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LOW TEMPERATURE ^{I}H NMR SPECTRA OF ASSOCIATED n-BUTANOL IN SOLUTION

N.S.GOLUBEV,S.F.BUREIKO and G.S.DENISOV

Institute of Physics,Leningrad State University,Petrodvorets,
I Maya IOO,Leningrad I98904,USSR

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ABSTRACT

^{I}H NMR spectra of solutions of n-butanol,$C_3D_7CH_2OH$, / IO^{-3} - IO^{-I} M / in a freon mixture,CDF_3+CDF_2Cl+$CDFCl_2$,have been obtained at 85-IOO K.The spectra proved not to depend on concentration and consist of two spin multiplets,a triplet /I:2:I/ and a quintet /I:3:4:3:I/.The conclusion has been drawn that under these conditions only one cyclic polimer with fast degenerated multiple proton transfer exists in the solutions.

INTRODUCTION

Association of alcohols in inert solvents is one of the most difficult problems of hydrogen bonding.On the basis of IR and NMR data,different authors proposed various schemes of equilibria in solutions,e.g.:cyclic dimers and open higher polimers [I-4]; open dimers and higher polimers of different types [5,6];cyclic trimers only [7-9];open dimers and cyclic tetramers [IO-I2]. /The latter is now considered as the most realistic model/.It is generally accepted that pure liquid alcohols consist of long open chains,which may account for their dielectric properties [I3]. Earlier NMR investigations were carried out by analysis of concentration and temperature dependencies of the averaged OH-proton chemical shift. In [I4-I7] we have shown that, at temperature as low as 80-I00 K, lifetimes of H-bonded complexes become large enough for the signals belonging to all kinds of complexes involved and a monomer to be observed separately. This makes the investigation of H-bonding equilibria similar to that carried out by means of optical spectroscopy, with the interpretation of NMR spectra being much easier.

In the present paper ^IH NMR spectra of self-associated n-butanol in a freon mixture, CDF +CDF_2Cl+$CDFCl_2$ /2:4:I/, liquid and of low viscosity down to 80 K, are reported. Two isotopic species of n-butanol, $C_3D_7CH_2OH$ and C_4D_9OH were used.

EXPERIMENTAL

The freons were obtained as described in [I8] and purified by repeated vacuum low temperature distillation. The technique of preparing samples for low temperature NMR in liquified gases was reported earlier [I8]. The spectra were recorded by a JEOL C-60 HL instrument / 60 MCps/ with TMS as an internal lock. Temperature in the region 80-I00 K was maintained and measured with accuracy ± I K. The concentration of butanol was varied in the range IO^{-3} - IO^{-I} M /these limits are determined by the sensitivity of the spectrometer and the solubility of n-butanol at 80 K/.

RESULTS AND DISCUSSION

^IH NMR spectra of thoroughly purified liquid $C_3D_7CH_2OH$ at 200-300 K /Fig.I,a/ consist of a doublet belonging to CH_2-protons / δ =3.60 ± 0.05 ppm, J=4.7 ± 0.I Cps / and an OH-triplet, with chemical shift of the latter strongly depending on temperature. Since proton exchange between OH-groups is unmeasurably slow

/which may be proved by spin-spin coupling/,slow molecular exchange would give rise to a separate high field signal of free terminal OH-groups./Indeed,in Raman spectra of liquid butanol the corresponding narrow ν_{OH} band may be observed even at 200 K/. So,there is no doubt that under these conditions the OH-multiplet is averaged;it belongs to the molecules in the state of rapid exchange between different polimer chains.

Diluting the alcohol with inert solvents /like hexane,CCl_4 or freons/ results in disappearance of the coupling.This effect might well be accounted for by some acidic impurities present in the solvents and accelerating proton exchange.There is,however, another explanation [I9] involving cyclic polimers as intermediates of the reaction.Formation of such cycles from long open chaines composing pure liquid alcohols must be extremely unfavourable in terms of free energy.

The fine structure in the spectrum of strongly diluted $C_3D_7CH_2OH$ appears at the temperature as low as 95 K / Fig.I,b /. However,the spectrum cannot be treated in terms of a simple A_2X system,which holds for the liquid alcohol.The spectrum of another isotopic species,C_4D_9OH,consist of a single line / δ =6.4 ±0.I ppm, Fig.I,c /.Thus,the components of the OH-multiplet for $C_3D_7CH_2OH$ cannot be attributed to non-equivalent protons,the splitting is due to spin-spin coupling.The spectrum reveals no changes in the concentration range IO^{-3} - IO^{-I} M.The dilution does not lead to any new signals,and no shift of the OH-multiplet is seen.This implies that only one complex is present in the solution.An alternative explanation,i.e.,equilibrium between several associates with their spectra absolutely coinciding seems to be unlikely.Indeed,this would require chemical shifts of OH-protons to coincide to the accuracy more than ± 0.2 per cent 6/as compared with the total chemical shift from the monomer,ca.

7 ppm [7] /.

The spin-spin structure of the signals / Fig.I,b / can be explained on the assumption of fast degenerated transfer of all the OH-protons in a polimer:

$$\ldots\mathrm{OH}\ldots\mathrm{OH}\ldots\mathrm{OH}\ldots \xrightleftharpoons{k} \ldots\mathrm{HO}\ldots\mathrm{HO}\ldots\mathrm{HO}\ldots$$

with $k=\tau^{-I} > 2\pi J=30$ Cps.The analysis of the spin density matrix [20] shows that,in the case of fast degenerated exchange,the A_2X spin system would be transformed into $A_2A_2'XX'$ / $J_{AX}=$ I/2 J; $J_{AA'}=J_{XX'}=0$/.The first order spectrum of the system consists of a triplet with intensity ratio I:2:I and a quintet I:3:4:3:I. Earlier,similar transformation of AX into $AA'XX'$ was reported [2I,22] for the degenerated double proton transfer inside a porphyrinic cycle with four equivalent ^{I5}N nuclei,and in [I5,23] for the cyclic dimer of formic acid.It seems likely that the multiple concert proton transfer is accomplished by tunnelling [24].

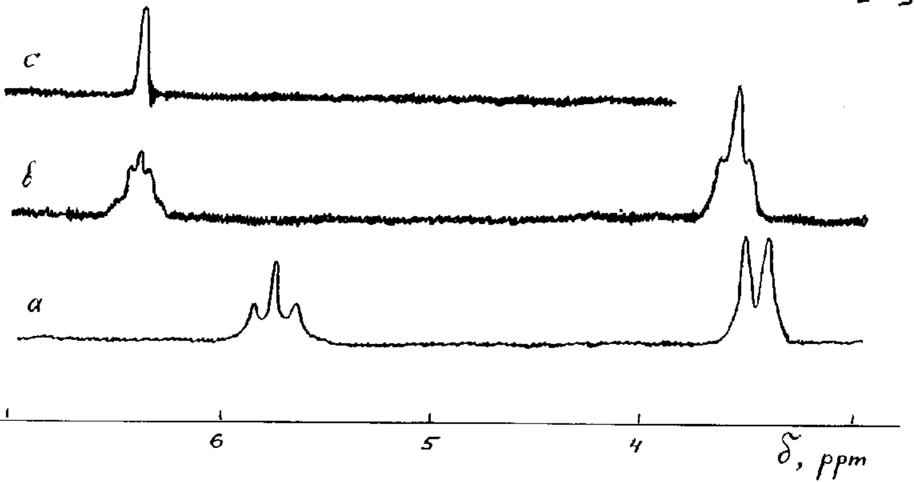
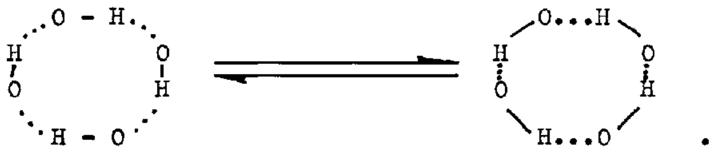


Fig.I. ^{I}H NMR spectra of pure liquid $C_3D_7CH_2OH$ at 220 K / a /, and of solutions containing 0.005 M $C_3D_7CH_2OH$ / b / and C_4D_9OH / c / in the freon mixture at 90 K.

It is to be emphasized that the spectrum / Fig.I,b / may be attributed only to a cyclic polimer.Indeed,the protons involved in an open chain would be non-equivalent.Even neglecting this fact / which may be reasonable for very long chains /,multiple proton transfer in a chain could not be degenerated,as the bipolar structure for low-polar media like freons must be unfavourable in terms of thermodynamics:

$$OH\dots OH\dots OH \not\rightleftharpoons O^{-}\dots HO\dots HOH^{+}\ .$$

Unfortunately,low temperature ^{I}H NMR is incapable of discerning cyclic trimer,tetramer and higher polimers.But bearing in mind the evidences [IO-I2],the supposition can be made that in diluted solutions at low temperature only cyclic tetramers exist in the solutions of n-butanol in inert solvents:



This may not hold for the system under different conditions /room temperature and concentrated solutions/.But it seems very likely that formation of some amount of similar cyclic complexes with fast multiple degenerated proton transfer is responsible for the acceleration of proton transfer on diluting alcohols.

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