

THE O-H AND O-D STRETCHING VIBRATIONS IN THE HYDRATES OF SODIUM AND POTASSIUM SACCHARINATE : SPECTRA-STRUCTURE CORRELATIONS

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ABSTRACT

The infrared spectra of the two hydrates of sodium saccharinate in the region of the O-H and O-D stretching vibrations of protiated and partially deuterated samples are considerably different. The less stable monoclinic form is obviously a higher hydrate which is easily converted into the more stable triclinic one. The observed infrared frequencies for the triclinic crystals are correlated with the crystallographically determined $O\cdots O$ and $O\cdots N$ distances. The infrared spectra of the sodium compounds in the region of the O-H and O-D stretching vibrations are compared with those of potassium saccharinate.

INTRODUCTION

In an attempt to recrystallize from ethanol the commercial crystals of sodium saccharinate hydrate (they are prepared from an aqueous solution), another crystalline form was obtained (ref. 1). It was found that the crystals recrystallized from water are monoclinic (ref. 1) whereas those obtained from ethanol have triclinic symmetry (space group $P1$, $Z = 6$) (ref. 2). The infrared spectra of the two different forms of sodium saccharinate in the region of the O-H and O-D stretching vibrations were found to be considerably different (ref. 1) and it was concluded that two different hydrates are in fact formed. It is not clear which of these has been studied by Natarajan and Subramanian in their recent work on the infrared spectra of sodium and potassium saccharinates (ref. 3).

As a part of our systematic studies of the structural and spectral properties of a series of metal saccharinates (ref. 1, 2, 4, 5), the results of the investigation of the infrared spectra of the hydrates of sodium and potassium saccharinates in the region

of O-H and O-D stretching vibrations are presently reported and correlated with the crystallographically determined (ref. 2) $O\cdots O$ and $O\cdots N$ distances in the triclinic $Na_3(C_7H_4NO_3S)_3 \cdot 2H_2O$.

EXPERIMENTAL

The crystals of $Na_3(sac)_3 \cdot 2H_2O$ (hereafter sac denotes a saccharinate ion) were prepared either by recrystallization from ethanol of the commercially available sodium salt or, according to the method described by Defournel (ref. 6), from warm aqueous solution of saccharine and sodium carbonate followed by recrystallization from ethanol. As shown (ref. 1), the recrystallization from water gives a hydrate whose composition was not determined with certainty but which is undoubtedly a hydrate higher than that obtained from ethanol. The hydrate of potassium saccharinate was prepared from warm aqueous solution of saccharine and potassium carbonate and recrystallized from both aqueous and ethanolic solutions. It was found that identical crystals were obtained irrespectively of the medium.

Partially deuterated compounds were prepared from suitable H_2O-D_2O or ethanol- D_2O mixtures.

The infrared spectra were recorded, from KBr pellets and Nujol mulls, at room and liquid-nitrogen temperature (RT and LNT respectively), on a Perkin-Elmer 580 infrared spectrophotometer. For LNT infrared measurements a VLT-2 (RIIC) cell was used. The powder X-ray diffractograms were obtained on a JEOL diffractometer.

RESULTS AND DISCUSSION

In the beginning of our work (ref. 1, 2) it seemed that the infrared spectra (recorded from KBr pellets) of the two crystallographically different forms of sodium saccharinate compounds were surprisingly similar (see Fig. 1 a, b). Afterwards it was shown, however, that the spectrum of the monoclinic form recorded in Nujol emulsion is different from that of the same crystalline form but recorded from KBr pellets (see Fig. 1 c, d). Such a difference was not observed in the case of the form with triclinic symmetry. Identical spectra of the monoclinic form were obtained by the two techniques when the time for the preparation of the KBr pellet was shortened (see Fig. 1 e, f).

The infrared spectra in the region of the O-H and O-D stretching vibrations of protiated and partially deuterated samples show that the monoclinic form is a higher (see Fig. 2) and less stable hydrate which can undergo a transition to the more stable triclinic form (see Fig. 3).

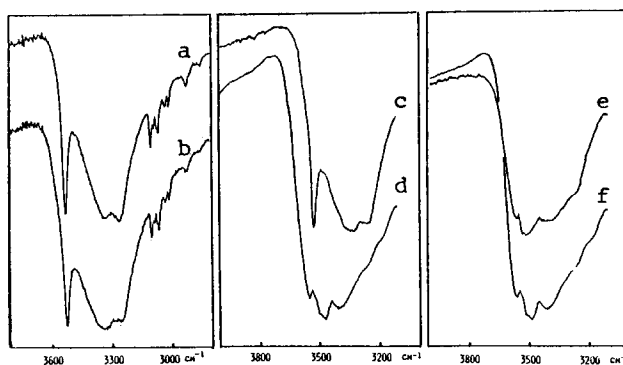


Fig. 1. The O-H stretching region in the RT IR spectra of the sodium saccharinate recrystallized from ethanol (a) and water (b, c, d, e, f) recorded from KBr pellets (a, b, c, e) and Nujol emulsions (d, f).

The crystal structure of the triclinic form of sodium saccharinate hydrate, $\text{Na}_3(\text{sac})_3 \cdot 2\text{H}_2\text{O}$, has been

determined in detail (ref. 2). In the unit cell there are three crystallographically independent six-coordinated Na cations, three saccharinate anions and two independent water molecules. Only one nitrogen atom belonging to a saccharinate anion is coordinated to one of the sodium cations (the nitrogens from the other two saccharinate anions are not part of the coordination spheres of the remaining two symmetrically non-equivalent sodium cations). This finding contradicts the conclusion made by Natarajan and Subramanian (ref. 3) that the disappearance of the $\nu(\text{N-H})$

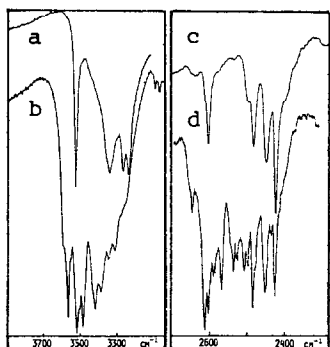


Fig. 2. The O-H (a, b) and O-D (c, d) stretching region in the LNT IR spectra of sodium saccharinate hydrate recrystallized from ethanol (a, c) and water (b, d).

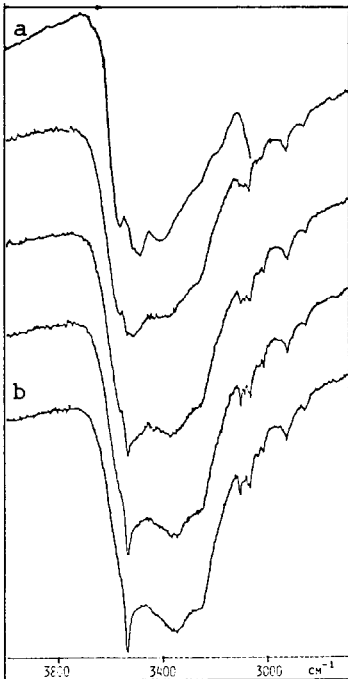


Fig. 3. The transition of the less stable monoclinic form (a) of the sodium saccharinate hydrate into the more stable triclinic one (b).

maxima in the spectra of the metal saccharinates suggested the existence of contact between the metal and nitrogen atoms.

Both independent water molecules are coordinated to sodium cations and, at the same time, participate in hydrogen bonding to the nitrogen atoms from saccharinate anions or to oxygen atoms belonging to the SO_2 and CO groups. The $\text{Ow}(1)\cdots\text{N}(1)$ and $\text{Ow}(1)\cdots\text{N}(2)$ distances are 283.3(3) and 286.9(3) pm, whereas the corresponding $\text{Ow}(2)\cdots\text{O}(33)$ and $\text{Ow}(2)\cdots\text{O}(31)$ distances have values of 274.6(4) and 290.8(3) pm, respectively (the labeling scheme of ref. 2 is used throughout). The existence of four independent O-H groups belonging to the water molecules in the structure is in a good agreement with the appearance of four infrared bands originating from $\nu(\text{O-D})$ modes of isotopically isolated HDO molecules (see Fig. 2 c).

Since all $\text{Ow}\cdots\text{A}$ (A denoting a proton acceptor) distances in the structure are *not* of the $\text{Ow}\cdots\text{O}$ type, it is difficult to make correlations between the frequencies of the $\nu(\text{O-D})$ modes of isotopically isolated HDO molecules and the hydrogen bond lengths using the eqn. 1 (ref. 7)

$$\nu/\text{cm}^{-1} = 2727 - 8.97 \cdot 10 \exp(-3.73 R/A) \quad (1)$$

Supposing that the bands with the highest (2604 cm^{-1}) and lowest (2425 cm^{-1}) frequencies (see Fig. 2 c) originate from the O-H groups involved respectively in the weakest ($R = 290.8 \text{ pm}$) and the strongest ($R = 274.6 \text{ pm}$) hydrogen bond of the $\text{Ow}\cdots\text{O}$ type, the calculated (using eqn. 1) values for the frequencies of the O-D stretching vibrations are 2552 and 2407 cm^{-1} . These two calculated frequencies are for 52 and 18 cm^{-1} higher than the experimentally

determined values (2804 and 2425 cm^{-1} respectively). On the other hand, when the experimental frequencies were substituted into eqn. 1, a fair agreement between the calculated and the experimentally determined $\text{O}\cdots\text{O}$ distances was obtained (Table 1).

TABLE 1

Experimental (ref. 2) and estimated (ref. 7) values for the $\text{O}\cdots\text{A}$ distances in $\text{Na}(\text{sac})\cdot 2\text{H}_2\text{O}$

$\text{O}\cdots$	A	R/pm (experiment)	R/pm (estimated)
$\text{O}\cdots(1)$	N(1)	283.3	?
$\text{O}\cdots(1)$	N(2)	286.9	?
$\text{O}\cdots(2)$	O(33)	274.6	276.0
$\text{O}\cdots(2)$	O(31)	290.8	300.7

Contrary to the case of sodium saccharinate, the crystals of the potassium salt recrystallized from water and from ethanol were found to be identical. In fact, their infrared spectra recorded at room temperature are similar to the spectrum of the triclinic form of sodium saccharinate (see Fig. 4). However, the spectral pictu-

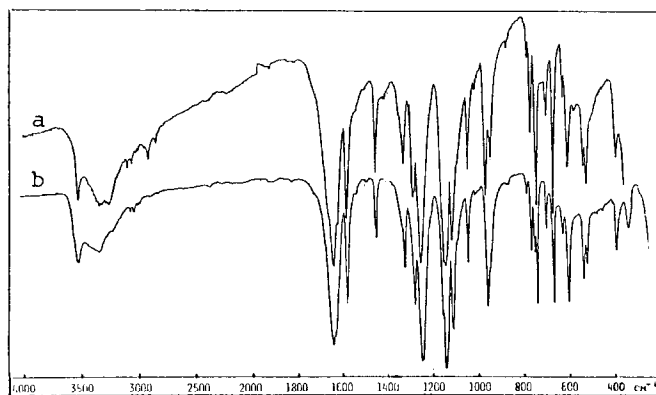


Fig. 4. The RT IR spectra of the hydrates of sodium (a) and potassium (b) saccharinate.

re in the O-H and O-D stretching region at LNT (see Fig. 5) as well as X-ray powder patterns (see Fig. 6) indicate that structural differences exist between these two compounds.

It should finally be noted that the RT frequencies reported by Natarajan and Subramanian (ref. 3) in the region of O-H stretching vibrations of H₂O molecules are in considerable disagreement with those found in our infrared spectra of the hydrates of sodium and potassium saccharinate. Some of their assignments are questionable as well.

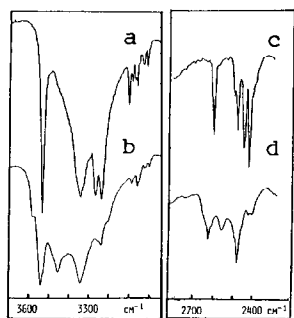


Fig. 5. The O-H (a, b) and O-D (c, d) stretching region in the LNT IR spectra of the hydrates of sodium (a, c) and potassium (b, d) saccharinate recrystallized from ethanol

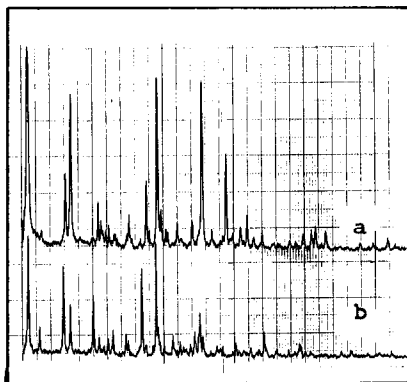


Fig. 6. The X-ray powder diagrams of the hydrates of sodium (a) and potassium (b) saccharinate.

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