Intramolecular Hydrogen Bonding in Protonated α-Halogeno-aldehydes: Nuclear Magnetic Resonance Study

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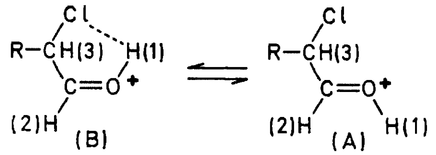
Summary The n.m.r. spectra of protonated α-chloroacetaldehyde and α-chlorobutyraldehyde in strong acid solution show the presence of two isomeric species, one of which can be explained in terms of intramolecular hydrogen bonding between the proton on oxygen and the chlorine atom.

THE intramolecular hydrogen-bonding between a hydroxy-group and an acceptor atom X (halogen or oxygen) at a β-carbon atom has aroused much interest in recent years in the field of conformational analysis. Such intramolecular interaction has been suggested in i.r. studies,[1] thermodynamic calculations, and dipole moment measurements[2] of 2-cyano-, 2-nitro-, and 2-halogenoethanols, and on ethylene glycol.[3]

The direct observation by n.m.r. spectroscopy of unequivocal internal hydrogen-bonding in protonated α-halogeno-aldehydes prompts us to publish our first results in the conformational analysis of α-halogeno-aldehydes in strong acid solvent systems.

Stable protonated aliphatic aldehydes[4a] and ketones[4b] have been described by G. A. Olah and his co-workers in the course of their n.m.r. investigation of hetero-atom substituted carbonium ions in the FSO_3H–SbF_5–SO_2 strong acid solution.[4c] Protonated aliphatic aldehydes have also been observed in HF–BF_3 acid solution by H. Hogeveen.[5]

When the α-chloro-aldehyde is dissolved in the extremely strong acid system: FSO_3H–SbF_5–SO_2 at −70°, the n.m.r. spectrum of this solution shows evidence for complete protonation on the carbonyl oxygen and for the presence of two isomeric species (A) and (B).



The spectrum of protonated chloroacetaldehyde (Figure 1) is: Form (A): O^+H proton appears at 16·00 p.p.m.† as a doublet of triplets; $J_{1,2}$ 9·0 Hz† (*cis*-olefinic), $J_{1,3}$ 0·8 Hz (*trans*-allylic). The aldehydic proton at 10·18 p.p.m. is a doublet ($J_{1,2}$), one of the lines being partly recovered by the acid and the other partly by the (B) form. The α-protons appear as the doublet ($J_{1,3}$) at 5·42 p.p.m. Form (B) shows the O^+H proton less deshielded at 15·50 p.p.m. as a doublet of triplets $J_{1,2}$ 20·0 Hz (*trans*-olefinic), $J_{1,3}$ 1·4 Hz (*cis*- allylic). The aldehydic proton is a doublet at 10·25 p.p.m. ($J_{1,2}$) and the two α-protons appear more deshielded than in the (A) form at 5·50 p.p.m.

The spectrum of protonated α-chlorobutyraldehyde (Figure 2) shows the same features: CH^5_3–CH^4_2–CH^3Cl–$CH^2O^+H^1$. Chemical shifts: (A): H(1) 16·00; H(2) 10·18; H(3) 5·4; H(4) 2·3; H(5) 1·2; (B): H(1) 15·40; H(2) 10·15; H(3) 5·4; H(4) 2·3; H(5) 1·2. Coupling constants: (A): $J_{1,2}$ 9·4, $J_{1,3}$ *ca.* 0·3; (B): $J_{1,2}$ 20·0, $J_{1,3}$ 0·7 Hz. The assignment of the structures (A) and (B) is readily made, using the size of the olefinic (*trans* > *cis*) and allylic couplings (*cis* > *trans*).[4a]

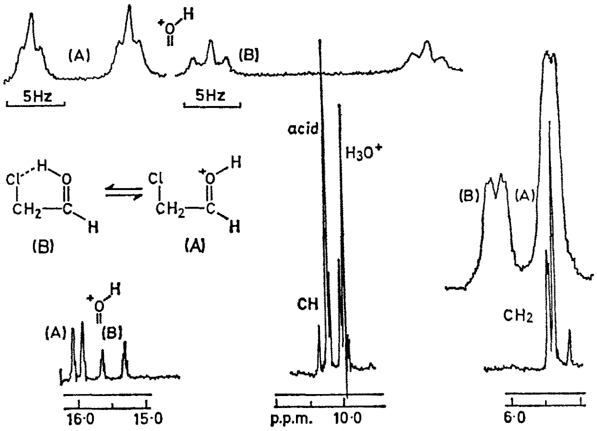


FIGURE 1

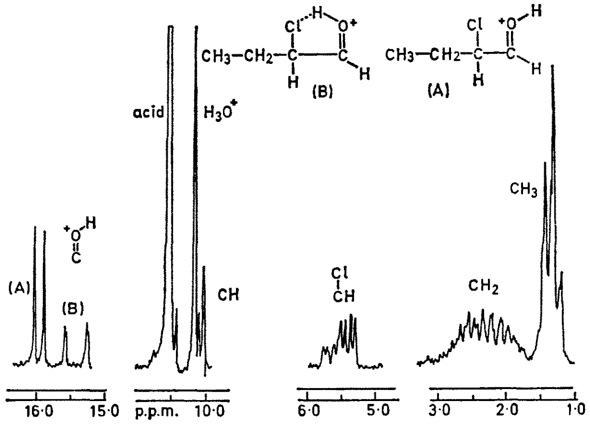


FIGURE 2

The existence of hydrogen bonding in structure (B) is strongly supported by the following facts:

(i) From the isomer ratio (A)/(B) in the protonated aliphatic aldehydes we see that the (A) form, in which the alkyl group is *trans* to the proton on oxygen, is favoured

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† All chemical shifts are given in p.p.m. from Me_4Si used as external capillary reference.

and is the only one detectable in aldehydes higher than acetaldehyde [(A): (B) = 80 : 20].[4a,5] α-Chloroacetaldehyde as well as α-chlorobutyraldehyde both show a ratio (A) : (B) = 65 : 35 indicating the presence of the (B) form despite the bulk of the RCHCl group.

(ii) From the chemical shifts of the $C=O^+H$ protons in protonated aliphatic aldehydes[4a] we see that the (B) form is more deshielded than the (A) form due to the steric effect of the R group.

In protonated α-halogeno-aldehydes the reverse is true. The (B) form is less deshielded than the (A) form. This can only be explained by the fact that the positive charge is delocalized through internal bonding of the proton on oxygen to the chlorine atom. The same effect is also observed in the CH_2 signal which is less deshielded in the (A) than in the (B) form [in the (B) form the charge density on the carbon atom is diminished by the vicinal chlorine hydrogen bond].

(iii) Protonated α-bromobutyraldehyde[7] in the same acid solution shows only the (A) form indicating that hydrogen bonding is not strong enough to be detected by the same technique.

(iv) The spectra of protonated α-chloro-aldehydes show temperature reversibility at −30°. The OH^+ proton exchanges with the acid solvent system, and the (A) and (B) form are no longer distinguishable. By lowering the temperature the original spectra appear again.

(v) The $J_{2,3}$ coupling which has been thoroughly investigated[6] in relation to the general problem of rotational isomerism about single bonds joining sp^2 to sp^3 hybridized carbon atoms was stated to be unable to be measured in protonated aliphatic aldehydes.[4a,5] We measured the coupling $2\cdot5 < J_{2,3} < 0\cdot5$ Hz, the size depending on the nature of the isomeric form and on the α-chloroaldehyde. Since in our case the (B) form is hydrogen bonded, internal rotation should be much more hindered than in the (A) form where hindered rotation is due only to dipole–dipole interaction. At present we can only conclude that the conformation is not identical in the (A) or (B) form on going from α-chloroacetaldehyde to α-chlorobutyraldehyde. Further work is in progress in this field on α-fluoro-, α-bromo-, α-chloro-, and α-iodo-aldehydes.[7]

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