

996. *Kinetics of Hydration of Aliphatic Aldehydes.*

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Catalytic constants for the hydrogen ion in the acid-catalysed hydration of aliphatic aldehydes have been found to be almost constant in a homologous series. Anomalies in the observed kinetics of the base-catalysed hydrations have been traced to the formation of appreciable quantities of addition compounds between the aldehydes and the catalysing bases. Evidence is presented for the existence of such compounds.

IN studies of the kinetics of hydration and dehydration of acetaldehyde Bell *et al.*<sup>1,2</sup> reported serious deviations from the usual Brönsted relation for the base-catalysed reaction, although the acid-catalysed reaction was normal. The present work concerns the kinetics of the acid-catalysed hydrations of acetaldehyde, propionaldehyde, and n- and iso-butyr-aldehyde; it also presents kinetic and spectrophotometric evidence for the existence in solution of addition compounds between aldehydes and bases, accounting for the apparent abnormal behaviour of the base-catalysed hydrations.

## EXPERIMENTAL

Reaction rates were measured at 25°, a thermal device being used similar to that described by Wyatt.<sup>3</sup> The reactants were rapidly mixed in a thermally insulated silver calorimeter, and the subsequent change in temperature (*ca.* 0.2°) was measured as a function of time. The "slow" rate of heat evolution, following an instantaneous temperature rise associated with the heat of solution of the free aldehyde, may be characterised by a first-order rate constant. This rate constant is identified with that for the approach of the system to the equilibrium condition where about 50% of any simple aliphatic aldehyde is in the form of the *gem*-diol hydrate.<sup>4</sup> Experimental rate constants were obtained from slopes of plots of  $\log(T_\infty - T_t)$  against time, where  $T_\infty$  and  $T_t$  refer to temperatures at infinite time and time  $t$ , respectively. Temperatures were measured with an S.T.C. F23 thermistor (*ca.* 1500  $\Omega$  at 25°) which formed one arm of a D.C. bridge, the out-of-balance current of which operated a Philips GM6020 D.C. microvoltmeter. Temperature changes of 0.001° could be readily detected in this way. The balancing time of the voltmeter was  $\sim 1$  sec. and, during kinetic experiments, readings were taken at intervals of 2 sec. with the aid of a calibrated metronome and a tape recorder.

Extinction coefficients of propionaldehyde in salt solutions were measured with a Hilger Uvispek spectrophotometer equipped with an electrically heated cell-block maintained at 25°.

Aldehydes used were laboratory-grade reagents purified by fractional distillation in an atmosphere of nitrogen. Other chemicals were of "AnalaR" grade.

## RESULTS

Kinetic results for hydration of propionaldehyde in acetate buffer solutions at ionic strength 0.20 are shown in Fig. 1, where the solid lines correspond to the following values of the catalytic constants in the rate expression:

$$k_e = k_0 + k_H[H^+] + k_{HOAc}[HOAc] + k_{OAc^-}[OAc^-], \quad (1)$$

where  $k_e$  is the experimental first-order rate constant for heat evolution  $k_0 = 0.021 \text{ sec.}^{-1}$ ,  $k_H = 980 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ ,  $k_{HOAc} = 0.45 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ , and  $k_{OAc^-} = 0.18 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ .  $k_0$  was determined independently by experiments in phosphate buffers at pH's close to 7. Some experiments were also carried out in formate buffers and we have found the catalytic constants  $k$  (for  $H\text{-CO}_2H$ ) 2.12 and  $k$  (for  $HPO_4^{2-}$ ) 2.30  $\text{l. mole}^{-1} \text{ sec.}^{-1}$ . All catalytic constants other than  $k_0$  were determined by trial-and-error curve-fitting on graphs similar to Fig. 1, and we estimate the error in our rate constants to be  $\pm 10\%$ . The bad fit with set V is probably related to the

<sup>1</sup> Bell and Higginson, *Proc. Roy. Soc.*, 1949, *A*, 197, 141.

<sup>2</sup> Bell, Rand, and Wynne-Jones, *Trans. Faraday Soc.*, 1956, 52, 1093.

<sup>3</sup> Wyatt, *J.*, 1960, 2299.

<sup>4</sup> Gruen and McTigue, preceding paper.

very high buffer ratio (10 : 1) with its very low acetic acid concentrations, which may have been lowered still further by traces of strong base in the sodium acetate used.

Values of  $k_H$  obtained for various aldehydes in dilute ( $\sim 10^{-3}M$ ) hydrochloric acid at very low ionic strengths are shown in Table 1. pH's were measured in each case immediately on completion of the reaction, with an E.I.L. direct reading pH-meter. This was made necessary by the inevitable small traces of carboxylic acid in the aldehydes, which significantly affected the pH of unbuffered solutions. In all cases the reaction was started by breaking a bulb

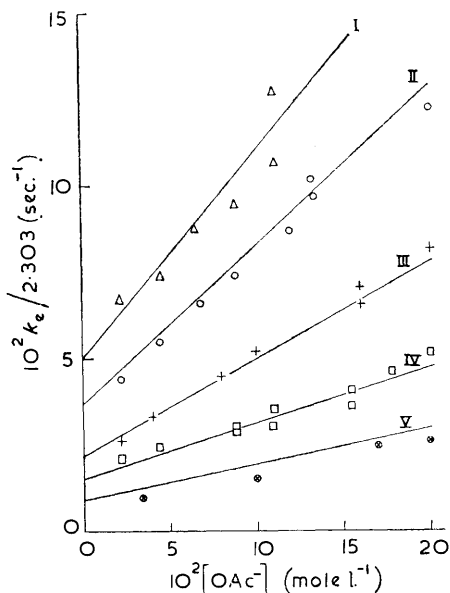


FIG. 1. Variation of first-order rate constants with concentration of acetate ion. Buffer ratios,  $[OAc^-]/[HOAc]$ : (I) 0.33, (II), 0.50, (III) 1.0, (IV), 2.0, and (V) 10.0.

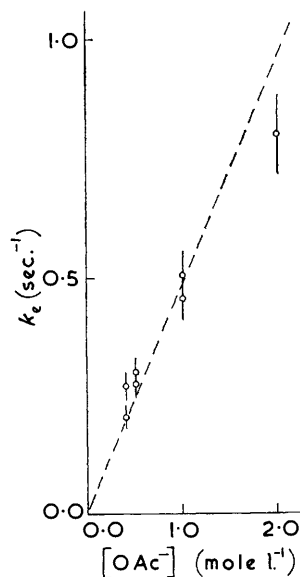


FIG. 2. Rate constants evaluated from evolution of heat on addition of propionaldehyde to sodium acetate solutions  $10^{-2}M$  in sodium hydroxide.

[Propionaldehyde]  $\sim 0.1 M$  in all cases.

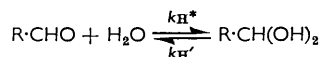
containing aldehyde into a stirred aqueous solution of the catalyst. The catalytic constants quoted in Table 1 are average values of a number of runs, the number in each case being given

TABLE 1.

$k_H$ , etc. for aldehydes in $\sim 10^{-3}M$ -HCl.				
R in R-CHO	Me	Et	Pr <sup>a</sup>	Pr <sup>b</sup>
$K_h$ .....	0.93	0.69	0.48	0.44
$k_H$ .....	1400	1200	1300	1200
$k_H^*$ .....	670	490	420	370
$k_H'$ .....	730	710	880	830
No. of runs .....	12	6	15	6

in the last row of the Table. The average deviation of individual rate constants from the mean was *ca.*  $\pm 5\%$ .

The observed rate constant,  $k_o$  ( $\approx k_H[H^+]$  at pH  $< 4$  in unbuffered solutions) is the sum of the forward and back rate constants  $k_H^*$  and  $k_H'$  in the reaction



We have the relation

$$k_H^* = k_H K_h / (K_h + 1), \quad (2)$$

where  $K_h$  is the equilibrium constant for the hydration <sup>a</sup> defined in such a way that

$$K_h = k_H^* / k_H' = [H]y_H / [A]y_A a_w \approx [H] / [A], \quad (3)$$

where H and A refer to the aldehyde hydrate and free aldehyde, respectively,  $a_w$  is the water activity, and the molar activity coefficients  $\gamma_H$  and  $\gamma_A$  will be close to unity at low ionic strengths if we take infinitely dilute aqueous solutions as our thermodynamic reference state.

The difference in the hydrogen-ion catalytic constants for propionaldehyde as determined in buffered and unbuffered solutions may be due to a salt effect or to a systematic error in our calculation of  $[H^+]$  in buffer solutions, for which we have used the simple formula

$$\log \gamma_{\pm} = -0.51I^{1/2}/(1 + I^{1/2}) \quad (4)$$

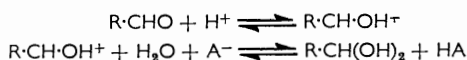
in calculating activity coefficients,  $I$  being the ionic strength.

The rate constants for heat evolution when propionaldehyde was added to various solutions of sodium acetate are recorded in Fig. 2. These solutions were all  $10^{-2}M$  in sodium hydroxide to ensure that the hydration reaction was effectively instantaneous. In the absence of acetate, in  $10^{-2}M$  hydroxide, all the heat released on dissolution of the aldehyde appeared in less than 2 seconds. Similar experiments with solutions of potassium monohydrogen phosphate revealed that all heat was evolved within 2 seconds.

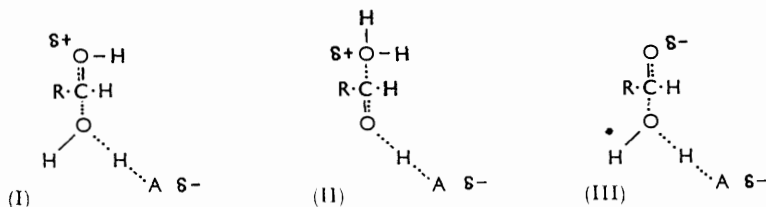
The extinction coefficients of solutions of propionaldehyde in solutions of potassium monohydrogen phosphate, sodium chloride, bromide, perchlorate, and acetate have been measured. The results obtained for sodium chloride, bromide, and perchlorate solutions are recorded and discussed elsewhere.<sup>4</sup> Some measurements were also made on solutions of sodium hydrogen carbonate, carbonate, and borate, but the comparatively low solubility of these salts rendered the results of indeterminate value. They are briefly referred to in the following discussion.

#### DISCUSSION

(A) *The Acid-catalysed Reaction.*—The mechanism of the acid-catalysed hydration of acetaldehyde has been discussed by Bell and Darwent;<sup>5</sup> here we merely draw attention to an additional mechanism which appears to have escaped attention:



*i.e.*, a pre-equilibrium proton transfer followed by a base-catalysed step—a mechanism formally similar to that postulated for enolisation of a ketone. The transition states for the rate-determining steps for the above mechanism (I) and that suggested by Bell and Darwent (II) are as shown. The effects of increasing the length of the hydrocarbon chain

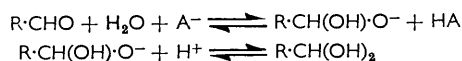


on the hydrogen-ion catalytic constants would be the same in either mechanism. Each mechanism requires the addition of a proton to the carbonyl-oxygen atom and nucleophilic addition of water to the carbonyl-carbon atom. Increasing the length of the hydrocarbon chain will increase the partial negative charge on both carbonyl-carbon and oxygen, and this will affect the rate of the proton-addition and water-addition in opposite directions. The observed similarity of the hydrogen-ion catalytic constants for the homologous series is therefore consistent with either mechanism.

The catalytic constants for formic and acetic acid determined for hydration of propionaldehyde indicate that, for this aldehyde at least, the exponent in the Brønsted relation is very close to that (0.54) found by Bell *et al.* for hydration of acetaldehyde,<sup>2</sup> and we should expect the butyraldehydes to behave similarly.

<sup>5</sup> Bell and Darwent, *Trans. Faraday Soc.*, 1950, **46**, 34.

(B) *The Base-catalysed Reaction.*—The mechanism suggested by Bell and Darwent<sup>5</sup> may be represented:



and the transition state in the rate-determining step may be represented as (III). This transition state differs by one proton from (I) and (II), and it is difficult to see how such a small difference could lead to the different behaviour of the acid- and base-catalysed hydrations with respect to the Brönsted relation, since deviations from this relation are usually regarded as arising from steric effects. Nucleophilic catalysis has been observed in many hydrolytic reactions,<sup>6</sup> but could scarcely be contributing to the catalysis of the hydration since this reaction is specifically the addition of a particular nucleophil, water, to a carbonyl centre. The origin of the kinetic discrepancy presumably lies in the ability of aldehydes to form addition compounds with nucleophils. The addition of  $\text{HSO}_3^-$ ,  $\text{CN}^-$ , and  $\text{NH}_3$  to aliphatic aldehydes is well known since each of these forms a stable solid adduct. Presumably, however, weaker nucleophils may add to aldehydes, even when the compounds formed are not sufficiently stable (as in the case of the hydrates themselves) to be isolated as solids at room temperature.

(C) *Nucleophilic Addition to Aldehydes.*—Since the observed extinction coefficient of an aldehyde in solution at 280  $\text{m}\mu$  is due to the free carbonyl group, formation of a hydrate or other nucleophilic adduct will lead to a lower extinction coefficient at this wavelength. We may express the observed extinction coefficient at 280  $\text{m}\mu$  in terms of the water activity of the medium, and various activity coefficients and equilibrium constants. Thus for the addition of any nucleophil, we have:



and the equilibrium constant

$$K_x = [\text{N}^-]y_{\text{N}}/[\text{A}]y_{\text{A}}[\text{X}^-]y_{\text{X}}, \quad (5)$$

where  $\text{X}^-$  and  $\text{N}^-$  refer to the nucleophil and nucleophilic adduct, respectively, and  $y_{\text{N}}$ ,  $y_{\text{A}}$ , and  $y_{\text{X}}$  are molar activity coefficients. Combining this equation with (3) we obtain:

$$[\text{A}]_{\text{an}} = [\text{A}]\{1 + K_{\text{h}}y_{\text{A}}a_{\text{w}}/y_{\text{H}} + K_{\text{x}}[\text{X}^-]y_{\text{X}}y_{\text{A}}/y_{\text{N}}\}, \quad (6)$$

where  $[\text{A}]_{\text{an}}$  is the analytical concentration of aldehyde in the solution. Thus

$$\epsilon = \epsilon_{\infty}/\{1 + K_{\text{h}}y_{\text{A}}a_{\text{w}}/y_{\text{H}} + K_{\text{x}}[\text{X}^-]y_{\text{X}}y_{\text{A}}/y_{\text{N}}\}, \quad (7)$$

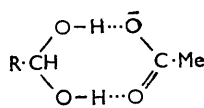
where  $\epsilon$  is the observed extinction coefficient of the aldehyde in any aqueous solution and  $\epsilon_{\infty}$  is the "true" extinction coefficient referred to the actual concentration of free aldehyde. We have

$$\epsilon = \epsilon_{\infty}[\text{A}]/[\text{A}]_{\text{an}} = \epsilon_{\infty}/(1 + K_{\text{h}}) \quad (8)$$

in pure water and we have used  $K_{\text{h}}$  data from Table 1 to calculate  $\epsilon_{\infty}$  for propionaldehyde.  $K_{\text{x}}$  values have been calculated by using equation (7).  $y_{\text{A}}a_{\text{w}}/y_{\text{H}}$  has been calculated from water activity data and the observed variations in the  $[\text{H}]/[\text{A}]$  ratios in concentrated solutions<sup>4</sup> of sodium chloride, bromide, and perchlorate, the assumption being that the anions of these salts do not add to aldehydes. This assumption is reasonable in view of (i) the low basic strength of these anions, and (ii) the observed increase in extinction coefficient with increasing salt concentrations, implying that the major effect of these salts is the reduction in water activity with increasing salt concentration and a corresponding decrease in the proportion of hydrate present. We can see no way of evaluating

<sup>6</sup> See, e.g., Jencks and Carriuolo, *J. Amer. Chem. Soc.*, 1961, **83**, 1743.

the activity coefficient ratio  $y_X y_A / y_N$  and we shall assume it to be unity to enable us to obtain a quantitative estimate of  $K_X$ . By assigning to  $K_X$  values of 0.10 for acetate addition and 0.45 for phosphate addition we can calculate "expected"  $\epsilon$  values for equation (7), and the calculated values are given by the solid lines in Fig. 3. In view of our assumptions regarding activity coefficients we regard the rough fit with our experimental points as an indication that nucleophilic addition of acetate and phosphate ions to propionaldehyde has occurred. Another possible interpretation of our spectroscopic data in acetate and phosphate solutions is that hydrogen-bonded complexes have formed between propionaldehyde hydrate and the anions, *e.g.*, (IV), which "stabilise" the hydrate relative



(IV)

to the free aldehyde in these solutions. Certainly part of the observed decrease in free aldehyde concentration may be due to this effect, but the observed rate of addition of acetate to the aldehyde could scarcely be due to the formation of such hydrogen-bonded species, which should be a very fast process. Other work with sodium carbonate, hydrogen carbonate, and borate suggests that nucleophilic addition occurs in these cases too, but the salt-concentration range

available was too small to be certain of this.

It is generally observed that the equilibrium constants for the addition of a chemically similar set of nucleophils to an electrophil are related to the nucleophil basic strengths by

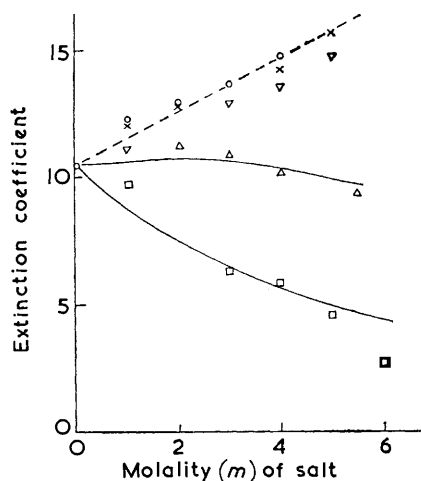


FIG. 3. Effect of salts on the apparent (broken line) and calculated (full line) extinction coefficients of propionaldehyde ( $\sim 0.03$  M) in water.

× NaCl, ○ NaBr, ▽ NaClO<sub>4</sub>,  
 Δ NaOAc, □ K<sub>2</sub>HPO<sub>4</sub>.

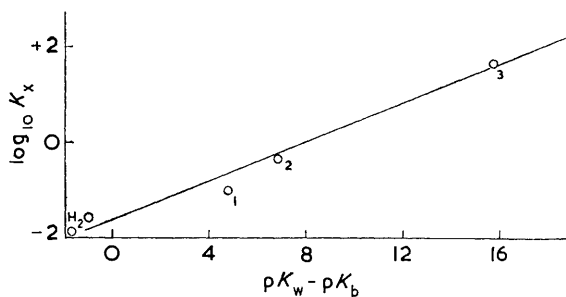


FIG. 4. Relation between the equilibrium constant for nucleophilic addition and the basicity constant of the nucleophil.

1, OAc<sup>-</sup>. 2, HPO<sub>4</sub><sup>2-</sup>. 3, OH<sup>-</sup>.

a linear free-energy relation. The four "oxygen" nucleophils which we now assume to add to propionaldehyde are water and the acetate, monohydrogen phosphate, and hydroxide ions. In Fig. 4,  $K_X$  is the equilibrium constant for nucleophilic addition, and  $K_b$  is the basicity constant of the nucleophil.  $K_X$  for water cannot be exactly determined, and we shall use  $K_b/55.5$  as an approximation to this quantity where 55.5 is the molar concentration of water in liquid water at 25°.  $K_X$  for hydroxide ions is  $K_a' K_b / K_w$  where  $K_a'$  is the acidity constant of propionaldehyde hydrate (taken as the same as that for acetaldehyde hydrate<sup>7</sup>).  $K_w$  is the ionisation constant of water. The fact that all the points fall close to a straight line (of slope 0.1) is a strong indication that we are dealing

<sup>7</sup> Bell and McTigue, *J.*, 1960, 2983.

with genuine examples of nucleophilic addition and, until further work is done, Fig. 4 should be a useful guide to the extent of nucleophilic addition of "oxygen" bases to aldehydes in aqueous solution.

(D) *Conclusions.*—The apparent effects of nucleophilic addition on the kinetic studies of aldehyde hydrations arise from the assumption that the reaction rate constant, measured from the slow evolution of heat when an aldehyde is rapidly mixed with a buffer solution, is due solely to hydration. In fact, there may also be addition to the aldehyde of the basic component of the buffer. Together, these two reactions may lead to a "distorted" first-order rate constant for heat evolution. Thus a base present in a mixture of catalysts can affect the rate of heat evolution in two ways; it can catalyse the hydration in the generally accepted fashion, and can add directly to the aldehyde to form a nucleophilic adduct. Separation of the two reactions from accurate kinetic data is always possible in principle, but the experimental error involved in the measurement of the quite large rate constants by thermal methods makes this possible in practice only when the two rates are very different. The rates of addition have been determined in solutions of ionic strength 0.5, 1.0, and 2.0 and hence the second-order rate constant for the addition obtained from the slope of the line in Fig. 2 does not refer to any particular ionic strength, and the non-linearity of the curve probably reflects a salt effect. Further, the measured rate constant is the sum of two rate constants (for the forward and the reverse reaction). In view of these uncertainties we estimate the second-order rate constant as  $0.5 \pm 0.2$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, referred to the analytical aldehyde concentration. Our observation that hydration proceeded at a measurable rate in sodium acetate solutions in the absence of added hydroxide gives a good indication that the nucleophilic adduct formed is ionised, since if it were un-ionised the solution would rapidly become alkaline within a fraction of a second after the start of the reaction, and no slow heat evolution due to hydration would be observed.

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