decomposed by the addition of sodium bisulfite. The resulting solution was concentrated *in vacuo* to a volume of 13 cc. The oxidation product appeared to be very soluble in the aqueous medium. However, extraction with three 30-cc. portions of chloroform yielded a white crystalline product melting at 137–141°. Recrystallization from benzene yielded the pure diester acid melting at 147–148°.

*Anal.* Calcd. for $C_{11}H_{17}O_7N$: C, 47.99; H, 6.23; N, 5.09; neut. equiv., 275. Found: C, 47.96; H, 6.21; N, 4.73; neut. equiv., 277.

DL-**Aspartic Acid.**—The acid diester was hydrolyzed by refluxing with concentrated hydrochloric acid for a period of four hours. After the removal of the excess hydrochloric acid *in vacuo* and neutralization until just acid to methyl red, the aspartic acid was isolated as blue copper salt. The DL-aspartic acid was recovered as described by Dunn and Fox[7] and melted with decomposition at 300°.

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(7) M. S. Dunn and S. W. Fox, *J. Biol. Chem.*, **101**, 493 (1933).

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## Complexing of Pyridine with Phenol and Other Acids in Benzene Solution[1]

BY C. GARDNER SWAIN AND JOHN F. BROWN, JR.

The complexing of pyridine with phenol, *p*-nitrophenol, 2,4-dinitrophenol, benzoic acid and 2-hydroxypyridine has been studied in benzene solution at 25° by a dynamic vapor pressure method. This supplements cryoscopic and kinetic data previously reported.[2] In solutions of pyridine and phenol, the data indicate the presence of 1:1 and 1:2 pyridine–phenol complexes, in agreement with the results of a freezing-point study on the pyridine–phenol system.[3] The following equilibria appear to be present.

$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$

(from the literature[4]) $K_x = 0.57\ M^{-1}$

$$C_5H_5N + C_6H_5OH \rightleftharpoons C_5H_5N{\cdot}C_6H_5OH \qquad K_y = 18.4\ M^{-1}$$

$$C_5H_5N + 2C_6H_5OH \leftrightarrows C_5H_5N{\cdot}2C_6H_5OH \qquad K_z = 109\ M^{-2}$$

The complexing of pyridine with several other acidic species was examined briefly, and the equilibrium constants for the formation of 1:1 pyridine–acid complexes are estimated in Table I.

TABLE I

THE COMPLEXING OF PYRIDINE WITH ACIDS IN BENZENE AT 25°

| Acid | Total acid, *M* | Total pyridine, *M* | Free pyridine, *M* | $K_y$, $M^{-1}$ |
|---|---|---|---|---|
| *p*-Nitrophenol | 0.0482 | 0.0396 | 0.0120 | 110 |
| 2,4-Dinitrophenol | .102 | .00989 | .00915 | 0.8 |
| Benzoic acid[a] | .100 | .0495 | .0197 | 210 |
| 2-Hydroxypyridine | .100 | .0099 | .0104 | 0.0 |

[a] $K_y$ based upon monomeric benzoic acid. The dimerization constant of the benzoic acid was calculated from literature data[5] to be 617 $M^{-1}$.

### Experimental

The complexing between pyridine and various acidic species in benzene solution was studied by slowly passing a fixed volume (about 4 liters) of dry, benzene-saturated air through 25 ml. of a benzene solution of pyridine and the acid in question, and then through 10 ml. of 0.10 *M* hydrochloric acid. This resulted in the transfer of about 2% of the free pyridine in the benzene solution to the aqueous acid. The latter was then boiled to expel traces of benzene, cooled, diluted to 25 ml. with 0.10 *M* hydrochloric acid, and examined in a spectrophotometer in the region 250–275 mμ to determine the pyridine concentration.

In some of the determinations where phenol was the acid, appreciable amounts of it were also carried over, and the observed extinction had to be corrected for light absorption by phenol. To do this, the phenol concentrations were determined from the extinction at 275 mμ, where there was negligible absorption by pyridinium ion.

Similar runs on solutions of pyridine alone in benzene showed that the amount of pyridine vaporized by the air stream and transferred to the aqueous acid was directly proportional to the pyridine concentration of the benzene solution; hence, knowing the amount of pyridine transferred to the aqueous acid made it possible to calculate the pyridine concentration of the benzene solution.

In calculating the values of $K_y$ and $K_z$ from the association measurements, a graphical method was used. Taking the results of any one association measurement, various values of the concentration of the 1:1 complex were assumed, and for each assumed value a pair of values of $K_y$ and $K_z$ was determined. Plotting these one against the other gave a curve on a plot of $K_y$ *vs.* $K_z$. From the other association measurements other curves were calculated, and their intersection gave the desired solution for $K_y$ and $K_z$, with a precision of ± 2%.

From $K_x$, $K_y$ and $K_z$, the amounts of free phenol and free pyridine in each solution in Table II were calculated by a method of successive approximations.

TABLE II

THE COMPLEXING OF PYRIDINE AND PHENOL IN BENZENE AT 25°

| Total phenol, *M* | Total pyridine, *M* | Free phenol (calcd.) | Free pyridine (calcd.) | Free pyridine (found) |
|---|---|---|---|---|
| 0.200 | 0.0099 | 0.159 | 0.00148 | 0.00150 |
| .100 | .0099 | .083 | .00302 | .00303 |
| .050 | .0099 | .042 | .00502 | .00500 |
| .209 | .103 | .096 | .0274 | .0276 |
| .104 | .103 | .042 | .0526 | .0528 |

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[1] For more complete experimental data see J. F. Brown, Jr., Ph.D. Thesis, M.I.T., July, 1950, pp. 178–183.

[2] C. G. Swain and R. W. Eddy, THIS JOURNAL, **70**, 2993 (1948).

[3] A. Bramley, *J. Chem. Soc.*, **109**, 469 (1916).

[4] E. N. Lassettre and R. G. Dickinson, THIS JOURNAL, **61**, 54 (1939).

[5] F. T. Wall and F. W. Banes, *ibid.*, **67**, 898 (1945).

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# NEW COMPOUNDS

### Preparation of 5-Nitro-2-chlorothiophene

5-Nitro-2-chlorothiophene was prepared from 2-chlorothiophene by a modification of the method of Babasinian.[1]

An ice-cold mixture of 50 g. of fuming nitric acid (sp. gr. 1.51) and 100 ml. of acetic anhydride was added dropwise over a period of 2.5 hours to a vigorously-stirred mixture of 50 g. of 2-chlorothiophene and 100 ml. of acetic anhydride in a one-liter flask cooled by an ice–salt mixture so that the temperature did not rise above 0°. An orange-colored precipitate formed. Stirring was continued an additional hour. The flask was then packed in an ice–salt mixture and allowed to stand in an ice-box for 24 hours. The mixture was then poured with stirring onto 400 g. of crushed ice. The yellowish-red oil was separated, dissolved in 500 ml. of petroleum ether, washed several times with sodium bicarbonate solution and with water, and decolorized with

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[1] V. S. Babasinian, THIS JOURNAL, **57**, 1763 (1935).