

RELAXATION STUDY OF STRONG HYDROGEN BOND LIFETIME IN GAS PHASE

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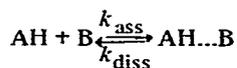
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Laser temperature jump and shock tube techniques have been used to measure the monomer-dimer relaxation time in the gas phase. With the former method, the lifetime of the cyclic dimer of acetic acid is found to increase from 3 μs at 315 K to 16 μs at 285 K. The activation energy has been determined to be $11.4 \pm 0.8 \text{ kcal mol}^{-1}$. A step-wise mechanism of dissociation is discussed.

1. Introduction

The interest in the study of the dynamics of hydrogen-bonded systems has increased during the last years because of its importance for the understanding of some fundamental questions concerning the nature and spectral properties of hydrogen bonding; for instance, the width and the shape of the proton donor $\nu_s(\text{AH})$ mode, the vibrational predissociation in hydrogen-bonded complexes. The lifetimes of hydrogen-bonded complexes in a condensed phase have been measured by various techniques, particularly by ultrasonic relaxation at room temperature, and by dynamic NMR at low temperatures [1-3]. In most cases, at room temperature, the rate of hydrogen bond formation



is limited by diffusion. As a rule, the bimolecular rate constants k_{ass} , are within the range 10^8 – $10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$, and the activation energy does not exceed $\Delta E_{\text{ass}} \approx 1$ – 3 kcal mol^{-1} and coincides with the activation energy of the diffusion [4-5]. To a first approximation, the rate of dissociation k_{diss} of complexes is determined by the energy of hydrogen bonding, and generally decreases as the energy increases. The lifetime of the complexes $\tau = k_{\text{diss}}^{-1}$ depends strongly on temperature, and its typical values increase from 10^{-6} – 10^{-11} s at $T \approx 300 \text{ K}$ to 10^{-2} – 10^{-3} s at $T \approx 130 \text{ K}$ [6,7].

It should be noted that even a neutral solvent may

play a vital role in the kinetics of processes due to the high rate of energy transfer in the condensed phase. For this reason, measurement of the lifetime of hydrogen-bonded complexes in the gaseous phase is the subject of considerable experimental and theoretical interest. Valuable information may be drawn by comparing the results of experiments in the gaseous phase, with the data obtained in solution, where the interaction between the molecules of a solvent and complexes is almost uninterrupted.

However, attempts to determine the dynamic characteristics of hydrogen bonds in the gaseous phase in a direct way have not been successful until recently. In fact, the first complete paper on measurements of the lifetime of complexes in a gas was published in 1982 [8]. The lifetimes of the cyclic dimer of trifluoroacetic acid at different temperatures have been estimated using dynamic NMR. Experimental data have shown that τ varied from 4×10^{-6} to $0.2 \times 10^{-6} \text{ s}$ in the temperature range 310–360 K. The authors evaluated the activation energy of monomolecular dissociation $\Delta E_{\text{diss}} = 12.6 \pm 0.5 \text{ kcal mol}^{-1}$ and $\Delta E_{\text{ass}} = 0.0 \pm 0.2 \text{ kcal mol}^{-1}$.

In the present study an attempt is made to investigate the monomer-dimer relaxation using the methods of shock tube and laser temperature jump in the gaseous phase.

2. Shock tube experiments

The kinetic experiments were performed using a shock tube with an infrared diagnostic system with a HeNe laser, W-lamps, and Nernst sources. Five measuring channels were employed simultaneously to measure the velocity of the wave and the variation in the concentration of the complexes behind the incident shock wave. The shock tube technique used in the present experiments has been described previously [9]. The light absorption at a selected wavelength (in the region from 2.5 to 6 μm), which was proportional to the component concentration, has been measured by cooled (77 K) InSb and GeAu detectors as a function of time. The response time of these detectors loaded with a 2 k Ω resistor was $\leq 1 \mu\text{s}$. Detector outputs were displayed on a five-trace oscilloscope. The shock conditions were calculated from the known initial conditions and the shock velocity. The initial pressure of gas mixtures was varied from 10 to 100 torr. The shock temperatures ranged between 320 and 400 K.

A few strongly hydrogen-bonded complexes have been studied: cyclic dimers of trifluoroacetic and acetic acids (the enthalpies of association of the complexes $\Delta H \approx 12\text{--}14 \text{ kcal mol}^{-1}$), and mixed complexes $\text{CF}_3\text{COOH}\dots\text{O}(\text{C}_2\text{H}_5)_2$ ($\Delta H = 8.4 \text{ kcal mol}^{-1}$) and $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}\dots\text{N}(\text{CH}_3)_3$ ($\Delta H = 8.8 \text{ kcal mol}^{-1}$) [10,11]. The relaxation measurements reported here, were performed in the ν_{OH} region around 4000–2500 cm^{-1} . The strong band of the complex appears at $\approx 3000 \text{ cm}^{-1}$ (with half-width $\Delta\nu_{1/2} \approx 300 \text{ cm}^{-1}$) for acids, and at $\approx 3170 \text{ cm}^{-1}$ ($\Delta\nu_{1/2} \approx 200 \text{ cm}^{-1}$) for alcohol.

The measurements of relaxation processes were performed in pure (AH + B) system and in dilute gas mixtures (AH + B) + Ar, H_2 , N_2 . The partial pressure of AH...B did not exceed 1–3 Torr. It should be noted that, as the dissociation of AH...B progresses, the gas cools, and the density of undissociated complexes increases behind the shock front. This effect produces a change in light absorption which is of an opposite sign compared to that produced by dissociation. As a consequence, during the relaxation process, the absorption of the ν_{OH} band of complexes falls in dilute gas mixtures and rises in the pure (AH + B) system.

The temporal resolution of the measuring system τ_0 was limited by the transit time across the parallel beam of probing radiation. $\tau_0 = S/U$, where U is the

shock velocity and $S = 1 \text{ mm}$ is the beam width. The value τ_0 reaches a minimum $\tau_0 \approx 1 \mu\text{s}$, for the gas mixtures containing H_2 , where $U \approx 10^6 \text{ mm/s}$, but under these conditions the temperature of the experiment is increased considerably ($T \geq 400 \text{ K}$).

Unfortunately, in all the systems within the temperature range 320–400 K, the decay of the complexes comes to an end at the front of the shock wave, and an estimate of the upper limit of the lifetimes $\tau \leq 1\text{--}2 \mu\text{s}$ is only possible. The experimental rate of the cyclic dimer dissociation cannot be predicted on the basis of the simplest collision model with $\Delta E_{\text{diss}} = \Delta H$, but can be explained on the supposition that the two hydrogen bonds do not break simultaneously. Two relaxation processes were observed by ultrasonic absorption in liquid acids and in concentrated solutions. One relaxation process was ascribed to the conversion of the cyclic dimer to an open dimer and the other to the conversion of the open dimer to the monomer [12,13].

3. Method of laser temperature jump. Results and discussion

As part of a general study of the dynamics of the systems with hydrogen bonding, in the present work, we have explored the possibilities of the recently devised laser temperature jump method of lifetime measurements in the gas phase. The heating of the gas mixture was due to the fast vibrational deactivation after the pulsed excitation of absorbing admixture molecules. The kinetic measurements were undertaken for acetic acid which has been studied extensively in solvents. The experimental procedure of the observation for monomer–dimer relaxation was similar to that used for shock tube experiments.

A block diagram of the apparatus is shown in fig. 1. The measurements of the relaxation process were performed in the gas mixture $\text{SF}_6 + \text{H}_2$ (or He) at pressures of 2, 30–90, and 50–250 Torr for SF_6 , H_2 and He, respectively, in the temperature region 310–290 K. The choice of SF_6 as the absorber molecules is made primarily due to its chemical inertness and intensive infrared absorption at the 944 cm^{-1} laser frequency. The foreign gas (H_2 or He) was used to ensure complete SF_6 vibrational deactivation within the response time and to increase the heat capacity of the mixture. The pressure of CH_3COOH was varied within the range 0.5–2.5 Torr.

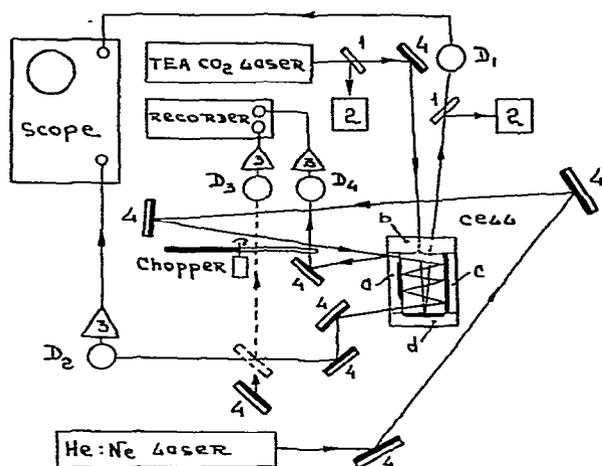


Fig. 1. Block diagram of the apparatus. 1 – beam-splitting plate, 2 – energymeter, 3 – amplifier, 4 – mirrors, D_1 – GeAu photoresistor, D_2 – InSb photoresistor, D_3, D_4 – pyroelectric detectors.

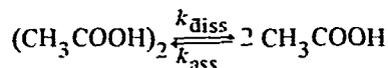
The SF_6 molecules (mode ν_3) were excited with a TEA pulsed CO_2 laser tuned to the P(22) line of the $10.6 \mu\text{m}$ transition of CO_2 . The laser radiation was directed into the temperature jump cell through the NaCl window b and uniformly filled the $1 \times 1 \text{ cm}$ cross section of the cell. It then passed through the cell of length 1.4 cm, was reflected back by the mirror d and focused on a GeAu (77 K) photoresistor D_1 , which was used to trigger the oscilloscope. The value of temperature jump ΔT was estimated using a small fraction of this radiation diverted by NaCl beam-splitting plates 1 to the energymeters 2 before entering the cell and on leaving it. The pulse energy did not exceed $\approx 20 \text{ mJ/cm}^2$, and the pulse fwhm was $\leq 200 \text{ ns}$ (laser mixture: 5 CO_2 : 1 N_2 : 20 He).

For probing, a HeNe laser ($\nu \approx 2950 \text{ cm}^{-1}$) with a typical power of 10 mW was used. The monitoring beam was collimated to a diameter of 1 mm and passed through a volume of the heated gas at an angle of $\approx 90^\circ$ relative to the exciting beam. A multipass system was used for the probe laser beam ($N = 19$, an effective path length of $\approx 20 \text{ cm}$). It consisted of two parallel mirrors, a and c, mounted on a glass plate. The mirror a was made of an Al coated quartz window with two gaps. The cell was placed in a vacuum chamber with windows for the pump and the probe beams. The time dependent signals obtained from the InSb (cooled to 77 K) detector D_2 were amplified and registered on the oscilloscope.

The full response time of the unit, with the detector loaded with a $1 \text{ k}\Omega$ resistance, was found to be $\approx 0.3 \mu\text{s}$.

Gas pressure was measured with a capacitance manometer. The acetic acid concentration was determined by IR absorption immediately in the cell using pyroelectric detectors D_3 and D_4 , fig. 1.

Quantitative information about the rate of dimer dissociation



was obtained under the condition of high dilution in the gas mixture, 2 Torr SF_6 + 90 Torr H_2 . Fig. 2 shows typical traces of the probe signal. The observed transient decrease in absorption of the ν_{OH} band of the dimers after the temperature jump did not deviate from a single exponential dependence. It should be noted, that the relaxation rate can be easily obtained from the experimental curves only at weak excitation, when the initial state is not far from equilibrium ($\Delta T/T$ is small). With the intensity of laser pulse increased considerably, a fast non-exponential decay was observed. The high sensitivity of the monitoring system (the threshold of the change in the dimer concentration being $\approx 0.01 \text{ Torr}$) allowed working with $\Delta T \lesssim 5^\circ$, i.e.

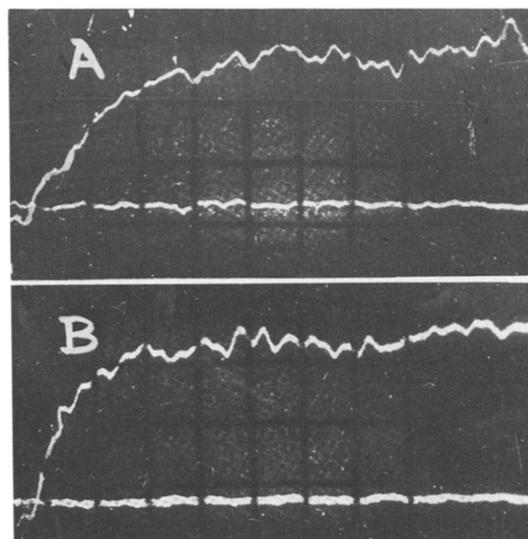


Fig. 2. Oscillogram of the process monomer-dimer relaxation in the system $\text{SF}_6 + \text{H}_2 + \text{CH}_3\text{COOH}$, $P_{\text{SF}_6} = 2 \text{ Torr}$, $P_{\text{H}_2} = 90 \text{ Torr}$, $T = 291 \text{ K}$, $\Delta T \approx 3^\circ$, sweep $1 \mu\text{s/cm}$. (A) $P_0 = 1.1 \text{ Torr}$, (B) $P_0 = 3 \text{ Torr}$.

when the relative change of the signal was small.

The characteristic monomer-dimer relaxation times τ_{rel} were determined from the semilogarithmic plots of the signal change $\ln \Delta I$ with time, where ΔI is the deviation of the signal from the equilibrium value. In linear approximation

$$\tau_{\text{rel}} = (4k_{\text{ass}}[P_m] + k_{\text{diss}})^{-1} \\ = \{k_{\text{diss}}[2(1 + 4P_0/K)^{1/2} - 1]\}^{-1}, \quad (1)$$

where P_m , P_d and $P_0 = P_m + P_d$ are the monomer, the dimer and the total CH_3COOH pressures, respectively. $K = P_m^2/P_d$ is the equilibrium constant. It was expected that the relative intensity of the signal (which was proportional to ΔT) depended on the foreign gas (H_2 or He) and its pressure. It was found that, to good accuracy, the τ_{rel} was independent of the H_2 pressure in the range $P > 50$ Torr. Therefore, one can suppose that the dissociation of the dimer is a monomolecular process within this pressure range.

On the other hand, τ_{rel} decreases greatly as the pressure (P_0) of the CH_3COOH increases, fig. 2. The typical τ_{rel} values at different pressures and temperatures are given in table 1. The pressure dependence and the temperature dependence, due to $K(T)$, of τ_{rel} is in accordance with formula (1). Unfortunately, the temperature of the experiment must be above ≈ 280 K because of the considerable adsorption of CH_3COOH , and below ≈ 320 K because τ_{rel} becomes shorter than the response time at $T > 320$ K. In this temperature interval the measured, τ_{rel} values range from 0.7 to 2.3 μs (at pressure $P_0 = 2.5$ –0.5 Torr).

Table 1

The typical values of observed relaxation times and calculated k_{diss}^{-1} for CH_3COOH

Temperature (K)	P_0 (Torr)	τ_{rel} (μs)	k_{diss}^{-1} (μs)
288	0.8	1.6	12.0
288	2.6	1.0	13.6
295	0.5	2.2	9.2
295	1.2	1.4	9.2
295	2.6	1.0	9.6
300	1.0	1.5	7.1
300	2.1	1.0	7.1
314	0.9	1.0	2.6
314	1.9	0.9	3.2

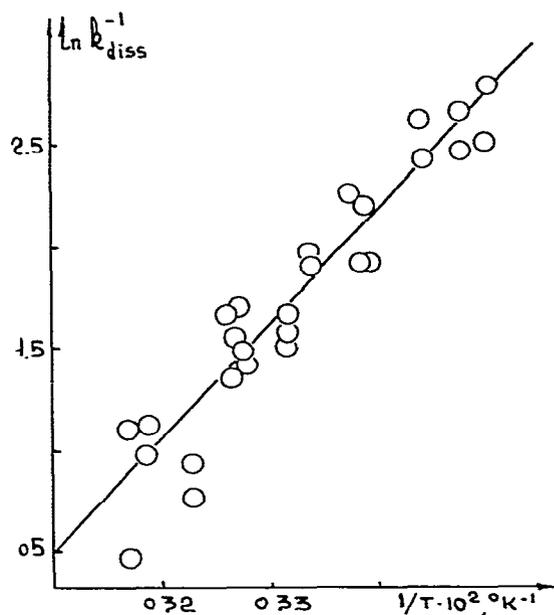
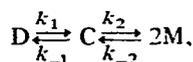


Fig. 3. Temperature dependence $\ln k_{\text{diss}}^{-1}$ for acetic acid.

The dimer lifetimes $\tau = k_{\text{diss}}^{-1}$ determined by the monomolecular dissociation process, were calculated using expression (1), (the value $\log K(\text{Torr}) = 11.1 - 3410/T$ was taken from ref. [14]). Indeed, as one can see, k_{diss} is independent of acid concentration within experimental error, table 1. It is obvious that calculation of k_{ass} would require a very accurate value of the equilibrium constant K .

The activation energy has been determined from the temperature dependence of the rate constant k_{diss} using the method of least-squares, fig. 3. The value obtained is $\Delta E_{\text{diss}} = 11.4 \pm 0.8$ kcal mol $^{-1}$, which is less than the enthalpy of this complex ($\Delta H = 15.5$ kcal mol $^{-1}$ [14], $\Delta E_{\text{ass}} = (0 \pm 1.5)$ kcal mol $^{-1}$).

The result is not inconsistent with the assumption that the same step-wise mechanism of the dimer dissociation operates both in the liquid and the gas phases:



where D and C are the closed and open forms of the dimer, M is the monomer. In this case, when the concentration of C is negligible, the effective activation energy

$$\Delta E_{\text{diss}}^{\ddagger} = \Delta E_1^{\ddagger} + [k_{-1}/(k_2 + k_{-1})](\Delta E_2^{\ddagger} - \Delta E_1^{\ddagger})$$

may be less than $\Delta E_1^{\ddagger} + \Delta E_2^{\ddagger} \approx \Delta H$, where ΔE_1^{\ddagger} is the activation energy of the conversion cyclic dimer $D \rightarrow$ open dimer, ΔE_2^{\ddagger} is the activation energy of the open dimer dissociation. It was observed that only the reaction type $D \rightleftharpoons C$ in acetic acid-acetone mixtures with $\Delta E_1^{\ddagger} = 9.1 \text{ kcal mol}^{-1}$ is indeed less than ΔH [12].

4. Conclusions

Two techniques, shock tube and laser temperature jump, were applied to measure the lifetimes of hydrogen bonds in the gas phase. The kinetic parameters of the acetic acid dimer dissociation are in accordance with the step-wise mechanism, though more thorough kinetic and thermodynamic measurements are needed for its better understanding.

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