

Acid Strengths of the Hydrates of Formaldehyde, Acetaldehyde and Chloral

BY R. P. BELL AND D. P. ONWOOD

Physical Chemistry Laboratory, Oxford

Received 13th February, 1962

The following pK-values have been measured in aqueous solution at 25°C: $\text{CH}_2(\text{OH})_2$ 13.27, $\text{CH}_3\text{CH}(\text{OH})_2$ 13.57, $\text{CCl}_3\text{CH}(\text{OH})_2$ 10.04. The results are discussed in terms of structural effects.

Many carbonyl compounds are appreciably hydrated in aqueous solution to gem-diols $\text{R}_1\text{R}_2\text{C}(\text{OH})_2$, this hydration being effectively complete for chloral and formaldehyde,¹ and its extent ascertainable from measurements of ultra-violet absorption for a number of other aldehydes and ketones.² The gem-diols are weak acids, giving rise to the ion $\text{R}_1\text{R}_2\text{C}(\text{OH})\text{O}^-$, which may also be regarded as being formed by the addition of hydroxide ions to the carbonyl compounds. Their dissociation constants should provide a direct measure of the inductive effects of the groups R_1 and R_2 , since steric effects will be inappreciable and there are no complications arising from the distribution of the charge of the anion between several atoms, as in the carboxylic acids or phenols. These advantages are also present in the monohydric alcohols, but these are even weaker acids, and it is difficult to measure their strengths accurately: nevertheless, recent work³ has provided interesting correlations. Approximate determinations have been reported for the hydrates of formaldehyde and acetaldehyde,⁴ and the present paper describes more accurate measurements for these substances and for chloral.

EXPERIMENTAL

The water used was doubly distilled in glass from dilute potassium permanganate, and was then de-oxygenated by passing oxygen-free nitrogen while boiling, and cooling in a stream of nitrogen. It was stored under nitrogen and had a specific conductivity of 10^{-6} mho cm^{-1} . Sodium hydroxide solution was prepared by dissolving A.R. sodium hydroxide in an equal weight of water and sucking the solution free from the insoluble sodium carbonate. After dilution with conductivity water it was stored in polythene vessels under nitrogen.

Two sources of formaldehyde were used, with identical results. The first was an A.R. 37 % aqueous solution. The second was prepared from trioxan, which was distilled with dilute sulphuric acid, and the distillate evaporated down *in vacuo* to give solid paraformaldehyde. This was depolymerized by distilling in a current of nitrogen and the formaldehyde absorbed in conductivity water. Acetaldehyde was fractionally distilled through a water-cooled reflux condenser in a current of nitrogen, and condensed in dry ice. Gram quantities were transferred to small bulbs which were sealed off under nitrogen. Solutions were prepared by breaking one of these bulbs under conductivity water. Chloral hydrate (Laboratory Reagent grade) was found to contain a negligible amount of acidic impurities, since an M/10 aqueous solution had pH 6. The concentration of these solutions determined by analysis indicated a high purity for the original solid, so that no purification was attempted.

The concentration of the formaldehyde solutions was estimated by titrating the alkali produced by reaction with sodium sulphite to give the bisulphite compound.⁵ Acetaldehyde was estimated by the bisulphite method of Clausen⁶ and chloral by cleavage and oxidation with alkaline iodine solution.⁷ The formaldehyde solutions contained about 0.07 mole % of formic acid, which was estimated by titration and allowed for in the measurements. Acetaldehyde solutions contained similar but more variable quantities of acetic acid, and it was found more convenient to neutralize these by adding dilute sodium hydroxide solution, the required amount being determined by a pilot titration. The sodium acetate thus introduced was allowed for.

Most of the measurements of acid strength depended on the effect of added aldehyde on the conductivity of dilute sodium hydroxide solution, as described by Long and Ballinger.³ All measurements were carried out at $25^\circ \pm 0.005^\circ$. The conductivity cell had an effective capacity of about 8 ml and a cell constant of about 0.5: it had two limbs, one of which contained the sodium hydroxide solution and the lightly platinized electrodes, while the other contained the aldehyde solution and enabled measurements to be made shortly after mixing the solutions. The conductivity was measured with a Tinsley bridge (type 4896) fed by a 1000 cycle valve oscillator, and the balance point was detected by a valve amplifier connected to a high impedance voltmeter. Calibration with potassium chloride solutions showed a reproducibility of 0.25 %. All operations were carried out in an atmosphere of oxygen-free nitrogen in order to avoid contamination by carbon dioxide and oxidation of the aldehydes. The measured conductivities of sodium hydroxide solutions agreed within experimental error with the equation used by Darken and Meier⁸ to represent their accurate measurements in the range 0.001–0.05 M, thus showing that carbon dioxide had been successfully excluded. All three aldehydes undergo slow chemical reaction in alkaline solution; formaldehyde to formate and methyl alcohol, acetaldehyde to acetaldol, and chloral to chloroform and formate. This was reflected in a change of conductivity with time, but at the low alkali concentrations used extrapolation back to the time of mixing involved an uncertainty of less than 0.5 %.

If the mobility of the anion $R_1R_2C(OH)O^-$ is known (l_A), then the change in conductivity can be used to determine the anion concentration x , since

$$\frac{\lambda_0}{\lambda_0 - \lambda} = \frac{b(l_{Na} + l_{OH})}{x(l_{OH} - l_A)} \quad (1)$$

where b is the stoichiometric concentration of sodium hydroxide (allowing for dilution by the added aldehyde solution), λ the measured conductivity after mixing, and λ_0 the conductivity of sodium hydroxide solution of concentration b . The mobilities are those appropriate to the concentration b , which was kept approximately constant for each aldehyde studied. The equilibrium constant of the reaction $R_1R_2C(OH)_2 + OH^- \rightleftharpoons R_1R_2C(OH)O^- + H_2O$ is then defined by

$$K' = x/(b-x)(\alpha a - x), \quad (2)$$

where a is the stoichiometric aldehyde concentration and α the fraction of aldehyde which is hydrated. The following procedure can then be used to evaluate l_A and K' . For each solution investigated, K' is calculated from eqn. (1) and (2) for a series of reasonable values of l_A , and K' is plotted against l_A . The plots obtained for the different solutions should all intersect in one point giving the true values of l_A and K' . In practice, this determines K' fairly accurately, but gives only an approximate value of l_A , which is in any case much less than l_{OH} .

With a sufficiently weak acid, such as acetaldehyde hydrate, it is possible to choose concentrations such that $x \ll \alpha a$, when (1) and (2) can be combined to give

$$\frac{1}{a} = \frac{\alpha K' \lambda_0 (l_{OH} - l_A)}{(\lambda_0 - \lambda)(l_{OH} - l_{Na})} - \alpha K'. \quad (3)$$

In this case $1/a$ is a linear function of $\lambda_0/(\lambda_0 - \lambda)$, and K' can be obtained from the intercept without any knowledge of l_A , which can be derived from the slope. Fig. 1 shows this plot for acetaldehyde.

The constant K' should be effectively independent of ionic strength at the low concentrations used, and the thermodynamic dissociation constant of $R_1R_2C(OH)_2$ is given by $K_a = K'K_w$. The results obtained for acetaldehyde and formaldehyde are given in table 1, most of the values being the average of 2-4 experiments. The corrections applied to $\lambda_0 - \lambda$ allow for the presence of formic acid in the formaldehyde and of sodium acetate in the acetaldehyde solution; they were calculated from the equivalent conductivities of sodium formate and sodium acetate at the appropriate concentrations.

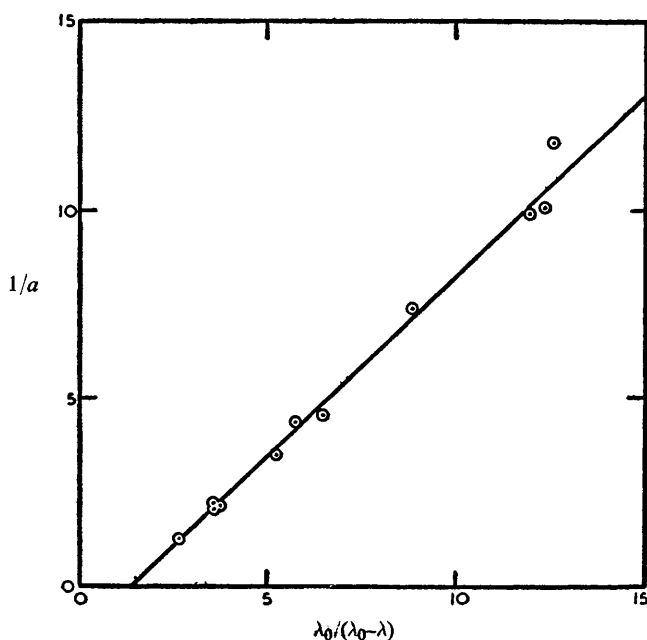


FIG. 1.

The conductivity method is not very suitable for chloral, since $K' \approx 8000$, and reaction with hydroxide ions goes almost to completion even at concentrations of about 2×10^{-3} M. The mean of nine experiments gave $pK_a = 10.0 \pm 0.1$, $I_A = 25$. A more accurate value was obtained by measuring the pH of buffered solutions with a Cambridge pH-meter. In calculating pK_a it was assumed that

$$pH = -\log [H^+] + \frac{0.5I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.1I,$$

using Davies' empirical expression⁹ for f_{\pm} . The results obtained are given in table 2.

DISCUSSION

The values of pK_a obtained for the hydrates of formaldehyde and acetaldehyde agree substantially with our earlier less accurate values.⁴ On the other hand, our value for chloral hydrate, 10.04, differs considerably from the value of 11 obtained by Euler¹⁰ from the conductivity of the ammonium salt and is closer to $pK = 9.77$, derived indirectly from kinetic measurements.^{10a} The new value invalidates the statement made by Bell and Higginson¹¹ that the catalytic power of chloral hydrate as an acid is greater than would be anticipated from its dissociation constant.

The values derived for the mobilities of the ions $R_1R_2C(OH)O^-$ are considerably smaller than those for simple carboxylate ions (e.g., 40 for acetate, 56 for formate). This can be partly attributed to the greater length of the carbon-oxygen bonds in the gem-diols and their

TABLE 1.—EFFECT OF ALDEHYDES ON CONDUCTIVITY OF DILUTE SODIUM HYDROXIDE SOLUTION AT 25°

10 ³ <i>a</i>	10 ⁴ <i>b</i>	10 ⁵ <i>λ</i> ₀	10 ⁵ (<i>λ</i> ₀ - <i>λ</i>)	
			obs.	corr.
FORMALDEHYDE				
55	210	815	125	124
75	178	704	127	126
99	178	716	168	167
101	153	610	145	143
191	167	684	239	236
201	153	612	216	212
383	164	671	312	305
1914	167	682	450	422
<i>K'</i> = 5.38, p <i>K</i> _a = 13.27, <i>I</i> _A = 29.				
ACETALDEHYDE				
84	22.3	77.9	5.37	6.18
98	22.3	76.5	3.79	6.19
101	14.8	50.5	2.82	4.22
135	14.8	51.2	5.08	5.78
220	20.8	71.6	8.46	11.0
228	14.8	51.4	7.70	8.95
284	22.3	78.0	13.7	15.0
441	20.8	73.3	18.6	20.6
458	14.8	51.4	11.6	15.7
481	20.8	72.9	16.6	20.0
784	20.8	72.2	23.6	26.6
<i>K'</i> = 2.72, p <i>K</i> _a = 13.57, <i>I</i> _A = 24.				

TABLE 2.—pH OF PARTLY NEUTRALIZED CHLORAL SOLUTIONS

a = total chloral concentration ;*r* = stoichiometric buffer ratio, [CCl₃CH(OH)₂]/[CCl₃CH(OH)O⁻] ; mean p*K*_a = 10.04.

10 ³ <i>a</i>	214	211	204	196	106	52.9	189	183	
<i>r</i>	263	129	69	44.7	40.7	34.7	33.1	26.3	
pH	7.59	7.88	8.15	8.36	8.38	8.45	8.48	8.60	
p <i>K</i> _{<i>a</i>}	10.02	10.00	10.02	10.04	10.01	10.01	10.03	10.06	
10 ³ <i>a</i>	98.6	177	51.6	171	94.7	166	161	50.3	
<i>r</i>	22.9	21.9	20.0	18.2	15.9	15.9	13.8	13.2	
pH	8.66	8.68	8.68	8.74	8.82	8.79	8.86	8.86	
p <i>K</i> _{<i>a</i>}	10.03	10.06	10.00	10.04	10.05	10.03	10.05	10.02	
10 ³ <i>a</i>	91.9	88.5	48.9	84.8	47.6	79.7	44.2	42.2	39.4
<i>r</i>	12.9	10.2	10.0	8.3	7.8	6.2	4.57	3.47	2.51
pH	8.90	9.01	8.99	9.11	9.11	9.25	9.35	9.49	9.62
p <i>K</i> _{<i>a</i>}	10.05	10.06	10.02	10.07	10.03	10.09	10.05	10.07	10.07

ions, but it is probably also significant that the negative charge is concentrated on one oxygen atom instead of being spread over two, as in the carboxylate ions: this could lead to greater solvation and an increase in effective ionic size. It should also be noted that the carbon atom of the carboxylate ion has three groups attached in a planar arrangement, while in the ions studied here there are four groups tetrahedrally arranged. The anions of the monohydric alcohols were found by Ballinger and Long³ also to be less mobile than the carboxylate ions.

It has been shown by Stewart and Van der Linden¹² that the acid strengths of compounds $X \cdot C_6H_4 \cdot C(OH)_2CF_3$ correlate well with the Hammett aromatic substituent constants σ . The appropriate constants for the present series are Taft's σ^* , derived for aliphatic substitution.¹³ His constants are relative to $CH_3 = 0$, and the appropriate values for our compounds are therefore $CH_2(OH)_2$, $2\sigma_H^* = 0.98$; $CH_3CH(OH)_2$, $\sigma_H^* = 0.46$; $CCl_3CH(OH)_2$, $\sigma_H^* + \sigma_{CCl_3}^* = 3.14$. On this basis our values of pK_a correlate well with σ^* , if $\rho^* = 1.4$, which is identical with the value found by Ballinger and Long³ for substituted methanols. We can in fact include both series in the same relationship if we take $\sigma^* = 1.28$ for the substituent OH, and allow statistically for the number of OH-groups. Extrapolating our own results to $\sigma^* = 0$ gives $pK_a \approx 14.5$ for $(CH_3)_2C(OH)_2$, the hypothetical hydrate of acetone. No hydration can be detected spectrophotometrically in aqueous acetone, and studies of isotopic oxygen exchange¹⁴ suggest that it takes place only to a very small extent: hence aqueous solutions of acetone would not be expected to show detectable acid properties.

¹ Bieber and Trümpler, *Helv. chim. Acta*, 1947, **30**, 1860.

² Bell and Clunie, *Trans. Faraday Soc.*, 1952, **48**, 439. Bell and McDougall, *Trans. Faraday Soc.*, 1960, **56**, 1281.

³ Ballinger and Long, *J. Amer. Chem. Soc.*, 1959, **81**, 1050, 2347; 1960, **82**, 795.

⁴ Bell and McTigue, *J. Chem. Soc.*, 1960, 2983.

⁵ Walker, *Formaldehyde*, 2nd edn. (Reinhold), p. 383.

⁶ Friedman, Cotonio and Schaeffer, *J. Biol. Chem.*, 1927, **73**, 341.

⁷ Kolthoff, *Pharm. Weekblad.*, 1923, **60**, 2.

⁸ Darken and Meier, *J. Amer. Chem. Soc.*, 1942, **64**, 621.

⁹ Davies, *J. Chem. Soc.*, 1938, 2093.

¹⁰ Euler and Euler, *Ber.*, 1903, **36**, 4255.

^{10a} Gustafsson and Johanssen, *Acta chim. Scand.*, 1948, **2**, 42.

¹¹ Bell and Higginson, *Proc. Roy. Soc. A.*, 1949, **197**, 141.

¹² Stewart and Van der Linden, *Can. J. Chem.*, 1960, **38**, 399.

¹³ Taft, *J. Amer. Chem. Soc.*, 1953, **75**, 4231.

¹⁴ Cohn and Urey, *J. Amer. Chem. Soc.*, 1938, **60**, 679.