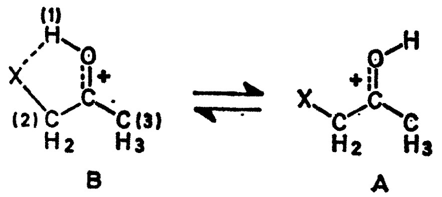
Intramolecular Hydrogen-bonding and Long Range Coupling in Stable Protonated Halogenoacetones

By R. JOST, P. RIMMELIN, and J. M. SOMMER*

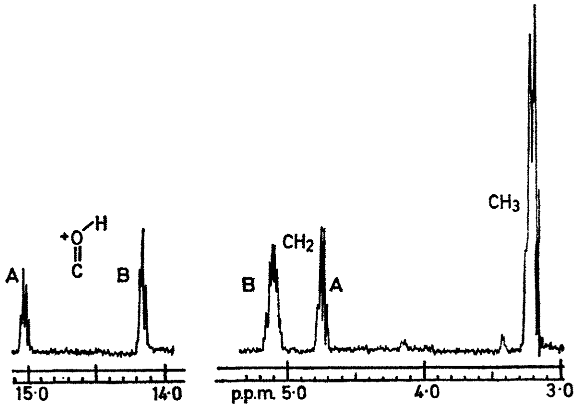
(*Laboratoire de Chimie Organique Appliquée, Associé au C.N.R.S., Institut de Chimie*, 1, *rue Blaise Pascal*, 67 *Strasbourg, France*)

Summary The n.m.r. spectra of four halogenoacetones (Me·CO·CH$_2$X; X = F, Cl, Br, or I) protonated in superacid media show strong long-range coupling through the sp^2 centre and intramolecular hydrogen bonding, both directly related to the electronegativity of the heteroatom X.

THE current interest in the carbonyl bond in stable protonated carbonyl compounds[1–3] as well as in the relation of the hydrogen bond strength to the electronegativity of the donor atom prompts us to publish results obtained by the n.m.r. study of the stable protonated halogenoacetones.



As reported earlier for α-chloro-aldehydes,[4] direct n.m.r. observation of the stable protonated species in SO$_2$–SbF$_5$–FSO$_3$H [5] shows the presence of two stereoisomers (A) and (B) in which the chemical shifts are different owing to greater charge delocalisation in (B) through the internal hydrogen bond.



FIGURE

The n.m.r. spectra of the four halogenoacetones in the strong acid solvent at −60 °C show good resolution (0·4 Hz) and structures (A) and (B) could be assigned in all cases *via* the allylic coupling constants $J_{1,2}$ or $J_{1,3}$ (*cis* ≫ *trans*).[1]

The n.m.r. spectrum of protonated bromoacetone in SbF_5–FSO_3H–SO_2 at −60 °C shows the following (see Figure.)

(A); C=OH$^+$ 14·15 p.p.m.,† q, $J_{1,3}$ 0·8 Hz; XCH_2 4·76 p.p.m., q, long range $J_{2,3}$ 1·4 Hz; and CH_3 3·20 p.p.m., m, $J_{2,3}$ and $J_{1,3}$, partly covered by CH_3 resonance of the B form.

(B); C=OH$^+$ 15·05 p.p.m., t, $J_{1,2}$ 0·8 Hz, XCH_2 15·16 p.p.m., octet, $J_{1,2}$; $J_{2,3}$ 1·4 Hz; and CH_3 3·2 p.p.m., t.

Proton exchange rates with the acid system remain very low up to −30 °C. At higher temperatures the C=OH$^+$ signals broaden and vanish and the signals from the two stereoisomeric forms coalesce. On lowering the temperature the original spectrum reappears.

Intramolecular hydrogen bonding in the form (B) is strongly supported by: (*a*) the (B):(A) ratio is 55:45 instead of *ca.* 20:80 expected from steric reasons[1] (*b*) in form (B) the strong charge delocalisation through the internal H-bond is reinforced by the strong shielding effect on the C=OH$^+$ proton (0·9 p.p.m. higher field) and the opposite effect on the methylene protons (0·4 p.p.m. lower field).

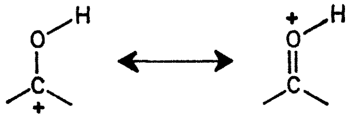
TABLE

X	(B):(A)	δ(C=OH$^+$) (B) form	$J_{2,3}$/Hz	Electro-negativity
F	>98:2	15·15	2·1	3·9
Cl	75:25	14·50	1·8	3·0
Br	55:45	14·26	1·4	2·8
I	15:85	14·06	0·8	2·5

The Table shows a high dependence of the (B):(A) ratio on the electronegativity of the X atom [in fluoroacetone only the (B) isomer is observed]. The free energy difference between the (A) and (B) form at −60 °C can be linearly correlated with the calculated electronegativity of the heteroatom.[6]

The C=OH$^+$ signal, which is known to be highly sensitive to electronic effects of the carbonyl substituents, shows also a linear correlation of its chemical shift with the electronegativity of X (Table).

The long range coupling $J_{2,3}$ is also related to the electronegativity of the α-heteroatom. The magnitude of this coupling through the sp^2 centre is unusually high in comparison with the same coupling in unprotonated halogenoacetones (<0·4 Hz) or in protonated aliphatic ketones (*ca.* 0·5 Hz).[1] We suggest that in the protonated halogenoacetones there is a higher contribution of the hydroxycarbonium form (I) mesomeric with the oxonium form (II); strong coupling (up to 7 Hz) through an sp^2 carbonium ion centre is well known.[7]



(I) (II)

As this study allows the direct observation of two isomers in equilibrium, one of which is internally hydrogen bonded, we believe, contrary to some earlier statements that: (*a*) the fluorine atom is not only large enough to give internal H-bonding[8] in a five-membered ring system, but is also by far the best donor atom in the halogen series, and (*b*) the chlorine atom is a better donor atom than bromine,[9] as shown by the (B):(A) ratio. The difference observed cannot be attributed to steric effects only as the van der Waals radii difference is much smaller.

(*Received, June 9th,* 1971; *Com.* 946.)

---

† All chemical shifts are relative to external Me_4Si.

[1] G. A. Olah, M. Calin, and D. H. O'Brien, *J. Amer. Chem. Soc.*, 1967, **89**, 3586.

[2] D. M. Brouwer, *Rec. Trav. chim.*, 1967, **86**, 879.

[3] A. M. White and G. A. Olah, *J. Amer. Chem. Soc.*, 1969, **91**, 2943.

[4] L. Thil and J. J. Riehl, P. Rimmelin, and J. M. Sommer, *Chem. Comm.*, 1970, 591.

[5] For a review see G. A. Olah, *Chem. Eng. News*, 1967, **45**, 76; G. A. Olah, M. A. White, and D. H. O'Brien, *Chem. Rev.*, 1970, **70**, 560.

[6] L. Pauling, 'The Nature of the Chemical Bond', Cornell University Press, 1960, p. 91; H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, 1955, **55**, 745.

[7] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. McIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, 1964, **86**, 1360.

[8] F. C. Marler and H. P. Hopkins, *J. Phys. Chem.*, 1970, **74**, 3164.

[9] P. J. Krueger and H. D. Mettee, *Canad. J. Chem.*, 1965, **43**, 2888.