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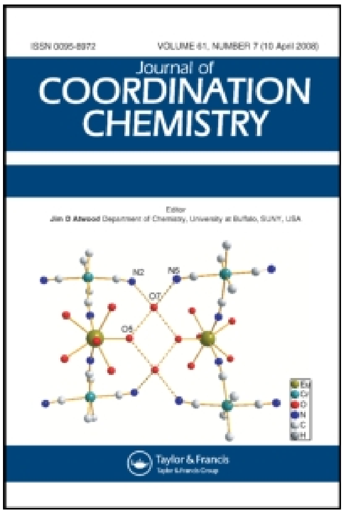

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THE THERMODYNAMICS OF PROTONATION OF SOME SULPHIDE CONTAINING DIAMINES IN AQUEOUS SOLUTION

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The protonation properties of 1,7-diaza-4-thiaheptane, 1,8-diaza-4-thiaoctane, 1,9-diaza-4-thianonane and 1,9-diaza-5-thianonane have been investigated potentiometrically and calorimetrically at 25°C in 0.5 mol dm^{-3} (K)NO_3 solution. Values for the protonation constants and for the thermodynamic functions ΔH° and ΔS° were determined. The results have been discussed. It has been found that the place of the thioether group in the aliphatic chain, connecting the two aminogroups, predominantly determines the behaviour of the diamines when protonated.

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INTRODUCTION

As part of an investigation[1] on equilibria in aqueous solution of sulphide containing amines, we have now undertaken the thermochemical study of the protonation of 1,7-diaza-4-thiaheptane, 1,8-diaza-4-thiaoctane, 1,9-diaza-4-thianonane and 1,9-diaza-5-thianonane. Values for the protonation constants and for the thermodynamic functions ΔH° and ΔS° were determined, to gain a better insight in the influence of the thioether group on the basic properties of the amino-groups.

EXPERIMENTAL

Syntheses

1,7-diaza-4-thiaheptane (($NH_2CH_2CH_2)_2S$, abbrev. 2,2-NSN) was prepared by a method already described.[2] 1,8-diaza-4-thiaoctane ($NH_2(CH_2)_2S(CH_2)_3NH_2$, abbrev. 2,3-NSN) was prepared as follows. A solution of 0.8 mole sodium hydrogensulphide in 0.250 dm^3 methanol was prepared by bubbling dry gaseous hydrogen sulphide through a methanolic sodium methoxide solution until the reaction with phenolphtaleine became negative, and refluxed for 3 hours with 201 g (0.75 mole) of N-(3-bromopropyl)-phtalimide. After cooling, the product (two liquid layers and crystals of NaBr) was poured into 1 dm^3 of boiling water. An oily product remained undissolved, which solidified upon standing at 0°C. This solid material was then dissolved in 0.500 dm^3 absolute ethanol, and ethyleneimine was slowly added, until the mercaptotest with sodium nitroprusside became negative. The reaction product was then hydrolized following the method described by Dwyer and Lions.[3] The finally obtained yellow oil was distilled under reduced pressure through a Vigreux column. The fraction constantly boiling at 85°C/2 mm Hg was taken. This fraction was refractionated again and only the middle cut was used for the determination of the molecular weight by a potentiometric titration with standardized nitric acid. Calcd. for $C_5H_{14}N_2S$: M.W. = 134.2; Found: 133.8. The dichloride salt of the amine was prepared. Anal. Calcd. for $C_5H_{16}Cl_2N_2S$: N, 13.5; Found: N, 13.6.

1,9-diaza-4-thianonane ($NH_2(CH_2)_2S(CH_2)_4NH_2$, abbrev. 2,4-NSN) was prepared by the same procedure. 0.75 mole N-(4-bromobutyl)-phtalimide was used for the reaction with sodium hydrogensulphide. B.p. of the obtained amine : 102°C/0.5 mm Hg. Calcd. for $C_6H_{16}N_2S$: M.W. = 148.3; Found: 148.1. The dichloride salt of the amine was prepared. Calcd. for $C_6H_{18}Cl_2N_2S$: N, 12.7; Found: N, 12.6.

1,9-diaza-5-thianonane ($NH_2(CH_2)_3S(CH_2)_3NH_2$, abbrev. 3,3-NSN) was also prepared by the same method. 0.75 mole N-(3-bromopropyl)-phtalimide was used for the reaction with sodium hydrogensulphide. The same product was used instead of

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ethyleneimine in the second stage of the synthesis. Here, 1.5 mole sodium ethoxide in dry ethanol was also added to obtain a precipitation of NaBr. B.p. of the obtained amine : 112°C/1 mm Hg. Calcd. for $C_6H_{16}N_2S$: M.W. = 148.3; Found: 148.6. The dichloride salt of the amine was prepared. Anal. Calcd. for $C_6H_{18}Cl_2N_2S$: N, 12.7; Found: N, 12.7.

Solutions

Solutions of the four amines were prepared with CO_2-free twice distilled water under a flow of nitrogen. Their titers were determined by potentiometric titration with standardized nitric acid. The end-point of the titrations was determined using Gran's method.[4] Solutions of potassium hydroxide and of nitric acid were prepared and standardized as previously described.[1] To all the solutions an appropriate amount of solid potassium nitrate was added, to bring the total nitrate concentration up to 0.5 mol dm^{-3}.

Potentiometric Titrations

pH Data were obtained by potentiometric titrations with the apparatus and $[H^+]$ – calibration method previously described.[1] For each titration, the cell contained 70.0 or 80.0 cm^3 of a solution in which known amounts of the amine and nitric acid were dissolved. The total nitrate concentration was 0.5 mol dm^{-3}. The solution was titrated with 0.9958 mol dm^{-3} KOH in 0.5 mol dm^{-3} KNO_3. All measurements were carried out at 25° ± 0.05°C. Experimental details are given in Table I.

Calorimetric Measurements

The calorimetric measurements were carried out with a LKB 8700/2 titration calorimeter, thermostatted at 25.000° ± 0.001°C. To determine the heats of protonation of the amines, the calorimetric vessel contained a solution of the amine with known concentration. The total nitrate concentration was 0.5 mol dm^{-3}. The solution was then stepwise titrated with 1.024 mol dm^{-3} HNO_3 in 0.5 mol dm^{-3} KNO_3. Experimental details are given in Table II.

Calculations

The protonation constants for each amine were calculated from selected data with a SIEMENS 4004 computer and an appropriate FORTRAN IV programme. The heats of protonation were calculated on a VARIAN 620/L–100 data machine and an appropriate FORTRAN IV programme. The details concerning the calculation procedures have already been reported.[1]

RESULTS

The values of log K, ΔH° and ΔS° for the two successive stages of protonation of the S-α,ω-diamines are given in Table III.

DISCUSSION

Comparing the thermodynamic functions of the

TABLE I
Experimental details for the potentiometric titrations

Amine	Millimoles amine	Millimoles HNO_3	$V(cm^3)^a$	Range $-\log [H^+]$
2,2-NSN	3.208	7.132	80.0	4.46[b] – 10.52
	1.604	3.910	80.0	4.34 – 10.64
	0.802	3.910	80.0	4.56 – 10.61
2,3-NSN	3.138	9.926	80.0	3.05 – 11.68
	1.527	9.926	80.0	3.21 – 11.72
	0.723	9.926	80.0	2.98 – 10.88
2,4-NSN	4.077	10.182	70.0	3.04 – 11.35
	2.039	5.091	70.0	3.74 – 11.43
	2.673	5.624	80.0	3.58 – 11.27
3,3-NSN	3.712	9.986	80.0	3.64 – 10.84
	1.856	6.274	80.0	3.58 – 10.79
	3.093	6.274	70.0	3.61 – 11.02

[a] Initial volume in the titration vessel.

[b] Values for $-\log [H^+]$ after the first addition of strong base.

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protonation of 2,2-NSN with those of 1,5-diaminopentane[5] (Table IV), one can see that for both stages the protonation constant is smaller, the enthalpy change is less exothermic and the entropy change is less favourable for 2,2-NSN. Thus the replacement of a methylene group by a sulphur atom reduces the electron density on both aminogroups, resulting in a lower basicity and less exothermic heat of protonation. Moreover, in the sphere of influence of an ammonium group, a carbon – sulphur bond looses more rotational entropy by chain – stiffening[6] than a carbon – carbon bond. These characteristics for the protonation of sulphur containing amines have already been shown for the protonation of 1-aza-4-thiapentane.[1]

At each protonation stage, 3,3-NSN, which has three methylene groups between the sulphur atom and the terminal aminogroups, is more basic and its heat of protonation is more exothermic than that of 2,2-NSN. This is due both to a larger positive inductive effect of the trimethylene chains upon the aminogroups and to the larger distance between the aminogroups and the electron withdrawing thioether group. The difference $\Delta H_2^{\circ} - \Delta H_1^{\circ}$ is smaller for 3,3-NSN (0.6 kJ mole^{-1}) than for 2,2-NSN (0.8 kJ mole^{-1}). This is in agreement with what has been found for α,ω-diamines[6], where the difference $\Delta H_2^{\circ} - \Delta H_1^{\circ}$ decreases with increasing chain length between the two terminal aminogroups. For the latter diamines, ΔS_1° becomes less favourable and ΔS_2° less unfavourable with increasing chain length.[6] For the S-α,ω-diamines 2,2-NSN and 3,3-NSN a similar trend is only found for ΔS_2°. On the other hand, ΔS_1° is more favourable for 3,3-NSN than for 2,2-NSN. This seems to indicate that for the first protonation stage, the distance between the thioether group and the ammonium group mainly determines the entropy change. As this distance increases, the loss of rotational entropy of the carbon – sulphur bond will decrease. Consequently, ΔS_1° will be more favourable for 3,3-NSN than for 2,2-NSN. At the second protonation stage, ΔS_2° for 3,3-NSN will be less unfavourable than for 2,2-NSN, since for both amines the

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TABLE II
Experimental details for the calorimetric titrations

Amine	Millimoles amine	V(cm^3)^a	Total volume HNO$_3$ added (cm^3)^b
2,2-NSN	7.200	81.00	14.00
	5.400	80.00	10.00
2,3-NSN	7.275	80.00	13.00
	5.454	80.00	10.00
2,4-NSN	7.115	70.00	13.00
	5.334	70.00	10.00
3,3-NSN	7.593	70.00	14.00
	5.694	70.00	11.00

[a] Initial volume in the titration vessel.
[b] Titer HNO$_3$: 1.024 mol dm^{-3} in 0.5 mol dm^3 KNO$_3$; addition in portions of 1.00 cm^3.

TABLE III
The protonation constants and the thermodynamic functions of the stepwise protonation of 2,2-NSN, 2,3-NSN, 2,4-NSN and 3,3-NSN[a,b]

Amine	log K_1	log K_2	$-\Delta H_1^{\circ}$	$-\Delta H_2^{\circ}$	ΔS_1°	ΔS_2°
2,2-NSN	9.682(2)^c	8.821(2)	54.1(3)	53.3(4)	3.8(8)	−9.9(1.0)
2,3-NSN	10.139(2)	9.161(2)	56.0(2)	54.8(3)	6.2(8)	−8.5(1.3)
2,4-NSN	10.440(2)	9.249(3)	57.6(2)	55.1(3)	6.6(8)	−7.8(1.4)
3,3-NSN	10.365(2)	9.628(2)	56.5(2)	55.9(3)	8.9(8)	−3.2(1.7)

[a] 25°C, 0.5 mol dm^{-3} [K]NO$_3$.
[b] ΔH° in kJ mol^{-1}, ΔS° in J K^{-1} mol^{-1}; standard state: 1 mol dm^{-3}.
[c] Value in parentheses is the standard deviation on the last significant figure.

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TABLE IV
The protonation constants and the thermodynamic functions of the stepwise protonation of 1,5-diaminepentane[a]

log K_1	log K_2	$-\Delta H_1°$	$-\Delta H_2°$	$\Delta S_1°$	$\Delta S_2°$
10.916	10.050	58.0	56.1	14.6	3.8

[a] 25°C, 0.5 mol dm^{-3} KNO_3, ref 5. $\Delta H°$ in kJ mol^{-1}, $\Delta S°$ in J K^{-1} mol^{-1}.

diprotonated form is symmetrical, so that chain-stiffening will decrease as the distance between the two ammonium groups increases. Within the series 2,2-NSN, 2,3-NSN and 2,4-NSN, there are two methylene groups between the first aminogroup and the thioether group, whereas the number of methylene groups between the second aminogroup and the thioethergroup increases steadily with one unit. Therefore we will make a distinction between these two aminogroups by adding the prefixes α or ω.

2,2-NSN : α-$NH_2(CH_2)_2S(CH_2)_2NH_2$-$\omega$
2,3-NSN : α-$NH_2(CH_2)_2S(CH_2)_3NH_2$-$\omega$
2,4-NSN : α-$NH_2(CH_2)_2S(CH_2)_4NH_2$-$\omega$

One can notice that for both protonation stages, the basicity and the heat of protonation increase steadily with increasing distance between the two aminogroups: thus in the order 2,2-NSN, 2,3-NSN, 2,4-NSN. This can be ascribed to an increasing positive inductive effect when the number of methylene groups increases. However, the difference $\Delta H_2°-\Delta H_1°$ increases with increasing distance between the α- and the ω-aminogroup ($\Delta H_2°-\Delta H_1°$: 0.8 kJ mol^{-1} for 2,2-NSN, 1.2 kJ mol^{-1} for 2,3-NSN and 2.5 kJ mol^{-1} for 2,4-NSN). Another fact is that for 2,3-NSN the values for both $\Delta H_1°$ and $\Delta H_2°$ are between those for 2,2-NSN and 3,3-NSN. Therefore, it seems reasonable to suggest that at the first protonation stage the $H(2,3\text{-}NSN)^+$ ion exists in two tautomeric forms, the one protonated on the α-aminogroup, and the other on the ω-aminogroup.

$$\underset{\text{I}}{\alpha-\overset{+}{N}H_3(CH_2)_2S(CH_2)_3NH_2-\omega} \rightleftharpoons$$

$$\underset{\text{II}}{\alpha-NH_2(CH_2)_2S(CH_2)_3\overset{+}{N}H_3-\omega}$$

The hypothesis of the tautomeric equilibrium enables us to explain the trends in the values for the thermodynamic functions of protonation.

The ω-aminogroup is steadily at a greater distance from the thioether group in the sequence 2,2-NSN, 2,3-NSN, 2,4-NSN. Owing to this, the microbasicity of the ω-aminogroup and, consequently the values for log K_1 and $-\Delta H_1°$ will increase in that sequence. At the second stage of protonation, the α-aminogroup will preferably be protonated in the same sequence. Since for the three amines the protonation of the α-aminogroup will be influenced to the same extent by the thioether group but to a much smaller extent by changing inductive effects, the increasing trends for log K_2 and $-\Delta H_2°$ will be much smaller. Thus the difference $\Delta H_2°-\Delta H_1°$ will increase in the sequence 2,2-NSN, 2,3-NSN, 2,4-NSN. With regard to the entropy changes, one can notice that the values for $\Delta S_1°$ become more positive in the order 2,2-NSN, 2,3-NSN, 2,4-NSN. This is in agreement with our previous finding that the entropy change becomes more favourable when the distance between the thioethergroup and the ammonium group increases. However, $\Delta S_1°$ for 2,3-NSN and 2,4-NSN remains less positive than for 3,3-NSN. This is indicative for the existence of the tautomeric equilibrium at the first protonation stage. For $\Delta S_2°$, there is only a slight increase (less negative) in going from 2,2-NSN to 2,4-NSN. This is in accordance with the protonation of predominantly the α-aminogroup at the second stage. Thus the entropy changes affirm the hypothesis of a tautomeric equilibrium at the first protonation stage of 2,3-NSN and 2,4-NSN.

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