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Influence of hydrogen bonding on the thermal behaviour of some amides and thioamides

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Abstract

The thermal behaviour of some oxamides and thiooxamides is studied by TGA and DSC techniques. The effect of the mass, the hydrogen bonding and the molecular structure on the T_{onset} and ΔH values is demonstrated. Special attention has been given on the nature (intermolecular versus intramolecular hydrogen bonds), the strength and the number of hydrogen bonds per molecule.

Keywords: Thermal analysis; Amides; Thioamides; Hydrogen bonds; Vibrational spectra

1. Introduction

Oxamides and thiooxamides form an important group of ligands in coordination chemistry [1], a remarkable characteristic of these ligands is their thermal stability and relatively high sublimation temperature. It is very well known that hydrogen bonding has a profound effect upon a wide variety of physical properties of some substances, for instance, the relatively high boiling points and ΔH_{vap} values in molecules exhibiting strong intermolecular hydrogen bonds. Since the publication of Pimentel and Mc Clellan's book [2], a great number of reviews and books on various aspects of the special role of inter- and intramolecular hydrogen bonding have been published [3–7].

We have studied hydrogen bonding in oxamides and thiooxamides extensively [4,8–12]. Strong intermolecular typical amide–amide hydrogen bonds have been observed for the oxamides. Intramolecular N–H $\cdots$ S associations successfully explain the thermal and chemical stability of dithiooxamides, as well as their dissociation constants [13] and H/D exchange rates for the thioamide function. The conclusions from the thermal measurements are further confirmed by the temperature-dependent solid state vibrational spectra for the insoluble compounds and by solution spectra where possible.

2. Experimental

The synthesis of the compounds under investigation has already been published [4,8–10,13]. Thermal analysis was performed on TA Instruments SDT 2960, TGA 2950 and DSC 2920. All experiments were performed under dry nitrogen atmosphere (50 ml min^{-1}

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for DSC, 100 ml min^{-1} for TGA and SDT) and the heating rate was 5 °C min^{-1}, except when stated otherwise in the text.

The thioamides under investigation are known as very good complexing agents and very soft bases. The zerovalent metals in the DSC cell are very soft bases and directly form complexes with the thioamides, resulting in a deterioration of the cell and considerable change in the cell constants.

TA Instruments recently developed a DSC/TGA upgrade for the SDT, where DSC values can be obtained, without any risk of deterioration of the instrument. All data for the thioamides have been obtained on this new DSC/TGA upgraded instrument. We measured several amides by DSC 2920 and the new DSC/TGA upgrade and adopted the DSC/TGA values to the DSC 2920 data. As the phase transitions for the compounds under investigation are all situated between 100 and 250 °C we restricted our calibration to two metals: indium (T_f = 156.60 °C, cell constant 1.0385) and tin (T_f = 231.93 °C, cell constant 1.0299). We used the average cell constant 1.034 for all measurements.

The temperature calibration was performed by measuring the melting temperature of the above mentioned metals. Each ΔH value given is the average of three measurements, for which the spread was always between 2 and 4% of the mean value. This is less accurate than what could have been expected form careful work with high class instrumentation, but we thought this was acceptable as we compare the results in a series of compounds with only the number and strength of the intermolecular hydrogen bonds as a variable component.

For all components $\Delta H^*_{total} = \Delta H_{fus} + \Delta H_{vap} + \Delta H_{decomp}$ or ΔH_{decomp}. The residue at the end temperature is for all compounds between 0 and 3%, indicating a small but comparable contribution in these ΔH^* values for most compounds.

For some products we could calculate these ΔH^*_{total} values without decomposition (at very low heating rates) and with increasing decomposition to about 3%, by increasing heating rates (see below). The differences in the obtained ΔH^* values are practically all within the acceptable error for the instrument.

The infrared spectra were recorded on a Bruker IFS 113v FT-spectrometer. The low temperature measurements were made with a self-designed liquid cooled cryostat, consisting of a copper sample holder with a small container, which can be filled with liquid nitrogen [4].

The activation energy for the thermal reactions was calculated from isothermal, non-isothermal TGA data and by applying the recently introduced modulated TGA method (TA Instruments) [14].

3. Results and discussion

3.1. The total enthalpies (ΔH_{total})

The ΔH^*_{total} values given in this paper all refer to the energy involved in the change from the solid state to the gas phase. This ΔH^*_{total} can also be the sum of $\Delta H_{melt} + \Delta H_{vap}$ and eventually some ΔH_{decomp}, a typical example is given for *N*,*N*′-dipropyloxamide. Fig. 1 gives the DSC curves at different heating rates (β-values). From this figure we can see that the compound is completely sublimed before the melting point at very low β-values, we further clearly observe the melting and evaporation of the compound at higher β-values.

From Table 1 we see an increased ΔH value at high heating rates but also a greater rest-mass due the partial decomposition of the compound by formation of nitriles. This increased ΔH^*_{total} at higher β-values must consequently be due to the greater percentage of decomposition at higher temperatures. All ΔH values given in this paper result from measurements with β-values ranging from 0.25 to 2 °C min^{-1}.

The enthalpy of sublimation is the energy, needed to overcome the intermolecular forces keeping the molecules together in the solid state. By decomposition of the compound, however, we need to break the

Table 1
DSC and TGA results from *N*,*N*′-dipropyloxamide at different heating rates

β (°C min^{-1})	ΔH^*_{total} (kJ/mol)	$T_{(dm/dT)max}$ (°C)	Residue (%)
0.25	91	139	3.8
0.5	92	148	4.6
1	92	146	6.8
2	91	165	8.4
5	92	170	8.2
10	92	192	13.7
15	95	200	15.3
20	98	203	18.8

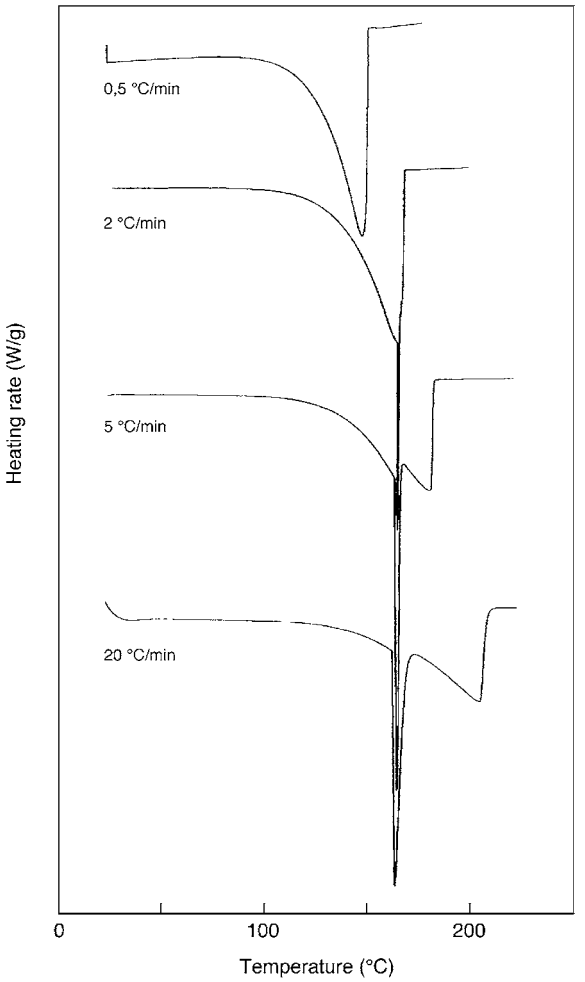


Fig. 1. Solid → gas phase transition for *N*,*N*′-dipropyloxamide at different heating rates.

primary chemical bonds within the molecule, generally resulting in a greater ΔH value at higher β-values as shown for the *N*,*N*′-dipropyloxamide molecule.

3.2. The influence of the molecular mass on the ΔH_{total}

Tetrasubstituted oxamides and thiooxamides are non-planar molecules, due to the steric hindrance between the alkyl group and the oxygen or sulphur of the adjacent amide or thioamide group. The two functional groups form a dihedral angle of about 90° [15–18] and exhibit no hydrogen bonding.

It is very well known that in a series of comparable compounds (comparable lattice energy) the ΔH increases with increasing molecular mass. This is clearly demonstrated in Table 2 for some tetrasubstituted compounds exhibiting similar crystal structures.

In the series **I**, **IV** and **V** (see Table 2) we change the mass of the molecule by substituting the methyl groups by ethyl and propyl, respectively. For series **I**, **II** and **III** we calculated comparable ΔH_{fus} values indicating comparable lattice energies and we clearly see that the T_{vap} and ΔH_{vap} values nicely obey this rule of increasing mass.

3.3. Influence of the intermolecular hydrogen bonding on ΔH^*_{total}

We have already published on the nature of the hydrogen bonding in oxamides and thiooxamides by infrared spectroscopy [4,8,11] and concluded that oxamides exhibit mainly intermolecular hydrogen bonds, while pure strong intramolecular hydrogen bonding has been observed for the dithiooxamides.

Table 2
T_{max} and ΔH values for some tetrasubstituted oxamides and thiooxamides

Product	$T_{(dm/dT)max}$ (°C)	$T_{onset_{fus}}$ (°C)	ΔH_{fus} (kJ/mol)	$T_{onset_{vap}}$ (°C)	ΔH_{vap} (kJ/mol)	ΔH_{total}[a] (kJ/mol)
$(CH_3)_2NCOCON(CH_3)_2$ **(I)**	183	78	18	187	52.5	70.5
$(CH_3)_2NCOCSN(CH_3)_2$ **(II)**	231	78	17	235	59	75
$(CH_3)_2NCSCSN(CH_3)_2$ **(III)**	256	137	21	260	60.5	82
$(C_2H_5)_2NCOCON(C_2H_5)_2$ **(IV)**	188	37	17	191	63	80
$(C_3H_7)_2NCOCON(C_3H_7)_2$ **(V)**	207	44	21	216	67	88

[a] $\Delta H_{total} = \Delta H_{fus} + \Delta H_{vap} + \Delta H_{decomp}$.

Table 3
The influence of the hydrogen bonding on the ΔH_{total} values

	ΔH_{total} (kJ/mol)	Number of internal H bonds
Oxamides		
$H_2NCOCONH_2$ (**I**)	109	4
$CH_3HNCOCONH_2$ (**II**)	89	3
$CH_3HNCOCONHCH_3$ (**III**)	83	2
$(CH_3)_2NCOCON(CH_3)_2$ (**IV**)	70	0
Monothiooxamides		
$H_2NCOCSNH_2$ (**V**)	Decomposed	4
$CH_3NCOCSNHCH_3$ (**VI**)	82	2
$(CH_3)_2NCOCSNH(CH_3)_2$ (**VII**)	77	0
Dithiooxamides		
$H_2NCSCSNH_2$ (**VIII**)	105 [20]	2
$CH_3HNCSCSNHCH_3$ (**IX**)	79	0
$(CH_3)_2NCSCSN(CH_3)_2$ (**X**)	85	0
Oxamic acids		
$H_2NCOCOOH$ (**XI**)	119 [20]	3
$CH_3HNCOCOOH$ (**XII**)	94.3	2
$(CH_3)_2NCOCOOH$ (**XIII**)	72.2	1

The planarity of the *N*-monosubstituted and *N*,*N*′-disubstituted compounds in the *S-trans* form and the non-planarity of the *N*-disubstituted compounds has also been confirmed by other techniques [16–18].

In Table 3 we compare the ΔH-values for some compounds exhibiting a different number of intermolecular hydrogen bonds. The TGA and DSC curves are for dithiooxamide (compound **VIII** in Table 3) given in Fig. 2. Dithiooxamide sublimes and starts to decompose at higher temperatures by the formation of H_2S and nitriles (νC≡N at 2224 cm^{-1}) even at heating rates of 0.25 °C min^{-1} with rest mass of about 16%. The ΔH for this compound has been published from Knudsen effusion measurements [19].

Monothiooxamide (compound **V**) also decomposes at higher temperatures as can be observed from the TGA–DSC curves given in Fig. 3. The isothermal decomposition of this compound at 125 °C is given in Fig. 4 and from the infrared spectrum of the rest compound (≈27%) we clearly observed the formation of oxamide (compound **I**). This let us conclude that the most important fragmentation process is the cleavage of the CC bond and the rearrangement of the two primary amide radicals to form oxamide. This CC cleavage for oxamide-like molecules has already been noticed in the study of the mass-spectra of oxamides [21,22].

The infrared spectra of pure oxamide (A) and the decomposition rest of monothiooxamide (B) are given in Fig. 5. All the fundamental vibrations of oxamide are present in the decomposition product, which means that the decomposition of monothiooxamide mainly results in the formation of oxamide.

The ΔH obtained for oxamide (compound **I**) is in good agreement with the literature data 109 kJ/mol [20,21] and 116 kJ/mol [19]. The influence of the hydrogen bonding on some ΔH values is given in Fig. 6. By comparing the oxamides (**I**–**IV**) we clearly see that the ΔH decreases at higher molecular masses and increases with increasing number of intermolecular hydrogen bonds, so the intermolecular hydrogen bonding is predominant in this series.

In the series of the dithiooxamides (**VIII**–**X**), we calculated the highest ΔH for dithiooxamide, exhibiting two intermolecular hydrogen bonds. The other dithiooxamides exhibit no intermolecular hydrogen bonds (see also Fig. 7) and we observe then the higher ΔH value for the compound exhibiting the highest mass.

Concerning the *N*,*N*′-disubstituted derivatives (**III**, **VI** and **IX**) we measured comparable ΔH values for increasing molecular masses. These comparable ΔH values can be explained by the number of intermolecular hydrogen bonds and their relative strengths.

The difference in the νNH modes in the infrared spectra of concentrated and diluted solutions provide a direct indication of the strength of the intermolecular hydrogen bonding ($\Delta\nu = \nu NH_{dil.solu.} - \nu NH_{conc.solu.}$).

Compound **III** exhibits two strong intermolecular hydrogen bonds ($\Delta\nu \approx 100\,cm^{-1}$), where $\Delta\nu = 0\,cm^{-1}$ for *N*,*N*′-disubstituted dithiooxamide (**IX**), as this molecule only exhibits intramolecular hydrogen bonds. In the *N*,*N*′-disubstituted monothiooxamide (**VI**) both the amide and the thioamide hydrogen atoms exhibit bifurcated hydrogen bonded systems, as the amide hydrogen atom shows more intramolecular character and the thioamide hydrogen more intermolecular character compared with the oxamide (**III**) and the dithiooxamide (**IX**), respectively. This monothiooxamide derivative (**VI**) consequently exhibits two intermolecular hydrogen bonds, but considerably weaker compared with the oxamide as the

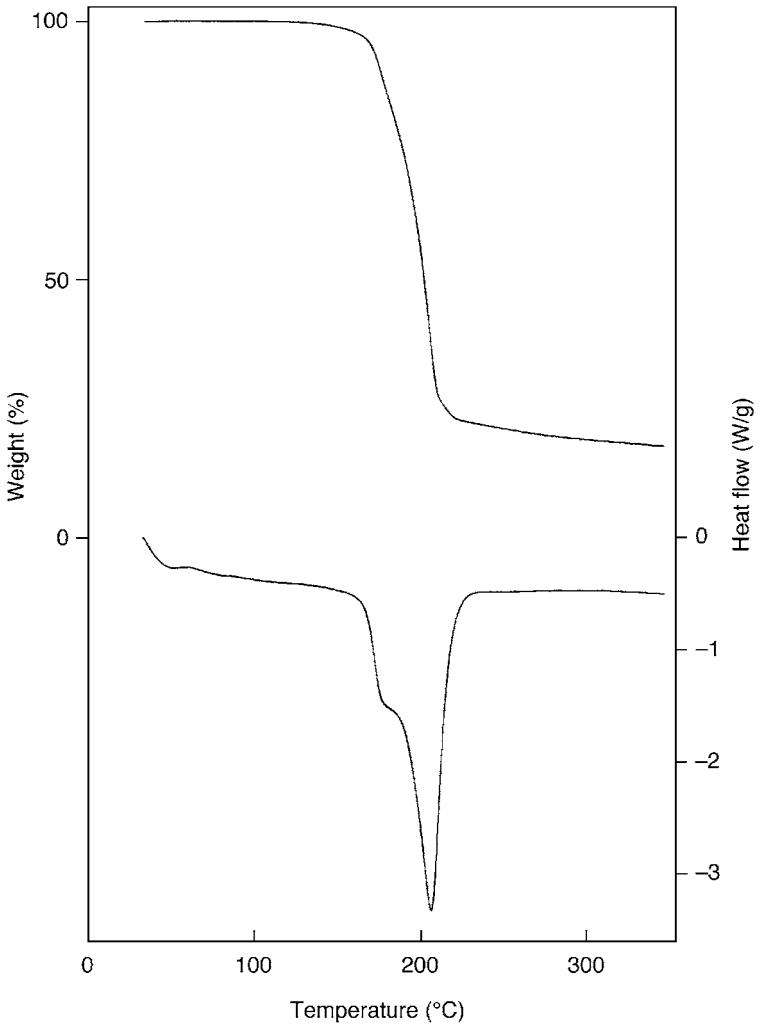


Fig. 2. TGA and DSC for dithiooxamide.

average $\Delta\nu$ is about 50% of the shift observed for the oxamide [23].

The importance of the number of intermolecular bonds is also clear from the series of oxamic acids (**XI**, **XII** and **XIII**) also given in Table 3. The oxamides (**I**, **II** and **III**) and the oxamic acids (**XI**, **XII** and **XIII**) exhibit comparable masses but the ΔH values are all greater for the oxamic acid compounds. This must be due to the difference in the lattice energy and the special strong character of the hydrogen bonding in carboxylic acids [24–26].

3.4. The hydroxy and aminoalkyl oxamides

We have already fully discussed the vibrational spectra and the hydrogen bonding in the hydroxyalkyl oxamides [22] and in oxalyldihydrazide (the NH_2 *N*,*N*′-disubstituted oxamide [27]). Fig. 7 summarises the geometry and data for some hydroxysubstituted oxamides, the oxalyldihydrazide and alkyl oxamides with comparable masses.

From the data also given in this figure we can see that the ΔH_{total} for hydroxy oxamides increases

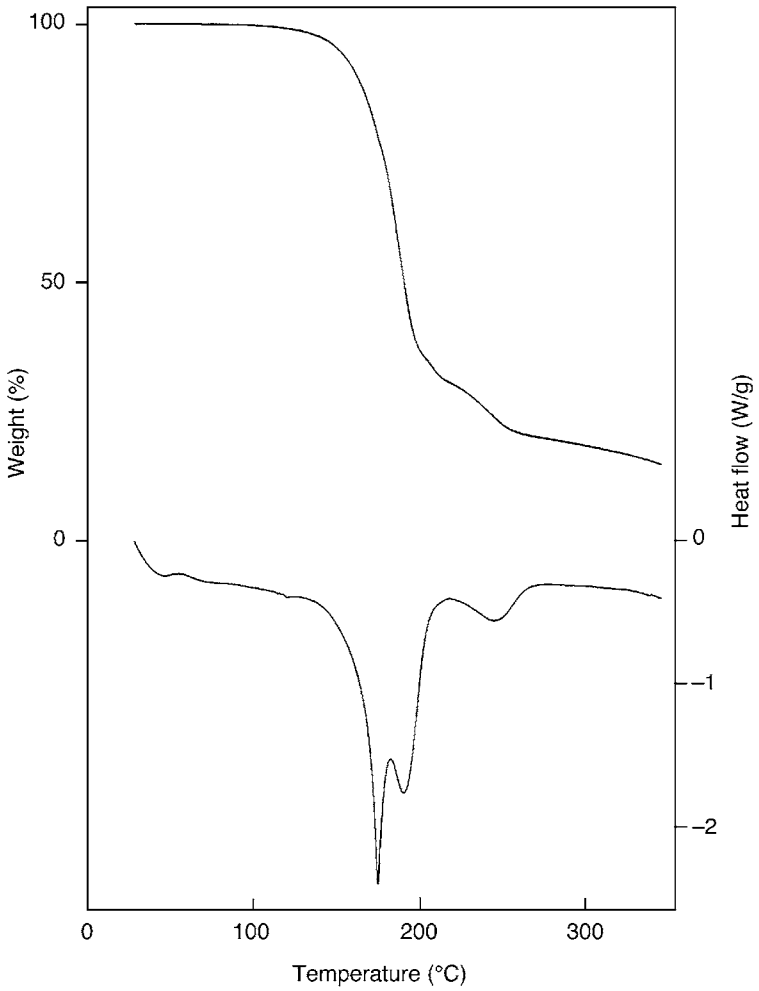


Fig. 3. TGA and DSC for monothiooxamide.

according to increasing molecular mass and that the ΔH value obtained is considerably greater than the value obtained for the alkylsubstituents with comparable masses. This is due to the different number of intermolecular hydrogen bonds as can be observed from Fig. 7.

Oxalyldihydrazide exhibits a molecular mass (118) comparable with the *N*,*N*′-dimethyloxamide (116), but exhibits six intermolecular hydrogen bonds compared with two for the methyl derivative. This compound decomposes at a very high temperature ($(\mathrm{d}m/\mathrm{d}T)_{\max} \approx 250\,^{\circ}\mathrm{C}$) compared with the $(\mathrm{d}m/\mathrm{d}T)_{\max} = 180\,^{\circ}\mathrm{C}$ for the sublimation of the methyl derivative.

3.5. Influence of the molecular structure on the strength and nature of the hydrogen bonding

The structures of *N*,*N*′-disubstituted oxamides were investigated using X-ray diffraction supported by calculations at the B3LYP/6–31++6** level [28], the structures for the different compounds all show a similar pattern in which hydrophilic layers (the peptide functional group) alternate with hydrophobic layers (the alkyl groups). Within these hydrophilic layers, neighbouring molecules are linked together by H bonds as given in Fig. 8.

The structures exhibit bifurcated N–H···O hydrogen bonds, in which weak intramolecular associations

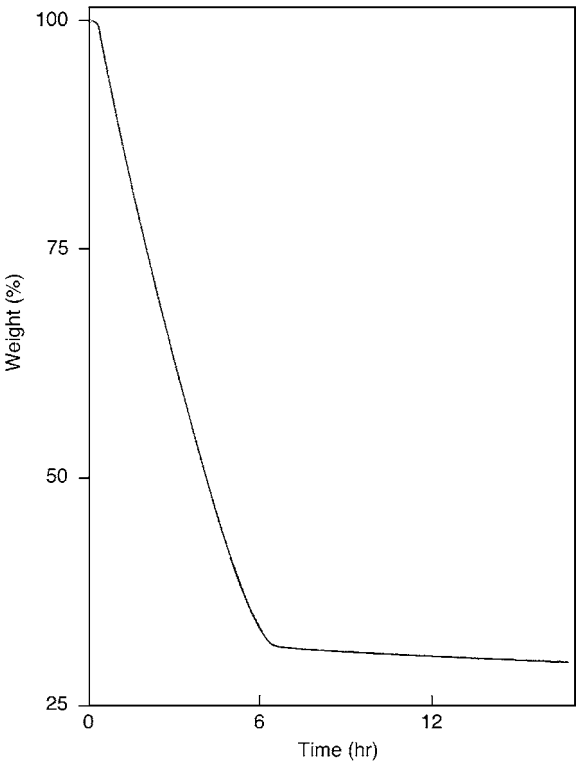


Fig. 4. Isothermal decomposition for monothiooxamide at 125 °C.

are combined with intramolecular hydrogen bonds. The weight of the intramolecular component strongly depends on the valence angle C–N–H (α in Fig. 8) and the NCO angle.

The contribution of the intramolecular character can also be derived from the difference in the νNH frequencies between the νNH of $CH_3CONHCH_3$ in dil. CH_2Cl_2 and those of the oxamides. This difference in given in Table 4 as the $\Delta\nu$ value. From these data we can see that the intramolecular character increases with the number of CH_3 groups on the α-carbon, which is a good measure of steric hindrance. By comparing compounds **II** (CH_3), **III** (C_2H_5), **V** (C_3H_7) and **VII** (C_4H_9) we clearly see the influence of molecular mass on the ΔH values. By comparing compounds **II** (CH_3), **III** (C_2H_5), **IV** (iC_3H_7) and **VI** (tC_4H_9) we observe a stronger intramolecular hydrogen bonding and consequently a weaker intermolecular character resulting in comparable ΔH values in this series, where the increased mass is compensated by the weaker intermolecular character of the hydrogen bonds.

3.6. The N,N′-di(n-hydroxy)phenyl oxamides

Another nice example of the influence of hydrogen bonding is the series of the *N*,*N*′-di(*n*-hydroxy)phenyl oxamides as given in Fig. 9. No solution spectra in CH_2Cl_2 could be obtained for these compounds due to the very low solubility; so for these compounds we obtained the solid state spectra of the νNH and νOH modes at different temperatures as given in Table 5.

Intramolecular distances hardly change, while the intermolecular distances considerably change at different temperatures, resulting in zero shifts for the

Table 4
Steric effects of the alkylsubstituents in *N*,*N*'-disubstituted oxamides (RHNCOCONHR)

	R						
	H (**I**)	CH_3 (**II**)	C_2H_5 (**III**)	iC_3H_7 (**IV**)	C_3H_7 (**V**)	tC_4H_9 (**VI**)	C_4H_9 (**VII**)
$\nu NH_{calc.}$ (cm^{-1})	3349*	3400	3400	3384		3374	
νNH in dil. CH_2Cl_2	**	3412	3399	3387		3377	
$\Delta\nu$ ($\nu_{CH_3CONHCH_3} - \nu_{NHdil.}$)		49	62	74		84	
α (calc.)	118.4	114.9	114.9	114.8		113.5	
∠NCO	126.6	126.4	126.4	126.6		127.2	
M.M.		116	144	172	172	200	200
ΔH_{total}		83	94	98	105	97	123
Number of CH_3 groups on α-carbon		0	1	2		3	

* 3349 = (ν asym NH_2+ν sym NH_2)/2
** Not soluble

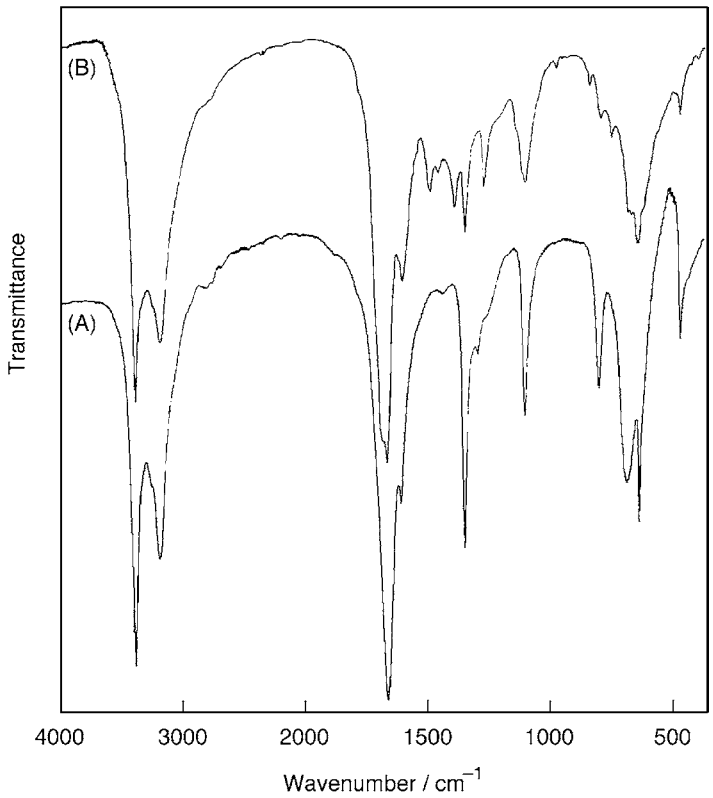


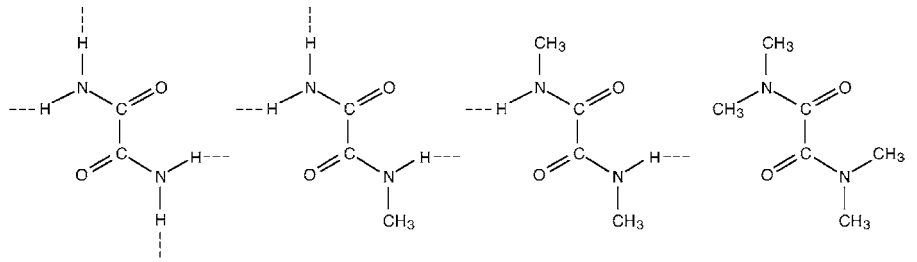
Fig. 5. Infrared spectra of oxamide (A) and the residue from the decomposition of monothiooxamide (B).

intramolecular and a shift to lower frequency (i.e., stronger hydrogen bonding) for the intermolecular hydrogen bonded systems at lower temperatures.

From Table 5 we can see that for the three compounds the O–H $\cdots$ O hydrogen bonding is intermolecular exhibiting comparable $\Delta\nu$(OH) values whilst the N–H $\cdots$ O hydrogen bonding is intramolecular ($\Delta\nu = 0$) for D2HPO due to the stabilisation by the formation of a five-membered ring as given in Fig. 9. This special kind of hydrogen bonding in D2HPO has already been given in an NMR and X-ray study [29,30]. So we can conclude that D2HPO

Table 5
The νNH and νOH frequencies of some hydroxyphenyloxamides

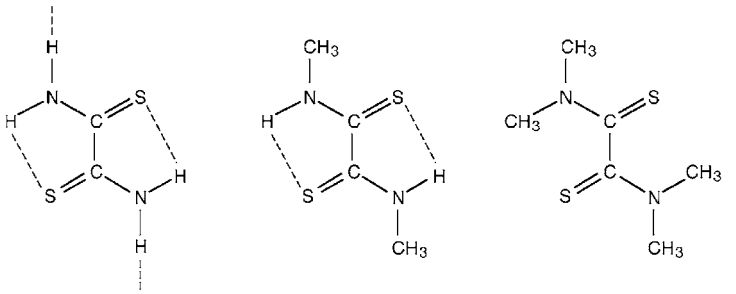
	D2HPO	D3HPO	D4HPO
νNH, 25°C	3356	3307	3295
νNH, −196 °C	3356	3299	3286
$\Delta\nu$ (NH)	0	8	9
νOH, 25 °C	3311	3340	3394
νOH, −196 °C	3291	3320	3372
$\Delta\nu$ (OH)	20	20	22
ΔH (kJ/mol)	205	Decomposed	Decomposed
T(dm/dT)max (°C)	301	335	360
Number of intermolecular H bonds	2	4	4



I (ΔH = 109) II (ΔH = 89) III (ΔH = 83) IV (ΔH = 70)

number of intermol. H–bonds :

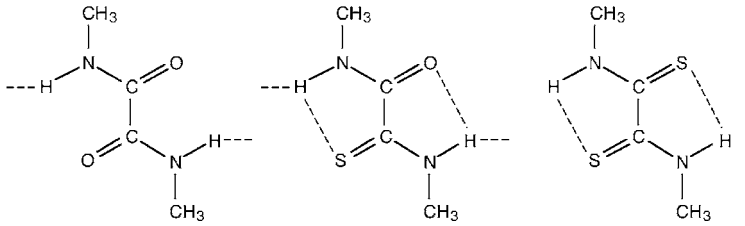
4 3 2 0



VIII (ΔH = 105) IX (ΔH = 79) X (ΔH = 85)

number of intermol. H–bonds :

2 0 0



III (ΔH = 83) VI (ΔH = 82) IX (ΔH = 79)

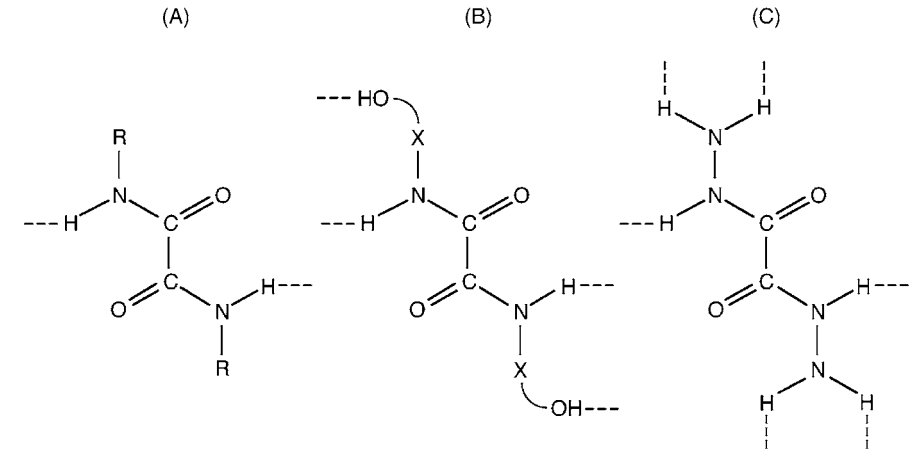
number of intermol. H–bonds :

2 (strong) 2 (weak) 0

$\Delta\nu^* = 100\ cm^{-1}$ $\Delta\nu^* = 77\ cm^{-1}$ (amide) $\Delta\nu^* = 0\ cm^{-1}$

$38\ cm^{-1}$ (thioamide)

Fig. 6. Influence of hydrogen bonding on some ΔH values.



		MM	$\Delta H_{subl.}$			MM	$\Delta H_{subl.}$	
R =	CH_3	116	89	X =	$(CH_2)_2$	176	146	MM = 118
	C_2H_5	144	94		$(CH_2)_3$	204	152	decompos.
	C_3H_7	172	105		$(CH_2)_4$	232	166	
	C_4H_9	200	125		$(CH_2)_5$	260	decomp.	
	C_5H_{11}	228	decomp.					
	C_6H_{13}	256	decomp.					

Fig. 7. Geometry and ΔH values for *N*,*N*′-disubstituted alkyloxamides (A), hydroxyalkyloxamides (B) and aminoalkyloxamides (C).

exhibits two intermolecular hydrogen bonded systems, while D3HPO and D4HPO exhibit four intermolecular hydrogen bonding interactions.

The TGAs at 5 °C min^{-1} for these three compounds are given in Fig. 10. The fact that D2HPO sublimes and D3HPO and D4HPO decompose at higher temperatures is due to the fact that D2HPO only exhibits two intermolecular hydrogen bonds. D3HPO and D4HPO exhibit four intermolecular hydrogen bonds; therefore, more energy is needed to overcome the intermolecular interactions, resulting in higher temperatures and decomposition of the products as indicated by the rest masses of D3HPO (33.7%) and D4HPO (17.5%) at 400 °C. The TGA–DSC curves for D2HPO are given in Fig. 11, the ΔH value has been calculated at 205 kJ/mol, and clearly shows a perfect sublimation process.

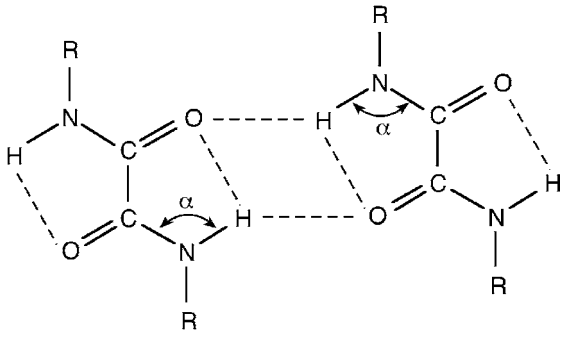


Fig. 8. Molecular arrangement of *N*,*N*′-dialkyloxamides.

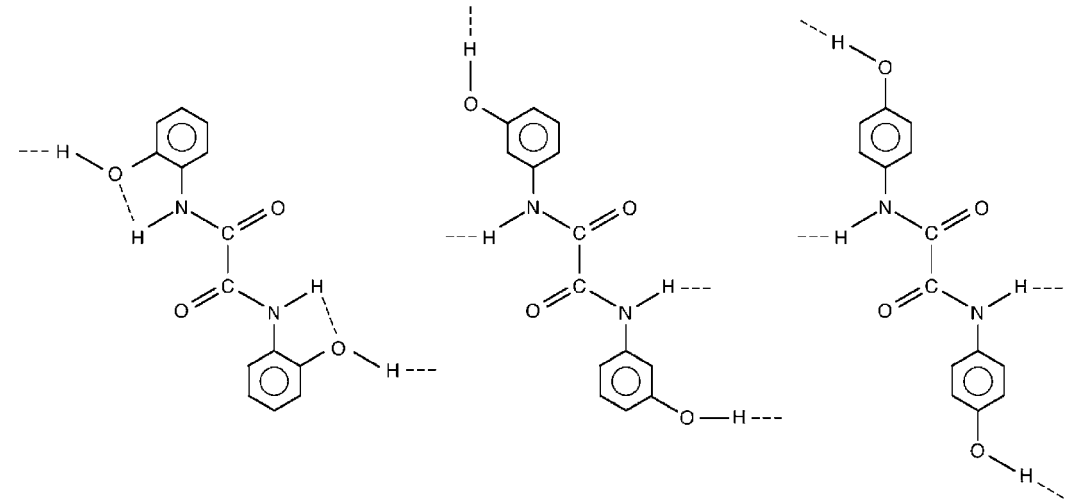


Fig. 9. Molecular geometry of *N*,*N*′-di(*n*-hydroxy)phenyl oxamides.

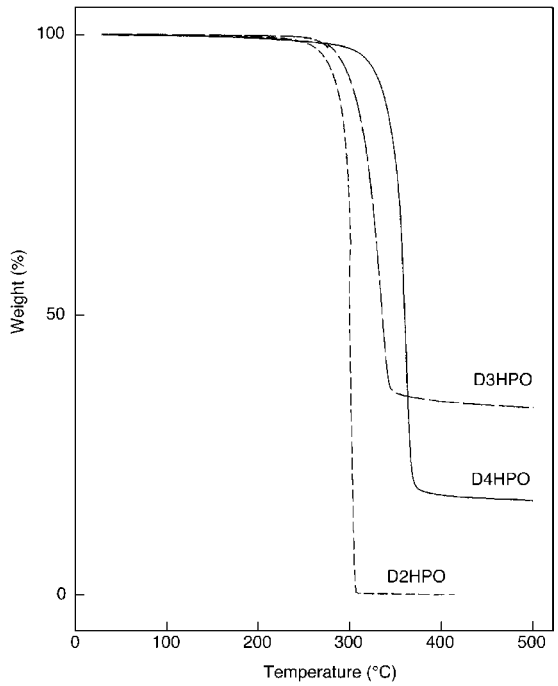


Fig. 10. TGA curves for D2HPO, D3HPO and D4HPO.

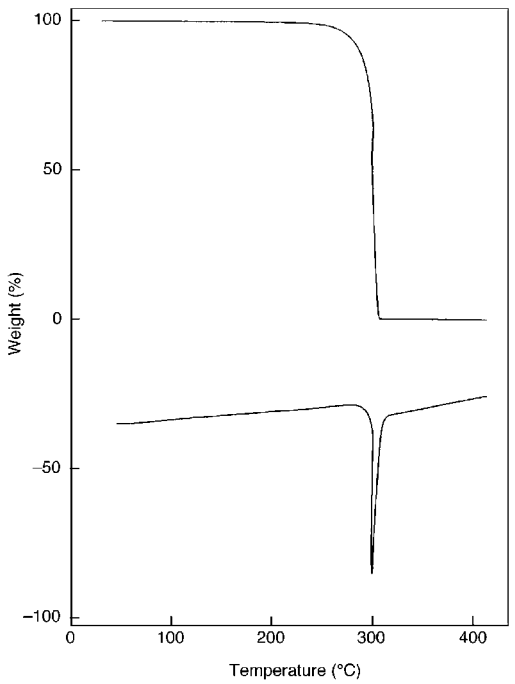


Fig. 11. TGA–DSC curves for D2HPO.

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