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Energetics and dynamics of H bonds in carboxylic acids studied by resonant photoacoustic spectroscopy

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Abstract: Dissociation rates of dimeric formic (methanoic)-, acetic (ethanoic)- and propionic acid in the gas phase were measured over the pressure range 0.01–100 mbar and for temperatures between 290 K and 325 K. Standing acoustic waves in a cylindrical cavity were excited by absorption of amplitude-modulated CO₂-laser radiation. Consistent sets of kinetic and thermodynamic properties of the dimer/monomer mixture were obtained from the parameters of the first radial acoustic resonances of the acoustic resonator.

1. Introduction

The vapor of the carboxylic acids consists of a mixture of monomers and dimers. The dimer is coupled via two H-bonds. Since the cyclic configuration is highly stabilized, higher polymers do not exist. Hence the carboxylic acids are relatively simple systems to investigate the energetics and dynamics of this type of chemical bond. This work is one of the few studies of hydrogen bonding between isolated molecules.

The kinetic parameter of the system can be determined from the speed of sound and the sound absorption [1],[2]. The sound wave of frequency ω introduces a time scale $1/\omega$ to the system. The equilibration processes achieved microscopically through intermolecular collisions follow this change with a characteristic time constant, the relaxation time τ . If the external macroscopic time scale becomes short compared with τ , the system cannot follow this external change and some degrees of freedom drop out of the distribution of energy. In this way the specific heat of the system changes and therefore the speed of sound shifts (dispersion). The change of state inside a sound wave follows the adiabatic compression and expansion. The pressure and the density are in phase in the case of very fast ($\tau \ll 1/\omega$) or very slow ($\tau \gg 1/\omega$) relaxation. However, if the external time scale $1/\omega$ and τ are of the same order of magnitude a phase lag occurs between pressure and density. Energy is removed from the sound wave but not fed back in phase. This process

leads to sound absorption. Therefore, relaxation processes can be detected by measuring the sound dispersion and sound absorption as a function of pressure and frequency.

2. Experimental

The first radial acoustic resonances of a cylindrical resonator were excited via CO_2 -laser radiation. The resonance frequency and the width of the resonance profile contain the information on the speed of sound and the sound absorption, respectively.

The resonator of 5 cm diameter and 6 cm length was machined from stainless steel. The amplitude modulated laser beam traversed the cell through ZnSe windows. The modulation was produced by an electrooptic device driven by a frequency synthesizer. The standing acoustic waves were detected by an electret microphone, which was positioned at the middle of the cylinder flush with the inner cylinder wall. The signal and the phase were recorded by a lock-in amplifier. The temperature was stabilized by a bath and could be determined with a precision of 0.03 K between 290 K and 325 K [3].

3. Results

The relaxation phenomena have an influence on the measured resonance parameters only in the low pressure range. Hence the data obtained for the high pressure range could be used to determine the equilibrium constants of the carboxylic acids. The typical pressure

Figure 1: The resonance frequency of the first radial mode of the cylinder as a function of pressure at 289 K, 304 K, and 323 K for pure acetic acid vapor.

and temperature dependence of the resonance frequency in pure carboxylic acid is shown in Fig.1.

The values obtained for the entropy S_{diss} and the enthalpy H_{diss} of dissociation are listed in Table 1.

The effects due to chemical relaxation are overlayed by the vibrational relaxation and the transport effects due to viscosity and thermal conductivity.

It is impossible to extract the kinetic parameters from the data obtained for the pure vapor in the case of acetic – and propionic acid. Therefore, we performed measurements with mixtures of He and the acids. The advantages of this method are:

Figure 2: Width of the resonance of the first radial mode in the cylinder as a function of the partial pressure of acetic acid in the presence of 9 mbar He at 304 K. The dashed line represents the contribution due to the chemical relaxation. The solid line represents the theoretical prediction. The points represent the measured values.

1. The speed of sound is much higher. We obtain ≈ 5 times higher resonance frequencies and therefore the region of chemical relaxation is shifted to higher pressures.
2. Helium is a relatively ineffective collision partner. This means that the relaxation processes are not much accelerated.
3. The classical losses are reduced drastically, because it is possible to work at relative high total pressures.
4. The specific heat of the mixture is much lower. This leads to an enormous enhancement of the effect and to a reduction of the effect of vibrational relaxation.

This method allows the investigation of fast relaxation processes. Fig. 2 gives an example for the pressure dependence of the width of the resonance in an acetic acid/He mixture. We are able to show for the first time that the dissociation process is a second order process and that it can be accelerated by adding inert gases. The dissociation rate constant is described by:

$$k_{diss} = k_0 \exp\left(-\frac{E_{act}}{RT}\right) [\epsilon_A p_A + p_{AA} + \epsilon_b p_b], \quad (1)$$

where E_{act} is the activation energy, ϵ_A and ϵ_b are the collision efficiencies of the monomer and the buffer gas relative to that of the dimer, and p_A, p_{AA} and p_b are the partial pressures of the monomer, the dimer and the buffer gas, respectively. The results are summarized in Table 1. The pressure dependence of the dissociation rate constant and the resulting

Table 1: Summary of the results for all acids under investigation

Parameter	Formic Acid	Acetic Acid	Propionic Acid
$S_{diss}(300K)$ (J/(mol·K))	159±2	151±2	150±3
$H_{diss}(300K)$ (kJ/mol)	59.6±0.5	62.6±0.6	61.3±0.5
k_0 (ns ⁻¹ mbar ⁻¹)	2.2±0.4	1.6±1	9.5±4
E_{act} (kJ/mol)	33±1	32±2	32±2.5
ϵ_A	0.5±0.2	0.84±0.2	1.2±0.5
ϵ_{He}	0.05±0.02	0.12±0.02	0.1±0.03
ϵ_{Ar}	0.08±0.02	0.18±0.02	0.21±0.03

activation energy, which corresponds to the dissociation energy of one H-bond, suggest a stepwise dissociation process due to bimolecular activation. A possible mechanism is slow dissociation of the cyclic dimer with two H-bonds into an open dimer with one H-bond and subsequent fast decay of the chain dimer into two monomers.

where D is a cyclic dimer with two H-bonds, C is an open dimer with one H-bond, M is the monomer and X is any possible collision partner.

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