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Hydrogen bond patterns in solid state carboxylic acids. Vibrational behaviour of the catamer pattern as exhibited by the N-alkyloxamic acids

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Abstract

The vibrational study presented in this publication shows that the *N*-alkyloxamic acids are hydrogen bonded through a catamer hydrogen bond pattern in the solid state. Two different hydrogen bond patterns are possible for these products, and these patterns can be very clearly distinguished by their vibrational behaviour. Deuteration and low temperature spectra make the assignment and characterisation more obvious.

Keywords: Catamer; Hydrogen bonding; Infrared; Oxamic acid; Raman

1. Introduction

Solid state carboxylic acids are known to exhibit different hydrogen bond patterns. Among these hydrogen bond patterns we can distinguish between cyclic acid dimers, acid catamers and heterogenic associations. The last type exhibits hydrogen bonds between the carboxylic acid function and another functional group. The purpose of this series of articles is to show that vibrational analysis is an ideal tool to study the different hydrogen bond patterns observed in solid state carboxylic acids. The first article in this series fully described the vibrational behaviour of the cyclic dimer hydrogen bond pattrern and introduced a new nomenclature for the carboxylic acid fundamentals [1]. The second publication described the heterogenic cyclic acid-amide hydrogen bond pattern as exhibited by succinamic and fumaramic acids [2-4]. In the present publication we report on the vibrational behaviour of the *N*-alkyloxamic acids and, consequently, on their hydrogen bond pattern, which to our surprise is very peculiar.

The occurrence of a carboxylic acid and a secondary amide functional group means that the compounds under investigation are perfect models to study the vibrational behaviour of both functional groups and to investigate their hydrogen bonding capabilities.

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2. Experimental

The *N*-alkyloxamic acids were prepared by adding one mole of RNH_2 (R is CH_3 , CD_3 , CH_2CH_3 , $(CH_2)_2CH_3$, $CH(CH_3)_2$, cyclopropyl or cyclopentyl) to one mole of diethyl oxalate in an alcoholic solution, under continuous stirring. The obtained oxalate monoamide is converted to the corresponding acid by adding, first, one mole of KOH and then one mole of HCl. The resulting products are purified by sublimation or by repetitive extractions with CHCl₃ in a Soxhlet apparatus. The compounds have all been characterised by mass spectrometry and ¹³C NMR spectroscopy. The spectra were excited by the 1064 nm line of a Nd-YAG laser operating at 200 mW. The scanning range was $50-3500 \text{ cm}^{-1}$. The spectra were recorded with a spectral slit width of 4 cm⁻¹, and for each spectrum 250 scans were recorded and averaged.

3. Results and discussion

3.1. Remarkable behaviour

Two totally different types of vibrational spectra are observed for N-methyloxamic acid: one

$$\begin{array}{cccc} \text{COOC}_2\text{H}_5 & +_{\text{RNH}_2} & \text{COOC}_2\text{H}_5 & +_{\text{KOH}} & \text{COOH} \\ | & \rightarrow & | & \rightarrow & | & +C_2\text{H}_5\text{OH} + \text{KCl} \\ \text{COOC}_2\text{H}_5 & ^{-C_2\text{H}_5\text{OH}} & \text{CONHR} & ^{+\text{HCl}} & \text{CONHR} \\ & & \text{Scheme 1.} \end{array}$$

The infrared spectra were recorded on a Bruker IFS 113v Fourier transform spectrometer, using a liquid nitrogen cooled MCT (4000-500 cm⁻¹) or a DTGS $(500-50 \text{ cm}^{-1})$ detector with a resolution of 1 cm^{-1} . The low temperature measurements were performed with a laboratory designed liquid nitrogen cooled cryostat, consisting of a copper sample holder with a small container which can be filled with liquid nitrogen [5]. This is surrounded by a jacket with KBr (4000-500 cm^{-1}) or polyethylene (500-50 cm^{-1}) windows and placed under vacuum, avoiding condensation on the sample when cooled. From the sample a pellet with KBr or polyethylene as a matrix was made, and this was mounted firmly upon the sample holder.

The solid state Raman spectra were recorded on a SPEX model 1403, 0.85 m double mono-chromator, Raman spectrometer. The spectra were excited by the 514.5 nm line of a Spectra Physics model 2020 argon ion laser operating at 500 mW. The scanning range was between 50 and 4000 cm⁻¹. The spectra were recorded at 1 cm⁻¹ intervals with a time constant at a spectral slit width of 4 cm⁻¹. The Fourier transform Raman spectra were recorded on a Bruker IFS 66v interferometer equipped with a FT Raman FRA 106 module. spectrum with a clear, distinct vOH band and another spectrum where vOH and vNH overlap. This is clearly illustrated in Fig. 1. Mass spectrometry and ¹H and ¹³C NMR spectroscopy indicate that the different vibrational spectra are due to the same molecule, namely *N*-methyloxamic acid. This product clearly appears in two different crystal modifications, and the clear differences in the vibrational spectra make us believe that different hydrogen bond patterns are responsible for the particular behaviour. Indeed, hydrogen bonding has a clear effect on the vibrational behaviour of these products. This phenomenon has been the subject of numerous studies, both experimental and theoretical [6].

In order to make the following discussion easier, we propose the following nomenclature for the different crystal modifications of N-methyloxamic acid. The crystal modification exhibited by N-methyloxamic acid after slow crystallisation and characterised through the typical vibrational behaviour as given in the left-hand side of Fig. 1 is assigned as the α -modification, and the righthand side of Fig. 1 gives the typical vibrational behaviour of the γ -modification which is obtained by rapid crystallisation. The sublimation temperatures observed by thermal analysis are 130°C for α -N-methyloxamic acid and 128°C for the γ -mod-



Fig. 1. The OH stretching region in the vibrational spectra of the α -modification (left) and the γ -modification (right) of *N*-methyloxamic acid. Infrared (upper spectra) and Raman (lower spectra).

ification of the methyl derivative. The sublimation tempreatures of both modifications are clearly different, indicating differences in the solid state hydrogen bond patterns.

The other N-alkyl substituted oxamic acids studied exhibit vibrational spectra comparable with those of the methyl derivative with this exception, that only the N-cyclopropyl derivative also exhibits the two different vibrational spectra. The ethyl, propyl and isopropyl derivatives give only vibrational spectra comparable with those of γ -N-methyloxamic acid (Fig. 2), and N-cyclopentyloxamic acid exhibits vibrational spectra of the α -modification type (Fig. 3).

The molecular symmetry of the *N*-alkyloxamic acids can be considered equal, especially when the alkyl groups are considered as point masses. The oxamic acid derivatives under investigation are planar owing to the steric hindrance between the two carbonyl groups for a non-planar structure. This results in a C_s point group, and all vibrations are infrared and Raman active. Additional symmetry can be introduced through hy-

drogen bonding, e.g. the molecular symmetry of formic acid monomer is C_s , but the cyclic formic acid dimer has C_{2h} symmetry.

3.2. Secondary amide functional group

The position of the typical amide bands in the vibrational spectra of both the α - and the γ -modification of the *N*-alkyloxamic acids clearly indicates that the secondary amide exhibits a *trans* conformation.

The NH stretching vibration for a *trans* secondary amide is expected in the 3300 cm⁻¹ region for solid state products. In the infrared spectra of the α -modifications vNH can be assigned to the medium intensity bands at 3362 cm⁻¹ (methyl derivative) and 3349 cm⁻¹ (cyclopentyl derivative). These bands shift about 10 cm⁻¹ to lower wavenumbers on cooling and they disappear on deuteration. The vNH vibrations are observed in the 3300 cm⁻¹ region for the γ -modification, and their shift on cooling is less clear because an overlap with the acid vOH vibrational band is observed.

As vNH usually can be described as an isolated vibration, the frequency can be associated directly with the strength of the hydrogen bond. Indeed, the formation of a hydrogen bond results in a decrease of the electron density of the NH bond, the NH bond is lengthened, the force constant of the NH stretching vibration lowers and the vibrational frequency decreases on hydrogen bond formation. Our first assumption is that the NH hydrogen bond is stronger in the γ -modification than in the α -modification.

Amide I and II bands are respectively expected in the 1680 cm⁻¹ and 1550 cm⁻¹ regions. In the infrared spectra of the *N*-alkyloxamic acids a very strong band is observed in the 1680 cm⁻¹ region and at slightly higher wavenumbers for the γ -modification. These bands are assigned to the amide I



Fig. 2. The OH stretching region in the infrared spectrum of γ -*N*-methyl- (upper), *N*-ethyl-, *N*-propyl-, and *N*-isopropylox-amic acids (lower).



Fig. 3. The OH stretching region in the infrared spectrum of α -*N*-methyl- (upper) and *N*-cyclopentyloxamic acid (lower).

fundamental; the corresponding Raman band has medium intensity, in contrast to the low intensity band in the Raman spectrum of potassium *N*methyloxamidate [7].

The band which can be assigned to the strongly coupled δ NH and ν CN vibration, amide II, is observed at higher wavenumbers (± 20 cm⁻¹) than the corresponding band in potassium *N*methyloxamidate. The intensity of the infrared amide II is markedly smaller for the carboxylic acid than for the potassium salt.

On deuteration, the changes typical of *trans* secondary amides are observed. Amide II', with mainly vCN character, is observed as the most intense Raman band in the 1490 cm⁻¹ region for all N-alkyloxamic acids. Amide III is observed in the 1250 cm⁻¹ region, and on deuteration we observe amide III', mainly δ ND character, at 940 cm⁻¹.

The νNR fundamental is observed in the infrared spectrum of the normal N-methyl-oxamic acid as a shoulder of the intense 1180 cm⁻¹ band. Through CH₃/CD₃ substitution and via a low



Fig. 4. The vNR behaviour on CH_3/CD_3 substitution (left) and on cooling (right) in the infrared spectra of x-N-methyloxamic acid.

temperature study, this band can be clearly distinguished, as can be observed in Fig. 4.

Amide V is usually assigned in the 750 cm⁻¹ region. Measurements at variable temperatures make the assignment of this fundamental straightforward, since a clear shift to higher wavenumbers is observed for π NH on cooling from room temperature to -196° C (Table 1).

3.3. Carboxylic acid function

The OH stretching vibration can be very clearly distinguished in both the infrared and the Raman spectra for the α -modification. On cooling, this band shifts to lower wavenumbers. It is difficult to distinguish the OH stretching vibration in the spectra of the γ -modification as ν NH and ν OH overlap. The high position for the ν OH indicates a weak hydrogen bond, and correspondingly we expect a low position for the π OH or acid IV fundamental.

The carboxylic acid carbonyl stretching vibrations (acid I) are observed at high wavenumbers, in contrast to the previous results, and we also observe a clear agreement between the infrared and Raman acid I frequencies. Acid I is shifted 10 cm⁻¹ to lower wavenumbers on deuteration, indicating a decoupling of δ OH as previously explained for the dicarboxylic acids [1]. Acid I is the most intense Raman band.

Acid II and III bands, with coupled vC-O and δOH character, are not observed at the expected positions, as we observed in earlier vibrational analyses of carboxylic acids [1]. The differences could be due to another hydrogen bond pattern or to different couplings of δOH and $\nu C-O$ and other symmetry coordinates. Acid II is observed in the 1360 cm^{-1} region and shifts to higher wavenumbers on cooling, and Acid III is observed in the 1180 cm⁻¹ region. On deuteration we observe acid II' at lower wavenumbers, and acid III' is observed in the 1050 cm⁻¹ region, except for the CD₃ derivative. For both modifications we observe acid III' for DOOC-CONDCD₃ in the 1005 cm⁻¹ region. This discrepancy is probably due to couplings with the CD_3 deformations.

The acid IV fundamental is expected in the 950 cm^{-1} region for strongly to very strongly hydro-

Table	1		
πNH	behaviour	on	cooling

Product	20°C	-100°C	196°C	
α-HOOC–CONHCH ₃	734 ms	744 ms	751 ms	
α-HOOC-CONHCD ₃	730 m	740 m	748 ms	
α-HOOC-CONH-cyclopentyl	730 m	734 m	739 ms	
α-HOOC−CONH−cyclopropyl	705 m			
γ-HOOC-CONHCH ₃	739 mw	747 mw	751 m	
γ-HOOC-CONHCD ₃	736 mw	745 mw	748 m	
γ-HOOC-CONHCH ₂ CH ₃	712 m	722 ms	727 m	
7-HOOC-CONHCH,CH,CH	716 m	719 m	721 s	
γ-HOOC-CONHCH(CH ₁),	711 mw	716 m	720 m	
γ-HOOC-CONH-cyclopropyl	718 m			

Table 2

Infrared πOH and πOD vibrations/cm⁻¹

Alkyl group	Acid IV			Acid IV'	
	20°C	- 100°C	-196°C	20°C	
α -modification					
CH ₃	842 m	848 m	853 m	608 mw	
CD ₃	841 m	848 m	852 m	608 mw	
cyclopentyl	839 mw,br	842 mw,br	845 m		
cyclopropyl	843 mw,br				
y-modification					
CH ₃	795 ms	804 ms	813 ms	582 m	
CD ₃	786 ms	800 ms	808 ms	582 mw	
CH ₂ CH ₃	793 ms,br	809 s	813 s	580 mw	
CH ₂ CH ₂ CH ₃	791 s,br	806 s,br	813 s	581 ms	
(CH ₂) ₃ CH ₃	795 m	806 m	811 m	577 m	
CH(CH ₃) ₂	765 m,br	773 m,br	778 m,br	545 ms	
cyclopropyl	767 m,br	,	,		

gen bonded carboxylic acids (ν OH below 3000 cm⁻¹). As we observe ν OH at higher wavenumbers in the products under investigation, we expect to find acid IV at lower wavenumbers. These fundamentals can be easily assigned through their temperature behaviour and through their characteristic behaviour on deuteration. We assign acid IV to the infrared bands in the 840 cm⁻¹ region for the α -modification, whereas this fundamental is assigned to a band in the 800 cm⁻¹ region for the γ -modification (Table 2). The difference in the acid IV position can be explained via the difference in hydrogen bond strength, as already mentioned for the ν OH behaviour. For the more weakly hydrogen bonded carboxylic acid (γ -mod-

ification), we observe a higher vOH position and consequently a lower acid IV position compared with the more strongly hydrogen bonded acid (α -modification).

From Table 2 we also observe that the acid IV position is not influenced by the alkyl group for the α -modification, whereas we observe a clear seric effect on the acid IV position for the γ -modification. This result indicates that there is an interaction between the carboxylic acid and the secondary amide groups for the γ -modification. This hypothesis is proved through the amide I vibration, which is observed at higher wavenumbers for the γ -modification than for the α -modification. Comparison with the ν NH wavenumbers



Fig. 5. Heterogenic cyclic acid-amide hydrogen bond pattern.

excludes a mide–amide hydrogen bonds for the γ -modification.

The clear agreement between infrared and Raman frequencies rules out any local inversion symmetry. One objection could be made; the relatively high vOH frequency, 3190 cm⁻¹ (α -modification) and 3290 cm⁻¹ (γ -modification), indicates that the OH hydrogen bonds are relatively weak. For strongly to very strongly hydrogen bonded carboxylic acids we expect vOH below 3000 cm⁻¹,



Fig. 6. Proposed hydrogen bond pattern for the α -N-alkylox-amic acids.



Fig. 7. Proposed hydrogen bond pattern for the γ -N-alkylox-amic acids.

giving rise to the well known broad vibrational band with several subbands. When local inversion symmetry is present for such strongly hydrogen bonded systems, a considerable difference is observed in infrared and Raman frequencies. For the N-alkyloxamic acids, however, vOH is observed at higher wavenumbers, and through the known vOH, rO....O relationship [8] we can conclude that the rO.....O distance in the crystalline Nalkyloxamic acids is in the 280–290 pm range, indicating weak hydrogen bonding. It can be questioned whether the difference between the infrared and the Raman frequencies will be large enough to be observed for such weak hydrogen bond interactions. In an earlier publication we described the vibrational behaviour of the cyclic formic acid dimer theoretically [9]. The results of this study indicate that, for a rO....O distance of 300 pm, we still expect a difference of at least 20 cm⁻¹ (harmonic approximation) between the infrared and the Raman active carboxylic acid carbonyl stretching vibrations. As we observe for both the α - and the γ -modifications of the N-alkyloxamic acids a clear agreement between the infrared and the Raman active acid I vibrations, we can rule out the cyclic dimer hydrogen bond pattern for both modifications.

A heterogenic hydrogen bond pattern similar to the one observed for malonamic and succinamic acids [2] can be excluded, since the secondary amide should be in the *cis* conformation (Fig. 5).

The Acid IV behaviour indicates that the carboxylic acid groups are hydrogen bonded through an acid-acid catamer pattern in the α -modification. Therefore we can propose the hydrogen bond pattern in Fig. 6. To propose a hydrogen bond pattern for the γ -modification is more difficult. On a vibrational basis we can conclude that the γ -modification of the N-alkyloxamic acids is hydrogen bonded through a heterogenic catamer pattern. A possible hydrogen bond pattern is given schematically in Fig. 7.

4. Conclusions

The vibrational behaviour of the N-alkyloxamic acids clearly indicates that these products can exhibit two different types of hydrogen bond pattern. These can be very readily distinguished becuase their vibrational behaviour is different. We assigned them as the α - and the γ -modification. The assignments of the OH and NH vibrational bands are obvious from low temperature measurements and spectra of deuterated products.

Vibrational analysis predicts an acid-acid catamer hydrogen bond pattern for the α -modification and a heterogenic acid-amide catamer association for the γ -modification of the the *N*-alkyloxamic acids.

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