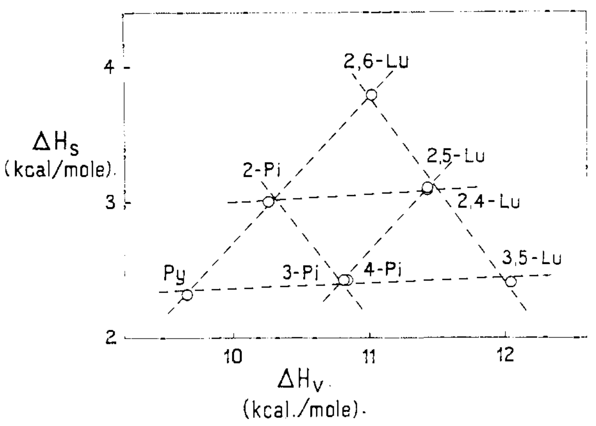

Fig. 1.—Plot of heats of solution *vs.* heats of vaporization for the pyridine bases.

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

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

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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).

[2] R. G. Charles, THIS JOURNAL, **76**, 5854 (1954); I. Poulsen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 1407 (1955); L. G. Sillén, *J. Inorg. & Nuclear Chem.*, **8**, 176 (1958); J. W. Linnett, *Discussions Faraday Soc.*, **26**, 15 (1958).

[3] H. C. Longuet-Higgins and C. A. Coulson, *J. Chem. Soc.*, 971 (1949).

[4] Part I of this series: L. Sacconi, P. Paoletti and M. Ciampolini, THIS JOURNAL, **82**, 3828 (1960).

chloride obtained was evaluated by means of the formation constants reported by Brown, McDaniel and Häfliger.[5] The heats so measured were corrected for the heat of dilution of HCl in water.[6]

The actual temperature changes which followed the opening of the bottle were of about 0.2° for all pyridine bases and of about 0.3 for piperidine and pyrrolidine. For these two bases it was necessary to make a correction for the reaction $H^+ + OH^- = H_2O$ in which the OH^- ions arise from the side reaction $B + H_2O = BH^+ + OH^-$. The amount of the correction was 1.5 and 1.8%, respectively. The neutralization heat of acridine was determined only in 50% ethanol, since this base is practically insoluble in water. The heat of dilution of 1.7 *m* hydrochloric acid in 50% ethanol was about 7261 cal./mole of HCl. The values of the neutralization heats reported here are the average of at least three measurements.

Results

The results of the measurements and the values of the acidity constants for the bases are reported in Table I. For some bases the values of the charge densitities on the nitrogen atom also are reported.

Table I

Thermodynamic Data for the Reaction $B_{(aq)}. + H^+_{(aq)}. \rightleftarrows B\cdot H^+_{(aq)}.$ at 25°

Base	$-\Delta F$ (cal./mole)	$-\Delta H$ (cal./mole)	$-\Delta S$ (e.u.)	pKa	Q_N[a]
Pyridine[e]	7050	4795 ± 10	7.55	5.17[b]	1.274
Pyridine (in 50% EtOH)	5970	5230 ± 30	2.50	4.38[b]	
2-Picoline[e]	8140	5990 ± 25	7.20	5.97[b]	1.494
3-Picoline[e]	7750	5640 ± 15	7.05	5.68[b]	1.368
4-Picoline[e]	8210	6020 ± 25	7.35	6.02[b]	1.521
2,6-Lutidine[e]	9210	7235 ± 25	6.60	6.75[b]	
3,5-Lutidine	8880	6815 ± 15	6.90	6.51[b]	
2,4-Lutidine	9260	7165 ± 15	7.00	6.79[b]	
3,5-Lutidine	8430	6365 ± 15	6.95	6.18[c,d]	
Quinoline	6550	5365 ± 15	3.95	4.80[b]	1.326
Isoquinoline	6910	5925 ± 15	3.30	5.07[b,d]	1.278
Acridine (in (50% EtOH)	5550	3480 ± 50	6.95	4.07[b,d]	1.431
Piperidine	15180	12190 ± 60	10.00	11.13[b]	
Pyrrolidine	15150	12370 ± 60	9.30	11.11[b]	

[a] *Cf.* D. Brown and M. J. S. Dewar, *J. Chem. Soc.*, 2406 (1953). [b] 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. [c] N. Ikerawa, Y. Sato and T. Maeda, *Pharm. Bull.*, **2**, 205 (1954); *cf. C. A.*, **50**, 994e (1956). [d] Corrected at 25°. [e] Recently C. T. Mortimer and K. J. Laidler, *Trans. Faraday Soc.*, **55**, 1731 (1959), reported values on these systems.

Discussion

The neutralization of a base in aqueous solution is to be considered a displacement reaction of a type

$$B(H_2O)_a + H(H_2O)_b{}^+ \rightleftarrows BH(H_2O)_c{}^+ + (a + b - c)H_2O$$

According to this scheme, the actual heat of reaction ΔH is made up of two effects, the heat of protonation and the heat of dehydration. The linking of the proton to the base molecule brings about a decrease in the number of free particles, while the displacement of water molecules results in an increase of this number. The positive values of ΔS show that in this case the latter effect outweighs the former and, on the whole, the number of free particles increases.

These concepts can be used to clarify and discuss the calorimetric data here obtained.

The plot of the ΔH values for pyridine, picolines and lutidines *versus* pK_a is linear, as shown in Fig. 1. This is due to the fact that the ΔS values are nearly equal for all these bases and would indicate that the number of water molecules displaced is the same for each base.

The ΔH values found for pyridine and 2-picoline are in fairly good agreement with those reported by Levi, *et al.*[7] They are −4.72 and −6.095 kcal./mole, respectively.

The ΔH values for the picolines increase in the order: 3- < 2- < 4-picoline. The introduction of a methyl group in 2- position in the pyridine ring results in an increase of the enthalpy of neutralization of 1.2 kcal./mole. This can be attributed to both the inductive effect, +I, and the mesomeric effect, +M, of the alkyl group which exerts an electron releasing effect. The same increase of 1.2 kcal. with respect to the pyridine has been found by H. C. Brown for the heat of neutralization of 2-picoline with methanesulfonic acid in nitrobenzene.[8]

The increase in the ΔH value for 3-picoline is lower, being equal to 0.85 kcal., probably because the mesomeric effect of the methyl group is not significant in this position. In 4-position, the methyl group produces the highest increase of 1.23 kcal. This can be explained in two ways: (a) because in 4-position the steric hindrance toward the oxonium ion, possible when the methyl group occupies the 2-position, is absent; (b) because in 4-position, the decrease in the inductive effect is outweighed by the increase in the mesomeric effect. This is due to the higher contribution of the *p*-quinoid structure with respect to that of the *o*-quinoid structure.

The latter explanation appears the most reasonable, while the influence of a steric hindrance of the methyl group in *ortho* on the oxonium ion seems negligible. In fact a second *o*-methyl group in 2,6-lutidine results in a further increase of the neutralization enthalpy of 1.24 kcal.

This absence of steric factors in the neutralization of picolines is also confirmed by the fact that the value of the ratio $R = \Delta H/Q_N$, where Q_N is the charge density on the nitrogen atom, is the highest for the 2-picoline.

Quinoline and isoquinoline have ΔH values higher than those expected on the basis of their pK_a (see Fig. 1). This is due to the low values of the corresponding ΔS, which would indicate the displacement of a lower number of water molecules. The heat of hydration subtracted from the heat of protonation is therefore lower and the over-all thermic effect higher.

The pK_a values for quinoline and pyridine, 4.80 and 5.17, respectively, appear to be anomalous[3]

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[5] 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.

[6] Selected Values of Chemical Thermodynamic Properties, Circular of the National Bureau of Standards No. 500.

[7] D. L. Levi, W. S. McEwan and J. H. Wolfenden, *J. Chem. Soc.*, 760 (1949).

[8] H. C. Brown and R. R. Holmes, This Journal, **77**, 1727 (1955).

because they vary in the opposite direction to the Q_N values, 1.33 and 1.27, respectively. On the other hand the ΔH values are not anomalous, being 5.36 and 4.79 for quinoline and pyridine, respectively. Unfortunately these values are not conclusive, because the reaction of neutralization is complicated by the displacement of water molecules.

The ΔH values for piperidine and pyrrolidine are lower than expected. The entropy values, on the other hand, are the highest of all the bases. This would indicate that a greater number of water molecules are displaced from these bases.

Acridine is too slightly soluble in water to allow calorimetric measurements to be made. The pK_a value for this base in 50% ethanol, equal to 4.07, is lower than that of pyridine, which is equal to 4.38 when measured under the same conditions. On the other hand, the Q_N value, 1.33, is higher than that of pyridine, 1.27. This anomalous behavior characteristic of the pK_a values in water is also exhibited by the heats of reaction ΔH in 50% ethanol, equal to 3.48 and 5.22 kcal., respectively, for acridine and pyridine. Here, too, the remarks made on quinoline are to be kept in mind.

It is interesting to compare the enthalpies of neutralization of pyridine, 2-, 3-, 4-picoline and 2,6-lutidine with methanesulfonic acid in nitrobenzene, as measured by Brown,[8] with the values obtained by summing up our heats of neutralization with the heats of hydration reported in our previous work.[4] The data obtained are:

	$\Delta H_{CH_3SO_3H}$	Heat of neutr. + heat of hydrat.
Pyridine	−17.1	−16.77
2-Picoline	−18.3	−19.37
3-Picoline	−17.8	−18.88
4-Picoline	−18.4	−19.28
2,6-Lutidine	−19.5	−21.78

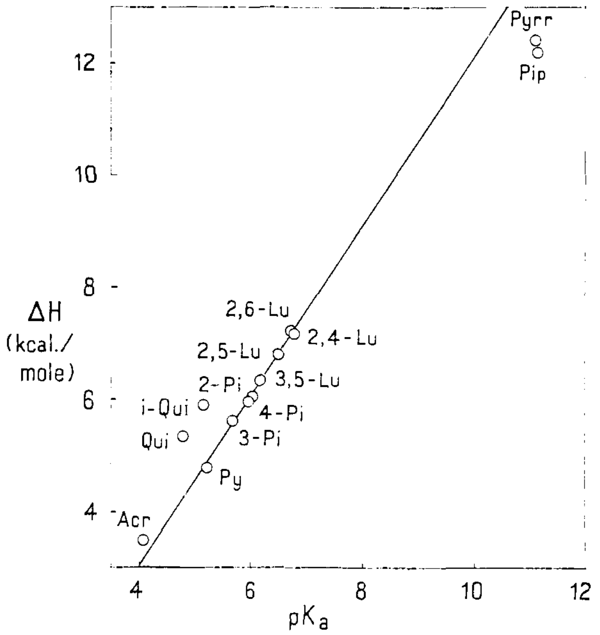

Fig. 1.—Plot of heats of neutralization *vs.* pK_a for the heterocyclic amines.

The agreement between both series is fairly good. Although it is probable that in the systems investigated by Brown, the solvation influences to some extent the heats of neutralization, the satisfactory agreement between the two series of values allows one to suppose that the hydrated proton when it reacts with the base displaces all the water bound to the nitrogen atom.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Chemistry of the Metal Carbonyls. III. The Reaction between Iron Pentacarbonyl and Tetraorganotin Compounds[1,2]

BY R. B. KING[3] AND F. G. A. STONE

RECEIVED DECEMBER 16, 1959

Organotin compounds of the type $R_x'SnR''_{4-x}$ (R′, alkyl group; R″, vinyl or phenyl group) react with iron pentacarbonyl in refluxing ethylcyclohexane to give yellow dialkyltin iron tetracarbonyl dimers, $[R_2'SnFe(CO)_4]_2$. Thus reaction between iron pentacarbonyl and either di-*n*-butyldivinyltin, di-*n*-butyldiphenyltin or tri-*n*-butylphenyltin affords di-*n*-butyltin iron tetracarbonyl, a compound identical with that previously obtained from di-*n*-butyltin dichloride and the anion $HFe(CO)_4^-$.

Until recently it appeared that iron would form complexes only with conjugated dienes, these being of the type $L \cdot Fe(CO_3)$. It is now evident, however, that under the appropriate reaction conditions iron carbonyls will react with the non-conjugated diene 1,5-cycloöctadiene, forming the very unstable compound $C_8H_{12} \cdot Fe(CO)_3$.[4]

The successful preparation of this diene complexe of iron led us to investigate the reaction between iron pentacarbonyl and dialkyldivinyltin compounds in an attempt to prepare compounds of the type $[R_2Sn(CH:CH_2)_2]Fe(CO)_3$. It was found that iron pentacarbonyl and di-*n*-butyldivinyltin did indeed react to give a yellow crystalline solid. However, the latter had the composition $C_{12}H_{18}O_4$

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(1) Previous papers in this series: T. A. Manuel and F. G. A. Stone, THIS JOURNAL, **82**, 366 (1960); R. B. King and F. G. A. Stone, *ibid.*, **81**, 5263 (1959).

(2) We are indebted to the Clark Fund of Harvard University for financial support of this work.

(3) National Science Foundation Predoctoral Research Fellow 1958–1960.

(4) T. A. Manuel and F. G. A. Stone, *Chemistry and Industry*, 231 1960.