BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1247—1248(1972)

The Formation of Solid Addition Compounds between Several *para*-Substituted Benzoic Acids and Piperidine

Setsuo KASHINO, Keiko KANEI, and Shigeo HASEGAWA
Department of Chemistry, Faculty of Science, Okayama University, Tsushima, Okayama

(Received August 27, 1971)

The formation of solid 1: 1 and 2: 1 addition compounds from benzoic acid and piperidine has previously been reported.[1]

This paper will describe the formation of the same type of addition compound from several *para*-substituted benzoic acids and piperidine, and will present some characteristic features of the infrared spectra of these compounds.

Experimental

Materials. The piperidine (GR-grade reagent) was used without further purification. The *p*-methyl-, *p*-chloro-, *p*-bromo-, and *p*-nitrobenzoic acids (each GR grade reagent) were recrystallized from benzene and dried over $CaCl_2$. Sodium salts of these substituted benzoic acids were prepared by the neutralization of the acids with a standard aqueous solution of sodium hydroxide. All the salts were dried at 110°C. The potassium hydrogen dibenzoate was prepared by the method described by Skinner *et al.*[2] The benzene was dried over metallic sodium and distilled.

The Addition Compound Formation. The 1: 1 addition compounds of *p*-methyl-, *p*-chloro-, *p*-bromo-, and *p*-nitrobenzoic acids with piperidine were prepared as follows: in a warm benzene solution of piperidine, an equimolar amount of the acid was dissolved. When the solution was then left to stand in a desiccator, crystals were separated out. They were recrystallized from benzene and then dried over $CaCl_2$.

p-Methylbenzoic acid–piperidine 1: 1 addition compound: mp 119°C.

Found: C, 70.45; H, 8.31; N, 5.86%. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33%.

p-Chlorobenzoic acid–piperidine 1: 1 addition compound: mp 121°C.

Found: C, 59.15; H, 6.46; N, 5.50%. Cacld for $C_{12}H_{16}NO_2Cl$: C, 59.63; H, 6.67; N, 5.80%.

p-Bromobenzoic acid–piperidine 1: 1 addition compound: mp 120°C.

Found: C, 50.16; H, 5.98; N, 4.82%. Calcd for $C_{12}H_{16}NO_2Br$: C, 50.37; H, 5.64; N, 4.89%.

p-Nitrobenzoic acid–piperidine 1: 1 addition compound: mp 158°C.

Found: C, 57.17; H, 6.25; N, 11.01%. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.10%.

The 2: 1 addition compounds of *p*-methyl-, *p*-chloro-, and *p*-nitrobenzoic acids with piperidine were prepared by dissolving equimolar quantities of each acid and the 1: 1 addition compound in hot benzene, and by then allowing the solution to cool; they were recrystallized from benzene and then dried over $CaCl_2$.

p-Methylbenzoic acid-piperidine 2: 1 addition compound: mp 113°C.

Found: C, 70.75; H, 7.48; N, 3.98%. Calcd for $C_{21}H_{27}NO_4$: C, 70.56; H, 7.61; N, 3.92%.

p-Chlorobenzoic acid–piperidine 2: 1 addition compound: mp 140°C.

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[1] S. Kashino, This Bulletin, **41**, 248 (1968).

[2] J. M. Skinner, G. M. D. Stewart, and J. C. Speakman, *J. Chem. Soc.*, **1954**, 180.

Found: C, 58.18; H, 5.20; N, 3.58%. Calcd for $C_{19}H_{21}NO_4Cl_2$: C, 57.30; H, 5.32; N, 3.52%.

p-Nitrobenzoic acid–piperidine 2: 1 addition compound: mp 177°C.

Found: C, 54.72; H, 4.88; N, 10.03%. Calcd for $C_{19}H_{21}N_3O_8$: C, 54.41; H, 5.05; N, 10.02%.

The Infrared Spectra. The infrared spectra were obtained by the usual KBr disk method at room temperature, using a Nihon-Bunko IR-S spectrophotometer.

Results and Discussion

In the infrared spectra of the 1: 1 addition compounds, no band characteristic of an un-ionized carboxyl group near 1700 cm^{-1} is observed, whereas antisymmetric and symmetric carboxylate stretching bands are observed near 1550 and 1400 cm^{-1} respectively. The peak positions of these bands are listed in Table 1, along with those of the corresponding sodium benzoates.

TABLE 1. THE CO_2^- STRETCHING FREQUENCIES OF THE *para*-SUBSTITUTED BENZOIC ACID-PIPERIDINE 1: 1 ADDITION COMPOUNDS (A) IN COMPARISON WITH THE CORRESPONDING SODIUM BENZOATES (B)

Substituent	Antisymmetric stretching ferquencies (cm^{-1})		Symmetric stretching frequencies (cm^{-1})	
	A	B	A	B
CH_3	1540	1540	1378	1414
H	1550[a]	1552[b]	1385[a]	1413[b]
Cl	1540	1436	1382	1406
Br	1525	1548	1375	1427
NO_2	1560	1578	—	—

a) Data from Ref. 1. b) Data from Ref. 3.

The spectra of the 1: 1 addition compounds were very similar to those of the corresponding sodium salts. Therefore, it may be concluded that the acid moiety in these 1: 1 addition compounds is almost fully ionized. However, it should be noted that the symmetric carboxylate stretchings of the addition compounds show lower values than those of the corresponding sodium salts. Since the vibrational frequency in a solid may be influenced by a number of factors,[3] no conclusive explanation of this behavior can be made. The X-ray crystallographic analysis of these adducts is now in progress.

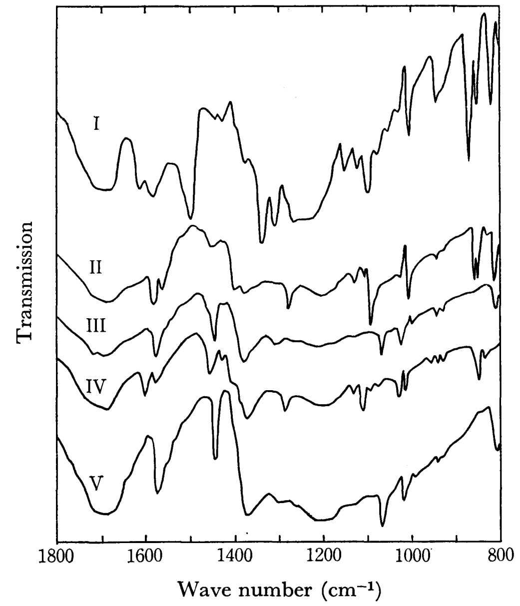

Fig. 1. Infrared spectra of the *para*-substituted benzoic acid-piperidine 2: 1 addition compounds (I—IV) and potassium hydrogen dibenzoate (V).
Substituent: I, NO_2; II, Cl; III, H; IV, CH_3

The infrared spectra of the 2: 1 addition compounds are shown in Fig. 1, along with those of potassium hydrogen dibenzoate.

The crystal structures of a series of acidic potassium salts of carboxylic acids have been studied by Speakman and his co-workers.[2,4–6] They have shown that, in many of these compounds, but not in potassium hydrogen di-*p*-nitrobenzoate,[4] the acid residues are joined to form dimers by a short and effectively symmetrical hydrogen bond.[2] According to Shrivastava and Speakman,[4] a characteristic feature of the infrared spectra of such compounds with a symmetrical hydrogen bond is a high background absorption spreading for several hundred wave numbers in the low-frequency region.

It may be noted here that all the present 2: 1 addition compounds apart from that of *p*-nitrobenzoic acid have a high background absorption in the region about 800—1100 cm^{-1}; these absorptions are very similar to those of the acidic potassium salts studied by Speakman and his co-workers.[2,5]

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3) J. H. S. Green, W. Kynaston, and A. S. Lindsey, *Spectrochim. Acta*, **17**, 486 (1961).

4) H. N. Shrivastava and J. C. Speakman, *J. Chem. Soc.*, **1961**, 1151.

5) H. H. Mills and J. C. Speakman, *ibid.*, **1963**, 4355.

6) J. C. Speakman, *Chem. Commun.*, **1967**, 32.