

NMR STUDY :HINDERED INTERNAL ROTATION IN STABLE
PROTONATED α - HALOACETOPHENONES .

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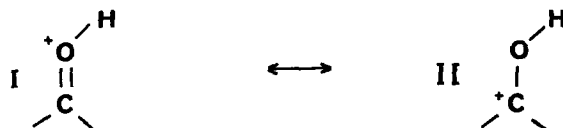
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During these last years dynamic nuclear magnetic resonance (DNMR) has been employed as a tool for estimation of the barrier to internal rotation about σ bonds possessing some π character ¹⁾. Benzaldehydes ²⁾ and acetophenones ³⁾ have received some attention but the low temperature of coalescence especially for acetophenones limited earlier studies to some compounds possessing strong releasing para substituents (p-MeO , p-dimethylamino).

The boron trihalide complexation of benzaldehydes has been shown recently ⁴⁾ to increase substantially the energy of the barrier , and stable protonation in the superacid medium ⁵⁾ increases the barrier even more drastically ⁶⁾.

Nevertheless NMR observation of protonated acetophenones showed no hindered internal rotation even at temperatures as low as - 110°C .

The strong long range coupling through the sp^2 center recently found in protonated α -haloacetones indicating a fair contribution of the hydroxy carbonium ion structure II,



in protonated α -halocarbonyls ⁷⁾, suggested this investigation of protonated α -haloacetophenones . The high barrier to internal rotation found in these compounds prompts us to publish our first results in this series .

When α -Fluoro p-Methyl Acetophenone is dissolved in the strong acid system : $SbF_5 - FSO_3H - SO_2$ at - 70°C , the nmr spectrum shows evidence for planarity of the protonated species (fig. 1) : The two ortho protons are non equivalent ($\Delta\nu = 20$ Hz) and the aromatic protons show an ACBB' pattern. The $C=OH^+$ proton appears at 13.0 ppm as a doublet ($J_{HF} = 7$ Hz), the CH_2^F protons as a doublet at 6.2 ppm ($J_{HF} = 25$ Hz) and the p-Me singlet appears at 2.8 ppm .

When the temperature is raised (fig. 2) the ACBB' pattern shows coalescence of the ortho protons at - 40°C and above - 10°C the nmr spectrum (AA'BB') is consistent with internal rotation about the C-C bond . The $C=OH^+$ proton remains a sharp doublet indicating that the free rotation at higher temperatures is not due to the deprotonation pro-

cess . The free energy of the barrier has been calculated by the Eyring rate equation ⁸⁾ at coalescence temperature and the results are summarized in Table I for a series of α -halo acetophenones . (X = F,Cl,Br,I , p-substituent = Me and Cl).

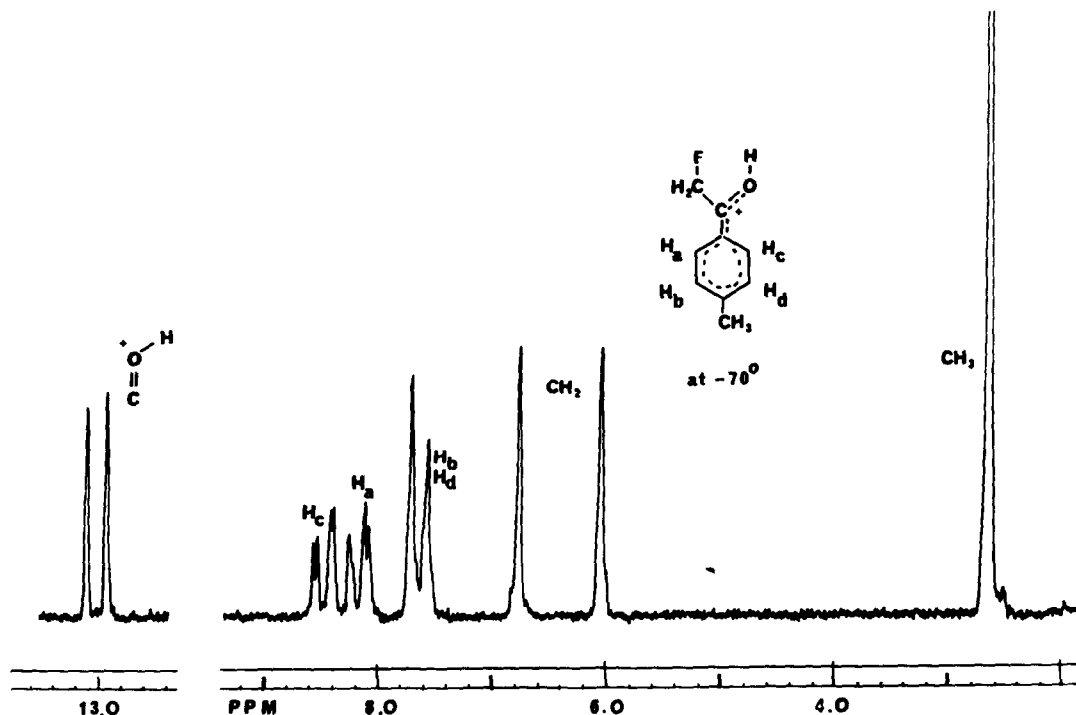


Fig. 1 . NMR spectrum of stable protonated α -fluoro p-Me acetophenone in $\text{FSO}_3\text{H} - \text{SbF}_5 - \text{SO}_2$ (the acid peak appearing at 10 ppm is omitted).

Due to the approximation made in the evaluation of ΔG_c at coalescence temperature the precision is limited to 0.5 Kcal/mole . Nevertheless we may assume that the errors in a same series are probably systematic and note that :

- a) ΔG_c is about 1 Kcal/mole higher if one replaces the p-Chlorine by a para-Methyl group.
- b) ΔG_c increases with the electronegativity of the halogen .

These results, which should be considered more as qualitative than quantitative will gain accuracy in further study when the rate of internal rotation will be evaluated in the whole temperature range by complete line shape analysis . In the same way it will be possible to know ΔH and ΔS which will shed some light on the nature of the barrier .

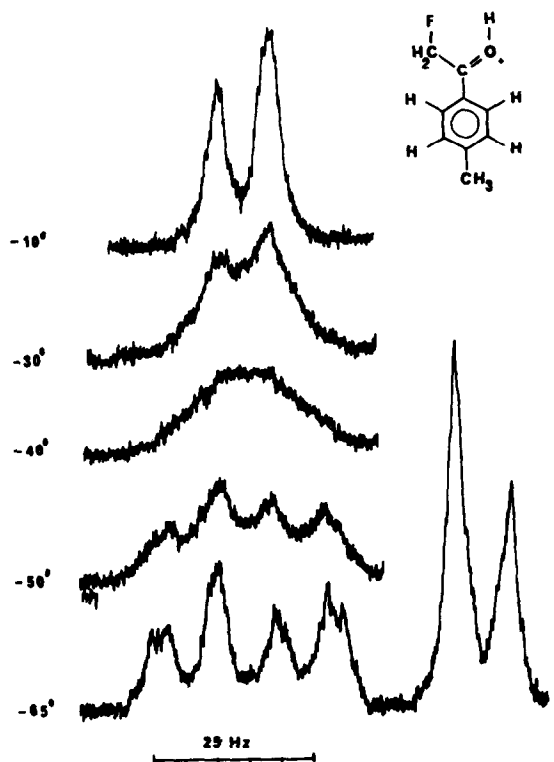


Fig. 2 . Temperature dependance of the AC protons in the stable Protonated α fluoro p-Me-acetophenone .

Table I

α - halo acetophenone	p - Me		p - Cl	
	ΔG_c	δ_{COH^+}	ΔG_c	δ_{COH^+}
F	12.45	12.93	11.28	13.40
Cl	12.42	12.70	11.20	12.70
Br	12.21	12.42	11.19	12.60
I	11.95	12.40	11.10	12.70

ΔG_c is given in Kcal/mole \pm 0.5 , δ is given in ppm from external TMS capillary .

which we intend to correlate with the Hammett's σ values and / or with the calculated basicity of these compounds. Indeed, if the charge delocalisation in the protonated species is well underlined by the chemical shifts, the nmr gives little or no information as to the relative importance of this effect if compared to the steric effects and the Hydrogen bonding of the COH^+ proton with the acidic solvent.

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