considerable hydrolysis of the halosilane[4,5]; it may react with silane–hydrogen accompanied by the nearly quantitative elimination of the hydrogen and the introduction of an alkoxy group in its place[6]; and it may cleave aryl and other sensitive substituents from the silicon atom. Previous efforts to minimize the effects of the hydrogen halides centered around its elimination from the system either by use of selective solvents[6] or hydrogen halide acceptors.[7] However, these procedures are not completely satisfactory.

Preparation of Diethoxydimethylsilane and Chloroethoxydimethylsilane.—Approximately 0.1 g. of aluminum chloride was added to a mixture of 124.0 g., 0.96 mole, of dimethyldichlorosilane and 142.0 g., 0.96 mole, of freshly distilled ethyl orthoformate. Heat was evolved and the mixture turned dark, and a gas boiling near room temperature was evolved. When the initial reaction subsided the mixture was heated at reflux for 16 hours. Further experimentation indicated that refluxing for this period of time was unnecessary.

Upon distillation there was recovered 32.8 g., 25.6%, of dimethyldichlorosilane. Chloro-(ethoxy)-dimethylsilane was obtained, b.p. 94–95° at 740.5 mm., $n^{25}D$ 1.3898, yield 74.4 g., 56.0%. A third fraction, diethoxydimethylsilane, also was obtained, b.p. 110° at 740.5 mm., $n^{25}D$ 1.3793, yield 22.5 g., 15.8%. The only other material present was ethyl formate.

(4) W. C. Schumb and D. F. Holloway, THIS JOURNAL, **63**, 2753 (1941).
(5) H. W. Post and H. M. Norton, *J. Org. Chem.*, **7**, 528 (1942).
(6) Martha E. Havill, I. Joffe and H. W. Post, *ibid.*, **13**, 280 (1948).
(7) S. W. Kantor, THIS JOURNAL, **75**, 2712 (1953).

Preparation of Diethoxymethylsilane.—To 148.0 g., 1.0 mole, of freshly distilled ethyl orthoformate was added 57.5 g., 0.5 mole, of methyldichlorosilane. An exothermic reaction set in immediately with the evolution of a gas. A water-bath was used to maintain a reaction temperature below 46°. The reaction subsided within one-half hour.

Distillation revealed the presence of the following ethoxysilanes in addition to ethyl formate: methyldiethoxysilane, b.p. 94° at 731.3 mm., $n^{25}D$ 1.3724, d^{25}_4 0.829; sp. ref. 0.2747, calcd. sp. ref. 0.2732; yield 54.8 g., 82%. *Anal.* Calcd. for $CH_3SiH(OC_2H_5)_2$: active H, 0.74; Si, 20.92. Found: active H, 0.78, 0.82; Si, 20.57, 20.59.

There was also obtained methyltriethoxysilane, b.p. 135–138° at 731.3 mm., $n^{25}D$ 1.3838–67, d^{25}_4 0.877; sp. ref. 0.2677, calcd. sp. ref. 0.2605; yield 14.2 g., 16%.

Ethoxylation of Phenyltrifluorosilane.—Phenyltrifluorosilane, 52.5 g., 0.324 mole, was heated with 218.0 g., 1.47 moles, of freshly distilled ethyl orthoformate in the presence of a catalytic quantity of anhydrous aluminum chloride for approximately 30 hours. The distillate contained the following ethoxysilanes in addition to ethyl formate and unreacted ethyl orthoformate: phenylfluorodiethoxysilane, b.p. 110° at 25 mm., $n^{25}D$ 1.4487, d^{25}_4 1.029; sp. ref. 0.2605, calcd. sp. ref. 0.2558; neut. equiv. 214, 217, calcd. neut. equiv. 214; yield 27.5 g., 39.6%.

There was also obtained phenyltriethoxysilane, b.p. 133° at 25 mm., $n^{25}D$ 1.4580, d^{25}_4 0.988; sp. ref. 0.2761, calcd. sp. ref. 0.2757; yield 44.5 g., 57.5%.

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Anabasine

BY ROBERT H. LINNELL

RECEIVED SEPTEMBER 9, 1953

A value for the second acid dissociation constant of α-(β-pyridyl)-piperidine has been determined spectrophotometrically. This compound is reduced polarographically when present as BH^+ *via* a 2-electron step. The Ilkcovic equation is obeyed.

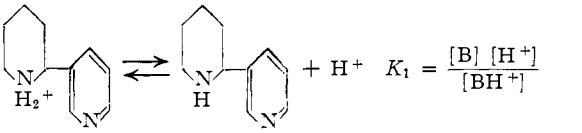
As part of a research program on nitrogen heterocyclic molecules it was necessary to study the polarographic reduction and ultraviolet solution spectra (to obtain the dissociation constant) of α-(β-pyridyl)-piperidine. As these results are of some general interest they are reported here.

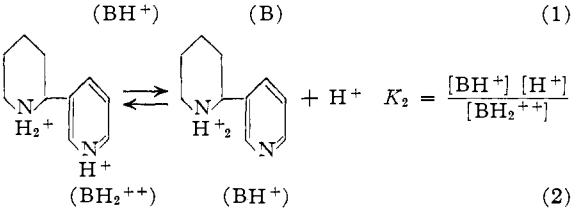
Experimental

All ultraviolet spectra were determined on a Beckman Model DU instrument; *p*H measurements were made with a Cambridge Instrument Co. portable *p*H meter. The polarograms were recorded photographically on a Sargent–Heyrovsky Model XII polarograph using a Heyrovsky Erlenmeyer type cell with Hg anode. The capillary characteristics were m = 1.62 mg./sec., t = 3.80 sec./drop (determined with 66.5 cm. open circuit, in distilled water). The anabasine was provided by Dr. Roark, U. S. Dept. of Agriculture and was used without further purification; it had the following physical constants: $n^{25}D$ 1.5387, m.p. 12.0±0.1° (determined with Cu–constantan thermocouple from time–temperature warming curves of frozen anabasine—cooling curves could not be used due to supercooling). All chemical reagents were analytical grade. The methylcyclohexane was purified with fuming H_2SO_4.

Results and Discussion

The ultraviolet solution spectra are shown in Fig. 1. The following equilibria are assumed to exist in aqueous anabasine solutions





The value of K_1 should be similar to that of piperidine since a substituent in the 3-position cannot

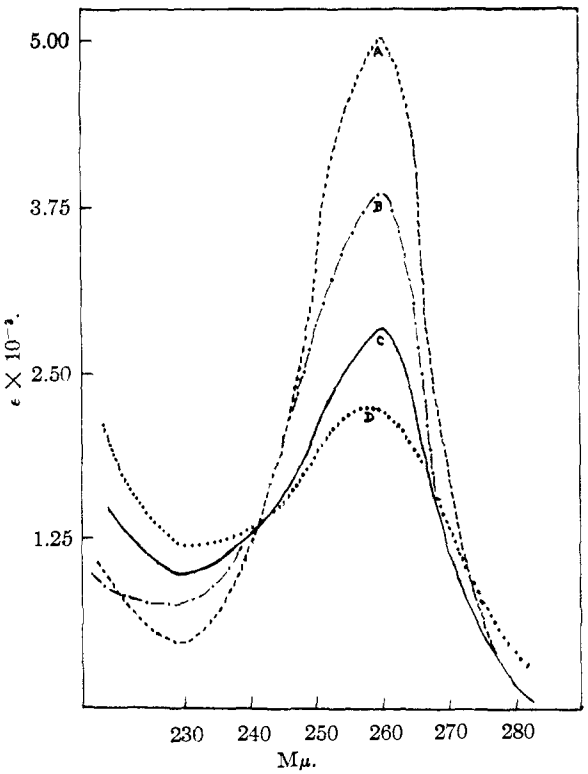


Fig. 1.—Ultraviolet spectra of anabasine; all solutions were approximately 2.5×10^{-4} mole anabasine per liter: A, 0.8 *N* HCl; B, *p*H 3.46 citric acid-Na_2HPO_4 buffer; C, *p*H 8.90 Na_2HPO_4; D, methylcyclohexane.

exert a great influence on the ring nitrogen. Therefore $pK_1 \cong 11.1$[1] and at *p*H 9.1, 99% of the anabasine will be in the form (BH^+) and a *p*H 13.1 is required to get 99% of the anabasine in the form (B). The change in the molar extinction coefficient of (B) and (BH^+) is very small compared to the difference between (BH^+) and (BH_2^{++}) as is to be expected since the second H^+ goes on the conjugated pyridine ring where several resonance structures are possible and hence the transition probability is much greater for the absorption act. It was accordingly not possible to experimentally determine K_1 by the spectrophotometric method. In Table I the data for pK_2 are given. These values were corrected for miss-match in the Beckman quartz cells and for ionic strength.[2] *pK* values were calculated according to the relationship

$$pK = p\mathrm{H} + \log \frac{\epsilon_x - \epsilon_{BH^+}}{\epsilon_{BH_2^{++}} - \epsilon_x} - \log \gamma_{BH^+} + \log \gamma_{BH_2^{++}}$$

where

ϵ_x = molar extinction coefficient of buffered soln. containing both BH^+ and BH_2^{++}

ϵ_{BH^+} = molar extinction coefficient of BH^+ obtained from *p*H 8.9 soln. (Na_2HPO_4 buffer)

$\epsilon_{BH_2^{++}}$ = molar extinction coefficient of BH_2^{++} obtained from strong acid soln.

$\log \gamma = -AZ^2\sqrt{u}$ where the contribution of BH^+ and BH_2^{++} to *u* were neglected. $A = 0.503$

(1) W. F. K. Wynne-Jones and G. Saloman, *Trans. Faraday Soc.*, **34**, 1321 (1938); L. W. Pickett, M. E. Corning, G. M. Wieder, D. A. Semenow and J. M. Buckley, THIS JOURNAL, **75**, 1618 (1953).

(2) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 117.

The value of pK_2 reported here can be compared with pK_2 values for the dipyridyls.[3] Anabasine (as BH_2^{++}) is a weaker acid than any of the corresponding dipyridyls (the values of K_2 given in reference 3 are not corrected for ionic strength and the correction must be estimated before comparison is made with the anabasine value reported here). Since the piperidine nucleus cannot exhibit resonance forms, it will influence the pyridine nucleus less than in the corresponding 2,3-dipyridyl. However, some electrostatic repulsion will still be found and this will make pK_2 for anabasine less than pKa for pyridine. This is experimentally found to be the case (pKa for pyridine = 4.2).

TABLE I

pK_2 OF ANABASINE—SPECTROPHOTOMETRIC METHOD

Buffer	*p*H	$\epsilon_{max} \times 10^{-3}$	pKa[a]
0.8 *N* HCl	..	5.18	..
Na_2HPO_4 + citric acid	2.88	4.52	3.19
Na_2HPO_4 + citric acid	3.46	3.84	3.19
Na_2HPO_4 + citric acid	4.08	3.12	3.14
Na_2HPO_4 + citric acid	4.49	2.98	3.31
Na_2HPO_4 + citric acid	4.69	2.85	3.16
Na_2HPO_4 + citric acid	4.90	2.83	3.28
Na_2HPO_4	8.90	2.73	..
0.1 *N* NaOH	..	2.90[b]	..
Methylcyclohexane	..	2.19	..
		Av.	3.21 ± 0.07

[a] The temperature varied from 28–31°. Except for the HCl solution the ionic strength of the buffers was no greater than 0.03. This is a corrected thermodynamic dissociation constant. [b] This value seems to be higher than expected. The reason for this is not clear at present.

Previous polarographic reduction studies[4] on the dipyridyls showed that the increase in $E_{1/2}$ values (*i.e.*, increasing difficulty of reduction) was in the order 4-sub.-pyridine ring < 2-sub.-pyridine ring < 3-sub.-pyridine ring. Since the anabasine has only the 3-substituted pyridine ring which can be reduced it is to be expected that it will have $E_{1/2}$ similar to 3,3-dipyridyl. Anabasine was not reduced in acetate buffer at *p*H 4 but a very well defined reduction wave was found in 0.10 *M* Na_2HPO_4 buffer with 0.10 *N* KCl supporting electrolyte. $E_{1/2}$ (applied voltage corrected for cell iR drop) = −1.70 volts. In Na_3PO_4 buffer no reduction took place. It appears that the BH^+ species is reduced while BH_2^{++} and B are not reduced under the experimental conditions used. The Ilkovic equation was obeyed over the concentration range 1×10^{-4} to 2×10^{-3} mole/l., where $i_d = 6.05 \times 10^{-3} \times Cua$ (C = mole/l.). For the dipyridyls[4] the constant in the Ilkovic equation was 5.45 for a 2-electron reduction; since it is reasonable to expect the diffusion coefficient for anabasine to be similar to the dipyridyls, the anabasine reduction also appears to involve 2 electrons. This is confirmed by log $(i/i_d - i)$ *vs.* $E_{d.e.}$ plots which were straight lines (indicating that the anabasine reduction may be reversible) whose slopes gave "*n*" values of 2.04–2.23. The temperature coefficient for i_d was found

(3) P. Krumholz, THIS JOURNAL, **73**, 3487 (1951).

(4) A. B. Zahlan and R. H. Linnell, *J. Org. Chem.*, to be published early 1954.

to be 3% per degree. A small maximum was found in the reduction wave but this did not interfere in the dilute solutions used in this study.

Acknowledgments.—The author thanks Mr. Alexander Kaczmarczyk for running the ultraviolet spectra and Dr. R. C. Roark for supplying the anabasine. The author is indebted to the Research Corporation for support which made this work possible.

BEIRUT, LEBANON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ultraviolet and Infrared Spectral Studies of Polyvinylpyrrolidone[1]

BY GERALD OSTER AND E. H. IMMERGUT

RECEIVED JULY 20, 1953

The ultraviolet spectra of polyvinylpyrrolidone (PVP), N-ethylpyrrolidone and N-vinylpyrrolidone are markedly dependent on *p*H at extreme *p*H values. N-Vinylpyrrolidone has a very pronounced absorption maximum at 235 mμ which is present only to a minute extent in the spectrum of the polymer and this is used as a method to follow the conversion of monomer to polymer during polymerization. Iodine exhibits strong interaction with PVP as shown by the alteration in the iodine spectrum at 290 mμ. Infrared spectra of PVP, N-ethylpyrrolidone and N-vinylpyrrolidone have similar absorption bands but the last-named compound also has a strong absorption at 6.13 μ corresponding to the vinyl group. The absorption peak of PVP at 5.96 μ is depressed on addition of KI.

Introduction

One of the most interesting products resulting from Reppe's technique for the handling of acetylene under pressure is polyvinylpyrrolidone (PVP). The importance of this water-soluble polymer lies not only in its usefulness as a blood plasma extender but also in the fact that like serum albumin, PVP binds certain drugs, dyes and toxins. Thus PVP acts as a carrier or vehicle for various substances in the blood stream and has been used as a retardant for drugs and as an eliminant for toxins.[2]

In particular, PVP combines strongly with anionic dyes of the fluorescein family, the binding increasing with increasing number and polarizability of the substituted halogens on the dye molecule.[3a,b] Similar binding properties have been observed for native serum albumin and for other proteins in the denatured state.[4-6] Of great practical importance in preventive medicine is the affinity of molecular iodine for PVP, since the resulting PVP–iodine complex retains the disinfectant properties of the iodine but eliminates its toxicity.

It is the purpose of the present paper to describe the ultraviolet and infrared spectra of PVP and closely related substances in an attempt to explain the peculiar binding properties of PVP.

Experimental

Two PVP samples, both of a number average molecular weight of about 40,000, were kindly supplied by the General Aniline and Film Corporation and by Schenley Laboratories. N-Vinylpyrrolidone (b.p. 96° at 14 mm.) and N-ethylpyrrolidone (b.p. 104° at 20 mm.) were supplied by the General Aniline and Film Corp.

Ultraviolet spectra were determined in a Beckman spectrophotometer. The fine structure illustrated in Fig. 1 was confirmed in a Carey recording spectrometer. The ultraviolet absorption is given in terms of optical densities per cm. path length; fused quartz cells one centimeter in path length were used throughout. Infrared spectra were determined on a Perkin–Elmer double beam spectrometer. Aqueous solutions of PVP were evaporated on silver chloride plates. Since no attempt was made to control the thickness of the films, the transmission data are given in arbitrary units. A sodium chloride liquid cell was employed for N-vinylpyrrolidone and N-ethylpyrrolidone.

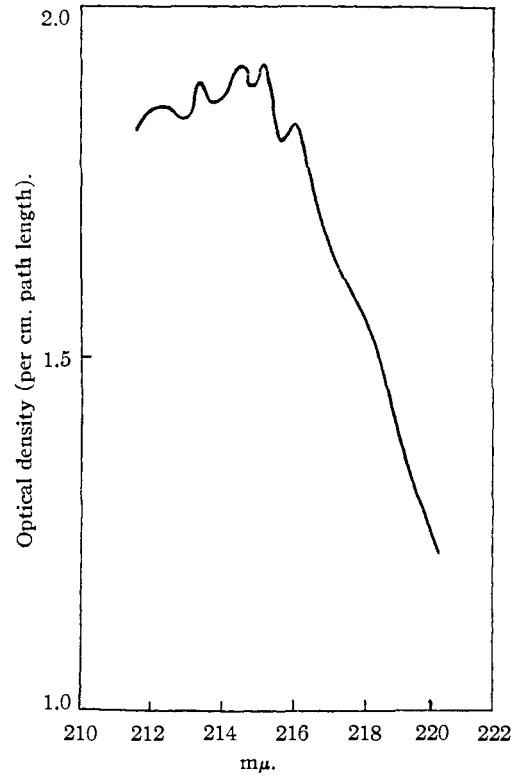


Fig. 1.—Ultraviolet spectrum of PVP in water (0.02%).

Results and Discussion

The fine structure of the ultraviolet spectra of PVP in water at relatively high concentrations (Fig. 1) is entirely reproducible. Very few poly-

(1) Presented at the 121st Meeting of the American Chemical Society, Buffalo, New York, April 19, 1952.

(2) "PVP-Polyvinylpyrrolidone," compiled and published by General Aniline and Film Corp., New York, 1951. This book contains abstracts of all the published work on PVP up to 1950.

(3) (a) G. Oster, *J. Polymer Sci.*, **9**, 553 (1952); (b) G. Oster and A. H. Adelman, data to be published.

(4) I. M. Klotz and J. M. Urquhart, THIS JOURNAL, **71**, 847 (1949).

(5) G. Oster and H. Grimmson, *Arch. Biochem.*, **24**, 119 (1949).

(6) G. Oster, *J. chim. phys.*, **48**, 217 (1951).