

STRUCTURE OF THE COMPLEXES OF FORMIC ACID WITH BUTANOL

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ABSTRACT

The interaction between formic acid (AH) and n-butanol (BH) in strongly diluted solutions has been studied by means of ^1H NMR and IR spectroscopy over the temperature range from 300 down to 80 K. A simple complex, $\text{AH}\cdot\text{BH}$, its cyclic dimer, $(\text{AH}\cdot\text{BH})_2$, as well as another cyclic complex, $\text{AH}\cdot(\text{BH})_2$, have been found to be in equilibrium. The 12-membered cyclic dimer, $(\text{AH}\cdot\text{BH})_2$, appeared considerably stable, being the only complex present in the solutions at 80 K. The rate of the degenerated multiple proton transfer inside the complex has been estimated to be higher than 10^5 s^{-1} at 80 K.

INTRODUCTION

A degenerated process of multiple proton transfer inside cyclic complexes with several hydrogen bonds (H-bonds) has often been considered as a stage of intermolecular proton exchange {1 - 10}. The possibility of the transfer to proceed through the tunneling effect has been extensively discussed {9 - 13}. In the case of strongly H-bonded symmetric systems, the low temperature limit of the rate, τ^{-1} , can be rather high. Thus, theoretical calculations {12} gave $\tau^{-1} \approx 10^7 \text{ s}^{-1}$ for the double proton transfer in formic acid dimer, with the potential energy barrier being less than 20 kcal per mole {13}. This estimate seems to agree with the experiment. Microwave evidence {11} has shown the upper limit for the τ^{-1} value not to exceed 10^{12} s^{-1} . On the other hand, low temperature NMR demonstrated {14, 15}, that the frequency of the double proton transfer in $(\text{HCOOH})_2$ must be higher than 10^3 s^{-1} even at 80 K, while the intermolecular proton exchange between the dimers proceeds slowly enough at the temperature as high as 130 K, being determined by dissociation of the dimers. Their life-time under these conditions was measured to be more than 1 s {4}.

The double proton transfer remains fast ($\tau^{-1} > 10^5 \text{ s}^{-1}$ at 80 K) even in the case of a strongly asymmetric cyclic dimer involving trimethylacetic and trifluoroacetic acids [16], where one of the two H-bonds was evaluated to be rather weak (about 3.2 kcal per mole). Only for weakly H-bonded systems involving NH...N hydrogen bonds, the process may become slow enough to be measured by NMR. There is some evidence for the tunneling mechanism of the process. Thus, the low temperature limit (5 s^{-1}) has recently been reported [17 - 19] for the rate of the simultaneous proton migration inside porphyrinic cycles.

Intermolecular proton exchange between carboxylic acids and alcohols has been widely examined [5 - 10, 19 - 21], under various conditions using different techniques. Most of the papers postulated cyclic complexes as intermediates of the reaction. Some of the complexes turned out to be stable enough for their IR spectra to be obtained. It was found [22 - 25], that strong carboxylic acids interact with alcohols in dilute solutions to give two types of complexes, $\text{AH}\cdot\text{BH}$ and $\text{AH}\cdot(\text{BH})_2$:



For the latter, the possibility of a cyclic structure with three H-bonds cannot be neglected. In [26] the IR spectra of an equimolar mixture, $\text{CF}_3\text{COOH} + \text{C}_4\text{H}_9\text{OH}$, have been recorded at successive stages of diluting the solution with CCl_4 . Strong self-association of the $\text{AH}\cdot\text{BH}$ complexes, having a proton-donor and a few proton-acceptor functions, has been detected. Various kinds of self-associates, both of open-chain and cyclic types, have been discussed.

The aim of the present paper was to obtain information concerning multiple proton transfer in cyclic complexes with more than two H-bonds. With this view in mind, we examined a carboxylic acid-alcohol system in strongly diluted solutions in inert solvents at low temperature (down to 80 K). Under these conditions, one would expect cyclic type of complexes to predominate. In previous papers [27,28] we demonstrated the advantage of low temperature NMR in liquified gases for investigation of multiple H-bonded complexes. At 80 - 100 K, intermolecular exchange processes are usually slow enough for unaveraged signals, belonging to all the non-equivalent OH-protons in different complexes to be observed separately. The spin-spin structure of the signals allows to obtain information about the rate of the degenerated proton transfer.

EXPERIMENTAL

^1H NMR spectra (60 MCps, a C-60 HL JEOL instrument) of solutions containing HCOOH and $\text{C}_4\text{D}_9\text{OH}$, were obtained in a liquid mixture, $\text{CDF}_3 + \text{CDF}_2\text{Cl} + \text{CDFCl}_2$ (2:4:1), of low viscosity down to 80 K. Formic acid was chosen because of a high proton spin-spin coupling value ($J_{\text{HH}} = 12$ Cps, {14}). In addition, IR spectra were recorded over the same temperature range. Butanol, $\text{C}_4\text{D}_9\text{OH}$, (99.3 % isotopic purity) was repeatedly distilled under low pressure at -30°C . The experimental technique of low temperature NMR spectroscopy, in liquified gases, as well as the procedure of obtaining and purifying the solvents used, has been reported in {28}.

RESULTS AND DISCUSSION

Fig. 1. represents the IR spectra of strongly diluted solutions of HCOOH in the spectral region from 1600 to 1800 cm^{-1} , where the absorption resulting from $\text{C}=\text{O}$ stretching vibrations ($\nu_{\text{C}=\text{O}}$) usually appears. The spectrum consists of the bands, 1756 and 1726 cm^{-1} , belonging to the monomer and the cyclic dimer, respectively. The addition of an equimolar amount of butanol does not affect the spectrum, though its excess does lead to a new band, 1733 cm^{-1} , which might be attributed (in accordance with {23}) to the $\text{AH}\cdot\text{BH}$ complex. Increasing the excess, as well as lowering the temperature, results in one more band, 1714 cm^{-1} , to appear. At the temperature as low as 200 K, this band is the only feature (over the region mentioned above) for the solution containing two $\text{C}_4\text{D}_9\text{OH}$

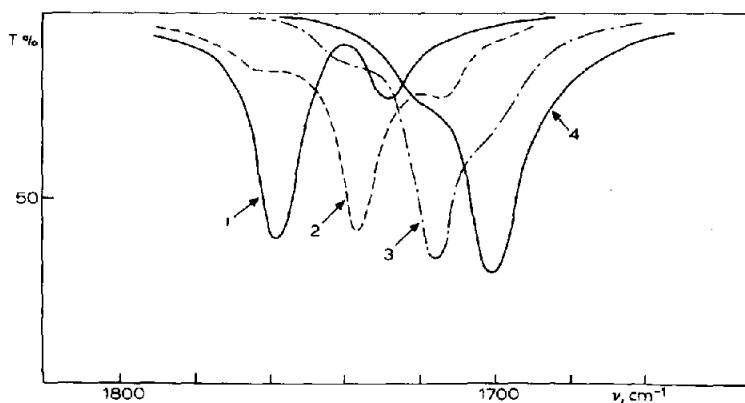
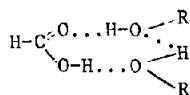


Fig. 1. IR spectra of a solution, containing $2 \cdot 10^{-3}$ M of HCOOH and $4 \cdot 10^{-3}$ M of $\text{C}_4\text{D}_9\text{OH}$, at 300 K (1), 240 K (2), 180 K (3), and 100 K (4).

molecule per one HCOOH molecule. The region, $3300 - 3700 \text{ cm}^{-1}$, shows no sharp band, which could be attributed to the stretching vibration of a "free" O-H vibrator, nor does it include any bands of butanol, monomeric or self-associated. This suggests the $\text{AH}\cdot(\text{BH})_2$ complex to be the only molecular form present in the solution under these conditions, all O-H vibrators of the complex being involved in H-bonding:



The existence of such complexes had been postulated by Grunwald {5} in analyzing the kinetics of intermolecular proton exchange in binary mixtures of carboxylic acids with alcohols. (It is to be noted, however, that the $\text{AH}\cdot(\text{BH})_2$ complex should not necessarily retain the cyclic structure when heated up to room temperature.)

With lowering temperature down to 150 K, the $\nu_{\text{C}=\text{O}}$ band of the $\text{AH}\cdot(\text{BH})_2$ complex, 1714 cm^{-1} , decreases in intensity in favour of a new band, 1700 cm^{-1} . At 80 - 120 K this feature remains alone in this spectral region. The band has to be ascribed to a third kind of complexes, which will be referred to as $(\text{AH}\cdot\text{BH}_2)$. (Experimental evidence for this formula will be given elsewhere). The $(\text{AH}\cdot\text{BH})_2$ complex can be characterized also by another feature, 1224 cm^{-1} ,

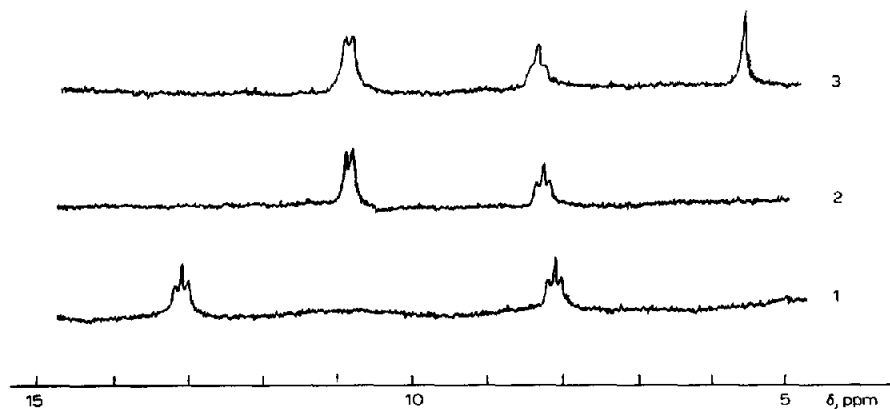
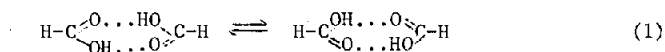


Fig. 2. ^1H NMR spectra (60 MCps, 80 K, a freon mixture as a solvent) of the solutions, containing $2 \cdot 10^{-3}$ M of HCOOH and $\text{C}_4\text{H}_9\text{OH}$ at the concentrations: 0.0 (1), $2 \cdot 10^{-3}$ M (2), and $4 \cdot 10^{-3}$ M (3).

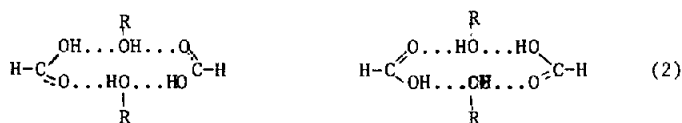
arising instead of the ν_{C-O} band, 1107 cm^{-1} , belonging to the monomer. The form of the vibration includes the stretching of the C-O bond and the "in plane" bending of the C-O-H valency angle. The involvement of the latter co-ordinate accounts for a high-frequency shift of the band when HCOOH forms an H-bond as a proton donor. In the cyclic $(\text{HCOOH})_2$ dimer the frequency of the vibration is 1210 cm^{-1} , for the AH·BH complex, this value was found to be 1175 cm^{-1} . One may say that in the $(\text{AH}\cdot\text{BH})_2$ complex the H-bonds, formed by HCOOH molecules, are likely to be stronger than those in $(\text{HCOOH})_2$.

The frequency of the "out of plane" bending vibration of the C-O-H angle, giving rise to the 600 cm^{-1} vibrational band of the monomer and 925 cm^{-1} of the dimer, for the $(\text{AH}\cdot\text{BH})_2$ complex is as high as 980 cm^{-1} , which implies a considerable increase in the H-bonding strength compare to that in $(\text{HCOOH})_2$ {29}.

^1H NMR spectrum of a diluted HCOOH solution in a freon mixture at 80 K consists of two triplets, $\delta = 13.1$ and 8.0 ppm, $J_{\text{HH}} = 6.0$ Cps. As shown in {14}, the spectrum corresponds to the cyclic dimer with the degenerated double proton transfer going on too fast in the NMR time scale:



If the process were hindered, the two signals would be doublets, for each of the OH-protons would be coupled with only one of the two CH-protons. On addition of an amount of butanol, The OH-signal of the dimer, $\delta = 13.1$ ppm, decreases in intensity, and another signal, $\delta = 10.7$ ppm, appears. The spectrum of the solution, containing the equimolar amounts of HCOOH and $\text{C}_4\text{D}_9\text{OH}$, consists of a doublet, $\delta = 10.7$ ppm, and a triplet, $\delta = 8.1$ ppm, $J_{\text{HH}} = 6.0$ Cps, with the integrated intensity ratio 2:1. Such a spectrum can well be consistent with a cyclic dimer of the AH·BH complex, i.e., the complex, suggested above, $(\text{AH}\cdot\text{BH})_2$, provided all the four protons transferred simultaneously and rapidly:



This condition satisfied, each of the OH-protons is now coupled with one of the CH-protons, while each of the CH-protons interacts with two OH-protons simultaneously.

To estimate the lower limit for the rate of the multiple proton transfer in the $(\text{AH}\cdot\text{BH})_2$ dimer, the difference in chemical shifts between the non-

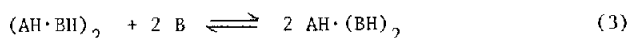
equivalent OH-protons is to be found. It has just been mentioned, that two of the four H-bonds, involved in the 12-membered cycle, must be stronger than those in the 8-membered cycle, $(\text{HCOOH})_2$.

Thus, the chemical shift of the acidic OH-protons is certain to be higher than 13 ppm. The other two H-bonds appear to be close (in terms of energy) to that in the complex of butanol with methylformiate, HCOOCH_3 , where the chemical shift under equal conditions was measured as 7.2 ppm. The difference in question would then be of about 6 ppm, which would give (as it was made in {16}) the following estimate:

$$\tau^{-1} > 10^5 \text{ s}^{-1} \text{ at } 80 \text{ K.}$$

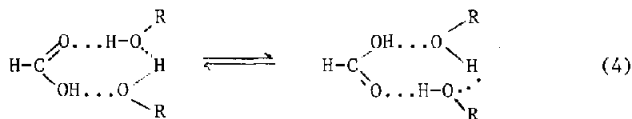
It is not impossible, though, that mutual influence of all the H-bonds, involved in the cycle, could result in decreasing the difference as compared to 6 ppm. Our estimate in this case may have to be weakened.

Addition of a small excess of $\text{C}_4\text{D}_9\text{OH}$ to the solution, containing $(\text{AH}\cdot\text{BH})_2$, at 80 K gives rise to another signal, $\delta = 5.6$ ppm, which should be ascribed to the self-associated alcohol. (The same signal can be observed in the spectrum of solutions, containing nothing but $\text{C}_4\text{D}_9\text{OH}$, in the freon mixture.) So the $(\text{AH}\cdot\text{BH})_2$ complex is not able to bind up an additional $\text{C}_4\text{D}_9\text{OH}$ molecule. The equilibrium



at 80 K is strongly shifted to the left, in accordance with the above IR data. The fact that the cooling of the solution leads, first, to formation of the $\text{AH}\cdot(\text{BH})_2$ complex and, then, to its dissociation into $(\text{AH}\cdot\text{BH})_2$ and B, being unusual, needs some explanation. The dissociation (3) is, beyond doubt, followed by increase in entropy. If it were exothermic, no marked amount of $\text{AH}\cdot(\text{BH})_2$ could be observed at any temperature. In the case of endothermic dissociation (3), cooling would bring out monotonously rising concentration of $\text{AH}\cdot(\text{BH})_2$. It should, however, be taken into account, that at room temperature butanol is mainly monomeric, while at 80 K it is completely associated. Therefore, at a certain temperature, the sign of the enthalpy (3) may reverse, thus making the reaction (3) go backwards.

The equilibrium (3) being strongly shifted to the left makes it impossible to estimate the rate of a hypothetical triple proton transfer in the $\text{AH}\cdot(\text{BH})_2$ complex:



Indeed, at about 200 K, when the vibrational band, 1714 cm^{-1} , indicating the complex, can be observed, NMR spectra appear to be of little use, since they contain no more than one averaged OH-signal.

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