

3,4-Di(2-pyridyl)furoxan. Pyridine-2-aldoxime (2 g.) was dissolved in 8*N* hydrochloric acid (15 ml.) at 0°. Chlorine was passed into the ice cold solution for 20 min. An excess of concd. aqueous sodium carbonate was added and the solution was warmed on a steam bath for 30 min. The solution was filtered and the brown solid was recrystallized from benzene/cyclohexane and from water to give 3,4-di(2-pyridyl)furoxan (0.5 g.; 27%), m.p. 169–170.5°. For analysis, see Table II.

Pyridine-2-aldoxime was dissolved in carbon tetrachloride or in ether, and chlorine was passed into the ice-cold solution for 20 min. The solution was filtered and the white solid was retained. The white solid was insoluble in organic solvents but soluble in water to give an acid solution.

The white solid was suspended in spectro-grade carbon tetrachloride and an excess of 10% aqueous sodium hydroxide was added to the ice-cold suspension. The mixture was allowed to stand at 0°, with occasional shaking, for 20 min. Part of the carbon tetrachloride layer was removed. The infrared spectrum of this solution showed only very weak absorption. On standing, the aqueous solution de-

posited 3,4-di(2-pyridyl)furoxan, m.p. 165–168° after recrystallization from water.

A portion of the white solid was allowed to stand at room temperature for 48 hr. It was then dissolved in water and the ice-cold solution was made alkaline. 3,4-Di(2-pyridyl)furoxan, m.p. 166–168° after recrystallization from water, was precipitated.

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The Basic Strength of Pyrrole

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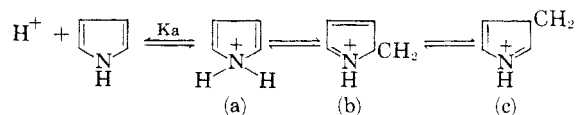
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The pK_a of pyrrole has been determined spectrophotometrically using the Hammett H_0 indicator method and is found to be -0.27 . The problems caused by the acid-catalyzed polymerization of pyrrole have been overcome by a back-extrapolation method and a differential plot.

It has long been recognized that pyrrole is a very weak base although no reliable measurement of its pK_a value has been made. Hall¹ established a relationship between the basicity constants of a series of bases in a nonaqueous solvent and water, and showed that by titrating the bases in glacial acetic acid, the pK_a values of certain bases, which could not be determined in aqueous solutions, could be predicted. Pyrrole was dissolved in glacial acetic acid and titrated conductometrically with perchloric acid; by inspecting the titration curve obtained, the approximate pK_a of pyrrole was reported to be $+0.4$. More recently, Tamres and co-workers² found that for a series of closely related compounds there was a linear relationship between the acidity constants and the ability of these compounds to form hydrogen bonds. For a number of compounds related to pyridine it was shown that $\Delta\nu = 14.8 pK_a + 136$, where pK_a is the acid dissociation constant of the compound and $\Delta\nu$ the frequency shift in cm^{-1} of the oxygen-deuterium stretching frequency in the infrared spectrum of methyl deuterioalcohol solutions. In the presence of pyrrole, $\Delta\nu$ was 161 cm^{-1} and therefore the pK_a of pyrrole is 1.7 if the above linear relationship is applicable. However, too much reliance cannot be

placed on acid dissociation constants obtained from studies on hydrogen bonding for a number of reasons. For example, different steric and solvation effects will be involved with different pyridine bases; there is also a fundamental difference between protonation of a pyridine type molecule where electrostatic forces are primarily involved, and hydrogen bond formation with such a compound in which a covalent bond is formed.² Moreover, in most pyridine type bases protonation takes place at the nitrogen atom, whereas in pyrrole it is possible that protonation takes place at a carbon atom. If carbon protonation occurs³ the above relationship between $\Delta\nu$ and pK_a is less likely to be valid.

In spite of the fact that pyrrole is an extremely weak base a certain amount of the protonated species (a), (b), or (c) is formed when pyrrole is



added to mineral acids. The protonated ion of pyrrole is highly unstable and undergoes polymerization very readily, one of the chief products of polymerization being the trimer, 2,5-dipyr-

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(3) H. A. Potts and G. F. Smith, *J. Chem. Soc.*, 4018 (1957).

rolypyrrolidine.³ The formation of polymers even in moderately strong acid solutions has been the main difficulty in the direct determination of the pK_a of the very weak base, pyrrole. This paper is concerned chiefly with the elimination of the experimental difficulties caused by polymerization and the determination of the pK_a of pyrrole by a spectrophotometric method.

EXPERIMENTAL

Materials. A sample of pyrrole was kindly supplied by Ansul Chemical Company, Wisconsin. The compound had the following physical constants: B.p. 131° at 760 mm. pressure; n_D^{20} 1.5091. Perchloric acid obtained from General Chemical Company, New York, was used to prepare a 6M stock solution. This solution was diluted appropriately and used in all the spectrophotometric measurements.

Apparatus. A Cary Model 14 spectrophotometer with 1 cm. silica cells was used for most of the preliminary work. Subsequent determinations were carried out with a Beckman Model DU spectrophotometer fitted with a photomultiplier attachment using matched 1 cm. silica cells.

Absorption spectrum of pyrrole. A stock solution containing 0.0522 g. pyrrole per l. of water was used to make up a series of solutions which ranged from 0.1 to 1.1M in perchloric acid, each solution being $6.22 \times 10^{-6}M$ in pyrrole. The absorption spectra of these solutions were determined using the Cary spectrophotometer. Fig. 1 shows the variation of the ultraviolet absorption spectrum of pyrrole with acidity, for three of the solutions used. The absorption maximum was $204 \pm 1 m\mu$ for all solutions; there was no measurable shift of the absorption maximum with variation in concentration of perchloric acid.

Variation of the absorption spectrum of pyrrole with time. Twenty-five-ml. portions of a stock aqueous solution of pyrrole containing 0.0506 g. pyrrole per l. were pipetted into a series of volumetric flasks containing water and perchloric acid. The final strength of the perchloric acid ranged from 5.0M to 0.10M. The time of mixing for all the solutions was kept constant. The absorbance of the solutions containing a constant amount of pyrrole was read at 205 $m\mu$ in a 1 cm. silica cell, and absorbance readings were taken at definite time intervals in order to determine the concentration of acid below which polymerization was not appreciable (Table I). All measurements were made at $25 \pm 1^\circ$.

RESULTS

Fig. 1 shows that the absorbance of the protonated form of pyrrole is appreciably greater than that of pyrrole. Therefore, it should be possible to determine the molar absorptivity of the cationic species of pyrrole, which is a proton donor, as well as the molar absorptivity of pyrrole, a proton acceptor, by measuring the absorbance of a solution at a sufficiently high and at a sufficiently low acidity, respectively. The molar absorptivity of the unprotonated pyrrole was readily measured in solutions that were 0.10 to 0.40M in perchloric acid. Preliminary experiments had shown that in solutions that were greater than 2.0M in perchloric acid, the protonated form of pyrrole was the predominant species present. However, if the solutions were greater than 1M in perchloric acid polymerization takes place (Table I), thus making the direct determination of the molar absorptivity

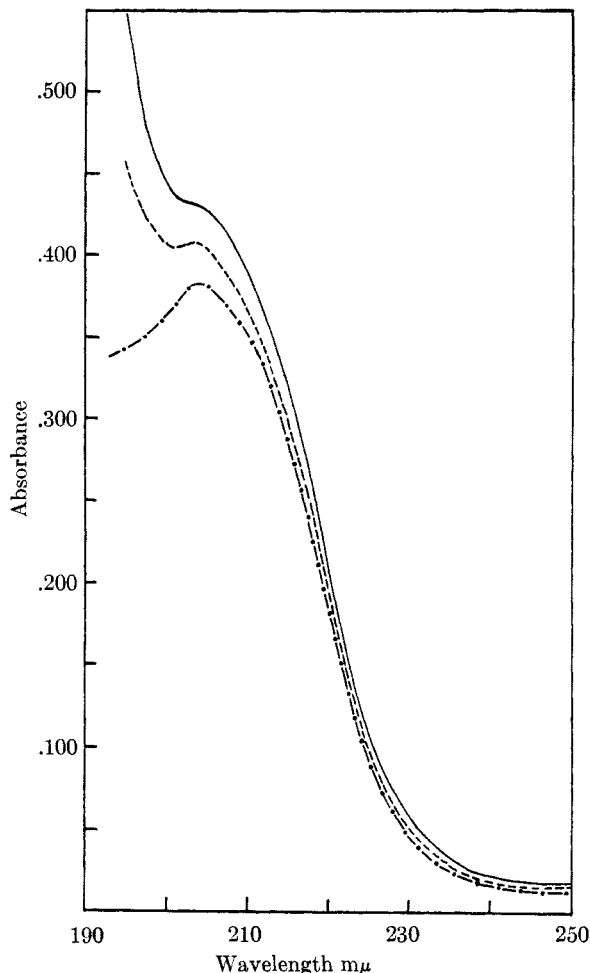
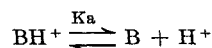


Fig. 1. The absorption spectrum of pyrrole ($6.22 \times 10^{-6}M$) in perchloric acid solutions. Legend.—1.00 M acid; ---- 0.500 M acid; -·-·- 0.100 M acid

of the protonated species impossible. An approximate value of the molar absorptivity of the protonated form of pyrrole was obtained by plotting the absorbance values of the solutions against time and extrapolating to zero time. In the case of solutions that were 1.0 to 2.0M in perchloric acid, the absorbance decreased relatively slowly with time and it was possible to extrapolate these values readily to zero time. If the perchloric acid concentration was greater than 2.0M there was a very rapid decrease in absorbance with time, thus introducing a great degree of uncertainty in the extrapolation. The best value for the molar absorptivity of the protonated form of pyrrole that was obtained by the extrapolation method was 7425, at 205 $m\mu$.

One of the most convenient methods of determining significant pK_a values of very weak bases is to make use of the H_0 acidity scale.⁴ If the ionization of the protonated form of pyrrole is represented by



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TABLE I
 VARIATION OF THE ABSORBANCE OF AN ACID SOLUTION OF PYRROLE ($7.54 \times 10^{-5}M$) WITH TIME

Molarity of Perchloric Acid	5.00	3.00	2.00	1.20	1.10	1.00	0.950	0.900
Time in Min.	Absorbance at 205 m μ							
0	0.562 ^a	0.558 ^a	0.560 ^a	0.522 ^a	0.505 ^a	0.497 ^a	0.490 ^a	0.487 ^a
4	0.475	0.518	0.555	0.512	—	—	—	—
5	—	—	—	—	0.504	0.495	0.490 ^a	0.487
6	0.460	0.495	—	—	—	—	—	—
8	0.450	0.485	—	—	—	—	—	—
10	0.450	0.477	0.540	0.504	—	—	—	—
20	0.450	0.470	0.528	0.498	0.498	—	0.486	0.486
30	0.450	0.467	0.520	—	—	—	—	—
40	—	—	—	0.488	0.494	—	0.484	0.485
50	—	—	0.510	—	—	—	—	—
60	—	—	0.506	0.486	0.492	0.493	—	—

^a Absorbance values extrapolated to zero time.

the absorbance of a solution containing both ionic species is given by

$$\epsilon \cdot C = \epsilon_{\text{BH}^+} \cdot C_{\text{BH}^+} + \epsilon_{\text{B}} \cdot C_{\text{B}}$$

where the total concentration of pyrrole in the solution is given by

$$C = C_{\text{BH}^+} + C_{\text{B}}$$

C_{BH^+} and C_{B} are the concentrations in moles per liter, of the forms BH^+ and B and ϵ , ϵ_{BH^+} , and ϵ_{B} the molar absorptivities at 205 m μ of a mixture of the two forms, of the protonated species and of the unprotonated species of pyrrole respectively. The ratio of the ionized to the unionized forms of pyrrole could be written as

$$\frac{C_{\text{BH}^+}}{C_{\text{B}}} = \frac{\epsilon_{\text{B}} - \epsilon}{\epsilon - \epsilon_{\text{BH}^+}}$$

This ionization ratio is related to the acid ionization constant of pyrrole and the acidity function of the medium by the equation

$$H_0 = pK_a + \log \frac{C_{\text{B}}}{C_{\text{BH}^+}}$$

or

$$H_0 = pK_a + \log \frac{\epsilon - \epsilon_{\text{BH}^+}}{\epsilon_{\text{B}} - \epsilon}$$

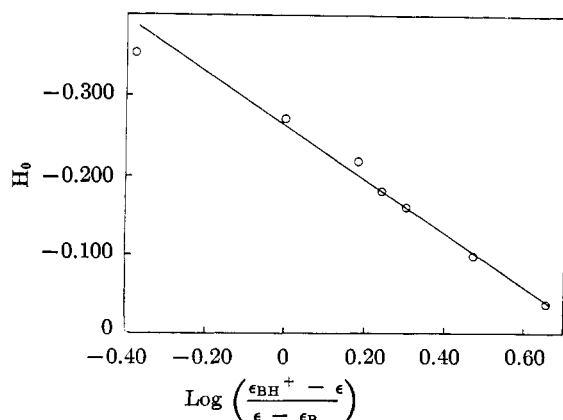


Fig. 2. Determination of pK_a using a linear plot

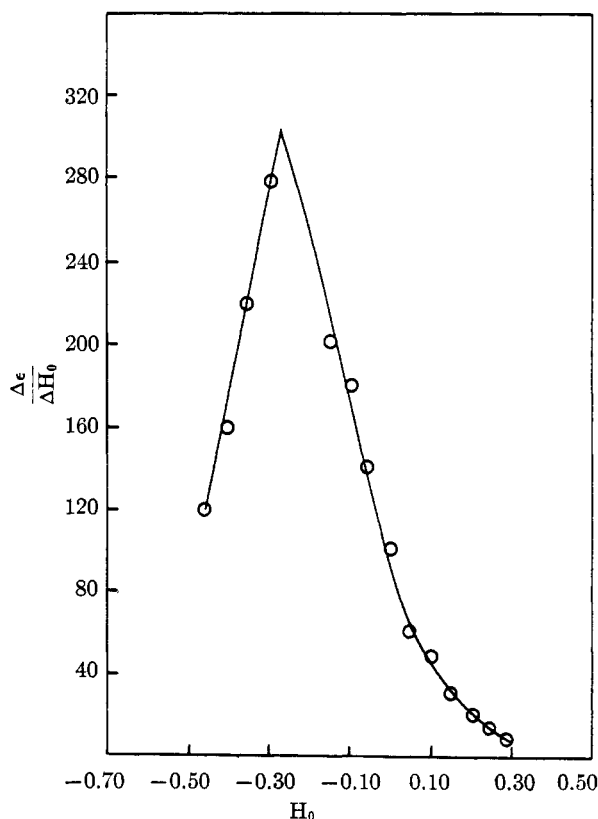


Fig. 3. Determination of pK_a using a differential plot

As the values of H_0 at selected molarities of perchloric acid have been determined,⁴ the value of pK_a can be calculated by a number of methods. If H_0 is plotted against ϵ , the value of H_0 at which $\epsilon = (\epsilon_{\text{BH}^+} + \epsilon_{\text{B}})/2$ gives pK_a ; or if H_0 is plotted against $\log (\epsilon - \epsilon_{\text{BH}^+})/(\epsilon_{\text{B}} - \epsilon)$ the intercept of the straight line obtained will give pK_a (Fig. 2). However, there is some uncertainty about the exact value of ϵ_{BH^+} since pyrrole polymerizes very rapidly in solutions that are greater than $2M$ in perchloric acid. It is possible to determine the pK_a of pyrrole even though the exact value of ϵ_{BH^+} is not known. If $d\epsilon/dH_0$ is plotted against H_0 the

value of H_0 at which $d\epsilon/dH_0$ reaches a maximum gives pK_a (Fig. 3). All values of H_0 were obtained from tables.⁴ The value of pK_a for pyrrole obtained from plots of the type shown in Figs. 2 and 3 is -0.27 .

DISCUSSION

The ultraviolet absorption spectrum of pyrrole in hexane consists of a strong band at $210\text{ m}\mu$ ($\epsilon = 15,000$) and a very weak band at $240\text{ m}\mu$ ($\epsilon = 300$).⁵ The high intensity absorption is probably due to $\pi \rightarrow \pi^*$ transitions but the low intensity band cannot be attributed to the presence of $n \rightarrow \pi^*$ transitions in pyrrole. It has been reported that this low intensity band was not observed in the spectra of a number of α and β -alkyl pyrroles in ethanol.⁶ On the other hand *N*-methylpyrrole has an absorption band in the $240\text{ m}\mu$ region⁷; this is probably due to the reduction in electronegativity of the nitrogen atom caused by the electron-releasing properties of the methyl group. This facilitates the participation of the nitrogen $2p$ electrons in conjugation with the π -electrons in the pyrrole ring. Fig. 1 shows the ultraviolet spectra

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of pyrrole in aqueous solutions containing perchloric acid. In no case was a low intensity band in the $240\text{ m}\mu$ region obtained. Therefore, on the basis of the ultraviolet spectra alone, it is apparently not possible to decide whether carbon protonation or nitrogen protonation occurs in pyrrole in the presence of acids.

The chemical reactions of pyrrole indicate that it is aromatic in character, the electrons on the nitrogen atom being delocalized on the four carbon atoms, thereby making the nitrogen atom a very poor proton acceptor. This, of course, implies that pyrrole should be a very weak base. This work has shown that pyrrole whose pK_a is -0.27 is a weaker base than has been expected. Unfortunately no pK_a values exist for related compounds for purposes of comparison. It would be of interest to determine the pK_a values of substances such as indole or carbazole, which should also be very weakly basic, and also the acid dissociation constants of substituted pyrroles, notably *N*-methylpyrrole.

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Studies in the Synthesis of 2,5-Diphenylpyrrole

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The synthesis of 2,5-diphenylpyrrole (III) from *trans*-1,4-diphenyl-2-butene-1,4-dione (I) via 1,4-diphenyl-1,4-butanedione (II) has been elaborated. Optimum conditions for the conversion of I to II have been found to be the palladium catalyzed pressure hydrogenation of I in isopropyl alcohol at room temperature. The pyrrole ring most effectively may be formed from II with ammonia under pressure at $140\text{--}145^\circ$.

The relative stability of 2,5-diphenylpyrrole (III) prompted us to include this compound in our investigations on new polymerizable heterocyclic compounds. Principally, there are two small-scale procedures for the synthesis of III, namely, by the ring-closing action of ammonia or ammonium acetate on either 1,4-diphenyl-1,4-butanedione^{1,2} (II) or ethyl phenacylbenzoylacetate.² For the planned investigations it was necessary to elaborate a route by which a pure grade of III could economically be synthesized in larger quantities. Such a path lay in the reaction sequence starting with *trans*-1,4-diphenyl-2-butene-1,4-dione (I), converting this into II and finally ring-closing this to III.

Chief difficulties in this reaction sequence were encountered particularly with the conversion of I

into II. Although a variety of methods for reducing I to II is known, the procedures either require costly reagents or give low yields or furnish II along with other by-products. The latter are frequently the result of a pronounced tendency of I to take a bimolecular course under certain reducing conditions. Thus, even in such reductions of I that superficially appear to proceed smoothly, for instance those effected by zinc,^{3,4} we found as by-product a colorless compound melting at 159° . It has twice the molecular weight of I but does not respond to any carbon-carbon double bond agents and is most probably 4,5-dibenzoyl-1,2-diphenyl-1,2-cyclohexanediol (IV).⁵

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