Table III. Typical Kinetic Data for the Reaction of 4-Chloroquinoline with *p*-Toluenethiol in Methanol[a]

Time, sec	NH_4CNS, ml	Reaction, %	$1/(a-x)$
0	4.84	0	34.42
130	4.72	9.92	38.21
275	4.62	18.18	42.07
405	4.53	25.62	46.28
555	4.45	32.23	50.79
747	4.37	38.84	56.27
1030	4.28	46.28	64.06
1450	4.20	52.89	73.10
2322	4.04	66.11	101.70

[a] Reaction solution, 0.0329 *M* in both reactants; temperature, 10°; resulting $k_{\mathrm{obsd}} = 2.87 \times 10^{-2}$, *k* in l. mole^{-1} sec^{-1}.

Kinetic Procedures. The reaction mixtures were prepared by weighing out a calculated amount of the substrate in a 25-ml volumetric flask, then adding about 15 ml of the solvent, a known volume of a standard solution of the thiol, and finally solvent to the mark. After shaking, the flask was immersed into a constant-temperature bath. Samples (2 ml) of the solution were withdrawn at appropriate time intervals and quenched in a separatory funnel containing ether and water. The ether layer was separated and washed with another 20 ml of water. The aqueous layers were combined, acidified with 6 *N* nitric acid, and analyzed for the chloride ion by the Volhard method. The extraction with ether was necessary in order to eliminate the sulfur compounds which interfere with the silver nitrate reagent. Data for a typical experiment are reported in Table III.

In the case of the reactions of the N-methyl-4-chloroquinolinium iodide, it was not possible to use the above-described procedure because of the high solubility of that compound in water; accordingly, the reactions were followed by an iodometric analysis of the unreacted thiol. Since color change in these conditions was not satisfactory by standard chemical methods, the titration end point was determined by an amperometric technique ("dead-stop method").

The Hydration of Acetaldehyde. I. Equilibrium Thermodynamic Parameters

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Abstract: The molar extinction coefficient for the n → π* absorption band of unhydrated acetaldehyde in aqueous solution has been measured directly, allowing spectrophotometric data to be used in the calculation of the value of the equilibrium constant for the hydration of acetaldehyde without making any assumption about the temperature dependence of $\Delta H°$ for that reaction. A combination of spectrophotometric and calorimetric data lead to the results for the hydration of acetaldehyde in pure water as solvent at 25°, $\Delta H° = -5.62 \pm 0.14$ kcal/mole and $\Delta S° = -18.7 \pm 0.5$ cal/mole deg (for a unit mole fraction standard state for water), while the corresponding average value of $\Delta C_p°$ over the temperature range 0–25° is -10 ± 5 cal/mole deg. The equilibrium constant is given equally precisely within experimental error by the two equations: $\log K_h = (1212.7/T) - 4.0412$ (which assumes $\Delta C_p° = 0$) and $\log K_h = (543.2/T) - 5.0330 \log T + 10.6594$ (which assumes $\Delta C_p° = -10$ cal/mole deg). The quoted uncertainties are 90% confidence limits.

The values of the thermodynamic parameters, particularly of $\Delta S°$ and $\Delta C_p°$, for the equilibrium addition of water to substrates in aqueous solution are of interest as bases for the interpretation of the corresponding activation parameters for hydrolysis reactions. For example, Kohnstam[1] has proposed that for solvolyses of alkyl halides and related compounds in mixed acetone–water solvents, the ratio, $\Delta C_p^{\ddagger}/\Delta S^{\ddagger}$, should be independent of the substrate for solvolysis *via* an SN1 mechanism and should have a lower value for solvolysis by way of an SN2 mechanism. The rationale for this mechanistic criterion is that both parameters are negative and that for SN1 solvolysis both are controlled by the increase in electrostatic solvation accompanying formation of the polar activated complex, while in SN2 solvolysis covalent binding of a solvent molecule will lower $\Delta S^{\ddagger}$ much more than $\Delta C_p^{\ddagger}$. That covalent binding of water does result in an entropy decrease of *ca.* 10–30 cal/mole deg seems well established,[2] but the absence of a similar large effect on the heat capacity is without experimental support (except that of Kohnstam's activation parameters) and seems based on the assumption that the value of $\Delta C_p°$ for covalently binding water will not differ by a large factor from that predicted for the loss of translational freedom arising from the combination of two mass points in the gas phase ($-5R/2$).

In view of the well-known large increases in heat capacity accompanying the solution of nonionic solutes in water[3-5] and of the changes in heat capacity which occur when substituents capable of hydrogen bonding to solvent are introduced,[6] this assumption would seem to be *a priori* a risky one. In fact, the only experimentally observed value of $\Delta C_p°$ for a simple covalent hydration appears to be that for the hydration of carbon dioxide, $CO_2 + H_2O \rightleftarrows H_2CO_3$, for which $\Delta C_p°$ is

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(1) G. Kohnstam, Special Publication No. 16, The Chemical Society, London, 1962, pp 179–195, and references cited therein.

(2) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, 1, 1 (1963).

(3) D. M. Himmelblau, *J. Phys. Chem.*, **63**, 1803 (1959).

(4) D. N. Glew and E. A. Moelwyn-Hughes, *Discussions Faraday Soc.*, **15**, 150 (1953).

(5) R. L. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, **73**, 1571 (1951).

(6) Compare, for example, $\Delta C_p° = -1$ cal/mole deg for ionization of ethanolammonium ion and $\Delta C_p° = +8$ cal/mole deg for methylammonium ion: ref 7, p 452.

(7) J. T. Edsall and J. Wyman, "Biophysical Chemistry," Vol. 1, Academic Press Inc., New York, N. Y., 1958, pp 550–590.

reported[7] to be −63 cal/mole deg. Although this value probably is not very precise, it hardly supports the contention that $\Delta C_p{}^\circ$ for such reactions should be small. Further, Kohnstam's criterion seems to work only for reactions in mixed solvents and fails for solvolysis in pure water.[1]

A reliable value of $\Delta C_p{}^\circ$ for such an equilibrium is required for the interpretation of the values of $\Delta C_p{}^\ddagger$ for the hydrolyses of carboxylate esters, which are currently being measured in these laboratories. The reversible hydration of a carbonyl group constitutes an even better model for these displacements at a trigonal carbon than for the displacements at a tetrahedral carbon to which Kohnstam's criterion refers, and the hydration of acetaldehyde

$$CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2 \quad (1)$$

was selected as the model reaction. This reaction has been widely studied[8] and several estimates of ΔS° are in the literature. However, these literature data do not permit an estimate of the value of $\Delta C_p{}^\circ$ to be made.

Since no available method for measuring the equilibrium constant

$$K_h = [CH_3CH(OH)_2]/[CH_3CHO] \quad (2)$$

for reaction 1 is sufficiently precise to allow a reliable value of $\Delta C_p{}^\circ$ to be determined from the temperature dependence of K_h, a combination of calorimetric measurements of the heat of hydration with measurements of K_h is required. Of the various possible methods for the measurement of K_h, ultraviolet absorption spectrophotometry appears most precise. Other methods such as nmr[9-12] give appreciably larger uncertainties.

Unfortunately, in order to evaluate K_h from measurements of the equilibrium value of the molar extinction coefficient, ϵ_∞, for the $n \rightarrow \pi^*$ carbonyl absorption band, the value of the extinction coefficient, ϵ_0, for unhydrated acetaldehyde in aqueous solution also must be known. The variation of ϵ_0 with solvent for analogous compounds[13] prohibits the use of the value found in nonaqueous systems. In order to solve this problem, Gruen and McTigue[14] chose that value of ϵ_0 (14.5 M^{-1} cm^{-1}) which led to a linear plot of log K_h *vs.* $1/T$, while Bell and Clunie[15] chose the value (17.0 M^{-1} cm^{-1}) which produced a slope of the plot of log K_h *vs.* $1/T$ which was in agreement with the value of ΔH_h calculated from calorimetric measurements. However, both of these approaches implicitly assume that $\Delta H^\circ{}_h$ is temperature independent, whereas it is the value of $\partial \Delta H^\circ/\partial T$ which is here sought. The only previous effort to measure ϵ_0 directly appears to have been that of Talvik and Kübar,[16] who obtained 14.2 M^{-1} cm^{-1}, but their result appears to be of low precision.

Experimental Section

Acetaldehyde. Eastman White Label acetaldehyde (100 g) was added to 5.0 g of magnesium oxide powder (previously dried by heating at *ca.* 60° for 12 hr on the vacuum line at $\leq 10^{-5}$ torr) and degassed by boiling under vacuum. The suspension was stirred magnetically for 0.5 hr at room temperature and the acetaldehyde then distilled three successive times on the vacuum line, retaining the middle two-thirds in each distillation. The product was stored under vacuum at *ca.* −20°, and samples were distilled on the vacuum line into thin-walled bulbs (for calorimetry) or breakseal tubes (for spectrophotometry) which were then sealed off. It was found that the mass of each sample could be determined with an uncertainty of no more than 0.3 mg (out of 800 mg in the bulbs and 100 mg in the tubes) by weighing the receiver before and after distillation and seal-off and applying an air buoyancy correction. Pure acetaldehyde was found to polymerize readily to a white elastomer when condensed from the vapor phase directly as a solid or when the liquid contacted a glass surface which was freshly blown or had been exposed to high vacuum for a long period. Polymerization was prevented by rinsing the bulb or tube with acetone, drying it by pumping for no longer than 10 min, condensing the acetaldehyde as a liquid in chloroform or fluorotrichloromethane slush, and allowing the glass surface which was heated during seal-off to be deactivated by exposure to acetaldehyde vapor before allowing the liquid to touch it. Samples prepared by this procedure contained less than 0.1% polymer (determined by breaking the bulb under water and weighing any precipitated solid) and about 0.0002% acetic acid (estimated from the change in pH observed when a bulb was broken in a sample of water).

Calorimetric Measurements. A 265-ml silvered dewar flask was used as a calorimeter, the contents being stirred magnetically. For each run, it was immersed in a water bath the temperature of which was near the anticipated final temperature of the calorimeter contents. The temperature inside the calorimeter was measured with a glass-enclosed thermistor probe (time constant, 2.5 sec) and an Industrial Instruments Model RC-18 conductivity bridge. The differences in temperature corresponding to measured differences in resistance were determined by measuring corresponding resistances and temperatures at 0.100° intervals (as defined by a Beckmann thermometer) and smoothing the data. Uncertainties in the measured resistance corresponded to temperature uncertainties of less than 0.001° at 25° and 0.0003° at 0°. Since the same temperature–resistance curve was used both for calibration of the calorimeter and measurements of the heat of hydration of acetaldehyde, uncertainties in the latter quantity arising from errors in temperature calibration should not exceed 0.3% (for a typical ΔT of 0.3°).

The calorimeter was calibrated by breaking bulbs of Baker and Adamson reagent potassium chloride (dried at 80° *in vacuo*) into 225.0 ml of water. (All water used in this work had been distilled in a metal still and then passed through an ion-exchange resin deionizing column.) The amount of KCl used was such that the composition of the final solution was $KCl \cdot 450H_2O$; the value of ΔH for this solution process was taken as 4.183 kcal/mole at 25°.[17] Uncertainties in this value are too small (*ca.* 0.2–0.3%) to be significant in this work.[18,19] The heat capacity of solid potassium chloride was assumed to be 0.16 cal/g deg.[20] The temperature increase arising from breaking the glass bulb was ≤0.1% of the smallest observed ΔT for either potassium chloride or acetaldehyde, and therefore was disregarded. Deviations of the final temperature of the KCl solution from 25.0° (never more than 1.5°) were corrected, using ΔC_p for the solution process as −36 cal/mole deg.[17] The total heat capacity of the calorimeter plus water was found to be 242.9 ± 0.9[21] cal/deg at 25.0°. The corresponding values for other temperatures were calculated from this number, assuming that the total change in heat capacity is due to the change in the heat capacity of the water. The water accounted for 92% of the total heat capacity, and the computed change over the range 0–25° was only 1%, so that errors from this assumption should be negligible.

Bulbs containing *ca.* 0.8 g of acetaldehyde were broken into the same quantity of water in the calorimeter as was used for the

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[8] For an excellent review, see R. P. Bell, *Advan. Phys. Org. Chem.*, **4**, 1 (1966).

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[13] M. Dertooz and J. Nasielski, *Bull. Soc. Chim. Belges*, **70**, 794 (1961).

[14] L. C. Gruen and P. T. McTigue, *J. Chem. Soc.*, 5224 (1963).

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[16] A. Talvik and I. Kübar, *Uch. Zap. Tartusk. Gos. Univ.*, **No. 95**, 31 (1960).

[17] S. Sunner and I. Wadsö, *Acta Chem. Scand.*, **13**, 97 (1959).

[18] R. J. Irving and I. Wadsö, *ibid.*, **18**, 195 (1964).

[19] S. R. Gunn, *J. Phys. Chem.*, **69**, 2902 (1965).

[20] Landolt-Börnstein, "Zahlenwerte und Functionen," Vol. 2, Part 4, 3rd ed, Springer-Verlag, Berlin, 1961, p 486.

[21] Confidence limits, 90%, calculated from the scatter in measurements on different samples.

calibration. The thermistor resistance was followed for a time period equal to 30 times the half-life for the hydration reaction. The measured resistance, R, was plotted as a function of time and the line defined by the points lying past 12 half-times was extrapolated back to the time, t_0, at which the bulb was broken. The difference between the value of this extrapolated resistance, R_{ex}, at t_0 and the value of R just before the bulb was broken was used to calculate the value of ΔH_s (for the reaction, $CH_3CHO_{(l)} \rightarrow CH_3CHO_{(aq)}$). A plot of $\ln (R - R_{ex})$ as a function of time was linear for more than seven half-times, indicating good first-order kinetics for the hydration, and the intercept of this plot at t_0 was used to calculate the value of $x\Delta H_h$ (where x is the fraction of acetaldehyde hydrated at equilibrium and ΔH_h is the enthalpy change for reaction 1). In calculating the value of $x\Delta H_h$ for the final temperature, it was assumed that the heat capacity of liquid acetaldehyde was 0.5 cal/g deg (by comparison to related compounds for which the specific heat is known[22]). The half-time for hydration at 25° was about 60 sec, and the water for the 0° runs was made 6.0×10^{-5} M in $HClO_4$ in order to make the half-time at that temperature also approximately equal to 60 sec. This should have allowed any small error in the measured ΔH values which arose from lag in the response of the calorimeter to cancel in the difference between the values for the two temperatures. The vapor space in the calorimeter was 23 ml, which, in combination with the vapor pressure data, requires that no more than 0.03% of the acetaldehyde escaped into the vapor phase during any calorimetric run.

Spectrophotometric Measurements. Optical densities were measured using a Cary Model 14 recording spectrophotometer. The linearity of the optical density scale was checked using solutions of potassium nitrate (Mallinckrodt AR, recrystallized once from water), and deviations were found to be less than 1% over the range used. Extinction coefficients reported in this paper are relative to an assumed extinction coefficient for KNO_3 in 0.1 F aqueous solution of 7.20 M^{-1} cm^{-1} at the absorption maximum (*ca.* 302 mμ). The cell was thermostated by circulating water and the temperature measured in a dummy cell which was identical with the cell used for the spectral measurements. Errors in reported temperatures should be <0.1°.

All spectral data reported for acetaldehyde were obtained on samples from which air was totally excluded. The silica absorption cell was fused *via* a graded seal to a borosilicate glass bulb into which a weighed quantity of solvent was distilled on the vacuum line before the bulb was sealed off. A known mass of acetaldehyde was contained in an evacuated breakseal tube also fused to the solvent bulb. The entire assembly was brought to a known temperature, the breakseal broken, the contents thoroughly mixed, and a sample of the resulting solution isolated in the absorption cell by a high-vacuum stopcock to prevent exchange of solute or solvent with the remainder of the solution in the bulb *via* the gas phase. In all cases, the value of the optical density at the absorption maximum was obtained by recording the optical density while scanning through the appropriate range of wavelength. From the known volume and temperature of the bulb and the vapor pressure data for aqueous acetaldehyde solutions (or Raoult's law for solutions in cyclohexane) a correction to the acetaldehyde concentration for the amount lost into the vapor phase was calculated. This correction for the aqueous solutions at 15° was 0.4% at equilibrium and 1.1% before any hydration had occurred.

The value of the maximum extinction coefficient for unhydrated acetaldehyde, ϵ_0, in heavy water solution was obtained by extrapolating the optical densities observed for the absorption maximum back to the time at which the breakseal was broken. The acetaldehyde vaporized immediately when the seal was broken, so that the difference between the time the seal was broken and the mean time for solution of the acetaldehyde should not exceed a few seconds. The first reading of the optical density was usually obtained at about 1.8 min after breaking the seal, while the half-time for the hydration reaction in D_2O at 15.0° is about 13 min.

No attempt was made to measure ϵ_0 from the more rapid hydration in H_2O. To facilitate equilibration, the solutions used for the measurement of ϵ_∞ for acetaldehyde in H_2O were 10^{-3} M in HCl. Values of ϵ for acetone (Mallinckrodt AR) in H_2O and D_2O were measured using solutions from which air was not excluded.

Vapor Pressure Measurements. Known amounts of water and acetaldehyde were distilled into a bulb on the vacuum line. The bulb and an attached mercury manometer were thermostated by immersion in a water bath and the contents of the bulb were stirred magnetically. Equilibrium total vapor pressures were read to the nearest 0.1 mm both for the solution and for the water before the acetaldehyde was added.

pH Measurements. All measurements of pH were made using a Beckman Research pH meter, Model 1019, which was standardized against borax and phthalate buffers at the same temperatures at which the pH values were to be measured; pH readings were reproducible to better than 0.005 unit.

Results and Discussion

Spectrophotometric Measurements. The extrapolated maximum value of ϵ_0 for CH_3CHO in D_2O (occurring at *ca.* 278 mμ) at 15° was 15.62 ± 0.27^{21} M^{-1} cm^{-1}. The maximum ϵ for acetone (occurring at *ca.* 265 mμ) was also measured and found to be 17.84 ± 0.11^{21} M^{-1} cm^{-1} for solutions in H_2O and 17.67 ± 0.10^{21} M^{-1} cm^{-1} for solutions in D_2O. It is known[8] that acetone is only 0.2% hydrated in aqueous solution, so that this difference should represent a true solvent effect on ϵ_{max}. Assuming that the ratio of ϵ_{max} for solutions in H_2O to ϵ_{max} for solutions in D_2O is the same for acetaldehyde and acetone, the value of ϵ_0 for CH_3CHO in H_2O is thus 15.77 ± 0.30^{21} M^{-1} cm^{-1}. By analogy with the known behavior of acetone,[14] this value of ϵ_0 was assumed to be temperature independent.

The equilibrium values of the maximum extinction coefficient of acetaldehyde in H_2O, ϵ_∞, are given in Table I as a function of temperature, along with the values of K_h calculated from eq 3 (which implicitly assumes ϵ

$$K_h = (\epsilon_0 - \epsilon_\infty)/\epsilon_\infty \qquad (3)$$

for acetaldehyde hydrate to be zero at 278 mμ).

Table I. Equilibrium Extinction Coefficients and Equilibrium Constants for Acetaldehyde in H_2O

Temp, °C	ϵ_∞, M^{-1} cm^{-1}		K_h		
	a	*b*	Obsd[c]	Calcd[d]	Calcd[e]
10.2	5.92	5.79	1.724	1.731	1.714
15.0	6.48	6.39	1.468	1.469	1.463
20.0	7.10	7.02	1.246	1.246	1.246
25.0	7.71	7.66	1.059	1.062	1.066
30.0	8.31	8.24	0.914	0.910	0.914
35.0	8.90	8.84	0.784	0.784	0.787
40.0	9.44	9.37	0.683	0.678	0.680
45.0	9.99	9.92	0.590	0.589	0.590
50.0	10.50	10.43	0.512	0.515	0.513

[a] From ref 15. [b] From this work. [c] Calculated from the values of ϵ_∞ and ϵ_0 found in this work. [d] From eq 4. [e] From eq 5.

Assuming the value of $\Delta C_p°$ for eq 1 to be zero, the least-squares equation of best fit for $\log K_h$ as a function of temperature is

$$\log K_h = (1212.7/T) - 4.0412 \qquad (4)$$

If the value of $\Delta C_p°$ is assumed to be −10 cal/mole deg (the value derived from the calorimetric measurements discussed below) and temperature independent, the corresponding equation is

$$\log K_h = (543.2/T) - 5.0330 \log T + 10.6594 \qquad (5)$$

Equations 4 and 5 give equally good fits to the experimental data; the sum of the squared deviations of the observed values of $\log K_h$ from those predicted by either equation is 2.3×10^{-5}.

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(22) Reference 20, p 307.

The values of K_h derived from similar spectrophotometric measurements and reported in the literature vary widely. For example, the values for 25.0° are 1.205,[15,23] 0.959,[14] and 0.874.[16] This spread is due primarily to the different values assumed for ϵ_0; the values of ϵ_∞ which may be reconstructed from the literature values of ϵ_0 and the corresponding equations for log K_h as a function of temperature do not differ widely from those reported here. The reconstructed values of ϵ_∞ from the work of Bell and Clunie[15] are included in Table I; for temperatures of 25° and above they parallel the values obtained in this work and are 0.7% higher, the deviation increasing to 2% at 10.2°. A similar parallelism is found in the ϵ_∞ values of Gruen and McTigue[14] (which are 3-5% lower than those obtained here) and of Talvik and Kübar[16] (which are 0-3% lower).

From the measurements on solutions of acetaldehyde in D_2O, the value of K_h at 15° for that solvent is 1.647 ± 0.019.[21] This gives an equilibrium solvent isotope effect, $K_h(H_2O)/K_h(D_2O)$, of 0.89, which may be compared to the value of 0.84 for 25° reported by Gruen and McTigue.[14]

In contrast to the earlier report[15] that the carbonyl n → π^* absorption band for acetaldehyde in hydrocarbon solvents shows no fine structure, pronounced vibrational splitting was observed in this work. The central maximum for solutions in cyclohexane fell at *ca.* 290 mμ and had ϵ 17.62 ± 0.12[21] M^{-1} cm^{-1}. However, two well-resolved maxima at *ca.* 282 and 297 mμ and two shoulders at 276 and 306 mμ were observed. The observed value of $\epsilon_{\max}$ did not change when the slit width was varied by a factor of 6 (maximum, 1 mm) around the value usually chosen. Similar behavior was observed for solutions in hexane.

Calorimetric Measurements. Table II lists the values of ΔH_s, $x\Delta H_h$, and the total enthalpy change, ΔH_T, which were observed. Also included are the corresponding parameters observed by Bell and Clunie.[15] In terms of the experimentally observed quantities, the value of ΔH_h for reaction 1 is given by eq 6 where

$$\Delta H_h = \epsilon_0(x\Delta H_h)/(\epsilon_0 - \epsilon_\infty) \qquad (6)$$

ϵ_∞ is the equilibrium maximum extinction coefficient calculated from the value of K_h given by eq 4 or 5. The uncertainties in $x\Delta H_h$ and ϵ_0 are known, but the uncertainty in ϵ_∞ is open to question. From the deviations of the observed values of K_h from those predicted by eq 4 or 5, the standard deviation of a single point from the curve of best fit is ±0.0018 in log K which implies an uncertainty in ϵ_∞ which is negligible compared to those in $x\Delta H_h$ and ϵ_0. A more realistically conservative estimation could be obtained by assuming that the relative 90% confidence interval around ϵ_∞ was equal to that found for ϵ_0 in D_2O. This procedure gives ϵ_∞ 7.64 ± 0.13 M^{-1} cm^{-1} at 24.9° and 4.56 ± 0.08 M^{-1} cm^{-1} at 0.5°. The corresponding values of ΔH_h then are −5.62 ± 0.14 kcal/mole at 24.9° and −5.38 ± 0.08 kcal/mole at 0.5°. These values of ΔH_h are in good agreement with the value implied by the temperature dependence of K_h; eq 4 gives ΔH_h = −5.55 kcal/mole as an average value over the range 10.2–50.0°, while eq 5 gives ΔH_h = −5.47 kcal/mole for 24.9°. The value of $\Delta S_h°$ corresponding to K_h and the calorimetric ΔH_h at 24.9° is −18.7 ± 0.5 cal/mole deg.

Table II. Results of Calorimetric Measurements

	At 0.5°		At 24.9°	
$-\Delta H_T$[a]	5.59 ± 0.03[b]	(5.64)[c]	4.18 ± 0.03	(4.40)
$-\Delta H_s$	1.76 ± 0.04	(1.96)	1.28 ± 0.04	(1.63)
$-x\Delta H_h$	3.82 ± 0.04	(3.68)	2.90 ± 0.03	(2.77)

[a] In kcal/mole. [b] All uncertainties are 90% confidence limits. [c] Values in parentheses are from ref 15 and refer to 0 and 25°.

From the slopes of the plots of log $(R - R_{ex})$ *vs.* t obtained from the calorimetric experiments, values of k_0 (the first-order rate constant for "uncatalyzed" hydration of acetaldehyde) and of k_H (the second-order rate constant for hydronium ion catalyzed hydration) can be estimated. The concentrations of H^+ and OH^- in the solutions were calculated from the observed pH, and small corrections (less than 4%) for the contribution of the hydroxide-catalyzed rate were made using the values of k_{OH} given by Bell and co-workers.[24,25] The value of k_0 was found to be 9.1 × 10^{-3} sec^{-1} at 24.8° and 2.3 × 10^{-3} sec^{-1} at 0.3°, and the value of k_H corresponding to 0.3° was 125 M^{-1} sec^{-1}.

Vapor Pressure Measurements. The partial pressures of acetaldehyde in equilibrium with aqueous acetaldehyde solutions were calculated from the observed total vapor pressure by assuming that the partial pressure of water obeyed Raoult's law (which is implied by the observation that the partial pressures of acetaldehyde so derived obey Henry's law) and that the vapor pressure of acetaldehyde hydrate was negligible (by analogy to that of the isomeric ethylene glycol). The Henry's law constants for acetaldehyde at various temperatures were: 0°, 1.11 atm; 10°, 2.00 atm; 20°, 3.70 atm; 30°, 6.59 atm; 40°, 10.8 atm.

In addition to providing the information necessary for calculating how much acetaldehyde escaped into the vapor phase in the calorimetric and spectrophotometric experiments, these data allow an independent check to be made of the accuracy of the calorimetric measurements. It may be shown that the temperature dependence of the observed Henry's law constant, k,

$$\frac{\mathrm{d}\ln k}{\mathrm{d}(1/T)} = \frac{1}{R}\left[\left(\frac{K_h}{K_h + 1}\right)\Delta H_h + \Delta H_s - \Delta H_v\right] \qquad (7)$$

is given by eq 7 where ΔH_v is the molar heat of vaporization of pure liquid acetaldehyde. For comparison, the value of ΔH_T determined in the calorimetric experiments is equal to $[K_h/(K_h + 1)]\Delta H_h + \Delta H_s$. Combining the value of ΔH_T determined for 25° with the literature value of ΔH_v for 21° (6.14 kcal/mole),[26] which should not be significantly different from that for 25°, gives a predicted value of d ln k/d(1/T) of −5.19 × 10^3 deg. The average value of d ln k/d(1/T) for the range 20–30° which corresponds to the observed Henry's law con-

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[23] The value of 1.5 which is widely quoted and attributed to ref 15 is inconsistent with the data therein.

[24] R. P. Bell and B. de B. Darwent, *Trans. Faraday Soc.*, **46**, 34 (1950).

[25] R. P. Bell, M. H. Rand, and K. M. A. Wynne-Jones, *ibid.*, **52**, 1093 (1956).

[26] C. F. Coleman and T. De Vries, *J. Am. Chem. Soc.*, **71**, 2839 (1949).

stants is $-(5.20 \pm 0.18) \times 10^3$, in good agreement with the calorimetric prediction.

Estimation of ΔC_p. The values of ΔH_h for 0.5 and 24.9° derived above imply an average value of ΔC_p for that interval of -10 ± 5 cal/mole deg. The uncertainty in this number was estimated from the known 90% confidence limits for ϵ_0, $(x\Delta H_h)_{0.5°}$ and $(x\Delta H_h)_{24.9°}$, and from the larger value for the uncertainty in ϵ_∞ discussed above. Errors in temperature were assumed negligible. If the error in ϵ_∞ is also assumed negligible, the 90% confidence interval for the average value of ΔC_p becomes 10 ± 4 cal/mole deg. The uncertainty in ΔC_p is appreciably smaller than the individual uncertainties in the two values of ΔH_h might at first suggest. This is due to the cancellation of a large part of the uncertainty in ΔH_h which arises from the uncertainty in ϵ_0 when the difference is taken. If the calorimetric data of Bell and Clunie[15] are combined with the values of K_h found in this work, the resulting value of ΔC_p is -9 cal/mole deg.

This value of ΔC_p clearly implies that the net contribution of solvation changes to ΔC_p for the hydration is small. The assumption made by Kohnstam[1] that the contribution to $\Delta C_p^{\ddagger}$ arising from covalent binding of the elements of water into an activated complex will be significantly smaller than the corresponding contribution to $\Delta S^{\ddagger}$ thus now has experimental support for reactions occurring in pure water as solvent. The failure of his mechanistic criterion for reactions in that solvent must therefore be due to large effects on $\Delta C_p^{\ddagger}$ and/or $\Delta S^{\ddagger}$ arising from solvation changes associated with charge separation rather than to any peculiar effects associated with covalent bond formation.

The calorimetric data also imply that for the solution of unhydrated CH_3CHO in water, $\Delta C_p = +20 \pm 3$ cal/mole deg. The data of Bell and Clunie imply $\Delta C_p = +13$ cal/mole deg. These positive values are about what would be anticipated for solution of a low molecular weight uncharged solute in water.

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The Hydration of Acetaldehyde.
II. Transition-State Characterization

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Abstract: Kinetic data on the hydrogen ion, hydroxide ion, and water-catalyzed hydration of acetaldehyde in aqueous solution have been analyzed by the $pK_a^{\ddagger}$ method and the following inferences drawn. The hydronium ion catalyzed reaction does not proceed *via* a mechanism involving rate-determining carbon–oxygen bond formation; it thus presumably involves rate-determining proton transfer. The data are consistent with a concerted mechanism for the other two catalytic paths in which the transition state is defined by rate-determining carbon–oxygen bond formation and all protons lie at potential minima. Assuming that the transition state for the hydroxide-catalyzed path has structure I, there are two approximately equally stable structures for the water-catalyzed transition state: II and III. (Hydrogen-bonded water molecules are omitted from all these structures.) The most probable average value of δ in the hydroxide- and water-catalyzed transition states lies between 0.5 and 0.6. The water-catalyzed transition state contains at least two strongly hydrogen-bonded water molecules (*i.e.*, this reaction probably proceeds *via* a push–pull mechanism), but the positions of the protons in the hydrogen bonds remain such that the charge distribution in the transition state closely approximates that shown in II and III.

The formally "uncatalyzed" or water-catalyzed hydration of acetaldehye

$$CH_3CHO + H_2O \longrightarrow CH_3CH(OH)_2$$

is in many ways analogous to the uncatalyzed hydrolysis of carboxylate esters, which is currently under investigation in these laboratories. Both show large solvent isotope effects ($k_{H_2O}/k_{D_2O} = 3.6$ for acetaldehyde dehydration at 0°,[1] and 3.8 for ethyl trichloroacetate hydrolysis at 20° [2]), both have very low entropies of activation [$\Delta S^{\ddagger} = ca.\ -38$ eu for acetaldehyde hydration (Tables I and II) and -43 eu for ethyl trichloroacetate hydrolysis[2]], both involve addition of water to a carbonyl group, and both additions are subject to acid and base catalysis. Since the transition states for the hydronium ion, hydroxide ion, and water-catalyzed hydration reactions differ stoichiometrically only in the numbers of protons and water molecules which they contain, it should be possible to characterize these transition states by the $pK_a^{\ddagger}$ approach.[3] Such an analysis for the aldehyde transition state should be simpler than that for the ester transition state, since there is one less oxygen atom which could serve as a site for protonation, and hence was attempted first.

The pseudo-first-order rate constant for acetaldehyde hydration in an aqueous solution containing the acidic

$$k = k_0 + k_H[H^+] + k_{OH}[OH^-] + k_{HA}[HA] + k_A[A^-] \qquad (1)$$

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(1) Y. Pocker, *Proc. Chem. Soc.*, 17 (1960).

(2) J. L. Kurz and M. E. DeBlois, unpublished observations.

(3) J. L. Kurz, *J. Am. Chem. Soc.*, **85**, 987 (1963).