[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Conductance, Dissociation Constant and Heat of Dissociation of Triethylamine in Water[1]

BY J. E. ABLARD, D. S. MCKINNEY AND J. C. WARNER

In connection with an investigation[1a] of the influence of base strength on the rate of reaction of alkyl halides with various bases, it became important to have accurate values for the dissociation constant of triethylamine in aqueous solutions over a range of temperatures. The available values[2,3,4] of the dissociation constant were determined at one temperature, 25°, by conductance measurements over a limited range of rather high concentrations. The investigation described below was undertaken to obtain a better value for the dissociation constant at 25° and also to obtain values of the constant at higher temperatures.

Experimental

A Grinnell Jones type bridge, constructed by the Leeds and Northrup Company as described by P. H. Dike,[5] was used for the measurement of conductivity. The arm ratio and individual resistors were checked and found to be within 0.001% of their nominal values. The audio oscillator and amplifier were constructed in this Laboratory. The oscillator frequency could be varied in eight steps from 500 to 3000 cycles, approximately. Its output was approximately 0.3 watt. A conventional audio amplifier circuit was used, with provision for variable attenuation and for tuning to the frequency of the oscillator. With this apparatus, the over-all accuracy of any particular resistance measurement (about 0.01%) is well within the experimental errors in determining the solution concentrations.

The thermostat was a 55-gallon drum filled with a mixture of kerosene and light oil, surrounded by an air jacket. The oil was heated by a bare nichrome wire, distributed evenly near the wall of the drum, and was stirred by a low speed propeller. Temperature was controlled by a toluene regulator of 700 ml. capacity. Air was circulated through the jacket, the temperature of which was maintained at 0.2 to 0.5° below the oil temperature, by means of a bimetallic regulator. The oil temperature was determined by Beckmann thermometers which had been calibrated against a Bureau of Standards resistance thermometer. The absolute temperatures recorded in these experiments are, therefore, probably accurate to 0.01°. For any single temperature, no variation in thermostat temperature occurred which was readable on the Beckmann thermometers.

It was early demonstrated that the conductivity of the amine solutions changed rapidly if in contact with rubber, so all parts used in making up the solution and the cell were of glass. All stopcocks were reground with 600 alundum and lubricated with powdered graphite, to avoid the possibility of amine being dissolved by stopcock grease.

We found the same variability in conductivity of triethylamine solutions as they stood in contact with the platinum electrodes of the conductivity cell as has been reported by Jones and Hughes[6] for ammonia in alcohol solutions and by Ogston[7] for diethylamine in alcohol solutions. We observed, however, a decrease in conductivity with time, instead of an increase as reported by the authors cited. Furthermore, the rate of change of conductivity increased with increasing temperature. This experience indicates the difficulty of making precise measurements of the conductance of solutions of volatile amines and ammonia. Finally, to overcome the difficulties mentioned above, a cell was designed so that the solution would flow slowly through the cell from a 500-ml. reservoir, also immersed in the oil-bath and maintained at the thermostat temperature. The first measurements with this arrangement were made by displacing the solution from the 500-ml. reservoir with purified nitrogen. It was then found that the later portions of the solution flowing through the cell contained less amine than the earlier portions of the same solution. This is easily explained since triethylamine in water shows very large positive deviations from Raoult's law. To prevent loss of the amine into the vapor space left in the reservoir as the solution flowed from it, the solution was displaced by distilled mercury.

The conductivity cell was patterned somewhat after that suggested by Jones and Bollinger,[8] taking precautions to eliminate the Parker[9] effect as far as possible. The solution was introduced at the bottom of the cell, which was shaped like a horizontal cylinder, and escaped through outlet tubes located at the top of the cell on each end. The outlet tubes and the corresponding electrode leads were extended along the axis of the cell two inches beyond the electrodes before being bent upwards. Each tube was four and one-half inches (11.5 cm.) from the electrode lead of opposite polarity. The cell constant was determined with hundredth demal potassium chloride solution. The cell constant calculated from the mean of 15 resistance readings on three separate solutions was 0.58934 cm.$^{-1}$.

Materials. Water.—Distilled water boiled and cooled under vacuum to remove carbon dioxide and stored under nitrogen, was used in making up all solutions. The maximum conductivity of the water was 2.5×10^{-6} mho/cm.

Potassium chloride for determining the cell constant was recrystallized twice from distilled water and fused

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[1] This paper is abstracted from a thesis submitted by J. E. Ablard to the Committee on Graduate Instruction, Carnegie Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science. [Original manuscript received November 2, 1938.]

(1a) Eagle and Warner, THIS JOURNAL, **61**, 480 (1939).

(2) Ostwald, *J. prakt. Chem.*, **33**, 364 (1886).

(3) Bredig, *Z. physik. Chem.*, **13**, 298 (1894).

(4) "International Critical Tables," Vol. VI, 1929, p. 277.

(5) Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

(6) Jones and Hughes, *J. Chem. Soc.*, 1197 (1934).

(7) Ogston, *ibid.*, 1023 (1936).

(8) Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

(9) Parker, *ibid.*, **45**, 1366, 2017 (1923).

just before weighing as recommended by Jones and Bradshaw.[10]

Triethylamine.—Eastman Kodak Co. triethylamine was distilled from solid potassium hydroxide, dried with magnesium perchlorate trihydrate and redistilled into a receiver protected from carbon dioxide of the air. The freshly distilled product (b. p. 88.7 to 89° at 760 mm.) was stored in sealed glass vials of about 1-ml. capacity. Titration of the triethylamine by breaking the vials directly into standard acid showed a purity of at least 99.8%. It is believed that the purity is even better than this since there was always some loss of amine by volatilization before reaction with the acid was complete.

Stock solutions of triethylamine were prepared by breaking the glass vials into conductivity water contained in a 3-liter reservoir, from which air had previously been displaced by purified nitrogen. Titration of portions of the stock solution with standard 0.01 N hydrochloric acid using rosolic acid as indicator established its concentration within 0.2%.

Dilution of Triethylamine Stock Solution and Measurement of Conductivity.—Weighed portions of the stock solution were placed in a 500-ml. reservoir over mercury, diluted to the desired concentration with weighed portions of conductivity water, mixed well and immersed in the thermostat. Care was taken to allow no air space over the solution, to avoid loss of amine. The 500-ml. reservoir was connected to the cell by a ground glass joint. After the solution had reached the thermostat temperature, it was allowed to flow through the conductivity cell, and bridge readings taken with successively increased flow rates until successive readings agreed within 0.1%. The remaining solution was used for dilution by weight with conductivity water, in the ratio of about one part triethylamine solution to three parts water, and conductivity measurements again taken. This process was repeated until the conductance of the solution was reduced to approximately ten times that of the conductivity water used. At least five separate stock solutions were made up and measured as described above, for each temperature.

Experimental Results

The experimental values of Λ for various concentrations of triethylamine at 25, 40 and 50° are shown in Table I. The dissociation constants K and Λ_0 values calculated from these data by a slight algebraic modification[11] of the Fuoss and Kraus[12,13] method are given in Table II, which also summarizes the necessary physical constants obtained from the literature.

The value of Λ_0 at 25° agrees well with that published by Bredig[3] obtained by means of ionic conductances, but the value of K is about 12.5% higher. It is also 20% higher than the value given in the "International Critical Tables."[4]

TABLE I

25° C.		40° C.		50° C.	
c, mole/liter	Λ	c, mole/liter	Λ	c, mole/liter	Λ
0.0000922	181	0.0000880	243	0.0000486	280
.000106	178	.0000898	259	.0000621	291
.000131	170	.000101	228	.000114	262
.000143	180	.000108	225	.000155	274
.000141	177	.000150	248	.000220	265
.000141	174	.000198	222	.000282	270
.000221	158	.000326	198	.000416	233
.000322	158	.000452	193	.000433	227
.000591	137	.000457	196	.000841	195.5
.000810	127	.000844	169	.001184	179.3
.000851	123	.00113	154	.001585	161.8
.000920	122	.00116	153	.002528	139.8
.000997	118	.00146	143	.003517	123.3
.00179	98.0	.00162	134	.00581	100.7
.00203	93.9	.00168	138	.00630	96.0
.00248	84.7	.00209	127	.00631	96.7
.00290	81.4	.00532	88.6	.00753	91.7
.00295	81.9	.00578	86.5	.00890	84.5
.00526	65.0	.00620	83.9	.0113	76.3
.00554	63.2	.00839	75.4	.0125	73.0
.00562	63.2	.00862	70.4	.01255	73.0
.00731	56.5	.00952	70.1		
.00760	55.6	.0115	64.0		
.00761	55.9				
.00763	55.1				
.00884	52.4				
.00950	50.7				
.00970	50.0				
.0137	43.0				
.01635	39.65				

TABLE II

T, ° K.	D^{14}	α	β	δ	η^{15}	Λ_0	$K \times 10$
298.1	78.57	106.65	0.5044	0.2918	0.008949	205	7.42
313.1	73.12	146.46	.5230	.3075	.006536	269	8.32
323.1	69.85	173.61	.5344	.3207	.005492	309	8.73

Since the above value of K contains the corrections for activity coefficient of the ions, it seems certain that the present value is the more accurate one.

Recently Shedlovsky[16] has proposed a modification of the Fuoss and Kraus procedure making use of an empirical equation which is valid to higher concentrations than the Debye–Hückel–Onsager limiting conductance equation. He finds that the two methods yield essentially the same result if the electrolyte is not too weak ($K \geq 10^{-4}$). He advocates that for weaker electrolytes, Λ_0 be calculated from the ion conductances obtained by measurements on strong electrolytes. For triethylamine this procedure, therefore, appears to offer no advantages over the comparatively simple methods used in this investigation.

Conclusion

The values of K and Λ_0 for triethylamine solutions in water have been obtained at 25, 40 and 50°. A mean value of the heat of dissociation in this temperature range is 1280 cal.

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(10) Jones and Bradshaw, THIS JOURNAL, **55**, 1780 (1933).

(11) J. E. Ablard, Thesis, "Equivalent Conductance, Dissociation Constant and Heat of Dissociation of Triethylamine," Carnegie Institute of Technology.

(12) Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

(13) Fuoss, *ibid.*, **57**, 488 (1935).

(14) Åkerlöf, *ibid.*, **54**, 4125 (1932).

(15) "International Critical Tables," Vol. V, 1929, p. 10.

(16) Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

While the authors recognize that the data are not as accurate at low concentrations as have been obtained in recent measurements on such materials as acetic acid, it is believed that this is due to the inherent difficulty in handling volatile amine solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Electron Sharing Ability of Organic Radicals. XI. *alpha*-Thienyl- and *alpha*-Mesitylpyrrolidines

BY J. G. KIRCHNER AND I. B. JOHNS

Studies on the alpha substituted pyrrolidines have been reported in earlier papers in this series.[1] In these chemical studies and in the insecticidal studies that have been carried along with them no α-substituted pyrrolidine has been used having an ionization constant lower than that of α-phenylpyrrolidine. In order to investigate these weaker bases α-thienyl- and α-mesitylpyrrolidine were prepared and their ionization constants determined.

The syntheses were accomplished by using the reaction of Cloke[2] as modified by Craig, Bulbrook and Hixon.[3]

Experimental

α-Thienyl-α-pyrroline.—Thiophene was treated with iodine and yellow mercuric oxide to yield the α-iodothiophene. From 24.3 g. (0.115 mole) of α-iodothiophene, 2.9 g. (0.115 atom) of magnesium, and 125 cc. of anhydrous ether a solution of α-thienylmagnesium iodide was prepared. As 12 g. of γ-chlorobutyronitrile in 125 cc. of ether was added a Grignard addition product precipitated and collected in the bottom of the flask as a dark liquid. After refluxing for thirty minutes the condenser was reversed, and xylene added as the ether distilled off. Heating this mixture for one hour changed the dark liquid to a gummy solid which was then hydrolyzed with a 10% solution of ammonium chloride. The xylene layer was separated, the water layer extracted with ether, and the latter combined with the xylene. Hydrochloric acid solution was used to recover the α-thienyl-α-pyrroline from the combined solvents. The acid solution was in turn washed with ether until the washings remained colorless and then heated to remove the ether. It was then treated with excess sodium hydroxide; the base extracted with ether and dried over solid potassium hydroxide. The compound was purified by crystallization from petroleum ether and by vacuum distillation. Four and eight-tenths grams of material boiling at 111.1–112.1° (4 mm.) was obtained, representing a yield of 27.5% based on the nitrile taken. α-Thienyl-α-pyrroline is a white crystalline solid melting at 57°.

Anal. Calcd. for C_8H_9NS: C, 63.54; H, 6.02; N, 9.24; S, 21.19. Found: C, 63.55; H, 6.09; N, 9.37; S, 21.10.

A picrate from alcohol melted at 197.7°.

α-Thienyl-α-pyrrolidine was obtained by reducing the above pyrroline with tin and hydrochloric acid. Four and three-tenths grams of base with excess tin and hydrochloric acid yielded 3.4 g. of the reduced compound: b. p. 88–89° (3 mm.); $n^{25}\mathrm{D}$ 1.5625.

Anal. Calcd. for $C_8H_{11}NS$: N, 9.14. Found: N, 9.10.

A picrate precipitated from ether solution and recrystallized from alcohol melted at 187.6°. It was found that picrates of these pyrrolidine bases precipitated from ether solutions with an ether solution of picric acid were much purer and required less recrystallizing than those prepared in alcohol solutions.

Reduction of the pyrroline was also attempted with sodium and alcohol. Two grams (0.013 mole) of base was treated with 4.2 g. of sodium and an excess of ethyl alcohol. During the reaction hydrogen sulfide was evolved, indicating that decomposition was taking place. Only a trace of an impure compound was recovered from the reaction mixture. Reduction of both rings probably occurred with the production of a highly unstable compound just as the complete reduction of α-pyrryl-α-pyrroline results in the spontaneously decomposable dipyrrolidine.[4] Likewise reduction of nicotine with sodium and alcohol results in the rupture of the pyrrolidine ring.[5]

α-Mesitylpyrroline was synthesized in the same general manner. A Grignard reagent was prepared from 24.9 g. (0.125 mole) of bromomesitylene and 3 g. (0.125 atom) of magnesium in 100 cc. of ether. In the preparation of this reagent it was necessary to heat the mixture for ten hours to complete the reaction. It was then cooled and 10.4 g. of nitrile added. A yield of 7.4 g. of pure base, representing 39.6% of the theoretical, was obtained. It is a colorless, rather unstable liquid which on standing turns dark red in color, b. p. 101–102° (cor.) (2 mm.).

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.36; H, 9.15. Found: C, 83.6; H, 9.15.

A picrate recrystallized from alcohol melts at 180° (cor.).

Reduction of α-mesitylpyrroline was accomplished by means of sodium and alcohol. Eleven grams of sodium was added to a solution of 7 g. of base in 100 cc. of ethyl alcohol. After completion of the reaction the mixture was acidified, and the alcohol distilled off in a vacuum. It was necessary to keep the temperature below 50° during this concentra-

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[1] Craig and Hixon, THIS JOURNAL, **53**, 4367 (1931); Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932); Goodhue and Hixon, *ibid.*, **56**, 1329 (1934).

[2] Cloke, *ibid.*, **51**, 1174 (1929).

[3] Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931).

[4] Craig, *ibid.*, **56**, 1144 (1934).

[5] Blau, *Ber.*, **26**, 628 (1893).