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HINDERED ROTATION OF PROTONATES OF AROMATIC ALDEHYDES.[1]

THE CHO: $^+$H PSEUDOSUBSTITUENT

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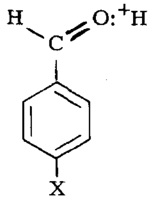
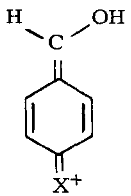
We have recently reported the formation of stable BF_3 complexes of aromatic aldehydes and some of their properties.[3] The establishment of the CHO: BF_3 group as a *pseudosubstituent* urged us to study the *protonates* of aromatic aldehydes I. We were particularly interested in finding out whether the group CHO: $^+$H may be regarded as a pseudosubstituent and to compare it with the CHO: BF_3 group.[4] A recent publication on the hindered rotation of three protonates of aldehydes[5] prompted us to report our results of the nmr spectra and the barrier to rotation about the $C_{aryl}-C_{formyl}$ bond of *para*-substituted benzaldehyde protonates. The expected relatively high barriers to rotation due to a partial π character of this bond (e.g, II) were evaluated by dynamic nmr and the heights of the barriers were found to be substituent dependent,[4] and higher than the free[6] and complexed[7] aldehydes.



I



II

An intensive study[8] of the basicity of benzaldehydes and acetophenones and of their pK_{BH^+} values has shown that the chemical shifts of the added proton of the CHO: $^+$H group correlate well with Hammetts σ^+ constants of the substituents of the aromatic ring. The Table shows our results for the chemical shifts, coalescence temperatures and ΔG^* values for seven benzaldehydes in a mixture of 90% v/v fluorosulfonic acid and 10% D_2O. The ΔG^* values at coalescence temperatures[9] were correlated with Hammetts σ^+ constants[10]; the correlation[11] (equation (1)) clearly shows that the height of the barrier is substituent dependent.[12] The ΔG^*

$$\Delta G^* = -4.86\,\sigma^+ + 14.4\,\frac{\text{Kcal}}{\text{mole}} \qquad (1)$$

$$(N = 6,\ CC = 0.940,\ STD = 0.66\,\frac{\text{Kcal}}{\text{mole}};\ \text{Slope} = -4.8)$$

values did not correlate with σ constants. Comparison of the ΔG^* values of the free,[6] BF_3-complexed[7] and the protonated aldehydes (Table) shows that the highest values are obtained for the protonates. This is probably due to the fact that the CHO: $^+$H group is the only one bearing virtually a positive charge. As an illustration the protonate of 4-methoxybenzaldehyde(anisaldehyde) exhibits an ACBB' spectrum at the probe temperature (31.5°C), its coalescence temperature is +60°C and only at +80°C an AA'BB' spectrum is obtained. On the other hand the coalescence temperature of 4-fluorobenzaldehyde protonate is −17°C. Substituting $\sigma^+ = 0.0$ for benzaldehyde protonate the ΔG^* value is estimated to be 14.4 $\frac{\text{Kcal}}{\text{mole}}$ which corresponds to a coalescence temperature of −1°C. It should be noted that the height of the barrier is concentration dependent; the higher the concentration the lower the barrier. This is probably due to the formation of associates in the strong acidic medium. The ΔG^* values at coalescence temperature of 4-methoxybenzaldehyde, 4-methoxyacetophenone and their protonates are: 9.9,[6] 6.5,[8] 17.9 and 12.0 $\frac{\text{Kcal}}{\text{mole}}$ respectively, and the corresponding values for 4-methoxybenzaldehyde-BF_3 complex and 4-methoxyacetophenone-BF_3 complex are 14.1 and 10.6 $\frac{\text{Kcal}}{\text{mole}}$ respectively. These results give an estimate of the electron withdrawing properties of the formyl groups of the free, protonated and BF_3-complexed aromatic carbonyl compounds. The nmr formyl proton chemical shifts of the aldehyde-BF_3 complexes correlated well (CC = 0.990)[11] with the formyl protons of the protonates, thus showing that the CHO: $^+$H group may be viewed as a pseudosubstituent of the aromatic ring.

TABLE: Nmr Data and Free Energies of the Barriers to Rotation in Protonated Benzaldehydes.[1]

Benzaldehyde	Chemical shift formyl proton[2]	Chemical shift aromatic protons			Coalescence temperature (°C)	ΔG^*, $\frac{\text{Kcal}}{\text{mole}}$
		ν_A	ν_B	$\Delta\nu$		
3,4,5-OCH_3	876.0		739.1		-8	14.1
4-iso-Propyl	916.1	826.1	765.1	61.0	+29	16.1
4-OCH_3	873.3		752.2[3]		+60	17.9
4-CH_3	907.1	830.1	767.2	62.9	+36	16.4
4-F	926.6		820.4[3]		-17	13.6
4-Cl	914.7	797.8	745	54.0	-11	13.9
4-Br	916.5	989.6	755.4	33.2	-9	14.0

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[1] At 100 MHz, in Hz from TMS, 0.3 M solutions in 90% v/v HSO_3F (+ 10% D_2O).

[2] At probe temperature (+31.5°C).

[3] Center of AA'BB' above coalescence.

References

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