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Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. VII.[1] Complex Isomerism in Several Anilinium Alkyl-substituted Picrates

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o-Chloroanilinium and *o*-bromoanilinium methylpicrates are obtainable not only as yellow-colored salts, but also as unstable, monotropic reddish-orange forms. Spectroscopic studies have revealed that the latter are charge-transfer complexes composed of the aniline molecule acting as an electron-donor and the acid molecule acting as an acceptor. Similar monotropic forms have been found in combinations of dimethylpicric acid with *o*-iodoaniline, *o*-bromoaniline, and *N,N*-dimethylamino-*p*-benzaldehyde.

About half a century ago, Hertel found that yellow-colored *o*-bromoanilinium picrate turns reddish-orange upon heating above 95 °C.[2] On the basis of the similarity in color and melting point with the corresponding *s*-trinitrobenzene complex, he concluded that the deeply-colored high-temperature form is a molecular compound composed of the aniline and the acid. As was confirmed by our spectroscopic examinations,[3] this is a charge-transfer complex in present-day terminology. The yellow picrate and the reddish-orange picric acid complex are enantiotropically related to each other. Hertel named this phenomenon "complex isomerism". Several more combinations including *o*-iodoanilinium picrate have been reported by Hertel to behave similarly.

With the hope of finding new organic compounds which exhibit solid-state transformations accompanied by a color change, we have examined series of anilinium methylpicrates and dimethylpicrates. These alkyl-substituted picric acids have been reported by Mariella *et al.* to form salts with aniline and its *N,N*-dimethyl derivative.[4] All of them have been noted to decompose at their melting points.

Experimental

Materials. The methylpicric acid and dimethylpicric acid were prepared by the nitration of *m*-cresol and 3,5-dimethylphenol respectively.[5] All the aromatic amines used in this work were commercially obtained. The anilinium alkyl-substituted picrates were precipitated by mixing the component compounds separately dissolved in chloroform or benzene.

Measurements. The vibrational and electronic spectra were measured as has been reported in the first paper of this series.[6] The X-ray measurements were made with a Toshiba recording diffractometer, Model ADG-301, using filtered copper radiation.

Results and Discussion

The combinations of methylpicric acid with *N,N*-diethyl-*m*-toluidine ($pK_a=7.12$), *N,N*-dimethyl-*o*-toluidine (6.11), *N,N*-dimethyl-*m*-toluidine (5.34), *N,N*-dimethylaniline (5.15), and *N*-methylaniline (4.85) give yellow compounds in both the solid and molten states. The presence of broad vibrational bands in the region from 2250 to 2750 cm^{-1} indicates that they are true phenolates formed by means of proton-transfer from the acid to the anilines. The solid products with the following seventeen anilines (arranged in the order of decreasing pK_a values) were also found to be salts: *p*-anisidine, *p*-phenetidine, *p*-toluidine, 2,4-dimethylaniline, *m*-toluidine, aniline, *o*-anisidine, *o*-phenetidine, *o*-toluidine, *m*-anisidine, *p*-chloroaniline, *m*-chloroaniline, 3-nitro-4-methylaniline (2.96), *o*-chloroaniline (2.71), *o*-iodoaniline (2.60), *o*-bromoaniline (2.55), and *m*-nitroaniline (2.46). The first twelve salts rapidly decompose below or at the melting points; therefore, the color of the melts could not be observed at all. On the other hand, the yellow salts derived from the last five turn red or reddish-orange upon melting. As will be described in the following paragraph, this color change can be attributed to the appearance of an additional electronic absorption near 500 nm. Moreover, the melting is accompanied by the replacement of the vibrational bands assignable to the NH_3^+ group by those characteristic of the NH_2 group. Therefore, we may conclude that these phenolates isomerize into complexes of the charge-transfer type at their melting points. Such an isomerization by melting has already been observed by us in some anilinium picrates and also in 2,4-dinitrophenolates.[6,7]

The lower limit of the pK_a range of aniline, in which the phenomenon of complex isomerization by melting is observable, has been shown to be close to the pK_a value of the acid component in the cases of the 2,4-dinitrophenolates.[7] On the other hand, the limit could not be determined in the cases of the picrates because of the lack of anilines in the desired pK_a range. Nonetheless, *p*-nitroaniline, the pK_a value of which is located a little above the value of picric acid, was found to form a charge-transfer complex. In the present case, the pK_a value of the acid component has not

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[1] Part VI: G. Saito and Y. Matsunaga, This Bulletin, **46**, 1609 (1973).

[2] E. Hertel, *Ann.*, **451**, 179 (1926).

[3] R. Osawa, E. Osawa, and Y. Matsunaga, Paper presented at the Symposium on Molecular Structures, October 1971, Kyoto.

[4] R. P. Mariella, M. J. Gruber, and J. Elder, *J. Org. Chem.*, **26**, 3217 (1961).

[5] C. E. Moore and R. Peck, *ibid.* **20**, 673 (1955).

[6] G. Saito and Y. Matsunaga, This Bulletin, **44**, 3328 (1971).

[7] N. Inoue and Y. Matsunaga, *ibid.*, **45**, 3478 (1972).

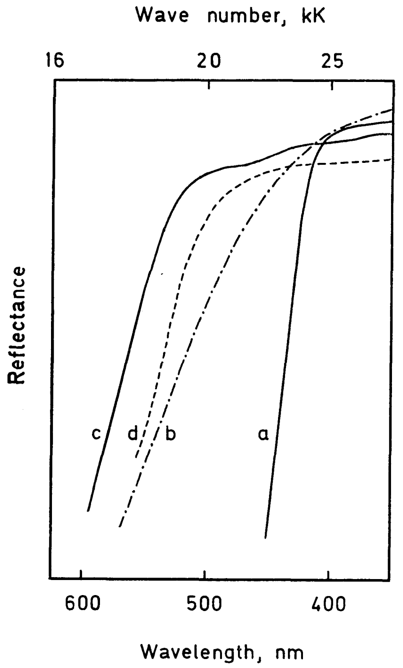

Fig. 1. Reflectance spectra, a) the stable yellow form of the *o*-chloroaniline-methylpicric acid complex, b) the same complex in the molten state, c) the unstable reddish-orange form, and d) the *o*-chloroaniline-*s*-trinitrobenzene complex.

been well established. Although Moore and Peck have reported that the acidity of methylpicric acid is considerably lowered (pK_a=2.8) as compared to that of picric acid itself,[5] this value may be in the range from 1 to 2, according to Mariella *et al.*[4]

When the reddish-orange melts of *o*-chloroanilinium and *o*-bromoanilinium methylpicrates are solidified, the color does not return to yellow. After storage at room temperature for several days; however, a gradual change to yellow became noticeable. Contrary to the case with most of the complex isomers studied by Hertel, these reddish-orange forms are monotropically related to the yellow forms. The melting point of the yellow form of the *o*-chloroanilinium methylpicrate was found to be higher than that of the reddish-orange form (101—102 *vs.* 72—73 °C), in accordance with Hertel's observation for the only complex isomers monotropically related to each other (4-bromo-1-naphthylamine-2,6-dinitrophenol; 91—92 *vs.* 85 °C).[8] For the *o*-bromoanilinium salt, the corresponding values are 102—103 °C and 74—75 °C. As is shown in Fig. 1, the reflectance spectrum of the yellow form of the *o*-chloroaniline complex has a strong absorption below 450 nm which is assignable to the methylpicrate ion. Upon melting, a broad absorption band covering the range from 450 to 570 nm appears. The unstable form shows a strong absorption in the same region as the melt does. The similarity between the spectrum of the reddish-orange form and that of the *s*-trinitrobenzene complex (shown by Curve d) indicates that this broad absorption band arises from the charge-transfer interaction between the amine and the acid. The weakness of the charge-transfer absorption in the melt may be explained by a partial dissociation of the complex to the component molecules at high experimental temperatures.

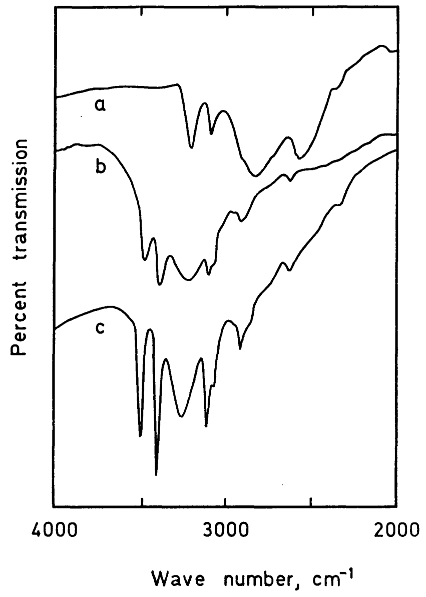

Fig. 2. Vibrational spectra, a) the stable yellow form of the *o*-chloroaniline-methylpicric acid complex, b) the same complex in the molten state, and c) the unstable reddish-orange form.

The examination of the vibrational spectra in the region from 2000 to 4000 cm^{-1} was more rewarding, and bands characteristic of the aniline and anilinium ion were well verified. In Fig. 2, the spectrum of the yellow form is compared with that of the melt and also with that of the reddish-orange form. The broad bands located at 2550 and 2820 cm^{-1} in the yellow form constitute the pattern characteristic of the anilinium ion. The sharp bands in the unstable form appearing 3250 and 3500 cm^{-1} may be assigned to the aniline, more particularly to a NH_2 stretching vibration. The spectrum of the melt consists of rather broad bands but is undoubtedly similar to that of the reddish-orange form, in accordance with the conclusion drawn on the basis of the electronic spectra. The behavior of the *o*-bromoanilinium methylpicrate resembles that of the above-mentioned *o*-chloroanilinium salt. On the other hand, the molten charge-transfer complexes of 3-nitro-4-methylaniline, *o*-iodoaniline, and *m*-nitroaniline reversibly isomerize into yellow salts upon solidification.

N,*N*-Dimethylamino-*p*-benzaldehyde, 2,5-dichloroaniline, and *p*- and *o*-nitroanilines, the pK_a values of which are the lowest among those of the anilines examined, ranging from −0.26 to 1.62, were found to form charge-transfer complexes in both solids and melts. These observations seem to be in accordance with the view that the pK_a value of methylpicric acid is in the range from 1 to 2.

Dimethylpicric acid forms yellow salts, which rapidly decompose below or at the melting points, with the following anilines: *p*-anisidine, *p*-phenetidine, 2,4-dimethylaniline, *N*-methylaniline, *m*-toluidine, aniline, *o*-anisidine, *o*-phenetidine, *o*-toluidine, *m*-anisidine, *p*-

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[8] E. Hertel and J. van Cleef, *Ber.*, **61**, 1545 (1928).

chloroaniline, *m*-chloroaniline, and 3-nitro-4-methylaniline. Their pK_a values are 2.96 or higher. The dimethylpicrates derived from *o*-chloroaniline, *o*-iodoaniline, *o*-bromoaniline, *m*-nitroaniline, and *N*,*N*-dimethylamino-*p*-benzaldehyde turn red or reddish-orange upon melting. Their melting points are consistently higher than those of the corresponding methylpicrates, 133—134 *vs.* 101—102, 96—97 *vs.* 89—90, 124—125 *vs.* 102—103, 123—124 *vs.* 110, and 99—100 *vs.* 82 °C respectively. The isomerization to complexes of the charge-transfer type was proved by spectroscopic examinations, as has been described for the cases of the methylpicrates. Among the five, the complexes of *o*-iodoaniline, *o*-bromoaniline, and *N*,*N*-dimethylamino-*p*-benzaldehyde were found to solidify without any color change. However, none of them was stable enough to be heated to the melting point. Even the physical measurements at room temperature could be carried out only for the last-mentioned complex. Thus, these complex isomers are also monotropically related to the yellow salts. The acidity of dimethylpicric acid has been estimated to be lower by 0.5 pK_a unit than that of methylpicric acid.[5] Nevertheless, we found that *N*,*N*-dimethylamino-*p*-benzaldehyde forms a charge-transfer complex with methylpicric acid, but a true phenolate with dimethylpicric acid. Charge-transfer complexes of dimethylpicric acid were obtained with 2,5-dichloroaniline and *p*-nitroaniline.

Hertel and Schneider have found that the complex isomers of 4-bromo-1-naphthylamine-2,6-dinitrophenol have crystal structures distinctly different from each other;[9] this is also the case with ours. The X-ray diffraction patterns are schematically presented in Fig. 3 for all the pairs examined. The longest spacings in the unstable forms of the methylpicrates are shorter than those in the stable yellow forms; *e.g.*, 7.2 Å *vs.* 9.2 Å in the isomers of the *o*-chloroaniline complex.

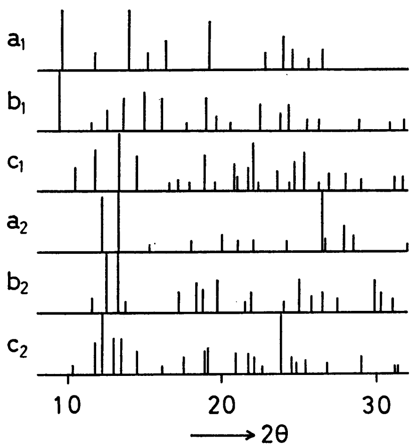

Fig. 3. X-Ray diffraction patterns, a) the *o*-chloroaniline-methylpicric acid, b) the *o*-bromoaniline-methylpicric acid, and c) the *N*,*N*-dimethylamino-*p*-benzaldehyde-dimethylpicric acid. The subscript 1 denotes the stable form and 2 the unstable form.

All the aromatic amines in the eight pairs of the complex isomers found by Hertel are halogenated derivatives.[2] The observations made by Hertel and also by us strongly suggest that the chance of finding complex isomers is high in the salts derived from halogenated amines, especially *o*-haloanilines. However, the amines in our five pairs of complex isomers include one free from halogen; that is, *N*,*N*-dimethylamino-*p*-benzaldehyde. In addition, a pair of complex isomers has been prepared by us with another amine bearing no halogen. When *o*-dianisidine is combined with tetranitrobiphenyl-4,4′-diol in a mole ratio of 1: 1, a yellow salt and a black complex of the charge-transfer type are obtained.[1]

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

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[9] E. Hertel and K. Schneider, *Z. Phys. Chem.*, **B13**, 387 (1931).