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THERMOANALYTICAL STUDIES ON SODIUM 1,2-NAPHTHOQUINONE OXIMESULFONATES

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ABSTRACT

Five sodium 1,2-nitrosonaphtholsulfonates were prepared or purified and their thermal behaviour studied by TG, DTG and DSC. Pyrolysis MS technique was used to identify evolved gases and FTIR to characterize residuals. The water contents depended on preparation and conservation. The decomposition was analysed in three stages which can be formed by one or more steps. The final product was sodium sulfate in air at 530 °C and the mixture of carbon and sodium sulfide at 950 °C in nitrogen. The structure effects on decomposition is discussed.

INTRODUCTION

The sulfonic acid derivatives of nitrosonaphthols have wide use in spectrofotometric and potentiometric titrations because of their ability to form stable and colourful complexes with many metal ions in aqueous solutions (ref.1-3). In particular, 2-nitroso-1-naphthol-4-sulfonic acid has proved to be an excellent ligand in ion pair extraction for the spectrofotometric determination of nickel in iron and steel (ref.4).

The sulfonated nitrosonaphthols may exist in two tautomeric forms: nitrosonaphthol and/or naphthoquinone oxime. Saarinen, Korvenranta and Näsäkkälä have studied the crystal structures of some sulfonated 1,2-nitrosonaphthols, having the tautomeric naphthoquinone oxime form (ref.5-9). On the other hand it can be regarded as a metal-nitrosonaphtholato structure in the ligand anions coordinated to copper(II) ion (ref.10-12).

In the present study TG, DTG and DSC were used to investigate thermoanalytical behaviour of sodium 1-nitroso-2-naphthol-4-sulfonate (abbr. L124), sodium 1-nitroso-2-naphthol-7-sulfonate (L127), disodium 1-nitroso-2-naphthol-3,6-disulfonate (nitroso-R-salt) (L123,6), sodium 2-nitroso-1-naphthol-4-sulfonate (nitroso-NW-salt) (L214), and sodium 2-nitroso-1-naphthol-5-sulfonate (L215). The numbering of naphthalene skeleton is shown in Fig.1. Pyrolysis MS technique was used to identify evolved gases and FTIR to characterize residuals.

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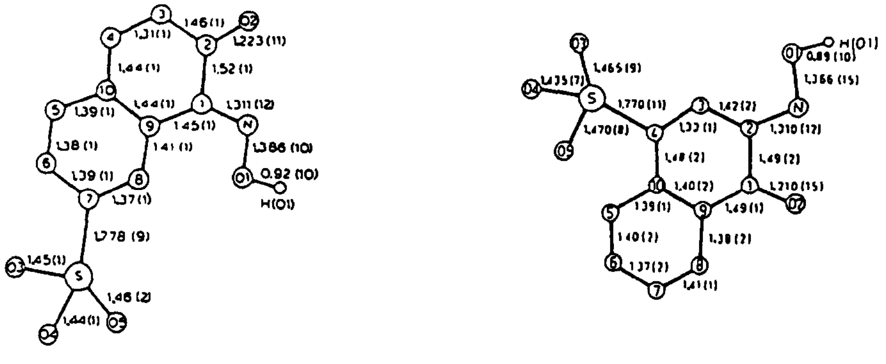

Fig.1. Schematic representation of the anion of the *anti*-configuration of 1,2-naphthoquinone-1-oxime-7-sulfonate($\rightleftharpoons$1-nitroso-2-naphthol-7-sulfonate) and 1,2-naphtoquinone 2-oxime-4-sulfonate ($\rightleftharpoons$2-nitroso-1-naphthol-4-sulfonate) showing atomic numbering and bond lenghts (ref.9,14).

EXPERIMENTAL

L123,6 and L214 were commercial products from Merck and purified by recrystallization three times from water. The preparation and purification of the other compounds have been described elsewhere (ref.14). The samples were kept in a desiccator containing silicagel or saturated K_2CO_3 (RH 44%). Carbon, nitrogen and hydrogen were analysed (first dried at 120 °C) by CARLO ERBA, ELEMENTAL ANALYZER 1106. In addition, potentiometric titrations were carried out for the verification of acid-base properties of these compounds.

TG and DSC were used in the measurement in the following hardware configurations (PE=Perkin-Elmer, HP=Hewlett-Packard):

TG: PE TGS-2, System 7/4, PE TADS MODEL 3700,
HP PLOTTER 7475A, PE TADS.TGS(software)
DSC: PE DSC-7, TAC 7/PC, EPSON PC AX 2,
HP PLOTTER 7475A, PE DSC7(software)

The TG curves were run from 1-18 mg of the samples in Pt-pans and in dynamic air or nitrogen with a flow rate of 40-60 cm^3 min^{-1}. The heating rate was 5 °C min^{-1} in the temperature range 20-950 °C. DSC were carried out at a heating rate of 5 °C min^{-1} to 550 °C using aluminum pans with holes, in dynamic air or nitrogen atmosphere.

Pyrolysis mass spectrometry was used to determine the composition of evolved gases by heating the solid sample in a quartz capillary tube in the direct inlet on a JEOL JMS 300D mass spectrometer equipped with JMA 2000H data system. The spectra were measured under electron ionization typical experimental conditions being: sample heating rate 5 °C min^{-1}, electron energy 70 eV and ionization current 300 μA.

The IR spectra (4000-600 cm^{-1}) were recorded with a NICOLET 20SXC FTIR spectrometer using KBr pellet technique.

RESULTS AND DISCUSSION

In general, nitrosonapthtol names are used for the compounds examined. In the following we prefer, however, names of the naphthoquinone oxime tautomeric forms because according to both solid state IR and ^{13}C NMR as well as liquid phase ^{13}C NMR results all these compounds exist mainly in the naphthoquinone oxime tautomeric form (Ref.1,13).

Inspection of the TG curves (Fig.2) in the dynamic air atmosphere reveals three main stages in the decomposition: an endothermic dehydration below 180 °C (Table 1), a split-off of nitrogen monoxide between 240-370 °C except compound (L214) which lost SO_2 and CO in this stage, and the third stage was the release of SO_2, CO, CO_2 and other minor decomposition products. Some water was released in the wide decomposition temperature range.

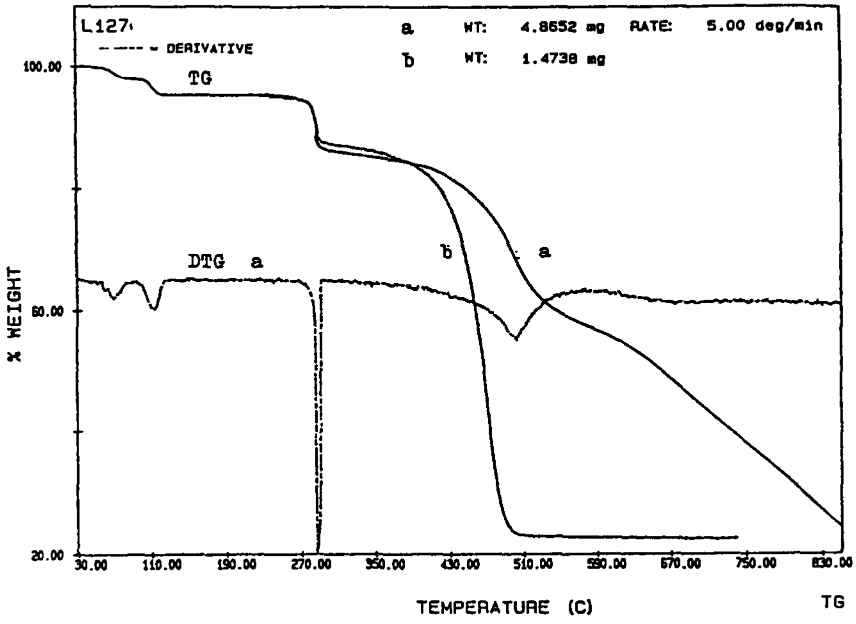

Fig.2. TG curves of sodium 1-nitroso-2-naphthol-7-sulfonate monohydrate in a dynamic nitrogen (a) and air (b) atmosphere.

L127 and L123,6 contained nearly one mole of water. L127 released water in two stages at 20-80 °C and 85-130 °C. In the first step 0.1-0.5 moles of water was lost depending on the preparation and conservation (0.5 mol in RH 44%). The DSC-curve gave 74 kJ mol^{-1} for the heat of dehydration of the second step. The dehydration of the compound L123,6 took place between 125-180°C. The corresponding heat of dehydration was 71 kJ mol^{-1}. The other compounds contained water within the 0 to 1.1 wt% range depending on the relative humidity of the surrounding.

Saarinen et al. have determined the crystal structures of potassium 1,2-naphthoquinone-1-oxime-7-sulfonate monohydrate (ref.10), potassium sodium bis(1,2-naphthoquinone-2-oxime-5-sulfonate) trihydrate (ref.8), disodium bis(1,2-naphthoquinone-2-oxime-5-sulfonate) trihydrate (ref.5) and potassium 1,2-naphthoquinone-2-oxime-8-sulfonate dihydrate (ref.7). According to them the cations are interconnected through a bridging water molecule. All the water hydrogen atoms contribute to hydrogen bonds to a neighbouring sulphonate oxygen and to one of free water oxygen which in turn can take part a hydrogen bond to oxime oxygen. The differences in the water contents between their and our studies are due to different conditions of preparing and conservation. Their products were crystals and measured after drying in air while ours were powders and conservated at least for four weeks before measuring.

TABLE1

The amount of water from TG curves in the studied compounds conservated in a desiccator containing saturated K_2CO_3 (RH 44 %) and silicagel.

Compound	Colour	$\log K^{o*}$	Temperature range (°C)	RH 44% Weight loss(%)	Silicagel Weight loss(%)
L124	orange	7.56	20-150	0.4	0.1
L127	yellow	7.74	20- 90	2.9	0.3
			90-130	3.1	3.1
L123,6	yellow	7.51	120-180	4.5	4.5
L214	yellow	6.63	20-160	0.1	0.1
L215	yellow	7.32	20-150	1.1	0.9

* Ref.15.

Although NO (or NOH) splitted off in the second stage, except in compound L214, the decompositions differed markedly from each other (Table 2). The weight loss of L124 depended on the heating rate and the mass of the sample. The DTG curve showed in this stage a poorly resolved double peak with a small sample both in air and nitrogen. Obviously, besides the loss of NO (NOH), also CNO (CNOH) splitted off partly. The calculated weight losses of these groups are 10.86 %

(11.22 %) and 15.21 % (15.57 %), respectively. Pyrolysis mass spectrometry verified this deduction. The increasing sample mass lowers the final temperature of this process. This is understandable because the corresponding DSC peak was exothermic both in air and nitrogen (Fig.3).

The decomposition of L127 differed from L124 in the way that now the mass loss varied 7.3-9.0 wt% and the DTG curve showed always a single peak. L127 expanded enormously in this stage which was not observed with the other compounds studied. Obviously, part of NO remained in the system or some NO bonds were broken with the formation of water. The mass loss was less than calculated (10.23 % with 1 mole H_2O) and the finding of NO at higher temperatures in the mass spectra gave support to this deduction. This process in DSC is followed immediately by an endothermic process in nitrogen and an exothermic process in air.

At the temperature range 300-360 °C L123,6 lost NOH 8.2-9.1 wt% which is more than the calculated 7.86 wt%. The MS studies showed that NO and H_2O were formed in this area. In DTG it gave rise to a single peak. DSC gave an exothermic peak which was followed by a partly simultaneous decomposition, exothermic in air and

TABLE 2

The TG and DSC data of the decomposition in the second stage in air (A) and nitrogen (N). The TG measurements were done with at least two different sample weights for each compound.

	TG			DSC			
Compound	Sample weight(mg)	Temperature range(°C)	Weight loss(%)	Sample weight(mg)	Temperature range(°C)	Peak temp.(°C)	Heat (J/g)
L124 A	1.92	250-318	12.7	1.83	260-297	291	
	18.01	245-286	14.9		297-320	305	-449*
N	11.78	244-309	13.4	1.94	251-297	286	-253
	18.65	244-289	13.8		297-327	300	111
L127 A	1.47	267-303	7.3	1.44	275-304	293	-404
	4.27	257-292	8.1				
N	2.13	263-300	7.6	1.73	267-300	283	-379
	4.87	266-292	9.0		300- ?	?	endo
L123,6A	2.56	320-365	8.2	1.45	329-359	352	-130
	15.63	300-360	8.9				
N	2.74	299-353	9.1	1.42	315-345	334	-34
	14.54	299-360	9.0		345-354	348	30
L214 A	2.86	254-355	22.0	2.35	303- -	333	
	12.38	253-355	21.6		- -360	345	-466
N	1.82	254-362	18.6	1.50	291-335	326	-2
	10.65	254-366	18.6		335-370	348	1
L215 A	2.57	277-356	8.1	1.30	323-361	348	-264
	9.26	277-354	8.1				
N	0.76	277-351	8.5	2.16	278-335	304	-6
	11.70	272-354	8.6		335-366	350	46

* 260-320 °C

endothermic in nitrogen.

According to the mass spectrum L214 evolved H_2O, SO_2 and CO (CO_2) at the temperature range 250-370 °C (FIG.4). The weight losses from the TG curve are 18% in nitrogen and 22% in air. The calculated amounts of 1/2 SO_2 and CO are 11.63% and 10.17%, respectively. On the basis of TG- and DTG-curves there existed three processes . At first a slight, about 1-2 %, mass-loss of water was observed and SO_2 and CO were released. TG curves in air and nitrogen were the same down to 82% sample mass residuals. After that, the sample weght decreased down faster in air than in nitrogen to 78 wt%. The burning of CO to CO_2 was the reason for this difference. There were no traces of NO in the mass spectra in this stage. The depedence of the decomposition on the relatively high dissociation constant was not studied.

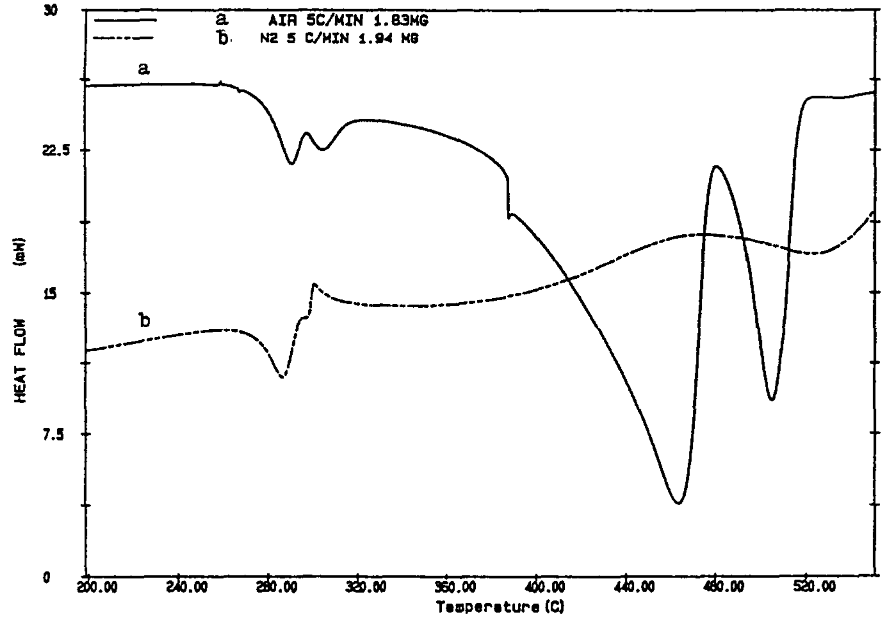

Fig.3. The DSC curves of L124 in air (a) and nitrogen (b).

L215 released NO (NOH) and water at the temperature range 260-360 °C. The calculated amount of NO is 10.79 %, which is more than the observed amount. The mass spectra showed that part of the NO was splitting off in the third stage.This process was clearly exothermic in air but in nitrogen only slightly exothermic. In comparison to the other cases the differencies were perhaps due to the immediately following endothermic steps, which partly covered the preceding

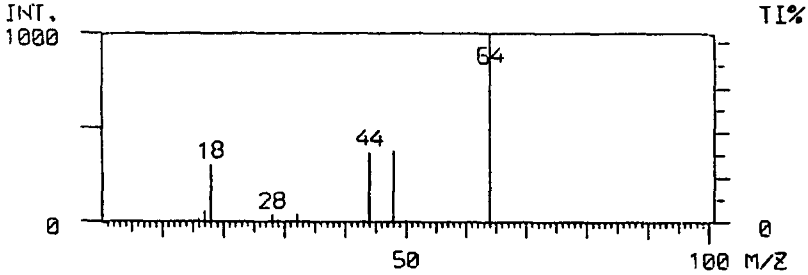

Fig.4. The 70 eV EI mas spectrum of the mixture of evolved gases from L214 at 325 °C.

process.

The differencies of decomposition in the second stage were connected with the differencies in structures and, especially, with hydrogen bonds. According to Saarinen et al. (ref.9) the NOH group is in the *anti*-configuration with respect to the CO group in L127, L214 and L215 in crystals. The distances calculated by us from the reported fractional atomic coordinates (ref.8,9,13) are: L127, O1...C8 = 2.8 Å; L214, O1...C3 = 3.45 Å and L215, O1...C3 = 2.63 Å or 2.72 Å. The *anti*-configuration has ben confirmed earlier for L123,6 (Ref.13) and now for L124 by ^1H NMR which shows a hydrogen bond between O(1)...H(C8). Obviously, the strong hydrogen bond weakens the C=N bond in oxime and makes it easy breakable at elevated temperatures. Some water was present in the mixture of evolved gases in this stage. If the N-O bond of the CNO group was broken, H_2O was formed with the assistance of hydrogen bond. The relatively long C1-C2 bond in these compounds gives possibility for breakage of the naphthalene ring system in the second stage and for the residual to reorganize in an exothermic process. The splitting-off of NO (NOH) or CO was endothermic. By comparing DT and DSC curves in nitrogen one can observe that at the beginning of this stage exothermic reorganization was the main process and at the end of the stage it was the endothermic cleavage of NO or CO .

The third stage varies remarkably depending on the heating atmosphere . In air the decomposition took place below 530 °C. The DTG curves showed in this stage three possible decomposition steps. There were also three exothermic peaks in the DSC curves. The residuals after the second stage released SO_2, CO, different kind of C_xH_y products and C, which burned in secundary reactions to CO, CO_2 and H_2O. The third step was mainly burning of carbon, which in large samples were retained as 2-3 atoms per molecule. The decompositions were partly simultaneous and the exothermic heat of the steps from DSC curves cannot be determined

TABLE 3

TG, DTG and DSC data of the decomposition in the third stage in air atmosphere.

	TG				DTG	DSC		
Compound	Weight (mg)	Temperature range (°C)	Weight loss(%)	Residual obs.calc.	Peaks (°C)	Weight (mg)	Peaks (°C)	T_f (°C)
L124	18.02	288-495	58.0	26.2 25.7	404	1.83	389,463,505	522
L127	1.47	306-522	63.1	25.7 25.3	480	1.44	480,498,531	541
L1236	15.63	360-530	50.2	36.2 36.0	438	1.45	473,499,511	522
L214	12.38	370-527	48.9	25.9 25.8	449	2.35	383,485,524	541
L215	9.27	354-515	64.5	25.9 25.9	445	1.30	472,501,513	533

exactly. A small sample decomposed at a somewhat higher temperature than a great sample.Obviously, exothermic reaction heat was the reason for these differencies. In all the cases the final product was sodium sulfate. The decomposition of L214 differed most from that of the other compounds. Now NO (NOH) was released instead of SO_2 and CO. Table 3 shows weight losses (%), observed and calculated residuals (Na_2SO_4) and final decomposition temperatures in TG , and the temperatures of peaks in DTG and DSC.

In nitrogen the decomposition differed considerably from that in air in this stage. All the peaks of the DSC were endothermic and there were several partly simultaneous decompositions. The main parts of the residuals were sodium sulfide and carbon. It was possible to find five broad DTG peaks after the second stage to 950 °C. The TG curves showed that the mixture of carbon and sodium sulfide decomposed further or vaporized over 950 °C.

IR SPECTRA

Some selected IR spectral bands (ref.16-18) of ligands under investigation are given in Table 4 and the spectrum of L124 is given as an example of these spectra (fig.5). The spectra of residuals were also recorded after the heating in 200 °C and after the second stage: L124; 314, L127; 298, L123,6; 360, L214; 362 and L215; 357 °C.

The heating to 200 °C changed the spectra in the 3500-3400 cm^{-1} region due to loss of water. After the second stage C-C stretching, skeletal distortion and C-H stretching and bending changed remarkably, showing the decomposition of the naphthalene skeleton in the second stage. In the same time the yellow or orange colour of the ligands changed to black.

The oxime bands, stretching C=N at 1665-1680cm^{-1},the bending OH at 1420-1400 cm^{-1} and the stretching N-O at 910-964 cm^{-1} had disappeared in L124, L127 and L215, and they were weak in L214 and L123,6 after the second stage. The carbonyl C=O bands at 1647-1648 cm^{-1} were retained at strong or medium intensities.

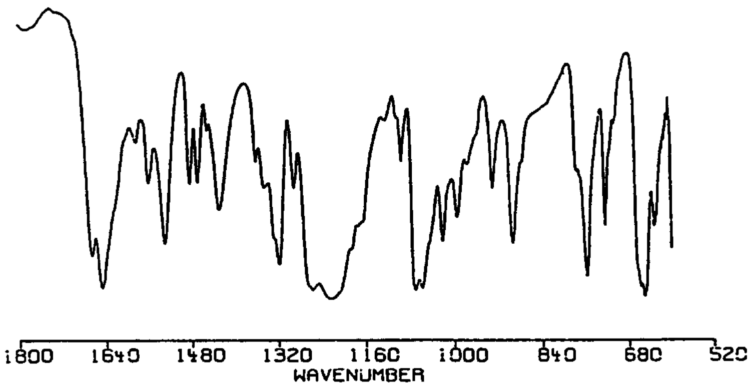

Fig.5. The characteristic part of the IR spectrum of L124.

TABLE 4

Selected bands in the IR spectra of sodium 1,2-naphthoquinone oxime sulfonates.

L124	L127	L123,6	L214	L215	assignment
1665s	1666s	1665s	1678s	1671	C=N (oxime) stretching
1647s	1648s	1638s	1675s	1664m	C=O stretching
1561m	1571s	1553s	1559m	1581m	C=C stretching
1430s	1444s	1450	1443s	1420s	O-H (oxime) stretching
1361	1388m	1357s	1348s	1384m	C=C stretching
1238s	1252s	1229s	1238m	1240s	
1188bs	1206bs	1200bs	1232bs	1227bs	SO_3^- asymmetrical (S-O) stretching
1165s	1170s	1175s	1206s	1205s	
1095w	1098m	1124m	1111m	1095m	OH deformation
1069s	1068s	1054s	1053s	1045s	SO_3^- symmetrical (C-S) stretching
931m	910m	964s	935s	940s	N-O (oxime) stretching
778s		741s	777s		OH and/or CH
758s	758s	727s	773s	760m	stretching
725s	725m	725m	721m		skeletal distortion
657s	647s	659s	652s	644s	SO_3^- and/or OH
649s	640s	659s	649s	635s	stretching

b, broad; s, strong; m, medium; w, weak

Asymmetric (S-O) stretchings showed three bands at 1170-1252 cm^{-1} which coalese after this decomposition to one broad strong band at the same or somewhat lower frequencies. The symmetric stretching appeared at 1024-1080 cm^{-1} and it was retained in the other cases except for L214. This exception was in agreement with the loss of SO_2 in the second stage. Now the C-S bond was broken and possibly sulfate was formed.

REFERENCES:

1. A.Vainiotalo, *Ann. Acad. Sci. Fenn., Ser. A, II* ,210 (1986) 15.
2. O.Mäkitie and H.Saarinen, *Ann. Acad. Sci.Fenn., Ser. A2,149* (1969) 1.
3. O.Mäkitie, H.Saarinen, L.Lindroos and K.Seppovaara, *Acta Chem. Scand., 24* (1970) 740.
4. S.Motomizu and K.Tôei, *Anal. Chim. Acta, 97* (1978) 335
5. M.Näsäkkälä, H.Saarinen and J.Korvenranta, *Finn. Chem. Lett.* (1977) 42.
6. H.Saarinen, J.Korvenranta and M.Näsäkkälä, *Finn. Chem. Lett.* (1977) 47.
7. J.Korvenranta, H.Saarinen, E.Näsäkkälä and M.Näsäkkälä, *Finn. Chem. Lett.* (1977) 52.
8. M.Näsäkkälä, H.Saarinen, J.Korvenranta and E.Näsäkkälä, *Finn. Chem. Lett.* (1977) 234.
9. H.Saarinen, J.Korvenranta and E.Näsäkkälä, *Acta Chem. Scand. A 31* (1977) 213.
10. H.Saarinen and J.Korvenranta, *Acta Chem. Scand. A 29* (1975) 409.
11. J.Korvenranta and H.Saarinen, *Acta Chem. Scand. A 29* (1975) 861.
12. J.Korvenranta and H.Saarinen, *Finn. Chem. Lett.* (1975) 115.
13. A.Vainiotalo and J.Vepsäläinen, *Magn. Reson. Chem. 24* (1986) 758.
14. J.Korvenranta, H.Saarinen and E.Näsäkkälä, *Finn. Chem. Lett.* (1977) 61.
15. H.Saarinen, *Ann. Acad. Sci. Fenn. Ser. A, II,* 170 (1973).
16. E.L.Lippincott and E.J.O'Reilly.Jr., *J. Chem. Phys., 23* (1955) 283.
17. H.M.M.Sire´n and M.M.Shapi, *Thermochim. Acta, 102* (1986) 239.
18. N.T.Abdel-Ghani, Y.M.Issa and S.A.Abdel-Latif, *Thermochim. Acta, 143* (1989) 37.