

# Dimerization of Carboxylic Acids in Solution up to High Pressures and Temperatures. 2. Benzoic Acid

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Benzoic acid in dilute solution of n-heptane and of CCl<sub>4</sub> is studied via high-pressure high-temperature IR spectroscopy on the C=O and O–H stretching fundamentals. Lambert-Beer's law is shown to be valid for the C=O modes of the acid monomer and of the hydrogen-bonded cyclic dimer, which enables the quantitative measurement of the dimerization equilibrium to a maximum pressure of 2 kbar and up to 175 °C. At identical pressure and temperature the dimerization equilibrium constant is larger in n-heptane than in CCl<sub>4</sub>. From the monomer-cyclic dimer equilibrium constants the pressure dependence of the dimerization enthalpy is determined and compared with direct information on both species as derived from their O–H fundamental mode absorption. Toward lower temperature the dimerization volume is decreasingly negative and, in CCl<sub>4</sub> solution,  $\Delta V$  even changes sign around 40 °C. Increasing pressure thus favours the dissociation of the hydrogen-bonded dimer into benzoic acid monomer molecules at ambient temperature.

## Introduction

The monomer-cyclic dimer equilibrium of carboxylic acids in dilute solution is an interesting model system for the study of association via hydrogen bonds [1–5]. By means of quantitative high-pressure high-temperature infrared spectroscopy, as has been shown for pivalic acid (PA) [6], the concentrations of monomer and cyclic dimer molecules may be determined within an extended pressure and temperature range from the characteristic carbonyl fundamentals. The simultaneous investigation of the O–H stretching modes enables further characterization of both species. High pressure favours the dimerization of PA. The (negative) dimerization volume, however, decreases toward lower temperature. It seemed interesting to apply the quantitative spectroscopic method to the study of another carboxylic acid. Within the present paper, the association of benzoic acid in dilute solution of n-heptane and of CCl<sub>4</sub> is studied via infrared spectroscopy on the C=O and O–H stretching fundamentals of monomer and dimer species to a maximum pressure of 2 kbar and up to 175 °C. The association thermodynamics at ambient pressure

and up to 60 °C has already been spectroscopically measured in CCl<sub>4</sub> and in cyclohexane solution [7, 8]. The influence of pressure on the dimerization of benzoic acid in n-heptane has been investigated by Suzuki and his group [9] at 25 °C up to 6400 bar. These authors report a positive dimerization volume of  $0.4 \pm 0.9 \text{ cm}^3 \cdot \text{mol}^{-1}$ .

## Experimental

The optical cell for operation up to 3300 bar and 350 °C with windows from single-crystalline sapphire or, for studies at wavenumbers below 2000 cm<sup>-1</sup>, from polycrystalline silicon is described in Ref. [6], where also details about the whole experimental set-up and about the experimental procedure are given.

Pressures are recorded within  $\pm 3$  bar. Temperatures are measured with a sheathed thermocouple inside the sample fluid to better than  $\pm 0.5$  °C. Spectra are taken on a NICOLET 5 DX Fourier transform interferometer.

Benzoic acid was of more than 99.5% purity (Fluka) and CCl<sub>4</sub> and n-heptane were of UVASOL quality (Merck). In order to prevent freezing and to avoid corrosion at higher temperature, experiments with CCl<sub>4</sub> as the solvent were performed only up to 1.25 kbar and 125 °C, respectively (see Ref. [6]).

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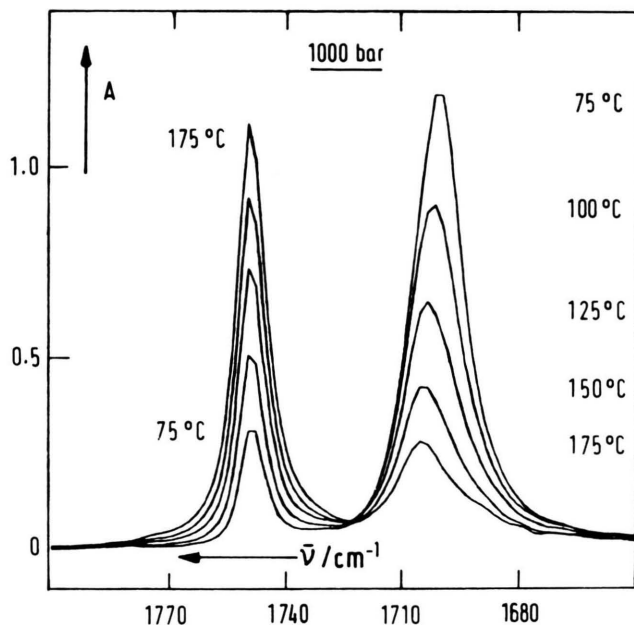


Fig. 1. Absorbance spectra in the carbonyl stretching region of a  $1.15 \cdot 10^{-2}$  molar solution of benzoic acid in n-heptane at 1000 bar and temperatures between 75 °C and 175 °C.

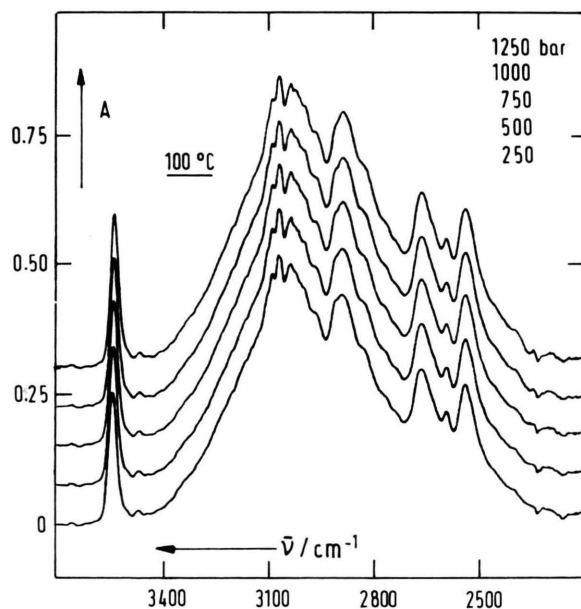


Fig. 2. Absorbance spectra in the O–H stretching region of a  $5.01 \cdot 10^{-2}$  molar solution of benzoic acid in  $\text{CCl}_4$  at 100 °C and pressures between 250 bar and 1250 bar (the curves are shifted in the baseline).

## Results

Experimental absorbance spectra between  $1650 \text{ cm}^{-1}$  and  $1800 \text{ cm}^{-1}$  of a  $1.15 \cdot 10^{-2}$  molar solution of benzoic acid (BA) in n-heptane measured at constant pressure (1000 bar) and temperature variation between 75 °C and 175 °C are shown in Figure 1. The band at  $1750 \text{ cm}^{-1}$  is due to the C=O stretching fundamental of monomeric BA and the  $1705 \text{ cm}^{-1}$  component is assigned to the C=O stretch of the cyclic BA dimer. With increasing temperature the monomer band increases and the dimer absorption decreases. An isosbestic point is observed close to  $1725 \text{ cm}^{-1}$ . The appearance of the experimental spectra measured at other pressures (up to 2 kbar) in n-heptane and up to 1.25 kbar and 125 °C in  $\text{CCl}_4$  is very similar to the data in Figure 1. The only difference being a very small change in band position which, however, occurs within the  $\pm 4 \text{ cm}^{-1}$  resolution of the spectrometer. Figure 2 shows experimental absorbance spectra in the O–H stretching region for a  $5.01 \cdot 10^{-2}$  molar BA solution in  $\text{CCl}_4$  at 100 °C and pressure variation between 250 bar and 1250 bar. The narrow band at  $3530 \text{ cm}^{-1}$  is due to the O–H fundamental in monomeric BA whereas the broad band between  $3400 \text{ cm}^{-1}$  and  $2300 \text{ cm}^{-1}$  is due to the O–H stretching fundamental in the dimer with absorption contributions from the C–H stretching fundamentals and from combination and overtone modes. The spectra in Fig. 2 are shifted in the baseline.

## Discussion

Several arguments indicate that in benzoic acid (BA) solution at pressures, temperatures, and concentrations as in the present paper, monomer and cyclic dimer molecules are, by far, the dominant species of the association equilibrium [8, 9]. Quantitative analysis of individual concentrations via IR spectroscopy in an extended pressure and temperature range requires Lambert-Beer's law to be valid: The molar integrated absorptivities (vibrational intensities)  $B$  of the characteristic modes in the monomer and dimer species should be independent of  $P$  and  $T$ .  $B$  is defined as

$$B = \int \varepsilon(\bar{\nu}) \cdot d\bar{\nu}, \quad (1)$$

where  $\varepsilon(\bar{\nu})$  is the molar absorptivity as a function of wavenumber  $\bar{\nu}$ .  $\varepsilon(\bar{\nu})$  is related to the experimental (decadic) absorbance  $A(\bar{\nu})$  by

$$\varepsilon(\bar{\nu}) = A(\bar{\nu}) / (c \cdot l) \quad (2)$$

with  $c$  and  $l$  being the concentration and the optical path length, respectively. Combination of (1) and (2) yields

$$\int A(\bar{\nu}) \cdot d\bar{\nu} = c \cdot l \cdot B, \quad (3)$$

which says that, if  $B$  is a constant, from the measured absorbance spectrum  $\int A(\bar{\nu}) \cdot d\bar{\nu}$ , at known optical path length, the concentration  $c$  is directly obtained. Thus it is interesting to measure  $B$ -values for monomer and dimer species in both absorption regions:  $B_M(\text{C=O})$ ,  $B_D(\text{C=O})$ ,  $B_M(\text{O-H})$ , and  $B_D(\text{O-H})$  and to carefully analyze whether these quantities remain constant within an extended range of pressures and temperatures. The result of the corresponding analysis of PA was that Lambert-Beer's law holds for the carbonyl stretching modes of the monomer and of the dimer and also for the O-H stretch of the monomer whereas it is violated for the O-H stretch of the dimer species [6].

The determination of these vibrational intensities from spectra is described in quite some detail for PA in [6]. Along the same lines, the monomer and dimer carbonyl intensities of BA (in n-heptane) are obtained to be

$$B_M(\text{C=O}) = 121 \pm 7 \text{ km} \cdot \text{mol}_M^{-1} \quad \text{and}$$

$$B_D(\text{C=O}) = 182 \pm 11 \text{ km} \cdot \text{mol}_M^{-1}.$$

These vibrational intensities are found to be independent of  $P$  and  $T$  in dilute fluid solution of n-heptane by plotting  $c_M + c_D$ , the sum of spectroscopically measured individual concentrations versus the total acid concentration  $c$  at identical pressure and temperature.  $c_M$  and  $c_D$  are obtained via (3) from the integrated absorbance between  $1725 \text{ cm}^{-1}$  and  $1825 \text{ cm}^{-1}$  (for the BA monomer) and between  $1642 \text{ cm}^{-1}$  and  $1725 \text{ cm}^{-1}$  (for the BA dimer).  $c$  is calculated from the precisely known BA concentration at ambient temperature and pressure,  $c_0$ , and from published PVT-data of the pure solvents, n-heptane [10] or  $\text{CCl}_4$  [11] according to

$$c = c_0 \cdot \varrho / \varrho_0, \quad (4)$$

where  $\varrho$  is the pure solvent density at  $P$  and  $T$  and  $\varrho_0$  is the corresponding value at ambient pressure

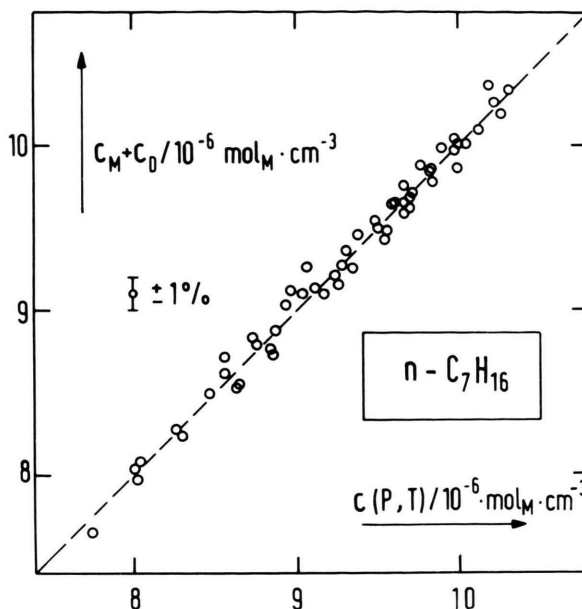


Fig. 3. Comparison of the spectroscopically measured sum of monomer and dimer concentrations,  $c_M + c_D$ , with the total acid concentration  $c$  at identical pressure and temperature (see text) for a series of experiments on benzoic acid in n-heptane.

and temperature. The agreement of  $c$  with  $c_M + c_D$  which, for a series of experiments on BA in n-heptane, is illustrated in Fig. 3, is very satisfactory. Thus, at least within the range of the present experiments Lambert-Beer's law is valid for the carbonyl stretching fundamentals of the monomer and cyclic dimer of BA in n-heptane. Individual concentrations,  $c_M$  and  $c_D$ , are thus directly available from the spectra.

Analysis of the carbonyl region measured for BA in dilute solution of  $\text{CCl}_4$  yields as monomer and dimer vibrational intensities:

$$B_M(\text{C=O}) = 122 \pm 5 \text{ km} \cdot \text{mol}_M^{-1} \quad \text{and}$$

$$B_D(\text{C=O}) = 213 \pm 9 \text{ km} \cdot \text{mol}_M^{-1}.$$

The monomer intensity, within experimental accuracy, agrees with the corresponding value in n-heptane whereas the dimer intensity is slightly larger. Plotting the sum of spectroscopically measured concentrations,  $c_M + c_D$ , against the total concentration  $c$ , for the whole pressure and temperature range, yields values close to the diagonal as in Fig. 3, which says that Lambert-Beer's law holds in  $\text{CCl}_4$  solution, too. Infrared spectroscopy on the C=O modes in both solvents thus enables quan-

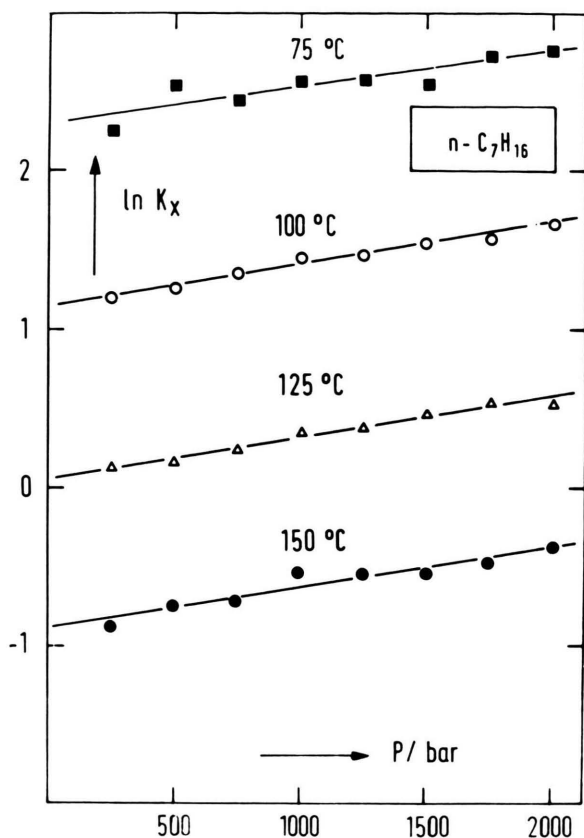


Fig. 4. Pressure dependence of the dimerization equilibrium constant  $K_x$  for benzoic acid in *n*-heptane solution ( $c_0 = 1.15 \cdot 10^{-2}$  molar).

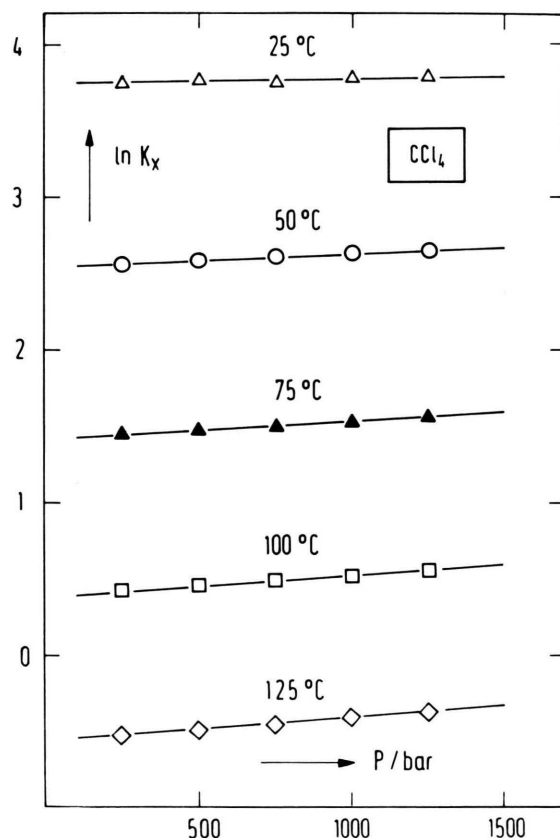


Fig. 5. Pressure dependence of the dimerization equilibrium constant  $K_x$  for benzoic acid in  $\text{CCl}_4$  solution ( $c_0 = 1.28 \cdot 10^{-2}$  molar).

titative analysis of monomer and cyclic dimer species up to high pressures and elevated temperatures.

The thermodynamic analysis is based on the equilibrium constant  $K_a$  in terms of activities,  $K_a = a_D/a_M^2$ , with the standard state of the solute being chosen as the hypothetical pure substance with interactions such as in an infinitely dilute solution. Assuming activity coefficients at low concentration as in the present study to be close to unity, the equilibrium constant  $K_x$  in terms of mole fractions becomes

$$K_x = x_D/x_M^2, \quad (5)$$

which after substitution of mole fractions by concentrations yields

$$K_x = c_D \cdot c/c_M^2 = K_c c. \quad (6)$$

$K_c$  is directly obtained from the spectroscopically measured concentrations, and the total acid concentration  $c$  is calculated according to (4).

The increase of  $\ln K_x$  toward higher pressure and lower temperature is illustrated for BA in *n*-heptane solution in Fig. 4 and for BA in  $\text{CCl}_4$  solution in Figure 5. The dimerization equilibrium constant  $K_x$  at identical temperature is larger in *n*-heptane than in  $\text{CCl}_4$ . This result, which has also been found for pivalic acid in *n*-heptane and in  $\text{CCl}_4$  solution [6], suggests that  $\text{CCl}_4$  is a less inert solvent for the BA monomer with the stronger attractive interactions being responsible for the lower  $K_x$  values [7].

The accuracy of the equilibrium constant data is estimated to be better than  $\pm 10\%$ . Their relative accuracy is considered to be sufficient for a study of the standard dimerization enthalpy  $\Delta H^0$  as a func-

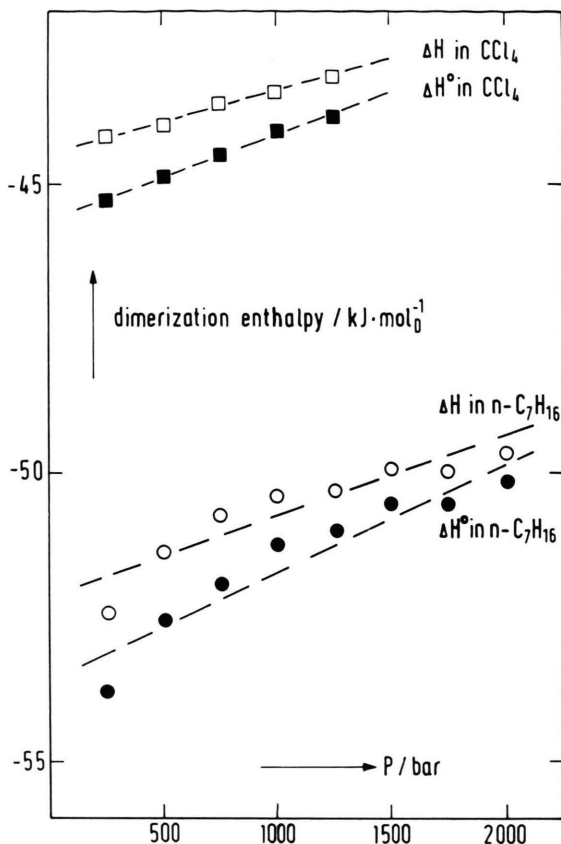


Fig. 6. Pressure dependence of the dimerization enthalpies  $\Delta H^0$  and  $\Delta H$  of benzoic acid in n-heptane and in  $\text{CCl}_4$ .

tion of pressure and of the standard dimerization volume  $\Delta V^0$  as a function of temperature:

$$-\Delta H^0 = (\delta(R \ln K_x) / \delta(1/T))_P \quad (7)$$

and

$$-\Delta V^0 = (\delta(RT \ln K_x) / \delta P)_T \quad (8)$$

Results for both solvents are given in Figs. 6 and 7. Dimerization enthalpy and dimerization volume are more negative in n-heptane than in  $\text{CCl}_4$  which, as has already been mentioned is due to the stronger interactions of the BA monomer with  $\text{CCl}_4$  than with n-heptane [6]. The remarkable observation from the data is the decrease of (negative) dimerization enthalpy toward higher pressure (Fig. 6) and the corresponding increase of (negative) dimerization volume toward higher temperature (Figure 7). Both effects have also been observed in PA [6]. Replacement of  $K_x$  in (7) and (8) by  $K_c$  yields  $-\Delta H$  and  $-\Delta V$ , respectively. The variation of  $\Delta H$

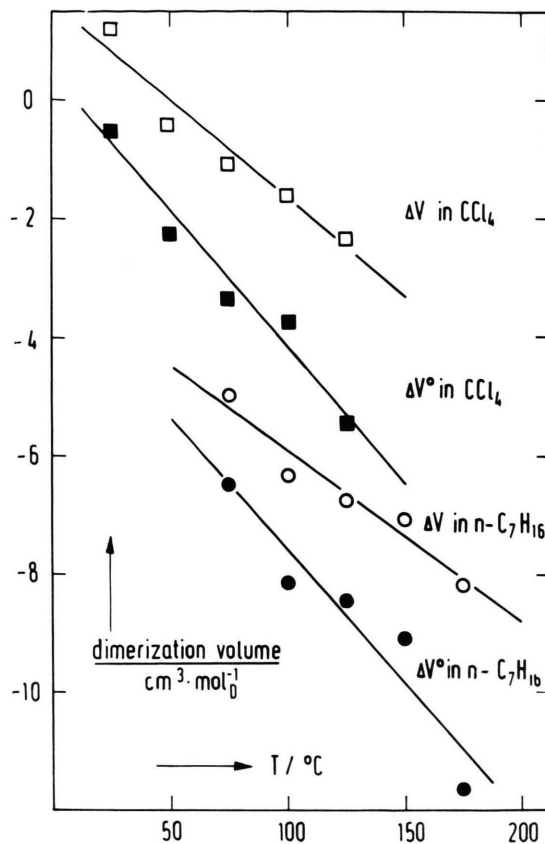


Fig. 7. Temperature dependence of the dimerization volumes  $\Delta V^0$  and  $\Delta V$  of benzoic acid in n-heptane and in  $\text{CCl}_4$ .

with  $P$  and of  $\Delta V$  with  $T$  is slightly weaker than the corresponding changes observed on  $\Delta V^0$  and on  $\Delta H^0$  as is shown in Figures 6 and 7. Linear extrapolation of the  $\Delta H$  data in  $\text{CCl}_4$  (Fig. 6) toward ambient pressure yields  $\Delta H = -44.5 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$ , which is in excellent agreement with the available literature data ( $-46.0 \text{ kJ} \cdot \text{mol}^{-1}$  [7] and  $-44.3 \text{ kJ} \cdot \text{mol}^{-1}$  [8]) and the value extrapolated from the n-heptane data (Fig. 6) for ambient pressure ( $\Delta H = -52.1 \pm 1 \text{ kJ} \cdot \text{mol}^{-1}$ ) is very close to the literature value of  $\Delta H = -54 \text{ kJ} \cdot \text{mol}^{-1}$  for BA in cyclohexane [7].

In order to see whether the observed changes of  $\Delta H^0$  with  $P$  and of  $\Delta V^0$  with  $T$  (for the same solvent) are essentially or even exclusively due to variations within the dimer, inspection of the O–H stretching region, which is known to be a sensitive probe of hydrogen bonds, seems to be in place. Analysis of the O–H fundamental region of BA in  $\text{CCl}_4$  demonstrates that Lambert-Beer's law is not



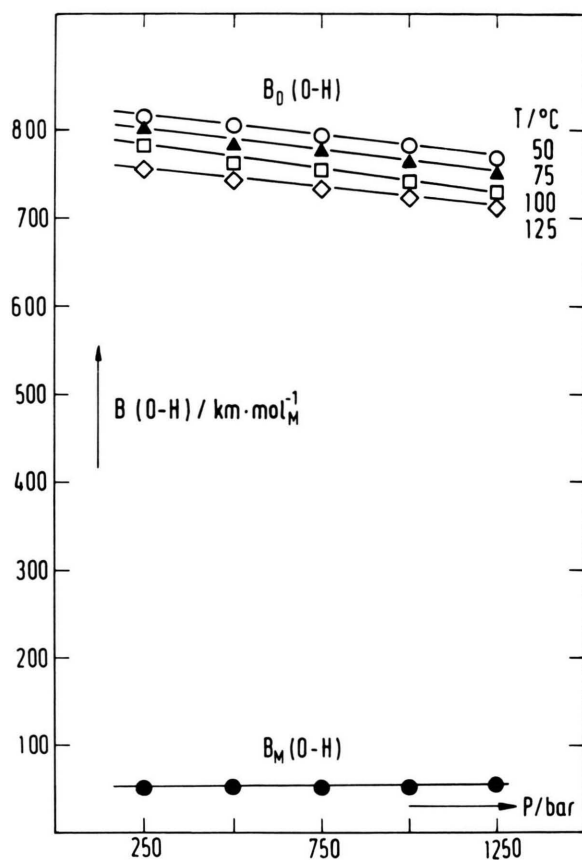


Fig. 8. Vibrational intensities  $B_M(O-H)$  and  $B_D(O-H)$  of benzoic acid monomers and cyclic dimers, respectively, in  $\text{CCl}_4$  solution ( $c_0 = 5.01 \cdot 10^{-2}$  molar) up to 1.25 kbar and 125 °C. The dimer intensity contains some absorption due to C–H stretching fundamentals and to combination and overtone modes in BA (see text).

valid for both species. To derive vibrational intensities for the monomer and dimer O–H vibrations, the integrated absorbance for the monomer (between  $3638 \text{ cm}^{-1}$  and  $3488 \text{ cm}^{-1}$ ) and for the dimer (between  $3488 \text{ cm}^{-1}$  and  $2142 \text{ cm}^{-1}$ ) is reduced by the individual concentrations,  $c_M$  and  $c_D$ , which are available from the carbonyl spectra, and by the known optical path length (see (3)). Results for  $B_M$  and  $B_D$  are given in Figure 8. As has been observed for pivalic acid [6], the vibrational intensity of the monomer O–H stretching mode, within the limits of experimental accuracy, is independent of  $P$  and  $T$ :  $B_M(O-H) = 53 \pm 2 \text{ km} \cdot \text{mol}^{-1}$ , whereas  $B_D(O-H)$  depends on both pressure and temperature. It should be noted that  $B_D(O-H)$  also contains vibrational intensity from the C–H stretching fundamentals and also from

combination and overtone modes in BA. This additional absorption, however, is considered to be independent of  $P$  and  $T$ . Thus the observed changes of  $B_D(O-H)$  with pressure and temperature should be essentially due to the O–H dimer mode. Lowering of the  $B_D(O-H)$  intensity, as it occurs toward the  $B_M(O-H)$  monomer intensity, is interpreted as an indication of weaker hydrogen bonds of the cyclic dimer. Higher pressures and higher temperatures thus decrease the hydrogen bond strength within the dimer species. This result agrees with the measured pressure dependence of  $\Delta H^0$  (Figure 6). The spectroscopic analysis of the association equilibrium via  $B_M(O-H)$  and  $B_D(O-H)$  thus enables the variation in the difference between the two states ( $\Delta H^0$ ) to be assigned to changes of the dimer species.

It may be concluded that the cyclic dimerization of BA in dilute solution is an interesting model system for the study of association via hydrogen bonds. The measured decrease of hydrogen bond strength toward higher pressure which has also been found in pivalic acid solutions [6] is in good agreement with observations on three-dimensional hydrogen-bonded systems such as ice or proteins where pressure is known to favour a transition from perfect to less stable hydrogen bonds. The pronounced difference in  $\Delta V$  between low and high temperatures (Fig. 7) suggests that more stable and certainly more planar hydrogen-bonded acid dimers have higher molar volume than the corresponding higher temperature species. At elevated temperatures increasing pressure thus clearly favours association to less perfect and probably less planar dimers. At lower temperatures the situation can be reached where  $\Delta V$  becomes positive which says that the dimer molar volume exceeds that of two monomer species. This is, indeed, observed for benzoic acid in  $\text{CCl}_4$  solution at 25 °C (Figure 7). The absolute value for  $\Delta V$  of BA in n-heptane at 25 °C does not agree with the literature value of  $\Delta V = 0.4 \pm 0.9 \text{ cm}^3 \cdot \text{mol}^{-1}$  [9]. A tendency toward positive  $\Delta V$  at low temperature is, however, clearly indicated for BA dissolved in n-heptane [9]. In the final paper of this series [12], the dimerization of acetic acid and trichloroacetic acid will be studied in n-heptane and in  $\text{CCl}_4$  up to high pressures and temperatures. In this forthcoming paper special attention will be paid to differences in dimerization equilibrium due to the special type of acid.

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