

HYDRATION CONSTANTS OF CARBONYL AND DICARBONYL COMPOUNDS.
COMPARISON BETWEEN ELECTROCHEMICAL AND NO ELECTROCHEMICAL
TECHNIQUES

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Summary

The values of the hydration equilibrium constants of carbonyl and α -dicarbonyl compounds given in the literature are reviewed; the experimental methods used to the calculation of these constants are discussed as well. The values of the corresponding constants of glyoxal, methylglyoxal and phenylglyoxal are discussed, the last by using a Taft-type correlation.

Carbonyl compounds are usually hydrated in aqueous solution:



This reversible hydration-dehydration reaction has been the objective of numerous papers due to its great chemical importance¹⁻¹⁰. Most of the values of the hydration constants, K_H , available till 1965 were compiled by Bell⁴. K_H values are increased by the presence of electroattractive substituents and decrease when bulky substituents are introduced. Bell proposed a relationship between the dissociation constant of the hydrate ($K_D=1/K_H$) and the Taft's parameters σ^* and E_s of the R_1 and R_2 substituents, that account for the electronic and steric effects of the substituents, respectively¹¹ (eqn. 2). A different approach^{5,6} was proposed using the electronic Taft parameter, σ^* , and the number of aldehydic protons, Δ (eqn. 3).

$$\log K_D = 2.70 - 2.6 \Sigma\sigma^* - 1.3 \Sigma E_s \quad (2)$$

$$-\log K_D = A \Sigma\sigma^* + B\Delta + C \quad (3)$$

Correlations obtained by using equation 3 are better than those found with equation 2. In any case, good partial correlations can be obtained between $\log K_D$ and $\Sigma\sigma^*$ for ketones ($\Delta=0$) and aldehydes ($\Delta=1$) separately⁶.

The main experimental techniques used in the calculation of K_H (or K_D) have been spectroscopic (UV-visible and NMR) and electrochemical (voltammetry). The most

extended method is UV-visible spectroscopy. The concentration of the unhydrated species is calculated from the absorption band appearing in the 260-300 nm region, in which the hydrate is transparent^{1,4,5,12}. The equilibrium constant is then obtained from the equation:

$$K_H = [R_1R_2C(OH)_2]/[R_1R_2CO] = (\epsilon_0 - \epsilon)/\epsilon \quad (4)$$

where ϵ_0 and ϵ are the molar absorptivities in the presence and the absence of hydration, respectively. The main difficulty resides in the determination of ϵ_0 , since in the usual experimental conditions the hydration reaction is fast^{4,8,10,13}. In most cases, ϵ_0 is assumed to have the same value to that obtained in cyclohexane. Nevertheless, the values of ϵ depend on the solvent⁵, and serious errors can be committed in the calculation of hydration constants.

NMR seems more appropriate than UV-visible spectroscopy, since the relative concentrations of both the free and hydrated species are obtained from the areas of the signals corresponding to each species. H^1 NMR^{5-7,9,10} and O^{17} NMR⁶ have been used, finding discrepancies between the values obtained from these techniques and those found by UV-visible spectroscopy. These differences are not always in the same direction, and no clear correlation can be established between the two series of values. Nevertheless, the K_H values obtained for the same compound by the different NMR techniques are consistent. Thus, it can be concluded that the K_H values obtained by the UV-visible spectroscopy are affected by errors not affecting to NMR measurements.

The use of polarographic limiting current, i_L , for the determination of K_D was proposed under the assumption that in polarographic conditions the reduction of the free form do not disturb the equilibrium between the free and hydrated forms^{14,15}. Nevertheless, i_L depends also on the dehydration rate, and the above assumption originates erroneous K_D values.

The linear potential sweep voltammetry has also been used for the calculation of K_H under the conditions in which the scan is high enough to that the hydration equilibrium is not perturbed^{2,3,12,16}. In this case, the limiting current is diffusion-controlled and the peak current value, i_p , is directly related with the concentration of the free species in the bulk solution. The main problem resides in which the relation between i_p and v (scan rate) depends on the electrode process. So, if the process is reversible¹⁷:

$$i_p = 2.72 \times 10^5 n^{3/2} A D_0^{1/2} c_0 v^{1/2} \quad (5)$$

where n is the number of electrons involved in the process. For irreversible processes¹⁸:

$$i_p = 3.03 \times 10^5 n (\alpha n_a)^{1/2} A D_0^{1/2} c_0 v^{1/2} \quad (6)$$

where αn_a accounts for the irreversibility of the process.

If the process is quasi-reversible, as in the case of most α -dicarbonyl compounds reductions¹⁹ equations 5 and 6 do not describe exactly the dependence of i_p on $v^{1/2}$ and the calculation of c_0 is affected by serious errors. This affects also to more sophisticated treatments as that used by Segretario et al.¹² and the K_H values are more similar to those obtained by UV-visible spectroscopy than to those obtained by NMR^{2,3,12}.

The K_H value found more frequently, if formaldehyde is taken apart, corresponds to diacetyl. The results obtained by NMR measurements are consistent, having a mean value of 2.05. The value reported by Wasa and Musha² is too high and this could be attributed either to the high concentration used, that could originate the polymerization of this compound in solution, or to that the scan rate was not fast enough to eliminate the influence of the preceding chemical reaction. On the other hand, the values obtained by Segretario et al.¹² by using linear sweep voltammetry concordate with those obtained by UV-visible spectroscopy rather than with those calculated by NMR. Measurements made by convolutive potential sweep voltammetry are in very good agreement with the NMR measurements²⁰ and this method takes advantage from the NMR method due to its simplicity and lower cost.

Hydration constants of glyoxal, methylglyoxal and phenylglyoxal

The value of the equilibrium constant of methylglyoxal calculated by Wasa and Musha² by LSV measurements is 2.7×10^3 . Nevertheless, this calculation was made by using equation 6 assuming $\alpha n = 1.48$. Moreover, the concentration of methylglyoxal used was 0.128 M, high enough to make important the contribution of the dimerization of this compound in solution²¹. It is easy to show that in these conditions, assuming that $K_H \gg 1$ we have:

$$K_H = [-1 + (1 + 8K_D c)^{1/2}] / 4c_0 K_D \quad (7)$$

where K_D is the equilibrium constant of the dimerization reaction and c is the overall concentration of the dicarbonyl compound. In addition $\alpha n = 1$, as can be inferred from electrochemical measurements²². With these data and taking into account those reported in reference 2 we have $K_H = 1.37 \times 10^3$, that is, around one half to that initially reported.

In this same way, the above authors calculate a value of 2.17×10^5 for the hydration of glyoxal at pH=9 and at a concentration of 2.52 M, using $\alpha n=1.48$. This last value is correct²³ but the dimerization reaction should be taken into account². In these conditions a value of $K_H=7.22 \times 10^4$ was obtained. The value of $K_H=2.07$ for the second hydration reaction of glyoxal was obtained by using convolutive potential-sweep voltammetry²⁰. Starting from this value, and taking into account that given above for overall hydration reaction, a value of c.a. 350 is obtained for the first hydration constant.

In the case of phenylglyoxal, the value of K_H must be high, as can be inferred from the value of the limiting current of the dc reduction wave corresponding to the unhydrated species in the pH range 2-6, which is less than 0.01 of the corresponding diffusion-controlled process. This means that it is necessary to use high phenylglyoxal concentrations, but this substance is strongly adsorbed on the mercury electrode and the I-E curves are seriously distorted by this effect. The aromatic ring absorbing strongly in the UV region precludes the use of UV-visible spectroscopy. An approximate value of K_H for this compound can be obtained from the correlation between structure and equilibrium constant for a series of nine aldehydes type R-CHO (R=CH₃, CH₃CH₂, COOH, COO⁻, CH₃CO, CHO, CH₂OH, CH(OH)₂, CH₃CONH). Since in all cases $\Delta=1$, the equation 3 could be used by including $B\Delta+C$ into a constant. Nevertheless, no good correlations were obtained and the following equation was applied:

$$\log K_H = A \sum F + B \sum R + C \quad (8)$$

where F and R are the Taft parameters including the inductive or field and resonance effects, respectively¹¹. The relation between $\log K_H$ values obtained with $A=2.08$, $B=6.57$ and $C=1.1$ and the experimental ones is acceptable. Two outliers can be observed corresponding to glyoxylate ion and acetamido-acetaldehyde, probably due to the presence of the charge in the first compound and of the nitrogen atom in the second compound. Using this correlation a value of $K_H \approx 400$ was obtained for phenylglyoxal

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