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**PYRIDINE:
PURIFICATION
AND TESTS FOR PURITY**

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ANALYTICAL CHEMISTRY DIVISION
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INTRODUCTION

The discovery of pyridine, C₅H₅N, was reported by Anderson in 1851¹. It resembles benzene in aromaticity and structural dimensions. The planar molecule is distorted to some extent from the regular hexagonal shape of the benzene molecule², owing to the presence of the heteroatom. Apparently, this has little effect on the aromatic nature of the material, for the resonance energy of pyridine has been calculated to be 31.9 kcal/mole as compared to 36 kcal/mole for benzene³. Molecular orbital calculations have indicated that the carbon atoms in pyridine are very close to being sp² hybridized⁴; the 'lone pair' electrons are only slightly involved in the π-electron system and are essentially localized on nitrogen⁵.

PROPERTIES OF PYRIDINE

Pyridine is a colourless basic substance with a fairly wide liquid range. It has a distinctive, somewhat disagreeable odour. It is miscible with the common organic solvents as well as with water. It forms numerous binary, ternary, and quaternary azeotropes with water and organic liquids^{6,7}. The pertinent physical constants are listed in *Table 1*.

Toxicity

Chronic exposure to pyridine vapour causes irritation of the mucous membranes and also affects the gastro-intestinal system; acute exposures may lead to unconsciousness^{2,3}. The odour of the material may be detected long before it becomes toxicologically important. Pyridine should be used with adequate ventilation.

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Table I. Physical properties of pyridine

Formula weight	79.10
Boiling point, °C	115.236 ^{a, b, 8} ; 115.256 ^{a, c, 9}
Melting point, °C	-41.71 ¹⁰
Molar heat ^d of:	
Formation	33.63 ^{e, 11} , 33.50 ^{e, 8} ; 23.95 ^{f, 11} , 23.89 ^{f, 12}
Combustion	-674.68 ^{e, 11} ; -665.00 ^{f, 11} , -664.95 ^{f, 12}
Hydrogenation	-45.30 ± 0.94 ³
Neutralization	14.4 ± 0.4 ^{e, 13} ; 13.6 ± 0.4 ^{h, 14}
Density, g/ml	0.98319 (20°), 0.97824 (25°), 0.97319 (30°) ¹⁵
Viscosity, cP	0.952 (20°), 0.884 (25°), 0.815 (30°) ¹⁵
Surface tension, dyne/cm (γ)	36.33 ^{i, 15} ; 37.86 ^{i, 16}
Refractive index	1.51016 (20°), 1.50745 (25°), 1.50466 (30°) ¹⁵
Dipole moment, Debye	2.20 ^h , 2.22 ^{k, 17}
Dielectric constant	12.5 ^{1, 18} ; 12.3 ^{m, 19} ; 13.04 ^{n, 20}
Specific conductance, mho/cm	< 1 × 10 ^{-9.21} (25°)
pK _b in water	8.81 ²² (25°)
Spectral cutoff	~290 nm

a—at 760.0 mm Hg.

b— $\log P = 7.04162 - 1374.103/(T + 215.014)$, P = vapour pressure (mm Hg), T = temperature (°C).c— $\log P = 7.05811 - 1384.99/(T + 216.296)$.

d—kcal.

e—gaseous.

f—liquid.

g—at 24°C in acetonitrile.

h—in benzene.

i—at 25°C; $dy/dT = -0.11$.j—at 15°C; $dy/dT = -0.144$.

k—in dioxane.

l—'high frequency'.

m—'low frequency'.

n—180 kHz.

TESTS FOR PURITY

Sulphur-containing impurities¹⁰ may be detected at less than 0.003 mole per cent by combustion analysis. Pyrrole, if present at levels above 1 p.p.m., may be detected by the formation of a noticeable colouration when an acidified sample of the pyridine is treated with *p*-dimethylaminobenzaldehyde¹⁰. Vapour phase chromatography with a column of ten per cent ethanolamine—five per cent *o*-phenylphenol on C-22 firebrick at 90°C permits successful resolution of water, the picolines, 2,6-lutidine and pyridine²⁴. Infra-red spectroscopy has been used to determine water in pyridine down to 0.01 mole per cent²⁵; Karl Fischer titration may also be used for water determination. Determination of total dissolved impurity in relatively pure samples of pyridine may be accomplished via the melting point curve technique⁸.

PREPARATION

From the time of its discovery, pyridine had been produced chiefly by high temperature pyrolysis; feedstocks included bone oil, petroleum and coal. Purification was tedious; from 15 tons of coal only 150 ml of pure pyridine were realizable²⁶. Not until the late 1950s did synthetic pyridine become commercially available. Since that time a variety of efficient preparative procedures have been achieved. Catalytic dehydrogenation of

PYRIDINE: PURIFICATION AND TESTS FOR PURITY

piperidine over palladium at 260°, for example, affords pyridine in 53 per cent yield²⁷; however, piperidine itself is not easily prepared, and the technique is thus of little commercial value.

More useful catalytic processes have been developed using various nitrogen and oxygen compounds to build the heterocycle. Most of the catalysts are based on silica and alumina and employ various additives. For example, an untreated silica-alumina catalyst (SAC) at 510° converts 1-cyanobutadiene-1,3 to 35 per cent crude pyridine²⁸. At 300° a gas stream containing ammonia, water and 3,4-dihydro-2-ethoxy-2H-pyran is converted to pyridine in 50 per cent yield when passed over SAC treated with boric and phosphoric acids²⁹; with a palladized SAC 66 per cent conversion is realized³⁰. Crotonaldehyde, formaldehyde, water, air and ammonia are combined over untreated SAC, affording 67 per cent pyridine and 7 per cent of the picolines³¹. Ammonia is combined with water and tetrahydrofurfuryl alcohol at 500° over a platinized SAC, producing pyridine in 48 per cent yield³².

Other catalyst systems have been used. For example, the last reaction, when carried out over a molybdenum trioxide catalyst at 400°, gives 69 per cent of a pyridine fraction³³. In another process, using a molybdenum-vanadium-alumina catalyst, methanol and 2,2'-dihydroxydiethylamine are combined at 520°, affording 42 per cent pyridine and 10 per cent picolines³⁴.

PURIFICATION

It would seem that the likely impurities in commercial pyridine are water and amines such as the picolines and the lutidines. The literature abounds with purification procedures, most of which involve various preliminary chemical and physical treatments prior to distillation.

Pyridine and zinc chloride form an adduct which can be easily recrystallized from ethanol³⁵; stable complexes of pyridine with mercuric chloride³⁶ and with ethyloximinocynoacetate³⁷ are also known. The free base can be subsequently liberated by treating these addition compounds with concentrated sodium hydroxide solution^{35b}. A drying step followed by distillation affords good product. Alumina, barium oxide, drierite, sodium or potassium hydroxide, and calcium hydride have been used as drying agents.

Steam distillation of AR grade pyridine dissolved in 1.2 equivalents of 23 per cent sulphuric acid has also been resorted to for removing contaminants¹⁰; the base was liberated and dried by using sodium hydroxide and was then fractionally distilled through a 50-plate Stedman column at a reflux ratio of 50:1. The product obtained was 99.5 per cent pure (b.pt 93.7–94.0°C/400 mm) with water as the major impurity; fractional freezing and redistillation of this material afforded 99.85 ± 0.03 mole per cent pyridine.

Repeated fractional freezing followed by refluxing over barium oxide and distillation gives reasonably pure pyridine, b.pt 114.5°C/740 mm¹⁷.

High purity pyridine was obtained by distilling Baker & Adamson (ACS reagent grade) product in an oxygen-free atmosphere through an 11 ft × 1 in. Helipak column. The lower-boiling pyridine-water azeotrope distilled first; later fractions (15 per cent of the total) were 99.92 per cent pure pyridine.

These fractions were degassed, dried over calcium hydride and finally distilled under vacuum to provide standard samples of pyridine¹⁵.

Elving and co-workers have found AR grade (Baker, Mallinckrodt or Merck) pyridine which was dried over Linde 4A molecular sieve for two to three days to be sufficiently pure for their polarographic work^{38,39}. In connection with their studies on reduction of acids^{39a} they observed a small pre-discharge wave (0.07 to 2.0 μA) when LiCl or LiClO_4 was used as the supporting electrolyte. The height of this wave appeared to depend on the individual batches of pyridine used. Furthermore, the height decreased with increasing acid concentration giving rise to a new wave, at a less negative potential, at its own expense; the latter wave assumed the height of the original pre-wave at ~ 0.02 mM acid concentration and remained constant thereafter. The observed decomposition potentials at which a current of 1 μA is attained for 0.1M solutions of LiCl , LiClO_4 , KSCN , NaI and $\text{NaB}(\text{C}_6\text{H}_5)_4$ are, respectively, -1.71 , -1.77 , -1.65 , -1.18 and -1.57 V versus a mercury pool anode. The decomposition potential in solutions of Et_4NClO_4 ^{39c} is appreciably more negative than in LiClO_4 solution. A pre-wave was also found in these solutions with an average height of 0.7 μA . In addition, a wave of negligible magnitude (~ 0.13 μA) has been observed both in LiClO_4 and Et_4NClO_4 solutions at a potential substantially less cathodic to be of any consequence insofar as the pyridinium ion reduction is concerned. From their studies on electrooxidation^{39b} in pyridine using the pyrolytic graphite electrode, the potential range appeared limited by the oxidation of pyridine or of an impurity, at ~ 1.4 V. versus the normal silver-silver nitrate reference electrode.

Recommended procedure

The following method⁴⁰ is recommended for obtaining pure pyridine. Karl Fischer reagent grade pyridine (Fisher) is to be kept over solid potassium hydroxide (~ 20 g/kg) for two weeks. The supernatant liquid should then be fractionally distilled over Linde 5A molecular sieve and solid potassium hydroxide at a reflux ratio of 20:1, using a Corad Vacuum-jacketed silvered column. The fraction boiling at 115.3° (cor. 760 mm Hg) should be collected and stored in glass containers. Using automatic burettes, the contents could be dispensed as required under pressure of dry, carbon dioxide-free nitrogen gas. The specific conductance of this product should be between 2.92×10^{-8} and 4.47×10^{-8} mho/cm at 25° . No water could be detected by Karl Fischer titration. In 0.1 M LiClO_4 solution a pre-discharge wave (0.16 μA) at ~ -1.6 V, accompanied by two small waves (0.10 and 0.03 μA) at ~ -0.7 V and -1.1 V, was observed using a d.m.e. between zero voltage and the decomposition potential of -1.8 V versus a mercury pool anode⁴¹.

Degassed samples of highly purified pyridine showed no appreciable decomposition after one year. Formation of a faint brown colouration was the sole detectable effect of a one year exposure of such samples to bright sunlight¹⁵.

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PYRIDINE: PURIFICATION AND TESTS FOR PURITY

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