The experimental procedure was that described in a report[4] on the ternary system Li_2SO_4–$Al_2(SO_4)_3$–H_2O at 0° except that the $Al_2(SO_4)_3$ used was air-dried recrystallized hydrated material. The compositions of many different batches of this material were practically the same, varying over the narrow range 53.4–53.7% $Al_2(SO_4)_3$, based on aluminum determinations. The average analysis corresponds to the composition 1 mole $Al_2(SO_4)_3$ to 16.5 moles H_2O. This is in agreement with observation reported by other investigators.[5,6] Mixtures of known composition were prepared from this analyzed material, anhydrous C.P. Na_2SO_4 and water, brought to equilibrium at 0°, analyzed for aluminum by the quinolate method[7] and for sodium by the magnesium uranyl acetate method.[8] Peculiar behavior was observed in mixtures made up to check the composition of the isothermally invariant saturated solution previously reported.[3] The analysis of the saturated solution of the first mixture differed markedly from that expected. Mathematical extrapolation[9] of the tie-line indicated that the solid phase was probably the pure alum. Four subsequent mixtures failed to yield a solid phase after stirring for 24 hours. The metastable condition of these mixtures was suspected. This led to the seeding of all the mixtures including the first one with a crystal of $Na_2SO_4 \cdot 10H_2O$. Then the analysis of the saturated solution of the first mixture changed markedly and a solid phase appeared in the latter ones. All other mixtures were seeded after stirring for 24 hours at 0°. The mixtures were stirred for 1 week before analysis of the solution, and the attainment of equilibrium was proved by constancy of composition on reanalysis after further stirring for 1 week.

The results of the analyses are tabulated in weight % in Table I, and plotted in the usual manner in Fig. 1 together with that portion of the previously reported data[3] which appears to be reliable. Also included in the table is the analysis of one filtered wet residue which differs somewhat from the theoretical composition of the alum, 15.50% Na_2SO_4, 37.33% $Al_2(SO_4)_3$. This is attributed to the incomplete removal of mother liquor and some loss of water by evaporation when the residue was filtered by means of suction on a porous glass filter in air at room temperature.

TABLE I

PARTIAL SYSTEM $Na_2SO_4(A)$–$Al_2(SO_4)_3(B)$–$H_2O(W)$ at 0°

Complex		Solution		
A, %	B, %	A, %	B, %	Solid phase
10.69	25.35	7.37	17.62	A·B·24W[c]
7.89	20.05	3.71	21.58	A·B·24W + A·10W
6.07	21.45	3.74	21.58	A·B·24W + A·10W
4.00	23.01	3.35	22.16	A·B·24W
2.86	24.88	2.09	24.13	A·B·24W
...[a]	...[a]	1.93	24.68	A·B·24W
3.31	26.85	1.87	25.55	A·B·24W
13.39[b]	37.99[b]			
3.70	29.87	1.00	27.12	A·B·24W + B·17W
1.56	27.99	0.99	27.16	A·B·24W + B·17W
0.400	30.99	0.435	27.34	B·17W

[a] Approximate complex. [b] Filtered wet residue. [c] Metastable.

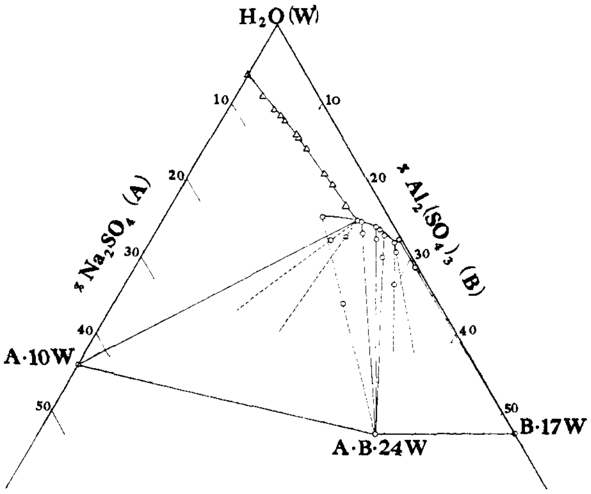


Fig. 1.—The ternary system Na_2SO_4–$Al_2(SO_4)_3$–H_2O at 0°: ○, this work; Δ, ref. 3.

Mathematical extrapolation[9] of the tie-lines of the complexes where the alum is the solid phase (in the order in which they are listed in Table I) to % Na_2SO_4 at 47.17% H_2O, the theoretical % H_2O in the alum, gives values of 15.73, 15.19, 15.57 and 15.22 as compared with the theoretical value of 15.50%. The composition of the metastable saturated solution changed markedly to 3.77% Na_2SO_4, 20.85% $Al_2(SO_4)_3$ on stirring for 48 hours after seeding. Reanalysis upon still further stirring was not possible because of the small amount of saturated solution remaining in the solubility tube. It is evident that the composition of the solution was still changing in the direction of that of the isothermally invariant solution saturated with respect to the alum and $Na_2SO_4 \cdot 10H_2O$. The congruent metastable solubility of soda alum at 0° can be estimated as 25.0% by weight on an anhydrous basis since the weight ratio Na_2SO_4:$Al_2(SO_4)_3$ in the metastable solution, 1:2.39, is close to that in the alum, 1:2.41.

DEPARTMENT OF CHEMISTRY
ST. JOHN'S UNIVERSITY
BROOKLYN 6, NEW YORK

Relative Basicities of Some Organic Nitrogen Bases

BY PHILLIP ROCHLIN, DANIEL B. MURPHY AND SAMUEL HELF

RECEIVED NOVEMBER 30, 1953

Although the 5-aminotetrazoles are generally represented, structurally, as primary amines I, their basicity appears never to have been determined quantitatively. It has been stated[1] that the basic nature of these compounds is masked in

---

(4) H. A. Horan and J. A. Skarulis, THIS JOURNAL, **61**, 2689 (1939).

(5) H. Bassett and T. Goodwin, *J. Chem. Soc.*, 2239 (1949).

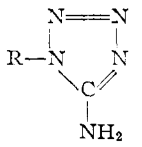
(6) D. Taylor and H. Bassett, *ibid.*, 4431 (1952).

(7) I. M. Kolthoff and E. B. Sandell, THIS JOURNAL, **50**, 1900 (1928).

(8) C. W. Foulk, H. V. Moyer and W. M. MacNevin, "Quantitative Chemical Analysis," McGraw-Hill Book Co., New York, N. Y., 1952, p. 436.

(9) A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

(1) R. M. Herbst, C. W. Roberts and E. J. Harvill, *J. Org. Chem.*, **16**, 139 (1951).



I, R = alkyl or aryl

some way; 5-aminotetrazole itself is ordinarily considered an acid by virtue of its replaceable ring hydrogen.[2]

Conant, Hall and Werner[3-7] found that many bases which were too weak to be titrated in water could be titrated successfully with perchloric acid in a glacial acetic acid medium. The use of this technique has enabled us to determine the relative basicities of a number of 1-substituted-5-aminotetrazoles and to calculate their *pK* values both in glacial acetic acid and in water. In this same investigation we have included also a number of other organic nitrogen compounds whose relative basicities either had not been reported previously, or were desired for purposes of comparison.

Experimental

Materials.—Glacial acetic acid, acetic anhydride and 70% perchloric acid were commercial analytical reagents used without further treatment. Acid potassium phthalate (NBSpH Standard Sample 185) was used for standardization of the perchloric acid solutions.

The 1-substituted-5-aminotetrazoles were prepared as described in the literature.[1] Diaminobiuret was prepared according to the method given in reference 8. Guanylurea sulfate and biguanide sulfate, received from American Cyanamid Co., were converted to the acetates before being titrated. All other nitrogen bases were commercial preparations, purified by recrystallization or redistillation where necessary.

Preparation of Acid Solution.—Fourteen ml. of perchloric acid and 36 ml. of acetic anhydride were stirred into about 500 ml. of glacial acetic acid. The solution was diluted to 1500 ml. with additional glacial acetic acid and allowed to stand overnight before standardization. Periodic redeterminations indicated little change from the nominal value of 0.11 *N*.

Procedure.—A Beckman *p*H meter, model M, with shielded glass (No. 4990) and saturated calomel (No. 4970) electrodes was used. A Sargent 4-volt potentiometer (Cat. No. S-30260) was inserted in the circuit between the *p*H meter and the calomel electrode. The apparatus was assembled so that e.m.f. values could be read directly from the potentiometer, the *p*H meter acting as a voltage amplifier and null-point indicator. The equipment was standardized with the potentiometer dials set at zero and all measurements were made with the *p*H meter needle at 0 mv. Use of this arrangement enabled us to obtain greater precision in the measurement of e.m.f. values, than could have been obtained with the usual line-operated *p*H meter.

Approximately 0.75 meq.[9] of the compound to be titrated was dissolved in 15 ml. of glacial acetic acid in a 50-ml. Pyrex beaker shielded with aluminum foil which was grounded to the shielded case of the *p*H meter. A 10-ml. Pyrex precision-bore buret (0.05-ml. subdivisions) connected by means of a ball and socket joint to an automatic-filling assembly, was used for the titrations. The apparatus was vented through a drying tube containing silica gel.

Titrations were carried out at 25 ± 2° and all volumes were corrected to 25° by use of the equation

$$V_{25°} \approx V_t(1 + 0.001063\,(25° - t))^{10}$$

where $V_{25°}$ is the corrected volume and V_t is the volume at temperature t°C.

Discussion

Values for the basicity constants were calculated according to the method of Hall.[7] At 25°, $p\mathrm{H}_{(\mathrm{HAc})} = (E_0 - E_\mathrm{m})/0.0591$, where E_0 is the potential at which $p\mathrm{H}_{(\mathrm{HAc})}$ equals zero and E_m is the measured potential at the mid-point of the titration.

Hall and Conant,[3] using a chloranil electrode, arbitrarily selected a potential of +0.566 v. for E_0. In order to correlate the present results with theirs, we decided to titrate several of their compounds using a glass–calomel system and by comparing the results, to calculate a "new" value for E_0. Seven of these compounds were selected at random on the basis of availability (some attempt having been made, however, to cover the entire *p*H range) and titrated. The results are shown in Table I.

TABLE I

DATA FOR CALCULATION OF E_0

	$pK'_{(\mathrm{HAc})}$[7]	E_m, v.	Calcd. E_0, v.
Urea	−0.93	0.601	0.546
Diphenylamine	− .74	.588	.544
p-Nitroaniline	− .36	.559	.538
o-Anisidine	+2.69	.379	.538
Guanidine	3.10	.374	.558
Diphenylguanidine	3.01	.371	.549
Piperidine	3.03	.367	.546
			0.545 ± 0.005̄

Table II lists $pK_{\mathrm{H}(\mathrm{H_2O})}$ values for the bases studied. These values have been predicted from Hall's semi-empirical curve[7] comparing $p\mathrm{H}_{(\mathrm{HAc})}$ values with values for pK_H in water. The pK_H values for the last few compounds are listed as >4.00 since Hall's correlation does not extend to bases in this range.

The shapes of the titration curves were similar to those plotted by Hall[7] and the bases could be divided similarly into three groups, *viz.*, the weakest bases including those whose curves showed no appreciable break: biuret and 1-amino-5-phenyltetrazole; the intermediate bases: from 1-(*p*-nitrophenyl)-5-aminotetrazole to diaminobiuret, including those whose curves showed both an initial rise and a break at the end of the titration; and the remaining group (strongest bases) whose curves showed no initial rise.

Several of the compounds which were expected to have more than one basic function could be titrated to one equivalent only. These included biuret, guanylurea and diaminobiuret. On the other hand, it required two milliequivalents of acid to titrate one millimole of biguanide.

All of the 1-substituted-5-aminotetrazoles fall into the "intermediate" group, with $pK_{\mathrm{H}(\mathrm{H_2O})}$ values from +0.34 (1-(*p*-nitrophenyl)-5-aminotetrazole) to 1.91 (1-isopropyl-5-aminotetrazole),

---

(2) E. Lieber, S. H. Patinkin and H. H. Tao, THIS JOURNAL, **73**, 1792 (1951), give a value of 1×10^{-6} for the acid dissociation constant of 5-aminotetrazole.

(3) N. F. Hall and J. B. Conant, *ibid.*, **49**, 3047 (1927).

(4) J. B. Conant and N. F. Hall, *ibid.*, **49**, 3062 (1927).

(5) N. F. Hall and T. H. Werner, *ibid.*, **50**, 2367 (1928).

(6) J. B. Conant and T. H. Werner, *ibid.*, **52**, 4436 (1930).

(7) N. F. Hall, *ibid.*, **52**, 5115 (1930).

(8) C. F. H. Allen and A. Bell, *Org. Syntheses*, **24**, 58 (1944).

(9) 0.75 meq. of 5-guanylaminotetrazole would not dissolve completely in 15-ml. of glacial acetic acid. The average E_m value (0.455 v.) was obtained from three titrations, *viz.*, 0.75 meq. in 25 ml. (E_m 0.458 v.) and 50 ml. (E_m 0.452 v.) (both incompletely soluble) and 0.125 meq. completely dissolved in 15 ml. (E_m 0.455 v.).

(10) N. A. Lange, "Handbook of Chemistry," 7th Ed., 1949, p. 1639.

TABLE II

RELATIVE STRENGTH OF BASES IN ACETIC ACID AND WATER

	E_m	$pH_{(HAc)}$	$pK_{H(H_2O)}$
Biuret (first equiv.)	0.700	−2.61	−0.88
1-Amino-5-phenyltetrazole	.685	−2.35	− .62
1-(*p*-Nitrophenyl)-5-aminotetrazole	.628	−1.39	+ .34
1-(*m*-Nitrophenyl)-5-aminotetrazole	.620	−1.26	.47
1-(*m*-Chlorophenyl)-5-aminotetrazole	.606	−1.03	.70
1-(*p*-Chlorophenyl)-5-aminotetrazole	.602	−0.95	.78
1-(*m*-Tolyl)-5-aminotetrazole	.584	− .65	1.08
1-Phenyl-5-aminotetrazole	.582	− .61	1.12
1-(*o*-Tolyl)-5-aminotetrazole	.575	− .50	1.23
1-Benzyl-5-aminotetrazole	.563	− .29	1.44
1-*n*-Propyl-5-aminotetrazole	.541	+ .07	1.80
1-Methyl-5-aminotetrazole	.540	.09	1.82
5-Aminotetrazole	.540	.09	1.82
1-Isopropyl-5-aminotetrazole	.535	.18	1.91
Biguanide (second equiv.)	.478	1.13	2.86
3-Aminotriazine-1,2,4	.465	1.36	3.09
5-Guanylaminotetrazole	.455	1.53	3.26
Guanylurea (first equiv.)	.426	2.03	3.76
Diaminobiuret (first equiv.)	.401	2.45	>4.00
Aniline	.394	2.57	>4.00
Biguanide (first equiv.)	.379	2.82	>4.00
1,4-Dimethyl-5-iminotetrazole	.368	3.01	>4.00

and the effect of the particular 1-substituent on the pK_H of 5-aminotetrazole seems to be what one would expect from the inductomeric influence of that group.

CHEMICAL RESEARCH SECTION
PICATINNY ARSENAL
DOVER, NEW JERSEY

The Effect of Temperature on the Density and Surface Tension of Monofluoroacetic Acid

BY JOSEPH J. JASPER AND PHILOMENA G. GRODZKA

RECEIVED NOVEMBER 13, 1953

In one of a series of related investigations carried out in this Laboratory, accurate surface tension data were required for the comparison of certain physico-chemical properties of the monohalogenated acetic acids at several temperatures. Search of the literature revealed the apparent unavailability of such data for most of these compounds and to correct this deficiency surface tension measurements were undertaken with the monofluoro-, monobromo- and monoiodoacetic acids. The last two of these were reported in the literature,[1] but due to difficulties of preparation data for the first of these could not be obtained. Since surface tension data for monofluoroacetic acid are still missing from the literature, the purpose of this investigation was to supply these data, together with corresponding densities, for an appreciable range of temperature.

Experimental

Preparation and Purification of the Compound.—The starting compound, sodium monofluoroacetate, was obtained from the Monsanto Chemical Company, and the monofluoroacetic acid prepared from it as follows[2]: 300 g. of the sodium salt was added to 800 ml. of water in a 3-liter erlenmeyer flask. To this was added slowly and with constant stirring, a solution containing 294 g. of sulfuric acid in 800 ml. of water. The resulting mixture was filtered and the filtrate extracted four times with 50-ml. portions of ether. The combined ether extracts were then dried with anhydrous sodium sulfate and the supernatant solution decanted. The ether was then removed by distillation, leaving a white crystalline solid which melted at 33°. The crystalline compound was then purified by repeated fractionations, first under partial vacuum and finally under high vacuum. The final product which was selected for use solidified into white transparent needles which melted at 35.3°. This value agrees closely with that of Swarts[3] who reported a melting point of 35.2° for this compound. The melting point was determined from a time–temperature diagram with a 150-g. sample, and the observed freezing time was approximately 50% of the total time of cooling. Since the monofluoroacetic acid was extremely hygroscopic, this operation, as well as all subsequent ones except the surface tension measurements, were carried out in an atmosphere of dry nitrogen.

A specially designed and constructed, glass wool insulated, constant temperature bath was used in this investigation. The stirring system was sufficiently efficient, and the thermoregulator sensitive enough to maintain a temperature constant to 0.02° at the lower temperatures and 0.05° at the higher temperatures of the investigation. The exact temperatures were determined with a series of NBS certified thermometers with two-degree ranges and scale divisions of 0.01°.

Measurement of Densities.—The densities were measured simultaneously with the surface tensions. A bicapillary pycnometer of the type described by Bauer[4] was used. It consisted of a 15-ml. bulb and two capillary tubes, each about 5 cm. in length, into which the liquid contents of the bulb could expand. The capillary tubes were equipped with ground-glass stoppers to prevent contamination of the contents from the surroundings. The molten compound was introduced into the pycnometer bulb with the aid of a glass syringe equipped with a hollow glass needle.

Measurement of Surface Tensions.—The surface tensions were measured by the capillary-height method under orthobaric conditions with a capillarimeter constructed according to the design of Jasper and Herrington.[5] The selection of the capillary tube, and the subsequent procedure employed in testing for constancy of bore, was similar to that of Harkins and Brown.[6] The capillary tube finally selected had a section 4.5 cm. in length with a radius which varied no more than one part per thousand. The average radius of this section from eleven measurements was 0.008211 cm. Since it is necessary that the reference surface of the liquid be approximately plane, equal care was taken in selecting the larger tube in which the reference surface was to be established. This tube had an inside diameter of 4.5 cm. which, according to Richards and Carver,[7] gives a surface sufficiently plane for accurate results. Tests for optical distortion through the walls of the apparatus gave negligible results.

The purified monofluoroacetic acid was transferred in the liquid state from the storage container to an all-glass distillation apparatus to which the capillarimeter was sealed. The compound was solidified with liquid nitrogen and the system evacuated to a high degree of vacuum. The first third of the distillate was rejected and the second third distilled into the reservoir bulb of the capillarimeter. The liquid in the capillarimeter was again solidified with liquid nitrogen, the system again evacuated, and the capillarimeter sealed off. The subsequent surface tension measurements were carried out with the compound in contact with its

---

(1) J. J. Jasper and L. Rosenstein, THIS JOURNAL, **64**, 2078 (1942).

(2) This method of preparation was followed by Clark D. Heenan, Director of the Pontiac Testing Laboratories, who prepared the compound for the author.

(3) F. Swarts, *J. chim. phys.*, **17**, 23 (1919).

(4) N. Bauer in Weissberger, "Physical Methods of Organic Chemistry," Vol. 1, 1st. Ed., Interscience Publishers, Inc., New York, N. Y., 1945, p. 80.

(5) J. J. Jasper and K. D. Herrington, THIS JOURNAL, **68**, 2142 (1946).

(6) W. D. Harkins and F. E. Brown, *ibid.*, **41**, 499 (1919).

(7) T. W. Richards and E. K. Carver, *ibid.*, **43**, 827 (1921).