential scanning calorimeter.

When chloroform was employed as the solvent and the mixture was kept in a refrigerator for a few days, the initially-appearing yellow crystals were replaced by red ones. This complex is of a 1:3 mole ratio and can be kept at room temperature without any noticeable change. Calcd for $C_6H_5NCl_2 \cdot 3C_6H_3N_3O_7$: C, 33.94; H, 1.66; N, 16.49; Cl, 8.35%. Found: C, 33.34; H, 1.50; N, 16.62; Cl, 7.79%. The NH_2 pattern in the vibrational spectrum demonstrates the absence of proton-transfer. As is shown in Fig. 1, the electronic absorption in the visible region is relatively weak if compared with that in the red 1:1 complex, but the location is essentially the same as that in the latter. Therefore, this 1:3 complex is undoubtedly

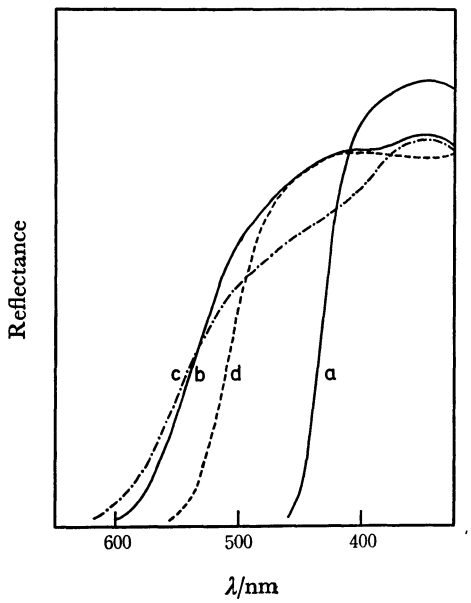

Fig. 1. Reflectance spectra of 2,5-dichloroaniline–picric acid; (a) the yellow 1:1 salt, (b) the red 1:1 complex, and (c) the red 1:3 complex, and (d) the spectrum of the corresponding *s*-trinitrobenzene complex.

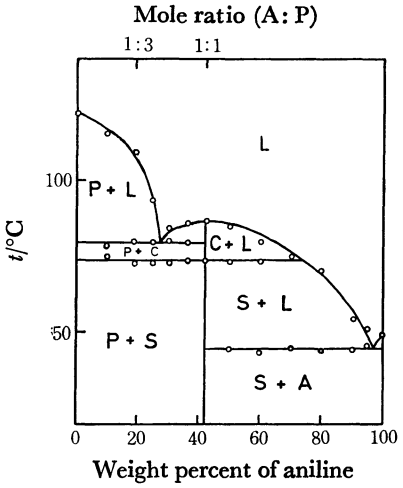

Fig. 2. The 2,5-dichloroaniline–picric acid phase diagram.

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of the charge-transfer type. An endothermic peak of about 4.8 kcal/mol was recorded at 69 °C in the thermogram. Once heated above this temperature, the color turns yellow after storage at room temperature for a few days.

The phase diagram of the 2,5-dichloroaniline–picric acid system was prepared by the calorimetric method in an effort to find out whether or not there is salt with a 1:3 composition. The results presented in Fig. 2 clearly indicate that the 1:1 salt and its isomeric complex of the charge-transfer type are the only compounds formed between picric acid and 2,5-dichloroaniline by direct fusion. At the composition of the red 1:3 complex, the room-temperature phase was a mixture of the 1:1 salt and picric acid. The eutectic point at which the 1:1 complex (C in Fig. 2) and picric acid (P) coexist with liquid (L) was found at 80 °C and at about a 27 weight percentage of aniline, and that at which the 1:1 salt (S) and aniline (A) coexist with liquid, at 45 °C and at a small weight percentage of the acid.

References

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