Polar and Steric Effects in the Stability of Silver Complexes of Primary Amines

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The complex-formation constants of alkylamines NRH_2 with Ag^I have been determined at 25 °C and I = 0.1 mol dm^{-3}, the background salt being mainly $[NRH_3][NO_3]$. The pK_a, $\log K_1$, and $\log \beta_2$ values are: R = Me, 10.64, 3.06, 6.78; Et, 10.66, 3.44, 7.34; Pr^i, 10.62, 3.64, 7.77; Bu^t, 10.66, 3.69, 7.87; Bu^s, 10.56, 3.65, 7.77; cyclopropyl, 9.06, 3.10, 6.43; cyclopentyl, 10.63, 3.61, 7.83; and cyclohexyl, 10.62, 3.72, 8.02. It is shown that these variations of pK_a and $\log K$ can be readily understood in terms of Taft's (1957) equation relating formation and rate constants to polar and steric effects. Correlations from this equation suggest that Ag^+ is much less susceptible to steric hindrance than is the proton.

ALTHOUGH many linear free-energy relations have been established for metal ions and amines, these have generally involved heterocyclic bases such as the substituted pyridines. Formation constants for heterocyclic bases can be analysed using Hammett sigma functions,[1] but the situation with primary aliphatic amines is more complex. Steric effects must also be taken into account, as attachment of substituents directly to the nitrogen of primary aliphatic amines can produce considerable steric hindrance.[2] Such hindrance can also occur for *ortho*-substituted heterocyclic bases, but one can easily study electronic effects alone by confining attention to the *meta*- and *para*-substituted forms where steric effects can be assumed to be constant.

The equation of Pavelich and Taft [3] below, which takes polar and steric effects into account, has been used highly successfully in organic chemistry to separate and correlate these effects. $\log K^0$ is the formation constant

$$\log K = \log K^0 + \rho^*\sigma^* + \delta E_s$$

(or in the case of reaction rates, rate constant) of the methyl substituent, in this case of methylamine, ρ^* and σ^* are analogous to the Hammett constants, δ represents the susceptibility of the reaction site to steric hindrance, and E_s is the tendency of the substituent to produce steric hindrance. It was recently proposed [4] that susceptibility to steric hindrance was an important factor in accounting for the low affinity of the proton or Ni^{II} for ligands such as chloride ion in water, as compared with that displayed by large ions such as Ag^I. It seemed the above equation might provide a means of testing this hypothesis. Accordingly, the formation constants of the silver(I) and nickel(II) ions were determined with a selection of primary amines designed to give as wide a range of σ^* and E_s values as possible. The amines studied were methylamine, ethylamine, isopropylamine, t-butylamine, s-butylamine, cyclohexylamine, cyclopentylamine, and cyclopropylamine. The last three are of particular interest as cyclization is commonly found [2] to produce much lower E_s values compared with other similar non-cyclic amines.

EXPERIMENTAL

All the reagents were obtained in high purity: methyl-, isopropyl-, cyclopropyl-, and cyclopentyl-amine from Merck; s-butyl- and cyclohexyl-amine from B.D.H.; t-butylamine from Fluka; and ethylamine from Hopkins and Williams. These were used without further purification to make up stock solutions which were standardized by titration with standard HNO_3. The 1 mol dm^{-3} stock solution of nitric acid was prepared from B.D.H. 'CVS' ampoules, and checked by titration against borax. The purity of the amines was found in all cases to be higher than 99% based on the weight of amine taken. A stock solution of silver nitrate was prepared from AnalaR $Ag[NO_3]$, and standardized by potentiometric titration.[5]

In the study of each system, the simple approach employed was to titrate 20 ml of 0.1N HNO_3 plus x ml 0.1N $Ag[NO_3]$ (x ranges from 5 to 1; $x = 0$ for pK_a determination) with *ca.* 0.2N amine in 0.1N HNO_3. This allows one to keep the background concentration of protonated amine high, which is essential for the prevention of hydrolysis. The ionic strength of 0.1 mol dm^{-3} is composed of 0.1N NO_3^-, with counter ions in the region of interest comprising almost entirely those of the protonated amine. Titrations were carried out with three different silver(I) concentrations, and pK_a determinations were carried out in duplicate or triplicate. A Radiometer G202B glass electrode was used, along with a Radiometer PHM 64 pH meter for monitoring the pH during the course of the titrations. The cell and other apparatus used were as described previously.[5] A stock solution of nickel(II) nitrate was prepared from Merck 'extra-pure' $Ni[NO_3]_2 \cdot 6H_2O$, and standardized by titration with edta (ethylenediaminetetra-acetate).

A computer program was written that calculated $\bar{n}$ from the potentiometric data for each of the three titrations with each amine, and then plotted the function $\bar{n}/(1 - \bar{n})[L]$ against $(2 - \bar{n})[L]/(1 - \bar{n})$, where [L] is the concentration of free ligand for that particular value of $\bar{n}$. A least-squares fit of the linear relationship for $0.2 < \bar{n} < 0.8$ and $1.2 < \bar{n} < 1.8$ yields K_1 as the intercept and β_2 as the slope.[6] No weighting scheme was necessary in the program for the latter step, as the linearity of the relations was excellent. The reliability of the procedure is shown by the excellent agreement obtained with published values for methylamine and ethylamine, even though these were obtained at an ionic strength (I) of zero. For neutral ligands, a change of I from 0 to 0.1 mol dm^{-3} should have very little effect.

For Ni^{II}, hydrolysis of the amine complexes was found to prevent formation-constant determination in a background of 0.1 mol dm^{-3} $[NRH_3][NO_3]$. In the case of cyclohexylamine, $\log K_1$ was determined as 2.0 ± 0.1 in 1 mol dm^{-3} cyclohexylammonium nitrate. The higher uncertainty reflects the fact that $\bar{n}$ did not rise above 0.1 in these experiments before hydrolysis set in.

RESULTS AND DISCUSSION

In the Table are set out the results obtained for the various amines, together with literature values, where available, for comparison. It is noted that while the pK_a values for the amines are almost invariant, there is a fairly large spread of log$K$ values for Ag^I. This can be explained using Taft's equation. If $\rho^* = 3.3$ and $\delta = 0.5$, the pK_a values of a wide selection of primary amines can be correlated reasonably well. The invariance of the pK_a of the amines is interpreted as a balance between polar (inductive) and steric effects. Thus t-butylamine has a favourable polar contribution, but, because of its bulkiness, has an unfavourable steric contribution, so that there is little difference in pK_a between it and methylamine.

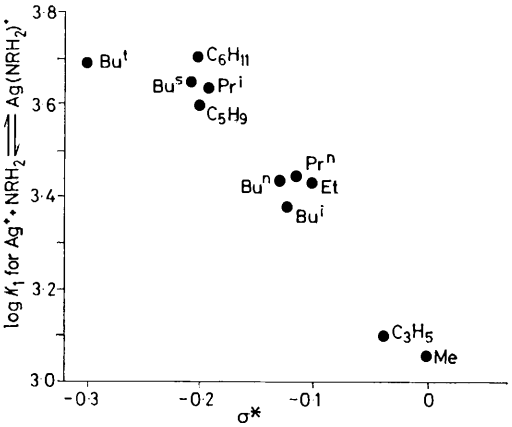
It is often found that the basicities of alkylamines in water do not relate well to gas-phase basicities. Thus, the order of increasing pK_a for the methyl-substituted amines in water is $N(CH_3)_3 < N(CH_3)_2H \sim N(CH_3)H_2$, while the order[7] of gas-phase basicity is $N(CH_3)H_2 \ll N(CH_3)_2H \ll N(CH_3)_3$. Part of this difference in order is attributable to quenching of the contribution from the polarizability of the alkyl group on transfer from the gas phase to aqueous solution.[8] The polarizability contribution stabilizes ions in the gas phase by distribution of charge over the whole ion, and is mainly dependent on the size of the substituents. This function is taken over by the highly polar solvent in aqueous solution, so that here polarizability effects are not observed.[8] However, one would still expect to see an inductive-effect order for alkylamines,[8] and its non-observance must be attributed to steric effects.

Values of pK_a and complex-formation constants with Ag^I for various amines NRH$_2$ at 25 °C and $I = 0.1$ mol dm^{-3}. Standard deviations are 3σ as indicated by the deviation of individual results from the three separate titrations from the mean value. Literature values, where available,[a] are shown for comparison

R =	Methyl	Ethyl	Isopropyl	t-Butyl	s-Butyl	Cyclopropyl	Cyclopentyl	Cyclohexyl
pK_a	10.644	10.662	10.623	10.663	10.559	9.064	10.625	10.617
	±0.005	±0.004	±0.008	±0.010	±0.003	±0.010	±0.003	±0.006
(lit.)	10.62	10.67	10.63	10.683	10.56	9.10	10.65	10.60
ΔH(lit.) [b]	−13.26	−13.71	−13.94	−14.39	−14.03	−11.72	−14.30	−14.26
logK_1	3.06	3.44	3.64	3.69	3.65	3.10	3.61	3.72
	±0.03	±0.03	±0.06	±0.06	±0.06	±0.08	±0.06	±0.08
(lit.)	3.07	3.46						
logβ_2	6.78	7.34	7.77	7.87	7.77	6.43	7.83	8.02
	±0.05	±0.05	±0.04	±0.03	±0.03	±0.05	±0.04	±0.05
(lit.)	6.89	7.35						

[a] R. M. Smith and A. E. Martell, ' Critical Stability Constants,' vol. 2, 'Amines,' Plenum Press, New York, 1975; J. J. Christensen, L. D. Hansen, and R. M. Izatt, ' Handbook of Proton Ionization Heats,' Wiley, New York, 1976. [b] Units are kcal mol^{-1}; 1 cal = 4.184 J.

It is of considerable interest that the log$K$ values for the Ag^I ion with primary alkylamines increase with more negative (electron-releasing) σ^* values as seen in the Figure. The log$K$ values are reasonably well correlated by the Taft equation when $\rho^* = 2.0$ and $\delta = 0.14$. The value for the ammonia complex is not well correlated using these parameters, but this is hardly surprising as even the pK_a values of ammonia, and primary, secondary, and tertiary amines cannot be correlated simultaneously using the Taft equation in its unmodified form. The increase in stability of the primary amine complexes of Ag^I as σ^* for the substituent becomes more negative, a trend not observed for pK_a, has to be attributed to the much smaller value of δ for Ag^I as compared with the proton. This result is in keeping with the suggestion[4] that the Ag$^+$ is less susceptible than the proton to steric hindrance to co-ordination, caused by the large hydration sphere and small size of the latter.



Relation between logK_1 (NRH$_2$) for complex formation with Ag^I and Taft[3] σ^* function. C_3H_5 = Cyclopropyl, C_5H_9 = cyclopentyl, and C_6H_{11} = cyclohexyl. Values for ligands not studied in this work are taken from the literature (see footnote *a* in Table). No σ^* values have been reported for the cyclohexyl or cyclopropyl groups, and those shown were estimated from the pK_a of the correspondingly substituted carboxylic acid, as discussed in ref. 2

That substitution of methyl groups on the α-carbon atom of primary alkylamines increases the stability of the complexes formed with the Ag$^+$ is in agreement with the observation[9,10] that the same process can lead to increased stability of the complexes formed with C-methyl-substituted ethylenediamines. The cyclohexyl substituent also produces considerable stabilization, the complexes of the first-row bivalent transition-metal ions with bicyclohexyl-1,1′-diamine being the most stable formed by these ions with any alkyl-substituted ethylenediamine derivative.[11] With all such substituted ethylenediamines, the increased stabilities of the complexes formed with the metal ions is not reflected by any increase in pK_a as compared with ethylenediamine itself, in the way found for Ag^I and primary amines. The evidence then is strong that Ag^+, in particular, and also first-row transition-metal ions, are able to form complexes of increased stability with more polar amines, where steric effects prevent an increase in pK_a.

Although the above results suggest that one might expect an increase in stability in passing from, say, methylamine to cyclohexylamine complexes of the first-row transition-metal ions, one would expect these increases to be small. The values recently published [12] for first-row bivalent metal ions with cyclohexyl- and cyclopentyl-amine are surprisingly high. Thus, $\log K_1$ for cyclohexylamine with Ni^{II} is reported as 5.9, compared with 2.7 for the ammonia complex. The corresponding values for Ag^I are only 3.7 and 3.3. In addition, our own measured value of 2.0 in 1.0 mol dm^{-3} $[NRH_3][NO_3]$ for cyclohexylamine does not agree with the reported values.[12] The previous studies were performed at a higher temperature (37 °C) and in perchlorate medium, but it seems unlikely that this could produce such a large difference, so that one is led to suggest that the complexes of cyclohexyl- and cyclopentyl-amine with the first-row bivalent metal ions should be re-investigated so as to clear up this disparity.

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