J. Am. Chem. Soc. 1994, 116, 9233–9240

Study of the Energetics and Dynamics of Hydrogen Bond Formation in Aliphatic Carboxylic Acid Vapors by Resonant Photoacoustic Spectroscopy

A. Winkler and P. Hess*

Contribution from the Institute of Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253, D-69120 Heidelberg, FRG

Received May 23, 1994[⊗]

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 and 325 K. Consistent sets of kinetic and thermodynamic data of the dimer/monomer mixture were obtained from the parameters of the first radial acoustic resonance of a cylindrical resonator. The standing acoustic waves were excited by absorption of amplitude-modulated CO_2-laser radiation. The entropy and enthalpy of dissociation of the equilibrium reaction $(R\text{–}COOH)_2 \rightleftharpoons 2R\text{–}COOH$ with R = H, CH_3, and CH_3CH_2, the rate constant of the dissociation of the dimer, and the mean relaxation time of the vibrational modes of the mixtures were determined by fitting a detailed model of the resonator to the measured values for the resonance frequency and the resonance broadening. The well-established value for the enthalpy of dissociation of about 60 kJ/mol was confirmed. It is nearly independent of the R group. For the first time the dissociation process in isolated propionic acid dimers was studied. The activation energy of the dissociation of the dimer was found to be 33 ± 1 kJ/mol for formic acid, 32 ± 2 kJ/mol for acetic acid, and 32 ± 2.5 kJ/mol for propionic acid. For the first time an accurate determination of the pressure dependence of the rate constant was possible. It was found that the system is in the second-order regime. The dissociation rate constant, the relative collision efficiency of the monomer, and the collision efficiencies of the noble gases increase with the number of C atoms. The rate constant was found to be 4.2×10^3 1/s for formic acid, 9.0×10^3 1/s for acetic acid, and 5.6×10^4 1/s for propionic acid in mixtures of 9 mbar of He and 1 mbar of acid at 300 K. The pressure dependence and the resulting 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.

Introduction

A large number of publications deal with the geometric structure, the energetics, and the spectroscopy of H bonds.[1,2] However, very few experiments have been carried out concerning the kinetics of this type of chemical bonding. Since the liquid state of carboxylic acids consists of dimers and the vapor is a mixture of monomers and dimers, where the dimer is coupled via two H bonds from the carbonyl oxygen of one monomer to the hydroxy hydrogen of the other, these acids represent an ideal system for investigating the basic principles of the association/dissociation process of these bonds in isolated molecules.

Most experiments have concentrated on ultrasonic studies of liquid carboxylic acid systems. Carsaro and Atkinson[3] deduced from ultrasonic measurements on acetic acid solutions in acetone and water that the observed relaxation effects are based on the reaction $D \rightleftharpoons C$, where D is the cyclic form of the dimer and the postulated species C was assumed to be a chain dimer with only one H bond. However, the intrinsic behavior of H bond relaxation cannot be extracted accurately from relaxation measurements in the liquid state. It was found that the solvent has a pronounced influence on the dissociation rate constant and the energetics of the system[4,5] and that H bonds between the acid and the solvent complicate the situation.[6,7]

These problems can be overcome by investigations of H bond relaxation in the gas phase, where isolated molecules interact. The first attempt to deduce the kinetics of the association/dissociation process in gaseous acetic acid from temperature jump experiments gave an activation energy somewhat lower than the dissociation energy but no information on details of the dissociation process.[8]

More information was obtained from temperature jump experiments on formic acid.[9,10] The activation energy was found to be approximately one-half the dissociation energy. However, this method yielded values for the dissociation rate constant with large uncertainties, so that no pressure dependence could be established.[9]

The basic questions which remain are the following: (1) Is the system $(R\text{–}COOH)_2 \rightleftharpoons 2R\text{–}COOH$ in the second-order regime at low pressure as expected? (2) What is the pressure dependence of the dissociation rate constant? (3) What value will be obtained for the activation energy if the available data are evaluated with the correct pressure dependence? (4) Is the dissociation process a stepwise reaction as proposed for the liquid? (5) What is the nature of the activation process? Is the dimer chemically activated or is the energy content only increased by vibrational and rotational energy transfer? (6) How do the rate constant and the activation energy depend on the R group?

In the present work, the kinetic parameters were obtained from precise measurements of the resonance frequency and the width

---

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) Schuster, P.; Zundel, G.; Sandorfy, C. *The Hydrogen Bond*; North-Holland: Amsterdam, 1976; Vols. I–III.

(2) Schuster, P., Ed. *Hydrogen Bonds*; Topics in Current Chemistry, Vol. 120; Springer-Verlag: Berlin, Heidelberg, New York, Tokyo, 1984.

(3) Carsaro, R. D.; Atkinson, G. *J. Chem. Phys.* **1971**, *54*, 4090. Carsaro, R. D.; Atkinson, G. *J. Chem. Phys.* **1971**, *55*, 1971.

(4) Tatsumoto, N.; Sano, T.; Matsunaga, N.; Tochigi, E.; Yusunaga, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2083.

(5) Schumann, O.; Hauptmann, P.; Kehlen, H. *Z. Phys. Chem.* (*Leipzig*) **1985**, *266*, 863.

(6) Rassing, J. *J. Chem. Phys.* **1972**, *56*, 5225.

(7) Sims, R. W.; Willcott, M. R.; Inners, R. *J. Chem. Phys.* **1979**, *70*, 4562.

(8) Voronin, A. U.; Gerasimov, I. V.; Denisov, G. S.; Rutkovski, K. S.; Tokhadze, K. G. *Chem. Phys. Lett.* **1983**, *101*, 197.

(9) Borchardt, D.; Caballero, J. F.; Bauer, S. H. *J. Am. Chem. Soc.* **1987**, *109*, 6651.

(10) Rutkovskii, K. S.; Bykov, M. G. *Khim. Fiz.* **1991**, *10*, 1457.

0002-7863/94/1516-9233$04.50/0

of acoustic resonance profiles for temperatures between 290 and 325 K and for pressures between 0.01 and 100 mbar. Standing acoustic waves in a cylindrical cavity were excited by absorption of amplitude-modulated laser radiation. Karbach et al.[11,12] demonstrated that the resonant photoacoustic method can be used to measure the effect of vibrational relaxation on the speed of sound and the sound absorption very precisely by evaluating the resonance frequency and the broadening of the resonance profile. The same method was employed later to investigate the kinetics of the reaction $N_2O_4 \rightleftharpoons 2NO_2$.[13,14] The resonance frequency at the maximum signal contains information about the speed of sound, and the broadening of the profile represents the sound absorption processes.

Theory

A full treatment of the theory of acoustic resonances in cylindrical cavities is given in ref 15. Here, only the main results are presented.

For an acoustic wave with the time dependence $\exp(i\omega t)$, the acoustic temperature change ϑ is governed by Kirchhoff's[16] fourth-order partial differential equation:

$$\frac{i\delta_T^{\,2}}{2}\left[1+\frac{i\gamma}{2}\left(\frac{\omega\delta_v'}{v_S}\right)^2\right]\nabla^4\vartheta + \left[1+\frac{i}{2}\left(\frac{\omega}{v_S}\right)^2(\gamma\delta_T^{\,2}+\delta_v'^2)\right]\nabla^2\vartheta + \left(\frac{\omega}{v_S}\right)^2\vartheta = 0 \quad (1)$$

Compared to Kirchhoff's original equation, which is valid only for ideal gases, some of the parameters here have a different meaning and some are complex. The complex value γ is the ratio of the isentropic to the isothermal speed of sound, the complex thermal penetration length is

$$\delta_T = \left(\frac{2\lambda}{\rho\omega T(\partial S/\partial T)_p}\right)^{1/2} \quad (2)$$

the real viscous penetration length is

$$\delta_v = \left(\frac{2\eta}{\rho\omega}\right)^{1/2} \quad (3)$$

and there is a related quantity $\delta_v' = (4/3)^{1/2}\delta_v$. ρ is the density, S is the entropy, λ is the thermal conductivity, and η is the kinematic viscosity. When the small effect of the isomerization reaction of the two forms of the monomer, which is documented for formic acid,[17] is neglected, the complex speed of sound v_S in a partially dissociated gas with monomers A and dimers AA is[15,18]

$$v_S^{\,2} = \frac{RT}{M}\left[1+\frac{R}{C_v}-\frac{p_{AA}}{p_{tot}}\,\frac{\left(1-\frac{D}{C_vT}\right)^2}{1+\frac{4p_{AA}}{p_A}+\frac{p_{AA}}{p_{tot}}\frac{D^2}{C_vRT^2}+\frac{i\omega}{k_{diss}}}\right] \quad (4)$$

where R is the universal gas constant, T is the temperature, M is the mean molar mass of the mixture, C_v is the mean specific heat, D is the dissociation energy, p_A and p_{AA} are the partial pressures of the monomer and the dimer, respectively, p_{tot} is the total pressure, ω is the frequency of the sound wave, and k_{diss} is the dissociation rate constant of the dimers. The real part of v_S corresponds to the speed of sound, and the imaginary part represents the damping of the sound waves. For slow relaxation ($\omega/k_{diss} \gg 1$), the chemical relaxation has no influence on the speed of sound and no damping is observed. The speed of sound becomes slower for fast relaxation ($\omega/k_{diss} \ll 1$). There is also no damping in this case. However, the damping becomes maximum when $\omega/k_{diss} = 1 + 4p_{AA}/p_A + (p_{AA}/p_{tot})[D^2/(C_vRT^2)]$. That means a dispersion step in v_S, and a bell-shaped absorption peak is expected as a function of ω/k_{diss}.

For the unperturbed problem ($\lambda = 0$, $\eta = 0$), eq 1 simplifies to

$$(\nabla^2 + k_p^{\,2})\vartheta = 0 \quad (5)$$

with $k_p^{\,2} = \omega^2/v_S^{\,2}$. The solution for cylindrical geometry is given by

$$\vartheta = \vartheta_0 J_m(k_r r)\cos(k_z Z)\begin{bmatrix}\sin(m\varphi)\\ \cos(m\varphi)\end{bmatrix} \quad (6)$$

with $k_p^{\,2} = k_r^{\,2} + k_z^{\,2} + (m/R_0)^2$, where R_0 is the radius of the cylinder and J_m is the Bessel function of order m. In the experiment, no azimuthal modes are excited and thus m is always zero and $J_m = J_0$. The pressure gradient normal to the wall $\vec{n}\cdot\vec{\nabla}p$ must vanish at the walls. This means

$$\left(\frac{\partial J_0(k_r r)}{\partial r}\right)_{R_0} = -J_1(k_r r) = 0 \quad (7)$$

The possible values of k_r are given by the zeros of the first-order Bessel function J_1 divided by R_0. The result for the first radial mode is $k_{100} = 3.8318/R_0$. We used the value $k_{100} = 152.9835$ m^{-1}, which was determined from calibration measurements for 1000 mbar of Ar at 304 K, where the speed of sound is known with high precision.[19]

There are additional contributions to the sound dispersion and absorption due to the thermal and viscous interactions of the gas particles with one another and with the resonator wall.[20] The calculation of the complex resonance frequency $\omega_{100} = \omega_r + i\Delta\omega/2$ of the first radial mode of a cylindrical resonator with radius R_0 and length L_0 gives

$$\omega_{100}^{\;2} = (k_{100}v_S)^2\left[1+(i-1)\frac{\delta_v+(\gamma-1)\delta_T\left(1+\frac{L_0}{R_0}\right)}{L_0} + \frac{i}{2}\left(\frac{\omega_r}{v_S}\right)^2((\gamma-1)\delta_T^{\,2}+\delta_v'^2)\right] \quad (8)$$

where γ, δ_T, δ_v, δ_v', and v_S are evaluated at the frequecy $\omega = \omega_r$.

The final result for the frequency dependence of the complex acoustic signal $A_{100}(\omega)$ is given by

$$A_{100}(\omega) = (\text{const})\frac{i\omega}{\omega^2-(\omega_r+i\Delta\omega/2)^2} \quad (9)$$

where the resonance frequency ω_r and the width of the resonance $\Delta\omega$ are given by $\omega_r + i\Delta\omega/2 = \omega_{100}$ for the mode under investigation. Equation 9 describes a Lorentzian profile.

Experimental Section

The experimental method is described in detail in some previously released reports.[13-15] The optimization of the experiment for the investigation of carboxylic acids and the additional possibility of studying complex gas mixtures are discussed in ref 15 in particular.

---

(11) Karbach, A.; Röper, J.; Hess, P. *Rev. Sci. Instrum.* **1984**, *55*, 892.

(12) Karbach, A.; Hess, P. *J. Chem. Phys.* **1985**, *83*, 1075; **1986**, *84*, 2945.

(13) Fiedler, M.; Hess, P. *J. Chem. Phys.* **1990**, *93*, 8693.

(14) Fiedler, M.; Hess, P. In *Photoacoustic, Photothermal and Photochemical Processes in Gases*; Hess, P., Ed.; Springer-Verlag: Heidelberg, Berlin, New York, 1989; pp 85–123.

(15) Winkler, A.; Mehl, J. B.; Hess, P. *J. Chem. Phys.* **1994**, *100*, 2717.

(16) Kirchhoff, G. *Ann. Phys. Chem.* **1868**, *134*, 177.

(17) Chao, J.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1978**, *7*, 363.

(18) Einstein, A. *Sitzungber. Phys.-Math. Kl.* **1920**, 380.

(19) Moldover, M. R.; Trusler, J. P. M.; Edwards, T. J.; Mehl, J. B.; Davis, R. S. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1988**, *93*, 85.

(20) Trusler, J. P. M. In *Physical Acoustics and Metrology of Fluids*; Adam Hilger: Bristol, Philadelphia, New York, 1991; pp 68–72.

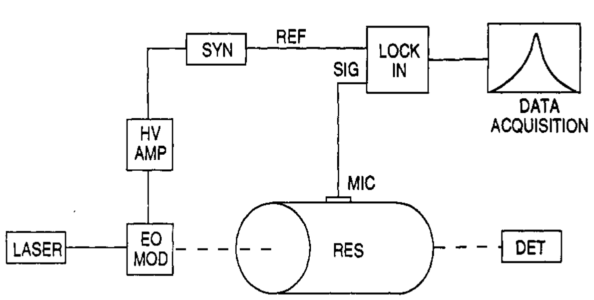

Figure 1. Scheme of the experimental setup. Photoacoustic part: laser, electrooptic modulator (EO-MOD), resonator (RES), microphone (MIC), and pyroelectric detector (DET). Electronic part: high-voltage amplifier (HV-AMP), frequency synthesizer (SYN), and lock-in amplifier (LOCK-IN).

A scheme of the apparatus is shown in Figure 1. The first radial acoustic resonance of a cylindrical resonator was excited by amplitude-modulated laser radiation of a waveguide CO_2 laser (Edinburgh Instruments, model WL8-Gt). The resonator of 5 cm diameter and 6 cm length was machined from stainless steel. The laser beam traversed the cell along the cylinder axis through ZnSe windows, which were pressed into openings of the cylinder wall on Teflon seals. An electrooptic modulator (Pockels cell) supplied by Electro Optic Development produced the amplitude modulation of the laser beam in the kilohertz range. A Sennheiser KE 4-211-2 electret microphone (sensitivity of 10 mV/Pa) with a diameter of 5 mm was mounted on a linear feedthrough halfway along the cylinder. For measurements the active surface of the microphone was positioned flush with the inner cylinder wall.

The modulation frequency was delivered by a computer-controlled frequency synthesizer (Philips, model PM 5190). It was amplified by a linear high-voltage amplifier (Electro Optic Development, model LA10C) to drive the Pockels cell. The microphone signal was amplified and filtered by an electronic filter (Ithaco 4213) with the high-pass cutoff set to 200 Hz and the low-pass set to 100 kHz. A computer-controlled two-phase lock-in amplifier (Ithaco 3961) recorded the signal and the phase. The frequency synthesizer output was used as an external reference.

The temperature was stabilized by a bath and could be determined with a relative precision of 0.03 K. The pressure was controlled by capacitance manometers (MKS Baratrons).

Carboxylic acid vapor was introduced into the acoustic resonator from a preparation cell which contained vapor in equilibrium with liquid. The preparation cell was pumped to freshen the vapor prior to every filling of the resonator. The purity was controlled by the measured vapor pressure and the measured resonance frequency, which depends strongly on the mean molar mass of the mixture and is therefore a powerful tool for detecting the presence of impurities ($\omega_r \propto 1/M^{1/2}$).

The resonance frequency ω_r was determined with a resolution in the 0.1%–2% range, depending on experimental conditions; the width of the resonance $\Delta\omega$ was typically determined to a fractional resolution of about $1/(2Q)$, where Q is the quality factor of the resonance given by $Q = \omega_r/\Delta\omega$. A typical resonance profile is shown in Figure 2.

The data evaluation method was studied intensively on formic acid.[15] In addition to kinetic information, it is possible to determine the equilibrium constant of the reaction $(R\text{–}COOH)_2 \rightleftharpoons 2R\text{–}COOH$ very precisely from the variation of the resonance frequencies measured in the high-pressure range, where the relaxation phenomena have no influence on the resonance parameters.

The kinetic information is obtained mainly from measurements on carboxylic acid/He mixtures. The theoretical model cannot be fit to the data under the assumption of a pressure-independent dissociation rate constant k_{diss} (first-order regime). As expected, the system is in the second-order regime. We assumed the dissociation rate constant to be described by

$$k_{diss} = k_a(T)[\epsilon_b p_b + \epsilon_A p_A + p_{AA}] \qquad (10)$$

where the temperature dependence of k_a is given by

$$k_a(T) = k_0 \exp\left(-\frac{E_{act}}{RT}\right) \qquad (11)$$

Here E_{act} is the activation energy and ϵ_i is the collision efficiency of gas component i relative to that of the dimer.

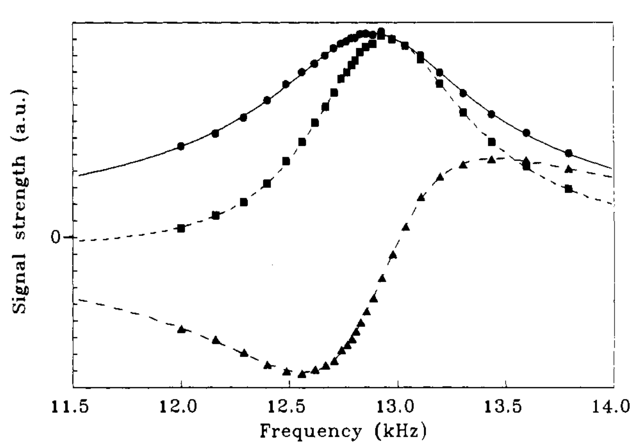

Figure 2. Typical acoustic resonance profile. The data were recorded in a mixture of 7 mbar of He and 0.7 mbar of propionic acid at 304 K. The dots, triangles, and squares represent the absolute value, the real part, and the imaginary part, respectively. The Q value is 15, the resonance frequency is 12 897 Hz, and the width of the resonance is 867 Hz.

The relaxation of the internal degrees of freedom (vibration, rotation) was also determined in these experiments. But this process has only an influence on the resonance parameters in the low-pressure region, where the available experimental data are not very accurate. In addition, the individual contributions of the different internal degrees of freedom cannot be resolved. Therefore, the phenomenon was treated only generally. The relaxation time τ was described by

$$\tau = \frac{p\tau}{p_A + p_{AA} + \alpha_b p_b} \qquad (12)$$

where α_b is the collision efficiency of the buffer gas for this process.

For formic and acetic acids, complete sets of the normal frequencies are available.[17] Therefore, the temperature dependence of the specific heat and the equilibrium constant could be included in the theoretical calculations of the resonance parameters. For propionic acid the estimation method of Joback described in ref 21 was applied to calculate the specific heats of the monomer and the dimer. The weak temperature dependence of the equilibrium constant was neglected for this acid. The thermal conductivities and the viscosities of the monomer and the dimer were calculated by the methods of Reichenberg and Roy-Thodos, respectively, described in ref 21. The transport coefficients of the noble gases were taken from ref 19. The thermal conductivities and the viscosities of the gas mixtures were calculated via the estimation techniques of Wassiljewa, combined with the proposals of Mason and Saxena, and the method of Wilkie, respectively (see ref 21).

The chemical relaxation effect in the pure acid could only be resolved as a separate peak in the case of formic acid. For acetic and propionic acids, this effect could be separated from other loss processes in mixtures with He. In the case of propionic acid, the determination of the equilibrium constant was less accurate because the precondensation effects influenced the results for the resonance frequency in the pure system even at relatively low pressures.[15,22]

For the calculation of the errors of the extracted parameters, the influence of uncertainties in the transport coefficients and the normal modes was investigated and we also performed a statistical error estimation based on the individual errors of the resonance parameters. In the cases of formic and acetic acids, the errors of the thermodynamic and the kinetic parameters due to uncertainties in the estimation of the specific heat and the transport coefficients are much larger than the errors obtained from the statistical error estimation. This indicates that resonant photoacoustic spectroscopy is a very accurate method.

Results

Resonance parameters were recorded as a function of the partial pressure of the acid for various temperatures between 290 and 325 K and He partial pressures up to 50 mbar.

---

(21) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of liquids and gases*, 4th ed.; McGraw-Hill Book Co.: New York, 1986.

(22) Mehl, J. B.; Moldover, M. R. *J. Chem. Phys.* **1982**, *77*, 455.

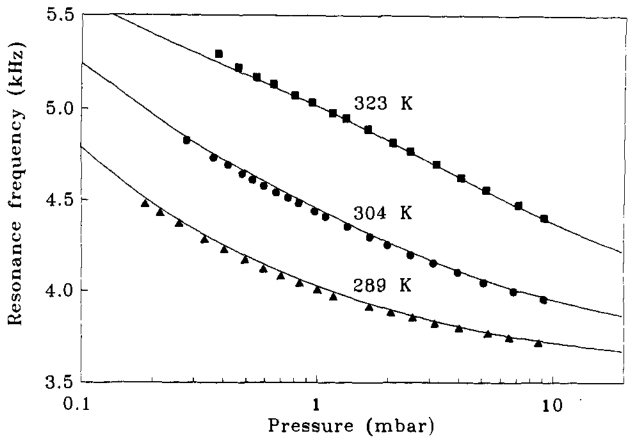

Figure 3. Resonance frequency of the first radial mode of the cylinder as a function of pressure at 289, 304, and 323 K for pure acetic acid vapor. The solid lines represent the theoretical prediction. The triangles, points, and squares represent the measured values.

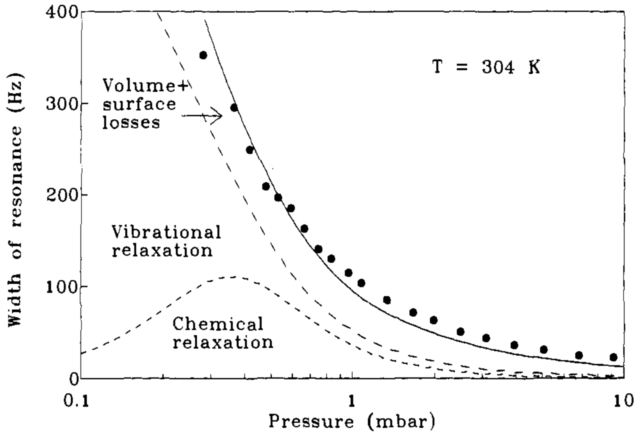

Figure 4. Width of the resonance of the first radial mode of the cylinder as a function of the pressure at 304 K for pure acetic acid vapor. The solid line represent the theoretical prediction. The points represent the measured values. The contributions of the different effects are cumulatively added.

Figure 3 shows the typical pressure and temperature dependences of the resonance frequency in pure acetic acid. The resonance broadening as a function of the pressure in pure acetic acid is shown in Figure 4. The chemical relaxation is fast and therefore occurs in the low-pressure region, where this effect is masked by classical loss effects. This problem is overcome by measurements on mixtures with He or Ar. Since the influence of the chemical relaxation on the complex sound velocity depends on $(1 - D/(C_vT))^2$, the effect is enhanced by the reduction of C_v (see eq 4). In addition, the thermophysical parameters of the mixture are dominated by the well-known values of the buffer gases so that the evaluation of the experimental resonance parameters becomes very precise. The typical behavior of the resonance frequency and the width of the resonance as a function of the partial pressure of acetic acid in a mixture with He is presented in Figures 5 and 6. The peak due to chemical relaxation is separated from the other loss processes and is much higher than in the pure system.

The data allow the thermodynamic equilibrium parameters and the pressure and temperature dependence of the dissociation rate constant to be determined. In addition, the collision efficiency of argon was obtained from measurements on mixtures of Ar and the acid under investigation.

Care must be taken with the adsorption/desorption processes of the acid molecules at the walls. When the carboxylic acid was admitted to the system, a drastic pressure decrease due to adsorption of the acid molecules on the wall was observed. If a buffer gas was admitted to the system after the partial pressure of the acid was stable, the opposite effect was observed. Acid molecules were removed from the surface. This was seen as a slow decrease of the resonance frequency with time, indicating that the pressure of the acid was increasing. Thus no accurate information about the actual partial pressure of the carboxylic acid is available. In spite of these difficulties, we were able to make useful measurements on formic acid for buffer gas pressures up to 1000 mbar. These measurements allowed an accurate estimation of the maximum width of the resonances. The measured values agree very well with the theoretical predictions.[15] This is shown in Figure 7.

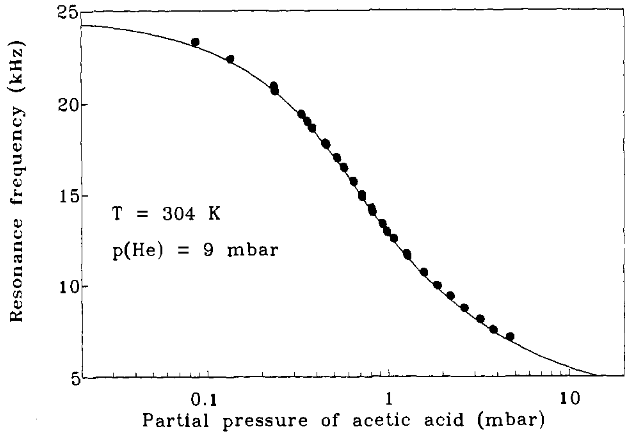

Figure 5. Resonance frequency of the first radial mode of the cylinder as a function of the partial pressure of acetic acid at 304 K in the presence of 9 mbar of He. The solid line represents the theoretical prediction. The points represent the measured values.

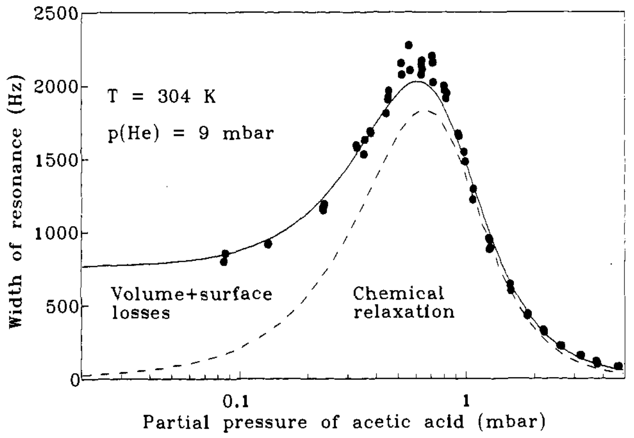

Figure 6. Width of the resonance of the first radial mode in the cylinder as a function of the partial pressure of acetic acid in the presence of 9 mbar of He at 304 K. The dashed line represents the contribution due to chemical relaxation. The solid line represents the theoretical prediction. The points represent the measured values. The approximations in eq 8 are responsible for the discrepancies between the measurement and the theory at the peak maximum.

To obtain the correct actual partial pressure of the acid in mixtures with noble gases, the cell was first filled with the noble gas, which showed no measurable adsorption effect, and then the acid was admitted to the system. This method introduced a limit for the working buffer gas pressure, which must be lower than the vapor pressure of the acid at the temperature of the preparation cell.

Formic Acid. A sample (Merck) with minimum purity of 98% containing probably about 2% water and small amounts of acetic acid (<0.05%) was used.

The acoustic resonances were excited by the 9R20 line (9.271 μm) of the CO_2 laser with an average power of 0.6 W. This wavelength was selectively absorbed by the monomer. The

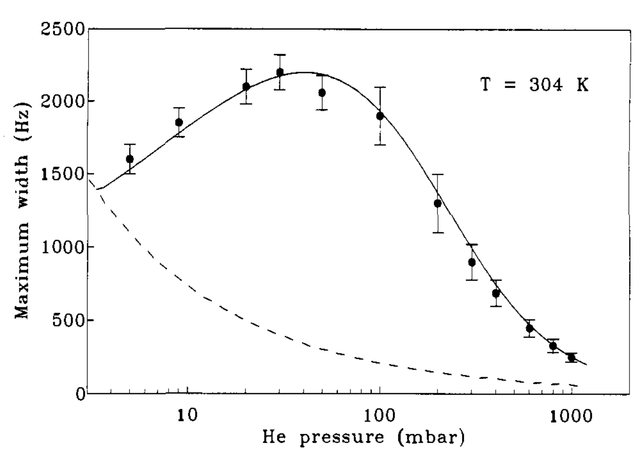

Figure 7. Maximum width of the resonance of the first radial mode of the cylinder for formic acid as a function of the He pressure at 304 K. The solid line represents the theoretical prediction. The points represent the measured values. The dashed line represents the maximum contribution of the surface and volume losses, which are always maximum for pure He.

minimum pressure in the pure system was 0.1 mbar and in mixtures with noble gases 0.01 mbar. Altogether we recorded about 900 acoustic resonance profiles.

The ratio r_Θ of the square of the product of the three principle moments of inertia of the monomer ($(\Pi\Theta_A)^2$) to that of the dimer ($\Pi\Theta_{AA}$) and the dissociation energy H_0^0 at 0 K were treated as free parameters. The values of H_0^0 at 0 K and $(\Pi\Theta_A)^2/\Pi\Theta_{AA}$ were computed to be 59.6 ± 0.5 kJ/mol and $6 \pm 2 \times 10^{-119}$ g^3·cm^6, respectively, compared to 61.59 kJ/mol and 1.39×10^{-118} g^3·cm^6, respectively, proposed by Chao and Zwolinski.[17] We obtain $S_{\text{diss}} = 159 \pm 2$ J/(mol·K) and $H_{\text{diss}} = 61.8 \pm 0.5$ kJ/mol at 300 K.

A consistent evaluation of the resonance parameters is also possible with the equilibrium constants given by Coolidge,[23] Halford,[24] Taylor and Bruton,[25] and Barton and Hsu.[26] A newer measurement[27] and the theoretically proposed values[17] give resonance frequencies that are too low, which means that the concentration of the dimer is overestimated.

The maximum half-width in mixtures with 10 mbar of He was observed for formic acid partial pressures around 2 mbar. The prefactor of the dissociation rate constant was determined to be $k_0 = 2.2 \pm 0.4$ ns^{-1}·mbar^{-1}, and the activation energy E_{act} is 33 ± 1 kJ/mol. We found $\epsilon_A = 0.5 \pm 0.2$. On the basis of estimated hard sphere diameters[21] of 3.9 Å for the monomer and 5.1 Å for the dimer, we estimate $\epsilon_A \approx 0.97$ if we assume strong collisions with 100% efficiency. That means about two times as many collisions of a dimer with a monomer are required to dissociate the dimer compared to collisions between two dimers. We obtain $\epsilon_{\text{He}} = 0.05 \pm 0.02$ and $\epsilon_{\text{Ar}} = 0.08 \pm 0.02$. With hard sphere diameters of 2.551 Å for He and of 3.542 Å for Ar,[21] we calculate that collisions with He are 40 times and with Ar are 12 times less effective than collisions between two dimers.

The average $p\tau$ value for vibrational and rotational relaxation is 10 ± 2 ns·bar for temperatures between 290 and 325 K. This means about 80 collisions are needed to equilibrate the inner degrees of freedom, if we assume a hard sphere diameter of the monomer of about 3.9 Å. The lowest normal vibrational mode of the monomer is 625 cm^{-1}.[17] For this wavenumber we estimate about 90–300 collisions from the Lambert–Salter plot presented in ref 28. This discrepancy can be explained by the small fraction of dimers present in the low-pressure region. The lowest normal mode frequency of the dimer is 68 cm^{-1}, which leads to a collision number on the order of 1. The collision efficiencies of He and Ar are $\alpha_{\text{He}} = 0.1 \pm 0.03$ and $\alpha_{\text{Ar}} = 0.2 \pm 0.02$.

Acetic Acid. The sample (Merck) had a purity of 99.8%. For the excitation of the sound waves, the 10P20-line (10.591 μm) of the CO_2 laser with an average output power of 1.2 W was used. This line is absorbed by the dimer. The minimum pressure in pure acetic acid was about 0.2 mbar, and in mixtures with He, about 0.03 mbar. Altogether about 900 acoustic resonance profiles were recorded.

Chao and Zwolinski[17] and Büttner and Maurer[27] have summarized 14 reports on the determination of the thermodynamic equilibrium parameters. In contrast to formic acid, there is only one data set, reported by Taylor,[29] which is consistent with the measured resonance frequencies.

For the equilibrium parameters, we obtain $r_\Theta = (4.5 \pm 0.9) \times 10^{-119}$ g^3·cm^6 and $H_0^0 = 63.51$ kJ/mol, corresponding to $S_{\text{diss}} = 150.60$ J/(mol·K) and $H_{\text{diss}} = 62.64$ kJ/mol at 300 K. These values are much closer to the values proposed by Chao and Zwolinski[17] ($r_\Theta = 6.6 \times 10^{-119}$ g^3·cm^6 and $H_0^0 = 64.04$ kJ/mol) as in the case of formic acid.

The maximum width of the resonance in mixtures with 10 mbar of He was typically observed for partial pressures of the acid of about 1 mbar, which indicates that the relaxation process is faster than in the case of formic acid. The prefactor of the dissociation rate constant is $k_0 = 1.6 \pm 1.0$ ns^{-1}·mbar^{-1}, and the activation energy is $E_{\text{act}} = 31.8 \pm 2.0$ kJ/mol. The relative collision efficiency of the monomer was computed to be $\epsilon_A = 0.84 \pm 0.2$, which is somewhat higher than for formic acid. With estimated hard sphere diameters of 4.6 Å for the monomer and 5.9 Å for the dimer, one would expect $\epsilon_A = 0.97$, when the collision efficiency is 100%.

Collisions with noble gases are about a factor of 2.3 more effective than for formic acid. We obtain $\epsilon_{\text{He}} = 0.12 \pm 0.02$ and $\epsilon_{\text{Ar}} = 0.18 \pm 0.02$, where Ar is again a more effective collision partner than He.

Due to the smaller lowest normal mode frequency[17] of the acetic acid monomer of 581 cm^{-1}, we expect faster relaxation of the internal degrees of freedom than for formic acid. The $p\tau$ value of 7.9 ± 2 ns·bar, compared to 10 ± 2 ns·bar for formic acid, is consistent with that assumption.

Propionic Acid. The measurements were performed with the 9R20 line of the CO_2 laser, which is absorbed by the monomer. The sample (Merck) contained a minimum of 99% propionic acid. The water content was about 0.3%. It was decreased by heating the sample and pumping the preparation cell several times.

Due to the low vapor pressure, the available pressure range was further restricted. About 500 acoustic resonance profiles were recorded.

The precondensation effects[15,22] have a large influence on the resonance frequency in the pure system. But this effect is reduced in measurements on He/acid mixtures because it decreases drastically with increasing He pressure and increasing frequency. Therefore, the equilibrium parameters were obtained from a simultaneous fit of the kinetic and thermodynamic parameters to the entire data set, including the data of mixtures with He. This method also delivers accurate values for the enthalpy of dissociation because the width of the resonance depends strongly on H_{diss}[15] (see eq 4), but includes some correlations between the different parameters. Thus, the determination of the parameters is not as accurate as in the cases of formic acid and acetic acid.

In addition, the chemical relaxation is much faster and therefore it is only observed at low pressures, where the quality factor of the resonances is relatively small. The maximum width of the

---

(23) Coolidge, A. S. *J. Am. Chem. Soc.* **1928**, *50*, 2166.
(24) Halford, J. O. *J. Chem. Phys.* **1942**, *10*, 582.
(25) Taylor, M. D.; Bruton, J. *J. Am. Chem. Soc.* **1952**, *74*, 4151.
(26) Barton, J. R.; Hsu, C. C. *J. Chem. Eng. Data* **1969**, *14*, 184.
(27) Büttner, R.; Maurer, G. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 877.
(28) Lambert, J. D. *Vibrational and rotational relaxation in gases*; Clarendon Press: Oxford, U.K., 1977; pp 63–65.
(29) Taylor, M. D. *J. Am. Chem. Soc.* **1951**, *73*, 315.

Table 1. Summary of the Results for the Entropy (S_{diss}) and the Enthalpy (H_{diss}) of Dissociation, the Prefactor of the Dissociation Constant (k_0), the Activation Energy (E_{act}), and the Relative Collision Efficiencies of the Monomer (ϵ_A), He (ϵ_{He}), and Ar (ϵ_{Ar}) at 300 K

	acid		
	formic	acetic	propionic
S_{diss} (J/(mol·K))	159 ± 2	151 ± 2	147 ± 3
H_{diss} (kJ/mol)	61.8 ± 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	0.8 ± 0.2	1.2 ± 0.5
ϵ_{He}	0.05 ± 0.02	0.12 ± 0.02	0.10 ± 0.03
ϵ_{Ar}	0.08 ± 0.02	0.18 ± 0.02	0.21 ± 0.03

resonance in mixtures with 10 mbar of He was in the pressure range of 0.3 mbar.

From the values of the equilibrium constant reported in the literature, only the data set of Taylor and Bruton[25] is consistent with the measured resonance frequencies. But the values for the width of the resonances predicted with this data set are too small. The values obtained for the thermodynamic parameters are $S_{diss} = 146.9 \pm 3.0$ J/(mol·K) and $H_{diss} = 61.3 \pm 0.5$ kJ/mol at 300 K.

The relative collision efficiency of the monomer is $\epsilon_A = 1.2 \pm 0.4$. With estimated hard sphere diameters of 5.1 Å for the monomer and 6.5 Å for the dimer, one would expect $\epsilon_A = 0.97$ under the assumption of 100% collision efficiency. Within the error bars now 100% efficiency is reached. The values of the collision efficiencies of the noble gases are nearly the same as for acetic acid. We obtain $\epsilon_{He} = 0.10 \pm 0.03$ and $\epsilon_{Ar} = 0.21 \pm 0.03$. The prefactor of the rate constant is $k_0 = 9.5 \pm 4.0$ ns^{-1}·mbar^{-1}. The activation energy is similar to those of the other acids. The value obtained is $E_{act} = 31.8 \pm 2.5$ kJ/mol.

The $p\tau$ value for the relaxation of the internal degrees of freedom was determined to be $p\tau = 20 \pm 5$ ns·bar. This value should be regarded as a rough estimate since it is mainly determined from the low-pressure data of the pure acid, where precondensation effects still influence the data.

Discussion

The results of all acids under investigation are summarized in Table 1. The values obtained for the equilibrium parameters agree very well with those reported previously.[17,30]

The prefactor of the dissociation rate constant, the relative collision efficiency of the monomer, and the collision efficiencies of the noble gases increase with the number of C atoms in the acid molecule. The noble gases are relatively ineffective collision partners, as expected. Ar is 1.7 times more effective than helium. The activation energy is nearly independent of the composition of the R group, and its value is about one-half the dissociation energy.

The chemical relaxation times for dissociation can be calculated via

$$\tau = \frac{1}{k_{diss}\left(1 + 4\frac{p_A}{K_p}\right)} \qquad (13)$$

The chemical relaxation becomes much faster with an increasing number of C atoms, corresponding to an increasing specific heat of the monomer. This can be seen from the values given for typical experimental conditions presented in Table 2 and the contribution of the chemical relaxation to the width of the resonance in Figure 8.

Table 2. Comparison of the Equilibrium Constant (K_p), the Corresponding Partial Pressures, the Specific Heat of the Dimer ($C_{v,dim}$), the Dissociation Rate Constant (k_{diss}), and the Chemical Relaxation Time (τ_{diss}) at 300 K, 1 mbar of Carboxylic Acid, and 9 mbar of He

	acid		
	formic	acetic	propionic
K_p (mbar)	3.91	0.93	1.01
p_{mon} (mbar)	0.83	0.60	0.62
p_{dim} (mbar)	0.17	0.40	0.38
$C_{v,dim}$ (J/(mol·K)	88.2	120	174
k_{diss} (10^4 1/s)	0.42	0.90	5.61
τ_{diss} (μs)	126	31	5.2

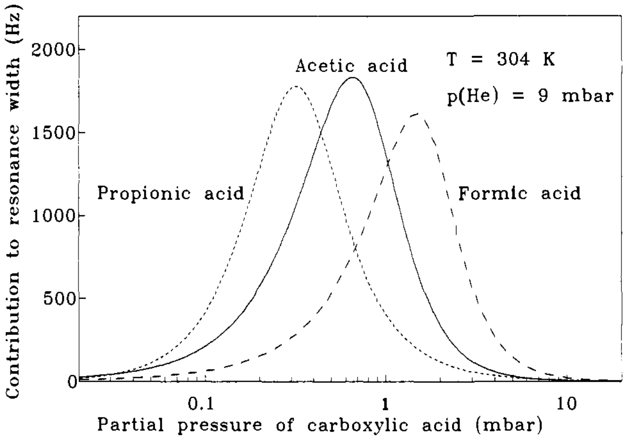

Figure 8. Contribution of the chemical relaxation effect to the width of the resonance of the first radial mode in the cylinder as a function of the partial pressure of the carboxylic acid in the presence of 9 mbar of He at 304 K.

A comparison with the kinetic data extracted for formic and acetic acids under comparable conditions from temperature jump experiments is given in Table 3. Borchardt et al.[9] investigated the chemical relaxation of formic acid in mixtures with Ar and some organic compounds that can participate in strong H···O bond formation for temperatures between 293 and 335 K. Initial formic acid partial pressures varied from 1.3 to 3.7 mbar, and the Ar pressure ranged from 6 to 800 mbar. Since we have derived the relative collision efficiency of the monomer and Ar, we can make a direct comparison. The values for the chemical relaxation times agree very well for high Ar pressures but show differences up to a factor of 10 for low Ar pressures.

Our results cannot be explained if the system is assumed to be in the first-order regime. As expected it is in the second-order regime and the pressure dependence of the rate constant is described by eq 10.

Rutkovskii and Bykov[10] worked with a large excess of H_2. Therefore, they were not able to establish the dependence of k_{diss} on the partial pressure of formic acid.

Voronin et al.[8] investigated the chemical relaxation in mixtures of H_2, SF_6, and acetic acid. Their results are also compared with the results of this work in Table 3. They obtained an activation energy of 48 ± 3.5 kJ/mol, which is much higher than the present result (32 ± 2 kJ/mol).

The data in Table 3 show that H_2 is a more effective collision partner than He. From comparison with the present experiment, we deduce $\epsilon_{H_2} = 0.07$ for formic acid and $\epsilon_{H_2} = 0.21$ for acetic acid. Comparable values and a higher efficiency of Ar were also observed for other reactions such as the isomerization $c\text{-}C_3H_6 \rightarrow CH_3CHCH_2$ ($\epsilon_{He} = 0.05$, $\epsilon_{H_2} = 0.12$, $\epsilon_{Ar} = 0.07$) and the dissociation $c\text{-}C_4H_8 \rightarrow 2C_2H_4$ ($\epsilon_{He} = 0.07$, $\epsilon_{H_2} = 0.10$, $\epsilon_{Ar} = 0.21$).[31]

---

[30] Clague, A. D. H.; Bernstein, H. J. *Spectrochim. Acta, Part A* **1969**, *25*, 593.

[31] Lambert, J. D. *Vibrational and rotational relaxation in gases*; Clarendon Press: Oxford, U.K., 1977; p 112.

Table 3. Comparison of the Dissociation Rate Constant (k_{diss}), the Corresponding Chemical Relaxation Time (τ_{diss}), and the Activation Energy (E_{act}) with the Results of Temperature Jump Experiments

	formic acid				acetic acid		
ref	9	10	this work	this work	8	this work	this work
temp (K)	294.5	293	294.5	293		300	
buffer gas	Ar	H_2	Ar	He	H_2	Ar	He
buffer gas pressure (mbar)	66.1	66.6	66.1	66.6		120	
pressure of acid (mbar)	1.9	1.7	1.9	1.7		1.3	
τ_{diss} (μs)	9.2	9.4	14	22	1.5	2.3	3.1
k_{diss} (10^4 1/s)	3.0	3.2	2.4	1.7	14.1	10.5	7.7
E_{act} (kJ/mol)	32 ± 4	41 ± 8	33 ± 1	33 ± 1	48 ± 3.5	32 ± 2	32 ± 2

Table 4. Comparison of the Measured Activation Energies (kJ/mol) in the Liquid and in the Gas Phase

		acid		
phase	ref	formic	acetic	propionic
gas	this work	33 ± 1	32 ± 2	32 ± 2.5
	8		48 ± 3.5	
	9	32 ± 4		
	10	41 ± 8		
liquid	3		38 ± 0.2	
	32	26 ± 1.3	33.8 ± 1.3	30.5 ± 1.3
	33		35.4	
	34			31.4
	35		37 ± 2	
	36			46

It should be mentioned that the activation energy was found to be significantly lower than the dissociation energy in all studies. In this respect the results of this work agree well with the results from temperature jump experiments. The activation energy is quite similar to the values observed in the liquid. A comparison is given in Table 4. Carsaro and Atkinson[3] found dissociation rate constants in mixtures of acetic acid and acetone of $k_{D\to C} = 3.37 \times 10^5$ 1/s and in solutions in water of $k_{D\to C} \approx 4 \times 10^5$ 1/s. These values are only about 4 times higher than the values measured in the gas phase in the presence of 120 mbar of H_2 or Ar. This demonstrates the great influence of the solvents on the kinetics of the dissociation. From the vapor phase data, one would expect much higher rates for such high densities.

The dissociation in the gas phase cannot be described by a simple Lindemann mechanism. Since the activation energy of the rate-determining step is about one-half of the dissociation energy, it must be a stepwise process as proposed for the liquid. E_{act} corresponds to the bonding energy of one H bond. Therefore, a noncyclic dimer with only one H bond is proposed as an intermediate state.

This was already proposed by Borchardt et al.[9] for formic acid. They observed an acceleration of the process when organic compounds which can participate in strong H···O bond formation were added. Therefore, they proposed the following process. The cyclic structure opens when a free monomer adds to one of the O···HO bonds of the dimer. By this means, one of the initial monomers is released and the remaining two monomers generate a chain structure which rapidly dissociates into two monomers.

However, this mechanism is not consistent with the present data because it predicts that the dissociation rate is proportional to the partial pressure of the monomer and that Ar and He should not affect the dissociation process. However, a fit of the theoretical model to the measured resonance parameters leads to inconsistencies for this assumption.

A process which is consistent with the entire available experimental data is the following: An activation of a dimer D with any possible collision partner X can break one H bond. A chain dimer C is generated. Additional collisions may transform this noncyclic dimer into a cyclic dimer or break the second H bond. The noncyclic dimer dissociates into two monomers.

The scheme of the process is as follows:

$$D + X \rightleftharpoons D^* + X \qquad (I)$$

$$D^* \rightleftharpoons C \qquad (II)$$

$$C + X \rightleftharpoons C^* + X \qquad (III)$$

$$C^* \rightleftharpoons 2M \qquad (IV)$$

Here D^* is a highly excited cyclic dimer and C^* is a highly excited chain dimer. To simplify the calculation of the dissociation rate, we combined the steps I and II, and III and IV.

$$D + X \rightleftharpoons C + X$$

$$C + X \rightleftharpoons 2M + X$$

The time derivative of the concentration of the cyclic dimer is given by

$$\frac{dc_D}{dt} = -k_{D\to C}c_Xc_D + k_{C\to D}c_Xc_C \qquad (14)$$

and for the chain structure one finds

$$\frac{dc_C}{dt} = -k_{C\to 2M}c_Xc_C + k_{2M\to C}c_Xc_M^{\ 2} + k_{D\to C}c_Xc_D - k_{C\to D}c_Xc_C \qquad (15)$$

If the steady-state hypothesis is applied to the concentration of C ($dc_C/dt = 0$), the overall change of the concentration of D becomes

$$\frac{dc_D}{dt} = -\left[k_{D\to C}\frac{k_{C\to 2M}}{k_{C\to D} + k_{C\to 2M}}\right]c_Xc_D + \left[k_{C\to D}\frac{k_{2M\to C}}{k_{C\to D} + k_{C\to 2M}}\right]c_Xc_M^{\ 2} \qquad (16)$$

Thus, the dissociation rate constant is given by

$$k_{diss} = \left[k_{D\to C}\frac{k_{C\to 2M}}{k_{C\to D} + k_{C\to 2M}}\right]c_X \qquad (17)$$

This describes the observed pressure dependence of k_{diss}.

The measured activation energy implies $k_{C\to 2M} \gg k_{C\to D}$ because otherwise it should be at least as large as the dissociation energy. This holds true also for the more detailed mechanism. Therefore

$$k_{diss} \approx k_{D\to C}c_X \qquad (18)$$

In this case, the experimental data give information only on the first reaction step and its temperature and pressure dependence. This is in agreement with the observed activation energy.

---

(32) Moriamez, C.; Moriamez, M.; Moreaux, A. *J. Chim. Phys.* **1966**, *63* (4), 615.

(33) Lamb, J.; Pinkerton, J. M. M. *Proc. R. Soc. London* **1949**, *A199*, 114.

(34) Lamb, J.; Huddart, D. H. A. *Trans. Faraday. Soc.* **1950**, *46*, 540.

(35) Khan, V. H.; Subrahmanyam, S. V. *Chem. Phys. Lett.* **1972**, *17*, 231.

(36) Tatsumoto, N. *J. Chem. Phys.* **1967**, *47*, 4561.

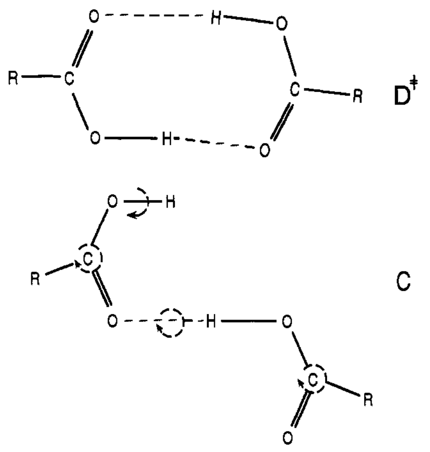

Figure 9. Proposed structure of $D^{\ddagger}$ and C. The different rotations are indicated.

Additional collisions are required because it is unlikely that the chain dimer has enough initial energy to dissociate by unimolecular decay. But we only have experimental information about the first reaction step. It is evident from the experimental results that a dissociation of a chain dimer into two monomers should be much faster than a regeneration of D ($k_{C\rightarrow D} \ll k_{C\rightarrow 2M}$).

Since there are no experimental data available for the next step(s), the following discussion is somewhat speculative. For the estimation of the entropy it is necessary to make some assumptions about the structure of the species.

The proposed structures of $D^{\ddagger}$ and C are presented in Figure 9. If we assume a low activation energy for $C \rightarrow D^{\ddagger}$ of about 3 kJ/mol and an activation energy of 30 kJ/mol for $C \rightarrow C^{\ddagger}$, then we need large entropy changes to fulfill $k_{C\rightarrow 2M} \gg k_{C\rightarrow D}$.

For $C \rightarrow D^{\ddagger}$ we estimate the following for formic acid: (1) entropy gain: one vibrational degree of freedom of about 260 cm^{-1}, $\Delta S = 6$ J/(mol·K); (2) entropy loss: (a) torsional frequency of one monomer[17] of 610 cm^{-1}, $\Delta S = -2$ J/(mol·K), (b) change of the product of the three moments of inertia, $\Delta S = -3$ J/(mol·K), (c) one free internal rotation of a monomer with an estimated reduced moment of inerta of $\Theta_{\text{red}} \approx 10^{-39}$ g·cm², $\Delta S = -27$ J/(mol·K), (d) rotation of a R—C═O group with $\Theta_{\text{red}} \approx 4 \times 10^{-39}$ g·cm², $\Delta S = -36$ J/(mol·K), (e) rotation of a R—C—O—H group with $\Theta_{\text{red}} \approx 4 \times 10^{-39}$ g·cm², $\Delta S = -36$ J/(mol·K), (f) change of the frequency in the stretched H bond, $\Delta S = -6$ J/(mol·K). Thus, $\Delta S_{\text{tot}} = -104$ J/(mol·K). This is similar to the estimate of Borchardt et al.[9] for the entropy difference between C and D (−92 J/(mol·K)). If we assume $\Delta S_{\text{tot}} = 20$ J/(mol·K) due to the lower frequency in the stretched bond for $C \rightarrow C^{\ddagger}$ then

$$\frac{k_{C\rightarrow 2M}}{k_{C\rightarrow D}} = 60 \tag{19}$$

at 300 K. That means that indeed $k_{C\rightarrow 2M} \gg k_{C\rightarrow D}$.

More illustrative is a geometrical argument. In the species C, the two monomers have many different possible configurations. However, only a few of these configurations can re-establish the cyclic dimer. Thus, collisions may more easily lead to bond breaking than the formation of a cyclic compound with a second H bond.

A proposed energy diagram is given in Figure 10. There is no information available about the depth of the minimum for the noncyclic dimer and the behavior of the potential curve between the noncyclic dimer and the two monomers.

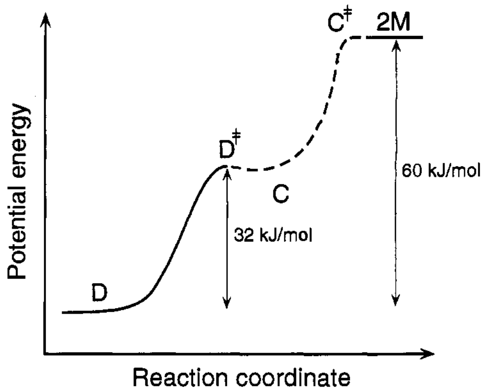

Figure 10. Enthalpy diagram for the dissociation of the carboxylic acid dimer in the gas phase.

The observed influence of noble gases also allows an explanation of why Borchardt et al.[9] observed the acceleration of the process by collisions with organic compounds. These substances have many degrees of freedom and should have a high collision efficiency.

The increase of the dissociation rate constant with the increase of the specific heat of the dimer can also be explained in view of the proposed mechanism. The energy transfer by collisions depends strongly on the number and the frequencies of the normal modes. A large number of vibrational modes or low-frequency normal modes of the dimer lead to a fast energy transfer and hence to a fast relaxation.

Conclusions

This work is one of the few experiments dealing with the dynamics of the association/dissociation process of the H bond in isolated molecules. Resonant photoacoustic spectroscopy offers the possibility of investigating fast relaxation processes in the microsecond range. The highest time resolution was achieved in experiments with added buffer gases. The fastest dissociation process was observed for propionic acid. We estimate that even 40 times faster processes could be detected. For the first time, the pressure dependence of the dissociation rate constant of hydrogen bonds in carboxylic acids was determined because the method provides information over a broad pressure range. The data give the first experimental evidence that the kinetics of the carboxylic acid dimer to monomer transformation are in the second-order regime at pressures below 100 mbar. Since we evaluate the data with the correct pressure dependence, the activation energy of the process is determined very precisely. This pressure dependence and the resulting activation energy, which corresponds to the dissociation energy of one H bond, suggest a stepwise dissociation process due to bimolecular activation. A possible mechanism, consistent with the entire experimental data, 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.

In addition to the kinetic parameters, the thermodynamic parameters were obtained from our data. The equilibrium constants agree very well with values reported in the literature. This is an important aspect since for many reaction systems the thermodynamic parameters are not very well-known.

Acknowledgment. Financial support of this research by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the European Union is gratefully acknowledged.