

INFLUENCE OF HYDROGEN BONDING ON SOME PHYSICAL CONSTANTS OF OXAMIDES AND THIOOXAMIDES

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(Received January 8, 1996; in revised form June 10, 1996)

Abstract

The influence of intermolecular hydrogen bonding on some physical constants is clearly shown by comparing some thermal data for simple oxamides and thiooxamides.

Keywords: activation energy, amides, enthalpy of sublimation, hydrogen bonding, thioamides

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 temperatures.

Since the publication of Pimentel and McClellan's book [2], a number of reviews on various aspects of hydrogen bonding have discussed the very special role of inter- and intramolecular hydrogen bonding [3-8]. The hydrogen bonding in oxamides and thiooxamides has extensively been studied [6, 9-11] and strong intermolecular amide-amide hydrogen bonds have been observed for the oxamides. Intramolecular (N-H...S) hydrogen bonds explain very well the thermal and chemical stability of dithiooxamides, as well as their dissociation constants and the H/D exchange rates for the thioamide function [12].

The aim of this article is to show the specific role of the intermolecular and intramolecular hydrogen bonding in the determination of some thermodynamic constants.

Experimental

The syntheses of the investigated compounds have already been published elsewhere [9, 10, 12]. Elemental analyses have been performed and confirm the pro-

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posed general formulae in all cases. No impurities have been detected. The products were then subjected to thermogravimetric and DSC measurements using a DuPont 951 Thermobalance and a DuPont DSC 910, monitored by a R90 controller as standard equipment.

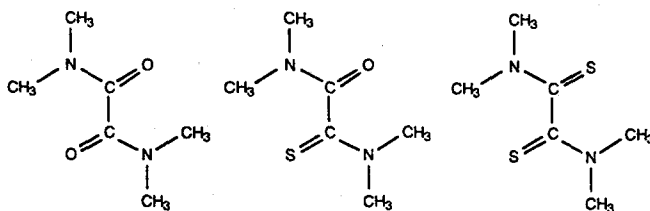
The E_a (activation energy) values have been calculated according to Ozawa [13] from the Arrhenius plot where $\ln\beta$ (β =heating rate, 1, 5, 10, 20°C min⁻¹) is plotted against $1/T$, for a given value of α (α =fraction reacted). The ΔH_{subl} data are calculated from the area under the DSC-curves after calibrating the instrument using the heat of fusion of pure Indium, by cutting out and weighting the peak (average of 3 measurements).

Results and discussion

N,N-disubstituted and N,N,N',N'-tetrasubstituted oxamides and thiooxamides are non-planar molecules, due to sterical hindrance between the methyl groups and the oxygen or sulfur of the adjacent amide or thioamide group, the two functional groups forming a dihedral angle of about 90° [14]. All the other compounds under investigation appear in a *trans*-planar conformation [9, 10, 12]. From the thermal analyses we get information about the stability of these solid products by comparing the sublimation process: we mainly concentrate on the peak temperature in the DTG curve at which the rate of loss of weight is maximum (T_{max}), the activation energy (E_a) and the enthalpy of sublimation (ΔH_{subl}) which give a good indication about the energy needed to overcome the intermolecular forces keeping the molecules together in the solid state [15].

Table 1 T_{max} and E_a values for N,N,N',N'-tetrasubstituted oxamides and thiooxamides

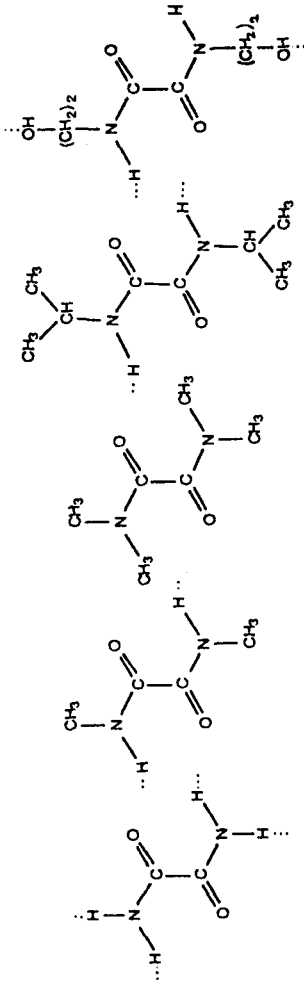
	(A)	(B)	(C)
M.M.	144	160	176
$T_{\text{max}}/^\circ\text{C}$	128	156	173
$E_a/\text{kJ mol}^{-1}$	67	80	90
Number of inter-molecular H-bonds	0	0	0



It is very well known that in a series of comparable compounds the sublimation occurs at higher temperatures and requires more energy with increasing mass. This effect is clearly demonstrated in Table 1 where T_{max} and E_a values for tetramethyl-

Table 2 T_{\max} , E_a and ΔH and values for some oxamides

	(D)	(E)	(A)	(F)	(G)
M.M.	88	116	144	176	176
$T_{\max}/^{\circ}\text{C}$	218	140	128	142	230
$E_a/\text{kJ mol}^{-1}$	111	99	67	111	160
$\Delta H/\text{kJ mol}^{-1}$	95.2	76.8	88	93	182
Number of intermolecular H-bonds	4	2	0	2	4



oxamide (A), tetramethylmonothiooxamide (B) and tetramethyldithiooxamide (C) are scheduled. These compounds all exhibit the same non-planar geometry [14], none of them is involved in any hydrogen bonding and they only differ in their molecular mass. As predicted the highest T_{\max} and E_a are observed for the dithio derivative exhibiting the highest molecular mass.

Oxamide, and N-monosubstituted oxamides (Table 2), appear as planar molecules and all exhibit comparable strong intermolecular amide-amide interaction by forming N-H...O hydrogen bridges [9, 10, 12]. Now two parameters, the molecular mass and the number and strength of the intermolecular associations, have to be considered to explain the observed tendencies in the sublimation processes.

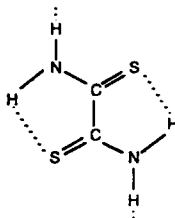
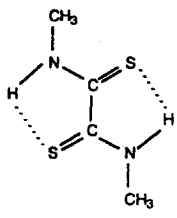
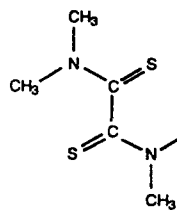
Compounds E and F both exhibit trans-secondary amide functions [14]. They have similar structures and are only different in the mass of the alkyl-substituent. The T_{\max} values are comparable but the isopropyl derivative (F) clearly exhibits higher E_a and ΔH_{subl} values (Table 2), which can be attributed to the higher mass. It seems that on one hand more energy has to be added to activate the individual molecules to a proper transition state (E_a) while on the other hand a larger amount of energy is needed to bring one mole of product from the solid state into the gaseous state (ΔH_{subl}) as the molecular weight of the products increases.

Table 3 T_{\max} , E_a and ΔH values for some N,N-disubstituted oxamides

	(H)	(I)	(A)
M.M.	116	130	144
$T_{\max}/^{\circ}\text{C}$	169	170	128
$E_a/\text{kJ mol}^{-1}$	115	112	67
$\Delta H/\text{kJ mol}^{-1}$	119	114	88
Number of intermolecular H-bonds	2	1	0

Compound G exhibits amide-amide and hydroxy-hydroxy intermolecular hydrogen bonds [8], and can be very well compared to F considering the structure and molecular mass, but differs in the number of hydrogen bonds. The hydroxy-substituted compound G clearly exhibits a higher T_{\max} , E_a and ΔH_{subl} . This can practically purely be ascribed to the strong supplementary hydroxy-hydroxy hydrogen bonds appearing in these molecules. These hydrogen bonds have to be broken and play a major role in the determination of these thermodynamic constants.

Table 4 T_{\max} and E_a values for some dithiooxamides

			
	(J)	(K)	(C)
M.M.	120	148	176
$T_{\max}/^{\circ}\text{C}$	179	130	173
$E_a/\text{kJ mol}^{-1}$	134	100	90
Number of inter-molecular H-bonds	2	0	0

By comparing D, E and A, in which both parameters (i.e. mass and number of intermolecular H-bonds) are varied, it becomes clear that the number of intermolecular associations is the dominating factor in the determination of T_{\max} , E_a and ΔH_{subl} . Indeed, while oxamide (D) has the lowest molecular mass, this ligand demonstrates the highest values for these thermal parameters, due to the presence of four intermolecular hydrogen bonds compared to only two for product E and none for A.

Table 3 schedules some N,N-disubstituted oxamides exhibiting similar geometries with dihedral angle between the amide groups of about 90° . Also from these data we can state that the T_{\max} and E_a and ΔH_{subl} are generally more dependent on the number of hydrogen bonds than on the molecular mass, although the difference between H and I is very small and is practically within the limits of error. Still, the influence of the hydrogen bonds in the series H \rightarrow I \rightarrow A is obvious.

We must keep in mind however that counting the number of associations can not always predict the thermal behaviour. It is important to specify the type of interaction.

Planar dithiooxamides exhibit strong intramolecular hydrogen bonds [6, 9]. As can be seen from Table 4, dithiooxamide (J) clearly shows higher T_{\max} and E_a values than the N,N'-disubstituted dithiooxamide (K). This is explained by the presence of two intermolecular associated hydrogen bonds in dithiooxamide, whilst the compared K only exhibits intramolecular hydrogen bonds which also exist in the liquid and gas phase. By comparing compound K and C we observe a higher T_{\max} for compound C due to the mass effect. The presence of intramolecular hydrogen bonds clearly has no effect. The E_a are comparable but both are significantly less than the value obtained for dithiooxamide.

From the other series (D, J and E, K) in which amides are compared with their thio-analogues no clear-cut tendencies for T_{\max} and E_a can be observed as both de-

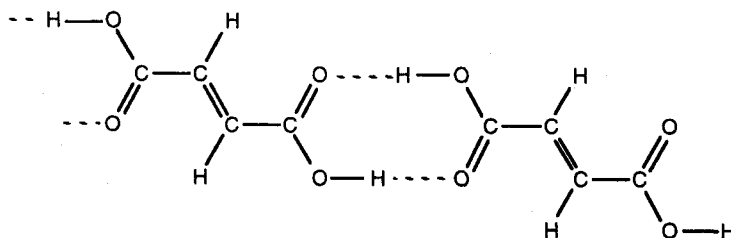


Fig. 1 Fumaric acid, $T_m = 282^\circ\text{C}$

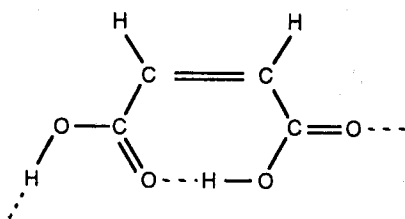


Fig. 2 Maleic acid, $T_m = 144^\circ\text{C}$

termining parameters change and it is obvious that these exert a different kind of influence on the different physical constants. Moreover the strength of the intermolecular interactions differs too much (see final remark in this discussion).

The ΔH_{subl} values could not be obtained for these dithiooxamides as they are known as very soft bases and immediately react with the very soft M^0 of the DSC-cell, producing very dark complexes and a deteriorated cell.

Remark

It has to be noted that these sequences can only be obtained for systems with similar hydrogen bond strengths. As for example in the series of the oxamic acids ($R_2\text{NCO-COOH}$), we can clearly conclude that these data are mainly dependent on the kind of hydrogen bonding in the acid function, which varies from acid dimers to acid catamers and acid-amide hydrogen bonds.

Recently Suzuki [16, 17] published on the thermal behaviour of maleic acid and fumaric acid and concluded that the difference in the melting points (T_m) is due to symmetry effects. In fumaric acid there is less crowding and less van der Waals strain as the two larger substituents in this trans isomer are located further apart than in the cis isomer, resulting in a higher T_m for the first.

Fumaric acid forms cyclic acid dimers in the solid state as given in Fig. 1 [18, 19], forming two intermolecular hydrogen bonds per molecule.

On the other hand, maleic acid forms intermolecular catamers and also intramolecular hydrogen bonds as can be seen from Fig. 2 [18, 20, 21], so only one intermolecular hydrogen bond per molecule is formed.

We calculated [22] that the hydrogen bond strength in the cyclic dimer of fumaric acid and in the catamer form of maleic acid are very well comparable. Considering the clear importance of the number of intermolecular hydrogen bonds in the melting process we can conclude that the difference in the melting points between maleic acid and fumaric acid is indeed due to the geometry, resulting in a different number of intermolecular hydrogen bonds and not to the weak van der Waals strain, presumed in maleic acid.

Conclusion

T_{\max} , E_a and ΔH_{subl} data of oxamides and thiooxamides clearly show the influence of hydrogen bonding in these compounds.

Intermolecular hydrogen bonds must be broken to form the vapour phase and considerably increase the T_{\max} , E_a and ΔH_{subl} , whilst the intramolecular hydrogen bonds are still present in the gas phase and do not exert any influence on these constants. For the relevant comparison one must consider hydrogen bonds with a similar strength.

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S. De Beukeleer wishes to thank N. F. W. O. for financial support. G. Thijs is thanked for technical assistance.

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