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The Reversible Addition of Water to Glycolaldehyde in Aqueous Solution

P. E. SØRENSEN

Chemistry Laboratory A, The Technical University of Denmark, Building 207, DK-2800 Lyngby, Denmark

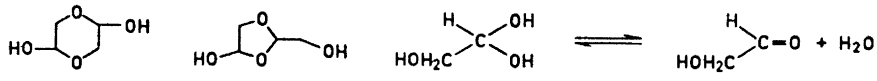
The kinetics of the reversible addition of water to glycolaldehyde in aqueous solution has been studied at 25°C ($I = 0.10 - 0.15$) using a scavenger technique by which the rate of dehydration was measured as a function of pH and total scavenger concentration. In the pH-intervals 2.6 – 6.0 and 6.0 – 8.5, semicarbazide ($pK_A = 3.65$), followed by spectrophotometry, and sulphite ($pK_A^{II} = 7.20$), followed by pH-stat, were used as scavengers, respectively. The reaction was found to follow the general pattern for hydration of carbonyl groups, showing general acid and base catalysis. The catalytic constants for H_2O, H^+, OH^-, SO_3^{2-}, HSO_3^-, $N^+H_3NHCONH_2$, and $NH_2NHCONH_2$ were determined.

Attempts were made to determine the hydration equilibrium constant partly by extrapolation of kinetic dehydration curves to zero time and partly by measuring the rate of hydration in aqueous dioxan and extrapolation to pure water. Results corresponding with about 90 % hydration were obtained.

Glycolaldehyde (2-hydroxyacetaldehyde) is often regarded as the simplest sugar. It appears in biological systems as a metabolic intermediate, in particular in the interconversion of sugars by the so-called transketolase reaction,[1–3] where glycolaldehyde, in combination with the coenzyme thiamine pyrophosphate, Mg^{2+}, and transketolase as enzyme, is transferred as "active glycolaldehyde". The existence of "active glycolaldehyde" has been proved by Datta and Racker [4,5] and the substance has been isolated by Holzer *et al.*[6]

Glycolaldehyde is a commercially available, white crystalline compound, which in the solid state undoubtedly exists as the dimer (I) (2,5-dihydroxy-1,4-dioxan) [7–10] as with other α-hydroxyketones and -aldehydes (*e.g.* 1,3-dihydroxyacetone and 2-hydroxypropionic aldehyde (lactaldehyde)). However, on dissolving the compound, a solvent- and time-dependent dissociation takes place. The rate of dissociation in water was first studied very roughly by McCleland [11] using a cryoscopic technique and found to be of first order. Bell and Hirst [12] studied the same reaction and its acid-base catalysis in more detail using microdilatometry and found it to be very similar to the dissociation of 1,3-

dihydroxyacetone.[13] In an equilibrated aqueous solution the glycolaldehyde molecules are expected to exist mainly in the hydrated form (IV) according to eqn. (1) because of destabilization of the carbonyl group, compared to that of acetaldehyde, which is about 60 % hydrated,[16] by the hydroxy group, but other species may also be present in the solution. For instance, Späth and Raschik [14] found evidence for the species (II) in pyridine solution by acetylation studies.



(I) (II) (IV) (III) (1)

Recently Michelson and Klæboe [10] and Collins and George [15] using vibrational and NMR-spectroscopy, respectively, report the existence of all the species (I)(9), (II)(17), (III)(4), and (IV)(70) in an equilibrated, aqueous solution. By integrating NMR-signals Collins and George found the distribution in a 0.1 M solution of glycolaldehyde in D_2O at 35°C in percentage as indicated in the parentheses. Some weaker unassigned bands were also observed in the NMR-spectrum indicating the presence of small concentrations of other at present unknown species.

The biological activity of glycolaldehyde and other carbonyl compounds active in biological systems, where the free carbonyl group is expected to participate in chemical reactions, is likely to be dependent on its degree of hydration and of the rate of hydration and dehydration. The nature of the hydration of carbonyl groups has been studied by many authors, in particular by Bell and coworkers.[16,17] The reaction is found to be general acid and base catalysed, except for the carbon dioxide hydration, where acid catalysis has not yet been observed with certainty.[18] Recently Bell, Millington, and Pink [19] and Bell and Critchlow [20] have demonstrated that the transition state for the uncatalysed hydration of 1,3-dichloroacetone in aqueous dioxan clearly consists of the carbonyl compound and three water molecules in a cyclic structure. The same conclusions are reached from determination of activation entropies for the system.[21]

The purpose of the present work is to give a quantitative treatment of the kinetics and equilibria of the hydration of glycolaldehyde. In a recent paper Barnes, Uden, and Zuman [22] find that the reduction current in the polarographic reduction of glycolaldehyde is governed by the rate of dehydration of the hydrated form. They give no quantitative kinetic data but their results seem to indicate that less than 10 % of glycolaldehyde is present in the non-hydrated form in dilute, aqueous solution.

EXPERIMENTAL

Glycolaldehyde (Fluka, *purum*), m.p. 90°C, was kept over silica gel in a desiccator and used without further purification. BDH Analar $Na_2SO_3.7H_2O$, $Na_2S_2O_5$, and semicarbazide were used for preparation of scavenger solutions. Analar NaCl for adjusting the ionic strength and doubly distilled water were used throughout.

Dehydration in the pH-range 6.0 – 8.5. In this pH-interval mixtures of bisulphite and sulphite ($pK_A^{II} = 7.20$) [29] were used as scavenger substance in connection with a pH-stat

technique (Radiometer, Copenhagen). The method was introduced and described by Bell and Evans [23] in their work on the hydration of formaldehyde in aqueous solution. It is based on the increase in pH associated with the addition reaction between sulphite ions and the carbonyl group.[24,26] If this addition is fast compared to the rate of hydration and sufficiently irreversible the dehydration becomes the rate determining step. Using a bisulphite solution as titrant the pH-stat technique offers two advantages as both pH and the total concentration of sulphite are kept constant during an experiment. At a certain pH a series of scavenger solutions in the concentration range $1 \times 10^{-2} - 5 \times 10^{-2}$ M ($I = 0.10 - 0.15$) was prepared from weighed amounts of bisulphite and sulphite and O_2-free redistilled water. 25 ml of the solution was placed in the reaction vessel (Type V 520) fitted with glass electrode (Type G 202 C), calomel electrode (Type K 401), burette and stirrer and was kept under an O_2-free atmosphere of nitrogen. For temperature control (25.0 ± 0.1°C) a thermostat jacket (Type V 525) with circulating water was used. The reaction was started by adding to the scavenger solution 100 or 200 µl of a 0.25 M equilibrated (25°C) aqueous solution of glycolaldehyde from small precision pipettes. Two or three experiments could be made in the same solution.

Dehydration in the pH-range 2.6 – 6.0. Here semicarbazide ($pK_A^I = 3.65$) [30] was used as a scavenger and the appearance of the free carbonyl group-semicarbazide-reaction product was followed spectrophotometrically at 226 nm, where it has a strong maximum of absorbance, and where none of the other species present in the solution absorb to an appreciable extent. For this purpose a Gilford 2400 recording UV spectrophotometer with thermostatted cell compartment (25.0 ± 0.1°C) was used. A scavenger solution of known pH and scavenger concentration ($2 \times 10^{-2} - 1 \times 10^{-1}$ M, $I = 0.1$) was thermostatted in a 1 cm silica reaction cell and the reaction was initiated by adding 1 – 5 µl of a 0.1 M equilibrated (25°C) aqueous solution of glycolaldehyde.

Hydration experiments. As the results of Barnes *et al.*[22] indicate, the pseudo 1. order hydration rate constant in aqueous solution may be expected to be at least ten times greater than that of dehydration and it was therefore necessary to use a fast registering kinetic technique. An attempt was made to determine the equilibrium constant for eqn. (1) approximately by measuring the hydration rate constant in aqueous dioxan (1:1) in a Durrum stopped flow apparatus (Palo Alto, California) and combine it with the dehydration rate in water. An approximately 0.1 M solution of glycolaldehyde in dioxan (BDH technical, purified by the method described by Bell and Jensen [27]) was refluxed for 4 h to ensure a considerable degree of monomerization of the dimer to free glycol aldehyde.[11] The solution was rapidly cooled to room temperature and transferred to syringe I in the flow apparatus. Pure water was used as the other reactant (syringe II). After mixing the liquids the concentration of the carbonyl group was followed spectrophotometrically at 285 nm where it has a maximum of absorbance.

For the same purpose a "t-jump"-technique was also tried (Durrum instrument). 4 – 5 kilovolts were discharged through equilibrated $10^{-3} - 10^{-1}$ M aqueous solutions of glycolaldehyde ($I = 0.1$), which gave instant temperature rises of about 5 – 10°C. The rate of reequilibration was followed at 285 nm.

RESULTS AND DISCUSSIONS

Dehydration. A typical kinetic curve from the dehydration experiments is shown on Fig. 1. It shows an instant increase in optical density or pH before the proper 1. order curve starts. This phenomenon is due to incomplete hydration and is discussed later. Plots of $\log|a_t - a_\infty|$ *vs.* time, where $a_0 < a_t < a_\infty$ (as defined in Fig. 1), gave good straight lines the slopes of which were determined by the method of least squares. The 1. order rate constant, k_{obs}, could be obtained from $k_{obs} = -\text{slope}/0.4343$. It represents the sum of all 1. order (pseudo 1. order) rate constants for all the parallel reactions participating in the dehydration. In the present system it can be written as follows:

$$k_{obs} = k_0 + k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_A\,[A] + k_B[B] \qquad (2)$$

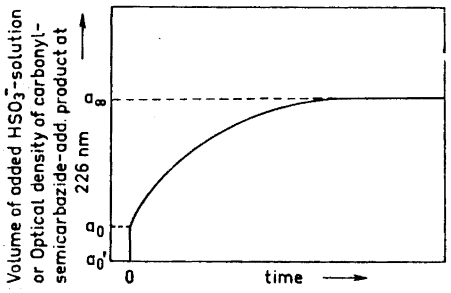


Fig. 1. Typical kinetic curve from the dehydration experiments.

where k_0 refers to the "spontaneous" dehydration, *i.e.* the reaction catalysed by the solvent (H_2O). k_{H^+}, k_{OH^-}, k_A, and k_B are catalytic constants (2. order rate constants) belonging to the dehydration reactions catalysed by H^+, OH^-, A, and B, respectively. In the present case A and B represent the acidic and the basic form of the scavenger, respectively.

Eqn. (2) can be transformed to:

$$k_{obs} = (k_0 + k_{H^+}[H^+] + k_{OH^-}[OH^-]) + \left(\frac{k_A [H^+] f_B f_{H^+}}{[H^+] f_B f_{H^+} + K_A f_A} + \frac{k_B K_A f_A}{[H^+] f_B f_{H^+} + K_A f_A}\right)([A] + [B]) \qquad (3)$$

where f denotes activity coefficients and K_A is the thermodynamic dissociation constant of the scavenger. Thus, by plotting k_{obs} *vs.* total concentration of scavenger at two different pH-values and combining the slopes, k_A and k_B can be determined. From a combination of intercepts of three of such plots k_0, k_{H^+}, and k_{OH^-} can be determined in principle, but the situation is usually somewhat simplified by the fact that, depending on pH and the relative magnitude of k_0, k_{H^+}, and k_{OH^-}, either $k_{H^+}[H^+]$ or $k_{OH^-}[OH^-]$ or both can be neglected.

The applicability of a scavenger technique requires that the first step in the consecutive kinetic system is entirely rate determining. Thus, if the scavenger concentration is not too small, changes of this concentration should not affect the rate, apart from possible catalytic effects, or the extent of the overall reaction. In the present system the sulphite ion seems to satisfy this criterion very closely except for the lower pH-values, where too high k_{obs}-values (Table 1), compared to the overall kinetic picture of the system, are observed. However, the kinetic curves obtained in this pH-region are not particularly well defined or reproducible, which may be due to the very small concentration of sulphite ion here, and therefore too much attention should not be paid to them. In the semicarbazide case far too low values for k_{obs} are obtained if the total scavenger concentration is less than about 3×10^{-2} M (Table 1) and further complications may appear if pH is too low because of deactivation of the scavenger by converting it to the protonated form.[23]

Table 1. Catalysis by scavenger species of dehydration of hydrated glycolaldehyde at 25°C. r_S = [A]/[B]. pH = values observed with the glass electrode. [H^+], [OH^-] = values calculated from buffer ratio or from observed pH[a]. Values of activity coefficients (I = 0.1) are taken from Kieland,[28] f_{H^+} = 0.83, f_{OH^-} = 0.76, $f_{SO_3^{2-}}$ = 0.37, $f_{HSO_3^-}$ = 0.78, and to a good approximation $f_{RNH_3^+}$ (semicarbazide) = f_{H^+}. k_{obs} is the mean value from at least two experiments. Figures in parentheses are obtained by extrapolation.

Sulphite (pK_A of bisulphite ion = 7.20)

r_S = 5.49, pH = 6.15 (calc. 6.14), [OH^-] = 0.132 × 10^{-7} M.

$10^5 \times$ ([A]+[B])(M)	0	487	1007	2012	2500
$10^4 \times k_{obs}$ (sec^{-1})	(120)	124	128	129	140
calc.	97	99	101	106	108

r_S = 1.74, pH = 6.66 (calc. 6.64), [OH^-] = 0.575 × 10^{-7} M.

$10^5 \times$ ([A]+[B])	0	507	1014	1520	2027	2535
$10^4 \times k_{obs}$	(118)	126	136	152	154	154
calc.	100	105	111	116	122	127

r_S = 0.692, pH = 7.05 (calc. 7.04), [OH^-] = 1.44 × 10^{-7} M.

$10^5 \times$ ([A]+[B])	0	500	1000	1507	2005
$10^4 \times k_{obs}$	(110)	124	152	160	164
calc.	105	114	122	131	140

r_S = 0.269, pH = 7.48 (calc. 7.45), [OH^-] = 3.72 × 10^{-7} M.

$10^5 \times$ ([A]+[B])	0	508	1003	1522	2005
$10^4 \times k_{obs}$	(115)	127	138	152	158
calc.	118	130	142	154	166

r_S = 0.145, pH = 7.60 (calc. 7.72), [OH^-] = 6.92 × 10^{-7} M.

$10^5 \times$ ([A]+[B])	0	504	1004	2010	3000	4000
$10^4 \times k_{obs}$	(145)	152	160	189	237	268
calc.	138	151	164	190	217	243

r_S = 0.069, pH = 8.02 (calc. 8.04), [OH^-] = 14.4 × 10^{-7} M.

$10^5 \times$ ([A]+[B])	0	502	999	1496	1998	2500
$10^4 \times k_{obs}$	(189)	200	216	228	237	252
calc.	182	197	211	225	240	253

r_S = 0.046, pH = 8.22 (calc. 8.31), [OH^-] = 21.9 × 10^{-7} M.

$10^5 \times$ ([A]+[B])	0	481	962	1922	2885	3845
$10^4 \times k_{obs}$	(238)	252	262	292	326	335
calc.	227	241	255	283	310	338

[a] From buffer ratio:

$$\log [H^+] = \log \frac{[A]}{[B]} - pK_A + \log \frac{f_A}{f_B f_{H^+}}$$

$$\log [OH^-] = \log \frac{[B]}{[A]} - pK_B + \log \frac{f_B}{f_A f_{OH^-}}$$

From measured pH:

$$[H^+] = \frac{10^{-pH}}{f_{H^+}}, \quad [OH^-] = \frac{10^{pH-pK_{H_2O}}}{f_{OH^-}}$$

Table 1. Continued.

variable buffer ratio.

$10^5 \times ([A]+[B])$	1000	1000	1000	1000
pH ($[OH^-] \times 10^7$)	8.29(25.7)	8.38(31.6)	8.44(36.3)	8.52(43.6)
$10^4 \times k_{obs}$	278	298	350	376
calc.	279	316	344	388

Semicarbazide ($pK_A = 3.65$)

$r_s = 1.20$, pH = 3.65, $[H^+] = 2.70 \times 10^{-4}$ M.

$10^4 \times ([A]+[B])$(M)	0	200	400	600	800	900	1000
$10^4 \times k_{obs}$ (sec^{-1})	(118)	121	131	140	146	145	158
calc.	118	126	133	140	148	152	155

$r_s = 0.363$, pH = 4.17, $[H^+] = 0.812 \times 10^{-4}$ M.

$10^4 \times ([A]+[B])$	0	20	40	60	80	100	200	300	400	600	800	900	1000
$10^4 \times k_{obs}$	(104)	71	81	87	96	98	104	110	114	119	127	128	130
calc.	103	103	104	104	105	105	107	109	112	116	121	123	125

$r_s = 0.123$, pH = 4.65, $[H^+] = 0.270 \times 10^{-4}$ M.

$10^4 \times ([A]+[B])$	0	200	400	600	800	900	1000
$10^4 \times k_{obs}$	(96)	94	104	104	111	113	108
calc.	99	102	105	108	111	113	115

variable buffer ratio.

$10^4 \times ([A]+[B])$	1000	1000	1000	1000	1000	500
pH($[H^+] \times 10^5$)	2.65(2.70)	2.80(1.91)	3.00(1.20)	3.20(0.76)	3.45(0.43)	5.23($\approx$0)
$10^4 \times k_{obs}$	362	315	243	214	172	100
calc.	376	308	248	208	175	101

Plots of the intercepts, $k_0 + k_{H^+}[H^+]$ and $k_0 + k_{OH^-}[OH^-]$, *vs.* $[H^+]$ and $[OH^-]$, respectively, are shown in Fig. 2. It is seen that the k_0-values obtained from the two extrapolations are indistinguishable, which may justify the applicability of the two scavengers to the system. It also shows that the presence of low concentrations of dimers of glycolaldehyde (dependent on the initial concentration of the aldehyde [11]) in the stock solutions used have no observable effect on the rates of dehydration.

Table 2 contains the collected velocity constants from the dehydration experiments. They are very similar to the corresponding values for the dehydration of hydrated formaldehyde [23] (1 – 4 times higher).

Table 2. Kinetic results from dehydration experiments.

Catalyst (acidic species)	K_A	k_A M^{-1} sec^{-1}	k_B M^{-1} sec^{-1}
H_3O^+	55.5	8.3	0.0096/55.5
HSO_3^-	6.2×10^{-8}	$\approx$0	0.30
$N^+H_3NHCONH_2$	2.24×10^{-4}	0.06	0.01
H_2O	1.8×10^{-16}	0.0096/55.5	6000

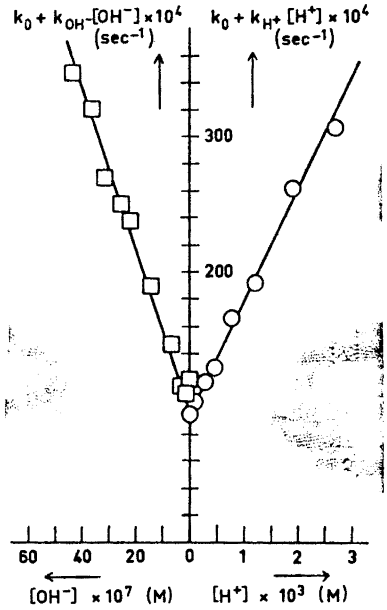


Fig. 2. Catalysis by hydrogen (○) and hydroxide (□) ions.

Hydration and equilibria. In principle the equilibrium constant K for eqn. 1 (K defined as $[CH_2OHCHO]/[CH_2OHCH(OH)_2]$) can be determined from the kinetic dehydration curves (Fig. 1) as $(a_\infty - a_0)/(a_0 - a_0')$. This procedure was used by Bell and Evans [23] for acetaldehyde and the results were shown to be in good agreement with those derived by other experimental methods. In the present case this method turned out to be less accurate, probably because of the higher degree of hydration of glycolaldehyde compared to acetaldehyde and because of the presence of dimers of varying concentration in the stock solutions used, which seems to affect the degree of hydration found. Thus, with sulphite (0.25 M stock solution) equilibrium constants varying from 0.1 to 0.3 were typical, whereas with semicarbazide (0.1 M stock solution) K was nearly always less than 0.1, which is in agreement with the findings of Barnes *et al.*[22]

Because of the qualitative character of these results and the obvious discrepancies observed it was desirable to attempt to measure K by a different technique. If, for example, the spontaneous rate constant for the hydration reaction in aqueous solution, k_0^{hydr}, can be determined, then $K = k_0^{dehydr}/k_0^{hydr}$, where k_0^{dehydr} is known from the dehydration experiments. At the beginning the "t-jump" method was thought to be a suitable one for this purpose as it was shown to be for formaldehyde by Schecker and Schulz.[31] However, the glycolaldehyde reequilibration rate turned out to be too slow so that secondary temperature changes started to influence the system.

As an alternative but less attractive method, k_0^{hydr} was now determined by a flow technique as described in the experimental section. Immediately after cooling the 0.1 M solution of glycolaldehyde in dioxan to room tempera-

ture it had an optical density compared to pure dioxan of 0.842 (light path 1 cm, 285 nm), which gradually declined to 0.349 during 48 h due to dimerization. Thus, dimerization is very slow compared with hydration and hence no corrections had to be made to k_0^{hydr}. The approach of the hydration reaction to equilibrium (25°) gave good and reproducible 1. order curves. The mean of the rate constants, k_{obs}, derived from four such curves was 4.9×10^{-2} sec^{-1}. Now k_{obs} equals $k_0'^{hydr} + k_0'^{dehydr}$, where $k_0'^{hydr}$ and $k_0'^{dehydr}$ are rate constants in 50 % water/dioxan (mol fraction $x_w = 0.83$). These values may be related to the appropriate constants in pure water by the following expression:

$$k_{obs} = k_0'^{hydr} + k_0'^{dehydr} = x_w^{n_h} k_0^{hydr} + x_w^{n_d} k_0^{dehydr} \quad (4)$$

where n_h and n_d are reaction orders with respect to x_w for hydration and dehydration, respectively. Such reaction orders are unknown for glycolaldehyde, but if it is assumed, which seems reasonable, that the mechanism for the hydration of glycolaldehyde is similar to that for the hydration of 1,3-dichloroacetone, then the reaction orders for the latter process ($n_h = 3.65$, $n_d = 2.79$), determined by Bell and Critchlow,[20] can be used as approximate values. Inserting all known values in eqn. 4 k_0^{hydr} is found to be 8.4×10^{-2} sec^{-1}, which gives $K = 0.11$ corresponding to 90 % hydration. This value can be compared to the one calculated from the following empirical expression given by Bell [16] and approximately valid for a large number of carbonyl compounds:

$$\log K_d = 2.70 - 2.6 \sum\sigma^* - 1.3 \sum E_s$$

where σ^* and E_s are Tafts polar and steric substituent constants and where the summations involve both the substituents in $R_1R_2C(OH)_2$, the methyl group representing the standard ($\sigma^* = 0$, $E_s = 0$). E_s- and σ^*-values for a number of substituents are collected in Leffler and Grunwald's book.[32] However, no E_s-value is given for the CH_2OH-group but if it is estimated to -0.15, which seems reasonable compared to the values -0.19 and -0.24 for the CH_2OCH_3- and the CH_2Cl-groups, respectively, $K_d = K$ is calculated to be 0.04 corresponding to 96 % hydration.

Because of the rather indirect methods of determining K, involving a number of assumptions, the quantitative aspect of the results should not be taken too seriously, although they can be regarded as qualitatively correct. However, it seems difficult to devise more reliable experimental methods for the present system.

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