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Metal Complex Formation in Non-hydroxylic Solvents. II. The Thermodynamics of the Equilibria between NiDBH and Primary Aliphatic Amines in Benzene[1,2]

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Received December 28, 1959

By means of spectrophotometric measurements the formation constants have been obtained for adducts of the complex diacetylbisbenzoylhydrazino-nickel(II) (NiDBH) with primary alkylamines in benzene. From the temperature coefficient of the constants, the enthalpy and the entropy changes associated with complex formation were calculated. The donor ability of the amine as well as the strength of the coördinate bond N–Ni increases regularly with the length of the alkyl chains and is proportional to the inductive effect of the substituents on the nitrogen as measured by the polar substituent constant σ^*. Steric factors are effective only for amines with branched groups. By using NiDBH as a reference acceptor in benzene solutions, the leveling effect of aqueous solutions of the pK_a values of alkylamines is eliminated and the actual relative donor affinity of the amines is revealed.

Introduction

Thermodynamic data on the relative base strengths of primary alkylamines are based mainly on measurements of acid–base equilibria in water and related hydroxylic solvents. Yet these equilibria are disturbed and complicated by solvation effects so that the interpretation of the results so obtained is rather doubtful. In the case of normal primary alkylamines, from methyl to n-octylamine, the polarity of the nitrogen atom increases with increasing chain length approaching an asymptotic limit. However, the pK_a values determined in water oscillate irregularly within a narrow range of values (Table I). Also the enthalpies of ionization in aqueous solutions of ammonia, methyl- and ethylamines,[3] which are the only ones reported, fail to show any regularity. In fact the ΔH_a value for methylamine is higher than those of ammonia and ethylamine.

Table I

Formation Constants of NiDBH Adducts with Primary Alkylamines in Benzene Solution

Amine, RNH_2, R—	log $K_{10°}$	log $K_{15°}$	log $K_{20°}$	log $K_{25°}$	log $K_{35°}$	log $K_{45°}$	pK_a	
Hydrogen	2.66 ± 0.04	2.47 ± 0.04	2.23 ± 0.05	2.11 ± 0.03		1.41 ± 0.06	9.27[a]	9.21[b]
Methyl	4.37 ± .03	4.16 ± .04	3.92 ± .04	3.75 ± .04			10.64	10.62
Ethyl	5.44 ± .04	5.24 ± .04	4.98 ± .05	4.80 ± .05			10.67	10.63
n-Propyl	6.57 ± .03		6.14 ± .03	5.90 ± .03		5.14 ± .04	10.58	10.53
i-Propyl	5.86 ± .03			5.20 ± .03		4.39 ± .02	10.63	
n-Butyl	6.73 ± .03	6.51 ± .02		6.07 ± .03		5.29 ± .04	10.61	10.59
i-Butyl	4.91 ± .03		4.45 ± .02	4.32 ± .02	3.86 ± .02	3.50 ± .01	10.42	
s-Butyl	4.71 ± .02	4.49 ± .02	4.23 ± .02	4.09 ± .02	3.67 ± .02	3.31 ± .03	10.56	
t-Butyl	4.01 ± .04	3.77 ± .02	3.58 ± .02	3.39 ± .03	3.02 ± .04	2.68 ± .04	10.45	
n-Amyl	6.59 ± .03	6.39 ± .03		5.96 ± .03	5.50 ± .04	5.14 ± .04	10.64	
i-Amyl	6.67 ± .03		6.22 ± .03	5.96 ± .03	5.54 ± .03	5.14 ± .03	10.64	
n-Hexyl	6.76 ± .03			6.10 ± .03	5.69 ± .03	5.33 ± .04		10.64[c]
n-Heptyl	6.80 ± .03			6.13 ± .04		5.36 ± .04		10.66
n-Octyl	6.74 ± .03			6.07 ± .03		5.30 ± .04		10.65
n-Nonyl	6.78 ± .03			6.12 ± .03		5.34 ± .04		10.64[c]
n-Decyl	6.82 ± .04			6.1 ± .03		5.36 ± .05		10.64

[a] N. F. Hall and M. R. Sprinkle, This Journal, **54**, 3469 (1932). [b] D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc.*, (*London*), **215**, 425 (1952). [c] C. W. Hoerr, M. R. McCorkle and A. W. Ralston, This Journal, **65**, 328 (1943).

This lack of regularity can be ascribed to the solvent effect. In fact, according to the Bjerrum and the Kirkwood and Westheimer theories,[4] the flexible alkyl chain permits the methyl group in ethylamine to approach the NH_2 group, thus modifying its electrostatic environment by direct action through the solvent.

The propylamine occupies a singular place having the lowest basic strength of all normal primary amines. This was attributed to a particularly favorable geometry of the molecule which allows the formation of a hydrogen bond between a methyl hydrogen atom and the nitrogen, thus lowering its basic strength.[5]

H. C. Brown, in his classic investigations on acid–base equilibria in the gas phase, found a slight increase in the heat of dissociation of monoalkylamine-trimethylboron with increasing length of the alkyl chain.[6] The free energy changes, however, present two irregularities at methyl- and ethylamine, the first value being higher than that of n-propylamine and the second being lower than that of methylamine.

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(1) This research was supported by the U. S. Department of the Army through its European Research Office, under Contract No. DA-91-508-EUC-304.

(2) For preceding article in this series, see L. Sacconi, G. Lombardo and P. Paoletti, *J. Chem. Soc.*, 848 (1958).

(3) W. S. Fyfe, *ibid.*, 1347 (1955).

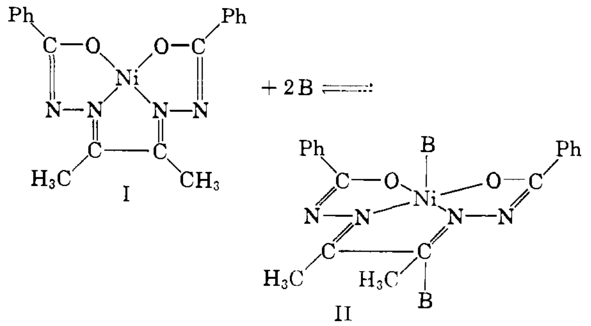
(4) N. Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923); J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938); *cf.* H. C. Brown, D. H. McDaniel and O. Häfliger, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., Publ., New York, N. Y., 1955, p. 622.

(5) H. C. Brown, M. D. Taylor and S. Sujishi, This Journal, **73**, 2464 (1951).

(6) H. C. Brown, Centenary Lecture delivered at Burlington House, June 2, 1955, *J. Chem. Soc.*, 1248 (1956).

In order to overcome the difficulties arising from the presence of hydroxylic solvents and to obtain reliable thermodynamic data on the donor properties of primary alkylamines, we decided to measure the donor abilities of such bases toward the complex compound diacetyl-bisbenzoylhydrazino-nickel(II) (NiDBH) in benzene. This tetracoördinate square planar complex (I) can add two molecules of base (B) to give a six-coördinate adduct (II) according to the equilibrium reaction

$$\text{NiDBH} + 2\ \text{Alkylamine} \rightleftarrows \text{NiDBH}\cdot 2\ \text{Alkylamine} \quad (1)$$



I

II

This equilibrium can be studied spectrophotometrically with great accuracy owing to the marked difference between the absorption spectra of I and II and the sharpness of the isosbestic point.[2] As the reaction of complex formation takes place in inert non-hydroxylic solvents, the complication arising from the use of solvating solvents is eliminated. Furthermore the large planar structure of the molecule of the NiDBH hinders the terminal methyl group of the alkylamines from approaching the NH_2 group of the same molecule with the formation of an intramolecular hydrogen bond. In this way the NiDBH complex, on account of its large steric requirements and the presence of a transition metal as a central atom, behaves as an ideal reference acceptor. It is highly suitable for the study of the structure of ligand molecules, possible steric strains, and of the bond type involved.

From spectrophotometric data the values of log K at different temperatures have been obtained. Then, from the temperature dependence of the formation constants the enthalpy and entropy changes were calculated. These thermodynamic quantities are necessary to evaluate the bond strength and the effect of the stereochemistry of both acceptor and ligands. It should be pointed out that ΔH and ΔS data for acid–base equilibria of alkylamines as well as other nitrogen bases are very scarce. The ΔH values were found to be constant within experimental error over the range of temperature investigated. The sharpness of the isosbestic point shows that no monoadduct NiDBH·B is present in the system. This is confirmed by the good reproducibility in the log K values calculated, for the different concentrations of base, according to the equilibrium reaction 1.

Experimental

Materials.—The alkylamines, which were good-quality commercial products, were purified by standard methods until their physical constants agreed closely with the values in the literature. They were dried on potassium hydroxide and fractionated through a Todd column of 40 theoretical plates and the constant boiling middle fractions collected. Methylamine and ethylamine were used without purification.

The concentration of the amines in the benzene solutions was determined by titration according to Fritz[7] and Pifer, Wollish and Schunal.[8]

The benzene was purified carefully by standard methods.

Spectrophotometry.—The absorptimetric data were obtained in the manner described in the previous paper[2] using a Beckman DU quartz spectrophotometer fitted with a thermostat-controlled cell compartment. Measurements were made at 10, 15, 20, 25, 35 and 45° in 1.00 cm. stoppered silica cells. In measurements at lower temperatures, especially during the hot season, care was taken to prevent the formation of moisture on the cells, by circulation of dried air in the cell compartment. The solutions used contained 10^{-4} mole per liter of the complex and known and varying amounts of each base. The solution used as a blank contained the same concentration of base as the sample.

The formation constants, log K, and the thermodynamic quantities ΔH, ΔF and ΔS were calculated in the manner reported in the above mentioned paper.[2] The optical densities were measured at the wave length of the absorption maximum of the upper limiting absorption curve. These maxima fall between 460 and 480 mμ.

The accuracy of the thermodynamic quantities is ΔF, ± 0.06; ΔH, ± 0.3 kcal./mole; ΔS, ± 0.7 e.u.

Results and Discussion

The results are given in Tables I and II.

TABLE II

THERMODYNAMIC FUNCTION FOR THE REACTION NiDBH + 2 Amine ⇄ NiDBH·2 Amine AT 25° IN BENZENE SOLUTION

Amine $R-NH_2$, R-	$-\Delta F$ (kcal./mole)	$-\Delta H$ (kcal./mole)	$-\Delta S$ (e.u.)	$-\Sigma\sigma^*$
Hydrogen	2.86	14.6	39.2	−1.47
Methyl	5.11	15.9	36.4	−0.98
Ethyl	6.34	16.5	33.3	− .88
n-Propyl	8.04	16.9	29.7	− .865
i-Propyl	7.09	17.3	34.2	− .79
n-Butyl	8.27	16.9	29.1	− .85
i-Butyl	5.89	16.6	35.9	− .885
s-Butyl	5.57	16.5	36.5	− .77
t-Butyl	4.62	16.1	38.5	− .68
n-Amyl	8.13	17.1	30.0	− .835
i-Amyl	8.13	17.2	30.3	
n-Hexyl	8.31	16.8	28.6	
n-Heptyl	8.35	16.9	28.8	
n-Octyl	8.27	16.9	29.1	
n-Nonyl	8.34	16.9	28.8	
n-Decyl	8.36	17.2	29.6	

The values of log K and therefore of $-\Delta F$ for normal amines increase fairly regularly up to *n*-butylamine and remain practically constant thereafter. The values of $-\Delta H$ start from 15.9 kcal./mole for methylamine and increase slowly with chain length approaching an asymptotic limit of *ca.* 17 kcal./mole starting with butylamine. This value is very close to the heat of dissociation of the adducts between *n*-primary alkylamines and trimethylboron in gas phase (18.5 kcal.).[6]

The variations of the ΔS values are analogous to that of $-\Delta F$ and $-\Delta H$. The entropy changes are negative in every case. This is due to: (i) a decrease in the number of molecules due to the binding of two amine molecules in the formation of

(7) J. Fritz, *Anal. Chem.*, **22**, 1028 (1950).

(8) C. W. Pifer, E. C. Wollish and M. Schunal, *ibid.*, **25**, 310 (1953).

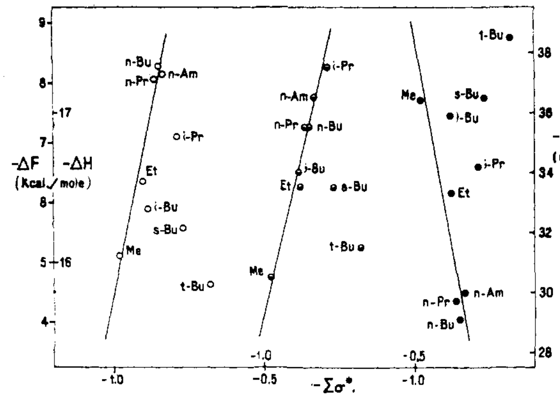


Fig. 1.—Free energy, enthalpy and entropy changes values for NiDBH·2-amine adducts plotted against the inductive substituent constant: O, $-\Delta F$ values; ⊖, $-\Delta H$ values; ●, $-\Delta S$ values.

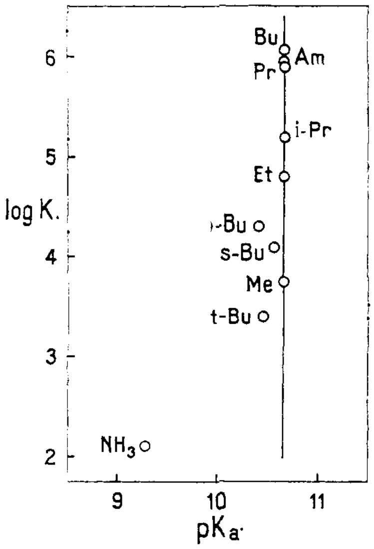


Fig. 2.—Log K values for NiDBH·2amine adducts plotted against pK_a.

the adducts; (ii) an over-all increase in rigidity of the system.

The main factors to be taken into consideration when discussing the behavior of aliphatic amines toward a reference acceptor are: (a) the polarity; (b) the steric requirements of the amines with respect to the reference acceptor.

It is well known that in the alkylamines the inductive effect ($+I$), and thus the polarity, increase with the length of the alkyl chain.[9] Taft has shown that the quantity $-\Sigma\sigma^*$ is a measure of the inductive electron releasing effect relative to the methyl group.[10] The values of $-\Sigma\sigma^*$ are in satisfactory agreement with the qualitative scale of polarity of the English school. For this reason we have correlated the values of $-\Sigma\sigma^*$ with those of ΔF, ΔH and ΔS for the primary alkylamines. The plots are reported in Fig. 1.

$-\Delta F$ values for *n*-alkylamines lie roughly on one straight line with a positive slope, that is, the stability of the adducts increases linearly with the polarity. This shows that steric effects are practically absent. The points for *iso*-, *sec*- and *tert*-alkylamines fall below the line showing that the adducts with these amines are less stable than expected on the basis of $-\Sigma\sigma^*$. This can be attributed to steric strain due to the branched alkyl chains, which interferes with the flat molecule of NiDBH. This steric hindrance is considered to be F-strain.

The $-\Delta H$ values also fall on a straight line with a slope of the same sign as that of $-\Delta F$. The relative stability of the adducts is thus in part an enthalpy effect. In this case, too, the points corresponding to branched alkylamines fall below the line given by the *n*-monoalkylamines. The closer the NH_2 groups are to the branching of the alkyl chain, the higher is the steric F-strain. This would signify that the bond strength for normal alkylamines is influenced only by the polarity of the amines and that only in the case of branched alkylamines are steric factors operative with consequent weakening of the bond strength.

The values of $-\Delta S$ also lie roughly on a straight line with a slope opposite to those of $-\Delta F$ and $-\Delta H$ for the amines. Thus the stability of the adducts appears to be mainly an entropy effect.

The entropy changes become less negative with the lengthening of the alkyl chain. This indicates that the rigidity of the adducts decreases with the introduction of new rotational modes of the alkyl chains due to the increasing number of carbon atoms. The *iso*-, *sec*- and *tert*-alkylamines show more negative entropy changes, in agreement with the idea of a greater rigidity in the adducts due to steric strains as indicated in the discussion of the $-\Delta H$ values.

The values of log K, ΔF, ΔH and ΔS for ammonia are situated far away from the lines corresponding to the alkylamines. This indicates that structural factors, other than steric and polarity, play an important role.

The log K values plotted against pK_a (Fig. 2) lie roughly on a straight line parallel to the ordinate axis and far away from each other. This means that, while the affinity of these amines for the proton varies irregularly with the length of the alkyl chain, the affinity for NiDBH increases markedly with chain length. Thus, aqueous solvents bring about a levelling effect which tends to equalize the values of pK_a for all primary alkylamines whereas the acceptor NiDBH in benzene causes a wide separation of the values of formation constants, *i.e.*, of donor affinities. This reference acceptor therefore behaves as a "detector" of the coördinating tendencies of the alkylamines.

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(9) C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

(10) R. W. Taft, Jr., This Journal, **74**, 3120 (1952); **75**, 4231 (1953).