[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Nitrogen Compounds from Petroleum Distillates. X. Purification of Nitrogen Bases with Zinc Chloride

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It is known that zinc chloride salts of the type $(Base)_2ZnCl_2$ dissociate at elevated temperatures with the liberation of the free base[1] and that zinc chloride salts of the type $(Base\cdot HCl)_2ZnCl_2$ dissociate into base, hydrochloric acid and zinc chloride with the base and acid recombining as a sublimate of base hydrochloride.[2]

The above principle has been incorporated in a procedure described in this paper, designed for the simultaneous removal from nitrogen bases of water, and other non-basic admixtures, including thio and phenolic compounds, and hydrocarbons.

The procedure reported represents improvement over processes described in patent literature[3] for the dehydration of organic nitrogen bases and furthermore permits the simultaneous elimination of substances, notably sulfur compounds, which are known to be catalyst poisons and which normally require separate processes[4] for their removal.

Experimental

General Procedure for Processing Pyridine or Quinoline and Other Types of Nitrogen Bases by Use of Zinc Chloride.—A mixture of the base and zinc chloride solution is maintained at 80° for one hour, or at least until salt formation is complete. The double salt, $(Base)_2ZnCl_2$, forms with evolution of heat and precipitates on cooling. Water and other volatile products are removed by distillation and, after the distillation flask has been connected with a dry condenser and dry receiver, the residual salt cake is heated to its dissociation temperature 320° and higher. Where this procedure is applied to produce anhydrous bases from salts of the type $(Base\cdot HCl)_2\cdot ZnCl_2$, it is necessary, as explained above, to add sodium hydroxide sufficient to neutralize the hydrochloric acid in combination with the nitrogen base and to precipitate a small amount of zinc hydroxide as a convenient indicator for the end-point of the reaction involved in acid neutralization.

Treatment of Pyridine

Sample 1.—To 50 cc. of pyridine (Eastman) ($n^{25}D$ 1.4988; b. p. 113.5–115.5°) in a 125-cc. Claisen distillation flask provided with a reflux condenser was added an excess of ground zinc chloride and the mixture was made slightly alkaline with sodium hydroxide and distilled. Water and hydrocarbon oil (approx. 4 cc. total) were eliminated by distillation at atmospheric pressure, and the last traces of impurities were removed at a pressure of 25 mm., absolute, and a bath temperature of 150°. After the equipment had been cleaned, dried and reassembled, the residual salt cake was heated to the dissociation temperature. The distillate ($n^{25}D$ 1.5046) gave a negative test for chloride and showed no change in refractive index after remaining in contact with solid sodium hydroxide for twenty-four hours.

Sample 2.—A more recent sample of pyridine ($n^{25}D$ 1.5052; b. p. 113.5–115.5°) was treated according to the procedure outlined above with the production of a material having a refractive index $n^{25}D$ 1.5066.

Sample 3.—This sample of base ($n^{25}D$ 1.4983, techn.) before treatment gave a negative test for sulfur but was found to contain about 1% hydrocarbon oil. The refractive index was raised to $n^{25}D$ 1.5047.

The refractive index of pure pyridine has been reported as $n^{21}D$ 1.50919,[5] $n^{25.2}D$ 1.50695,[6] and $n^{25}D$ 1.5068.[7]

Amplified Distillation of Pyridine Obtained Through Pyrolysis of the Zinc Chloride Salt.—A portion (50 cc.) of pyridine ($n^{24}D$ 1.5066) from Sample 2 above was subjected to amplified distillation[8] using 20 volumes of a hydrocarbon oil fraction boiling evenly over an 82–126° range. This mixture was fractionated with a 10:1 reflux ratio through a packed column (carding teeth) into 100-cc. cuts. Determination of the refractive index ($n^{25}D$ 1.5068) and melting point of the picrate (167°) of the basic material contained in the hydrocarbon oil fractions distilling below 110° revealed it to be pure pyridine. The refractive index ($n^{25}D$ 1.5028) and the melting point of the picrate (143°) lead to the conclusion that the material isolated from the higher boiling hydrocarbon fraction was a mixture of the picolines.

Zinc Chloride Treatment of Petroleum Bases.—A 10-cc. fraction of crude petroleum bases ($n^{25}D$ 1.4990) of b. p. 210–215° and with a sulfur content of 0.21% was processed in the manner described. The forerun contained an appreciable amount of hydrocarbon oil and other impurities, and at an elevated temperature the anhydrous bases ($n^{25}D$ 1.5002) distilled free of sulfur.

Numerous other experiments performed on fractions of petroleum bases of different origin and of varying boiling points served to confirm the efficiency of the zinc chloride

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(1) Wilhelm Lang, *Ber.*, **21**, 1578 (1888).

(2) M. Wyler, *ibid.*, **60**, 398 (1927); G. R. Lake and J. R. Bailey, THIS JOURNAL, **55**, 4144 (1933).

(3) Barrett Co. and Downs, U. S. Patent 1,290,124 (January 7, 1919); Koppers Co., Sperr and Brown, U. S. Patent 1,414,441 (May 2, 1922); Koppers Co. and Huff, U. S. Patents 1,416,205 and 1,416,206 (May 16, 1922). *Cf.* H. Maier-Bode and J. Altpeter, "Das Pyridin und seine Derivate in Wissenschaft und Technik," Wilhelm Knapp, Halle, Germany, 1934, p. 294.

(4) Hydrierwerke, A.-G., German Patent 541,923 (January 16, 1932) (*Frdl.*, XVIII, 627 (1933)); Kruber and Schmitt, German Patent 551,606 (June 2, 1932) (*Frdl.*, XIX, 809 (1934)).

(5) Bruhl, *Z. physik. Chem.*, **16**, 193 (1895).

(6) Zawidzki, *ibid.*, **35**, 129 (1900); through "I. C. T.," Vol. VII, p. 80.

(7) Eguchi, *Bull. Chem. Soc. Japan*, **3**, 241 (1928).

(8) Bratton, *et al.*, *Ind. Eng. Chem.*, **28**, 424 (1936).

process in dehydration and final purification of cyclic nitrogen compounds of basic type.

Summary

A simple economical method involving the use of zinc chloride is presented for the purification of basic nitrogenous substances. The process includes the removal in one operation of water hydrocarbons, thio and phenolic bodies and other associated non-basic admixtures. The process permits the recovery and re-use of the zinc chloride.

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The Photochemical Decomposition of Aliphatic Alcohols in Aqueous Solution

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The absorption spectra and the photochemical decomposition of methyl and ethyl alcohols in the gaseous state have been investigated recently. The absorption spectra consist of continuous bands, extending from 2000 Å. to the far ultraviolet.[1] The photochemical decomposition is consequently a dissociation process, which takes place according to the scheme[2,3]

$$\mathrm{ROH} + h\nu \longrightarrow \text{aldehyde} + \mathrm{H_2} \qquad (1)$$

According to Patat this is the primary process, since no hydrogen atoms (formed for example according to RO + H) could be detected by the parahydrogen method.

It seemed interesting to investigate the photochemical decomposition of the aliphatic alcohols also in solution in order to determine the primary process and to obtain some information about the interaction of photochemically formed products with the water.

Experimental

A water-cooled vertically burning mercury lamp was used as light source, surrounded concentrically by two reaction vessels, as used already in previous investigations.[4,5] The light intensity was usually checked by determining the decomposition of monochloroacetic acid. Although the decomposition of monochloroacetic acid takes place also in the region 2600–2000 Å., in which the alcoholic solutions do not absorb light, it was found that the intensity of the mercury arc in the short wave length region (below 2000 Å.) was proportinal to the intensity of light which is active in the hydrolysis of monochloroacetic acid. Two mercury arcs of different sizes were used. The one had a quantum output of 1.5×10^{19} per second, the other about $3\text{–}5 \times 10^{18}$ per second. The number of alcohol molecules decomposed per second was about 20–40 times smaller.

The alcoholic solutions were made from purest alcohol and distilled water, their concentration was usually 1 to 3 molar. Aqueous solutions of methyl alcohol, ethyl alcohol, propyl alcohol and isopropyl alcohol were investigated, the first two of these solutions more in detail.

Experiments with Methyl and Ethyl Alcohols

After the aqueous solutions of these two alcohols were illuminated with the full light of the mercury arc for some time, gas was evolved, which proved to be pure hydrogen without any carbon monoxide or dioxide content. This suggests that the decomposition of methyl and ethyl alcohol also in solution takes place according to

$$\mathrm{CH_3OH} + h\nu \longrightarrow \mathrm{H_2CO} + \mathrm{H_2}$$
$$\mathrm{CH_3CH_2OH} + h\nu \longrightarrow \mathrm{CH_3CHO} + \mathrm{H_2}$$

In fact in all cases formation of aldehyde could be proved qualitatively. For the quantitative determination different methods were used: formaldehyde was determined either according to Romijn by oxidation with alkaline iodine solution or by oxidation with hydrogen peroxide to formic acid and titrating the acid with sodium hydroxide; or according to Ripper[6] with bisulfite and iodine. The latter method and the reaction with hydroxylamine sulfate was used for the estimation of acetaldehyde. The results obtained by the different methods were in satisfactory agreement.

Tables I and II contain the results of some experiments on the decomposition of methyl and ethyl alcohols.

TABLE I

EXPERIMENTS WITH 2 MOLAR AQUEOUS SOLUTIONS OF METHYL ALCOHOL

Minutes, illuminated	Moles H_2, evolved	Moles, aldehyde found	Intensity: number of $ClCH_2COOH$, decomposed
210	4.0×10^{-3}	2.1×10^{-3}	2.6×10^{18} sec.$^{-1}$
140	2.8×10^{-3}	1.1×10^{-3}	..
280	6.4×10^{-3}	2.7×10^{-3}	..
150	3.9×10^{-3}	2.5×10^{-3}	3.6×10^{18} sec.$^{-1}$
240	5.7×10^{-3}	3.0×10^{-3}	4.0×10^{18} sec.$^{-1}$
15	..	0.4×10^{-3}	3.1×10^{18} sec.$^{-1}$

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(1) G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

(2) See Farkas's communication to K. E. Bonhoeffer, *Z. Elektrochem.*, **40**, 425 (1934).

(3) E. Patat, *ibid.*, **41**, 494 (1935).

(4) L. Farkas and O. J. Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 124 (1932).

(5) L. Farkas, *ibid.*, **B23**, 89 (1933).

(6) *Cf.* G. Wagner, *Biochem. Z.*, **194**, 441 (1928).