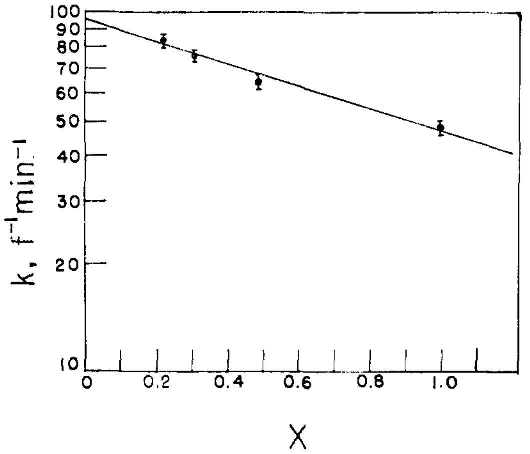

Fig. 3.—Effect of the fraction $(HClO_4)/(HClO_4) + (NaClO_4)$ on the rate-conditions as in Fig. 2.

it is hard to say whether these values are reasonable or not.

Discussion

A complete treatment of the (H^+) data in terms of the usual two term rate law requires data on the hydrolysis of Co^{+3}. There appears to be considerable question as to the actual state of affairs[8,9] so that no discussion can be given at this time. The possibility that only a medium effect is involved warrants further investigation in view of the data obtained.

Comparison of the results obtained here with the similar reaction for $Co(NH_3)_6(II)$–$Co(NH_3)_6(III)$ is of interest.[10] For the latter case *E* exp. is 13.5 kcal./mole and ΔS^* is calculated to be −41 e.u. The relative slowness compared to the aquo case seems to be due to the ΔS^* term (−41 e.u. compared to − 13 e.u.). It should be pointed out, however, that in the ammine case the path $Co(NH_3)_6{}^{+2}$–$Co(NH_3)_5(NH_2)^{+2}$ is postulated.

The effect of D_2O is about the same as found in the Fe(II)–Fe(III) case. An unambiguous explanation of this effect has not yet been given.

Data under strictly comparable conditions for purposes of comparison are rather scarce. In Table III are given some numbers concerning rates for aquo ions. The values of *k* are for the rate law term $k[M(H_2O)_x{}^{+2}][M(H_2O)_y{}^{+3}]$ and are obtained from plots similar to those in Fig. 2. The value in the cobalt case is an estimate involving the assumption that the over-all activation energy would be close to that for the single path involved.

Table III

Comparison of Exchange Data at 25°

System	k (f^{-1} sec.$^{-1}$)	E(kcal./mole)	ΔS^* e.u.	μ
V(II)–V(III)[a]	1×10^{-2}	13.2[d]	−25[d]	2.0
Fe(II)–Fe(III)[b]	4.2	9.9	−25	0.5
Co(II)–Co(III)	*ca.* 5	13.2[d]	−13[d]	1
Cr(II)–Cr(III)[c]	Less than 2×10^{-5}	...	...	1

[a] K. V. Krishnamurty and A. C. Wahl, This Journal, **80**, 5921 (1958). [b] J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952). [c] A. Anderson and N. A. Bonner, This Journal, **76**, 3826 (1954). [d] Values are for over-all reaction.

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[Contribution from the Institute of General Chemistry, the University of Palermo, Palermo, Italy]

Thermochemical Studies. I. Thermodynamic Functions of Solutions of Pyridine Bases in Water[1]

By L. Sacconi, P. Paoletti and M. Ciampolini

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The heats of solution of pyridine, picolines, lutidines, piperidine and pyrrolidine in water at 25° have been determined by direct calorimetric measurements, using a non-isothermic calorimeter. By combining the values so obtained with the known values of free energy changes the entropies of solution have been calculated. The thermodynamic functions of hydration have been calculated on the basis of the heat of vaporization values. The data so obtained favor the hypothesis of hydrogen bonding between the bases and the water molecules. The affinity of the bases toward water appears to be essentially an entropy effect. The anomalous values of the heats of solution for 2-substituted picolines and lutidines afford further evidence for the existence of hydrogen bonding between the molecules of the base.

As is well known, the ionization of organic acids and bases is very suitable for obtaining useful information on the structural parameters of the molecules and for investigating the interionic effects in solution.[2] The pyridine bases, on the other hand, are very suitable for studying the relation between physical properties and molecular structure.

While the values reported in the literature on the dissociation constants of pyridine bases in water are numerous,[3] very few data are available on the heats and entropies of neutralization of such bases.

On this account we thought it important to measure calorimetrically the enthalpies of neutralization in water of these pyridine bases in order to obtain all the thermodynamic functions associated with the neutralization. On the other hand, such functions depend largely on the amount of hydration of the bases because neutralization is accom-

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(1) Presented at the 8th National Congress of the Società Chimica Italiana held jointly with the Society of Chemical Industry, Turin, May 1958 (Abstracts of Communications, Division of Physical Chemistry, p. 87).

(2) H. C. Brown, D. H. McDaniel and O. Häfliger, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 567.

(3) "Stability Constants," Part I, Special Publication No. 6, The Chemical Society, London, 1957.

panied by detachment from the bases of some water molecules of solvation. For this reason we have first determined by direct calorimetric method the heats of solution of the bases and then calculated the heats and entropies of hydration.

The results of these investigations are reported here.

Experimental

Materials.—The pyridine bases were good quality commercial products which were dried over sodium metal and fractionally distilled at high reflux ratio through a Todd column packed with glass helices. Only the middle cuts were used, the refractive indices of which were in agreement with the literature values.[4-8] The following values for $n^{25}D$ were found: pyridine, 1.5075; 2-picoline, 1.4980; 3-picoline, 1.5038; 4-picoline, 1.5030; 2,6-lutidine, 1.4952; 2,5-lutidine, 1.4982; 2,4-lutidine, 1.4983; 3,5-lutidine, 1.5035; piperidine, 1.4535 (20°); pyrrolidine, 1.4425 (20°).

Apparatus and Method.—A non-isothermic calorimeter similar to the one described by Davies, Singer and Staveley[9] and improved in many details was employed. Its capabilities have been tested by measurements of the heat of solution of potassium chloride in water, in the molar ratio 1:167 at 25°. The mean of ten determinations was 4195 ± 5 cal./mole. The values reported in the literature, corrected for this dilution, are: 4184 ± 8,[9] 4187.[10]

In order to measure the heats of solution, the bases were placed in the bottle and the dewar flask was filled with doubly distilled water. The amounts of the base and of water were weighed carefully to obtain solutions of molar ratio 6×10^{-4}. Generally 3 g. of the base was placed in the bottle and about 920 g. of water in the dewar flask. The base was dissolved within 20 seconds after the bottle was opened. The temperature rise following the opening of the bottle ranged between 0.07 and 0.11° for all the pyridine bases. For piperidine and pyrrolidine the rise in temperature was about 0.19°. Usually three determinations of the ratio $Q_{\text{curr}}/\Delta R_{\text{curr}}$ were made for each measurement, and the average of the values so obtained was used. Q_{curr} is the amount of heat supplied by the heating resistance and ΔR_{curr} the corresponding increase in the thermometric resistance. The values of molar heats of solution ΔH_s, shown in Table II, are the average of at least three measurements for each base. The reproducibility was of ± 0.2–0.9%. The heats of solution for piperidine and pyrrolidine were corrected for the heats of dissociation. The amounts of this correction, 3.3 and 2.9% respectively, were calculated using the known pK_a values and the measured heats of neutralization.[11] For the other bases this correction was found to be quite negligible.

The entropies of solution were obtained by combining the experimental heats of solution with the corresponding free energy values reported by Andon, *et al.*[12] Calculation of the heats of hydration ΔH_h has been carried out by subtracting from the heats of solution of the liquid base in water the heats of vaporization at the same temperature.

For pyridine, the picolines and the 2,6-lutidine the heats of vaporization at 25° of Andon, *et al.*[13] were used. The heats of vaporization for the other three lutidines have been derived from the accurate vapor pressure data of Coulson, *et al.*[8]

TABLE I

FUNCTIONS OF HYDRATION OF HETEROCYCLIC BASES AT 25°

Base	Heat vaporiz. (kcal./mole)	$-\Delta F_h$[a] (kcal./mole)	$-\Delta H_h$ (kcal./mole)	$-\Delta S_h$ (e.u.)
Pyridine	9.656[b]	0.423	11.98	38.7
2-Picoline	10.258[b]	.355	13.28	43.3
3-Picoline	10.811[b]	.498	13.24	42.7
4-Picoline	10.834[b]	.659	13.27	42.3
2,6-Lutidine	11.018[b]	.325	14.82	48.6
2,5-Lutidine	11.432[c]	.441	14.54	47.3
2,4-Lutidine	11.421[c]	.587	14.51	46.7
3,5-Lutidine	12.043[c]	.566	14.46	46.6
Piperidine	8.92[d]	...	15.29	..
Pyrrolidine	8.24[d]	...	14.52	..

[a] Ref. 12. [b] Ref. 13. [c] Ref. 8. [d] Ref. 14 and 15.

TABLE II

THERMODYNAMIC FUNCTIONS OF SOLUTION IN WATER OF HETEROCYCLIC BASES AT 25°

Base	ΔF_s[a] (cal./mole)	$-\Delta H_s$ (cal./mole)	$-\Delta S_s$ (e.u.)
Pyridine	1709 ± 8	2320 ± 10	13.50 ± 0.06
2-Picoline	2145 ± 4	3020 ± 15	17.30 ± .06
3-Picoline	2374 ± 3	2430 ± 15	16.10 ± .06
4-Picoline	2243 ± 8	2435 ± 15	15.70 ± .08
2,6-Lutidine	2588 ± 5	3800 ± 15	21.40 ± .07
2,5-Lutidine	2791 ± 4	3110 ± 15	19.80 ± .06
2,4-Lutidine	2669 ± 7	3085 ± 5	19.30 ± .04
3,5-Lutidine	3054 ± 4	2415 ± 5	18.35 ± .03
Piperidine		6365 ± 15	
Pyrrolidine		6280 ± 50	

[a] Ref. 12.

The heats of vaporization for piperidine and pyrrolidine were obtained from the well-known formula of Hildebrand[14] using the boiling points reported in the literature.[15]

Excepting the last two bases the uncertainty in the values of heat of vaporization has been estimated to be of the order of 0.1 kcal./mole.[13] The errors attaching to ΔH_h values are the same as those attaching to the heats of vaporization, since the uncertainties in the heats of solution term are small in comparison with the uncertainties in the heats of vaporization.

The entropies of hydration ΔS_h have been obtained by combining the values of ΔH_h with the ΔF_h values given by Andon, *et al.*[12] As the errors in the ΔF_h values range from 6 to 16 cal./mole, the resulting error in the entropy of hydration can be assumed to be *ca.* 0.4 e.u.

Discussion

Thermodynamic Functions of Hydration.—The heats of hydration ΔH_h, given in Table I, are negative. This is evidence that the bases studied are highly hydrated in aqueous solution through the formation of hydrogen bonding. The existence of hydrogen bonding between pyridine and water is supported by the negative temperature coefficient of the heats of solution of this base in water.[16] This indicates that thermic motion hinders the formation of such bonds. The existence of such bonds has recently been investigated by infrared measurements both on aqueous[17] and chloroform[18] solu-

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[14] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold Publishing Corporation, New York, N. Y., 1955, p. 427.

[15] "Handbook of Chemistry and Physics," 37th Ed.

[16] M. E. Baud, *Bull. Soc. Chim.*, **5**, 1022 (1909).

[17] E. A. Coulson, J. L. Hales and E. F. G. Herington, *J. Chem. Soc.*, 2125 (1951).

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tions. Furthermore some pyridine hydrates of definite composition have been isolated long ago.[19]

The $-\Delta H_h$ values for pyridine bases can be collected into three different groups: pyridine, 11.98; picolines, 13.24–13.28; lutidines, 14.46–14.82 kcal./mole. As is evident, the ΔH_h values are practically constant for the three picolines and the four lutidines. The introduction of a methyl group results in an increment of about 1.3 kcal./mole. The values of ΔH_h increase roughly with the basic character of the pyridine bases. This would indicate that the water molecules are bound mainly to the nitrogen atom. Piperidine, whose pK_a is more than twice that of pyridine (pyridine, $pK_a = 5.23$; piperidine, $pK_a = 11.13$) has an enthalpy of hydration only a little higher than that of pyridine. Probably the higher hydrophilic character and donor power of the secondary nitrogen is counterbalanced by the higher hydrophobic character of the paraffin ring.

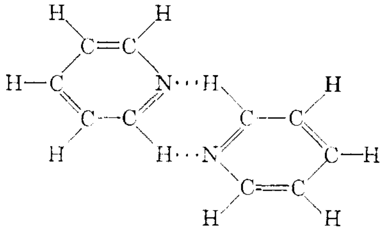
The ΔH_h values determined by us are 0.3–1.0 kcal./mole higher than the corresponding data obtained by Andon, *et al.*,[12] from the temperature coefficient of free hydration energy determined by a transpiration method.

The entropy of hydration is strongly negative for all the bases investigated. This is in accordance with a decrease in the number of molecules following hydration and an increased rigidity of the system. Also the entropies of hydration $-\Delta S_h$ fall into three groups of values: pyridine, 38.7; picolines, 42.3–43.3; lutidines, 46.6–48.6 e.u.; moreover within each isomeric series, the values decrease slightly in the order: $o- > m- > p-$. Andon, *et al.*,[12] ascribed this to an *ortho* effect. From our data, however, it could be attributed rather to an inductive effect, which decreases as the distance of the CH_3 group from the nitrogen atom increases.

Since the $-\Delta F_h$ values increase in the opposite order ($o- < m- < p-$), we conclude that the stability of the hydrates is essentially an entropy effect.

Thermodynamic Functions of Solution.—The heats of solution ΔH_s are in every case negative. This shows that the exothermic effect due to hydration outweighs the endothermic effect which corresponds to the energy used to move away the molecules in the course of the dissolution. The $-\Delta H_s$ values of 2-substituted pyridines are the highest within a series of isomers. Non-2-substituted pyridines (3- and 4-picoline, 3,5-lutidine) or mono-2-substituted (2,5- and 2,4-lutidine) have, within experimental error, the same ΔH_s value. Each introduction of one *o*-methyl group in the pyridine nucleus results in a ΔH_s increment of 600–700 cal./mole. So $-\Delta H_s$ for 2-picoline is *ca.* 600 cal./mole higher than $-\Delta H_s$ for 3- and 4-picoline; that of 2,6-lutidine (twice 2-substituted) is higher by about 700 cal./mole than the ΔH_s values for 2,5- and 2,4-lutidine (mono-2-substituted) and *ca.* 1400 cal./mole higher than that of 3,5-lutidine.

To explain this fact it must be remembered that pyridine is generally considered to be associated in the liquid state. It is quite likely that this association takes place through hydrogen bonding between the nitrogen atom and one hydrogen in *ortho* according to the scheme



These bonds are of the type already postulated for the isoxazole.[20] They could take place because of the contribution of some ionic structures of the type:

This mechanism of the association of pyridine molecules is analogous to that suggested for hydrocyanic acid.

When a methyl group replaces a hydrogen atom in *ortho*, the possibility of the formation of such bond between two molecules of base decreases and disappears when both *ortho* positions are occupied by two CH_3 groups. It must be remembered that the solution heat is equal to the difference between the heat of hydration and the heat of vaporization. While the heat of hydration, as shown above, is almost constant for the different isomers, the heat of vaporization is lower for *ortho* isomers. In fact, in this case, the interaction between the molecules which must be overcome is weaker, because intermolecular hydrogen bonds are fewer or completely lacking. Consequently the heat of solution, ΔH_s, will be lower for non-*ortho*-substituted isomers. On the other hand, the anomalous character of the *ortho* isomers is evident even in the values of the heat of vaporization (Table I).

Interesting remarks can be made on Fig. 1, where the values of the heats of solution are plotted against the heats of vaporization. The points for the non-*ortho*-substituted pyridines fall roughly on a lower line, parallel to the abscissa; the points for the mono-*ortho*-substituted bases are situated on an upper line, roughly parallel to the former and midway between this and the point corresponding to the di-*ortho*-substituted base: 2,6-lutidine. The ΔH_s values for the picolines and the lutidines fall on two approximately parallel lines. Finally, the values for the homologous series with increasing number of *ortho* CH_3 groups (pyridine, 2-picoline, 2,6-lutidine; 3-picoline, 2,5-lutidine; 4-picoline, 2,4-lutidine) fall also on two parallel lines.

The ΔH_s values for piperidine and pyrrolidine are three times higher than those for the pyridines, owing to the lower heat of vaporization as well as the higher heat of hydration. The lower heat of vaporization for these secondary bases can be attributed to their failure to form intermolecular hydrogen bondings.

The values of the entropy of solution also fall on three levels corresponding to pyridine, picolines

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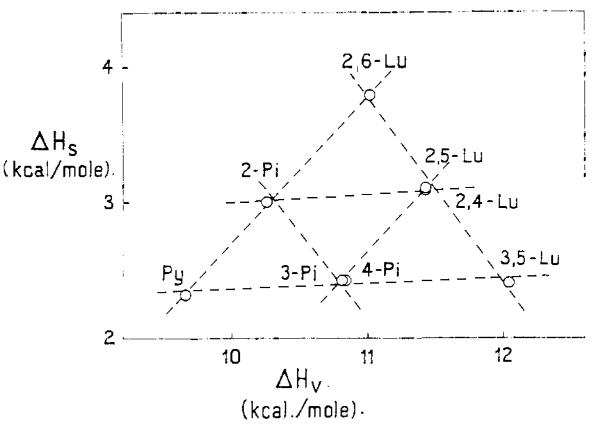

Fig. 1.—Plot of heats of solution *vs.* heats of vaporization for the pyridine bases.

and lutidines. The entropy changes are the highest for 2-substituted bases and then decrease as the CH_3 groups move away from the nitrogen atom. Thus $-\Delta S_s$ values decrease in the order: picoline, *o*- > *m*- > *p*-; lutidines, 2,6- > 2,5- > 2,4- > 3,5-.

The more negative value of the entropy of solution for 2-substituted pyridines is to be ascribed both to the greater hydration entropy and to the lower association of these bases. In fact, for the non-2-substituted pyridines, the decrease in the number of free particles due to hydration of these bases is partly counterbalanced by the increase in the number of molecules due to the dissociation of the associated molecules. As a consequence the value of ΔS_s is lower in non-*ortho*-substituted bases than in *ortho*-substituted ones.

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[CONTRIBUTION FROM THE INSTITUTE OF GENERAL CHEMISTRY, THE UNIVERSITY OF PALERMO, PALERMO, ITALY]

Thermochemical Studies. II. Thermodynamic Quantities of Neutralization of Pyridine Bases in Water[1]

BY L. SACCONI, P. PAOLETTI AND M. CIAMPOLINI

RECEIVED NOVEMBER 30, 1959

The heats of neutralization in water of a series of pyridine bases have been determined by calorimetric measurements. For pyridine, monomethyl-pyridines and dimethyl-pyridines, a linear relationship between the heats of neutralization and basicity constants is observed. This is not the case for piperidine and pyrrolidine or for quinoline and iso-quinoline, The calorimetric data so obtained are discussed in terms of electronic and steric factors. The influence of hydration on the neutralization heat is examined and discussed. The heat of neutralization in water for pyridine, picolines and 2,6-lutidine, with allowance being made for the heat of hydration, is roughly equal to the heat of neutralization of these bases in nitrobenzene.

The ionization of acids and bases is one of the few reversible reactions suitable for studying the effect of structure on chemical behavior. In this field many data on ionization constants of nitrogen bases have been collected. On the contrary, comparatively few data on the other thermodynamic functions of such equilibria, and particularly on enthalpy and entropy changes, are reported. Furthermore, the few data available on the neutralization heats have not been obtained, as a general rule, by direct calorimetric measurements, but through the temperature coefficient of free energy. It is generally agreed today that the enthalpy values obtained by non-calorimetric methods are sometimes unreliable.[2] Furthermore the importance of the heats of reaction in determining many structural parameters is widely accepted.

Longuet-Higgins and Coulson,[3] for instance, pointed out the necessity of correlating the charge density on the nitrogen atom of organic bases with the neutralization enthalpies instead of with the free energies. In fact the procedure of correlating free energy and density charge is carried out because of the lack of calorimetric data, but it is vitiated by assuming that the entropy values are constant. To avoid these shortcomings and to collect calorimetric data of primary importance in the comprehension of the acid-base interaction, we have determined by calorimetric methods the heats of neutralization with hydrochloric acid in aqueous solution of the pyridine bases already investigated by us in a previous work.[4] We also have measured the heats of neutralization of quinoline, isoquinoline and acridine. By combining the ΔH values so obtained with the ΔF values, the corresponding ΔS values have been calculated.

Experimental

Materials.—The aqueous solutions employed for measuring the heat of neutralization of the bases were those obtained in the course of measurements of the heats of solution. HCl solutions were stored in a bottle which had contained concd. hydrochloric acid for at least one year. The molality of HCl (about 1.7 *m*) was determined gravimetrically as silver chloride and was checked during the measurements; the variations never exceeded 0.06%.

Apparatus and Procedure.—The calorimeter and the techniques already described were employed.[4] The weight of hydrochloric acid placed in the bottle was determined from the increase in the weight of the bottle. An excess of hydrochloric acid was employed and the amount of hydro-

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(1) Presented at the 8th National Congress of the Società Chimical Italiana held jointly with the Society of Chemical Industry, Turin, May 1958 (Abstracts of Communications, Division of Physical Chemistry, p. 87).

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