

Strong Covalent Hydration of Terephthalaldehyde

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Spectrophotometric and electroanalytical studies indicate that one of the formyl groups of terephthalaldehyde in aqueous solution is present in about 23% as a geminal diol. Stronger covalent hydration of CHO in terephthalaldehyde than in *p*-nitrobenzaldehyde is attributed to a strong resonance interaction between the two formyl groups.

Covalent addition of water to aliphatic carbonyl compounds has been investigated in considerable detail.^{1–7} With some of the aldehydes, the hydration is so strong that they are present in aqueous solutions in more than 99% in the hydrated form. Strong covalent hydration has also been observed in aqueous solutions of aldehydes, bearing a formyl group on a π -deficient aromatic ring.^{7–11} On the other hand, aldehydes where the formyl group is located on a benzenoid aromatic or π -excessive heteroaromatic ring have been for a long time assumed to remain in aqueous solutions practically unhydrated.⁷ Hence, for example, benzaldehyde as well as 3- and 4-chlorobenzaldehydes are less than 1% hydrated.¹² This was attributed to a considerable resonance stabilization of the unhydrated form. For most substituted benzaldehydes the nucleophilic additions were observed only in the presence of stronger nucleophiles, such as hydroxide or alkoxide ions.^{7,13–16}

The first indication that the covalent hydration of benzaldehydes can be increased by an introduction of an electron-withdrawing group was deduced from the shape of the pH dependence of limiting currents of *o*- and *p*-nitrobenzaldehydes.^{17–19} Limiting reduction currents of these aldehydes in the medium pH range indicate that they are present in equilibrium at least in 8–10% in hydrated form. The measurements of limiting currents in this pH range depend also on the rate of dehydration yielding the electroactive unhydrated form. Hence more of the aldehyde can be reduced than is present in equilibrium and only the lower limit of concentration of the hydrated form can be obtained. Spectrophotometry indicated the following concentrations of the hydrated form present in aqueous solutions: for 3-nitrobenzaldehyde, 9.9%¹² and 7.4%;¹⁵ for 4-nitrobenzaldehyde, values vary from 11.5 to 23%,²⁰ with 14.5% as the most reliable value.¹² Recent electrochemical studies^{21,22} indicated that in aqueous solutions of terephthalaldehyde one of the formyl groups present in equilibrium is more than 15% in the hydrated form at 25 °C. Due to the dynamic character of electrolysis, where some of the electroactive unhydrated forms can be generated during the experiment, only the lower limit of concentration of the hydrated form can be estimated, as mentioned above. Furthermore, electroreduction is a heterogeneous process, and it is not possible a priori to exclude that the equilibrium of a reaction established within the electrical field of the electrode may differ from that in the bulk of the solution. The application of NMR for investigation

of hydration–dehydration equilibria of terephthalaldehyde was prevented by the limited solubility of the aldehyde in aqueous solutions. The use of UV spectra for investigation of such equilibria is reported in this study. The absorbance at about 300 nm, corresponding to the forbidden $n \rightarrow \pi^*$ transition within the carbonyl group, proved less suitable for this purpose. To this absorbance not only the two formyl groups of the unhydrated form but also the single formyl group of the monohydrated form contribute. The hydration of the second formyl group in the monohydrated form can be neglected due to the negligible electron-withdrawing effect of the $\text{CH}(\text{OH})_2$ group. On the other hand, following the absorbance at about 260 nm, corresponding to the electronic transitions involving the PhCO grouping, proved useful.

Three independent approaches were used in investigation of the hydration–dehydration equilibria: (a) absorbance of terephthalaldehyde in an aqueous solution was compared with absorbance in aprotic solvents at equimolar concentrations; (b) absorbance of terephthalaldehyde in an aqueous solution was compared to the absorbance observed in an equimolar aqueous solution of isophthalaldehyde, which is less than 3% hydrated; (c) spectra of terephthalaldehyde were recorded in mixtures of water and acetonitrile of varying concentrations of the organic cosolvent.

To ensure that in all studied reactions the absorbance was measured after the equilibrium between terephthalaldehyde and water was established, a preliminary kinetic study of the covalent addition of water was carried out. Neither a stop-flow or a temperature-jump method was available, but the addition of water to terephthalaldehyde was sufficiently slow to allow using conventional spectrophotometric equipment. The reaction mixture was prepared by adding a stock solution of terephthalaldehyde in acetonitrile to water or water–acetonitrile mixtures, rapid mixing for 10 s, and recording the spectra every 5 or 10 s. In all instances the plots of $\log(A - A_\infty) = f(t)$ (where A is absorbance at time t and A_∞ at equilibrium) were linear. This indicates that the establishment of the equilibrium between terephthalaldehyde and water follows first-order kinetics. The first-order rate constants of formation of the hydrated species varied between 6 and $9 \times 10^{-3} \text{ s}^{-1}$ and thus were several orders of magnitude smaller than those reported¹² for nitrobenzaldehyde.

By use of the absorbance at 262 nm at equilibrium, the following values for equilibrium hydration constants $K_h = [\text{C}(\text{OH})_2]/[\text{CO}]$ were found: (a) from comparison of this

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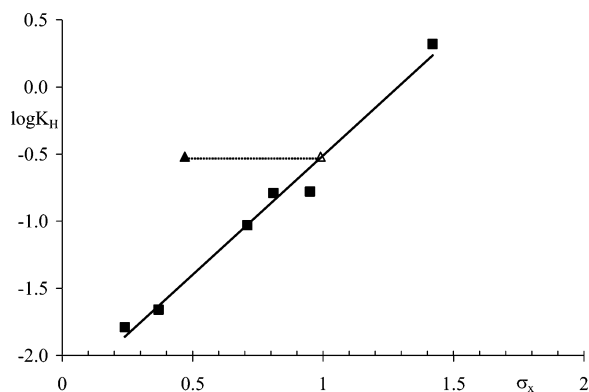


Figure 1. Effects of substituents on hydration of benzaldehydes. Dependence of $\log K_H$ on Hammett substituent constants σ_x . $K_H = [X-\text{Ph}-\text{CH}(\text{OH})_2]/[X-\text{Ph}-\text{CH}=\text{O}]$: (■) average values of K_H reported in the literature used for $\log K_H = \rho\sigma_x$; (▲) K_H for p -CHO and $\sigma_{p\text{-CHO}} = 0.47$; dotted line indicates the shift to fit the LFER; (△) K_H for p -CHO and $\sigma_{p\text{-CHO}} = 0.98$.

absorbance with molar absorptivity of terephthalaldehyde in acetonitrile solution $K_h = 0.31$; (b) from comparison with absorbance of isophthalaldehyde $K_h = 0.27$; (c) from the dependence of absorbance of terephthalaldehyde on concentration of water in acetonitrile $K_h = 0.39$. The difference observed for the latter value may be due to the fact that the equilibrium is established in a solution containing about 0.5% acetonitrile rather than in pure water.

With reported¹² average values of the hydration constant K_h , obtained for chloro- and nitrobenzaldehydes, a good fit ($r^2 = 0.98$) was obtained for the linear plot of $\log K_h = f(\sigma_x)$ (Figure 1). This Hammett plot has a slope $\rho = 1.75$, in good agreement with the value $\rho = 1.71$ reported by McClelland¹² based predominantly on his experimental data. Using for terephthalaldehyde the mean value²³ $\sigma_{p\text{-CHO}} = 0.47$, the mean value of $K_h = 0.3$ shows a significant deviation from the linear plot (Figure 1). To obtain a good fit for the experimentally found value of $K_h = 0.3$, it would be necessary to use substituent constant $\sigma_{p\text{-CHO}}^- = 0.98$. This is within the range 0.94 and 1.04 reported for the substituent constant $\sigma_{p\text{-CHO}}^-$.²³ The need to use $\sigma_{p\text{-CHO}}^-$ rather than $\sigma_{p\text{-CHO}}$ indicates strong resonance interaction between the two formyl groups. Notably, such interaction is absent in p -nitrobenzaldehyde, where the experimentally found average value of $K_h = 0.22$ shows a good correlation using the plots of $\log K_h = \rho\sigma$ when the value of $\sigma_{p\text{-NO}_2} = 0.71$ was used instead of $\sigma_{p\text{-NO}_2}^- = 1.25$.

Thus the stronger hydration observed for terephthalaldehyde indicates a strong resonance interaction between the two formyl groups in terephthalaldehyde. This interaction increases the

positive charge on the carbonyl carbon that is attacked by the water molecule. The resulting effect of the p -CHO on hydration of the second CHO group is even larger than the effect of a p -NO₂ group.

Attempts to compare covalent hydration with additions of aliphatic alcohols to terephthalaldehyde were unsuccessful. These additions took place faster than the addition of water but resulted in at least two equilibria. As hemiacetals and acetals both involving a single and/or two formyl groups were formed simultaneously, a quantitative treatment of processes involved was currently not possible. Qualitatively, the reactivity increased in the sequence 2-propanol < 1-propanol < ethanol.

Unexpectedly strong hydration of terephthalaldehyde is currently compared with that of o -phthalaldehyde, where unhydrated, acyclic monohydrated, and cyclic hemiacetal forms are simultaneously present in aqueous solutions.

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