Temperature dependent near-UV molar absorptivities of aliphatic aldehydes and ketones in aqueous solution

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Abstract—Temperature dependent molar absorptivities are reported for acetone, 2-butanone, 2-pentanone, 3-pentanone, acetaldehyde, propionaldehyde, and *n*-butyraldehyde in aqueous solution. Molar absorptivities are given at eight temperatures in the range $6.5-69.5^{\circ}$ C for wavelengths greater than 200 nm, a spectral resolution of 2.0 nm, and a spacing of 2.5 nm. For both ketones and aldehydes a shift to shorter wavelengths of approximately 10 nm is observed in the aqueous phase absorption spectrum relative to that found in the gas phase. For the ketones, there is an increase in the total intensity of the spectrum of approximately 5% over the range of temperatures studied. For the aldehydes a much larger change in the intensity of the absorption spectrum is observed, due to the temperature dependence of the hydration reaction

 $RCHO + H_2O \rightleftharpoons RCH(OH)_2; K_{hvd} = [RCH(OH)_2]/[RCHO].$

The change in the spectral intensity with temperature is used to determine thermodynamic parameters for the hydration reaction, giving the following results (at 25°C): acetaldehyde, $K_{byd} = 1.13 \pm 0.06$, $\Delta H = -19.7 \pm 0.6 \text{ kJ/mol}$, $\Delta S = -65.0 \pm 2.5 \text{ J/mol-K}$; propionaldehyde, $K_{hyd} = 1.02 \pm 0.06$, $\Delta H = -20.8 \pm 0.8 \text{ kJ/mol}$, $\Delta S = -69.6 \pm 3.1 \text{ J/mol-K}$; *n*-butyraldehyde, $K_{hyd} = 0.50 \pm 0.05$, $\Delta H = -27.0 \pm 2.2 \text{ kJ/mol}$, $\Delta S = -96.5 \pm 8.2 \text{ J/mol-K}$. The implications of these results for aqueous phase atmospheric chemistry are discussed.

INTRODUCTION

ALDEHYDES and ketones represent important trace constituents in the troposphere. While there has been extensive study of the gas phase photochemistry of these compounds, much less is known concerning their photochemistry in aqueous solution [1-3]. Aldehydes and ketones are efficiently scavenged by water, and are also produced by chemical reaction in raindrops [4]. Several aldehydes and ketones, including formal-dehyde, acetaldehyde, acetone, and 2-butanone, have been found in fog, mist, cloud-water, and rainwater [5-14]. Aqueous phase photolysis of aldehydes and ketones is a potential source of organic free radicals, and may also provide a mechanism by which rainwater becomes supersaturated in carbon monoxide [15].

An additional factor in the absorption of actinic UV radiation by aldehydes and ketones in aqueous solution is the equilibrium that exists between the free and hydrated forms of the compounds

$$RCHO + H_2O \rightleftharpoons RCH(OH)_2; K_{hvd} = [RCH(OH)_2]/[RCHO]$$
(1)

$$RCOR' + H_2O \rightleftharpoons RC(OH)_2R'; K_{hyd} = [RC(OH)_2R']/[RCOR'].$$
(2)

The hydrated (gem-diol) compound formed by reactions (1) or (2) does not absorb in the actinic UV. On the other hand, the gem-diol form of the aldehydes can react with the hydroxyl radical by a process that results in the formation of organic acids [16, 17]

$$RC(OH)_2 + OH \xrightarrow{O_2} RCOOH + H_2O + HO_2.$$
(3)

It has been suggested that reaction (3) is the main source of organic acids in the troposphere [18-20]. If this is correct, then the rate of formation of organic acids will be sensitive to changes in the equilibrium between the free and *gem*-diol forms of aldehyde molecules with temperature. Over 99% of aqueous phase formaldehyde exists in the *gem*-diol form [21, 22]. For larger aldehydes there are roughly equal amounts of the free and *gem*-diol forms in solution, while for ketones only a small fraction of the molecules exist in the *gem*-diol form [21].

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This paper reports the results of measurements of the temperature dependent near-UV absorption spectrum of aliphatic aldehydes and ketones in aqueous solution. The compounds investigated are acetone, 2-butanone, 2-pentanone, 3-pentanone, acetaldehyde, propionaldehyde, and *n*-butyraldehyde. The molar absorptivities that are obtained are compared to results found for the gas phase spectra of these compounds. For the aldehydes, the change in the intensity of the spectrum with temperature is used to determine thermodynamic parameters for the hydration reaction, which are compared with previous results.

EXPERIMENTAL

Carbonyl compounds were obtained from Aldrich at the following minimum purity: acetone (99.9%), 2-butanone (99%), 2-pentanone (97%), 3-pentanone (99%), acetaldehyde (99.5%), propionaldehyde (99%), and *n*-butyraldehyde (99%). Samples of each compound were dried over molecular sieve 4A and then distilled at reduced pressure. Compound purity was checked by UV-vis and FTIR spectral measurements and gas chromatographic analysis. No impurities were found after distillation.

Aqueous solutions of each carbonyl compound were prepared in high purity ($R > 15 \text{ M}\Omega/\text{cm}$) deionized water using standard volumetric techniques. Experiments were carried out using both air saturated and nitrogen saturated water. For the ketones, no difference was observed in solutions prepared using air or nitrogen saturated water. A majority of the ketone measurements were therefore carried out using air saturated water. For the aldehydes, it was found that in solutions prepared using air saturated water a slow chemical reaction took place producing a new compound with a strong absorption centered at 220 nm. This compound was identified as the carboxylic acid formed by oxidation of the aldehyde in solution. For solutions prepared in nitrogen saturated water no carboxylic acid formation was observed. Therefore, only data obtained in nitrogen saturated water were used in the determination of aldehyde molar absorptivities.

Absorption measurements were made in the double beam mode on a Shimadzu 265 UV-vis spectrophotometer with a temperature regulated cell holder. A matched set of quartz cuvettes with a 1.000 cm path length was used to contain the sample and reference solutions. Solution temperature was measured to $\pm 0.1^{\circ}$ C using a calibrated thermocouple sensor. Data were obtained at wavelengths in the range 200-350 nm at a spacing of 2.5 nm and a spectral bandwidth of 2.0 nm. Measurements were carried out at the following eight temperatures: 6.5, 11.2, 20.8, 30.5, 40.2, 50.1, 59.8, and 69.5°C. Absorption values were corrected for changes in the density of the sample solution with temperature using data on the temperature dependence of the density of pure water [23] (since the maximum concentration of carbonyl compound used in the measurements was 0.12 M, the relative density change of the experimental solutions with temperature should be approximately the same as that found for pure water). A total of 12-18 different concentrations of carbonyl compound were used in the determination of the temperature dependent molar absorptivities for each compound.

Molar absorptivities were found from the experimental data using the Beer's law relationship

$$a = (1/\ell) \,\mathrm{d}A/\mathrm{d}c,\tag{4}$$

where a is the molar absorptivity (in units of L/mol-cm, base 10), ℓ is the path length of the cell, A is the experimental absorbance, and c is the concentration of carbonyl compound (in units of mol/L). Data with A > 1 were excluded from the determination of the absorption coefficients. For data with A < 1 no systematic deviations from Beer's law were observed.

RESULTS AND DISCUSSION

The results of the experimental measurements are a set of molar absorptivities for each of the carbonyl compounds at eight experimental temperatures, in the wavelength region 200-350 nm. The results are discussed in detail below. The complete set of molar absorptivities are available from the authors upon request.



The precision of the molar absorptivities, determined by finding the standard deviation in the molar absorptivity at each wavelength and temperature, is 0.5% + 0.004 L/mol-cm. By reporting a single value for the precision of the results, small differences in precision from molecule to molecule or for the same molecule at different wavelengths or temperatures have been ignored. The major sources of systematic error (and their estimated magnitude) are believed to be in the preparation of solutions (0.2%)and the determination of the path length for the sample cuvette (0.1%). Absolute error in wavelength, based on a calibration of the spectrophotometer using the vapor phase spectrum of benzene, is estimated to be ± 0.2 nm. Absolute error in the molar absorptivities was estimated by periodically determining the molar absorptivity of potassium dichromate, measured in acidic aqueous solution, at wavelengths corresponding to the peaks and valleys in the dichromate spectrum (235, 257, 313, and 350 nm). Dichromate solutions were prepared using standard techniques [24]. Absorbance measurements were made for six or more solutions of varying dichromate concentration, and molar absorptivities were found using the same procedure used to analyze the aldehyde and ketone data. Based on the agreement between the experimental and literature [24] values for the molar absorptivities for dichromate, absolute error in the molar absorptivities due to instrumental error is estimated to be less than 1%.

The absorption spectra for acetone, 2-butanone, 2-pentanone, and 3-pentanone at 20.5°C are given in Fig. 1. For the ketones, the changes in the spectrum with temperature are small. The main changes in the spectrum are a shift in the peak of the spectrum to longer wavelengths with increasing temperature, and an overall increase in the intensity of the spectrum with temperature. These changes are summarized in Tables 1 and 2. Note that the intensity of the spectrum has been defined by the expression

$$I = \int a(\nu)/\nu d\nu, \tag{5}$$

where a(v) is the molar absorptivity, given as a function of frequency, and the integral is over the absorption band. An extrapolation procedure has been used to determine the shape of the absorption band at short wavelengths, where overlap with a more intense higher energy band occurs. Because the overlap of the near-UV absorption band and the higher energy absorption band is small, the error introduced by this extrapolation procedure should also be small.

A comparision of the ketone spectra in solution against the results obtained in the gas phase spectra of the compounds [25] reveals that there is a shift in the solution spectra to shorter wavelengths by about 10 nm compared to the gas phase spectra. Since the observed electronic transition in these molecules is an $n \rightarrow \pi^*$ transition, with the transfer of an electron from a nonbonding orbital of the oxygen atom to an antibonding π -orbital

T(°C)	$\lambda_{\max}(nm)$					
	Acetone	2-Butanone	2-Pentanone	3-Pentanone		
6.5	264.7	266.8	269.7	269.8		
11.2	264.8	267.0	269.9	270.0		
20.8	264.9	267.2	270.2	270.2		
30.5	265.1	267.6	270.6	270.6		
40.2	265.2	267.9	271.1	271.0		
50.1	265.4	268.2	271.4	271.4		
59.8	265.6	268.6	271.8	271.7		
69.5	265.8	268.9	272.1	272.2		
Gas†	276.0	277.9	280.0	279.7		

Table 1. Maximum wavelength* vs temperature for ketone spectra

* Obtained from a plot of absorption coefficient vs wavelength. \dagger From Ref. [25], at $T = 27^{\circ}$ C.

delocalized over the carbonyl group [26], the carbonyl group is less polar in the excited state than in the ground state. This results in a larger net stabilization of the ground electronic state in water, and therefore leads to a shift of the spectrum to shorter wavelengths in aqueous solution relative to the gas phase spectrum [27].

An overall increase in the intensity of the solution spectrum in comparison to the gas phase spectrum is also observed in the present results. This intensity increase is most likely to be the result of solute-solvent interaction. The electronic transition that takes place in these molecules is dipole forbidden, but becomes allowed due to vibronic coupling [26]. Solute-solvent interaction should increase vibronic coupling, and therefore lead to an increase in intensity in the solution phase spectrum relative to that found in the gas phase spectrum. Vibronic coupling would also account for the increase in the intensity of the spectrum with temperature, since such coupling increases with increasing vibrational excitation, and therefore with increasing temperature.

The temperature dependent absorption spectra for acetaldehyde, propionaldehyde, and *n*-butyraldehyde are given in Figs 2–4. As was the case for the ketone spectra, the aldehyde solution spectra are shifted to shorter wavelengths by about 10 nm relative to the gas phase spectra. The most obvious change in the absorption spectra is the increase in spectral intensity with increasing temperature, due primarily to the increasing fraction of free aldehyde molecules present in solution. If it is assumed that the absorption intensity of free aldehyde molecules is independent of temperature, then the equilibrium constant for the hydration of the aldehyde in solution, reaction (1), is given by the expression

$$K_{\text{hyd}}(T) = [\text{RC(OH)}_2] / [\text{RCHO}] = (I_0 - I_T) / I_T,$$
 (6)

T(°C)	Intensity					
	Acetone	2-Butanone	2-Pentanone	3-Pentanone		
6.5	2.990	3.374	4.10	3.706		
11.2	2.998	3.390	4.11	3.722		
20.8	3.021	3.418	4.14	3.753		
30.5	3.040	3.442	4.16	3.781		
40.2	3.058	3.461	4.18	3.811		
50.1	3.077	3.483	4.21	3.840		
59.8	3.094	3.505	4.23	3.866		
69.5	3.109	3.528	4.24	3.889		
Gast	2.600	2.852	3.076	2.929		

Table 2. Intensity* vs temperature for ketone spectra

* Spectral intensity is defined by Eqn (5), and has units of L/mol-cm.

† From Ref. [25], at $T = 27^{\circ}$ C.



Fig. 2. Temperature dependent absorption spectrum for acetaldehyde. Spectra are at the following temperatures (in °C, from bottom to top): 6.5, 11.2, 20.8, 30.5, 40.2, 50.1, 59.8, 69.5, --- gas phase spectrum, at $T=27^{\circ}$ C, from Ref. [25].



Fig. 3. Temperature dependent absorption spectrum for propionaldehyde. Spectra are at the following temperatures (in °C, from bottom to top): 6.5, 11.2, 20.8, 30.5, 40.2, 50.1, 59.8, 69.5. --- gas phase spectrum, at $T=27^{\circ}$ C, from Ref. [25].



Fig. 4. Temperature dependent absorption spectrum for *n*-butyraldehyde. Spectra are at the following temperatures (in °C, from bottom to top): 6.5, 11.2, 20.8, 30.5, 40.2, 50.1, 59.8, 69.5. --- gas phase spectrum, at $T = 27^{\circ}$ C, from Ref. [25].

Table 3. Intensity* and maximum wavelength† vs temperature for aldehyde spectra

	Acetaldehyde		Propionalde- hyde		<i>n</i> - Butyralde- hyde	
T(°C)	λ_{max}	IT	λ_{max}	IT	λ _{max}	IT
6.5	277.4	1.022	278.0	1.228	284.1	1.581
11.2	277.2	1.122	278.4	1.354	284.1	1.734
20.8	277.2	1.329	278.5	1.607	284.4	2.028
30.5	277.3	1.535	278.9	1.857	284.6	2.297
40.2	277.6	1.729	279.0	2.094	284.8	2.531
50.1	277.8	1.912	279.4	2.306	285.1	2.721
59.8	278.0	2.079	279.9	2.501	285.4	2.871
59.5	278.2	2.232	280.1	2.679	285.8	2.985
Gas‡	288	2.385	289	2.840	293	2.939

* Spectral intensity is defined by Eqn (5), and has units of L/mol-cm.

[†]Obtained from a plot of molar absorptivity vs wavelength.

 \ddagger From Ref. [25], at $T = 27^{\circ}$ C.

where I_T is the experimental spectral intensity at temperature T, and I_0 is the spectral intensity in the absence of the hydration reaction.

Experimental values for the temperature dependent spectral intensities of the aldehydes are given in Table 3. Because I_0 cannot be determined directly from experiment, it has been chosen as the value that results in the smallest standard deviation in the slope of the van't Hoff plot of $\ln(K_{hyd})$ vs 1/T. It is also assumed in the data analysis that there is a

Compound	Present results	Literature	
Acetaldehyde			
$I_0(L/mol-cm)^b$	3.02 ± 0.08		
K _{hyd}	1.13 ± 0.06	1.02, ^c 0.94, ^d 1.06, ^e 1.2, ^g 1.38, ^h 1.2, ⁱ 1.2 ^k	
$\Delta H(kJ/mol)$	-19.7 ± 0.6	-23.5°	
$\Delta S(J/mol-K)$	-65.0 ± 2.5	-78.2°	
Propionaldehyde			
$I_0(L/mol-cm)^{b}$	3.47 ± 0.09		
K _{hyd}	1.02 ± 0.06	0.68,° 0.77, ^d 1.8, ^f 0.714, ^g 1.24, ⁱ 0.83 ^j	
$\Delta H(kJ/mol)$	-20.8 ± 0.8	-21 ^j	
$\Delta S(J/mol-K)$	-69.6 ± 3.1	-70 ^h	
n-Butyraldehyde			
$I_0(L/mol-cm)^b$	3.23 ± 0.09		
K _{hyd}	0.50 ± 0.05	0.388,° 0.426, ^g 0.58, ⁱ 0.83 ^j	
$\Delta H(kJ/mol)$	-27.0 ± 2.2	-21 ⁱ	
$\Delta S(J/mol-K)$	-96 ± 8	70 ^j	

Table 4. Thermodynamic parameters for the aldehyde hydration reaction^a

* All values are given at $T = 25^{\circ}$ C.

^b Spectral intensity is defined by Eqn (5), and represents the intensity of the aldehyde spectrum at 25° C in the absence of the hydrolysis reaction.

^c Ref. [28].	^h Ref. [33].
^d Ref. [29].	¹ Ref. [34].
^e Ref. [30].	ⁱ Ref. [35].
^f Ref. [31].	^k Ref. [36].
^g Ref. [32].	

5% increase in the value of I_0 in going from the lowest to the highest temperature, as is observed in the corresponding ketone data, for which the hydration reaction is negligible.* Thermodynamic parameters for the hydration reaction are then determined from the slope and intercept in the van't Hoff plot.

The results of the above analysis are given in Table 4. Error limits in the results represent one standard deviation in the values for I_0 , K_{hyd} , ΔH , and ΔS . Also given in the table are previously reported values for the thermodynamic parameters, determined using a variety of methods, including UV spectroscopy [28, 30, 32], NMR spectroscopy [29, 31, 33, 34], calorimetry [30], and kinetic measurements of the forward and reverse rate constants for reaction (1), monitored by UV spectroscopy [35, 36]. In most cases only values for the equilibrium constant have been reported. For cases where the equilibrium constant has been given at a temperature different than 25°C, the value of ΔH obtained in the present results have been used to adjust the reported value of K to that expected at 25°C.

The values for K_{hyd} obtained in the present study are in good agreement with previous results. For the enthalpy and entropy change for the hydration reaction, only one set of values have previously been reported for each compound. The values for ΔH and ΔS obtained in the present study for propionaldehyde are in good agreement with those reported by BUSCHMANN et al. [35]. However, there is a significant difference between the present results and those found by BUSCHMANN et al. for *n*-butyraldehyde [35], and by Kurz for acetaldehyde [30]. While the reasons for the disagreement are not known, it should be noted that the present results should be more accurate than previous 'UV spectroscopic determinations of the equilibrium constant and thermodynamic parameters, since they make use of the integrated intensity of the absorption band to determine thermodynamic parameters, instead of measurements at a single wavelength. Also, the results obtained for the equilibrium constant by Buschmann et al. for both propionaldehyde and *n*-butyraldehyde in UV kinetic measurements [35] differ from those found in the same laboratory by NMR spectroscopic measurement [34].

The results from the present study have implications for the fate of aliphatic ketones and aldehydes in the troposphere. For aliphatic ketones, the shift in the absorption spectrum to shorter wavelengths in aqueous solution and the reduction in the quantum yield for photodissociation expected for molecules in solution implies that direct photodissociation should be slow in comparison to the rate of photodissociation found in the gas phase. Since the half-life of gas phase aliphatic ketones with respect to photodissociation has previously been estimated to be in excess of 10 h [25, 37], aqueous phase photodissociation should be a minor process for the removal of aliphatic ketones from the environment. For aliphatic aldehydes, the above factors plus the formation of the gem-diol by a substantial fraction of the aldehydes in solution means that direct photodissociation of aliphatic aldehydes should also be slow. However, formation of organic acids by the reaction of aldehydes in aqueous solution, reaction (3), may change significantly with temperature, due to the shift in the equilibrium constant for the aldehyde hydration reaction with temperature. Based on the present results, the fraction of aldehyde molecules in the gem-diol form in going from 25 to 0°C changes from 53 to 70% for acetaldehyde, from 50 to 69% for propionaldehyde, and from 33 to 57% for nbutyraldehyde. Therefore, with the exception of formaldehyde, the conversion of aliphatic aldehydes into organic acids in aqueous solution will be significantly affected by the change in the fraction of molecules in the gem-diol form with temperature.

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^{*} If I_0 is treated as a temperature independent constant, the thermodynamic parameters obtained for the hydrolysis reaction are as follows: acetaldehyde ($K_{hyd} = 1.35$, $\Delta H = -19.2 \text{ kJ/mol}$, $\Delta S = -62.0 \text{ J/mol-K}$); propionaldehyde ($K_{hyd} = 1.22$, $\Delta H = -20.2 \text{ kJ/mol}$, $\Delta S = -66.1 \text{ J/mol-K}$); *n*-butyraldehyde ($K_{hyd} = 0.61$, $\Delta H = -25.3 \text{ kJ/mol}$, $\Delta S = -89.1 \text{ J/mol-K}$). A comparison of these results with those presented in Table 4 shows that treating I_0 as a temperature independent constant has only a small effect on the calculated values for K_{hyd} , ΔH , and ΔS .

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