The Solid Complex Formation of Benzoic Acid with Piperidine

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A study of the carboxylic acids - amines system in benzene led Bruckenstein and Saito[1] to identify the 1 : 1, 2 : 1, and 3 : 1 acid-base adducts in solutions. Moreover, with regard to benzoic acid and piperidine, they identified the 1 : 1 and 2 : 1 acid-base adducts in benzene by infrared study.

The present study will deal with the formation and identification of solid complexes of benzoic acid (HA) with piperidine (B). It was found that the 1 : 1 and 2 : 1 benzoic acid - piperidine complexes exist in the solid state. The 1 : 1 complex (B·HA) was formed from a cyclohexane solution containing equimolar amounts of benzoic acid and piperidine. The complex is highly hygroscopic. When the complex is exposed to the atmosphere, it forms a complex (B·HA·H_2O) with a benzoic acid - piperidine - water ratio of 1 : 1 : 1. The infrared spectra in the KBr disks of the 1 : 1 and 1 : 1 : 1 complexes were very similar. As is shown in Table 1, however, their X-ray diffractions are apparently different.

The melting-point diagram for the benzoic acid-piperidine system is shown in Fig. 1. This shows the existence of a molecular compound with an acid-base ratio of 2 : 1. The complex (B·HA·HA) was isolated from a cyclohexane solution containing benzoic acid and piperidine in a mole ratio of 2 : 1. The X-ray diffraction data of the complex are given in Table 1.

The infrared data of these solid state complexes are given in Table 2, along with the data of Bruckenstein and Saito[1] for a benzene solution. As may be seen in Table 2, the infrared absorptions of the 1 : 1 complex in the solid state are almost identical with the absorptions in a benzene solution, though the ν-CO_2^- absorptions in the solid state shift to slightly higher frequencies. The 1 : 1 complex shows ν-CO_2^- absorptions, but no absorptions of ν-C=O. This indicates that the 1 : 1 complex has an ionic structure in the solid state as well as in a solution.

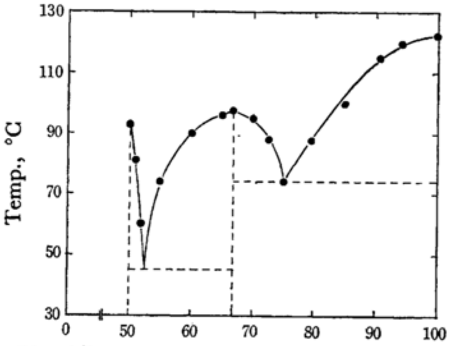

Fig. 1. The melting point diagram for the system benzoic acid - piperidine.

Table 1. X-ray diffraction data of the solid complexes between benzoic acid (HA) and piperidine (B)

B·HA		B·HA·H_2O		B·HA·HA	
2θ(°)	$H/H°$	2θ(°)	$H/H°$	2θ(°)	$H/H°$
11.56	7	13.52	20	9.85	26
13.92	7	14.25	18	10.60	21
15.05	46	15.20	10	14.40	12
16.72	19	17.20	29	16.06	16
18.35	21	18.40	100	17.50	34
19.40	39	19.30	34	19.34	100
20.70	100	20.65	22	21.35	13
21.90	18	21.90	14	22.80	19
22.60	47	22.85	16	24.10	30
23.95	7	23.40	58	25.45	5
24.90	8	24.60	58	26.70	11
25.70	15	25.40	19	27.55	10
26.80	47	27.10	27	28.75	14

θ=Bragg angles.
$H/H°$=relative height of diffraction peak.

The infrared data of the 2 : 1 complex suggest that the complex has both C=O and CO_2^- groups. The main absorptions of the 2 : 1 complex in the solid state are also observed in a solution, though some absorptions observed in a solution disappear in the solid state.

The facts presented above give clear evidence of the existence of solid complexes between benzoic acid and piperidine.

Experimental

Materials. The piperidine (E. P.-grade reagent) was used without further purification. The benzoic acid was recrystallized from cyclohexane and dried at 100°C for one hour. The cyclohexane was dried over metallic sodium and distilled.

The Complex Formation. The 1 : 1 complex was prepared as follows: To a warm (*ca.* 60°C),

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1) S. Bruckenstein and A. Saito, *J. Am. Chem. Soc.*, **87**, 698 (1965).

TABLE 2. INFRARED DATA OF THE COMPLEXES BETWEEN BENZOIC ACID (HA) AND PIPERIDINE (B)

Frequency, cm^{-1} (observed absorbance)				
B·HA		B·HA·HA		Assignment
a	b	a	b	
—	—	1720 (0.10)	1730 (0.10)	ν-C=O
—	—	—	1690 (0.12)	ν-C=O
1630 (0.15)	1620 (0.13)	—	1620 (0.13)	—
1600 (0.25)	1590 (0.09)	1595 (0.10)	1590 (0.13)	ν-CO_2^-
1550 (0.30)	1540 (0.10)	—	1540 (0·14)	ν-CO_2^-
—	—	1455 (0.10)	—	ν-CO+δ-OH
1385 (0.50)	1368 (0.31)	1385 (0.10)	1368 (0.35)	ν-CO_2^-

a : Data of the solid complexes in KBr disk, present studies.
b : Data of the complexes in benzene solution, Bruckenstein and Saito.[1)]
ν : Streching. δ: Bending.

saturated solution of 2.9 g of benzoic acid in cyclohexane, an equimolar amount (2.0 g) of piperidine in the same solvent was added. After the solution had stood at room temperature for about one hour, colorless needles of the complex separated out. These needles were recrystallized repeatedly from cyclohexane, and then dried *in vacuo* over $CaCl_2$; mp 93—94°C. The complex was not subjected to elemental analysis, since it was highly hygroscopic. The complex was then exposed to the atmosphere overnight to form the 1 : 1 : 1 benzoic acid - piperidine - water complex; mp 51—52°C.

Found: C, 64.60; H, 8.61; N, 6.21%. Calcd for $C_{12}H_{17}NO_2(H_2O)$: C, 63.96; H, 8.50; N, 6.22%.

The 2 : 1 complex was prepared by a method virtually identical with that described for the 1 : 1 complex, but here the mole ratio of benzoic acid to piperidine was 2 : 1. Colorless needles, mp 97—98°C.

Found: C, 69.42; H, 7.31; N, 4.22%. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.08; N, 4.25%.

Identification. In all the experiments the 1 : 1 complex was treated in a dry box. The IR spectrum was obtained according to the usual KBr disk method. The X-ray powder-diffractometry was made with a Rigaku Denki diffractometer, Geigerflex, by the use of Cu$K\alpha$ radiation. For the melting-point diagram, a mixture of the 1 : 1 complex and benzoic acid in appropriate proportions was ground in a mortar and then sealed into capillaries. The melting point was obtained by the usual method.

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