

Spectrochimica Acta Part A 56 (2000) 2653-2658

SPECTROCHIMICA ACTA PART A

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# Temperature dependent near-UV molar absorptivities of glyoxal and gluteraldehyde in aqueous solution

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Received 14 August 1999; received in revised form 28 April 2000; accepted 28 April 2000

#### Abstract

Molar absorptivities have been determined for glyoxal and gluteraldehyde in aqueous solution. Absorptivities are reported at eight temperatures in the range 5–70°C for wavelengths greater than 200 nm. For glyoxal the data indicate did less than 0.02% of the glyoxal molecules exist in the free dialdehyde form, and that at 25°C approximately 98% of the molecules are hydrated at both carbonyl groups, results that are consistent with previous experiments. For gluteraldehyde hydration of the two carbonyl groups occurs in an independent manner. The following thermodynamic data are found for gluteraldehyde hydration:  $\Delta H = -35.8 \pm 1.3$  kJ mole<sup>-1</sup>,  $\Delta S = 103 \pm 7$  J (mole K)<sup>-1</sup>, and  $K = 7.5 \pm 2.0$ . The results for gluteraldehyde are compared with previous results obtained for the hydration of aliphatic aldehydes. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Glyoxal; Gluteraldehyde; Dialdehyde; Gem-dial; Hydration

### 1. Introduction

Aliphatic aldehydes are important trace constituents in the Earth's atmosphere. In water aldehydes can form hydrates by the process:

R-CHO ↔ R-CH(OH)<sub>2</sub>  
$$K_{hyd} = [R-CH(OH)_2]/[R-CHO]$$
(1)

The equilibrium between free and hydrated aldehydes and the dependence of the equilibrium constant for hydration on temperature can play an important role in the chemistry of these compounds; in cloudwater, rainwater, and other atmospheric droplets [1-4] and can affect other chemical processes occurring there [5-7].

One method that has been used to study the hydration reaction is absorption spectroscopy. Since hydration removes the C=O chromophore, changes in the near UV absorption spectrum with temperature can be used to determine the equilibrium constant for hydration. In two previous studies [8,9] we have used absorption spectroscopy to determine thermodynamic information on the hydration reaction for several aliphatic aldehydes.

Dialdehydes have also been detected in the atmosphere. For example, glyoxal is typically

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present in cloudwater in micromolar concentrations [10–13], and has been observed at concentrations as high as 276  $\mu$ m 1<sup>-1</sup> in urban atmospheres [12]. As is the case for aldehydes, hydration can be expected to play a role in the chemistry of glyoxal in atmospheric droplets. While larger dialdehydes such as gluteraldehyde have not been detected in the atmosphere, such compounds have been suggested as intermediates in the oxidation of cyclic olefins [14]. The study of the hydration reaction of gluteraldehyde is also of interest in determining the degree of independence with which hydration of the two dicarbonyl groups proceeds when separated by several carbon atoms.

The present work reports measurements on the temperature dependence of the near UV absorption spectrum of glyoxal and gluteraldehyde in aqueous solution. For glyoxal the results indicate that a majority of the molecules are hydrated at both carbonyl groups. For gluteraldehyde the temperature dependent spectra are used to determine thermodynamic information on the hydration reaction, which is compared with previous results for aliphatic aldehydes.

# 2. Experimental

The experimental procedure used in the present measurements is a modification of that used in previous studies of the absorption spectra of carbonyl compounds [8,9] and is summarized here. Stock solutions of glyoxal (Aldrich, 40% by weight) and gluteraldehyde (Aldrich, 25% by weight) were used to prepare more dilute aqueous solutions of the compounds using high purity ( $R > 15 \text{ M}\Omega \text{ cm}^{-1}$ ) deionized water by standard volumetric techniques. The water was saturated with nitrogen before use to prevent oxidation of the dialdehyde during the course of the measurements. No evidence of oxidation was noted.

All absorption measurements were performed on a Shimadzu-265 UV-visible spectrophotometer with a temperature regulated cell holder. Data were obtained at the following eight temperatures: 6.5, 11.2, 20.8, 30.5, 40.2, 50.1, 59.8, and 69.5°C. Solution temperatures were measured to a precision of  $\pm 0.1^{\circ}$ C using a calibrated thermocouple sensor. Data were obtained at a total of 14 concentrations in the wavelength range 200–430 nm for glyoxal and 13 concentrations in the wavelength range 200–350 nm for gluteraldehyde. Experimental absorbances were corrected for the change in density of water with temperature [15]. Molar absorptivities were calculated from the experimental data using the differential form of Beer's law:

$$a = (1/\ell) \mathrm{d}A/\mathrm{d}c \tag{2}$$

where *a* is the molar absorptivity (in units of 1 (mole cm)<sup>-1</sup>, base 10),  $\ell$  is the path length of the cell (in cm), *A* is the measured absorbance, and *c* is the concentration of compound in solution (in units of mole 1<sup>-1</sup>). Measurements were limited to concentration of less than 0.4 mole 1<sup>-1</sup> for gly-oxal and less than 0.2 mole 1<sup>-1</sup> for gluteralde-hyde, and data with A > 1 were not used in the determination of molar absorptivity. For A < 1 no systematic deviations from Beer's law were observed in the data.

## 3. Results and discussion

The results of the experimental measurements are a set of molar absorptivities at eight experimental temperatures in the wavelength range 200–430 nm for glyoxal and 200–350 nm for gluteraldehyde. The absorption spectra are displayed in Figs. 1 and 2. The complete set of molar absorptivities are available from the authors on request.

The precision in the molar absorptivities, determined from the standard deviation in the results, is  $0.5\% + 0.006 \text{ l} \text{ (mole cm)}^{-1}$ . The major sources of systematic error in the measurements and their estimated magnitude are in solution preparation (0.2%), compound purity (0.2%), and measurement of the pathlength of the absorption cell (0.1%). The absolute error in molar absorptivities due to instrumental error is believed to be less than 1% based on the results from periodic calibration of the spectrophotometer against standard solutions of potassium dichromate [8,16]. Absolute error in wavelength, based on calibration of the spectrophotometer using the vapor phase spectrum of benzene, is estimated at  $\pm 0.2$  nm.

Since glyoxal is a dicarbonyl compound it can exist in aqueous solution as the free molecule or can be hydrated at one or both of the carbonyl groups. The processes involved are:

## CHOCHO $\leftrightarrow$ CHOCH(OH)<sub>2</sub>

$$\leftrightarrow CH(OH)_2 CH(OH)_2 \tag{3}$$

The equilibrium constant for the above process can be written as  $K_1 = [CHOCH(OH)_2]/$ [CHOCHO] for hydration of the first carbonyl group and  $K_2 = [CH(OH)_2CH(OH)_2]/$ 



Fig. 1. Temperature dependent absorption spectrum for glyoxal. 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. Absorption spectra, magnified by a factor of 10.



Fig. 2. Temperature dependent absorption spectrum for gluteraldehyde. 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.

 $[CHOCH(OH)_2]$  for hydration of the second carbonyl group. An overall hydration constant,  $K_{hyd}$ , can be defined by the relationship  $K_{hyd} = K_1K_2$ , as has been done in previous work on glyoxal hydration.

Comparison of the aqueous phase glyoxal spectra in Fig. 1 with the spectrum observed in the gas phase [17] and in *n*-heptane [18] shows that the lowest energy absorption band, centered at 430 nm, has completely disappeared. The disappearance of this band, which has been assigned as an  $n_{-} \rightarrow \pi_3$  transition involving molecular orbitals extending over both carbonyl groups [19], indicates that only a negligible fraction of free glyoxal molecules exist in aqueous solution. Similar behavior has been observed in aqueous solutions of biacetyl, and has been used to determine the equilibrium constant for hydration in that molecule [20].

If it is assumed that the intensity of the 430 nm absorption band for free glyoxal molecules in aqueous solution is approximately the same as in the gas phase, as is the case for aliphatic aldehydes [8,9,21], then the fraction of glyoxal molecules that do not undergo hydration, based on the error limits on absorptivity given above, is < 0.0002 ( $K_{hyd} > 5000$ ). This is in accord with qualitative observations by Buxton et al. [22] on the reaction of glyoxal in oxygenated aqueous solutions following pulse radiolysis, the anomalously high Henry's law constant for glyoxal in water [23,24], and the experimental value  $K_{hyd} = 7.2 \times 10^5$  recently reported by Montoya and Mellado [25].

The first absorption band appearing in the aqueous phase spectrum of glyoxal occurs at 290 nm. Although a weak absorption band appears in the gas phase spectrum of glyoxal at approximately the same wavelength, it is unlikely that the band observed in aqueous solution corresponds to the band observed in the gas phase. This is because the fraction of glyoxal molecules that exist in the free dialdehyde form in aqueous solution is, based on the argument presented above, extremely small. Instead, the band observed in solution is most likely due to the presence of the partially hydrated species CHOCH(OH)<sub>2</sub>. While there have not, to our knowledge, been any theo-

retical calculations for the electronic states and corresponding absorption spectrum of the partially hydrated molecule, the presence of a carbonyl group in CHOCH(OH)<sub>2</sub> would be expected to produce an absorption band in this wavelength region, based on comparison with the spectra observed for aliphatic aldehydes in solution [8,9].

Because the overlap between the weak band at 290 nm and a much stronger absorption band centered at  $\lambda \cong 200$  nm it is difficult to obtain precise information an the intensity of the long wavelength band. However, it is clear from examination of the spectra in Fig. 1 that the intensity of the 290 nm band increases with temperature, indicating some conversion of CH(OH)<sub>2</sub>CH(OH)<sub>2</sub> into CHOCH(OH)<sub>2</sub>. If the 290 nm band is due to CHOCH(OH)<sub>2</sub> and has an intensity similar to that observed for aliphatic aldehydes then the fraction of glyoxal molecules existing in the partially hydrated state is, at 25°C, approximately 0.02, which would mean that  $K_1 > K_2$ .

For gluteraldehyde there are also two sites where hydration can occur:

$$CHO(CH_2)_3CHO \leftrightarrow CHO(CH_2)_3CH(OH)_2$$
$$\leftrightarrow CH(OH)_2(CH_2)_3CH(OH)_2$$
(4)

The equilibrium constants for the above processes are  $K_1 = [CHO(CH_2)_3CH(OH)_2]/[CHO(CH_2)_3CHO]$  and  $K_2 = [CH(OH)_2(CH_2)_3CH(OH)_2]/[CHO(CH_2)_3CH(OH)_2].$ 

The weak absorption band centered at 280 nm seen in Fig. 2, arises from an  $n \rightarrow \pi^*$  transition in either of the two carbonyl groups, which due to the separation between them act as independent chromophores. The change in intensity of this band with temperature indicates that the relative number of free, partially hydrated, and fully hydrated gluteraldehyde molecules changes with temperature. If it is assumed that hydration occurs independently at the two carbonyl groups in gluteraldehyde then an equilibrium constant for hydration can be written as  $K = [R-CH(OH)_2]/$ [R-CHO], where R represents the remainder of the molecule. Evidence supporting this assumption is presented below. Note that because the carbonyl groups in gluteraldehyde are equivalent

*K* is related to  $K_1$ ,  $K_2$ , and  $K_{hyd}$  by the expressions  $K_1 = 2$  *K*,  $K_2 = K/2$ , and  $K_{hyd} = K_1K_2 = K^2$ .

Based on the assumption that hydration of the carbonyl groups in gluteraldehyde takes place in an independent manner the value for K can be determined by the method previously used in the analysis of absorbance data for aliphatic aldehydes [8]. The intensity of the 280 nm absorption band is defined as:

$$I(T) = \int a(v, T)/v \, \mathrm{d}v \tag{5}$$

where the integral is over the absorption band. Absorptivities for the 280 nm band have been corrected for overlap with a second band at shorter wavelength by fitting the long wavelength side of the second band to a Gaussian and then subtracting the absorptivities of the second band from the band at 280 nm. The intensities calculated for the 280 nm band by this procedure are relatively insensitive to the form of the Gaussian used to model the shorter wavelength band. If  $I_0$  is defined as the intensity of the 280 nm band in the absence of hydration, then:

$$K = [I_0 - I(T)]/I(T)$$
(6)

Since  $I_0$  cannot be directly found from experiment, it is chosen as the value giving the smallest standard deviation in the slope of the van't Hoff plot of ln *K* versus 1/T. As in previous work a 5% increase in the value of  $I_0$  in going from the lowest to the highest experimental temperature is assumed based on the intensity changes observed for aliphatic ketones in solution, where hydration is negligible.

The van't Hoff plot corresponding to the best fit of the experimental intensity information is given in Fig. 3. Based on this plot  $I_0 = 7.85 \pm 1.4$ ,  $\Delta H = 38.5 \pm 1.3$  kJ mole<sup>-1</sup>,  $\Delta S = 103 \pm 7$  J (mole K)<sup>-1</sup>, and K (at 25°C) =  $7.5 \pm 2.0^1$ .

<sup>&</sup>lt;sup>1</sup> If  $I_0$  is treated as a temperature independent constant, the thermodynamic parameters obtained are as follows:  $I_0 = 8.39 \pm 1.5$ ,  $\Delta H = -36.1 \pm 1.5$  kJ (mole)<sup>-1</sup>,  $\Delta S = -104 \pm 7$  J (mole K)<sup>-1</sup>, and  $K = 8.0 \pm 1.7$ . Comparison with the results given in the paper shows that treating  $I_0$  as a temperature independent constant has only a small effect on the values reported for thermodynamic parameters.



Fig. 3. Plot of In K versus 1/T for gluteraldehyde. K is found using Eq. (6), with  $I_0$  and I(T) determined as discussed in the text.

The above analysis is based on the assumption that hydration occurs independently at the two carbonyl groups in gluteraldehyde. Three arguments supporting this assumption can be given based on the results of the data analysis. First, the error in the slope in the van't Hoff plot for the gluteraldehyde data is approximately the same as observed previously in the analysis of data for aliphatic aldehydes, where only one carbonyl group is present. Second, there is no systematic curvature in the van't Hoff plot as would be expected if hydration of one carbonyl group affected the hydration of the second carbonyl group. Finally, the value for  $I_0$  found for the gluteraldehyde data is about twice that found for aliphatic aldehydes, where  $I_0$  fall in the range 3.0-3.6. This is as expected if the concentration of independent carbonyl groups in gluteraldehyde is twice the concentration of gluteraldehyde molecules.

The thermodynamic data for hydration of gluteraldehyde can be compared with that previously obtained for hydration of aliphatic aldehydes [8,9]. The entropy change for hydration of gluteraldehyde is approximately the same as that found for the larger aldehydes such as *n*-butryaldehyde  $(-96 \pm 8 \text{ J} \text{ (mole } K)^{-1})$ , isobutryaldehyde  $(-95 \pm 7 \text{ J} \text{ (mole } K)^{-1})$ , *n*-pentanal  $(-87 \pm 7 \text{ J} \text{ (mole } K)^{-1})$  and *n*-hexanal  $(-91 \pm 8 \text{ J} \text{ mole } K)^{-1})$ . Buschmann and coworkers [26] have suggested that the aldehyde hydration reaction should be written as:

$$R-CHO + nH_2O \rightarrow RCH(OH)_2 + (n-1)H_2O$$
(7)

and that  $\Delta S \cong -n$  (25 J (mole K)<sup>-1</sup>) for reaction. Assuming this is correct then four water molecules are involved in the hydration of each carbonyl group in gluteraldehyde. The enthalpy change for gluteraldehyde hydration is 8–10 kJ (mole)<sup>-1</sup> larger in magnitude than that observed for the aliphatic aldehydes listed above. The difference may be due to the presence of a second carbonyl group in gluteraldehyde, which makes the R group attached to the aldehyde less electron donating than the corresponding R group in the aliphatic aldehydes, thereby favoring hydration.

#### References

- [1] W.L. Chameides, J. Geophys. Res. 88 (1984) 4739.
- [2] Y.G. Adewuy, S.-Y. Cho, R.-P. Tsay, G.R. Carmichael, Atmos. Environ. 18 (1984) 2413.
- [3] D.J. Jacob, J. Geophys. Res. 91 (1986) 9807.
- [4] S.N. Pandis, J.H. Seinfeld, J. Geophys. Res. 94 (1989) 1105.
- [5] P. Carlier, H. Hannachi, G. Mouvier, Atmos. Environ. 20 (1986) 2079.
- [6] T.M. Olson, M.R. Hoffmann, J. Phys. Chem. 92 (1988) 533.
- [7] T.M. Olson, M.R. Hoffmann, Atmos. Environ. 23 (1989) 985.
- [8] H. Xu, P.J. Wentworth, N.W. Howell, J.A. Joens, Spectrochim. Acta 49A (1993) 1171.
- [9] Y.Y. Sham, J.A. Joens, Spectrochim. Acta 49A (1995) 247.
- [10] V.A. Isidorov, I.G. Zenkevich, B.V. Ioffe, Atmos. Environ. 19 (1985) 1.
- [11] J.W. Munger, J. Collett, B.C. Daube, M.R. Hoffmann, Atmos. Environ. 23 (1989) 2305.
- [12] J.W. Munger, J. Collett, B.C. Daube, M.R. Hoffmann, Atmos. Environ. 24B (1990) 185.
- [13] J.W. Munger, D.J. Jacob, B.C. Daube, L.W. Horowitz, W.C. Keene, B.G. Heikes, J. Geophys. Res. 100 (1995) 9325.
- [14] S. Hatakeyama, M. Ohno, J. Weng, H. Takagi, H. Akimoto, Environ. Sci. Technol. 21 (1987) 52.
- [15] G.S. Kell, J. Chem. Eng. Data 20 (1975) 97.
- [16] W.S. Brickell, in: A. Knowles, C. Burgess (Eds.), Practical Absorption Spectrometry, Chapman and Hall, New York, 1984 chapter 13.
- [17] C.N. Plum, E. Sanhueza, R. Atkinson, W.P.L. Carter, J.N. Pitts, Environ. Sci. Technol. 17 (1983) 479.
- [18] C.L. Carpenter, L.S. Forster, J. Phys. Chem. 62 (1958) 874.

- [19] E. Drent, J. Kommanduer, Chem. Phys. Lett. 14 (1972) 321.
- [20] K. Miyata, K. Nakashima, M. Koyanagi, Bull. Chem. Soc. Jpn. 62 (1989) 367.
- [21] R.-P. Bell, Adv. Phys. Org. Chem. 4 (1966) 1.
- [22] G.V. Buxton, T.N. Malone, G.A. Salmon, J. Chem. Soc. Faraday Trans. 93 (1997) 2889.
- [23] E.A. Betterton, M.R. Hoffman, Environ. Sci. Technol. 22 (1988) 1415.
- [24] X. Zhou, K. Mopper, Environ. Sci. Technol. 24 (1864) 1990.
- [25] M.R. Montoya, J.M.R. Mellado, Port. Electrochim. Acta 13 (1995) 299.
- [26] H.J. Buschmann, E. Dutkiewicz, W. Knoche, Ber. Bunsenges Phys. Chem. 86 (1982) 129.