The Influence of Hydration on Base Strength. Part V.[1] Hydrazines and Oxyamines. Heats of Solution and Thermodynamics of Ionization of the 20 Methyl and Ethyl Substituted Hydrazines. Isomerization Equilibria for Unsymmetrical Hydrazinium Ions. Substituent Constants (σ^* Values) for Amino-groups

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Calorimetric heats of solution in water and in 0·1M-hydrochloric acid are presented for the 20 methyl and ethyl substituted hydrazines. Their difference is given as the heat of neutralization of each hydrazine. The base strengths (pK_a) of these hydrazines were determined at five temperatures between 10 and 40° and at several ionic strengths, permitting extrapolation to values at zero ionic strength ($pK_a{}^0$) and calculation of the heats of ionization. An equation is presented by means of which the $pK_a{}^0$ data are correlated with a root mean square deviation *ca.* 0·15 p*K* unit in terms of inductive substituent constants (Taft σ^*) and hydration parameters dependent on the number of hydrogens on each nitrogen of a hydrazinium ion. It is shown how the equation can be used to calculate heats of ionization, changes in heat capacity on ionization of amines and hydrazines, and equilibrium constants for tautomerization of hydrazinium ions. The changes in heat capacity appear to be only a function of the difference between the σ^* constants for hydrogen and the substituents replacing it. Calculated equilibrium constants for the tautomerization: $R^1R^2\overset{+}{N}HNR^3R^4 \rightleftharpoons R^1R^2N\overset{+}{N}HR^3R^4$ are presented for 26 unsymmetrical hydrazines, including phenylhydrazine. Published $pK_a{}^0$ data for six oxyamines are correlated with a root mean square deviation of 0·08 p*K* unit.

PREVIOUSLY,[1] equations were developed by means of which the base strengths of 77 aliphatic amines, 25 *N*-substituted anilines, and eight methyl and ethyl substituted hydrazines could be correlated by means of substituent constants measuring inductive effects (Taft σ^* constants [2]), and hydration parameters dependent on the number of hydrogens, *n*, attached to positive nitrogen in the ammonium, anilinium, or hydrazinium ion. In the case of hydrazinium ions, $R^1R^2\overset{+}{N}HNR^3R^4$, additional hydration parameters dependent on the number of hydrogens, *m*, attached to the adjacent nitrogen (R^3, R^4 = H or alkyl) were needed for a good correlation.

Data for only eight methyl and ethyl substituted hydrazines were available at that time, whereas there are 20 such compounds. In this paper the correlation is extended to all 20 of the methyl and ethyl substituted hydrazines, to 10 hydrazines with electronegative substituents, which were studied by Pollet and Vanden Eynde,[3] and to published data for six oxyamines.[4] In addition, heats of solution and neutralization, and thermodynamic data pertaining to the ionization of the 20 methyl and ethyl substituted hydrazines are presented.

EXPERIMENTAL

Materials.—Hydrazine (anhydrous; 97%) was obtained from Matheson, Coleman and Bell. It was dried overnight with calcium hydride and then distilled, b.p. 113°,[5] from fresh calcium hydride in glassware oven-dried at 115°. The sources and preparations of the other hydrazines are described elsewhere.[6] All were dried with calcium hydride and distilled from fresh calcium hydride in oven-dried glassware just before use in the heat of solution measurements.

Calorimeters.—Two calorimeters were used in this work. Calorimeter 1 consisted of a nest of two Styrofoam cups (150 ml) (total wall thickness 5 mm). With it, water or 0·1M-HCl (*ca.* 100 g) was used. The temperature rise was measured with a Beckmann-type thermometer covering the range 22—28°, made and calibrated by Kessler and Co. Stirring was done by hand by means of a horizontal glass loop surrounding the thermometer, having a vertical handle, and fashioned from a glass rod (3 mm). The calorimeter

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[1] F. E. Condon, *J. Amer. Chem. Soc.*, (*a*) Part I, 1965, **87**, 4481; (*b*) Part II, p. 4485; (*c*) Part III, p. 4491; (*d*) Part IV, p. 4494.

[2] R. W. Taft, jun., in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, pp. 536*ff*.

[3] R. Pollet and H. Vanden Eynde, *Bull. Soc. chim. belges*, 1968, **77**, 341.

[4] T. C. Bissot, R. W. Parry, and D. H. Campbell, *J. Amer. Chem. Soc.*, 1957, **79**, 796.

[5] V. C. Bushnell, A. M. Hughes, and E. C. Gilbert, *J. Amer. Chem. Soc.*, 1937, **59**, 2142.

[6] F. E. Condon, D. C. Thakkar, and T. B. Goldstein, *Org. Prep. Procedures Internat.*, 1973, **5**, 233.

was provided with a cover made from a sheet of polyethylene (0·9 mm thickness) and having a 1 cm hole in the centre for the thermometer, a 5 mm hole at one side for the stirrer handle, and another 5 mm hole opposite the first to serve as an injection port for the hydrazine sample. It was calibrated by means of mixing experiments using known amounts of warm and cold water. Its apparent heat capacity, including the stirrer and thermometer, was 2·7 ± 0·5 cal K^{-1}.

Some of the hydrazines acted as solvents for Styrofoam, however, especially the tetra-alkylhydrazines, which dissolved in water relatively slowly. For this reason, a second calorimeter 2 was also used. It consisted of a cup (250 ml) moulded from a Melamine resin (wall thickness 3 mm), and encased in Styrofoam for insulation. With it, water or 0·1M-HCl (*ca.* 200 g) was used. Stirrer, thermometer, and cover were the same as with calorimeter 1. Its apparent heat capacity, with stirrer and thermometer, was 8·0 ± 0·7 cal K^{-1}.

Both calorimeters were supported in glass beakers weighted with plaster of Paris for mechanical stability. The plastic cups used in these calorimeters provided advantages over glass or metal of lower thermal conductivity and lower mass, resulting in very low apparent heat capacities, only 3—4% of the totals calculated with the water or 0·1M-HCl added. They gave results with hydrazine in good agreement with the value determined with more sophisticated equipment.[5]

Procedure for Heat of Solution.—Calorimeter 1 was charged with boiled, distilled water (100 g) at *ca.* 25°, accurately weighed, and was set up with cover, stirrer, and thermometer in place. Stirring was begun; and thermometer readings were taken at 30 s intervals until a steady rate of change was observed. At the next 30 s mark, a sample of the hydrazine (1—2 ml) was injected beneath the surface of the water by means of an oven-dried Pasteur pipette. The hydrazine was contained in a distilling flask (50 ml) supported in a Styrofoam cup with a 50° thermometer, graduated to 0·1°, beside it; the temperature at the time of sampling was recorded to the nearest 0·01°. Stirring was continued, while time and temperature readings were made at 30 s intervals until a constant rate of change was observed. The temperature rise was determined from time–temperature plots in the usual way. This was usually in the range 0·500—1·000°.

The amount of hydrazine used was then determined by titration of aliquot portions of the solution with 0·1M-HCl, using Bromphenol Blue as indicator. End points were sharp and reproducible within 0·2%. The total heat capacity of the systen was calculated as the sum of that due to the water, the calorimeter constant, and a small contribution from the hydrazine added. For the specific heat of water, 0·9982 cal g^{-1} K^{-1} was used.[7] (Since the specific heat of water is given in ref. 7 as 4·1796 J g^{-1} K^{-1}, a conversion factor of 4·187 J cal^{-1} is appropriate to this work.) The specific heat of each alkylhydrazine was estimated as 0·6—0·7 cal g^{-1} K^{-1} on the basis of available data, which indicate 12 cal mol^{-1} K^{-1} for an amino-group and 8 cal mol^{-1} K^{-1} for a methylene group.[8] The heat absorbed was calculated as the product of the rise in temperature and the total heat capacity. A small correction was applied if the initial temperature of the hydrazine differed from the temperature of the water in the calorimeter. The corrected heat absorbed was divided by the number of moles of hydrazine to get the molar heat of solution.

The same procedure was used with calorimeter 2, except that water (200 g) and a correspondingly larger amount of the hydrazine (*ca.* 0·02 mol) were used. Several determinations were made with each compound, in which the quantity of hydrazine used was varied within a factor of two, the initial temperature was varied within the limits 23—27°, and the two different calorimeters were used. The average deviation from the mean was *ca.* 50 cal mol^{-1} in most cases.

Procedure for Heats of Neutralization.—The procedure for determining the heats of neutralization was like that for heats of solution, except that 0·1M-HCl was used instead of water; and the amount of hydrazine was insufficient to react with all the acid. The excess of acid was then determined by titration of aliquot portions with 0·1M-NaOH to a Bromphenol Blue endpoint. The amount of hydrazine used could then be calculated from the amount of acid neutralized. The specific heat of the solution was estimated as 0·9982—0·080*m* cal g^{-1} K^{-1}, where *m* was the molality of chloride ion in the solution (*ca.* 0·1). This estimate reproduces very nearly the specific heats of solutions of hydrochloric acid,[9] hydrazinium chloride,[10] and ammonium nitrate [11] in the range 0—0·20*m*, allowances being made for differences in the energy units used by different workers. Several determinations were made with each compound; the average deviation from the mean was *ca.* 100 cal mol^{-1} in most cases.

The heats of neutralization were calculated as the difference between the heat of solution in acid and in water. It is clear that this result would not be sensibly affected by the presence of traces of water in the hydrazine, although each of the experimental quantities might be so affected. The uncertainty in these values is *ca.* 110 cal mol^{-1} $(\overline{100^2 + 50^2})^{\frac{1}{2}}$.

pK_a Determinations.—The pK_a of each hydrazine was determined by means of pH measurements on buffer solutions containing equimolar amounts of hydrazinium ion and free base. Measurements were made on seven or eight solutions with ionic strengths in the range 0·0004—0·6 ($I^{\frac{1}{2}}$ *ca.* 0·02—0·8), and at five temperatures, 10, 17·5, 25, 32·5, and 40°. The general procedure was as follows.

Ca. 500 ml of an approximately 0·1M solution of the hydrazine was prepared; its concentration was determined by titration with 0·1M-HCl to a Bromphenol Blue endpoint. *Ca.* 400—450 ml of this solution was carefully measured with a burette into a narrow-mouthed bottle (1 l) with a rubber stopper, the calculated amount of 0·1M-HCl required for half-neutralization of the hydrazine was added, and the solutions were mixed thoroughly. From this stock buffer solution, samples (60 ml) differing in ionic strength were prepared and were kept in jars (100 ml) with screw caps and large enough to take the pH meter electrodes. One sample was the stock buffer solution itself, with $I^{\frac{1}{2}}$ *ca.*

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[7] 'Handbook of Chemistry and Physics,' 53rd edn., ed. R. C. Weast, The Chemical Rubber Co., Cleveland, Ohio, 1972, p. D128; after N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Res. Nat. Bur. Stand.*, 1939, **23**, 197.

[8] (*a*) D. W. Scott, G. D. Oliver, M. E. Gross, W. N. Hubbard, and H. M. Huffman, *J. Amer. Chem. Soc.*, 1949, **71**, 2293; (*b*) J. G. Aston, H. L. Fink, G. J. Janz, and K. E. Russell, *ibid.*, 1951, **73**, 1939; (*c*) J. G. Aston, G. J. Janz, and K. E. Russell, *ibid.*, 1951, **73**, 1943; (*d*) J. G. Aston, J. L. Wood, and T. P. Zolki, *ibid.*, 1953, **75**, 6202.

[9] F. T. Gucker, jun., and K. H. Schminke, *J. Amer. Chem. Soc.*, 1932, **54**, 1358.

[10] A. W. Cobb and E. C. Gilbert, *J. Amer. Chem. Soc.*, 1935, **57**, 35.

[11] F. T. Gucker, jun., F. D. Ayres, and T. R. Rubin, *J. Amer. Chem. Soc.*, 1936, **58**, 2118.

0·2. 20 ml of this was diluted to 80 ml to give a solution with $I^{\frac{1}{2}}$ *ca.* 0·1. 60 ml was bottled and the other 20 ml was diluted to 80 ml to give a solution with $I^{\frac{1}{2}}$ *ca.* 0·05. The procedure of sampling and four-fold dilution was repeated so as to give a solution with $I^{\frac{1}{2}}$ *ca.* 0·025; and sometimes once more to give a solution with $I^{\frac{1}{2}}$ *ca.* 0·0125. Solutions with $I^{\frac{1}{2}} > 0\cdot2$ were prepared by adding 1, 2, 4, and 7 (or 8) ml of 4·0M-KCl to 59, 58, 56, and 53 (or 52) ml, respectively, of the stock buffer solution. The ionic strength of each solution was approximated as the molarity of the chloride ion, which was nearly enough equal to molality for our purposes.

In the cases of triethylmethyl- and tetraethyl-hydrazine, because of their low solubilities, the stock buffer was prepared from *ca.* 0·01M-hydrazine solutions and 0·03M-HCl.

The pH measurements were made with a Leeds and Northrup model 7664 pH meter equipped with calomel and glass electrodes, using procedures recommended by the American Society for Testing Materials.[12] The solutions and samples of standard buffers with pH 7 and 4 were brought to temperature; and the electrodes were aged at the same temperature for *ca.* 1 h. After setting the instrument to the pH of the standard buffer, pH 7, at the operating temperature, the electrodes were rinsed with distilled water and dried with tissue. Without rinsing the electrodes between solutions, the pH of each hydrazine buffer was then measured rapidly in succession, from the one with lowest ionic strength to the highest. Since the difference in pH between successive solutions was only *ca.* 0·04 unit, it was felt that less error was introduced, and greater reproducibility was actually observed, by not rinsing the electrodes between solutions than if a distilled water rinse were used. The standard buffer, pH 4, was finally used as a check of instrument calibration.

The order in which the measurements at the several temperatures was made was usually 10, 17·5, 25, then 40, 32·5, and 25° again. Reproducibility of the two sets of measurements at 25° then served as an indication of stability of the solutions throughout the series of measurements. In some cases, it was necessary to prepare a second set of buffers for the measurements at the higher temperatures in order to achieve good agreement between the two sets of measurements at 25°.

Plots of pH against $I^{\frac{1}{2}}$ at each temperature were linear within experimental error (0·02 pH unit). They were, however, subjected to a smoothing procedure, as follows. Small adjustments in the ' best ' straight lines through the points at the several temperatures were made so that the following three conditions were met. (i) The slopes of the lines were all the same. (ii) The difference in pH values at the two extreme temperatures, 10 and 40°, were within 0·01 unit of a quotient, $13{,}525/\Delta H_n$, where ΔH_n is the calorimetric heat of neutralization in cal mol^{-1}. (iii) The variation of pH with temperature, for any given ionic strength, was linear with respect to T^{-1}. Except for some of the solutions of very lowest ionic strength, which served mainly as a preparatory rinse for the electrodes, the actual pH values seldom differed by more than 0·02 unit from the resulting smoothed curves. The justification for this smoothing procedure stems from the rather large uncertainty in our pH data and is as follows.

(i) The variation of pH with ionic strength results from the variation of the activity coefficient of the hydrazinium ion, f_{BH^+}. For the ionization, $BH^+ + H_2O \rightleftharpoons B + H_3O^+$, equation (1) applies and when $C_B = C_{BH^+}$ and $f_B = 1$

$$K_a^0 = a_B a_{H_3O^+}/a_{BH^+} = C_B f_B a_{H_3O^+}/C_{BH^+} f_{BH^+} \qquad (1)$$

equations (2) and (3) are obtained where $pH_{\frac{1}{2}}$ stands for the

$$-\log K_a^0 = pK_a^0 = pH_{\frac{1}{2}} + \log f_{BH^+} \qquad (2)$$

$$pH_{\frac{1}{2}} = pK_a^0 - \log f_{BH^+} \qquad (3)$$

pH of a half-neutralized solution of the base, B. If the Debye–Hückel limiting law for a 1 : 1 electrolyte,[13] $-\log f_{BH^+} = AI^{\frac{1}{2}}$, were to apply, the slope of our plots of $pH_{\frac{1}{2}}$ against $I^{\frac{1}{2}}$ would have been 0·51 ($A = 0\cdot511 \pm 0\cdot015$, in molal units, in the range 10—40°).[14] The slope was usually *ca.* 0·35, however (see Table 1). For a straight line with a slope of 0·35, the modified Debye–Huckel equation, $-\log f_{BH^+} = 0\cdot51I^{\frac{1}{2}}/(1 + 0\cdot50I^{\frac{1}{2}})$, is a good approximation.* It differs from the straight line, $-\log f_{BH^+} = 0\cdot01 + 0\cdot35I^{\frac{1}{2}}$, by no more than 0·02 unit in the range I = 0—1, and by only 0·01 unit in the extrapolation to $I = 0$. Since the uncertainty in our pH measurements was 0·02 unit, however, we have preferred the simple linear treatment of the data, with slope invariant between 10 and 40°, over a more rigorous Debye–Hückel form.

(ii) It became apparent early in this work that the variation of pK_a with temperature was that to be expected from the calorimetric heat of neutralization (which is the negative of the heat of ionization). Thus hydrazine and tetramethylhydrazine were among the first of the compounds studied; and the change in pK_a between 10 and 40° was *ca.* 0·7 pK unit for the former and *ca.* 0·2 pK unit for the latter, in agreement with the results of calorimetric measurements. That is, neglecting small changes in heat capacity on ionization [see (iii) below and the Results and Discussion section], the heat of ionization, ΔH_i, is related to the pK_a values at two temperatures, T_1 and T_2, by equation (4). For temperatures of 10 and 40°, the extremes in this work, this

$$\Delta H_i = \frac{2\cdot303RT_1T_2}{T_2 - T_1}(pK_{a_1} - pK_{a_2}) \text{ cal mol}^{-1} \qquad (4)$$

becomes (5). An uncertainty of 0·01 pK unit in the

$$\Delta H_i = 13{,}525(pK_{a_1} - pK_{a_2}) \text{ cal mol}^{-1} \qquad (5)$$

difference in pK_a values at the two extreme temperatures, therefore, corresponds to an uncertainty of 135 cal mol^{-1} in the heat of ionization by this method. As the uncertainty in each of our pK_a values is 0·02 unit, however, the uncertainty in their difference is $(\overline{0\cdot02^2} + \overline{0\cdot02^2})^{\frac{1}{2}}$, or *ca.* 0·03 unit; and the corresponding uncertainty in the heat of ionization is *ca.* 400 cal mol^{-1}. As the uncertainty in the calorimetric heat of neutralization is only *ca.* 110 cal mol^{-1}, we have used the calorimetric data as a guide in selecting preferred values for the pK_a values at the extreme temperatures, within the range allowed by the experimental error.

(iii) A linear relationship between pK_a^0 and T^{-1} is observed for ammonium ion, but not for the methylammonium ions because of changes in heat capacity upon ionization.[15]

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* Since the constant, B, in the modified Debye–Hückel equation, $-\log f_{BH^+} = AI^{\frac{1}{2}}/(1 + B\mathring{a}I^{\frac{1}{2}})$, is *ca.* 0·33 (ref. 14), an ' ion-size parameter,' å of *ca.* 1·5 Å is indicated. The value is comparatively low (ref. 12, p. 53).

[12] R. G. Bates, ' Determination of pH,' Wiley, New York, 1964, ch. 11, especially pp. 376—379.

[13] P. Debye and E. Hückel, *Z. Phys.*, 1923, **24**, 185.

[14] Ref. 12, p. 406.

[15] D. H. Everett and W. F. K. Wynne-Jones, *Proc. Roy. Soc.*, 1941, *A*, **177**, 499.

The deviations from linearity are small, however, and within our experimental error of 0·02 pK unit. The precision of our data was not high enough, therefore, to justify a more complex treatment to evaluate changes in heat capacity upon ionization.

RESULTS AND DISCUSSION

The experimental results and some derived data are presented in Table 1, and a comparison of some of our pK_a data with those available from the literature is made in Table 2.

TABLE 1

Heats of solution and neutralization, enthalpies and entropies of ionization, and base strengths of the methyl and ethyl substituted hydrazines

Hydrazine		$-H_s$ (25°)/	$-H_{s+n}$ (25°)/	$-H_n$ (25°)/	ΔH_i^0/	pK_a^0			$\frac{dpK_a}{dI^{1/2}}$ [a]	$-\Delta S_i^0$/cal
Code no.[b]	Formula	cal mol^{-1}	cal mol^{-1}	cal mol^{-1}	cal mol^{-1}	10°	25°	40°		mol^{-1} K^{-1}
0000	H_2NNH_2	3900 [c]	13,680	9780	9730	8·33	7·95	7·61	0·28	3·7
1000	MeNHNH$_2$	6210	14,480	8270	8260	8·17	7·85	7·56	0·33	8·2
2000	EtNHNH$_2$	6550	15,160	8610	8650	8·25	7·91	7·61	0·31	7·2
1010	MeNHNHMe	8300	15,300	7000	7030	7·76	7·49	7·24	0·29	10·7
2010	EtNHNHMe	8640	15,925	7285	7180	7·78	7·50	7·25	0·33	10·1
2020	EtNHNHEt	10,590	17,440	6850	6900	7·82	7·55	7·31	0·36	11·5
1100	Me$_2$NNH$_2$	7970	13,700	5730	5690	7·34	7·12	6·92	0·35	13·4
2100	EtMeNNH$_2$	8510	14,470	5960	5950	7·53	7·30	7·09	0·38	13·4
2200	Et$_2$NNH$_2$	8960	15,400	6440	6490	7·81	7·56	7·33	0·40	12·9
1110	Me$_2$NNHMe	9370	13,800	4430	4460	6·75	6·58	6·42	0·33	15·2
2011	EtNHNMe$_2$	10,350	14,700	4350	4330	6·75	6·58	6·43	0·32	15·5
2110	EtMeNNHMe	10,000	14,100	4100	4190	7·01	6·85	6·70	0·35	17·4
2120	EtMeNNHEt	10,100	14,200	4100	4060	6·97	6·81	6·67	0·38	17·5
2210	Et$_2$NNHMe	10,560	15,340	4780	4600	7·32	7·14	6·98	0·36	16·9
2220	Et$_2$NNHEt	10,600	15,300	4700	4870	7·27	7·08	6·91	0·38	16·3
1111	Me$_2$NNMe$_2$	9960	12,400	2440	2440	6·20	6·10	6·02	0·30	19·7
2111	EtMeNNMe$_2$	9980	12,970	2990	2980	6·50	6·38	6·28	0·38	19·2
2121	EtMeNNEtMe	9670	12,740	3070	3110	6·86	6·74	6·63	0·39	20·5
2211	Et$_2$NNMe$_2$	10,290	13,800	3510	3520	7·02	6·88	6·76	0·37	19·7
2221	Et$_2$NNEtMe	*d*	13,620		4330	7·47	7·30	7·15	0·33	18·9
2222	Et$_2$NNEt$_2$	*d*	13,000		5950	7·54	7·31	7·10	0·34	13·5

[a] Variation of pK_a with the square root of the ionic strength, I. [b] The first two digits of the code no. give the numbers of carbons in the alkyl substitutents on N-1, the second two digits give the numbers of carbons in the alkyl substituents on N-2. [c] Literature value, 3890 cal mol^{-1} (ref. 5). [d] Not determined because of low solubility in water.

TABLE 2

Comparison with literature values

Hydrazine Code no.	pK_a (25°) This work	Literature pK_a
0000	7·95	8·10,[a] 7·94,[b] 8·07,[c] 8·11[d]
1000	7·85	7·87,[c] 8·14[d]
2000	7·91	7·99,[c] 7·95[e]
1010	7·49	7·52[c]
1100	7·12	7·21[c]
2100	7·30	7·30[e]
2020	7·55	7·78[c]
2200	7·56	7·71[c]
1110	6·58	6·56,[c] 6·78[f]
1111	6·10	6·30[f]

[a] G. Schwarzenbach, *Helv. Chim. Acta*, 1936, **19**, 178; 20°. [b] N. Yui, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), 1941, **20**, 256 (*Chem. Abs.*, 1941, **35**, 4660); pK_a^0 at 25°. [c] R. L. Hinman, *J. Org. Chem.*, 1958, **23**, 1587; 30°; ionic strength *ca.* 0·01. [d] M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*, 1967, **89**, 2327; 30°; ionic strength 1·0. [e] H. H. Stroh and H. G. Scharnow, *Chem. Ber.*, 1965, **98**, 1588; 25°; 0·1M solution. [f] J. B. Class, J. G. Aston, and T. S. Oakwood, *J. Amer. Chem. Soc.*, 1953, **75**, 2937; temperature and ionic strength not specified; temperature assumed to be 25° in converting from K_b value reported.

Heats of Solution.—Some interesting regularities are apparent in the heats of solution in water, H_s, and in acid, H_{s+n}. The latter quantity varies relatively little with structure, all values lying within the range 12·4—17·4 kcal mol^{-1}; and 17 of the 21 values lie within the narrower range 13·0—15·4 kcal mol^{-1}. The value for 1,2-diethylhydrazine is exceptionally large; and this compound is unique in other ways. It undergoes autoxidation to azoethane with extreme ease; and it reacts relatively rapidly with carbon tetrachloride to give azoethane and chloroform.[16] All these phenomena are related manifestations of a high susceptibility of the nitrogens to attack by an electrophilic reagent (the proton, oxygen, and the carbon of CCl_4).

The heat of solution, H_s, which is one component of H_{s+n}, varies over a wide range, between 3·9 and 10·6 kcal mol^{-1}. The other component of H_{s+n} is the heat of neutralization, H_n, and it, too, varies widely, but in a complementary fashion, between 9·8 and 2·4 kcal mol^{-1}. It is the complementary variation in these components that leads to a nearly constant value for their sum.

The heat of solution shows a fairly regular progression from *ca.* 4 for hydrazine, to *ca.* 6 for monoalkylhydrazines, to *ca.* 8 kcal mol^{-1} for dialkylhydrazines (excepting the anomalous 1,2-diethylhydrazine), and to *ca.* 10 kcal mol^{-1} for tri- and tetra-alkylhydrazines. The values seem to reflect a difference between the heat of formation of hydrogen bonds between the hydrazine and water and the heat of formation of hydrogen bonds within the liquid hydrazine itself. Where the latter are plentiful, as in H_2NNH_2, the net enthalpy change on solution in water is small (3·9 kcal mol^{-1}); where they are absent, as in Me$_2$NNMe$_2$, a large enthalpy release (10 kcal mol^{-1}) is

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[16] F. E. London and R. Krugley, unpublished observations.

observed on solution in water. No quantitative correlation could be made, however, in terms of constant values for the heats of formation of N–H···N, N–H···O, and N···H–O type hydrogen bonds.

Correlation of pK_a^0 *Data.*—The pK_a^0 values at each of three temperatures, 10, 25, and 40°, are well correlated by an equation of the form (6) which is like one developed

$$\mathrm{p}K_a^0 = C + (A + Bn)\log n + (F + Gm)\log(m+1) + 0{\cdot}08(m+1)\sum_{j=1}^{2}\sigma_j^* - [\rho^* - 0{\cdot}08n - 0{\cdot}03(m+1)]\sum_{i=1}^{3}\sigma_i^* - \log n + \log(1 + K_T^0) \qquad (6)$$

earlier.[1,†] Some changes toward an increase in rigour have been made, however, which will be described herein. The genesis of equation (6) is outlined in the Appendix.

In equation (6), pK_a^0 is the negative logarithm of the thermodynamic equilibrium constant for ionization of a hydrazinium ion as usually defined (see Experimental section); n is the number of hydrogens attached to the protonated nitrogen in the hydrazinium ion; m is the number of hydrogens attached to the adjacent nitrogen, only singly protonated hydrazines being considered; $\Sigma\sigma_i^*$ is a sum of substituent constants,[2] one for each of the groups (or hydrogen atoms) attached to the proton-accepting nitrogen in the hydrazine; $\Sigma\sigma_j^*$ is the same for the adjacent nitrogen, but excluding a constant for the amino-group, which becomes an aminium group in the hydrazinium ion; ρ^* is a reaction constant;[2,17] A, B, C, F, and G are empirical correlation constants evaluated as described later herein; and $K_T^0 = K_{a_1}^0/K_{a_2}^0$, the equilibrium constant for the tautomerization (7).

$$\mathrm{R^1R^2\overset{+}{N}HNR^3R^4} \rightleftharpoons \mathrm{R^1R^2N\overset{+}{N}HR^3R^4} \qquad (7)$$

(1) (2)

$$K_T^0 = [(2)]/[(1)] = K_{a_1}^0/K_{a_2}^0; \quad K_{a_2}^0 > K_{a_1}^0; \ \mathrm{p}K_{a_1}^0 > \mathrm{p}K_{a_2}^0 \qquad (8)$$

The term $\log(1 + K_T^0)$ replaces a $\log s$ term used earlier; † its use represents a departure from the earlier treatment toward a more rigorous treatment of hydrazine ionization in solution. In the earlier treatment, only one of the two protonated forms of the hydrazine shown in equation (7) was assumed to be present. In the present treatment, both forms are assumed to be present in tautomeric equilibrium, the individual pK_a^0 values are calculated by equation (6), and K_T^0 therefrom. The term $\log(1 + K_T^0)$ is easily derived;[18] it represents an enhancement of the base strength (p$K_{a,\mathrm{exptl}}^0$) due to the availability of two sites for protonation, *i.e.* equation (9). It maximizes at

$$\mathrm{p}K_{a,\mathrm{exptl}}^0 = \mathrm{p}K_{a_1}^0 + \log(1 + K_T^0) \qquad (9)$$

0·301 pK unit when the two sites are equivalent (s = 2 in the $\log s$ term used earlier), falls off rapidly as the difference p$K_{a_1}^0$ − p$K_{a_2}^0$ increases, and becomes <0·01 pK unit when that difference exceeds *ca.* 1·6 pK units.‡

In equation (6), the term $-\rho^*\Sigma\sigma_i^*$ measures inductive effects on the base strength of an amine resulting from modification of the substituents attached to the proton-accepting nitrogen, including in the case of a hydrazine an amino- or modified amino-group as a substituent. The group of terms $(A + Bn)\log n + 0{\cdot}08n\Sigma\sigma_i^*$ measures effects of hydration by hydrogen bonding at the protonated nitrogen. It is the 'relative net hydration energy' (in pK units), that is, the difference between the hydration energies of aminium ion and amine, relative to trimethylamine as zero.[1] The group of terms $(F + Gm)\log(m+1) + 0{\cdot}08(m+1)\Sigma\sigma_j^* + 0{\cdot}03(m+1)\Sigma\sigma_i^*$ measures effects of hydration by hydrogen bonding at the second nitrogen of a hydrazine. It, too, is a 'net hydration energy', relative to that for tetramethylhydrazine.§ The term, $-\log n$, is a statistical correction;[19] and the constant, C, is an idealized or correlative pK_a^0 for trimethylamine, all other terms being zero in this case.[21]

The constants for equation (6) in its various applications are gathered in Table 3. In evaluating them for use in this work, the constants C and ρ^* at 25° were taken without change from the earlier work,[1b] and their variation with temperature was assumed to be normal. Thus the constant C represents a theoretical value for the pK_a^0 of trimethylamine.[21] The experimental pK_a^0 for trimethylamine decreases by 0·65 unit between 10 and 40°, which corresponds to its heat of ionization of 8·8 kcal mol^{-1}.[15] With this and the value of C at 25°, and assuming a linear relation between pK_a^0 and T^{-1}, values for C at 10 and 40° were readily obtained. A reciprocal relationship between ρ^* and the absolute temperature, $\rho_1^*/\rho_2^* = T_2/T_1$, was assumed, as has been found for other reaction constants of this type.[22]

The constants, A, B, F, and G, and the σ^* values for the amino-groups were treated as adjustable parameters.¶ Treating the σ^* values of the amino-groups as

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† See equation (5) of ref. 1*c*. An error in the sign before the term, $0{\cdot}08m\ \Sigma\sigma_j^*$, in that equation is corrected here.

‡ For evaluation of pK_a values by equation (6), a graph of $\log(1 + K_T)$ against the difference p$K_{a_1}^0$ − p$K_{a_2}^0$ was prepared, from which the needed values could be readily obtained.

§ The coefficient 0·03 before the last term of this group represents a change from the 0·016 used earlier [see equation (5) of ref. 1*c*]. It results from applying to 0·08 the commonly observed loss factor, 1/2·8, instead of 1/4·9 used earlier, for the transmission of inductive effects through an intermediate atom.[20] Also, '$(m + 1)$' replaces 'm' in two places, to provide needed dependence of the hydration energies of tetra-substituted hydrazines on the nature of the substitutents, which was lacking in the earlier equation. Hydration takes place then by virtue of the lone pair of electrons on the unprotonated nitrogen.

¶ Actually, the 'relative raw net hydration energies' (Table 3) were treated as adjustable parameters; and the constants A, B, F, and G were ultimately evaluated from those yielding the best fit of equation (6) to the experimental data.

[17] L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96; *Chem. Rev.*, 1935, **17**, 125.

[18] M. I. Kabachnik, T. A. Mastrukova, A. E. Shipov, and T. A. Melentyeva, *Tetrahedron*, 1960, **9**, 10, and references therein.

[19] S. W. Benson, *J. Amer. Chem. Soc.*, 1958, **80**, 5151.

[20] R. W. Taft, jun., *J. Chem. Phys.*, 1957, **26**, 93.

[21] H. K. Hall, jun., *J. Amer. Chem. Soc.*, 1957, **79**, 5441. The constant C differs slightly from the experimental pK_a^0 for trimethylamine, as it is derived from an empirical correlation of data for 31 tertiary amines.[1b]

[22] (*a*) H. H. Jaffe, *Chem. Rev.*, 1953, **53**, 191; (*b*) R. W. Taft, jun., and I. C. Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343.

adjustable parameters represents a departure from earlier procedure, where a single value, 0·62, was used for all the amino-groups.[1c] Then it was necessary, however, to postulate a base-weakening dehydration accompanying protonation of a hydrazine, as in Figure 1. Its contribution to pK_a was —1·46 units (at 30°).

TABLE 3

Constants for equation (6)

	pK_a, 25° 70 amines [a] Ref. 1*b*	pK_a, 25° 20 anilines Ref. 1*b*	pK_a, 30° 9 hydrazines Ref. 1*c*	p$K_a{}^0$, 31 hydrazines 10° This work	25°	40°	p$K_a{}^0$, 25° 6 oxyamines
Standard deviation	0·185	0·26	0·06	0·176 [b]	0·157 [b]	0·145 [b]	0·08
Constant *C* (pK_0)	9·61	5·36 [c]	9·50	9·95	9·61	9·30	9·61
A	10·92	0·75	7·34	6·14	5·95	5·84	9·24
B	—0·778	1·55	0·42	0·95	0·78	0·60	—0·25
F			1·47	1·41	1·36	1·31	0
G			0·26	0·45	0·37	0·29	2·93
ρ*	3·38	3·35 [d]	3·38 [e]	3·56	3·38	3·22	3·38
$(A + Bn)\log n$ [f]							
$n = 2$	2·82	1·16	2·46	2·42	2·26	2·12	2·63
$n = 3$	4·10	2·58	4·10	4·29	3·95	3·64	4·05
$n = 4$	4·70	(4·18) [g]	(5·43) [g]	(5·98) [g]	(5·46) [g]	(5·02) [g]	(4·95) [g]
$(F + Gm)\log(m + 1)$ [f]							
$m = 1$			0·52	0·56	0·52	0·48	
$m = 2$			0·95	1·10	1·00	0·90	
$(F + Gm)\log(m + 2)$							
$m = 1$							1·40

[a] Including ammonia, but excluding hydrazine and seven other amines listed in ref. 21 having substituents with large steric requirements and giving a difference between calculated and experimental pK_a values >0·50 unit. [b] For the 21 hydrazines listed in Table 1 only. A correlation coefficient, $r = 0{\cdot}951$, between calculated and experimental values at 25° was calculated. It is rated ' satisfactory.'[22a] [c] Theoretical pK_a for *NN*-dimethylaniline. [d] In this case the substituent effect term in equation (6) reads $(\rho^* - 0{\cdot}16n)\Sigma\sigma^*$ rather than $(\rho^* - 0{\cdot}08n)\Sigma\sigma^*$. [e] A value of 3·32 would be more appropriate for the temperature (30°); but its use would necessitate revisions in the constants *A*, *B*, *F*, and *G* also. [f] These are the ' relative raw net hydration energies,' that is, unrefined by terms in $\Sigma\sigma^*$ and are the same for all amines or hydrazines of a given class or substitution pattern, in p*K* units.[1c] (1 p*K* unit = 1365 cal at 25°.) [g] Not physically significant.

The σ* value (0·62) was based on a σ_I constant of 0·10 and carried with it a large uncertainty.† The possibility was considered that $\sigma^*_{(NH_2)} = 1{\cdot}09$, which would have made unnecessary the dehydration postulate.[1c] Since that time, some larger values of σ* for amino-groups have appeared in the literature, in the range, 1·0—1·7.[3,25] In this paper, therefore, the dehydration postulate has been shelved and the larger σ* values for amino-groups needed for correlation of the data without it have been adopted. The well-established values of σ* for H (0·49), Me (0·00), and Et (—0·10) were also used.[2]

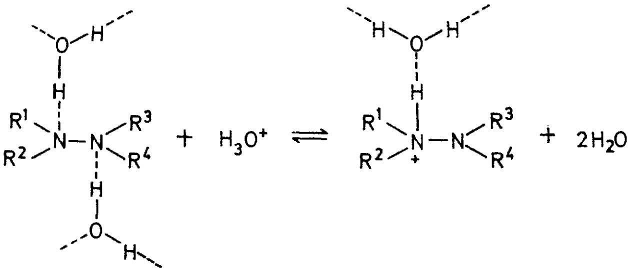

FIGURE 1 Postulated dehydration accompanying protonation of a hydrazine, which may be base-weakening by 1·48 pK_a units at 25°

With values for the constants *C* and ρ* in hand, preliminary estimates of σ* for some of the amino-groups could

TABLE 4

Preliminary estimates of σ* values for amino-groups

Temp. (°C) *C*, and ρ*	Source hydrazine	*p*$K_a{}^0$	σ* Values for Me$_2$N	EtMeN	Et$_2$N
10, *C* 9·95, ρ* 3·56	1111	6·20	1·17		
	2111	6·50	1·18		
	2121	6·86		1·08	
	2211	7·02	1·11		
	2221	7·47		0·98	
	2222	7·54			0·98
25, *C* 9·61, ρ* 3·38	1111	6·10	1·16		
	2111	6·38	1·17		
	2121	6·74		1·07	
	2211	6·88	1·10		
	2221	7·30		0·97	
	2222	7·31			0·99
40, *C* 9·30, ρ* 3·22	1111	6·02	1·15		
	2111	6·28	1·15		
	2121	6·63		1·05	
	2211	6·76	1·08		
	2221	7·15		0·96	
	2222	7·10			1·00
Averages			1·14 ±0·03	1·02 ±0·05	0·99 ±0·01

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† The relationships, $\sigma_{I(X)} = 0{\cdot}45\sigma^*_{(XCH_2)}$,[23] and $\sigma^*_{(X)} = 2{\cdot}8\sigma^*_{(XCH)_2}$,[20] yield the relationship, $\sigma_{(X)}{}^* = 6{\cdot}2\sigma^*_{I(X)}$ (not valid for hydrogen and alkyl groups).[24] $\sigma_{I(NH_2)} = 0{\cdot}10$ was found to correlate well with ^{19}F chemical shifts in the n.m.r. spectra of *m*- and *p*-substituted fluorobenzenes.[2,22b] It may reflect the electron release by resonance of an aromatic amino-group. If so, a $\sigma^*_{(NH_2)}$ value calculated from it would be too low for use with aliphatic amino-groups.

[23] R. W. Taft, jun., *J. Amer. Chem. Soc.*, 1957, **79**, 1045; R. W. Taft, jun., and I. C. Lewis, *ibid.*, 1958, **80**, 2431.

[24] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

[25] A. Ya. Kaminskii and S. S. Gitis, *Tr. Konf. Po Probl. Primeneniya Korrelyatsion Uravnenii v Org. Khim.*, 1962, 206 (*Chem. Abs.*, 1964, **61**, 4182c).

be made by use of equation (6) and the experimental pK_a^0 values for tetra-alkylhydrazines at the three temperatures, 10, 25, and 40°, since the hydration terms in equation (6) vanish in the case of a tetra-substituted hydrazine. The results were essentially temperature independent, as shown in Table 4. This rather remarkable result is in accordance with previous conclusions that σ-constants are temperature invariant [22] and vindicates our earlier assumptions regarding the temperature dependencies of the constants C and ρ^*. These preliminary estimates were modified slightly after use with all the data; the values providing the best (least squares) fit of the data to equation (6) are shown in Table 5.†

TABLE 5

σ* Constants for amino-groups

Group (no.) [a]		σ* Constant		Group (no.) [a]		σ* Constant	
		This work [b]	Lit.[c]			This work [b]	Lit.[c]
H_2N		1·20	0·62 [d]	$PhOCH_2CH_2NH$	(III)	1·42	1·07
MeNH		1·15	0·86, 1·018 [e]	EtO_2CCH_2NH	(IV)	1·60	1·39
EtNH		1·22		$NCCH_2CH_2NH$	(V)	1·69	1·32
Me_2N		1·16		$CHF_2CF_2CH(CH_3)NH$	(VI)	1·76	1·43
EtMeN		1·08		$HC{\equiv}CCH_2NH$	(VII)	1·83	1·43
Et_2N		1·00		CF_3CH_2NH	(VIII)	1·81	1·55
$HOCH_2CH_2NH$	(I)	1·32	1·01 [f]	$CHF_2(CF_2)_3CH_2NH$	(IX)	1·83	1·53
$PhCH_2NH$	(II)	1·35 [g]	1·02	$PhCH(CF_3)NH$	(X)	1·97	1·69

[a] Identifying numbers of Pollet and Vanden Eynde (ref. 3) also pertain to corresponding hydrazines in Figure 2. [b] Value giving the best fit of available hydrazine pK_a^0 data to equation (6) without the base-weakening dehydration effect of Figure 1. If that effect is real and equivalent to −1·48 pK units at 25°, all these σ* constants would be *ca.* 0·46 unit smaller. [c] From ref. 3 unless otherwise indicated. These may be regarded as approximate values for the *hydrated* amino-group. See text. [d] Ref. 21. [e] Ref. 25. [f] Calculated by us by the method of Pollet and Vanden Eynde.[3] [g] Interpolated value; a value of 1·74 would yield the best fit to equation (6) but seems too high.

Included in Table 5 are new σ* constants for amino-groups (I)—(X) having strongly electronegative substituents, which are provided by equation (6) and the pK_a^0 data of Pollet and Vanden Eynde.[3] The σ* constants provided by those authors are given for comparison. They may be regarded approximately as σ* constants for the *hydrated* amino-groups, since Pollet and Vanden Eynde did not separate hydration and inductive effects as we have done,‡ nor did they use the statistical terms, log n and log $(1 + K_T^0)$, which appear in equation (6). They assumed protonation only at the NH_2 group in these hydrazines, which may not be correct, as we will show later. The revised σ* constants for (I)—(X), correlate well with those for the other six amino- and alkylamino-groups derived here. Furthermore, all the values correlate well with the values for Et (−0·10), Me (0·00), and H (0·49), given earlier, and with values for OH (1·88) and OMe (1·81), derived later in this work.

It should be emphasized that the σ* constants in Table 5 are valid only to the extent that the dehydration postulate (Figure 1) is invalid. If the dehydration is actually base-weakening by, say, 1·48 pK units (at 25°), then σ* constants lower than those shown by *ca.* 1·48/3·2 = 0·46 unit would yield as good a correlation of the data. {The divisor 3·2 is an average value of the multiplier of $\Sigma\sigma^*$ in equation (6) $[\rho^* - 0{\cdot}08n - 0{\cdot}03(m + 1)]$}.

Calculation of pK_a^0 by use of equation (6) is illustrated in Table 6; and the resulting correlation at 25° is shown in Figure 2. The correlations at 10 and 40° yield similar figures. The average deviations (from the line with unit slope) were 0·143, 0·128, and 0·117 pK unit at 10, 25, and 40°, respectively. The standard (root mean square) deviations are given in Table 3. The largest deviation was 0·33 unit (with triethylmethylhydrazine at 40°). In all other cases, the magnitude of the deviation was <6% of the total inductive effect component

TABLE 6

Calculations of pK_a^0 by equation (6)

	EtNHNHEt, 25°	Me_2NNH_2, 25°	
		$pK_{a_1}^0$	p$K_{a_2}^0$
C	9·61	9·61	9·61
$+ (A + Bn)\log n$	2·26		3·95
$+ (F + Gm)\log(m + 1)$	0·52	1·00	
$+ 0{\cdot}08(m + 1)\,\Sigma\sigma_j^*$	0·06	0·24	0·00
Sub-total	12·45	10·85	13·56
$- [\rho^* - 0{\cdot}08n - 0{\cdot}03$ $(m + 1)]\,\Sigma\sigma_i^*$	−5·09	−3·85	−6·66
Sub-total	7·36	7·00	6·90
$- \log n$	−0·30		−0·43
Sub-total (p$K_{a_1}^0$, p$K_{a_2}^0$)	7·06	7·00	6·42
$+ \log(1 + K_T^0)$	0·30	0·10 [a]	
pK_a^0,calc	7·36	7·10	
pK_a^0,exptl	7·55	7·12	
Deviation	0·19	0·02	

[a] Read from a graph of $\log(1 + K_T^0)$ against the difference, p$K_{a_1}^0$ − p$K_{a_2}^0$.

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† Only the data at 25° were used in finding the σ* constants for the six amino-groups (and the constants, A, B, F, and G) which minimized the sum of the squares of the differences between calculated and experimental pK_a values. These were then used with the data at 10 and 40° to find the new 'best' values of A, B, F, and G for those temperatures. Any alternative could only worsen the correlation at 25°.

‡ The σ* constants in Table 5 are for the unhydrated amino-group if the hydrazinium ion is as pictured in Figure 1, where the positive charge on adjacent nitrogen effectively neutralizes the hydrogen-bonding capacity of the unshared pair on NR^3R^4. If the group is hydrated at the unshared pair, however, as is implicit in the use of '$(m + 1)$' terms in equation (6), the hydration may stabilize the hydrazinium ion by *ca.* 0·5 pK unit. (Reference to Table 3 shows that hydration of NHR adds 0·5 and hydration of NH_2 adds 1·0 pK unit.) Then the σ* constants for unhydrated amino-groups would have to be 0·15—0·16 unit larger than those in Table 5.

(term in σ_i^*; see Table 6 for example) and was a much smaller percentage of the total hydration effect, which has been estimated as at least 6 pK units for a tertiary amine.[1b]

The deviations appear to be randomly distributed and could be caused by steric effects or electronic interactions among substituents. The resulting correlation, however, strongly supports the view that the variations among base strengths of amines in aqueous solution are almost wholly the result of large, and opposing, structural and hydration effects. Essentially the same conclusion has been reached from studies of gas-phase basicities provided by pulsed ion cyclotron resonance techniques.[26]

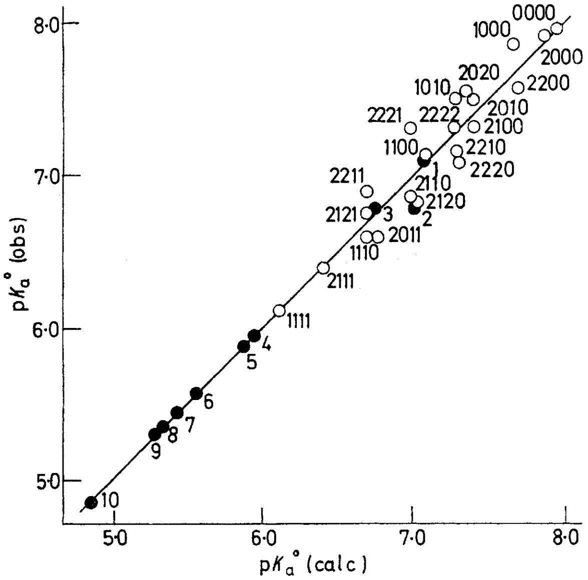

FIGURE 2 Correlation of base strengths of hydrazines at 25° by means of inductive substituent constants (Taft σ^*) and hydration parameters

Temperature Dependence of pK_a^0.—Everett and Wynne-Jones [15,27] have carefully determined the dependence of pK_a^0 on temperature for ammonia and methylamines. They found that, whereas for ammonia the relation between pK_a^0 and T^{-1} was linear, indicating no change in heat capacity on ionization, for the methylamines the relation is not linear, indicating that the ionization of methylammonium ions is accompanied by a change in heat capacity, ΔC_p. The values were 8·0, 23·1, and 43·8 cal K^{-1} mol^{-1} for methylamine, dimethylamine, and trimethylamine, respectively.[15] They suggested that the strongly hydrophobic character of the alkyl groups in the substituted amines is responsible for the large positive values of ΔC_p. Further analysis of our equation (6) provides striking confirmation of this view and furnishes estimates of ΔC_p in fair agreement with the experimental values.

Examination of Table 3 shows that the 'relative raw net hydration energies' (footnote *f*) bear a linear relation to T^{-1}, like the constants, C and ρ^*. By differentiation of equation (6) with respect to temperature, making use of these temperature dependencies [and neglecting small temperature dependencies of K_T^0 and the reaction constants 0·08 and 0·03 in equation (6)], there is obtained equation (10) in which A'_n and B'_m are constants which are the derivatives with respect to T^{-1} of the

$$\mathrm{d}pK_a^0/\mathrm{d}T = -C'/T^2 - A'_n/T^2 - B'_m/T^2 + (\rho^*/T)\sum_{i=1}^{3}\sigma_i^* \qquad (10)$$

'relative raw net hydration energies' (each dependent on n or m) and $C' = \mathrm{d}C/\mathrm{d}T^{-1}$, also a constant. From thermodynamics for ionization accompanied by a change in heat capacity, there may be derived equation (11)[27,28]

$$\mathrm{d}pK_a^0/\mathrm{d}T = -(\Delta H_i^0{}_{298} - 298\Delta C_p)/2{\cdot}303RT^2 - \Delta C_p/2{\cdot}303RT \qquad (11)$$

in which '298' corresponds to 25°. Comparison of equations (10) and (11) shows that the identifications (12) and (13) can be made.

$$\Delta H_i^0{}_{298} - 298\Delta C_p = 2{\cdot}303R(C' + A'_n + B'_m) \qquad (12)$$

$$\Delta C_p = -2{\cdot}303R\rho^*\sum_{i=1}^{3}\sigma_i^* \quad \text{(relative to Me}_3\text{N} = 0) \qquad (13)$$

Equation (12) indicates that hydration makes substantial contributions to the net enthalpy of ionization (defined as $\Delta H_i^0{}_{298} - 298\Delta C_p$); and equations (12) and (13) together permit evaluation of these contributions and of the enthalpy of ionization at 25°, $\Delta H_i^0{}_{298}$. The contributions of hydration for different classes of amines and hydrazines are shown in Table 7. Values of $\Delta H_i^0{}_{298}$ calculated by use of equation (12) and (13) were in fair agreement with values of ΔH_i^0 in Table 1.

TABLE 7

Contributions of hydration to enthalpy of ionization of amines and hydrazines

	$2{\cdot}303R(A'_n + B'_m)$/kcal mol^{-1} [equation (12)]			
m	$n = 1$	$n = 2$	$n = 3$	$n = 4$
0	0	4·06	8·80	12·99
1	1·08	5·14	9·88	
2	2·70	6·76	11·50	

Equation (13) indicates that changes in heat capacity on ionization are associated with structural changes only, and the equation permits a calculation of these. The equation gives directly a value relative to that for trimethylamine, which is easily converted into a value relative to that for ammonia, for which the experimental value is zero. Results for methylamine, dimethylamine, and trimethylamine are 7·5, 15·1, and 22·7 cal K^{-1} mol^{-1}, respectively, in fair agreement with the experimental

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[26] (*a*) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 4724; (*b*) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *ibid.*, p. 4728.

[27] D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35**, 1380.

[28] F. E. Condon, in 'Catalysis,' ed. P. H. Emmett, Reinhold, New York, 1958, p. 146.

values of Everett and Wynne-Jones. Applied to the hydrazines listed in Table 1, equation (13) gives values for ΔC_p ranging from $-11{\cdot}0$ cal K^{-1} mol^{-1} for hydrazine to $+10{\cdot}4$ cal K^{-1} mol^{-1} for tetraethylhydrazine.

Tautomerization Equilibria of Hydrazinium Ions.—In this work we have adopted the reasonable point of view that both ions derivable from an unsymmetrical hydrazine are present in solution in tautomeric equilibrium [equation (7)]. The correlation by equation (6) required calculation of the tautomerization equilibrium constant $K_T{}^0$ or at least its negative logarithm p$K_T{}^0$ [equation (14)]. We are encouraged by the apparent accuracy of

$$\mathrm{p}K_T{}^0 = \mathrm{p}K_{a_1}{}^0 - \mathrm{p}K_{a_2}{}^0 \qquad (14)$$

equation (6) to present the results of these calculations, even though we know of no direct experimental proof of the existence of both ions in solution for any of these hydrazines.

TABLE 8

Tautomerization equilibria of hydrazinium ions in water at 25° [a]

$$R^1R^2\overset{+}{N}HNR^3R^4\ (aq)\ (1) \rightleftharpoons R^1R^2\overset{+}{N}NHR^3R^4\ (aq)\ (2)$$

Hydrazine	R¹	R²	R³	R⁴	p$K_T{}^0$	% (1) at equil.	Hydrazine	R¹	R²	R³	R⁴	p$K_T{}^0$	% (1) at equil.
1000	Me	H	H	H	0·40	72	2211	Et	Et	Me	Me	0·15	59
2000	Et	H	H	H	0·95	90	2221	Et	Et	Et	Me	0·07	54
2010	Et	H	Me	H	0·55	78		Ph	H	H	H	−3·12 [b]	0·08
1100	Me	Me	H	H	0·58	79		(I) [c]	H	H	H	0·25	64
2100	Et	Me	H	H	0·64	81		(II)	H	H	H	0·32 [d]	68
2200	Et	Et	H	H	0·74	85		(III)	H	H	H	0·23	63
1110	Me	Me	Me	H	0·17	60		(IV)	H	H	H	−0·54	22
2011	Me	Me	Et	H	−0·38	29		(V)	H	H	H	0·05	53
2110	Et	Me	Me	H	0·25	64		(VI)	H	H	H	−0·22	38
2120	Et	Me	Et	H	−0·31	33		(VII)	H	H	H	0·00	50
2210	Et	Et	Me	H	0·33	68		(VIII)	H	H	H	−0·60	20
2220	Et	Et	Et	H	−0·23	37		(IX)	H	H	H	−0·43	27
2111	Et	Me	Me	Me	0·07	54		(X)	H	H	H	−0·72	16

[a] Calculated by means of equation (6). [b] The pK_a for the ion $Ph\overset{+}{N}H_2NH_2$ was calculated as 2·15 by use of appropriate constants from Table 3, and $\sigma^*_{(Ph)} = 0{\cdot}60$; and the p$K_a$ for phenylhydrazine, 5·27, reported by H. Stroh and G. Westphal, *Chem. Ber.*, 1963, **96**, 184, was used for the ion $PhNH\overset{+}{N}H_3$. [c] Numbered substituents identifiable by reference to Table 5. [d] Based on $\sigma^* = 1{\cdot}35$ for the benzylamino-group; but see footnote *g*, Table 5.

The results are presented in Table 8, together with the calculated percentage of one of the tautomers present at equilibrium at 25° for all the unsymmetrical hydrazines considered here. Phenylhydrazine has been included for comparison. The results indicate that substantial amounts of both isomers of the aliphatic hydrazinium ions are present, even for those with a strongly electronegative substituent (I)—(X); and the assumption made by Pollet and Vanden Eynde [3] of protonation only at the NH_2 group may not be correct.

Oxyamines.—For oxyamines, $R^1R^2NOR^3$, we have rewritten equation (6) with $(m + 2)$ in place of $(m + 1)$ because of the possibility that there is a water of hydration at each of the two unshared pairs on oxygen in the oxyamminium ion $R^1R^2\overset{+}{N}HOR^3$ (*cf.* footnote on p. 1118).† We have used the resulting equation to correlate the p$K_a{}^0$ data for hydroxylamine and its five methylated derivatives reported by Bissot *et al.*[4] (See Figure 3.) We have treated the constants, *A*, *B*, *F*, and *G*, and the σ^* constants for OH and OMe as adjustable parameters. The resulting σ^* constants for OH (1·88) and OMe (1·81) are consistent with reported σ_I values of *ca.* 0·30.[29] The 'relative raw net hydration energies' were about the same as those for amines with $n = 2$ or 3 (see Table 3). Hydration of the OH group was found to contribute to the base strength 1·4 p*K* unit more than hydration of the OMe group, whereas in hydrazines, hydration of the NHMe group adds only 0·5 p*K* unit more than hydration of the NMe_2 group. The difference indicates a 1·2 kcal mol^{-1} difference in the strengths of O–H ⋯ O and N–H ⋯ O hydrogen bonds in these circumstances.

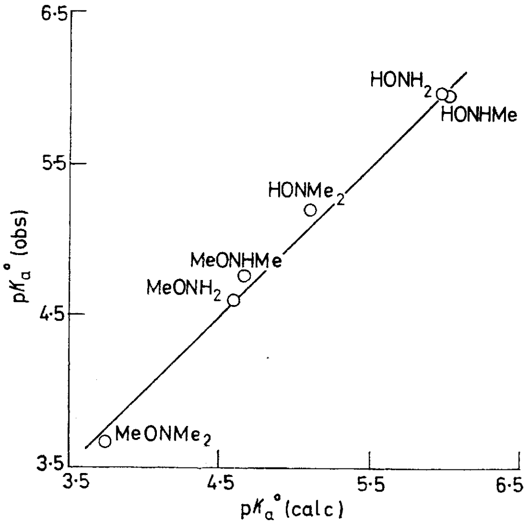

FIGURE 3 Correlation of base strengths of oxyamines by means of inductive substituent constants (Taft σ*) and hydration parameters

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† The term log $(1 + K_T{}^0)$ in the resulting equation would be applicable only with oxyamines having two sites with similar basicity, such as $MeONHCH_2CH_2ONH_2$.

[29] P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

APPENDIX

Genesis of Equation (6).—The linear free energy relationship [2,17] $\log K = \log K_0 + \rho\sigma$ in the form $\mathrm{p}K_\mathrm{a} = \mathrm{p}K_{\mathrm{a}_0} - \rho^*\Sigma\sigma^*$ was found to hold for aliphatic amines, a different equation being required for each class of amine.[21] In comparing amines of different classes, and to allow for the presence of more than one basic site, the statistical terms, $\log n$ and $\log (1 + K_\mathrm{T})$, explained in the text, must be included. Addition of these terms does not give an equation applicable to all classes of amines, however. The effect of replacing successively the hydrogens of ammonia, hydrazine, or hydroxylamine is first to increase (or affect little) and then to decrease base strength, that is, a non-linear dependence on n, the number of hydrogens attached to nitrogen in the ammonium ion.[1,4,21] Such a non-linear dependence may be expressed as a power series in n, $\mathrm{f}(n) = cn + dn^2 + en^3$, as a logarithmic function, $\mathrm{f}(n) = (A + Bn) \log n$, and in other ways,[1b] with the number of terms needed to provide for ammonia and the three different classes of amines. Recognition of this function as a measure of hydration effects subject to influence by the nature of the substituents attached to nitrogen invites addition of a term, $nf\Sigma\sigma^*$, as a measure of these influences, where f is a ' reaction constant ', like ρ^* above. Resulting equations of the form (15) where C stands for $\mathrm{p}K_{\mathrm{a}_0}$, were found to reproduce well the pK data for 77 amines (with f 0·08) and 20 anilines (with f 0·16).[1b] For hydrazines, oxyamines, and presumably for other amines with hydrophilic substituents, there is

$$\mathrm{p}K_\mathrm{a} = C - \rho^*\Sigma\sigma^* + (A + Bn) \log n + nf\Sigma\sigma^* - \log n + \log (1 + K_\mathrm{T}) \quad (15)$$

added a function of m, the number of hydrogens on a substituent amino- or oxy-group, of the same form as the function of n described earlier, and a distinction is made between substituents attached to the protonated nitrogen, σ_i^*, and substituents attached to adjacent nitrogen or oxygen, σ_j^*. Equation (15) then becomes (16) which, with

$$\begin{aligned}\mathrm{p}K_\mathrm{a} = C &- \rho^*\Sigma\sigma_i^* + (A + Bn) \log n + nf\Sigma\sigma_i^* \\ &- \log n + \log (1 + K_\mathrm{T}) + (F + Gm) \log (m + 1) \\ &+ (m + 1)f\Sigma\sigma_j^* + (m + 1)(f/2{\cdot}8)\Sigma\sigma_i^* \quad (16)\end{aligned}$$

f 0·08, is the equivalent of (6). For further details, the preceding text and earlier work [1] should be consulted.

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