Thermodynamic and Activation Parameters in the Reversible Hydration of 1,3-Dichloroacetone in Dioxan

By **R. P. Bell** * and **P. E. Sörensen**, Department of Chemistry, University of Stirling, Scotland

The reversible hydration of 1,3-dichloroacetone in aqueous dioxan has been studied spectrophotometrically at 12 temperatures between 277 and 333 K. Rates and equilibrium constants were measured at two water concentrations for the uncatalysed reaction, and the rate of the reaction catalysed by benzoic acid was studied at a single water concentration. The enthalpy and entropy of hydration agree with previous results in aqueous solution, and the magnitude of the entropy change can be interpreted statistically. The entropy of activation for the uncatalysed reaction is consistent with a cyclic transition state containing two extra water molecules, and the less negative value for catalysis by benzoic acid supports the view that the catalyst replaces one water molecule in the transition state.

THERE is now good evidence that in the uncatalysed reaction $R^1R^2CO + H_2O \rightleftharpoons R^1R^2C(OH)_2$ the transition state contains water molecules (probably two) in addition to the one which reacts, and that in the catalysed reaction one or more of these is replaced by a molecule of catalyst. This evidence derives mainly from the kinetic order with respect to water dissolved in a non-aqueous solvent [1-3] and also from a study of the isotope effects.[3] The structure of the transition state should also be reflected in the entropy of activation, and the present paper described a study over a range of temperatures of a system already studied at 25 °C.[1,3]

EXPERIMENTAL

Spectroscopic grade dioxan was purified as described by Bell and Critchlow.[3] It was stored under dry nitrogen and used within two weeks of distillation. The required

---

[1] R. P. Bell, J. P. Millington, and J. M. Pink, *Proc. Roy. Soc.*, 1968, *A*, **303**, 1.

[2] H. Dahn and J.-D. Aubort, *Helv. Chim. Acta*, 1968, **51**, 1348.

[3] R. P. Bell and J. E. Critchlow, *Proc. Roy. Soc.*, 1971, *A*, **325**, 35.

amounts of water and catalyst (if any) were added to the storage flask, and the solution was delivered directly into the reaction cell. The 1,3-dichloroacetone used was mainly the commercial product previously tested for purity.[3] Attempts to purify it by distillation at atmospheric pressure (b.p. 174—175 °C) were unsuccessful, since the product gave reaction velocities which were higher than normal, and which varied with the concentration of ketone; this is probably due to the catalytic effect of small quantities of hydrogen chloride formed during distillation. Distillation under reduced pressure gave a product having kinetic properties identical with those of the original sample, which was therefore used directly in most of the experiments. AnalaR benzoic acid was recrystallised twice from water and dried *in vacuo*.

Both equilibrium and kinetic determinations were made by measuring the absorbance at 285 nm due to the carbonyl group by means of a Unicam SP 500 recording spectrophotometer. (For solutions containing benzoic acid a wavelength of 300 nm was used to avoid absorption by the acid.) The cell compartment was thermostatted at 12 temperatures between 277 and 333 K by circulating water from a thermostat. A thermocouple in a second cell served to measure directly the temperature difference between the cells and the thermostat, which was as much as 1 K at the extremes of the range. At these extreme temperatures the uncertainty in the cell temperature was ±0·2 K, falling to ±0·05 K close to room temperature. The thermostat thermometer was calibrated against an N.P.L. standard. For experiments below room temperature dry air was passed through the cell compartment to prevent condensation of moisture.

The reaction was initiated by dissolving solid ketone in a mixture of dioxan, water, and catalyst (if any) already brought to the correct temperature in a 1-cm cell in the cell compartment. Dissolution and mixing was effected by a platinum wire stirrer, which was then removed and the cell sealed with Parafilm; reliable absorbance readings could be taken within *ca.* 30 s. The initial absorbance D_0 in the uncatalysed reactions could thus be obtained by a small back extrapolation, not exceeding 2%. The ketone concentration was about 0·03M; it was not known accurately since the weight of ketone was only a few mg, but the mean molar absorptivity for 63 experiments at two water concentrations was 29·8 at 285 nm, which is very close to the values of 29·3 ± 0·2 and 29·0 ± 0·6 previously reported.[3,4] The final absorbance D_∞ was measured after 10—12 half-lives and remained constant for a similar period. A plot of lg $(D_t - D_\infty)$ against t was strictly linear for at least 4—5 half-lives: its intercept at $t = 0$ gives lg $(D_0 - D_\infty)$ and its slope $-0{\cdot}4343k$, where k is the first-order velocity constant for the approach to equilibrium, equal to $k_h + k_d$, where k_h and k_d refer to the hydration and dehydration reactions respectively. The dissociation equilibrium constant is defined as $K_d = [K]/[K,H_2O] = k_d/k_h$, where K represents the ketone. We then have, in terms of measurable quantities, the equations (1).

$$K_d = D_\infty/(D_0 - D_\infty),\ k_h = k(D_0 - D_\infty)/D_0,\quad k_d = kD_\infty/D_0 \qquad (1)$$

For the uncatalysed reaction these equations were applied to each individual experiment. Essentially the same results are obtained if a mean value of K_d is taken for each set of experiments at a given temperature and water concentration.

The results for the uncatalysed reaction at two water concentrations are given in Table 1. Each entry represents the mean of 2—6 experiments. The values of k at 298·03 K ($x_w = 0{\cdot}1744$) and 297·98 K ($x_w = 0{\cdot}2858$) agree excellently with the equation previously found to fit experimental values at 298·15 K over a wide range of x_w [equation (2) of ref. 3].

TABLE 1

Uncatalysed reaction

$x_w = 0{\cdot}1744$, $C_w = 2{\cdot}35$ mol dm^{-3} at 298 K.

T/K	K_d	10^5k/s^{-1}	10^5k_h/s^{-1}	10^5k_d/s^{-1}
$277{\cdot}6_5$	0·524	2·33	1·53	0·80
$283{\cdot}4_5$	0·630	3·23	1·98	1·25
$288{\cdot}3_5$	0·873	4·61	2·46	2·15
$293{\cdot}1_1$	1·01	5·61	2·79	2·82
$298{\cdot}0_3$	1·20	7·15	3·25	3·90
$302{\cdot}9_2$	1·42	8·41	3·47	4·94
$307{\cdot}8_5$	1·72	10·5	3·86	6·64
$312{\cdot}7_5$	2·12	13·6	4·36	9·24
$317{\cdot}7_5$	2·58	17·7	4·94	12·8
$322{\cdot}6_5$	2·83	19·9	5·20	14·7
$327{\cdot}7_5$	3·56	26·0	5·70	20·3
$332{\cdot}4_3$	4·22	31·7	6·10	25·6
$x_w = 0{\cdot}2858$, $C_w = 4{\cdot}28$ mol dm^{-3} at 298 K.				
$277{\cdot}6_5$	0·371	11·4	8·28	3·07
$283{\cdot}6_5$	0·467	15·6	10·6	4·95
$288{\cdot}3_5$	0·579	20·7	13·1	7·60
$293{\cdot}0_9$	0·689	26·2	15·6	10·7
$297{\cdot}9_8$	0·841	34·0	18·5	15·5
$302{\cdot}8_5$	0·972	42·4	21·5	20·9
$307{\cdot}2_5$	1·17	53·9	24·9	29·0
$312{\cdot}8_5$	1·45	70·6	28·8	41·8
$318{\cdot}0_5$	1·73	85·1	31·2	53·9
$322{\cdot}4_5$	2·09	112	36·1	75·4
$327{\cdot}2_5$	2·39	132	38·8	92·7
$333{\cdot}2_5$	2·91	173	44·3	129

The experiments on catalysis by benzoic acid were carried out at a fixed water content and a fixed catalyst concentration. The rate of the catalysed reaction k^c was calculated as $k - k_0$, where k is the observed composite velocity constant and k_0 is the constant for the uncatalysed reaction at the same temperature and water content. k_0 Was obtained from the least squares analysis described in the next section. Since these reactions are fairly fast at the higher temperatures (half-lives down to 1 min) it is impossible to observe reliable values of D_0, and hence of K_d. K_d Was therefore calculated from the least squares analysis of the values for the uncatalysed reaction; previous work[3] indicates that it is unaffected by low concentrations of catalyst, and in fact at the six lowest temperatures the observed values of K_d are in good agreement with the calculated ones. We then have the equations (2).

$$k_h^c = (k - k_0)(1 + K_d)^{-1},\ k_d^c = k - k_0 - k_h^c \qquad (2)$$

The results are given in Table 2.

DISCUSSION

The plots of lg K_d, lg k_h or lg k_d against $1/T$ are in several instances noticeably curved, indicating finite values for ΔC_p or $\Delta C_p^\ddagger$. However, no curvature is evident in the plots for the catalysed reaction, or for K_d at the lower water concentration, where the experimental accuracy is somewhat lower. These conclusions

---

[4] P. Greenzaid, Z. Rappoport, and D. Samuel, *Trans. Faraday Soc.*, 1967, **63**, 2131.

are confirmed by a statistical treatment of the experimental data, following Kohnstam.[5] For the sake of consistency each set of data was computer fitted by least squares to an equation of the type (3) though the

$$\ln K\ (\ln k) = \mathrm{A} + \mathrm{B}T^{-1} + \mathrm{C}\ln T \qquad (3)$$

standard errors found for C show that in some instances no significant value can be assigned to it. The values of ΔH, ΔS°, ΔC_p, E_a, $\Delta S^\ddagger$, and $\Delta C_p^\ddagger$ (all at 298 K) were then derived from those of A, B, and C by standard procedures.[5] It is convenient initially to omit the concentrations of water and catalyst, which remain constant in each series of experiments; K_d is then dimensionless and k_h and k_d remain as first-order constants, so that no problems arise in the choice of a standard state for ΔS° and $\Delta S^\ddagger$. These concentrations are of course considered in interpreting the values of the parameters, which are collected in Table 3.

TABLE 2

Reaction catalysed by benzoic acid

$x_w = 0{\cdot}1744$, $C_w = 2{\cdot}35$ mol dm^{-3}, [acid] = 0·0515 mol dm^{-3} at 298 K

T/K	K_d	10^5k/s^{-1}	10^5k_0/s^{-1}	$10^5k_h^c$/s^{-1}	$10^5k_d^c$/s^{-1}
$277{\cdot}3_5$	0·517	21·9	2·37	12·9	6·63
$284{\cdot}0_5$	0·685	35·4	3·41	19·0	13·0
$288{\cdot}0_7$	0·806	46·1	4·20	23·2	18·7
$292{\cdot}9_5$	0·983	67·4	5·40	31·2	30·8
$297{\cdot}9_3$	1·20	95·2	6·91	40·2	48·1
$303{\cdot}5_2$	1·48	137	9·03	51·6	76·4
$308{\cdot}3_7$	1·78	195	11·3	66·0	118
$313{\cdot}4_5$	2·15	255	14·2	77·0	164
$318{\cdot}2_5$	2·55	359	17·4	96·2	245
$322{\cdot}0_2$	2·93	422	20·4	102	299
$327{\cdot}2_5$	3·51	720	25·2	154	541
$333{\cdot}4_5$	4·35	1010	32·0	183	795

TABLE 3

Thermodynamic and activation parameters at 298 K

ΔH and E_a in kJ mol^{-1}. ΔS°, $\Delta S^\ddagger$, ΔC_p, and $\Delta C_p^\ddagger$ in J mol^{-1} K^{-1}

	ΔH	ΔS°	ΔC_p
Dissociation equilibrium			
$x_w = 0{\cdot}1744$	28·8 ± 0·7	105 ± 2	71 ± 73
$x_w = 0{\cdot}2858$	28·2 ± 0·3	105 ± 1	80 ± 29
	E_a	$\Delta S^\ddagger$	$\Delta C_p^\ddagger$
Kinetics of uncatalysed reaction			
Hydration, $x_w = 0{\cdot}1744$	20·1 ± 0·5	−271 ± 2	−301 ± 54
Dehydration, $x_w = 0{\cdot}1744$	49·0 ± 1·0	−174 ± 4	−251 ± 112
Hydration, $x_w = 0{\cdot}2858$	24·5 ± 0·3	−242 ± 1	−259 ± 30
Dehydration, $x_w = 0{\cdot}2858$	52·7 ± 0·5	−149 ± 2	−176 ± 47
Kinetics of catalysed reaction			
Hydration, $x_w = 0{\cdot}1744$	36·1 ± 0·9	−197 ± 3	−40 ± 101
Dehydration, $x_w = 0{\cdot}1744$	64·9 ± 0·7	−99 ± 2	+31 ± 72

Table 3 shows that ΔH for the dissociation of the hydrate has the same value at the two water concentrations employed. It is also indistinguishable from the value $\Delta H = 29$ kJ mol^{-1} obtained by Greenzaid *et al.*[4] in their recalculation of the results of Bell and McDougall[6] for the equilibrium in aqueous solution.

Interpolation from the calorimetric results of Goates and Sullivan[7] shows that the partial molal enthalpy of water in our two dioxan solutions is about −0·1 and +0·9 kJ mol^{-1} respectively, relative to pure water. This is consistent with closely similar values for the enthalpy of dehydration in water and in aqueous dioxan, since the enthalpies of transfer of the ketone and its hydrate are likely to be small and partly self-cancelling.

Since it is well known that the hydrates of aldehydes and ketones are definite compounds (*gem*-diols) containing one water molecule,[8] the standard entropy of dehydration should be referred to the reaction $\mathrm{K,H_2O} \rightleftharpoons \mathrm{K} + \mathrm{H_2O}$, and its value will depend upon the choice of standard state. For a standard state of 1 mol dm^{-3} the correct values are obtained by adding $R\ln C_w$ to the values of ΔS° in Table 3, giving $\Delta S^\circ = 113$, 118 J mol^{-1} K^{-1} for the two water concentrations. These values are effectively the same, and it is interesting to note that a value of 118 is also obtained by the addition of $R\ln 55{\cdot}5$ to the value of ΔS° given by Greenzaid *et al.*[4] for dissociation of the hydrate in aqueous solution. A large entropy increase is of course expected for the dissociation of one molecule into two, and it has been recently pointed out by Page and Jencks[9] that a cancellation of several factors leads to very similar values for gas and solution reactions of this type. In the present instance calculation of the gain in translational entropy gives 116 J mol^{-1} K^{-1} for a standard state of 1M. If we include rotational terms, the production of a freely rotating water molecule would contribute a further 44 J mol^{-1} K^{-1}; however, this would be off-set by 37 J mol^{-1} K^{-1} if the two OH groups in the diol are assumed to undergo free internal rotation. Actually it is more realistic to suppose that in dioxan solution both the water molecules and the OH groups are prevented from rotating, so that the translational contribution is dominant.

In considering the kinetic parameters it is sufficient to examine either the hydration or the dehydration reaction; we shall deal with the dissociation of the hydrate. Considering first the uncatalysed reaction, although there is no formal change in the number of molecules on forming the transition state, Table 3 shows a large negative value of $\Delta S^\ddagger$. This is good evidence for the binding of extra water molecules in the transition state, and the values obtained are consistent with the formulation $\mathrm{K,H_2O} + 2\mathrm{H_2O} \longrightarrow \mathrm{K,3H_2O}^\ddagger$ suggested previously.[1,3] On this basis the entropy of activation (standard state 1M) is obtained by adding $-2R\ln C_w$ to the values in Table 3, giving −188 and −175 J mol^{-1} K^{-1} for the two water contents; it is doubtful whether these two values differ significantly, and a mean value of −181 J mol^{-1} K^{-1} may be assumed. As before, it is probably justifiable to assume that the rotation of the water molecules and the internal rotation of the OH

---

[5] G. Kohnstam, *Adv. Phys. Org. Chem.*, 1967, **5**, 121.

[6] R. P. Bell and A. O. McDougall, *Trans. Faraday Soc.*, 1960, **56**, 1281.

[7] J. R. Goates and R. J. Sullivan, *J. Phys. Chem.*, 1958, **62**, 188.

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

[9] M. I. Page and W. P. Jencks, *Proc. Nat. Acad. Sci. U.S.A.*, 1971, **68**, 1678.

groups are effectively frozen, and a calculation of the change in rotational entropy gives −206 J mol^{-1} K^{-1}. This is numerically somewhat greater than the observed value of −181, but it has been pointed out by Page and Jencks[9] that cyclic transition states will frequently have low-frequency stretching and bending modes which can make a considerable contribution to their entropy. In our proposed transition state, shown as Figure (a), the ring contains eight atoms and is held together by hydrogen bonds, so that the contribution of 25 J mol^{-1} K^{-1} is reasonable. In any case, the assumption that two extra water molecules are bound in the transition state gives considerably better agreement with experiment than if either one or three are assumed to be bound.

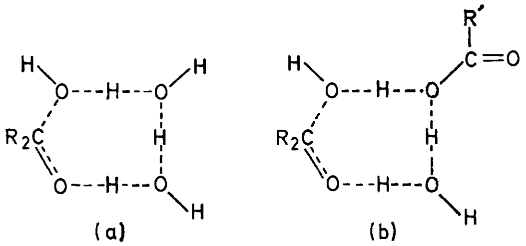

FIGURE Transition states for (a) uncatalysed, and (b) catalysed reactions. They have been drawn with the protons symmetrically placed, but this is not meant to imply any particular degree of proton transfer

The activation energy for the dehydration reaction is slightly but significantly greater at the higher water content. This can also be related to the incorporation of extra water in the transition state, since water in dioxan is appreciably associated,[10] and its degree of association increases with concentration. A similar change is apparent for the hydration reaction, but for the equilibrium (involving only one water molecule) no difference is detectable. The value of $\Delta C_p^\ddagger$ is too inaccurate to merit discussion, but it is consistent with the general observation[5] that $\Delta C_p^\ddagger$ and $\Delta S^\ddagger$ are of the same sign and similar magnitude when water molecules are bound in the transition state.

Turning to catalysis by benzoic acid, the decrease in kinetic order with respect to water (compared with the uncatalysed reaction) was at first interpreted by the replacement of two molecules of water in the transition state by one of carboxylic acid.[1] However, it was later realised that carboxylic acids are hydrated to a considerable extent in aqueous dioxan, so that a more realistic scheme is $A,H_2O + K,H_2O \rightleftharpoons K,A,2H_2O^\ddagger \rightleftharpoons A,H_2O + K + H_2O$, where A is the acid catalyst. The structure of the proposed transition state is shown in Figure (b). This formulation was supported by a study of hydrogen isotope effects[3] and will be used in interpreting our observed activation entropies; the hydration of carboxylic acids in aqueous dioxan has been confirmed by freezing point measurements in this laboratory.[11]

Since the reaction is certainly first order with respect to catalyst, the activation entropy for a standard state of 1M is obtained by adding $-R \ln [A]$ to the values in Table 3, giving −73 J mol^{-1} K^{-1} for the dehydration reaction. This is numerically considerably smaller than the value for the uncatalysed reaction, reflecting the fact that the formation of the transition state now involves 2 molecules ⟶ 1 molecule, rather than 3 molecules ⟶ 1 molecule. In fact, E_a for the catalysed reaction is 13 kJ mol^{-1} *greater* than for the uncatalysed one, so that the catalyst owes its effectiveness to its ability to bring with it one of the water molecules required for the transition state, rather than to a lowering of activation energy. The calculated change in translational entropy for the above reaction scheme is −134 J mol^{-1} K^{-1}, leaving 61 J mol^{-1} K^{-1} to be accounted for in terms of changes in rotations and vibrations. This is larger than the corresponding quantity for the uncatalysed reaction, but is similar to the values given by Page and Jencks[9] for the formation of cyclic products or transition states from two molecules.

We thank the Leverhulme Trust for a Fellowship awarded to P. E. S., Statens naturvidenskabelige Forskningsråd for financial support, and Dr. B. A. Timimi for valuable discussions.

[2/721 *Received, 27th March,* 1972]

---

[10] R. P. Bell and J. H. Wolfenden, *J. Chem. Soc.*, 1935, 822.
[11] To be published.