Kinetics of the Addition of Hydroxide Ions to Substituted Benzaldehydes

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Rates and equilibria have been investigated for the addition of hydroxide ions to ten substituted benzaldehydes in aqueous solution at 25 °C. Enthalpies of reaction are also reported, and the extent of hydration of five of the aldehydes. The rates of addition of hydroxide ions are almost proportional to the corresponding equilibrium constants; the rate of dissociation of the adduct is almost unaffected by substitution. It is concluded that the state of the carbon–oxygen bonds in the transition state corresponds closely to that in the adduct, but that the state of solvation of the transition state resembles that of the initial reactants.

THERE have been several recent investigations of equilibria in the addition of hydroxide ions to substituted benzaldehydes [1-3] and it has been proposed to use such equilibria for establishing an acidity function scale.[3] We have found that these processes have half-lives in the range 0.1—1 ms, and they are thus conveniently investigated by the temperature-jump technique. The present paper reports velocity constants for the forward and reverse reactions of ten compounds, and compares them with the corresponding equilibrium constants. Enthalpies of reaction have also been determined, as well as the extents of hydration of several of the aldehydes.

EXPERIMENTAL

The substituted benzaldehydes were all derived from commercial specimens, and their characteristics are given in Table 1. The values recorded for $\lambda_{max.}$ and $\varepsilon_{max.}$ are for neutral aqueous solutions at 25 °C and refer to $\pi \longrightarrow \pi^*$ transitions in the benzaldehyde molecules. The molar absorptivities are mostly in fair agreement with those obtained by Greenzaid [1] on the basis of a single measurement for each compound, though the discrepancies are larger for compounds (3) and (9). For the latter our value agrees well with that of Bover and Zuman,[2] and for compounds (1) and (5) all three sets of values are in reasonable agreement. Compound (8) has also been studied by Bunnett and his co-workers,[4] with results agreeing with our own and those of Greenzaid.

Solutions were made with deionized freshly distilled water free from carbon dioxide and inorganic materials were of AnalaR grade.

TABLE 1

Compounds investigated

	Benzaldehyde	Purification	λ_{max} nm	$10^{-2}\varepsilon_{max}$ $dm^3 mol^{-1} cm^{-1}$
(1)	3-Chloro	Distillation *in vacuo* and partial freezing	249	108
(2)	3,4-Dichloro	Recryst. H_2O	260	124
(3)	2-Chloro	Distillation *in vacuo*	253	92
(4)	2,4-Dichloro		264	115
(5)	3-Nitro	Recryst. H_2O	233	216
(6)	2-Nitro		225	118
(7)	4-Chloro-3-nitro	Recryst. H_2O	245	178
(8)	2,6-Dichloro		255	57
(9)	4-Nitro	Recryst. H_2O	268	151
(10)	2-Chloro-5-nitro	Recryst. H_2O	240	204

Equilibrium Measurements.—These were made by measuring the absorbances (wavelengths given in Table 1) of solutions containing 10^{-5}—10^{-4}M aldehyde and sodium hydroxide in the range 0.005—2.5M, depending on the value of the equilibrium constant. For hydroxide concentrations below 0.25M the ionic strength was made up to 0.25M by the addition of sodium chloride. The solutions were made alkaline just before measurement so as to minimize the effect of slow side-reactions. Measurements were made in 1 cm silica cells in a Unicam SP 500 spectrophotometer with the cell compartment at 25 ± 0.1 °C and allowance was made at the lower wavelengths for absorption by hydroxide ions. A single solution of each compound (in 0.1 or 0.25M sodium hydroxide) was also studied at five to

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[1] P. Greenzaid, *J. Org. Chem.*, 1973, **38**, 3164.

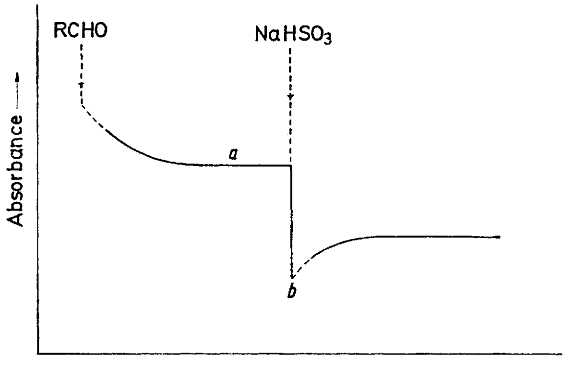
[2] W. J. Bover and P. Zuman, *J.C.S. Perkin II*, 1973, 786.

[3] W. J. Bover and P. Zuman, *J. Amer. Chem. Soc.*, 1973, **95**, 2531.

[4] J. F. Bunnett, J. H. Miles, and K. V. Nahabedian, *J. Amer. Chem. Soc.*, 1961, **83**, 2512.

ten temperatures in the range 10—46 °C. The absorbance at 25 °C remained unchanged after a temperature cycle.

For five of the compounds the position of the equilibrium $RCHO + H_2O \rightleftharpoons RCH(OH)_2$ [K_2 in equation (1)] was investigated by a modification of the first of the three methods recently reported by Sayer.[5] This involves adding a small volume of a solution of the aldehyde in acetonitrile to an aqueous acetate buffer and following the change of absorbance which takes place over the first few minutes. An excess of hydrogen sulphite is then added, and the change of absorbance again observed. The results of a typical experiment are shown schematically in the Figure. The molar absorptivity of the unhydrated aldehyde is obtained by extrapolating the initial first-order curve back to zero time, and that of the hydrogen sulphite compound from the steady value attained at the end of the experiment, which is close to zero for compounds not containing a nitro-group, but considerable for the nitrobenzaldehydes. The steady value reached after the addition of the solution of aldehyde in acetonitrile (point *a* on the diagram) refers to a solution of composition $(1 - x)RCHO + xRCH(OH)_2$, where x is the equilibrium fraction of hydrate. Immediately after the addition of hydrogen sulphite (point *b* on the diagram) the composition of the solution is $xRCH(OH)_2 + (1 - x)RCH(OH)SO_3H$, since only the unhydrated aldehyde reacts rapidly with hydrogen sulphite, and the corresponding absorbance is obtained by a short back-extrapolation of the second first-order change. The change of absorbance between *a* and *b* thus corresponds to the conversion of $(1 - x)RCHO$ into $(1 - x)RCH(OH)SO_3H$, and since the molar absorptivities of these species are known x can be calculated. For some of the compounds studied no change was observed beyond point *b*: this implies that the absorptivities of $RCH(OH)_2$ and $RCH(OH)SO_3H$ are indistinguishable, as was assumed by Sayer.[5] The method gave consistent results when the concentrations of buffer and hydrogen sulphite were varied.



Determination of the extent of hydration

The two kinetic portions of the curve in the Figure offer in principle an independent method of estimating the extent of hydration. The initial change refers to the approach to equilibrium, and the observed rate constant is therefore the sum of those for hydration and dehydration. The change after point *b* represents only the dehydration reaction, since it may be assumed that the unhydrated aldehyde is scavenged by hydrogen sulphite as soon as it is formed.[6] Combination of the two rate constants thus yields the hydration equilibrium constant K_2.* This method was practicable only for compound X, where it gave $K_2 = 0.62$; *cf.* $K_2 = 0.67$ by the method of the last paragraph.

Kinetic Measurements.—These were made with a Durrum-Gibson temperature-jump spectrophotometer. They employed the same solutions as the equilibrium measurements (wavelengths given in Table 1), though it was not possible to use concentrations of sodium hydroxide greater than 0.12M, since a further decrease in the resistance of the cell results in optical disturbances when the discharge is passed. The reaction cell was thermostatted at 20 °C and reached 25 ± 0.2 °C after the discharge. This was achieved by measuring the absorbance of a 4×10^{-5}M-solution of compound (9) in sodium hydroxide at 20 and 25 °C, and then finding the value of the capacitor voltage (4.8 kV) which produced the same change of absorbance in this solution on discharge. Since these fast reactions presumably have low activation energies accurate temperature control is not necessary.

The first-order relaxation constants were obtained from a logarithmic plot of the absorbances read manually from the oscilloscope traces. Experiments were carried out in duplicate.

RESULTS

Equilibria.—In aqueous alkaline solution an aldehyde is involved in three equilibria [reactions (1)], of which only

$$\begin{aligned}
&\underset{A}{RCHO} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{B}{RCH(OH)O^-}, \\
&\qquad\qquad K_1 = \frac{k_1}{k_{-1}} = \frac{[B]}{[A][OH^-]} \\
&\underset{A}{RCHO} (+ H_2O) \underset{\text{slow}}{\rightleftharpoons} \underset{C}{RCH(OH)_2}, \\
&\qquad\qquad K_2 = \frac{[C]}{[A]} \qquad (1) \\
&\underset{C}{RCH(OH)_2} + OH^- \underset{\text{fast}}{\rightleftharpoons} \underset{B}{RCH(OH)O^-} (+ H_2O), \\
&\qquad\qquad K_3 = \frac{K_1}{K_2} = \frac{[B]}{[C][OH^-]}
\end{aligned}$$

two are independent. The direct interconversion of A and C is relatively slow, but is accomplished indirectly in alkaline solution by a combination of $A \rightleftharpoons B$ and $B \rightleftharpoons C$, the second of which can be assumed to be very fast. Since the ratio [C] : [A] depends only on the temperature, the measurements of absorbance can yield only a composite equilibrium constant K, defined in equation (2),

$$K = \frac{K_1}{1 + K_2} = \frac{[B]}{([A] + [C])[OH^-]} = \frac{\varepsilon_0 - \varepsilon}{\varepsilon - \varepsilon_\infty} \cdot \frac{1}{[OH^-]} \qquad (2)$$

where ε_0 and ε refer to neutral and alkaline solutions respectively; ε_∞ refers to the anion B, and represents the limiting value at sufficiently high [OH^-]. It is readily shown that equation (2) is valid for any values of the molar absorptivities of the species A, B, and C. Previous

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* Strictly speaking the two kinetic observations do not refer to exactly the same conditions, because of the presence of hydrogen sulphite in the second process, but it is easily seen that its catalytic contribution will be small.

[5] J. M. Sayer, *J. Org. Chem.*, 1975, **40**, 2545.

[6] R. P. Bell and P. G. Evans, *Proc. Roy. Soc.*, 1966, *A*, **291**, 297.

studies[1-3] have also measured K, but have identified it with K_1 on the assumption that K_2 is negligibly small. As shown by Sayer[5] and by our own measurements this assumption is not always justified.

If equation (2) were strictly obeyed over the whole concentration range, values of K and ε_∞ could be obtained from the slope and intercept of a linear plot of ε against $(\varepsilon_0 - \varepsilon)/[OH^-]$. In practice, however, these plots are not always linear over a large range, curvature being particularly marked for compounds (4), (6), (7), and (10); as pointed out by Bover and Zuman[3] such variations in K can be accounted for by the non-ideal thermodynamic properties of concentrated alkaline solutions. For the purpose of interpreting kinetic measurements we have therefore preferred to use the above type of plot for extrapolation to obtain ε_∞, and then to calculate K by applying equation (2) to the result for solutions of moderate concentrations, usually 0.25 or 0.10M-sodium hydroxide. The values of ε_∞ are given in Table 2: they are effectively zero for compounds not containing a nitro-group. The values of K obtained by this method are also given in Table 2. They are mostly in fair agreement with the rather discordant results of earlier studies.[1-3]

TABLE 2

Summary of equilibrium results at 25 °C

Compd.	ε_∞ * / dm³ mol⁻¹ cm⁻¹	K / dm³ mol⁻¹	K_2	K_1 / dm³ mol⁻¹	$-\Delta H$ / kJ mol⁻¹
(1)	*ca.* 0	1.25	0.01	1.26	31
(2)	*ca.* 0	2.33	(0.02) †	2.4	28
(3)	*ca.* 0	2.44	(0.02) †	2.5	32
(4)	*ca.* 0	6.4	(0.06) †	6.8	34
(5)	3 280	7.4	0.08 ‡	8.0	30
(6)	3 070	9.1	0.11	10.0	30
(7)	4 030	14.8	(0.15) †	17	32
(8)	*ca.* 0	15.2	0.16	18	33
(9)	6 760	15.3	0.15	18	29
(10)	2 180	35	0.64	57	22

* Wavelengths given in Table 1. † Interpolated values. ‡ Value from ref. 1.

The equilibrium constant K_2 is difficult to measure accurately. The use of ^1H n.m.r. measurements is attractive in principle, but is hindered by the low solubility of the compounds in water. Sayer[5] has obtained consistent results for compound (9) by three different methods, and we have applied one of these to several other compounds, as described in the Experimental section. The results are given in Table 2: as might be expected, K and K_2 increase in parallel, and values of K_2 for the remaining compounds have been interpolated. Our value for compound (9) agrees fairly well with that of Sayer,[5] but values for compounds (1) and (6) derived from polarographic measurements[7,8] are much greater than our own, and seem improbably high. The resulting values of K_1 are also tabulated. In principle values of K_3 could also be given, since $K_3 = K_1/K_2$, but these would be subject to large uncertainties when K_2 is small. As will be shown later, the interpretation of the kinetic results is not sensitive to the exact values taken for K_2.

Enthalpies of Reaction.—These were determined by applying the equation $\Delta H = -R\,d(\ln K)/d(1/T)$ to the measurements on a single solution over a range of temperatures and are given in Table 2. This enthalpy is the effective value in the temperature-jump experiment, but is a composite quantity, being given by equation (3). Even

$$\Delta H = \Delta H_1 - K_2\Delta H_2/(1 + K_2) \qquad (3)$$

if ΔH_1 and ΔH_2 are temperature-independent ΔH will vary with temperature, on account of the temperature dependence of K_2 according to equation (4). However, insertion

$$d\Delta H/dT = -K_2(\Delta H_2)^2/(1 + K_2)^2RT^2 \qquad (4)$$

of typical values[9] for ΔH_2 shows that this variation would be barely detectable over the ranges of temperature investigated, which agrees with experiment.

TABLE 3

Kinetic results for 2-chloro-5-nitrobenzaldehyde (10)

Mean $k_1 = 22 \times 10^4$ dm³ mol⁻¹ s⁻¹, $k_{-1} = 0.38 \times 10^4$ s⁻¹

$10^3[OH^-]$/dm³ mol⁻¹	5	10	15	20	40	60	80	100
$10^{-2}k$/s⁻¹	26	35	57	67	115	142	222	265
$10^{-4}\,k_1$/dm³ mol⁻¹ s⁻¹	25	19	23	22	21	19	23	23

TABLE 4

Summary of kinetic results at 25 °C

Compound:	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
$10^{-3}\,k_1$ / dm³ mol⁻¹ s⁻¹	6.6	17	15	39	48	41	72	70	83	220
$10^{-2}\,k_{-1}$ / s⁻¹	50	72	59	58	51	45	42	40	47	38
K_1	1.26	2.4	2.5	6.8	8.0	10.0	17	18	18	57

Reaction Kinetics.—In the reaction scheme (1) it will be assumed that the second reaction is too slow to contribute to the observed rate, while the third process is always at equilibrium. The standard relaxation treatment then yields equation (5) for the observed first-order rate constant

$$\begin{aligned} k &= k_1[OH^-] + \frac{k_{-1}K_3[OH^-]}{1 + K_3[OH^-]} \\ &= k_1[OH^-] + \frac{k_{-1}(1 + K_2)K[OH^-]}{K_2 + (1 + K_2)K[OH^-]} \qquad (5) \end{aligned}$$

k. Since further $K = K_1/(1 + K_2) = k_1/k_{-1}(1 + K_2)$, provided that K_2 is known, kinetic measurements over a range of hydroxide ion concentration should yield values for k_1, k_{-1}, K, and K_1 without recourse to any other equilibrium measurements. However, in practice the range and

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[7] E. Laviron, H. Troncin, and J. Tirouflet, *Bull. Soc. chim. France*, 1962, 524.

[8] R. G. Barradas, O. Kutowy, and D. W. Shoesmith, *Canad. J. Chem.*, 1974, **52**, 1635.

[9] R. P. Bell, *Adv. Phys. Org. Chem.*, 1966, **4**, 1.

accuracy of the kinetic measurements is not sufficient to achieve this, and it is more satisfactory to use the directly measured value of K. Equation (5) can be transformed into (6), which was applied to the individual values of k and k_{-1} then calculated as $k_1/K(1 + K_2)$.

$$k_1 = k\{K_2 + (1 + K_2)K[\mathrm{OH}^-]\}/[\mathrm{OH}^-](1 + K_2)(1 + K[\mathrm{OH}^-]) \quad (6)$$

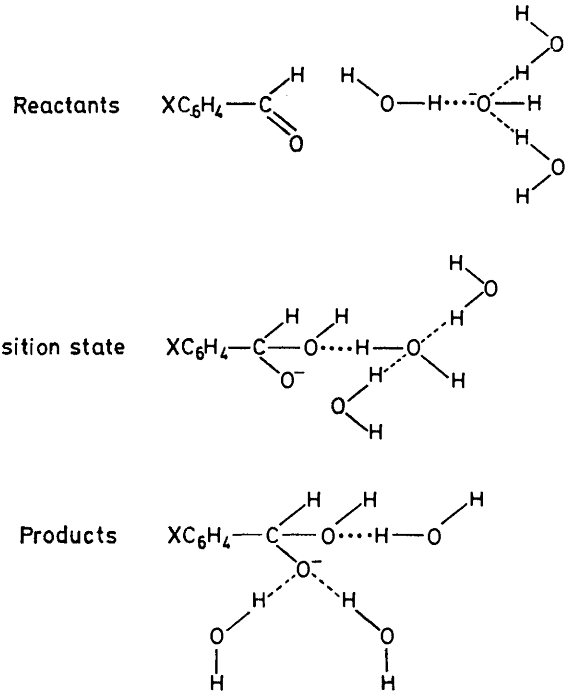
The validity of equation (6) may be illustrated by the detailed results for compound (10), which was studied over a large range of hydroxide ion concentrations, and for which the effect of the hydration equilibrium (K_2) is particularly marked. The results are given in Table 3, which shows that the calculated values of k_1 show no trend with concentration. If the results are treated on the assumption that $K_2 = 0$, the resulting values of k_1 vary systematically over a three-fold range. The results of applying equation (6) to the observed rates for all the compounds are collected in Table 4. Although the smaller values of K_2 are not known with any accuracy, this leads to little uncertainty in k_1 and k_{-1}; moreover, since K_1 and k_1 are affected in the same sense by changes in K_2, correlations between them will not be appreciably disturbed.

DISCUSSION

Equilibria.—Greenzaid [1] and Bover and Zuman [2] have shown that for *meta*- and *para*-substituents their values of K can be correlated with the appropriate sigma constants, and the same is true of our own values of K and K_1. All the values of ΔH in Table 2 correspond to an exothermic process. As shown by equation (3), ΔH is a composite quantity involving both ΔH_1 and ΔH_2. Values of ΔH_2 are not available for the compounds studied, but a general survey [9] of the addition of water to carbonyl compounds gives an average of $\Delta H_2 = -24$ kJ mol^{-1} for six compounds. If this is combined with the values of ΔH and K_2 in Table 2 we find an average value of $\Delta H_1 = -32$ kJ mol^{-1}, with no clear trend along the series.

This last value can be combined with K_1 to yield the standard entropy change for the addition of hydroxide ion, giving an average value of -89 J mol^{-1} K^{-1}. This decrease is somewhat smaller than the average decrease for the addition of water to carbonyl compounds,[9] which amounts to -122 J mol^{-1} K^{-1} after correction to a standard state of 1 mol dm^{-3}. This is probably because the negative oxygen in $\mathrm{RCH(OH)O^-}$ is less hydrated than the hydroxide ion, though this will be partly compensated by hydrogen bonding of solvent to the OH group. In the addition of a water molecule changes in solvation will be less important because of the absence of a net charge.

Kinetics.—The salient feature of the results in Table 4 is that the forward rate constant k_1 increases steadily along the series, being approximately proportional to the equilibrium constant K_1, while the reverse rate k_{-1} shows little, if any, trend with K_1. On a simple view (for example in terms of Leffler's principle [10]) this suggests that the transition state is very product-like, whereas the reverse conclusion would be reached from the observation that the forward reaction is considerably exothermic. This kind of contradiction can often be resolved by supposing that the energy of the system depends on two parameters which develop at different rates as the system passes along the reaction co-ordinate, and which are differently affected by substitution.[11] In the present instance the first parameter could be the orders or lengths of the two C–O bonds (sensitive to substitution), and the second some index of the interaction of the system with the solvent (insensitive to substitution). The observed facts can then be explained by the above Scheme, in which it has been assumed that the hydroxide ion in aqueous solution exists mainly as $\mathrm{OH(H_2O)_3}^-$,[12,13] though this is not a necessary feature of the explanation. The conversion of reactants into transition state consists largely in changes in the C–O bonds, with little solvent reorganisation, and will therefore be sensitive to the nature of the substituent X. On the other hand, the change products ⟶ transition state involves little change in the carbon–oxygen system, and consists essentially in the removal of water molecules from the negative oxygen into a position suitable for solvating the hydroxide ion which is eventually produced: its rate will therefore be little affected by the nature of X. This picture is consistent with the discussion of reaction entropies given in the preceding paragraph. An analogous interpretation has been given for proton transfers,[14] in which it is suggested



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[12] J. T. Edward and I. C. Wang, *Canad. J. Chem.*, 1962, **40**, 399.

[13] G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, 1963, **85**, 2376.

[14] See particularly contributions by W. J. Albery, R. A. Marcus, and M. M. Kreevoy in *Chem. Soc. Faraday Symposium*, 1975, vol. 10.

that re-solvation precedes proton transfer for uphill reactions, and conversely for downhill reactions, in agreement with the above sequence.

We have not been able to measure activation energies, but these can be estimated if the pre-exponential factor of k_1 is equated to the diffusion-controlled value, 4×10^{10} dm^3 mol^{-1} s^{-1}. This gives E_1 *ca.* 34 kJ mol^{-1} (average value), and hence E_{-1} *ca.* 66 kJ mol^{-1} for the reverse reaction. The latter is a reasonable value for the proposed resolvation process, and is similar to values derived for various proton-transfer reactions by applying Marcus theory to the curvature of Brönsted plots.[15-18]

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