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Charge-transfer and Proton-transfer in the Formation of Molecular Complexes. II.[1] Kofler's Ternary Molecular Complex

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The interaction between an aromatic amine and picric acid generally results in the formation of a yellow-colored 1: 1 salt by means of proton-transfer. By adding pyridine to a mixture of α-naphthylamine and picric acid, Kofler isolated a red-colored complex, the composition of which happened to be α-naphthylamine-pyridine-picric acid (1: 1: 1).[2] To explain the deep color of this mixed picrate, he assumed that the pyridine molecule is bound to the hydroxy group of picric acid, while the aromatic amine interacts with the nitro groups of the acid. So far, however, no spectroscopic study of this ternary molecular complex has been reported.

As is shown in Fig. 1, the vibrational spectrum of the 1: 1 salt derived from α-naphthylamine and picric acid, examined as a Nujol mineral oil mull, has sharp bands at 3075 and 3200 cm^{-1} and broader ones in the

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[1] Part I: G. Saito and Y. Matsunaga, This Bulletin, **44**, 3328 (1971).

[2] A. Kofler, *Z. Elektrochem.*, **50**, 200 (1944).

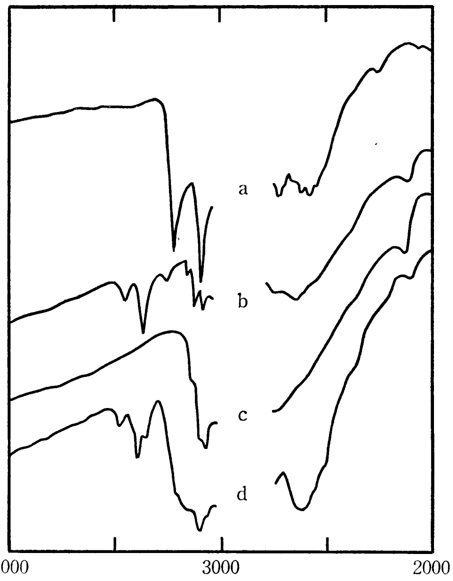

Fig. 1. Vibrational spectra; (a) α-naphthylamine-picric acid (1:1), (b) α-naphthylamine-pyridine-picric acid (1:1:1), (c) pyridine-picric acid (1:1), (d) α-naphthylamine-picric acid (2:1).

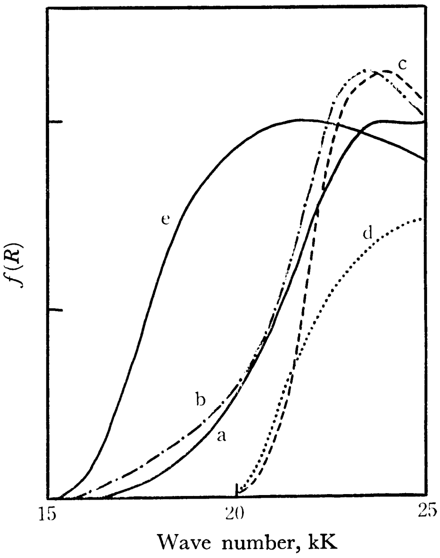

Fig. 2. Diffuse reflection spectra; (a) α-naphthylamine-pyridine-picric acid (1:1:1), (b) α-naphthylamine-picric acid (2:1), (c) α-naphthylamine-picric acid (1:1), (d) pyridine-picric acid (1:1), (e) α-naphthylamine-*s*-trinitrobenzene (1:1).

region from 2500 to 2800 cm^{-1}. This pattern is typical of picrates of primary amines. The first one is assigned to the picrate ion, and the second, to a NH_3^+ stretching frequency.[3] In the spectrum of the ternary complex, bands due to the amine appear at 3250, 3350, and 3450 cm^{-1} instead of at the above-mentioned locations. Although the spectrum in Fig. 1 presents no conclusive evidence for the protonation of pyridine, the pattern in the region below 1700 cm^{-1} includes that of the yellow-colored pyridinium picrate. Thus, the examination of the vibrational spectrum leads to the conclusion that the complex consists of pyridinium picrate and α-naphthylamine. This conclusion is in accordance with the fact that the pK_a value of pyridine is higher than that of the amine, *i.e.*, 5.22 *vs.* 3.92.[4] Kofler also reported the preparation of an orange-colored α-naphthylamine-picric acid (2: 1) complex, "semipicrate" in his nomenclature. As may be expected, its vibrational spectrum indicates the presence of both NH_2 and NH_3^+ groups in this complex (see Curve d in Fig. 1).

Both the ternary molecular complex and the 2: 1 complex are deeply colored. The diffuse reflection spectra given in Fig 2 clearly show that a broad weak absorption, the maximum of which is located around 20 kK, appears upon the incorporation of pyridine or additional α-naphthylamine into the 1: 1 salt. The new absorption must be due to a charge-transfer interaction. The electron donor is undoubtedly α-naphthylamine. As the locations of the absorption maximum are nearly identical, the acceptor component is possibly a common species, namely, the picrate ion. A comparison with the spectrum of the *s*-trinitrobenzene complex suggests that the picrate ion is as strong as trinitrobenzene as an acceptor. The strength of picric acid is comparable with that of *s*-trinitrobenzene; therefore, it may be argued that the acceptor-strength is not much affected by the ionization. Further evidence to support this conclusion will be presented in a subsequent paper.[5] On the basis of this spectroscopic study, one may conclude that, in Kofler's ternary complex, a proton is transferred from picric acid to pyridine and that the interaction between α-naphthylamine and the picrate ion is of the charge-transfer type. It must be added that the explanation suggested by Kofler, of course in the terminology at that time, is in essential agreement with the present conclusion.

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

[4] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London (1965), pp. 124 and141.

[5] G. Saito, and Y. Matsunaga, This Bulletin, submitted.