Monoalkali Phenolic Salts of 3,5-Dinitrosalicylic Acid

By BARRY CLEVERLEY

(*Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone, New Zealand*)

Summary Spectroscopic evidence is presented which suggests that monoalkali 3,5-dinitrosalicylates are phenolic salts.

THE C=O stretching vibration of crystalline salicylic acid absorbs strongly at 1660 cm^{-1}. It is replaced, in the spectrum of the crystalline monopotassium salt, by two strong bands at 1597 and 1396 cm^{-1}, assigned to the asymmetric and symmetric CO_2^- stretching vibrations. The monoalkali metal salts of substituted salicylic acids are also carboxylates.[1]

3,5-Dinitrosalicyclic acid appears to be an exception.† The spectra of its monoalkali metal salts all retain a strong band above 1674 cm^{-1} (see Table) where the C=O stretching frequency of the acid absorbs.‡ They have no symmetric CO_2^- stretching frequency near 1400 cm^{-1}, and a band of medium intensity near 1600 cm^{-1} can be assigned to an aromatic ring-stretching vibration. Additional evidence that the salt is a phenolate is provided by the absence of bands which, in the spectra of the alkali salicylates, have been assigned to the O–H stretching vibration.[2]

If the monoalkali metal salts of 3,5-dinitrosalicylic acid are phenolates, the dimetallic salts must then be carboxylates. The dipotassium and dilithium salts were prepared, and their spectra were found to have a pair of bands, at 1630 and 1390 cm^{-1}, and 1627 and 1399 cm^{-1}, corresponding to the CO_2^- stretching frequencies‡

TABLE. C=O Frequencies of monoalkali 3,5-dinitrosalicylates

Li	Na	K	Rb	Cs
1708	1699	1706	1705	1691 cm^{-1}

Although these results have been obtained using crystalline solids, they are unlikely to be greatly affected by the physical state of the sample. It was found that monolithium 3,5-dinitrosalicylate, which is very soluble, has nearly the same spectrum as an aqueous solution§ as it has as a crystalline solid.

The symmetric CO_2^- stretching vibrations near 1400 cm^{-1}, being relatively little affected by the polar and steric effects of substituents, are a reliable indicator of a CO_2^- substituent.[3] Asymmetric CO_2^- stretching vibrations always absorb strongly 50—150 cm^{-1} below the frequency of the corresponding CO_2H group,[4] and it would be contrary to all expectation for the asymmetric CO_2^- stretching vibration of the 3,5-dinitrosalicylate ion to be 17—24 cm^{-1} higher than the C=O frequency of the corresponding acid.

† Mono- and di-alkali salts were prepared by methods first reported by H. Hübner, *Annalen*, 1879, **195**, 43. It was found that mono-Na, -K, -Rb, and -Cs salts could also be prepared by boiling a solution containing equivalent weights of the acid and an alkali halide. Satisfactory metal analyses were obtained for both K salts. The action of mineral acids on the salts regenerated 3,5-dinitrosalicylic acid.

‡ Paraffin pastes and KBr pellets.

§ Concentrated solution between fluorite plates.

The increase of the C=O frequency that is observed when the OH group of 3,5-dinitrosalicylic acid is replaced by O^- may be explained as the removal of bonding between the oxygen atom of the carbonyl group and a phenolic proton.

The phenolic character of 3,5-dinitrosalicylic acid clearly resembles that of picric acid, NO_2 and CO_2 groups having quite similar steric and chelating properties. The comparatively high pK_2 of 3,5-dinitrosalicylic acid¶ may be explained as the combined effect of electron release from the phenoxide ion and bonding of the carboxylic hydrogen with O^-.

I.r. spectra show that the monopotassium salts of 3-nitro- and 5-nitro-salicylic acids are typical carboxylates.‡

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¶ 3,5-dinitrosalicylic acid, $pK_2 = 7{\cdot}4$; benzoic acid, $pK = 4{\cdot}2$; salicylic acid, $pK_1 = 3{\cdot}0$; (G. Kortüm, W. Vogel, and K. Andrussow, *Pure Appl. Chem.*, 1960, **1**, 187).

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