

1,1'-Oxydiethanol in Aqueous Solution

By G. SOCRATES

(Department of Polymer Science and Technology, Brunel University, Acton, London, W.3)

Summary 1,1'-Oxydiethanol has been directly observed by n.m.r. spectroscopy in acidic aqueous solutions of acetaldehyde.

THE presence of 1,1'-oxydiethanol in aqueous solution has been detected by ^1H n.m.r.

acetaldehyde, of course, exhibit not only n.m.r. signals of acetaldehyde but also of 1,1-dihydroxyethane. In the presence of acid catalyst, these signals are broadened due to the fast reversible hydration. However, for aqueous solutions rich in acetaldehyde, the hydrate signals are sharper^{2,3} than predicted by theoretical calculations of

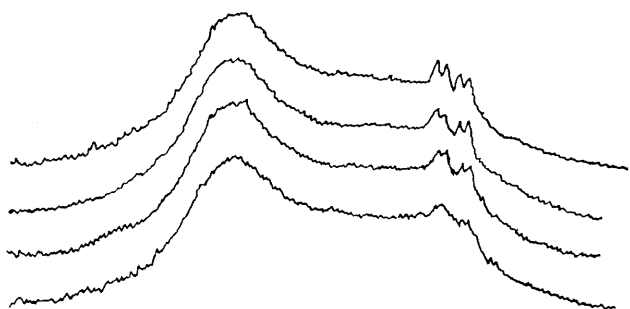


FIGURE 1. Time-dependence of spectra, the new doublet's appearance being clearly observed in 2.5 M-acetaldehyde with $4 \times 10^{-2}\text{M}$ hydrochloric acid.

The reversible hydration of carbonyl groups to form *gem*-diols is well known. Recently Bell¹ published a comprehensive review of the subject. The reversible hydration of acetaldehyde to form 1,1-dihydroxyethane has been found to be anomalous. Aqueous solutions of

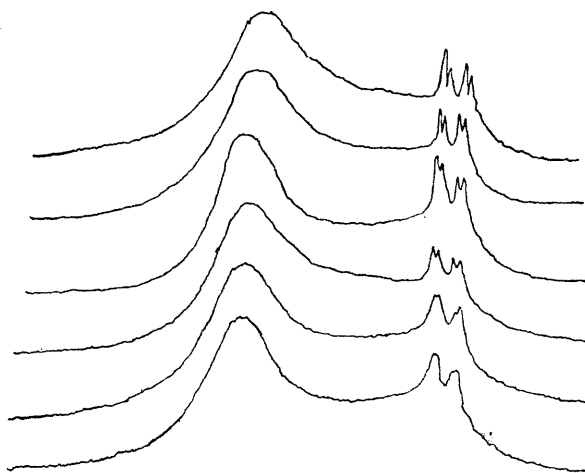
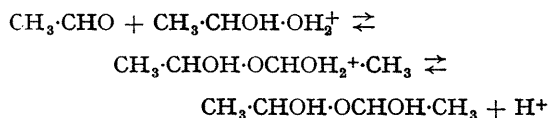


FIGURE 2. Time-dependence of spectra, the new doublet's appearance being clearly observed in 5.3 M-acetaldehyde with $6 \times 10^{-2}\text{M}$ hydrochloric acid.

spectra.⁴ To explain the anomalous hydration of acetaldehyde, Ahrens and Strehlow³ postulated the formation of a hemihydrate, 1,1'-oxydiethanol.



The methyl doublets of acetaldehyde and 1,1-dihydroxyethane were found to be at 2.27 and 1.34 p.p.m., respectively, using the sodium salt of 3-trimethylsilylpropanesulphonic acid as an internal standard. The respective coupling constants were also measured and found to be 2.84 and 5.4 Hz. The solutions of acetaldehyde with hydrochloric acid were prepared and examined immediately. The spectra were observed to be time-dependent, the changes

which occurred being complete in about 10 min. Under conditions of good resolution, an additional doublet was observed to appear with time in the region of the methyl resonance of 1,1-dihydroxyethane. The chemical shift and coupling constant of this doublet were found to be 1.37 p.p.m. and 5.2 Hz., respectively. Typical examples of spectra exhibiting these changes are those of 2.5M-acetaldehyde with 4×10^{-2} M-hydrochloric acid and of 5.3M-acetaldehyde with 6×10^{-2} M-hydrochloric acid (Figures 1 and 2).

The new signals may be attributed to the methyl resonance of 1,1'-oxydiethanol. According to Shoolery's rules,⁵ the methyl resonance of 1,1'-oxydiethanol would be expected to be in the region of the hydrate methyl resonance which is at 1.34 p.p.m. There is evidence that formaldehyde, dichloroethanal, and fluoral also form similar hemihydrates.⁶

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⁶ S. Bezzi, N. Dallaporta, G. Giacometti, and A. Ilicato, *Gazzetta*, 1951, **81**, 915; P. Skell and H. Suhr, *Chem. Ber.*, 1961, **94**, 3317; K. Moedritzer and J. R. Van Wazer, *J. Phys. Chem.*, 1966, **70**, 3025; M. Natterer, *Monatsh.*, 1882, **3**, 449.