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CO-laser photoacoustic spectroscopy on dimerization of fatty acid molecules

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Abstract: Absorption spectra of fatty-acid molecules with carbon number below five were recorded as a function of temperature and partial pressure in the 1560-1950 cm^{-1} wavelength range using photoacoustic spectroscopy with a CO laser as radiation source. A special Helmholtz PA cell providing good temperature uniformity and stability was developed and used to study flowing gaseous mixtures at varying temperatures. Dimerization enthalpies ΔH for acetic (ΔH = 60.8 ± 3.5 kJ/mole), propionic (ΔH = 62.4 ± 4.0 kJ/mole), acrylic (ΔH = 61.0 ± 3.5 kJ/mole) and butyric (ΔH = 58.7 ± 1.0 kJ/mole) acid agree well with values obtained by other methods.

1. INTRODUCTION

Since hydrogen bonds play a key role in chemistry and biology there is a great interest in hydrogen-bonded molecules. Simple examples of such systems are fatty acid dimers. Owing to their geometry and strong H-bonds, two monomers build a planar ring (see Fig.1) with a C_{2h} symmetry which is stable even at room temperature. The binding enthalpies of these dimers are on the order of a few kT which means that their concentration in a gas sample is negligible when the temperature is increased to 50°C above that of the ambient. For this reason, fatty acid molecules are well suited to study chemical equilibrium reactions with relatively simple spectroscopic techniques.

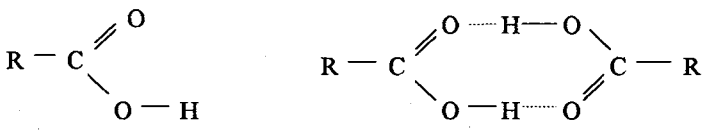

Figure 1: Fatty-acid monomer (R represents a chain of carbon atoms) Fatty-acid dimer

For approximately 60 years numerous studies on the dimerization enthalpies of various fatty acid molecules have been made. In earlier studies, authors selected the so called P-V-T method and measured the binding enthalpies ΔH for the lowest two fatty acids (e.g., formic and acetic acid) in undiluted gas samples [1,2,3]. The disadvantage of this method is that errors due to wall adsorption have to be taken into account. In the last thirty years spectroscopic techniques, e.g., Infrared [4,5], FTIR [6] and Raman [7] spectroscopies were used to obtain ΔH, as fatty acids absorb strongly in the infrared region and exhibit well separated bands of monomers and dimers. However, these previous spectroscopic measurements were

performed on stationary gas mixtures and are thus prone to adsorption effects resulting from a change of equilibrium between monomers (m) and dimers (d) (partial pressure changes during a typical measuring time of one or two hours). In this paper results of first spectroscopic measurements on flowing gas mixtures, avoiding thus problems associated with wall adsorption, are being discussed.

2. THEORY

The theoretical treatment used in this work to determine dimerization enthalpies of fatty acids (m = monomer, d = dimer) is essentially that of Pross and van Zeggeren [5]. For a reaction

$$m + m \leftrightarrow d \tag{1}$$

one can define the equilibrium constant K_p

$$K_p = \frac{p_d}{p_m^2} \tag{2}$$

(where p_d,p_m are the partial pressures of dimers and monomers). When replacing the partial pressures by corresponding concentrations c_d and c_m, one has:

$$K_p = \frac{c_d}{c_m^2 RT} = \frac{n_d}{n_m^2} * V_{cell} * \frac{1}{X} \tag{3}$$

(where n_d,n_m represent the number of dimers and monomers, V is the volume of the PA cell and X is the mixing ratio). The second expression of eq.(3) considers the case when measurements are made in a continuous stream of fatty acid molecules diluted at different mixing ratios X in synthetic air (80% N_2/ 20% O_2). From eq.(3) one can derive the Van't Hoff law:

$$\left[\frac{d\ln K(T,p)}{d(1/T)}\right]_p = \frac{d\ln\left[\left(c_d / c_m^2\right) * \frac{1}{T}\right]}{d(1/T)} = \frac{\Delta H}{R} \tag{4}$$

By measuring concentrations of monomers and dimers using photoacoustic spectroscopy (PAS), the dimerization enthalpies can be derived directly from Van't Hoff's law by plotting $\ln(c_d/(c_m^2*T)$ versus 1/T.

3. EXPERIMENTAL

3.1 The apparatus

The dimerization enthalpy ΔH of fatty acid molecules was determined using photoacoustic spectroscopy (PAS) with a modified set-up used previously for trace gas analysis [8]. The spectral range of our instrument was extended by reducing the temperature of the CO-laser (Edinburgh Instruments PL03) to 230K using ethanol as cooling liquid. The laser now emits on 90 transitions with a maximum output power of 3.1 Watt within the 1650 to 1950 cm^{-1} wavenumber range. The laser radiation is modulated by a mechanical chopper and split on a beam divider. A minor fraction is directed toward a pyroelectric detector while the remaining part traverses the photoacoustic cell before being detected by a power meter to allow simultaneous measurements of photoacoustic and transmitted signals. The microphone and detector signals are processed with Lock-in Amplifiers (Ithaco Dynatrac 393) and are recorded on a personal computer via a control work station (Keithley S 570). The entire system is automated using a IBM AT computer.

3.2 PA cell and gas filling system

The PA chamber consists of an inner copper cell surrounded by a stainless steel jacket, both are placed in a thermostat bath (temperature can be varied from 275 to 350K with an accuracy of ± 0.5K). The condenser microphone (Brüel & Kjaer Type 4179, sensitivity 107 mV/Pa) is connected to the inner cell via a thin pipe in order to avoid its heating. At a frequency of about 400 Hz this cell acts as a Helmholtz resonator (see Fig. 2).

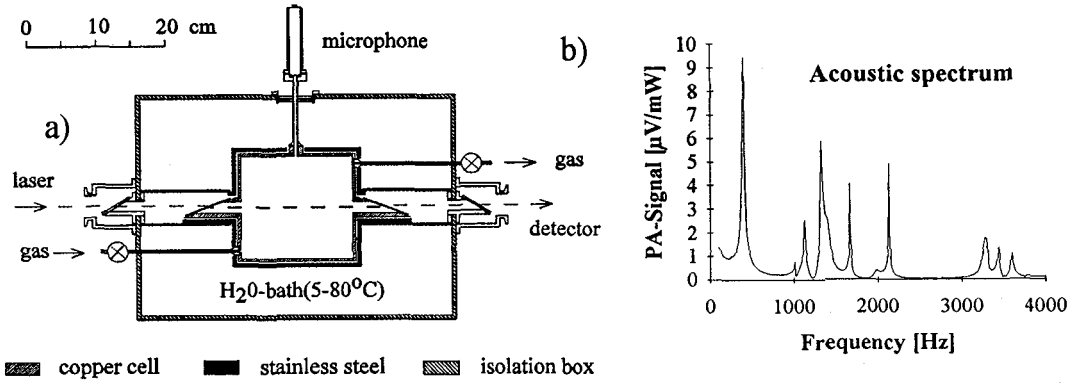

Figure 2: Photoacoustic cell (a) and its acoustic spectrum (b)

The measurements were performed on continuously flowing streams of gaseous fatty acid molecules buffered in synthetic air (80% N_2/20% O_2) at atmospheric pressure. The mixture was prepared by diluting fatty acid vapor from a washing bottle (at a flow rate of ca. 1-10 ml/min) with synthetic air (flow rate of 1 l/min) in a gas mixing unit (MKS Instruments). Such gas system prevents effects of adsorption since the walls of our PA cell get saturated with fatty acid molecules and do not reduce the partial pressure even during extended periods of measurement.

4. RESULTS

From the PA spectra recorded at different temperatures (Fig.3) and based on Van't Hoff's law, enthalpies of dimerization ΔH of fatty acid molecules with carbon number below five were derived.

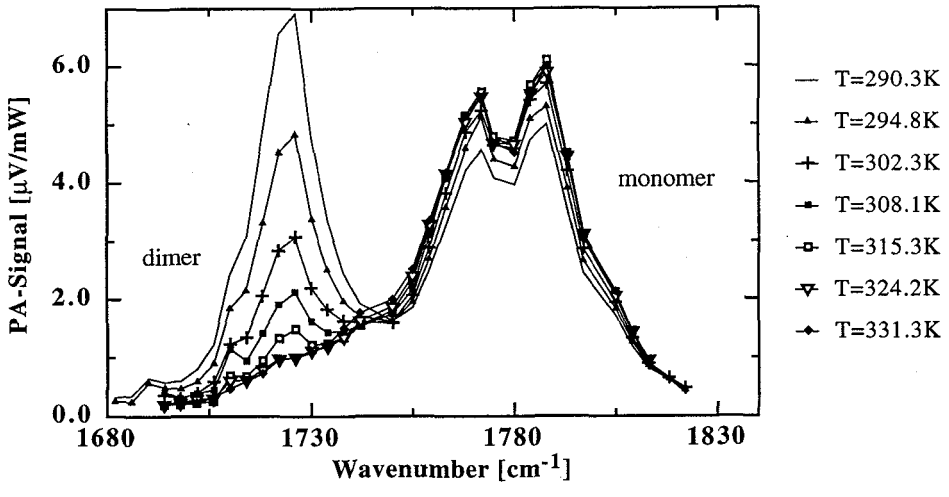

Figure 3: Photoacoustic spectra of propionic acid at different temperatures

Figure 3 above shows normalized PA signals obtained for propionic acid. A decrease of the dimer band absorption with increasing temperature is clearly manifested. Obtained ΔH data are in agreement with those reported by various authors using other methods (see Table 1) including most recent measurements of Winkler et al. [9].

Table 1: Dimerization enthalpies ΔH of various fatty acids

Fatty acid	ΔH [kJ/mole]	authors	method
acetic acid	61.5 ± 2.5	this study	PAS
	62.6 ± 0.6	Winkler et al.[9]	PAS
C-COOH	70.3 ± 3.2	Pross / van Zegerren[5]	IR-Spectroscopy
	60.3 ± 2.5	Jaffe / Rose[6]	Raman
propionic acid	62.3 ± 2.5	this study	PAS
C-C-COOH	61.3 ± 0.5	Winkler et al.	PAS
acrylic acid	61.0 ± 3.5	this study	PAS
C=C-COOH	77.4	Büttner / Maurer[3]	P-V-T
butyric acid	58.4 ± 1.0	this study	PAS
C-C-C-COOH	64.9 ± 3.0	Clague / Bernstein[4]	IR-Spectroscopy

5. OUTLOOK AND CONCLUSION

The PA spectroscopy with a CO-laser has been applied for the first time to flowing mixtures of fatty acid vapors buffered in synthetic air. Besides obtainig dimerization enthalpies ΔH, the objective of our present studies is to determine absolute line intensities of monomer and dimer absorption. Finally, anticipated PA studies on binary mixtures of fatty acids and water vapor are expected to provide new insights into processes of association in such samples.

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References

[1] Ritter H., Simons J., *J. Amer. Chem. Soc.* **67** (1945) 757-762
[2] Johnson J., Nash L., *J. Amer. Chem. Soc.* **72** (1950) 547-556
[3] Büttner R., Maurer G., *Ber. d. Bunsenges. Phys. Chem.* **87** (1983) 877-882
[4] Clague A., Bernstein H., *Spectrochimica Acta* **25A** (1969) 593-596
[5] Pross A., van Zegerren F., *Spectrochimica Acta* **16** (1960) 563-569
[6] Jaffe D., Rose N., *Spectrochimica Acta* **47A** (1991) 1695-1705
[7] Gauffrès R., Maillols J., Tabacik V., *J. Raman Spectr.* **11** (1981) 442-448
[8] Bernegger S., Sigrist M.W., *Infrared Phys.* **30** (1990) 375-429
[9] Winkler A. et.al., *Dig. 8th Int. Top. Meeting on Photoacoustic and Photothermal Phenomena*, Point-à -Pitre (Guadeloupe, F), Jan 22-25,1994, paper GO-04