BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(4), 1020—1021 (1974)

Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. VIII.[1] Benzidine–2,4-Dinitrophenol Complexes

Gunzi Saito* and Yoshio Matsunaga**

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received July 17, 1973)

Synopsis. The simultaneous operation of charge-transfer and proton-transfer interactions was demonstrated in the orange complex and also in the brown complex of a 3 : 2 composition. The former one quickly becomes the yellow monohydrate of the 1 : 1 salt upon exposure to air.

Buehler and Heap have reported that the benzidine–2,4-dinitrophenol (1 : 1) complex is brown when it is prepared in absolute ethanol, while it is yellow when 95% ethanol is employed as the solvent.[2] The latter complex contains 1 mol of water. As the first pK_a value of the diamine is higher than the value of the dinitrophenol (namely, 4.95 *vs.* 4.09), it does not seem likely that the brown-colored complex is of the charge-transfer (CT) type.[3] We can also eliminate the possibility that this "1 : 1 complex" is of the same type as the brick red-colored *o*-tolidine–picric acid (1 : 1) complex previously described by us.[4] If the brown benzidine-dinitrophenol complex belongs to Case 1 of CPT complexes as defined in a previous paper, a part of the diamine molecule acts as a proton-acceptor, while the other part has a CT interaction with the dinitrophenolate anion. The electron-donor strength of the monoprotonated benzidine can be essentially determined from that of the unprotonated part. By analogy with the case of the picrate anion,[4–7] the acceptor strength of the dinitrophenolate anion can be expected to be close to that of *m*-dinitrobenzene; therefore, the color of the 1 : 1 complex cannot be deeper than that of the aniline–*m*-dinitrobenzene complex. The observation the above-mentioned workers is undoubtedly in disagreement with this expectation.

By mixing equimolar amounts of the component compounds separately dissolved in hot chloroform which contains 0.05% of water according to the manufacturer, a yellow complex was obtained. Calcd for $C_{12}H_{12}N_2 \cdot C_6H_4N_2O_5 \cdot H_2O$: C, 55.96; H, 4.66; N, 14.51%. Found: C, 56.06; H, 4.70; N, 14.37%. When the solvent was dried with calcium chloride and the mixture was kept in a refrigerator, an orange-colored complex appeared. This complex quickly turned yellow upon exposure to air. After the color change, the composition was in good agreement with that of the monohydrate of the 1 : 1 complex. Found: C, 56.06; H, 4.84%. The brown complex was isolated at room temperature from a dried chloroform solution containing the diamine in excess and also from an absolute ethanol solution as has been reported by Buehler and Heap. Calcd for $3C_{12}H_{12}N_2 \cdot 2C_6H_4N_2O_5$: C, 61.69; H, 4.78; N, 15.22%. Found: C, 61.96; H, 4.95% (from chloroform) and C, 62.61; H, 4.78; N, 15.20% (from ethanol).

The vibrational spectrum of the yellow monohydrate clearly indicates the presence of water by a band at

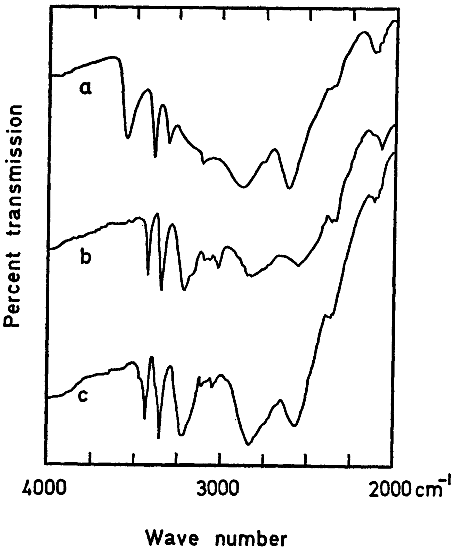

Fig. 1. Vibrational spectra, a) the yellow benzidine–2,4-dinitrophenol complex, b) the orange complex, and c) the brown complex.

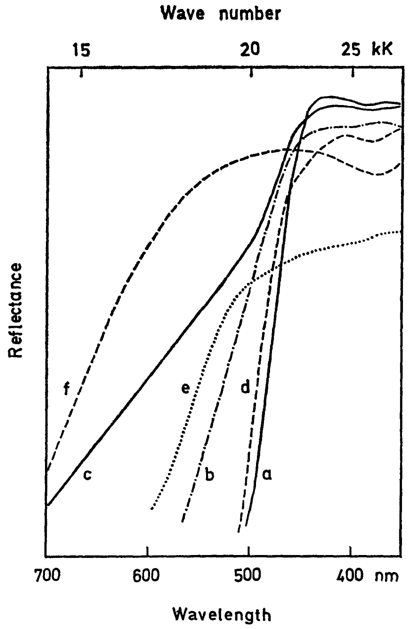

Fig. 2. Reflectance spectra, a) the yellow benzidine–2,4-dinitrophenol complex, b) the orange complex, c) the brown complex, d) sodium 2,4-dinitrophenolate, e) the aniline–*m*-dinitrobenzene complex, and f) the benzidine–*m*-dinitrobenzene complex.

---

* Present address: Department of Chemistry, Emory University, Atlanta, Georgia, 30322, U.S.A.

** To whom inquiries may be addressed.

3550 cm^{-1}, that of the NH_2 group by bands at 3320 and 3395 cm^{-1}, and that of the NH_3^+ group by those in the region from 2500 to 3000 cm^{-1}. As is shown by the spectrum in Fig. 1, the newly-found orange complex is undoubtedly free from water. In accordance with the composition, bands assignable to both the NH_2 and NH_3^+ groups are also detected in the orange- and brown-colored complexes.

The diffuse reflectance spectrum of the yellow complex is similar to that of sodium dinitrophenolate. Therefore, it may be concluded that the monohydrate is a salt formed by means of the proton-transfer from the phenol to the diamine. The orange complex exhibits an additional absorption band located close to the CT band in the aniline–*m*-dinitrobenzene complex (see Fig. 2). On the other hand, the location of the additional absorption band appearing in the brown 3 : 2 complex can be well compared with that of the CT band in the benzidine–*m*-dinitrobenzene complex. On the basis of these spectroscopic observations, we may conclude that the deeply-colored complexes are of the CPT type, but belong to different cases.$^{4)}$ In both complexes, the electron-acceptor is the dinitrophenolate anion. The electron-donor in the orange complex is the monoprotonated benzidine cation, while that in the brown complex is the diamine molecule.

Buehler and Heap have concluded the composition of the brown complex to be 1 : 1 on the basis of the nitrogen content, which does not depend much on the mole ratio. Their results, 14.94 and 14.92%, seem not to be inconsistent with the newly-assigned composition, for which N is 15.22%.

References

1) Part VII: N. Inoue and Y. Matsunaga, This Bulletin, **46**, 3345 (1973).
2) C. A. Buehler and A. G. Heap, *J. Amer. Chem. Soc.*, **48**, 3168 (1926).
3) N. Inoue and Y. Matsunaga, This Bulletin, **45**, 3478 (1972).
4) G. Saito and Y. Matsunaga, *ibid.*, **46**, 714 (1973).
5) Y. Matsunaga and G. Saito, *ibid.*, **45**, 963 (1972).
6) G. Saito and Y. Matsunaga, *ibid.*, **45**, 2214 (1972).
7) Y. Matsunaga, *ibid.*, **46**, 998 (1973).