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Spontaneous cyclo-trimerization of propionaldehyde in aqueous solution

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ABSTRACT

The equilibrium between propionaldehyde + propane-1,1-diol + 2,4,6-triethyl-1,3,5-trioxane has been characterized, for the first time, in aqueous solution using NMR techniques. The diffusion coefficients and the molar percentages at different temperatures have been also reported.

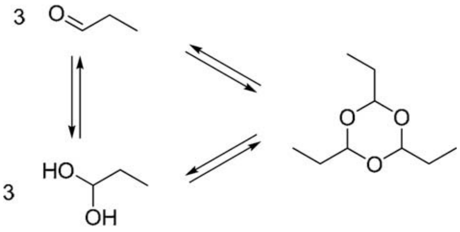
1. Introduction

1,3,5-Trioxanes have many applications in different fields of chemical industry, for example, as constituents of a stabilizing solution in color photography, as burning regulators in fumigants, as carriers for insecticides, and as the basis for many polymers and copolymers.[1] 1,3,5-Trioxanes could be formed by cyclo-trimerization of aldehydes like acetaldehyde, propionaldehyde, isobutyraldehyde, isovaleraldehyde, and 4-tert-butylbenzaldehyde.[2] There are a large number of efficient catalysts for this reaction.[3]

Although 1,3,5-trioxanes have been widely characterized and studied in synthetic purposes, their participation in the aqueous equilibrium formed between aldehydes and gem-diols only is described in the case of formaldehyde and acetaldehyde.[4]

The formation of *gem*-diols by reversible hydration of the carbonyl group of ketones and aldehydes is well known.[5] As well, from a chemical engineering point of view it was studied the solubility of trioxane in water[6] and the vapor-liquid equilibrium of the binary system trioxane + water and the ternary system formaldehyde + trioxane + water.[7]

The purpose of the present study was to investigate, by different Nuclear Magnetic Resonance (NMR) techniques, the possible coexistence of propionaldehyde, propane-1,1-diol, and 2,4,6-triethyl-1,3,5-trioxane when propionaldehyde is dissolved in D_2O (Scheme 1). NMR is the most powerful and widely utilized technique for determining molecular structure. Pulsed gradient spin-echo (PGSE) diffusion NMR spectroscopy was developed to measure diffusion coefficients and deduces the hydrodynamic radii of molecules in solution.[8] In 1992, C. S. Johnson included the PGSE sequence in a two-dimensional NMR experiment in which one dimension represents the regular chemical shift information and the second dimension separates species by particle size.[9] This 2D experiment is now referred to as diffusion-ordered NMR spectroscopy (DOSY). After discovering the benefits of DOSY, it is easy to appreciate why one polymer chemist has called this technique ‘chromatography by NMR’ since NMR spectra of individual components of a complex mixture are easily resolved based upon their diffusion properties.[10]



Scheme 1.

We have used ^{1}H NMR, ^{13}C NMR, COSY, TOCSY, and DOSY experiments to confirm for the first time the existence of trioxane in solution and we have studied the influence of temperature on the equilibrium of the three species in solution.

The initial purpose of the present study was to investigate the influence of temperature on the equilibrium of the hydration of propionaldehyde by ^{1}H-NMR. The spectrum of propionaldehyde 0.5 M in D_2O, at 25 °C (Fig. 1), consists of a singlet at 9.70 ppm, a multiplet at 2.57 and a triplet at 1.06. From consideration of inten-

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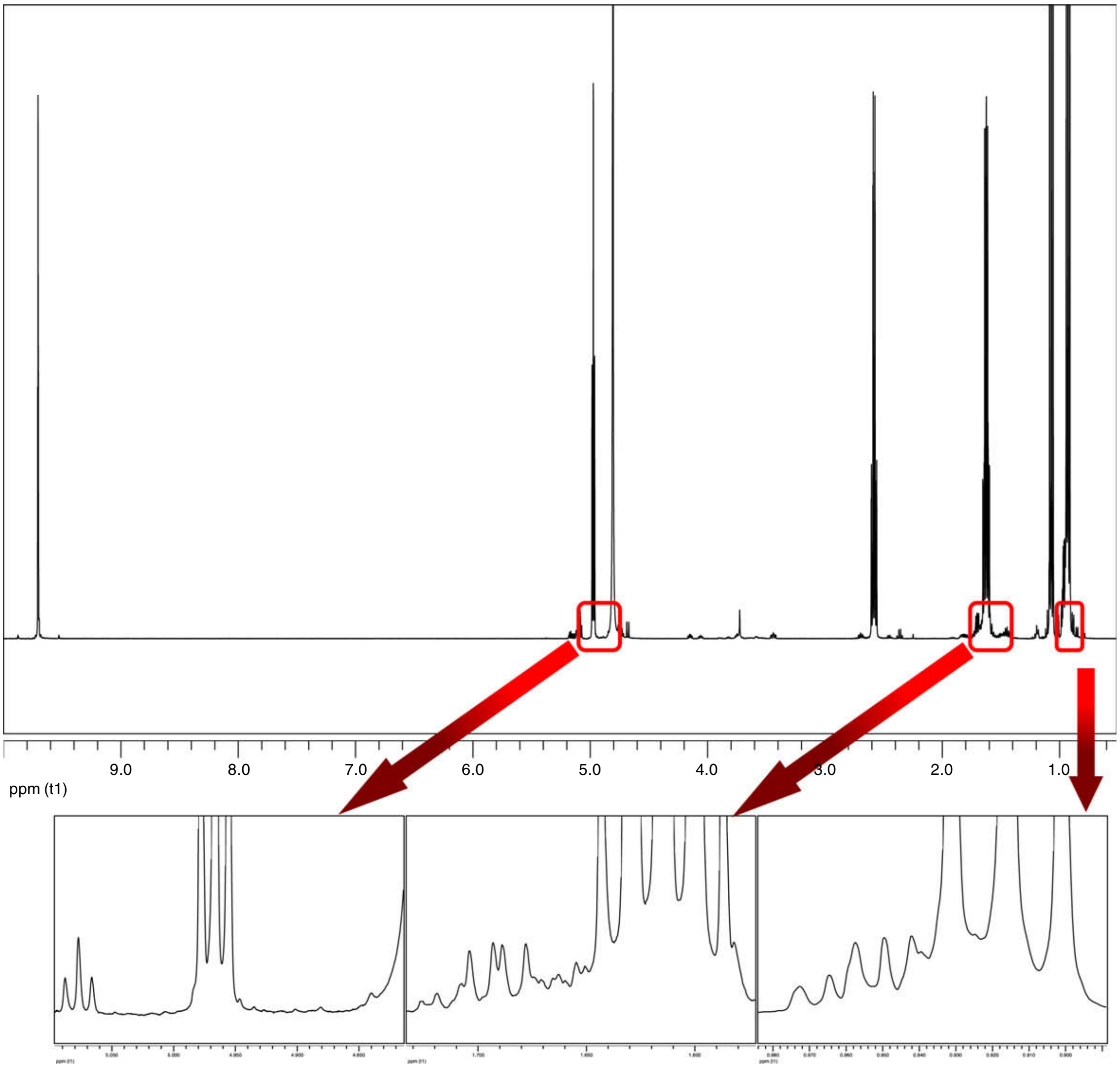


Figure 1. ^{1}H NMR spectrum of propionaldehyde 0.5 M in solution at 25 °C.

sities, chemical shifts, and coupling constants, these resonances may be assigned to the aldehydic, methylene, and methyl proton resonances, respectively.

The additional signals, a triplet at 4.97 (J = 5.5 Hz), a complicated multiplet at 1.61, and a triplet at 0.91 may be assigned to methine, $CH(OH)_2$, methylene and methyl protons of the hydrate of propionaldehyde, propane-1,1-diol. This is consistent with the assignments given to the NMR spectra of aqueous solutions of propionaldehyde.[4] Surprising, we found 3 more signals with low intensity at 5.08 (triplet, J = 5.4 Hz), 1.69 (multiplet) and 0.96 (triplet).

The influence of the temperature on the ^{1}H-NMR signals shows that for low temperature (T < 15 °C) there is a significant spectral overlap with the D_2O proton resonance at 4.8 ppm. Increasing the temperature allow us to distinguish two signals. One of them corresponds to methylene ($CH(OH)_2$) of the gemdiol. The other signal corresponds to a different molecule. Experimental ^{13}C NMR signals at 102.3 ppm, 25.8 ppm, and 7.6 ppm obtained for trioxane are in good agreement with those reported in the literature.[3i]

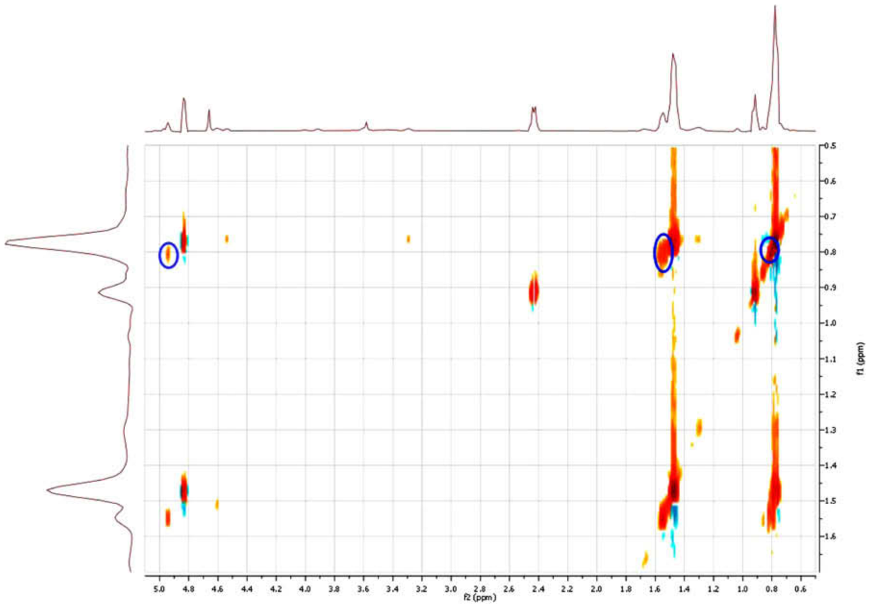
From the COSY and TOCSY experiments (Fig. 2) we can confirm that the three new signals are from the protons of the same molecule, that is, there must be present a third substance in solution.

Kurt Moedritzer and John R. Van Wazer in 1966,[11] observed that when anhydrous formaldehyde was dissolved in deuterium oxide, four to five peaks (plus a generally small resonance due to trace amounts of H_2O) appeared in the proton nuclear magnetic resonance spectrum. From the relative areas of these methylene resonances, one of which is due to trioxane, two equilibrium constants completely describing the system were calculated.

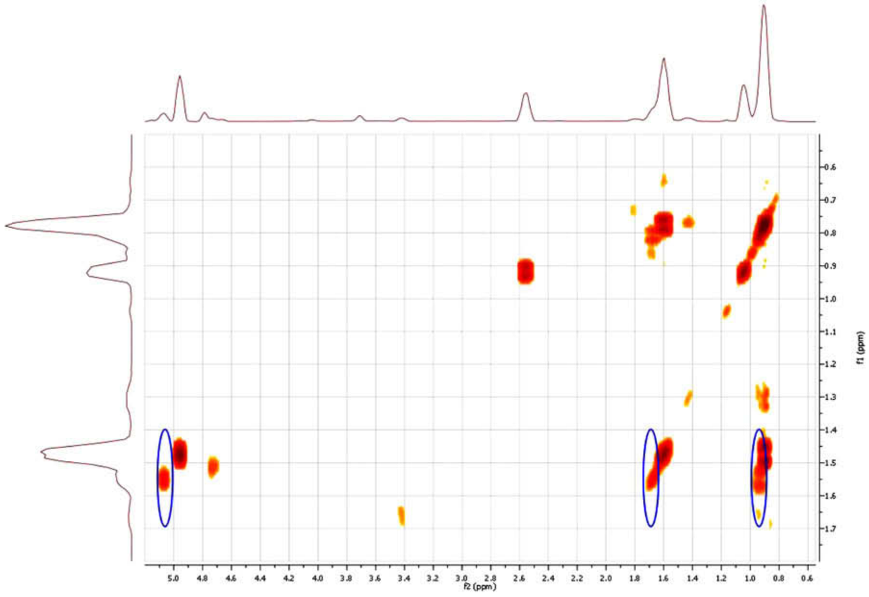
Diffusion ordered spectroscopy (DOSY) relies on differences in translation diffusion as a means to separate components in a solution mixture. We performed DOSY experiments at 25 °C to confirm the coexistence of the three substances in solution. In addition the diffusion of the signals that corresponds with the new molecule corresponds with the lowest diffusion coefficient. We obtained a mean diffusion values (D in $cm^2\ s^{-1}$) of 1.12×10^{-5} for the propionaldehyde, 8.11×10^{-6} for the propane-1,1-diol, and 5.52×10^{-6} for the 2,4,6-triethyl-1,3,5-trioxane (Fig. 3).

Repeating the influence of temperature (between 5 and 50 °C) at different concentrations of propionaldehyde all the obtained results are compatible. From the integrals of the ^{1}H NMR spectra at each temperature the relative concentration of propionaldehyde, propane-1,1-diol, and 2,4,6-triethyl-1,3,5-trioxane were obtained.

The aqueous equilibrium of propionaldehyde + propane-1,1-diol + 2,4,6-triethyl-1,3,5-trioxane has been characterized for the first time. The new species 2,4,6-triethyl-1,3,5-trioxane could play an important role when propionaldehyde is in aqueous solution, so this fact must be considered in further studies. A resume of species



TOCSY



COSY

Figure 2. Portion of ^{1}H-TOCSY(top) and ^{1}H-COSY (bottom) spectrum of propionaldehyde 0.5 M in D_2O at 25 °C. Signals corresponding to trioxane are marked in blue.

distribution at different temperatures in the equilibrium is given in Figure 4, so the equilibrium constant can be easily obtained. As Figure 4 shows, at lower temperature propane-1,1-diol is predominant. As temperature increases the relative concentration of diol decreases and the relative concentration of aldehyde increases. We must emphasize that the concentration of 2,4,6-triethyl-1,3,5-trioxane is practically constant (~10%) at all temperatures.

2. Experimental

The NMR measurements were performed on a 500 MHz spectrometer Varian INOVA equipped with gradient probe test tubes. Signal post-processing was performed with MestReC software.[12] The samples were prepared using D_2O (99.9%), supplied by Aldrich, as solvent. The samples were prepared by weighing the proper amount of propionaldehyde and the corresponding volume of D_2O for the four concentrations used (0.02, 0.04, 0.1, and 0.5 M). ^{13}C NMR NMR spectra were recorded with the aid of a coaxial tube filled with DMSO-d_6 to lock on the deuterium signal. The tubes were sealed with tightened Teflon caps and equilibrated at the corresponding temperature in each case. All the experiments were carried out at controlled probe temperatures in 5 mm NMR. For ^{1}H-NMR experiments we varied the temperature between 5 °C and 55 °C (±0.5 °C). ^{13}C NMR, COSY, and TOCSY were realized at 25 ± 0.5 °C.

The DOSY spectra were acquired with the standard stimulated echo pulse sequence using LED and bipolar gradient pulses. The gradient strengths (G) were changed from 2.1 to 64.3 G cm^{-1} in 20 steps, and the duration time of the gradient pulse (δ) was kept constant at 2 ms. To obtain reliable results of the diffusion

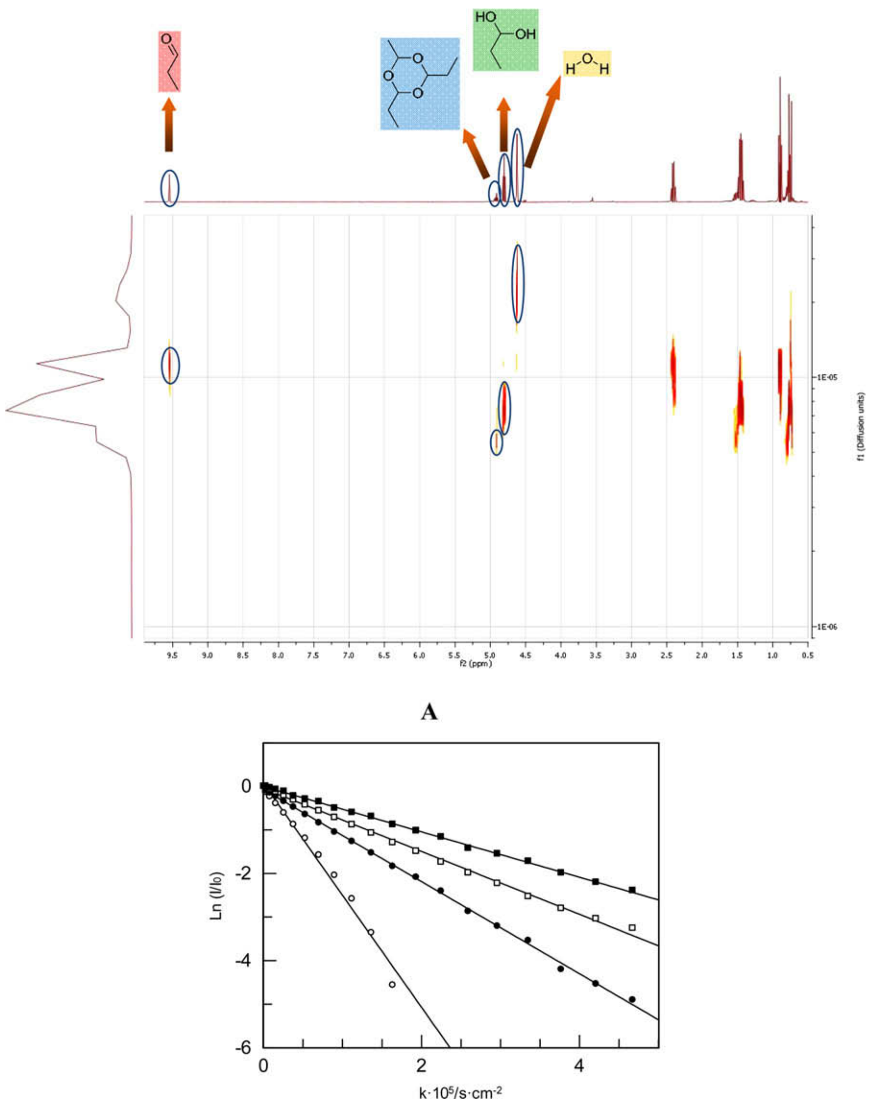


Figure 3. (A) Portion of 500-MHz ^{1}H-DOSY display for a 0.5 M solution of propionaldehyde in D_2O at 25 °C. (B) Plots of Ln(I/I_0) versus k showing the fits to experimental data.

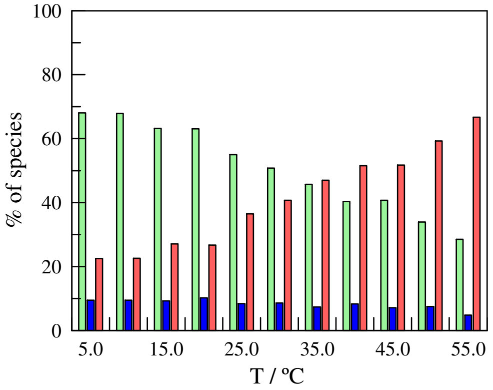


Figure 4. Variation of the percentage of propionaldehyde (🟥), propane-1,1-diol (🟩), and 2,4,6-triethyl-1,3,5-trioxane (🟦) with T. Initial concentration of propionaldehyde is 0.5 M.

coefficient, the diffusion time (the time between leading edges of the field gradient pulses, Δ) of the experiment was optimized for each sample to a value between 20 and 100 ms. The raw data were processed using the MestreC program (Mestrelab Research inc.).

For molecules undergoing unhindered random motion and for a single species the attenuation of the signal intensity is given by

$$I = I_0 \exp\left[-\gamma^2 G^2 \delta^2 (\Delta - \frac{\delta}{3}) D\right] \qquad (1)$$

In Eq. 1, I denotes the observed intensity, I_0 is the intensity in the absence of gradient pulses, γ is the magnetogyric ratio, and the rest of the quantities are defined above. The experimental data were analyzed using a nonlinear least squares fitting procedure (program Grafit 5.0, Erithacus Software Ltd.) to extract the D from an exponential decay.

Acknowledgments

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