

THE CONCENTRATION DEPENDENCE OF HYDROXYL PROTON  
MULTIPLICITY IN THE PMR SPECTRA OF THE  $\beta$ -CHLOROETHANOLS

By D. W. Slocum and C. A. Jennings\*

Department of Chemistry and Biochemistry  
Southern Illinois University, Carbondale, Illinois 62901

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Pmr studies of hydrogen bonding<sup>1</sup> have usually dealt with one of two possible phenomena: 1) the shift of hydroxyl proton absorption upon dilution with a solvent,<sup>2</sup> or 2) multiplicity of the hydroxyl proton in specially purified solvent systems<sup>3</sup>. Both of these phenomena are dependent upon a number of variables rendering comparison of independent studies difficult. This study reports simultaneous observation of the hydroxyl proton chemical shift and multiplicity changes upon dilution of a series of chloroethanols in a hydrogen bonding and a non-hydrogen bonding solvent.

The results, summarized in Table I, serve to 1) correct existing literature, 2) provide pmr evidence for intramolecular hydrogen bonding and 3) suggest that hydrogen bonding may be necessary for the observation of hydroxyl proton multiplicity.

The observation of an upfield shift of the hydroxyl proton resonance upon dilution in a non-hydrogen bonding solvent is now generally accepted to be the result of a gradual decrease in the concentration of oligomer alcohol structure with a resulting increase in the concentration of trimer, dimer and even monomer species.<sup>2c</sup> The observation of multiplicity in the hydroxyl proton resonance is less accountable and appears now to be dependent upon a number of experimental criteria. In DMSO strong hydrogen bonding between alcohol and solvent apparently reduces the proton exchange sufficiently to permit observation of the hydroxyl proton coupling.<sup>3c,d</sup> As a result, primary and secondary alcohols give well resolved triplets and doublets, respectively. In a later attempt to apply this method of classification, a number of alcohols having strong electron withdrawing substituents gave unreliable results.<sup>3g</sup> It was reported that even after treatment with carbonate the following alcohols still gave sharp singlets (s), or broad singlets (b) in DMSO: 2,2,2-trichloroethanol (s) ethyl lactate (b), 2-cyanoethanol (b) and trans-2-bromocyclo octanol (s). The authors concluded that ...

\*NASA Fellow, Southern Illinois University, 1969-1970.

"structure and perhaps geometry are important as well as electronegativity." In contrast to the reported absence<sup>3,4</sup> of hydroxyl proton multiplicity for 2,2,2-trichloroethanol in DMSO it has been reported that multiplicity was readily obtained in  $\text{CCl}_4$ <sup>5</sup>, a poor hydrogen bonding solvent.

From the experimental results summarized in Table I, it can be noted that the multiplicity of the hydroxyl proton resonance was dependent upon the concentration of alcohol in most instances. However, in DMSO ethanol exhibited triplet structure for the hydroxyl proton

Mole %	$\text{Cl}_3\text{C CH}_2\text{OH}$	$\text{Cl}_2\text{CH CH}_2\text{OH}$	$\text{ClCH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{OH}$
100	334-t (344-t)	298-bs (298-bs)	292-bs (292-bs)	309-t (309-t)
80	324-t (347-bs)	292-bs (309-bs)	290-bs (297-bs)	300-t (285-t)
66	318-t (366-bs)	287-bs (320-bs)	285-t (300-bs)	293-t (274-t)
50	308-t (390-bs)	278-bs (333-bs)	277-t (302-t)	283-t (265-t)
33	293-t (403-bs)	267-t (345-t)	266-t (306-t)	267-t (261-t)
20	271-t (411-t)	-- <sup>c</sup> (353-t)	249-t (309-t)	246-t (258-t)
10	-- <sup>c</sup> (414-t)	217-t (356-t)	-- <sup>c</sup> (310-t)	211-t (257-t)
5	208-t (415-t)	193-t (357-t)	168-t (310-t)	158-t (256-t)
2	164-t (416-t)	146-t (357-t)	153-t (311-t)	92-bs (255-t)
1	154-t (416-t)	139-t (358-t)	135-t (311-t)	57-bs (255-t)
0.5	146-t	126-t	102-t	
0.2	145-t	124-t	101-t	
a) DMSO data in parenthesis. t = triplet, bs = broad singlet.				
b) The pmr spectra reported in this study were obtained on a Varian A 56/60 Spectrometer operating at 60 MHz and 26.5°. All chemical shift values are reported as Hz downfield from TMS.				
c) Exact chemical shift not determined due to second order coupling with methylene protons.				

resonance over the entire concentration range, whereas in  $\text{CCl}_4$  this triplet collapsed to a broad singlet at concentrations below five mole percent. Introduction of chlorine atoms at

the  $\beta$ -position of ethanol produced significant variation of these observations. For the chloroethanols multiplicity was generally found only over the lower portion of the concentration range in both DMSO and  $\text{CCl}_4$ . Also for 2-chloroethanol and 2,2,2-trichloroethanol, multiplicity was obtained over a larger concentration range in  $\text{CCl}_4$  than in DMSO. In addition to 2,2,2-trichloroethanol, multiplicity over a modest concentration range was also found for ethyl lactate and 2-cyanoethanol. Traynham and Knesel<sup>3g</sup> had reported the absence of multiplicity for these alcohols in DMSO leading to the suggestion that the multiplicity criteria for alcohol classification failed for alcohols with electron withdrawing substituents. Table I shows that alcohols with electron withdrawing groups will exhibit hydroxyl proton multiplicity but over a reduced range of concentration.

Substitution of halogen at the  $\beta$ -position of ethanol affects the hydroxyl proton in two opposing directions with respect to exchange and multiplicity. The resulting increased acidity<sup>6</sup> of the hydroxyl proton should increase exchange and decrease the probability of observation of multiplicity whereas the increased opportunity for internal hydrogen bonding<sup>7</sup> with the halogen should diminish exchange and increase the probability of observation of multiplicity. Only in DMSO would the solvent be expected to compete effectively at lower concentrations with the internal halogen for hydrogen bonding with the hydroxyl proton.

From the observation that multiplicity for the chloroethanols was observed over a greater concentration range in  $\text{CCl}_4$  than in DMSO it appears that the increased chance of internal hydrogen bonding may outweigh the increase in acidity of the hydroxyl proton. In DMSO, since internal hydrogen bonding would not be expected to compete with the stronger solute-solvent interactions, the increased acidity factor assumes prime importance in increasing exchange. Hence it seems logical that at least over the higher portion of the concentration range in DMSO multiplicity of the hydroxyl proton would not be detectable. In  $\text{CCl}_4$ , however, weak solute-solvent interactions apparently do not compete with the internal hydrogen bond interaction and exchange is less probable; hence, multiplicity is observed over a larger concentration range.

These studies corroborate the conclusions reached by ir studies,<sup>7</sup> namely, that dilute solutions of the chloroethanols exist mostly in a conformation that permits an intramolecular hydrogen bond. The pmr technique of identifying alcohols<sup>3</sup> now must consider conformational and dilution factors and perhaps can safely ignore electronic factors. Moreover, these observations lead to the conclusion that intramolecular hydrogen bonding diminishes hydroxyl

proton exchange and such interaction is characterized by the increased probability of observation of hydroxyl proton multiplicity.

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