azeotropes of certain of the trimethylsilyl ethers with their corresponding alcohols have been determined.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Catalytic Synthesis of Pyridine

BY CHARLES HOWARD KLINE, JR.,[1] AND JOHN TURKEVICH

The main source of pyridine is coal tar. In view of the small percentage of pyridine in this source, 0.1%,[1a] it was thought desirable to investigate various synthetic methods. The catalytic syntheses of pyridine have been extensively reported in both scientific and patent literature.[2] Nearly all of these processes fall into three classes: (a) the reaction of unsaturated hydrocarbons such as ethylene and acetylene with ammonia or hydrogen cyanide, (b) the condensation of aldehydes or ketones with ammonia, and (c) the condensation of ethanol with ammonia. Though previous investigations have indicated favorable operating conditions for the production of pyridine, no satisfactory process has been developed. Low yields, expensive reagents, and lack of specificity in the reactants are the chief drawbacks. It would appear no less difficult to purify pyridine from the products of these reactions than directly from coal tar.

Before embarking on an investigation of the synthesis of pyridine it was thought worth while to investigate the theoretical implications of the various processes. The infra-red spectrum of pyridine vapor was examined, an assignment of vibrational frequencies made and the thermodynamic properties of pyridine were calculated.[3]

Using these results the standard free energy changes at various temperatures were calculated for fifteen reactions in which pyridine is formed. These are given in Table I and because of the uncertainty in the heats of combustion should be used to indicate general trends. On the basis of this table the following general conclusions may be reached.

1. Over the whole temperature range of interest pyridine is unstable with respect to its decomposition products. Insofar as possible, catalysts must be chosen to minimize coking.
2. Syntheses based on acetylene are favorable throughout the whole temperature range.
3. Synthesis from ethylene and hydrogen cyanide is a favorable reaction over the whole temperature range considered.
4. Synthesis from pentane and ammonia is thermodynamically favorable only above 475°. Pentene, however, because of the increased energy content of the double bond over the single bond at moderate temperatures, shows a favorable equilibrium above about 400°, while pentadiene-1,4 with two double bonds would probably show a negative standard free energy change for the reaction in the liquid state at 25°.
5. Syntheses producing water as well as pyridine such as reactions 9 to 15 of Table I require a much lower temperature for favorable equilibria than similar reactions involving corresponding hydrocarbons.
6. Syntheses from formaldehyde and acetaldehyde are thermodynamically favorable even at room temperature.
7. Syntheses from furfural and its derivatives are thermodynamically favorable at room temperature.

Besides these conclusions based on available data, others may safely be drawn by reason of the close analogy between pyridine and benzene. Like benzene, pyridine is a resonating molecule being stabilized by a resonating energy of 43 kcal. and is the stable high temperature form for nitrogen carbon compounds just as benzene is the stable high-temperature form for C_6 hydrocarbons. This is supported by the fact that pyridine and benzene are products of the pyrolysis of coal tar. Just as equilibria at sufficiently high temperatures favor the formation of benzene from hexane and cyclohexane[4] it is very probable that the equilibria also favor the production of pyridine from amylamine and similar compounds at high temperatures.

Kinetic considerations suggest that an efficient process would involve the least number of reactant molecules. Thus the cyclization of amylamine, the reaction of pentamethylene oxide and ammonia or the reaction of pentadiene and ammonia are susceptible of greater catalytic control than the reaction of three molecules of acetylene with one molecule of hydrogen cyanide. The mathematical argument for this view derived from considerations of absolute reaction rate theory[5] will be the subject of another publication from the Princeton Laboratories. Thus, five-carbon chained carbons were deemed as suitable

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(1) Ensign, U. S. N. R.

(1a) "Reilly Coal Tar Chemicals," Reilly Tar and Chemical Corporation, 1940.

(2) A good review of the literature is found in H. Maier-Bode and J. Altpeter, "Das Pyridin und seine Derivate in Wissenschaft und Technik," Halle, 1934, p. 6; W. Schmidt, Beaser and Manchen, German Patent 695,472; Natta, Mattei and Bartoletti, *Chem. Ind.* [Milano], **24**, 81–85 (1942).

(3) P. C. Stevenson and J. Turkevich, *J. Chem. Phys.*, **11**, 328 (1943); C. H. Kline, Jr., and J. Turkevich, *ibid.*, **12**, 303 (1944).

(4) Taylor and Turkevich, *Trans. Faraday Soc.*, **35**, 921–934 (1939).

(5) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, New York, N. Y., 1942.

TABLE I

STANDARD FREE ENERGY CHANGES FOR VARIOUS PYRIDINE SYNTHESES (IN KCAL. PER MOLE)

		25°C. 298.1°K.	126.9°C. 400°K.	326.9°C. 600°K.	426.9°C. 700°K.	526.9°C. 800°K.	726.9°C. 1000°K.
1	$5C + 5/2\ H_2 + 1/2\ N_2 \rightarrow C_5H_5N$	+40.5	+44.6		+57.3		+71.7
2	*n*-Pentane $+ NH_3 \rightarrow C_5H_5N + 5H_2$		+56.1	+15.0	+ 4.0	− 7.1	−29.6
3	Pentene-1 $+ NH_3 \rightarrow C_5H_5N + 4H_2$		+19.0	+ 5.0	− 2.3	− 9.7	−24.6
4	Pentadiene-1,4* $+ NH_3 \rightarrow C_5H_5N^* + 3H_2$	+ 7.6*					
5	$2C_2H_2 + HCN \rightarrow C_5H_5N$	−86.2	−78.2	−62.2		−54.2	
6	$2C_2H_4 + HCN \rightarrow C_5H_5N + 2H_2$	−17.3	−23.2	−34.7		−46.3	
7	$3/2\ C_2H_2 + CH_3CN \rightarrow C_5H_5N + 1/2H_2$	−57.7	−53.0	−43.5		−34.0	
8	$5/2\ C_2H_2 + NH_3 \rightarrow C_5H_5N + 3/2H_2$	−80.0	−74.6	−64.1		−53.7	
9	$5/2\ C_2H_5OH + NH_3 \rightarrow C_5H_5N + 5/2\ H_2O + 4H_2$		+ 8.2	− 6.2		−19.9	−33.0
10	*n*-Amyl alcohol $+ NH_3 \rightarrow C_5H_5N + H_2O + 4H_2$		+23.1	+ 5.1		−12.5	−30.0
11	$CH_2O + 2CH_3CHO^* + NH_3 \rightarrow C_5H_5N^* + 3H_2O^* + H_2$	−38.2*					
12	Furfural* $+ NH_3 + H_2 \rightarrow C_5H_5N^* + 2H_2O^*$	−39.9*					
13	Furfuryl alcohol* $+ NH_3 \rightarrow C_5H_5N^* + 2H_2O^*$	−26.7*					
14	Tetrahydrofurfuryl alcohol $+ NH_3 \rightarrow C_5H_5N^* + 2H_2O^* + 2H_2$	− 9.0*					
15	Pentanediol-1,5* $+ NH_3 \rightarrow C_5H_5N^* + 2H_2O^* + 3H_2$	− 9.2*					

* Material is in the liquid state.

NOTES.—Since the large uncertainty in the heat of combustion of pyridine makes small corrections meaningless, the data have not been reduced to a common basis of molecular weights, physical constants, etc. SOURCES OF DATA: *Pyridine*, spectral analysis of this paper; Parks, Todd and Moore, THIS JOURNAL, **58**, 398 (1936). *Graphite:* Rossini and Jessup, *J. Research Nat. Bur. Stds.*, **21**, 511 (1938); Kelley, "Contributions to the Data on Theoretical Metallurgy. II. High-temperature Specific Heat Equations for Inorganic Substances," U. S. Bureau of Mines Bulletin 371, 1934; Rossini, *J. Research Nat. Bur. Stds.*, **22**, 410 (1939). *Hydrogen:* Rossini, *J. Research Nat. Bur. Stds.*, **22**, 410–411 (1939); Kelley, *op. cit.*; Giauque, THIS JOURNAL, **52**, 4816 (1932). *Nitrogen:* Kelley, *op. cit.;* Kelley, "Contributions to the Data on Theoretical Metallurgy. I. The Entropies of Inorganic Substances," 1932, U. S. Bur. of Mines Bulletin 350. *Pentane and pentene-1:* Thacker, Perkins and Miller, *Ind. Eng. Chem.*, **33**, 587 (1941). *Ammonia: ibid.;* Rossini and Bichowsky, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936; "International Critical Tables," Vol. VII, p. 239; Thompson, *Trans. Faraday Soc.*, **37**, 344–352 (1941). *Pentadiene-1,4:* Parks, Todd and Shomate, THIS JOURNAL, **58**, 2505–8 (1936). *Acetylene:* Rossini and Bichowsky, *op. cit.;* Kassel, THIS JOURNAL, **55**, 1351–63 (1933); Gordon, *J. Chem. Phys.*, **6**, 219–220 (1938). *Hydrogen cyanide:* Rossini and Bichowsky, *op. cit.;* Gordon, *J. Chem. Phys.*, **5**, 30–32 (1937). *Ethylene:* Rossini and Bichowsky, *op. cit.;* Thompson, *loc. cit. Acetonitrile:* Rossini and Bichowsky, *op. cit.;* Thompson, *loc. cit. Ethyl Alcohol:* Francis, *Ind. Eng. Chem.*, **20**, 283–285 (1928). *n-Amyl Alcohol:* Parks, Huffmann and Barmore, THIS JOURNAL, **55**, 2733–40 (1933); Francis, *loc. cit. Furfural, Furfuryl Alcohol, Tetrahydrofurfuryl Alcohol, Pentanediol-1,5:* Miller, *Iowa State College Journal of Science*, 10, 91–93 (1935). *Water:* "International Critical Tables," Vol. VII, p. 232. *Formaldehyde and Acetaldehyde:* Parks and Huffmann, "Free Energies of Some Organic Substances," Ed. 2, pp. 156, 161. The heat of combustion of pyridine was taken to be 659,900 cal. per mole, *cf.* Parks, Todd and Moore, *supra*.

starting materials for the catalytic production of pyridine. In particular, amylamine was chosen as the particular derivative from the readily available C_5 cut of the petroleum industry; the derivatives of furfurol, from likewise available pentosans of the agricultural waste products.

It should be pointed out that piperidine can be readily converted to pyridine.

Experimental Procedure

The apparatus used was the standard catalytic apparatus developed at Princeton.[6] Unless otherwise stated the rate of introduction of the liquid was 12.6 ml./hr., that of ammonia was 6.3 g./hr. The amount of catalyst was 42 ml. The gaseous products of the reaction were analyzed by an Orsat apparatus. If two layers of liquid products were present these were separated and each layer was distilled separately in a specially constructed Vigreux type still of five theoretical plates, 0.4 ml. hold up and 30 cc. capacity. Analysis of appropriate cuts was carried out by determination of refractive index on an Abbe refractometer, density on a Westphal balance and standard methods of organic qualitative analysis. The determination of pyridine was carried out using the method of Spacu[7] based on the precipitation of the pyridine as a complex thiocyanate and titration of the excess thiocyanate by the Volhard method. This method was found to give excellent results for water-pyridine solutions but failed when piperidine was to be determined also.

Materials

Alumina was Alorco Activated Alumina of 8–14 mesh. Before initial use the catalyst was heated at about 400° in a stream of air and then flushed with nitrogen.

Copper on Alumina.—Sufficient C. P. cupric nitrate was dissolved in distilled water and evaporated on Alorco Activated Alumina to give 10% of the metal per weight of alumina. The material was heated till no more brown fumes of nitrogen oxides were evolved, introduced into the catalyst tube and then heated in a stream of air for several hours at 400°. Before use the catalyst was flushed with nitrogen for one hour, reduced with hydrogen at 200° and then heated or cooled to the desired temperature in a stream of hydrogen. After each run the catalyst was flushed with nitrogen, burnt off overnight with air at 400°, flushed with nitrogen and reduced again at 200°.

Nickel on Alumina.—Fifteen per cent. of nickel metal on alumina was prepared and treated in a manner similar to that used for the copper on alumina catalyst. This catalyst was reduced in a stream of hydrogen for one hour at 300°.

Chromium Oxide on Alumina.—This catalyst was prepared by evaporating a sufficient quantity of ammonium dichromate on Alorco Activated Alumina to give a 10% chromic oxide per weight of alumina. The catalyst was heated in air to 475° before use, flushed with nitrogen for

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[6] C. H. Kline, Jr., Thesis, Princeton, 1943.

[7] Spacu, *Z. anal. Chem.*, **64**, 330–342 (1924); Tallantyre, *J. Soc. Chem. Ind.*, **49**, 466–8T (1930).

one hour and reduced in a stream of hydrogen at 475°. After each run the catalyst was flushed for one hour with nitrogen, burnt off at about 400–475° with air, flushed with nitrogen and reduced with hydrogen at 475°.

Silica gel was obtained from the Davison Chemical Corporation, Baltimore, Maryland. It was 10–16 mesh and previous to use was dried at 400°. Its revivification schedule was the same as that of alumina.

Thoria Gel.—Three moles of 0.1 molar ammonium hydroxide was added dropwise over a period of ten hours to 0.65 mole (one pound) of thorium nitrate dodecahydrate in a 0.1 molar solution. The solution was stirred by a stream of filtered air. After the precipitate had settled, 100 ml. concentrated ammonium hydroxide was added and the solution was again stirred and let settle. The supernatant liquid was withdrawn and the gel washed with three 24-liter portions of distilled water to incipient peptization. The filtered gel was dried for three days at 100°. The material was 6–12 mesh and was activated by heating to 400°. Its strong dehydrogenating action on alcohol at 460° showed that the material was of high activity.

Ammonia was ordinary synthetic ammonia. It was dried over soda-lime and filtered through cotton.

Diethylamine was prepared from Eastman Kodak Co. diethylamine hydrochloride by treatment with aqueous sodium hydroxide, distillation, drying over solid sodium hydroxide and redistillation. The cut used had a boiling point range 55.4–55.7°.

***n*-Amylamine** was obtained from the Paragon Testing Laboratories and is characterized by $n^{20}\mathrm{D}$ 1.4080 and d^{20}_4 0.7612.

Furfuryl alcohol obtained from the Quaker Oats Company was purified by treatment with 20% sodium hydroxide, first at 0° and then for three hours at 80°. After salting out the alcohol with excess sodium and magnesium sulfates, the alcohol layer was dried with anhydrous magnesium sulfate and distilled at 20 mm. pressure. The boiling point under those conditions is 80–81°, $n^{20}\mathrm{D}$ 1.4868. There was only very slight coloration with aniline acetate and three months of standing on a well-lit laboratory desk produced but a slight straw coloration.

Tetrahydrofurfuryl alcohol was purified by taking the commercial grade of the Quaker Oats Company and distilling at about 15 mm. pressure, discarding the material boiling above 80° and redistilling the low-boiling fraction. The boiling point at 12 mm. is 69°, while at 15 mm. it is 74°. The $n^{20}\mathrm{D}$ 1.4520 and d^{20}_4 1.0550.

Dihydropyrane was prepared by the catalytic dehydration over activated alumina at 350° of commercial tetrahydrofurfuryl alcohol. There was no drop in catalytic activity after forty hours of operation. The dihydropyrane layer was separated, dried over anhydrous sodium sulfate and distilled through a 16-plate column packed with glass helices and vacuum jacketed. The fraction boiling between 84–85° at 751.4 mm. pressure was collected. The product had the characteristics: d^{20}_4 0.9242, $n^{20}\mathrm{D}$ 1.4391.

Pentamethylene oxide was prepared by hydrogenating dihydropyrane over nickel on alumina at 350°, refluxing the product with 20% sulfuric acid for four hours, treating the non-aqueous layer successively with sodium bicarbonate and anhydrous sodium sulfate and finally distilling through a five-plate column. The boiling point is 85.3–86.0°, the $n^{20}\mathrm{D}$ 1.4200 and d^{20}_4 0.8855.

Experimental Results

Attempted Cyclization of Amines.—Diethylamine was passed over chromium oxide on alumina at 465° at a rate of 8 ml./hr. for 3.5 hours. Gas was evolved at a rate of 50 ml./min. and consisted of 82% hydrogen, 5% unsaturated and 12% saturated. The high content of hydrogen indicates that the catalyst was acting as an efficient dehydrogenating agent. At best, however, only traces of pyrrole were formed. Although the liquid gave a positive splinter test, the identification test with isatin and the test of Montignie were both negative. Titration with iodine indicated negligibly small traces of pyrrole.[8] The liquid had the strong nauseating odor of nitriles and isonitriles. Another run at the lower temperature of 375° gave substantially the same results.

n-Amylamine was passed over chromium oxide on alumina at 400° for two hours. Gas was evolved at a rate of 50 ml./min. and consisted of 14% brine soluble gases (ammonia, hydrogen cyanide, etc.), 24% unsaturated hydrocarbons, 55% hydrogen and 7% saturated hydrocarbons. The liquid product was about 50% of the liquid feed. On careful fractionation it gave a flat at 32° which decolorized bromine water and whose index of refraction $n^{20}\mathrm{D}$ 1.3811 suggested its identification as pentenes. A further plateau at 80–82° seemed to be acetonitrile. Finally the plateau at 110–125° from its extremely nauseating smell and boiling point was identified as *n*-amyl isocyanide. No pyridine was found.

Reaction of Furfuryl Alcohol with Ammonia.—Ammonia alone does not attack furfuryl alcohol either in the liquid or the vapor phase up to 475°.

Attempts to catalyze the reaction in the liquid phase with anhydrous copper sulfate resulted in rapid resinification both at room temperature and at 100°. Dilution of the furfuryl alcohol with anhydrous ethanol prevented the resinification even at 72° but no pyridine was formed. Similarly no pyridine was found after a month of treatment at room temperature of furfuryl alcohol with excess concentrated aqueous ammonia.

Condensation was then attempted at 475° in the vapor phase over activated alumina and over chromium oxide on alumina. Extensive dehydration of the alcohol occurred and ammonium carbonate was formed. No pyridine could be detected in the liquid products, which consisted largely of unreacted furfuryl alcohol and water. An extensive deposit of carbon was formed on the catalyst in the first stages of the process and this poisoned the catalyst for further reaction. Furthermore, such fouled catalyst lost its ability to dehydrate absolute alcohol at 350°. A comparative study of the behavior of furfuryl alcohol *without* the ammonia on activated alumina showed that furfuryl alcohol disproportionates into silvane (15%) and furfural (*ca.* 14%) as reported by R. Paul.[9] Furthermore, this dehydration is accompanied by the same type of extensive carbonization of the catalyst as in the presence of ammonia. These experiments were carried out with specially purified furfuryl alcohol. The silvane was determined by analytical distillation and the index of refraction $n^{20}\mathrm{D}$ 1.4320, while the furfural was determined by an analysis of the 168°

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(8) Meyer, "Nachweis und Bestimmung organischer Verbindungen," Julius Springer, Berlin, 1932.

(9) Paul, *Bull. soc. chim.*, [5] **2**, 2220–2227 (1933).

cut colorimetrically with aniline acetate and the index of refraction.[10] As the experiments with furfuryl alcohol were uniformly unsuccessful in producing even traces of pyridine, work was transferred to the more promising and more stable tetrahydrofurfuryl alcohol.

Reaction of Tetrahydrofurfuryl Alcohol with Ammonia.—The products of this reaction were an oily and an aqueous layer. These were separated, and the oil layer was subjected to analytical distillation. The aqueous layer was ether extracted and also subjected to distillation. The various runs on the different catalysts produced essentially the same distillation pattern. The following cuts were made.

A. Material boiling below the 92° plateau: This amounted to less than 10% of the product and contained 20% water. Judging from its non-basic character it must consist of hydrocarbons, di- and tetra-hydropyranes. It was not investigated any further.

B. Material of the flat boiling at 92° which was identified as the water–pyridine azeotrope (three moles of water to one of pyridine) by its boiling point, its unmistakeable odor of pyridine, the melting point of its picrate 163–165° and the mixed melting point 163–165° of this picrate with equal amount of pure pyridine picrate (m. p. 163–165°).

C. Plateau boiling at about 106° consisted of a small amount of pyridine in piperidine. A portion of this cut was converted into the picrate. Repeated careful fractional crystallization from ethanol gave two types of crystals. The less soluble picrate (*ca.* 0.78 g.) melted at 163–165° and gave with an equal amount of pure pyridine picrate (m. p. 163–165°) a melting point of 163–165°. The more soluble fraction (2.15 g.) had a melting point of 147–149° and a mixed melting point of 146–149° with an equal amount of known pure piperidine picrate (m. p. 147–149°). This definitely identifies piperidine as the material of this distillation plateau especially since the boiling point of piperidine is 105.8°.

D. A further plateau was obtained in the region 125–130°. This material is characterized by erratic temperature fluctuation during distillation and a concomitant production of a white solid similar to ammonium carbonate in appearance. Undoubtedly one is dealing with a substance which is decomposing on distillation. The close agreement of the indices of refraction from this cut but of various runs over different catalysts, suggests that one is dealing with a rather pure material. The following qualitative tests were carried out on this material. At room temperature it is a thick, viscous liquid of a highly unpleasant odor. It fumes in air, evolving ammonia on standing. Its *p*H is greater than 8.4 by phenol red and less than 9.3 by thymolphthalein. Nitrogen is shown to be present by fusion with sodium. It is sparingly soluble in water, soluble in ether and in 5% HCl. It decolorizes bromine water and precipitates MnO_2 from potassium permanganate. It does not reduce Fehling solution. Attempts to crystallize the picrate resulted only in a red oil. The material was not a pyrrole because cadmium chloride gave no reaction while hydrochloide acid gave a dark red solution instead of a polymer. This material seemed to be an amine because treatment with sodium nitrite and hydrochloric acid at 0° gave a light oil which on warming to room temperature evolved nitrogen and dissolved in water. The product so obtained reduced Fehling solution and gave a slight precipitate with dinitrophenylhydrazine. Furthermore, the disagreeable odor of the original material turned into one reminiscent of quince. Further confirmation of the basic character of the original material was the formation of precipitates with acetyl chloride, and also with dry hydrogen chloride in ether, and its reaction with methyl iodide. These derivatives, however, turned gummy and could not be recrystallized. The substance was not further investigated.

The residue was material which boiled above 165°. It consisted in part of unreacted tetrahydrofurfuryl alcohol boiling at 169°, uncorrected, since its index of refraction was $n^{20}\text{D}$ 1.4527 while that of the pure alcohol was 1.4520 and its density d^{20}_4 is 1.0538 while that of the pure material is 1.0550. Another portion was obtained by vacuum distillation of the residue at 20 mm. pressure. Heating up to 250° produced an orange oil which was soluble in 6 *N* hydrochloric acid, alcohol, benzene and tetrahydrofurfuryl alcohol but which did not dissolve in 10% sodium hydroxide. It was not further investigated but consisted undoubtedly of higher molecular material and of secondary and tertiary amines. The material which did not distill up to 250° under 20 mm. pressure solidified on cooling to room temperature.

The reaction between tetrahydrofurfuryl alcohol and ammonia was studied on the following catalysts and at the following temperatures:

	Temp., °C.
Activated alumina	300, 350, 400, 450
Chromium oxide on alumina	300, 350, 400, 450
Copper on alumina	350
Nickel on alumina	250, 300, 400
Silica gel	300, 350, 400
Thoria	400

Thoria and silica did not give any pyridine or piperidine. The addition of chromium oxide, nickel or copper did not appreciably affect the catalytic activity of activated alumina so far as the yields of pyridine or piperidine are concerned. The following are the results which were obtained with activated alumina during the course

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(10) $n^{20}\text{D}$ for furfuryl alcohol is 1.4868, while for furfural it is 1.5255: Dunlop and Trimble, *Ind. Eng. Chem.*, **32**, 1000 (1942).

of a three-hour run and are typical of results obtained when using an alumina support.

Temp., °C.	% Pyridine	% Piperidine	% X
300	1.9	0	1.4
350	1.8	5	13
400	2.9	8	0
450	Trace	Trace	0

It is seen from the above results that the best yields of pyridine and piperidine are obtained on activated alumina at 400°.

Reaction of Dihydropyrane with Ammonia.—There was little or no reaction on chromium oxide–alumina catalyst at 350°. At 400° distillation of the products showed plateaux at 75, 91, 105 and 130°. By methods described in the experiments on tetrahydrofurfuryl alcohol, the latter three were found to have the same composition as previously found, *i. e.*, pyridine–water, azeotrope, piperidine, and the same unknown compound. The plateau at 75° which came over in two layers was found to be pentamethylene oxide (n^{20}_{D} 1.4190 found, while for pentamethylene oxide it is 1.4200). This compound appears to have resulted from the hydrogenation of part of the dihydropyrane feed. The yields were 0.9 mole per cent. of pyridine, 8.9 mole per cent. of piperidine and 10 mole per cent. of pentamethylene oxide. There was a smaller loss of the initial feed as cracked gases or carbon on the catalyst than in the case of tetrahydrofurfuryl alcohol. The general similarity of this reaction to that between tetrahydrofurfuryl alcohol and ammonia makes it probable that both proceed by the same mechanism. In particular the existence of a plateau at 130° on the distillation of the reaction products of both reactions makes it likely that this unknown substance is readily derived from both tetrahydrofurfuryl alcohol and from dihydropyrane.

Reaction of Pentamethylene Oxide and Ammonia.—At 350° there was little reaction on activated alumina, the product being essentially unchanged pentamethylene oxide. At 400° there was some (10%) material boiling below 100° and a plateau at 106° corresponding to 16% yield of piperidine. These results agree with those reported by Yur'ev.[11] The yields for the condensation of pentamethylene oxide with ammonia were not much greater than those found with tetrahydrofurfuryl alcohol and dihydropyrane.

Summary

1. Free energy values were calculated on the basis of spectroscopic data for various methods of synthesis of pyridine.
2. Amylamine and diethylamine do not cyclicize to aromatic bases in the vapor phase over chromium oxide on alumina.
3. Furfuryl alcohol does not react with ammonia to give pyridine in the liquid phase at low temperature nor in the vapor phase over alumina or chromium oxide on alumina at high temperatures.
4. Tetrahydrofurfuryl alcohol reacts with ammonia in the vapor phase to give at 400° over alumina 3% pyridine and 8% piperidine. Higher boiling material and an unknown nitrogenous substance boiling at 130° are produced in considerable amounts.
5. Dihydropyrane and ammonia react over chromium oxide on alumina in the vapor phase at 400° to give 1% pyridine and 9% piperidine.
6. Pentamethylene oxide and ammonia react over alumina at 400° to give 16% piperidine and traces of pyridine.

[11] Yur'ev, Pervova and Sazonova, *J. Gen. Chem.*, *U. S. S. R.*, **9**, 5904 (1939).

PRINCETON, N. J. RECEIVED JULY 14, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Kinetics of the Hydrion Catalyzed Esterification of Some Substituted Benzoic Acids with Cyclohexanol[1]

BY R. J. HARTMAN,[2] H. M. HOOGSTEEN[2] AND J. A. MOEDE[3]

The type of esterification in which this investigation is concerned may be represented as

$$\mathrm{ROH} + \mathrm{R'COOH} + \mathrm{H}^+ \rightleftarrows \mathrm{R'COOR} + \mathrm{H_2O} + \mathrm{H}^+$$

where R is the cyclohexyl radical and R′ is a monosubstituted phenyl radical. Many qualitative studies have been carried out wherein attempts have been made to show the relationship between the nature and position of the substituent on the benzene ring and the rate of esterification.[4–12] Hammett[13] has expressed this relationship by the equation

[1] This paper is constructed from a thesis presented by Harold Martin Hoogsteen to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry. Original manuscript received June 14, 1943.

[2] Present address: The Dow Chemical Company, Midland, Michigan.

[3] Present address: Radford Ordnance Works, Radford, Virginia.

[4] Goldschmidt, *Ber.*, **28**, 3224 (1895).

[5] Goldschmidt and Udley, *Z. physik. Chem.*, **60**, 728 (1907).

[6] Ingold and Ingold, *J. Chem. Soc.*, 756 (1932).

[7] Rolfe and Hinshelwood, *Trans. Faraday Soc.*, **30**, 935 (1934).

[8] Evans, Morgan and Watson, *J. Chem. Soc.*, 1168 (1935).

[9] Newling and Hinshelwood, *ibid.*, 1357 (1936).

[10] Fairclough and Hinshelwood, *ibid.*, 598 (1939).

[11] Datta, Day and Ingold, *ibid.*, 838 (1939).

[12] Hughes, Ingold and Masterman, *ibid.*, 840 (1939).

[13] Hammett, THIS JOURNAL, **59**, 96 (1937).