[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

The Physical and Chemical Properties of the Methylhydroxylamines[1]

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Free hydroxylamine and all its O- and N-methyl derivatives have been prepared in pure form. Melting points, vapor pressures and heats of vaporization have been determined for the entire series. Values are those expected from considerations of hydrogen bonding. The basic constants for the series have been determined. Variations in the series are compared to variations found in the series ammonia and the methylamines.

Although all the methyl derivatives of hydroxylamine have been mentioned in the early literature, the physical and chemical properties of these materials are for the most part either inaccurately described or unknown. Since these properties were important in delineating the conditions for the reaction of the hydroxylamines with diborane, and since the properties of the bases are of interest in their own right, a study of the pure methyl-substituted hydroxylamines has been conducted. Results are reported herein.

Experimental

a. The Preparation of Hydroxylamine and its Methyl Derivatives. 1. **Hydroxylamine.**—The free base was liberated from a suspension of hydroxylammonium chloride in butanol, using sodium butoxide as the base.[2] The salt was thoroughly dried at 110° before use. Since the free base undergoes rapid decomposition at temperatures above 15° and is very hygroscopic, it was stored under anhydrous butanol at −10° until used. Cold samples were filtered rapidly, washed with cold anhydrous ether, and weighed in a special vacuum-jacketed weighing bottle.

2. **O-Methylhydroxylamine.**—Methoxyamine hydrochloride (Eastman Organic Chemicals) was treated with an excess of 50% KOH in a small one-piece distillation apparatus. The fraction boiling at 45–50° was distilled onto KOH pellets contained in a receiver which was immersed in an ice-water-bath. The free base was then decanted into a tube containing BaO and equipped with an ₮ joint. The tube was attached to the line and the O-methylhydroxylamine was allowed to stand in contact with the BaO for several days. The CH_3ONH_2 prepared in this manner was contaminated with small amounts of other amines, chiefly ammonia. These were removed by fractional condensation, effected by holding the first trap at −63°, the second at −79°, and the third at −196°. The desired component was retained in the second trap.

3. **O,N-Dimethylhydroxylamine.**—The literature directions[3] for preparation were followed without modification. The hydrochloride salt was recrystallized from absolute alcohol by the addition of dry ether. The melting point was 115–116° (literature 115–116°). The free base was prepared in the following manner. A few milliliters of 50% KOH was frozen in the bottom of a tube which was equipped with an ₮ joint. The amine hydrochloride was placed on top of the frozen solution and the tube attached to the vacuum line. After evacuating the tube, it was allowed to warm up to room temperature. The contents were mixed by agitating a small iron-cored stirring bar with a magnet. The free O,N-dimethylhydroxylamine was then distilled into another tube containing BaO and was dried for several days before using. No further purification was required since all fractions had identical vapor pressure. As an extra check on the identity and purity of the material, the molecular weight was checked by vapor density. The value observed, 61.7 (theory 61.10), was within the experimental error of the measurement.

4. **O,N,N-Trimethylhydroxylamine.**—The trimethyl derivative was prepared as described by Jones and Major,[4] using the reaction of methyl iodide with the O,N-dimethylhydroxylamine.

The ether solution was filtered and phenyl isocyanate was added to remove any unreacted CH_3ONHCH_3. The ether and the free O,N,N-trimethylhydroxylamine were distilled out and dry HCl passed into the ether solution. The recrystallized hydrochloride salt had a melting point of 122.5–123.5° (literature 123°). The free base was prepared and dried using the method described for the previous amine. No further purification was required. The molecular weight was measured by vapor density as 76.2 (theory 75.11).

5. **N-Methylhydroxylamine.**—The N-methylhydroxylamine was prepared as described in the literature.[5–7]

The N-methylhydroxylamine is a solid of rather low volatility at room temperature. The material required a large number of fractional condensations before a portion was obtained whose vapor pressure did not change upon further fractionation. Because of the low vapor pressure, the purity was checked by a nitrogen analysis rather than by molecular weight (observed 29.69% N; theory 29.77% N).

6. **N,N-Dimethylhydroxylamine.**—This hydroxylamine was prepared by the action of a methyl Grignard reagent upon ethyl nitrate in ether solution.[8] After hydrolysis, the amine was removed by steam distillation and collected in dilute HCl. The resulting solution was evaporated to dryness and the crude hydrochloride was purified by two to four crystallizations from an ether–alcohol mixture. The salt was thoroughly dried under high vacuum. The melting point observed was 103–106°. Hepworth[8] listed a melting point of 102°, while Cope and co-workers[9] reported 106.5–109°.

The free anhydrous $HON(CH_3)_2$ could not be prepared using the distillation or extraction method described by Hepworth.[8] The product obtained boiled at around 93.5°. A boiling point of 94.5 to 95.5° was reported by Hepworth for the "pure" base. On the other hand a molecular weight measurement and a titration of a weighed sample of the fraction boiling at 93.5° indicated that a significant amount of water was still present in the amine.

A new procedure for preparing the free base utilized displacement of the weakly basic N,N-dimethylhydroxylamine from its dry hydrochloride salt by liquid ammonia. A quantity of the recrystallized $HON(CH_3)_2 \cdot HCl$ was dried at room temperature for several hours under high vacuum. An excess of anhydrous ammonia, dried over sodium, was distilled into the tube and stirred until the solution was clear. The mixture of ammonia and the hydroxylamine was then distilled away from the ammonium chloride and separated by fractional condensation. The $HON(CH_3)_2$ was retained in a trap maintained at −80°. The displacement was quantitative since the remaining hydrochloride salt would not reduce silver nitrate.

The melting point and boiling point of the anhydrous material were raised considerably, m.p. 17.7° as compared to 0°, b.p. 100.7° as compared to 93.5°. Nitrogen analyses, 22.56 and 22.70% N, are in agreement with the theoretical value of 22.94%. The molecular-weight values of this

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[1] Abstracted from dissertations submitted to the Horace H. Rackham School of Graduate Studies of the University of Michigan by D. H. Campbell and T. C. Bissot in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] C. D. Hurd, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 87.

[3] (a) L. W. Jones, *Am. Chem. J.*, **20**, 38 (1898); (b) R. T. Major and E. E. Fleck, THIS JOURNAL, **50**, 1479 (1928).

[4] L. W. Jones and R. T. Major, *ibid.*, **50**, 2742 (1928).

[5] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., Inc., London, 1948, p. 704.

[6] L. Semper and L. Lichtenstadt, *Ber.*, **51**, 933 (1918).

[7] C. Kjellin, *ibid.*, **26**, 2377 (1893).

[8] H. Hepworth, *J. Chem. Soc.*, **119**, 255 (1921).

[9] A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949).

amine, determined over a range of temperature, show that there is considerable association in the vapor phase.

Temp., °C.	Apparent. mol. wt.
59.0	73.0
64.8	70.5
69.4	69.2
98.3	64.6

The values approach the theoretical molecular weight of 61.09 at the higher temperatures. This anhydrous base was found to be quantitatively absorbed by alkaline drying agents such as BaO and KOH pellets. Since the amine and water also apparently form a low boiling azeotrope, they cannot be separated conveniently by ordinary distillation techniques.

b. Physical Properties. 1. Melting Points.—The melting points for the O,N-dimethyl- and the O,N,N-trimethylhydroxylamines were determined using the magnetic plunger method first described by Stock.[10,11]

The melting points of the N-methyl- and the N,N-dimethylhydroxylamine were determined visually in the same apparatus that was used to determine vapor pressures. A National Bureau of Standards calibrated mercury thermometer was used to measure the temperature. The results are recorded in Table I.

TABLE I

MELTING POINTS, BOILING POINTS, HEATS OF VAPORIZATION AND TROUTON CONSTANTS OF METHYL-SUBSTITUTED HYDROXYLAMINES

Compound	M.p., °C.	B.p., °C. (760 mm.)	ΔH_{vap}, cal./mole at 760 mm.	$\Delta H/T$, e.u. at 760 mm.
$HONH_2$	33[a]	...	....	..
$HONHCH_3$	38.5[b]	115.0	11,880	30.6
$HON(CH_3)_2$	17.6	100.6	9,670	25.9
CH_3ONH_2	−86.4	48.1	7,710	24.0
$CH_3ONH(CH_3)$	−97.0	42.3	7,440	23.6
$CH_3ON(CH_3)_2$	−97.2	30.0	6,410	21.1

[a] Data of C. A. Lobry de Bruyn, *Rec. trav. chim.*, **10**, 100 (1891); and J. W. Bruhl, *Ber.*, 26, 2508 (1893). [b] Kjellin[7] reported a melting point of 42°, but his observations appear to have been rather crude since his boiling point was seriously in error and extensive purification in this investigation failed to raise the melting point above the value reported above.

2. Vapor Pressures and Related Constants of Hydroxylamine and its Methyl-substituted Derivatives.—The details of the measurement varied with the temperature range.

(a) **−80 to 0°.**—Two-phase slush baths of chloroform, chlorobenzene, carbon tetrachloride and ice-water were used to maintain temperatures of −63.5, −45.3, −22.8 and 0°, respectively. A Dry Ice–isopropyl alcohol mixture gave −78°. For intermediate temperatures a large bath of isopropyl alcohol was cooled to the desired temperature. This bath was well stirred and the temperature measured with an alcohol thermometer. Since alcohol thermometers are often unreliable the one used in these measurements was calibrated each time it was used against two-phase slush baths of CCl_4, C_6H_5Cl and H_2O.

A mercury manometer was used to measure the pressures, which were read to the nearest 0.1 mm. with a cathetometer.

(b) **0° Room Temperature.**—A large, well-stirred water bath was used. A mercury thermometer with 0.01° graduations, which had been calibrated and certified by the National Bureau of Standards, was used to measure the temperature of the bath.

(c) **Above Room Temperature.**—An immersible tensimeter designed after the one described by Burg and Schlesinger[12] was used to determine vapor pressures. The tensimeter was immersed in a constant-temperature bath controlled to ±0.05°. Two National Bureau of Standards calibrated thermometers, −5 to 50° and 50 to 110°, were used with stem corrections applied where they were significant.

The vapor pressure data were fitted to an equation of the form

$$\log_{10} P = -A/T + B - C \log T$$

Data are summarized in Tables II to VI. The heats and entropies of vaporization at the boiling point were estimated from the vapor pressure data. Comparative physical data for all the methyl derivatives of hydroxylamine are summarized in Table I.

TABLE II

THE VAPOR PRESSURE OF O-METHYLHYDROXYLAMINE

Empirical equation $\log_{10} P = -2433.7/T + 23.9284 - 5.3746 \log T$

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.	ΔP, (obsd.)
−63.5	0.75	0.69	−0.06
−45.3	3.55	3.76	+ .21
−22.8	20.5	20.7	+ .2
−20.4	24.2	24.4	+ .2
−17.6	29.0	29.2	+ .2
−13.3	38.2	38.5	+ .3
−10.4	45.6	46.1	+ .5
− 6.8	56.4	57.0	+ .6
0.0	83.9	83.8	− .1
9.4	138.8	138.5	− .3
10.1	143.5	143.6	+ .1
12.6	162.9	162.5	− .4
14.4	177.3	177.4	+ .1
16.0	192.1	192.6	+ .5
17.7	208.4	208.6	+ .2
19.1	222.8	222.6	− .2
20.1	233.6	232.7	− .9
21.1	243.9	245.4	+1.5
24.8	291.1	290.5	−0.6
29.8	362.9	363.7	+0.8
34.9	451	450	−1
40.3	561	561	0
44.8	670	668	−2
48.2	761	765	+4

TABLE III

THE VAPOR PRESSURE OF O,N-DIMETHYLHYDROXYLAMINE

Empirical equation $\log_{10} P = -2282.9/T + 22.1065 - 4.7976 \log T$

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.	ΔP, calcd. − obsd.
−45.2	6.1	6.0	−0.1
−42.0	8.0	8.0	0
−36.5	11.8	11.7	− .1
−31.4	16.8	17.0	+ .2
−27.0	23.1	23.0	− .1
−22.6	30.6	30.8	+ .2
−18.0	40.8	41.2	+ .4
−13.3	54.9	54.5	− .4
− 7.3	77.8	77.2	− .6
− 4.2	91.5	92.0	+ .5
0.0	114.4	115.3	+ .9
4.0	141.1	141.3	+ .2
8.0	173.2	173.5	+ .3
12.0	210.9	210.7	− .2
16.0	253.8	253.7	− .1
19.7	301.4	301.0	− .4
23.9	361.5	361.7	+ .2
28.0	430.4	431.0	+ .6
32.9	526.6	527.1	+ .5
37.5	630.2	631.1	+ .9
42.4	765	762.6	−2.4

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[10] A. Stock, *Ber.*, **50**, 156 (1917).

[11] R. S. Sanderson, "Vacuum Manipulations of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[12] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1937).

Table IV

The Vapor Pressure of O,N,N-Trimethylhydroxylamine

Empirical equation $\log_{10} P = -2296.9/T + 27.3690 - 6.8151 \log T$

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.	ΔP, calcd. − obsd.
−78.5	0.9	0.9	0
−63.5	3.6	3.9	+0.3
−45.2	17.3	16.8	− .5
−39.0	26.5	25.8	− .7
−35.0	35.5	33.7	−1.8
−29.8	47.5	46.8	−0.7
−25.2	61.7	61.5	− .2
−20.0	81.5	82.9	+1.4
−14.1	113.6	113.4	−0.2
− 9.3	144.4	145.8	+1.4
− 4.8	186.0	181.3	−4.7
0.0	226.9	227.7	+0.8
3.9	270.7	271.0	+ .4
8.3	328.0	328.7	+ .7
11.8	379.1	379.8	+ .7
15.9	448.0	448.1	+ .1
20.0	525.4	524.9	− .5
23.3	597.5	595.3	−2.2

Table V

The Vapor Pressure of N-Methylhydroxylamine

Solid phase—empirical equation $\log_{10} P = 13.7/T - 4.261 + 5.63 \times 10^{-5} T^2$

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.	ΔP, calcd. − obsd.
0.0	0.9	1.0	+0.1
5.0	1.5	1.4	−0.1
10.0	2.0	2.0	0
15.0	2.9	2.9	0
20.0	4.2	4.2	0
25.0	6.1	6.1	0
30.0	9.0	9.0	0
35.0	13.5	13.4	−0.1

Liquid phase—empirical equation $\log_{10} P = -2597/T + 9.570$

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.	ΔP, calcd. − obsd.
20.0^a	5.2	5.2	0
25.0^a	7.3	7.3	0
30.0^a	10.0	10.1	+0.1
35.0^a	13.9	13.9	0
40.0	19.1	19.0	−0.1
45.0	25.8	25.4	− .4
50.2	34.6	34.7	+0.1
55.0	45.4	45.4	0
60.0	59.8	59.7	−0.1
65.0	76.8	77.8	+1.0

^{a} Supercooled liquid.

c. **Chemical Properties.** 1. **The Base Strength of Hydroxylamine and its Methyl-substituted Derivatives.**—The hydrochloride salts of the amines were carefully purified and dried. A quantity was weighed out and diluted to obtain a solution which was approximately 0.0025 *M*. A 100-ml. aliquot was transferred to a four-necked flask. The central neck contained a stirrer; two necks were used for the electrodes, while the fourth was used for the buret. A Beckman model G *p*H meter with a combination glass–calomel electrode system was carefully standardized against a potassium acid phthalate buffer. Both the four-necked titration flask and the buffer solution were thermostated at 25 ± 0.1°.

The dilute solution of the amine hydrochloride was then titrated with 0.05 *N* NaOH from a 5-ml. microburet. The *p*H of the solution was recorded after the addition of each 0.2 ml. of base; near the endpoint much smaller increments were taken.

Table VI

The Vapor Pressure of N,N-Dimethylhydroxylamine

Empirical equation $\log_{10} P = -3780.1/T + 39.4125 - 10.2693 \log T$

Temp., °C.	Pressure, mm. Obsd.	Pressure, mm. Calcd.	ΔP, calcd. − obsd.
17.6	13.0	13.0	0.0
19.1	14.5	14.4	−0.1
25.2	21.4	21.4	.0
29.8	28.5	28.6	.1
34.7	38.0	38.1	.1
40.3	52.4	52.5	.1
44.9	67.3	67.3	.0
50.3	90.1	89.8	− .3
55.1	114.6	114.2	− .4
60.2	146.0	146.8	.8
65.1	183.3	183.8	.5
70.2	229.7	231.2	1.5
75.1	284.4	285.2	0.8
80.2	351.7	351.2	− .5
85.0	427.0	426.3	− .7
90.0	521	518	−3

The pK_a of the amine was then calculated over the middle third of the titration curve. Values rarely deviated by more than 0.005 *pK* unit from their average. The titrations were repeated using 100-ml. aliquots of the same hydrochloride solution and adding weighed amounts of KCl to vary the ionic strength of the solution. The averages from these titrations were then plotted as a function of the square root of the ionic strength and the extrapolated value of pK_a at infinite dilution was obtained.

The glass electrode was used in this study because of its simplicity and because of errors arising from the reducing action of hydroxylamine on the noble metal salts of the usual reference electrode.[13] In order to estimate the magnitude of the errors in the procedure, the constant for NH_4OH was determined using the same procedure. The value obtained, pK_b 4.73, is in reasonably good agreement with the precision value of Bates and Pinching,[14] who reported a value of 4.751. In view of the inherent errors in the glass electrode, such as the asymmetry potential, and the uncertainties in standardizing the *p*H meter, the error which has been assigned to the pK_b values of these hydroxylamines is ±0.02 *pK* unit. Data are summarized in Table VII.

Discussion

Brown and co-workers[15] have found that the series of methylamines displays the same order of base strengths when trimethylborane is used as the reference acid, as it does when one uses the proton. If the inductive effect of the methyl group were the only factor in determining the strength of the base, the order expected would be $NH_3 < NH_2CH_3 < NH(CH_3)_2 < N(CH_3)_3$. The order actually observed with a proton and with trimethylborane as reference acids is $NH_3 < N(CH_3)_3 < NH_2CH_3 < NH(CH_3)_2$. A number of theories have been proposed to explain this order of base strengths of alkyl amines.[16-18] The opinion is divided as to whether the inductive effect of the alkyl group is opposed by a steric factor or by solvent interaction. Brown[15] has argued that the decrease in the basic-

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[13] D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 97.

[14] R. G. Bates and G. D. Pinching, Res. Paper 1982, *J. Research Natl. Bur. Standards*, **42**, 419 (1949).

[15] H. C. Brown, H. Bartholomay and M. D. Taylor, This Journal, **66**, 435 (1944).

[16] A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1293 (1949); R. B. Bell and A. F. Trotman-Dickenson, *ibid.*, 1288 (1949).

[17] R. G. Pearson, This Journal, **70**, 204 (1948); R. G. Pearson and F. V. Williams, *ibid.*, **76**, 258 (1954).

[18] K. S. Pitzer and R. Spitzer, *ibid.*, **70**, 1261 (1948).

TABLE VII

pK_a VALUES FOR AMMONIA, HYDROXYLAMINE AND METHYL-SUBSTITUTED HYDROXYLAMINES

Compound	Ionic strength	$\sqrt{\mu}$	Av. apparent pK_a	Value of pK_b at infinite diln.
NH_3	0.058	0.241	9.310	
	.0213	.146	9.298	
	.0025	.050	9.277	
	.00	.00	9.27	4.73 ± 0.02
$HONH_2$	.0226	.150	6.012	
	.0075	.087	5.997	
	.0023	.048	5.985	
	.00	.00	5.97	8.03 ± 0.02
$HONHCH_3$	.0226	.150	6.002	
	.0100	.100	5.968	
	.0034	.058	5.969	
	.0026	.051	5.983	
	.00	.00	5.96	8.04 ± 0.02
$HON(CH_3)_2$	.0626	.252	5.276	
	.0212	.145	5.246	
	.0026	.051	5.218	
	.00	.00	5.20	8.80 ± 0.02
CH_3ONH_2	.100	.316	4.674	
	.044	.210	4.652	
	.022	.148	4.639	
	.0091	.095	4.601	
	.00216	.047	4.611	
	.00	.00	4.60	9.40 ± 0.02
CH_3ONHCH_3	.0615	.248	4.780	
	.205	.143	4.768	
	.00223	.048	4.752	
	.0	.00	4.75	9.25 ± 0.02
$CH_3ON(CH_3)_2$	.0672	.259	3.746	
	.0206	.144	3.704	
	.00223	.047	3.671	
	.00	.00	3.65	10.35 ± 0.02

ity of $(CH_3)_3N$ is due to a steric strain, operating at the back of the molecule, through three bulky methyl groups on the small central atom (B-strain). Trotman-Dickenson[16] has noted that the replacement of hydrogens on the amine by alkyl groups reduces the hydration energy for the ammonium ion form, since the bonding between the amine ion and solvent is through the hydrogens of the former.

The base strengths of hydroxylamine and its methyl derivatives display the same order as ammonia and its methyl derivatives. In Fig. 1 the pK_a values of the methylamine series and the experimental values for the hydroxylamines are plotted as a function of the number of substituents replacing hydrogen on the nitrogen atom. The oxygen atom is somewhat smaller than a methyl group, but it is much larger than the hydrogen atom. Therefore, hydroxylamine is placed in the vertical row with methylamine rather than with ammonia, since the steric relationships would be more nearly comparable.

The similarity between the two series of hydroxylamines and the methylamine series is immediately apparent. The inductive effect of the methyl group in going from one to two substituents is small and is zero in the hydroxylamines containing the OH group. In going from two to three substituents there is a large decrease in the base strength for all three series.

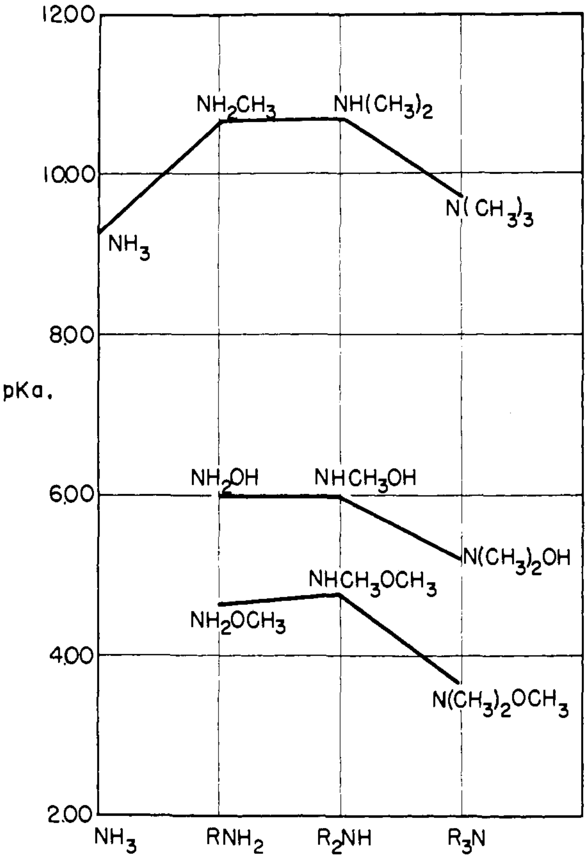

Fig. 1.—The pK_a values for CH_3, OH and OCH_3 substituted amines.

The electron-withdrawing power of the hydroxyl group is seen to reduce the electron-donating power of the nitrogen by a large amount. The difference between the hydroxyl and the methoxy series is much smaller. On the basis of an inductive effect alone it would be expected that O-methylhydroxylamine would be slightly stronger than hydroxylamine, but the converse is seen to be true. This anomalous effect of the methoxy group is known in other instances. An example is methoxyacetic acid, CH_3OCH_2COOH (pK_a 3.48), which is a stronger acid than glycolic acid, $HOCH_2COOH$ (pK_a 3.82).

The values obtained for either hydroxylamine series can be rationalized in terms of the steric strain-model or the solvation model. The correlation with the steric model is obvious. On the other hand one might argue that if solvation were the important factor, one would expect a different order with the amines containing an OH group, since the OH should be very important in the bonding with the solvent. Since, however, the OH group is present in all members of the series, the pK_a of the entire group would be lowered and the replacement of an H by a CH_3 group as one moves through the series would affect solvation terms in a manner comparable to that observed when CH_3 replaces an H in the simple amine series.

The base strengths of hydroxylamine and meth-

TABLE VIII

A COMPARISON OF THE "TROUTON CONSTANT" AT A PRESSURE OF 200 MM. WITH THE HILDEBRAND–TROUTON CONSTANT AT A UNIFORM VAPOR CONCENTRATION OF 0.00507 MOLE/L. FOR A SERIES OF AMINES

Compound	ΔH_{vap} 200 mm., cal./mole	T, ° A.	$\Delta H_{vap}/T$	Temp. for vap. concn. of 0.00507 mole/l.	P for vap. concn., mm.	ΔH_{vap} at this temp., cal./mole	$\Delta H/T$	Ref.
NH_3	5,860	216	27.1	200	63	6,041	30.2	*a*
CH_3NH_2	6,770	240	28.2	224	71	6,860	30.5	*b*
$(CH_3)_2NH$	7,100	252	28.2	236	75	7,330	31.1	*c*
$(CH_3)_3N$	6,090	245	24.8	227	72	6,150	27.0	*c*
N_2H_4	10,230	351	29.1	337	106	10,280	30.5	*d*
NH_2OH	16,600	361	46.0	352	111	17,266	49.0	*a*
NH_2OCH_3	8,400	290	29.0	273	87	8,483	31.0	*e*
H_2O	10,070	340	29.6	325	102	10,202	31.3	*a*
CCl_4 (ref.)	7,680	311	24.7	294	93	7,938	27.0	*a*

[a] D. R. Stull, *Ind. Eng. Chem.*, **39**, 540 (1947). [b] Aston, *et al.*, THIS JOURNAL, **59**, 1743 (1937). [c] T. E. Jordan, "Vapor Pressures of Organic Compounds," Interscience Publishers, New York, N. Y., 1954, pp. 176, 178. [d] L. F. Audrieth and B. A. Ogg, "Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 74. [e] This investigation.

oxyamine have been reported previously in the literature. The basic ionization constant usually reported for hydroxylamine[19,20] is the early value of Winkelbleck,[21] 6.6 × 10^{-9}, corresponding to a pK_b of 8.18. The pK_b value, 7.40, given by Ishikawa and Aoki[22] appears to be erroneous. The value closest to that found in this investigation (8.03) is that of Kolthoff and Stenger[23] who listed the pK_b of hydroxylamine as 7.97. The ionization constant for methoxyamine of 2.4 × 10^{-5} reported by Vodrazka[24] corresponds to a pK_a of 4.62. This is within the assigned error of the value obtained, pK_a 4.60.

Data summarized in Table I show that the replacement of hydrogen by a methyl group on the oxygen lowers the boiling points and the melting points of the compounds. The removal of the relatively strongly protonic hydrogen on the oxygen eliminates hydrogen bonding through the hydroxyl group. The same effect, though to a much smaller degree, is expected upon replacement of one of the hydrogens on the nitrogen by a methyl group. For comparable compounds the Trouton constant and the boiling point are reduced by substitution of methyl for hydrogen on nitrogen.

Although it is frequently assumed that the entropy of vaporization for a liquid under a constant pressure of one atmosphere (Trouton constant) is related to the degree of association in the liquid phase, Hildebrand[25] showed that the entropy of vaporization at a constant vapor phase concentration is of more fundamental significance. The so-called Hildebrand–Trouton constant is the entropy of vaporization at a constant vapor phase concentration of 0.00507 mole/l. The Hildebrand–Trouton constant for a group of amines is compared with the value of $\Delta H_{vap}/T$ at 200 mm. pressure for the same series in Table VIII. It will be noticed that according to the Trouton–Hildebrand constant all the amines except the trimethyl derivatives show a roughly comparable degree of association in the liquid phase prior to vaporization, a fact which may be ascribed to hydrogen bonding.

The value of 49.0 e.u. calculated from the literature data for the vapor pressure of hydroxylamine deserves further consideration. In comparison to the corresponding constants for the closely related water, hydrazine, ammonia and O-methylhydroxylamine (Table VIII), this value is unusually high. In view of the instability of free hydroxylamine above 10°, it is almost certain that the high value of ΔS indicates some decomposition of the sample during the vapor pressure measurement. Such an error in vapor pressure would result in a low value for the boiling point. The data for the more stable methyl derivatives of hydroxylamine suggest that the true boiling point of hydroxylamine is indeed above the recorded value of 111°. For N-methylhydroxylamine the value is 115° and for the N,N′-dimethylhydroxylamine the value is 100.6°. These values suggest 125° as a more reasonable boiling point for the pure H_2NOH.

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