

## The Base Strength of Hydrazoic Acid

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In his early work on the base strength of nitrogen compounds Hantzsch<sup>1</sup> investigated the cryoscopic behaviour of hydrazoic acid in concentrated sulfuric acid. From his measurements he concluded that in 100% H<sub>2</sub>SO<sub>4</sub> hydrazoic acid takes up three protons to form H<sub>3</sub>N<sub>3</sub><sup>+++</sup>. (Strictly speaking he stated that the salt N<sub>3</sub>H<sub>4</sub>(HSO<sub>4</sub>)<sub>3</sub> is formed.)

Recalculation of Hantzsch's data shows that at most two protons are taken up. Using the value<sup>2</sup> -10.6 for Hammett's acidity function  $H_0$  for 100% H<sub>2</sub>SO<sub>4</sub> we can from Hantzsch's data estimate the dissociation-constant for the acid H<sub>2</sub>N<sub>3</sub><sup>++</sup>. We get  $pK = -10.1$ , but this value should undoubtedly be taken with some reservation.

Since it is of importance to know the base strength of hydrazoic acid in order to study the mechanism of, *e. g.*, the Schmidt reaction<sup>3,4</sup> we have determined the dissociation constant for the acid H<sub>2</sub>N<sub>3</sub><sup>+</sup> at 25.0°C by the following simple technique. HN<sub>3</sub> was equilibrated between a sulfuric acid phase and a chloroform phase, and the concentrations of HN<sub>3</sub> and H<sub>2</sub>N<sub>3</sub><sup>+</sup> in the two phases were determined chemically<sup>5</sup>.

We use the symbols

|   |  |
|---|--|
| [HN <sub>3</sub> ] <sub>s</sub>               | concentration of HN <sub>3</sub> in the sulfuric acid phase                            |
| [H <sub>2</sub> N <sub>3</sub> ] <sub>s</sub> | concentration of H <sub>2</sub> N <sub>3</sub> <sup>+</sup> in the sulfuric acid phase |
| [HN <sub>3</sub> ] <sub>c</sub>               | concentration of HN <sub>3</sub> in the chloroform phase                               |

The concentration of H<sub>2</sub>N<sub>3</sub><sup>+</sup> in the chloroform phase is neglected. We also neglect the concentration of the ion H<sub>3</sub>N<sub>3</sub><sup>+++</sup> in both phases. The justification for this lies in the experimental data given below.

Defining two distribution constants:

$$f = \frac{[\text{HN}_3]_s + [\text{H}_2\text{N}_3^+]_s}{[\text{HN}_3]_c}$$

$$n = \frac{[\text{HN}_3]_s}{[\text{HN}_3]_c}$$

we have, as a simple consequence of the definition<sup>6</sup> of  $H_0$ :

$$pK = H_0 + \log \left( \frac{f}{n} - 1 \right). \quad (1)$$

$pK$  is the negative logarithm of the dissociation constant of the acid H<sub>2</sub>N<sub>3</sub><sup>+</sup>.

Since we neglect the concentration of H<sub>3</sub>N<sub>3</sub><sup>+++</sup> the distribution-constant  $f$  can be determined directly and proves to be constant over the range 25–40% H<sub>2</sub>SO<sub>4</sub>. We conclude therefore that in this range  $f = n$ . The value of  $n$  is (accidentally) equal to one,  $n = 1.00 \pm 0.04$ .

Assuming that  $n$  will be constant equal to one also for higher sulfuric acid concentrations we can determine an approximate value of  $pK$  from the measurement of  $f$ , using eqn. (1). Under this assumption we obtained as an average of six measurements  $pK = -6.21$  (see Table I).

Table I.

| % H <sub>2</sub> SO <sub>4</sub> | $H_0$ | $f$   | $pK$  |
|----------------------------------|-------|-------|-------|
| 77.96                            | -6.55 | 3.22  | -6.20 |
| 78.12                            | -6.57 | 4.22  | -6.07 |
| 78.54                            | -6.64 | 3.84  | -6.19 |
| 81.20                            | -7.04 | 6.66  | -6.29 |
| 83.76                            | -7.44 | 15.80 | -6.27 |
| 84.56                            | -7.54 | 19.95 | -6.26 |

$f$  is the distribution constant for hydrazoic acid between sulfuric acid and chloroform.

This approach is of course somewhat unsatisfactory, since we only know that  $n$  is constant over the range 25–40% H<sub>2</sub>SO<sub>4</sub>. We therefore proceeded to treat  $n$ , for higher sulfuric acid concentration, as an unknown, constant only over a small range in  $H_0$ .

Using the first four measurements for which  $H_0$  is practically constant we determined the value of  $n$  by requiring that the mean square deviation of  $pK$ , regarded as a function of  $n$ , be minimum. This gives a value for  $n$  slightly below one ( $n \sim 0.98$ ), but the correction in  $pK$  introduced in this way is immaterial. The above value for  $pK$  is therefore the best estimate of the dissociation constant we can give on basis of this method.

For higher concentrations of sulfuric acid we find unexpectedly small values of  $f$  (*e. g.*,  $f \sim 85$  for 95% H<sub>2</sub>SO<sub>4</sub>), indicating that  $n$  decreases rapidly with increasing concentration of sulfuric acid. This effect, which has nothing to do with the basicity

of  $\text{HN}_3$ , makes the present method unsuitable for studying the dissociation constant of, e. g.,  $\text{H}_3\text{N}_3^{++}$ . Similar effects have recently been reported by Deno and Perizzolo<sup>7</sup>.

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## The Chemistry of the Natural Order Cupressales

### XIX\*. The Occurrence of Manool in *Cupressus sempervirens* L.

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During routine examinations of the heartwood extractives of the conifers belonging to the genera *Cupressus* and *Chamaecyparis*, the heartwood of the Mediterranean cypress *Cupressus sempervirens* has been subjected to a brief study. Like Di Modica and Rossi<sup>1</sup> we have found that the main neutral constituents are carvacrol methyl ether and cedrol. The high boiling material, rather surprisingly gave manool<sup>2(I)</sup>. This diterpene alcohol is characteristic of a section of the genus *Dacrydium*, N. O. Podocarpaceae, and this is the first time it has been found in another genus of the conifers. Minor neutral constituents of the wood extractives are *d*-borneol, *d*-bornyl

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acetate and sesquiterpenes. From the acid material carvacrol,  $\beta$ -thujaplicin and nootkatol were isolated.

*Experimental.* Melting points were taken on the Koflerblock. Only upper limits of b.p. range of the fractions are given.

Finely divided heartwood (4.8 kg, from Le Lavandou, Provence, S. France) was extracted with acetone for 48 h. The acetone was removed and the residue poured, with vigorous stirring, into a tenfold volume of ether, which was filtered, concentrated and similarly poured into light petroleum. The filtered solution was successively shaken with 5% aqueous potassium hydroxide, 10% ethanolic potassium hydroxide and water. The alkaline fractions were combined, washed with light petroleum, acidified and extracted with light petroleum. The combined neutral solutions and the acid solution were dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent evaporated. The neutral fraction yielded 276 g (5.8%) of a slightly coloured oil (N) and the acid fraction 20.4 g (0.4%) of a yellow brown oil (A).

The neutral oil, N, (166 g) was fractionally distilled through a vacuum jacketed, packed column. Pressure 26 mm. Back pressure 10 mm. Fraction  $\text{N}_1$ , b. p. up to 104°, 1.9 g;  $\text{N}_2$ , 109°, 11.4 g;  $\text{N}_3$ , 110°, 70.0 g;  $\text{N}_4$ , 140°, 16.6 g;  $\text{N}_5$ , 162°, 9.6 g;  $\text{N}_6$ , 172°, 15.2 g;  $\text{N}_7$ , 178°, 2.1 g;  $\text{N}_8$  (at lower pressure), 5.0 g. The remainder, after a simple distillation at lower pressure, yielded a distillate  $\text{N}_9$  (31.9 g) and a residue (2.3 g, discarded).

Fractions  $\text{N}_{1-2}$  deposited a solid (2.5 g) which was recrystallized from ligroin and from nitromethane and sublimed. M. p. and mixed m. p. with *d*-borneol 204–207° (sealed tube, uncorr.),  $[\alpha]_D^{22} + 36.5^\circ$  ( $\text{CHCl}_3$ ; *c* 1.7).

Judging from the distillation curve the non-crystalline part of  $\text{N}_2$  and fraction  $\text{N}_3$  (total 79 g) contained the same compound, namely carvacrol methylether. Demethylation with HBr followed by etherification with chloroacetic acid yielded carvacroxy acetic acid, m. p. and mixed m. p. 150–152°. Fraction  $\text{N}_4$  and the non-crystalline part of  $\text{N}_5$  (see below) were combined (23.7 g) and distilled through a spinning band column. Pressure 26 mm.

Fraction  $\text{N}_{41}$ , b. p. up to 118°, 3.24 g,  $[\alpha]_D^{22} + 6.6^\circ$ ,  $n_D^{21}$  1.4973;  $\text{N}_{42}$ , 120°, 3.59 g, +18.0°, 1.4882;  $\text{N}_{43}$ , 120°, 3.03 g, +29.5°, 1.4716;  $\text{N}_{44}$ , 128°, 2.31 g, +18.3°, 1.4800;  $\text{N}_{45}$ , 142°, 2.16 g, -7.7°, 1.4968;  $\text{N}_{46}$ , 144°, 2.96 g, -17.8°, 1.5003;  $\text{N}_{47}$ , 156°, 1.17 g, -22.8°, 1.5029;  $\text{N}_{48}$ , 173°, 2.76 g, -17.8°, 1.5071;  $\text{N}_{49}$ , tailings/10 mm 1.31 g, +8.5°; Residue 1.25 g.