BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3478—3479 (1972)

Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. III.[1] 2,4-Dinitrophenol Complexes with Various Anilines

Nobuaki INOUE and Yoshio MATSUNAGA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received April 22, 1972)

When picric acid is combined with a number of the derivatives of aniline, the acid-base interaction generally predominates in both the solid and molten states. However, we found earlier that the complexes with the following four anilines can be essentially of the charge-transfer type above the melting points: *o*-chloroaniline, *m*-nitroaniline, 3-nitro-4-methylaniline, and *N*,*N*-dimethylamino-*p*-benzaldehyde.[2] Their pK_a values are rather low, in the range between 1.6 and 3.0.

2,4-Dinitrophenol is weaker than picric acid as a proton-donor; that is, the pK_a value of the former phenol is higher, at least by 3, than that of the latter. If the range of pK_a values of anilines, in which the phenomenon of complex isomerization by melting is observable, is essentially determined by the balance between the pK_a value of a polynitrophenol and those of anilines, one would expect the range observable with 2,4-dinitrophenol to be shifted higher by approximately the above-mentioned amount than that found with picric acid. Hertel's observation that this dinitrophenol forms a yellow complex with *o*-anisidine (pK_a=4.52) and a red one with *p*-bromoaniline (pK_a=3.86) seems not to be inconsistent with this anticipation.[3]

We attempted to prepare molecular complexes of 2,4-dinitrophenol with about thirty derivatives of anilines. The complexes dissolve well into most organic solvents. Chloroform was often found to be suited for the isolation. The solid complexes were obtained, with the nineteen anilines arranged in the order of decreasing pK_a value as is shown in Table 1.[4] Ten anilines from *p*-anisidine to *m*-anisidine, the pK_a values of which are above 4.20, were found to form yellow-colored complexes with 2,4-dinitrophenol. The presence of a NH_3^+ pattern in their vibrational spectra indicates that they are salts formed by means of proton-transfer from the phenol to the anilines. All of them turn orange or red upon melting. The isomerization was confirmed by measuring the vibrational and electronic spectra above the melting points. For example, Fig. 1 presents the vibrational spectra in the region from 2000 to 4000 cm^{-1} of the *p*- and *m*-anisidine complexes in the solid and molten states. By a comparison with the spectra of the corresponding anilinium chloride, two broad bands appearing at about 2600 and 2900 cm^{-1} in the spectra of the solid complexes were assigned to the NH_3^+ group. This pattern has been well known to be typical of picrates of primary amines.[5] Upon melting, the above-mentioned broad bands disappear and several sharp bands are observed in the region from 2850 to 3450 cm^{-1} (see Curves b and d). The bands at 2840, 2950, 3350, and 3450 cm^{-1} arise from the aniline, and those at 3100 and 3250 cm^{-1}, from the phenol. The two located at 3350 and 3450 cm^{-1} can be assigned to the NH_2 group. These solid complexes exhibit electronic absorptions only below 500 nm; however, the appearance of an absorption band in the

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[1] Part II. Y. Matsunaga and G. Saito, This Bulletin, **45**, 963 (1972).

[2] G. Saito and Y. Matsunaga, *ibid.*, **44**, 3328 (1971).

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

[4] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution", Butterworths, London (1965), pp. 58—91.

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

TABLE 1. 2,4-DINITROPHENOL COMPLEXES WITH VARIOUS ANILINES

Aniline	pK_a	Color below mp	mp	Color above mp
p-Anisidine	5.34	Bright yellow	117 —118	Red
p-Phenetidine	5.20	Dark yellow	110	Red
p-Toluidine	5.09	Yellow	111 —112	Red
2,4-Dimethylaniline	4.90	Yellow	89 — 90	Red
m-Toluidine	4.68	Yellow	92 — 93	Red
Aniline	4.59	Yellow	78 — 80[a)]	Red
o-Anisidine	4.52	Yellow	85 — 86	Red
o-Phenetidine	4.43	Golden yellow	76 — 77	Red
o-Toluidine	4.39	Yellow	54.5— 55	Orange
m-Anisidine	4.20	Yellow	73 — 74	Red
p-Chloroaniline	3.99	Red	57.5— 58.5	Red
p-Bromoaniline	3.86	Red	70[b)]	Red
3-Nitro-4-methylaniline	2.96	Orange	73	Orange
o-Chloroaniline	2.71	Orange	51	Orange
o-Iodoaniline	2.60	Orange	55	Orange
o-Bromoaniline	2.55	Orange	54	Orange
m-Nitroaniline	2.46	Yellow	79	Yellow
N,N-Dimethylamino-*p*-benzaldehyde	1.62	Red	87 — 88	Red
p-Nitroaniline	0.99	Yellow	96.5	Yellow

a) 78—79°C by Hertel, Ref. 3. b) Reported by Hertel, Ref. 3.

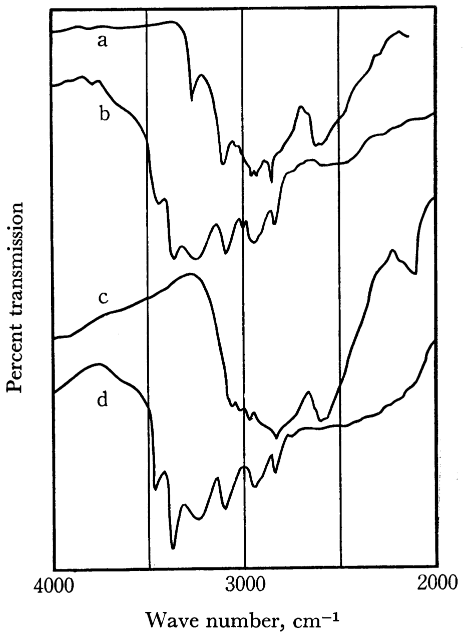

Fig. 1. Vibrational spectra, a) the *p*-anisidine-2,4-dinitrophenol at room temperature, b) the same above the melting point, c) the *m*-anisidine-2,4-dinitrophenol at room temperature, and d) the same above the melting point.

region from 500 to 600 nm was noted in the melts. The corresponding *m*-dinitrobenzene complex could be isolated only with unsubstituted aniline. The similarity in spectrum between the molten 2,4-dinitrophenol complex and the *m*-dinitrobenzene complex suggests that the band appearing upon melting is due to the intermolecular charge-transfer interaction. No change in color was observed upon the melting of the rest of the solid complexes. Their vibrational spectra indicate the absence of proton-transfer either in the solid state or in the molten state. These nine complexes may be supposed to be of the charge-transfer type.

The lower limit of the pK_a range where the phenomenon of complex isomerization by melting is observable appears to be very close to the pK_a of 2,4-dinitrophenol, 4.09.[6)] The results given in Table 1 show that a complex is of the proton-transfer type when the pK_a value of aniline is higher than this and that a complex is of the charge-transfer type when the pK_a value of aniline is lower. It must be added that such a coincidence is not necessarily seen with other phenols. On the basis of the vibrational spectrum, the *p*-nitroaniline-picric acid complex was found to be of the charge-transfer type. Although the pK_a values reported for picric acid are rather scattered, ranging from 0.22 to 0.708,[6)] *p*-nitroaniline has a pK_a value higher than they.

On the other hand, the upper limit of the pK_a range could not be established with the present phenol. Possibly, it is located higher than the upper limit observed with picric acid, the 2.96 of 3-nitro-4-methylaniline, by approximately the difference between the pK_a values of these two phenols.

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6) G. Kortüm, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworths, London (1961), pp. 452, 453.