Hydration Study of Acetaldehyde and Propionaldehyde

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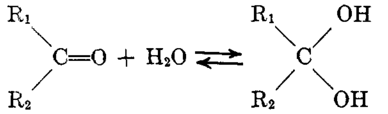
The presence of the hemihydrate of acetaldehyde, which has previously been suggested to be responsible for the unusual hydration kinetics observed, was detected by nmr spectroscopy for dilute, as well as rich, aqueous solutions of acetaldehyde. The sharp nuclear magnetic resonances observed for solutions of acetaldehyde with high acid concentration were explained by the presence of paraldehyde. In addition, the proton exchange of protonated 1,1-dihydroxyethane with water was detected. The hydration of propionaldehyde was also studied in order to determine whether its behavior was similar to that of acetaldehyde. The equilibrium constant K_h = [EtCHCO]/[EtCH(OH)$_2$] was determined. The catalytic constants for the hydrogen ion in the acid-catalyzed hydration and dehydration were found to be 460 and 650 l. mol^{-1} sec^{-1}, respectively.

The formation of *gem*-diols by the reversible hydration of the carbonyl group of ketones and aldehydes is well known and has been the subject of a large number of publications. A recent and comprehensive review of various aspects of the hydration of carbonyl groups has been published by Bell.[1]



(1)

In dilute aqueous solution, the equilibrium constant of hydration has been correlated by Bell with Taft

$$K_h = \frac{[R_1R_2CO]}{[R_1R_2C(OH)_2]}$$

polar and steric substituent constants, σ^* and E_s, respectively,[2-4] for a number of carbonyl-containing compounds. Even though the range of the equilibrium constant K_h extends over eight orders of magnitude, a reasonable correlation is obtained.

The hydration of carbonyl groups has been found to be catalyzed by acids and bases. It has been suggested that the mechanism of the hydration involves several water molecules.[5-8]

The hydration of acetaldehyde to form the hydrate, 1,1-dihydroxyethane, has been found to be anomalous. In dilute aqueous solution, in the presence of acid catalyst, the acetaldehyde and 1,1-dihydroxyethane proton magnetic resonance signals are broad owing to the fast reversible hydration of the carbonyl group. However, in acetaldehyde-rich mixtures, the hydrate signals observed are sharp, even though the acetaldehyde signals are broad. In order to explain this, Ahrens and Strehlow suggested that the hemihydrate $CH_3CH(OH)OCH(OH)CH_3$ is formed in acetaldehyde-rich aqueous solutions.

$$CH_3CHO + CH_3CH(OH)OH_2^+ \rightleftharpoons CH_3CH(OH)OCH(OH_2)^+CH_3 \rightleftharpoons CH_3CH(OH)OCH(OH)CH_3 + H^+ \quad (2)$$

The purpose of the present study was to investigate this and other apparently unusual occurrences in the acid-catalyzed hydration of acetaldehyde. An investigation was also made to determine whether propionaldehyde behaved in a similar fashion, the equilibrium constant of the hydration of propionaldehyde being determined. The hydrogen ion dependent rate constants of both the hydration and dehydration processes at 34.5° were computed.

Experimental Section

The Perkin-Elmer R10 high resolution nuclear magnetic resonance spectrometer was employed, using a 60-MHz probe. The magnetic assembly was thermally insulated at 34.5°.

The aldehydes were purified by distillation under reduced pressure. Bromothymol blue indicated that aqueous solutions of the purified aldehyde were neutral, thus showing the absence of acids which could be produced by oxidation. The samples prepared were allowed to attain the temperature of the magnet assembly. Owing to signal-to-noise considerations, all the solutions employed in the kinetic study were 1.5 mol l.$^{-1}$ propionaldehyde. The acid catalyst employed was prepared from hydrochloric acid (analytical reagent) and the solutions were standardized with sodium tetraborate (analytical reagent), using methyl red as indicator.

Results and Discussion

Acetaldehyde.—From the nmr spectra of aqueous acetaldehyde, the chemical shifts of the methyl doublet and aldehyde quartet were found to be τ 7.73 and 0.22 and those for the corresponding protons in the hydrate to be τ 8.66 and 4.69, employing the sodium salt of 3-trimethylsilylpropanesulfonic acid as internal standard. Aqueous solutions of acetaldehyde in the presence of hydrochloric acid at various concentrations of both aldehyde and acid were studied, and the solutions were prepared and examined immediately. In some cases, the spectra were observed to alter with time, and the changes in the spectra were complete within minutes of the preparation of the mixture. Typical examples are the spectra of 2.5 *M* acetaldehyde with 0.04 *M* hydrochloric acid and 5.3 *M* acetaldehyde with 0.06 *M* hydrochloric acid. Originally, both methyl doublets were broad. However, under conditions of good resolution, two doublets were observed to appear in the region of the originally broad hydrate methyl doublet. The chemical shifts of the two doublets are τ 8.63 and 8.66, and the coupling constants are 5.4 and 5.2 Hz, respectively.

The spectra may be explained as follows. Both methyl resonances of acetaldehyde and 1,1-dihydroxyethane are broad owing to fast reversible hydration. The doublet which appears at τ 8.63 may be attributed to a new compound that is formed with time and is probably the hemihydrate. The latter may be ex-

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pected to have a doublet in the region of the hydrate methyl resonances. The other doublet at τ 8.66 is due to the hydrate methyl resonance. There is evidence to support the formation of a hemihydrate, since formaldehyde,[9-11] dichloroethanal,[11] and fluoral[12] form similar hemihydrates. If the acetaldehyde–acid solutions are neutralized, a typical spectrum of an aqueous solution of acetaldehyde is obtained, thus showing that the reactions occurring are reasonably fast and reversible, as would be expected of the reaction forming the hemihydrate. By reasonably fast, it is meant that the rate constant is of the order of minutes. This is in agreement with the observed appearance of the doublet at τ 8.63.

The spectra of aqueous acetaldehyde-rich solutions in which the acid catalyst concentration is less than 0.1 *M* also change with time. The acetaldehyde proton resonances remain broad, but only one sharp doublet at τ 8.63 is observed. Neutralization of these solutions results in the nmr spectrum being typical of an aqueous solution of acetaldehyde at the concentration studied. Acetaldehyde-rich solutions in which the acid concentration is greater than 0.1 *M*, when neutralized, exhibit, in addition to the typical aqueous acetaldehyde solution spectrum, a doublet at τ 8.63 and a quartet at τ 4.69. The latter two signals may be attributed to paraldehyde.

The nmr spectra of 5.3 *M* acetaldehyde with hydrochloric acid at various concentrations exhibit a number of interesting features. In the concentration range 0–0.020 *M* hydrochloric acid, the broadening is consistent with the reversible hydration of acetaldehyde (Figure 1), and also with the computed theoretical spectra.[13] By comparing the experimental and theoretical spectra of the acetaldehyde and 1,1-dihydroxyethane resonances, the mean lifetimes of both the acetaldehyde and the hydrate are obtained. Hence, the hydrogen ion dependent rate constants for the hydration, 520 l. $\text{mol}^{-1}\ \text{sec}^{-1}$, and the dehydration, 540 l. $\text{mol}^{-1}\ \text{sec}^{-1}$, were computed.[14,15]

With further increase in the hydrochloric acid concentration, from 0.020 to 0.20 *M* (Figure 1), the widths of both methyl doublets increase. The doublet in the region of τ 8.6, however, remains relatively sharp, which is not in agreement with reversible hydration. The observed sharpness of this doublet may be attributed to the formation of a hemihydrate. When using 1 *M* acetaldehyde solutions for a similar study, both the acetaldehyde and the hydrate methyl doublets were observed to collapse, the hydrate doublet collapsing at a concentration of about 0.06 *M* hydrochloric acid. The theoretically computed and the experimental spectra were consistent over a much wider range of acid concentration than those for higher acetaldehyde concentrations. This fact is added proof of compound hemihydrate formation, since in acetaldehyde–dilute aqueous solutions the concentration of hemihydrate is expected to be low.

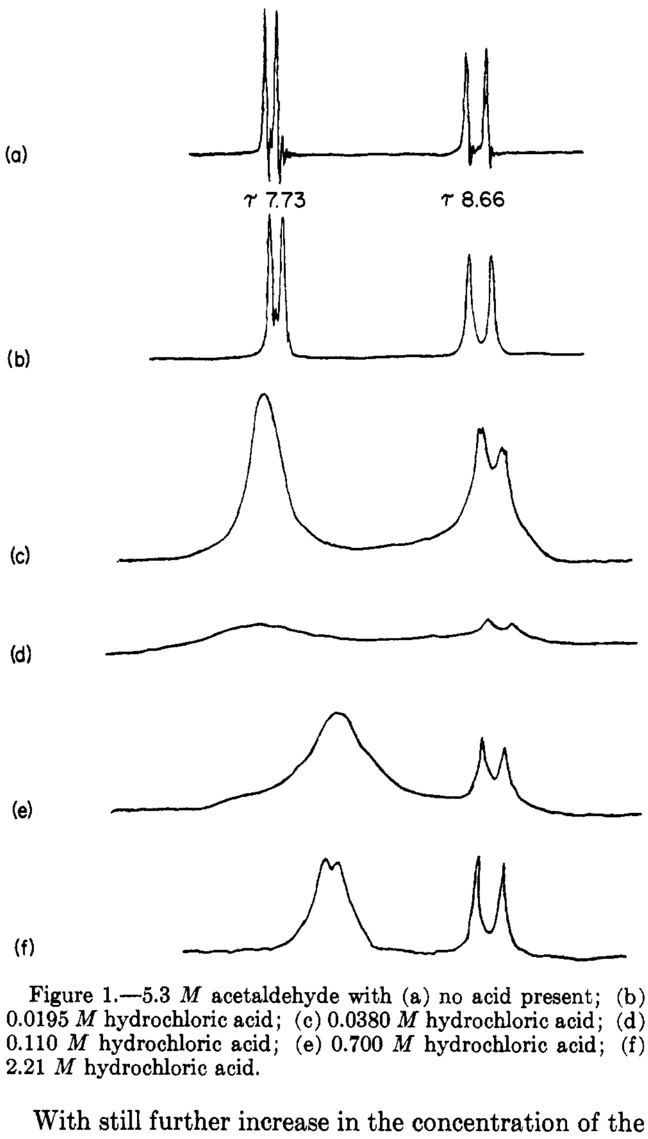

Figure 1.—5.3 *M* acetaldehyde with (a) no acid present; (b) 0.0195 *M* hydrochloric acid; (c) 0.0380 *M* hydrochloric acid; (d) 0.110 *M* hydrochloric acid; (e) 0.700 *M* hydrochloric acid; (f) 2.21 *M* hydrochloric acid.

With still further increase in the concentration of the hydrochloric acid (0.20–2.0 *M*) in the 5.3 *M* acetaldehyde solutions, the methyl signals do not appear to coalesce. Instead, the signal widths are observed to decrease. Finally, with 3.5 *M* hydrochloric acid, two doublets at τ 8.63 and 8.03 (with coupling constants 5.2 and 4 Hz respectively), a broad signal at τ 1.66, and a quartet at τ 4.96 (buried under the water resonance) are observed. Proton double resonance shows that when irradiating at τ 1.66 the doublet at τ 8.03 collapses, thus indicating that the protons producing these resonances are coupled.

The explanation of the observations made is as follows. The signals of acetaldehyde and 1,1-dihydroxyethane have coalesced, the doublets coalescing to the signal at τ 8.03 and the quartets coalescing to the signal at τ 1.66. The signals at τ 8.63 and 4.96 are due to paraldehyde, which is formed at these acid concentrations. Increase in the acid concentration makes the signal at τ 4.96 observable.

In 4 *M* hydrochloric acid, the two doublets and the quartet are sharp. The signal at τ 1.66 remains broad even at very high acid concentrations (10 *M*). This may be attributed to reactions 3–5. Unfortunately,

$$CH_3CH(OH)OH_2^+ + H_2O \rightleftharpoons CH_3CH(OH)_2 + H_3O^+ \quad (3)$$

$$CH_3CH(OH)OH_2^+ + CH_3CH(OH)_2 \rightleftharpoons CH_3CH(OH)_2 + CH_3CH(OH)OH_2^+ \quad (4)$$

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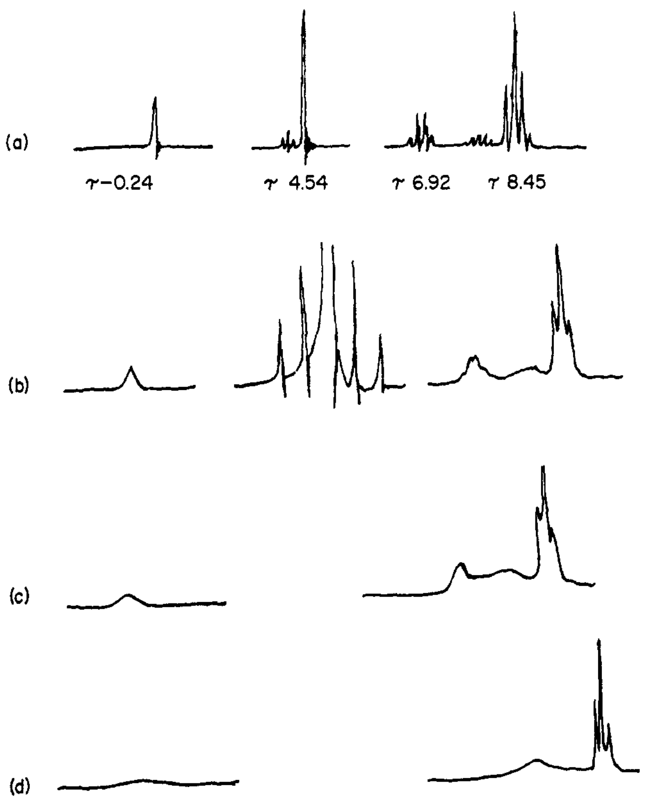
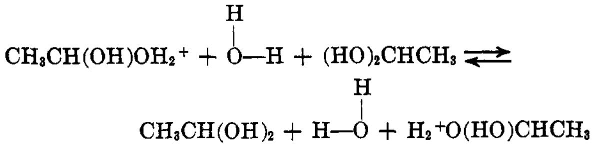


Figure 2.—The nmr spectra of aqueous propionaldehyde at various hydrochloric acid concentrations: (a) 0.005 *M* hydrochloric acid (propionaldehyde in heavy water); (b) 0.003 *M* hydrochloric acid; (c) 0.080 *M* hydrochloric acid; (d) 0.160 *M* hydrochloric acid.



$$CH_3CH(OH)OH_2^+ + \overset{\overset{H}{|}}{O}{-}H + (HO)_2CHCH_3 \rightleftarrows CH_3CH(OH)_2 + H{-}\overset{\overset{H}{|}}{O} + H_2{}^+O(HO)CHCH_3 \quad (5)$$

since the slow exchange state is not observed, the kinetics cannot, without undue difficulty, be studied by nmr.

The ratio of the concentration of paraldehyde to the concentration of acetaldehyde, as determined from the ratio of the intensities of the methyl doublets for 5.3 *M* acetaldehyde with 4 *M* hydrochloric acid, is 0.16.

A number of important points have thus been deduced.

(i) A hemihydrate is formed not only in aqueous acetaldehyde-rich solutions but even in dilute solutions.

(ii) Paraldehyde is formed with increase in acetaldehyde and acid concentrations, but this is not responsible for the sharpness of the doublet at τ 8.6 at low concentrations of aldehyde and acid.

(iii) The unusual narrowing of the doublet resonances has now been explained.

(iv) Proton exchange of protonated 1,1-dihydroxyethane with water must be responsible for the broad signal at τ 1.66 which is observed for solutions containing high acid concentrations.

Propionaldehyde.—The nmr spectrum of propionaldehyde consists of a triplet at τ 8.45, a quartet of triplets at τ 6.92, and a triplet at τ −0.24, employing the sodium salt of 3-trimethylsilylpropanesulfonic acid as reference. From consideration of intensities, chemical shifts, and coupling constants, these resonances may be assigned to the methyl, methylene, and aldehydic proton resonances, respectively.

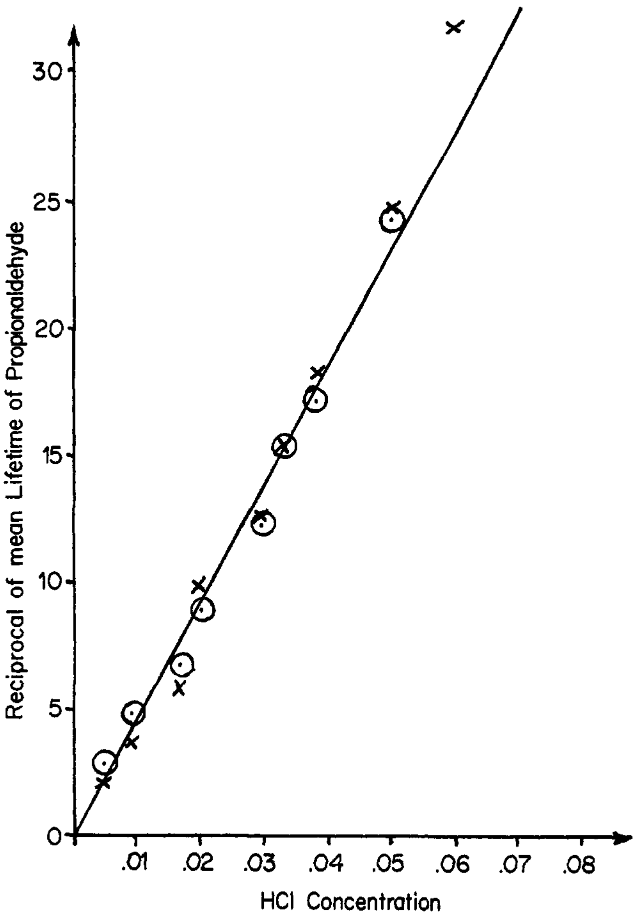


Figure 3.—The graph of the reciprocal of the mean lifetime of propionaldehyde against hydrochloric acid concentration. Points denoted by × were determined from the aldehydic proton resonance, points denoted by ⊙ from the methylene quartet of propionaldehyde.

The spin–spin coupling constant between the methylene and methyl protons was found to be 7.5 Hz, and that between the aldehydic and methylene protons, 1.3 Hz.

The spectrum of propionaldehyde in heavy water (Figure 2a) had additional signals: a triplet at τ 8.59, a complicated multiplet at τ 7.92, and a triplet at τ 4.54. These signals may be assigned to the methyl, methylene, and methylyne, $CH(OH)_2$, protons of the hydrate of propionaldehyde, 1,1-dihydroxypropane. This is consistent with the assignments given to the nmr spectra of aqueous solutions of other aldehydes.[15–20]

Employing the proton double resonance technique, the coupling constant between the methyl and methylene protons of the hydrate was found to be 7.0 Hz. Proton decoupling of the resonance at τ 7.92 was observed by irradiating and saturating the methylyne triplet. The coupling constant between the methylene and methylyne protons was found to be 5.5 Hz. On addition of acid catalyst, the methylene resonance of propionaldehyde in Figures 2a and 2b no longer appears to be a quartet with each component split into a triplet.

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Instead, a quartet with the usual second-order splitting is observed. It would therefore seem that the small splitting of the methylene protons by the aldehydic protons, together with the second-order splitting of the quartet, have produced these four triplets. Also, the triplet of the aldehydic proton resonance of propionaldehyde in Figure 2a has collapsed to give a sharp signal. The changes in the resonances of the methylene and aldehydic protons may be explained by the fact there are two possible magnetic environments for the protons: (i) in propionaldehyde; (ii) in 1,1-dihydroxypropane. Owing to the reversible hydration, protons experience a rapid interchange of these environments. From the collapse of the aldehydic proton triplet, the mean lifetime of propionaldehyde was calculated to be 450 msec.

The equilibrium constant K_h was determined to be 1.4 from the ratio of the intensities of (i) the aldehydic and methylyne proton resonances and (ii) the methylene proton resonances of propionaldehyde and its hydrate. This value is in good agreement with that obtained by the ultraviolet photometric technique.[21] The equilibrium constant did not vary with concentration. The lowest concentration observed was determined by the detection limits of the instrument and the highest concentration, about 6 mol l.$^{-1}$ of propionaldehyde, by solubility.

Various changes were observed in the spectra obtained on addition of hydrochloric acid to the aqueous solution of propionaldehyde. The methylene quartets, the methyl triplets and the aldehydic resonances all broadened (see Figures 2a–d), owing to the hydration–dehydration exchange which became more rapid.

The reciprocal of the mean lifetime of propionaldehyde was obtained by observing the aldehydic and methylene resonances of propionaldehyde and comparing these with theoretical spectra which had been computed for various lifetimes. The theoretical triplets and quartets were computed from the imaginary part of the total complex magnetization as determined by McConnell's method.[13]

The reciprocal of the mean lifetime of propionaldehyde is plotted against the hydrochloric acid concentration in Figure 3. The straight-line graph obtained indicates a rate law of the type

$$\text{specific rate} = k_0 + k_{H^+}[H^+]$$

where k_0 is the spontaneous rate constant and k_{H^+} is the hydrogen ion dependent rate constant. This is consistent with the general acid–base catalysis observed for the hydration of carbonyl-containing compounds.

For the hydration, the hydrogen ion dependent rate constant was 460 l. mol^{-1} sec^{-1}, as determined from the slope of the straight line obtained in Figure 3.

It is reasonable to assume that the spontaneous rate constants for the hydration and dehydration are small compared to the hydrogen ion dependent rate constants. Therefore, the equilibrium constant K_h was employed to estimate the hydrogen ion dependent rate constant, which was found to be 650 l. mol^{-1} sec^{-1}. These results are in good agreement with those of Gruen and McTigue,[7] who employed a thermal method.

No anomalous behaviour similar to that of acetaldehyde was observed for the hydration of propionaldehyde.

Registry No.—Acetaldehyde, 75-07-0; propionaldehyde, 123-38-6.

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Mechanism of Ozonation Reactions. IV. Carbon–Nitrogen Double Bonds

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A study of the mechanism of the ozonation of carbon–nitrogen double bonds has been carried out using product analysis data and competitive rate studies on dimethylhydrazones, oximes, and Schiff bases. It was found that variation of Y in I ($XC_6H_4CR{=}NY$) had a much larger effect on relative rates than variation of X. A generalized mechanism involving initial electrophilic attack of ozone on the carbon atom of the carbon–nitrogen double bond is proposed, and some specific suggestions are made as to pathways in the breakup of initial adducts. In all cases the complete reaction pathways are quite complex. Carbon–nitrogen double bonds, if properly substituted, are as reactive toward ozone as are carbon–carbon double bonds.

Previous work in this series has included one paper involving nitrones, a system which formally contains a carbon–nitrogen double bond.[3] At that time we showed that relative rate studies could be useful in distinguishing between nucleophilic and electrophilic ozone attack in such systems.

The literature contains ozonation studies on several other classes of compounds containing carbon–nitrogen double bonds in both acyclic and heterocyclic compounds. Acyclic systems include Schiff bases,[4] ni-

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