хим. физ. 1982, 1 (7), с. 967 - 971

Sov. J. Chem. Phys., Volume 1 (7), 1984, pp. 1679-1690
0733-2831/84/0107-1679$25.00/0

Printed in the United Kingdom

DETERMINATION OF THE LIFETIME OF THE CYCLIC DIMER OF TRIFLUOROACETIC ACID IN THE GAS PHASE

N.S. GOLUBEV, G.S. DENISOV, and R. SHIMKUS

Leningrad State University
Leningrad

^{1}H NMR spectra of trifluoroacetic acid in the gas phase have been obtained at pressures ranging from 20 to 500 torr and temperatures from 40 to 90° C at working spectrometer frequencies of 80, 270 and 360 MHz. It has been concluded that the signal broadens with frequency growth due to monomer-dimer relaxation. Consequently, the cyclic dimer lifetimes (10^{-7}-10^{-6} s) can be determined. The dimer dissociation reaction is monomolecular, and the pressure range in which the order of the reaction changes from the first to the second is below 70 torr. The activation energy of dissociation (E_{dis} = 12.6 ± 0.5 kcal/mol) approaches the total energy of two hydrogen bonds (12.2 kcal/mol). The dimer formation process is of an activationless character (E_{as} = 0.0 ± 0.2 kcal/mol). The kinetic data are in accord with the synchronous as well as the consecutive mechanism of the fission of two bonds when, in the latter case, internal rotation around the remaining hydrogen bond in the open dimer occurs much more rapidly than its fission. Certain preference was given to the stage mechanism (with intermediate formation of an open dimer) on comparing the data obtained both in the gas phase and in solution.

(Received October 5, 1981)

To understand several fundamental problems connected with the nature of the hydrogen bond and its manifestations in experiments, it is important to study the kinetic characteristics of complexes with the hydrogen bond. Determination of the lifetime of the complexes in the gas phase (the complexes being unperturbed by the medium) is of the greatest interest. The values of this lifetime are more easily calculated theoretically, and the mechanisms of the processes which occur in the gas phase can, in principle, be studied more thoroughly. All the presently available experimental data refer to liquids and solutions [1-4]. We do not know a single case when the lifetime of a complex in the gas phase was successfully determined. In Ref. [5], the kinetics of monomer-dimer relaxation in carboxylic acid vapors was studied by the shock wave method, and only the upper boundary of the dimer lifetime was determined, $\tau < 10^{-5}$ s, at 100° C.

In this work, an attempt is made to determine the lifetime of the cyclic CF_3COOH dimer in the gas phase from the width of the averaged NMR signal of the ^1H monomer and dimer in strong magnetic fields. Besides the monomer-dimer relaxation, i.e., the process of establishing the corresponding equilibrium, the cause of signal broadening is spin-rotational relaxation as well as proton exchange with the molecules of admixtures (e.g., water). Broadening caused by a rapid

($\tau^{-1} >> 2\pi|\nu_A - \nu_B|$) interconversion of two forms, A and B, is distinguished by its quadratic dependence on the difference of the resonance frequencies and, consequently, on the field intensity [6]

$$\Delta\nu_{1/2}=4\pi n_A^2 n_B^2(\nu_A-\nu_B)^2(\tau_A+\tau_B), \qquad (1)$$

where n_A and n_B are the relative numbers of the resonating nuclei with frequencies ν_A and ν_B in the specimen volume. The line width determined by spin-rotational relaxation can only diminish as the intensity grows [7], but it does not depend on the intensity in the case of "strongly narrowing lines." Therefore, in order to elucidate the nature of line broadening, we compare the spectra taken in three working frequencies: 80, 270 and 360 MHz (the spectrometers used were Varian CFT-20, Bruker HX-270 and WH-360). At 80 MHz, monomer-dimer relaxation, whose frequency is known to be higher than 10^5 s^{-1} [5], cannot make a measurable contribution to the observed line width when the difference of the chemical shifts of the monomer and the dimer is less than 10 ppm [8]. In this case, the line width is wholly determined by spin-rotational relaxation and slower exchange processes.

Traces of water in acid vapors noticeably affect the spectrum. However, water molecules are virtually completely bound and the chemical shift of the signal is reproduced with an accuracy of 0.01 ppm, while the width, with an accuracy of about 5%, when a small excess of trifluoroacetic anhydride is added. Anhydride (ca. 5% excess) was added to CF_3COOH, which was sublimated twice in vacuum at -40°C. Afterwards, the acid was placed into a glass vacuum apparatus, cooled with liquid nitrogen, and evacuated to 10^{-3} torr. Glass ampoules containing capillary tubes with D_2O inside (for stabilizing resonance conditions) were sealed to the apparatus. Then they were evacuated to 10^{-5} torr, filled with trifluoroacetic anhydride vapors, and left to stand for several hours until the adsorbed water was completly replaced by CF_3COOH. The surface treated in this way was enlarged 20 times by filling the ampoule with glass spirals. However, this did not change the signal width and location within the limits of the measurement error. When the ampoules were evacuated again, they were filled with acid vapors. The gases were metered with a deformation gas-discharge monometer VDG-1 to an accuracy of 3-5%. Afterwards, the ampoules were disconnected and put into the spectrometer probe. From 10^4 and 10^5 accumulations were required for recording the spectrum with the signal to noise ratio being about 30, depending on the acid concentration.

When the frequency is 80 MHz and the pressures range from 70 to 500 torr, the line width is constant (ca. 0.5 Hz) and is determined by the field heterogeneity. When the pressure diminishes from 70 to 20 torr, this width grows to 10 Hz. However, the broadening is eliminated when argon is added (pressure is 10-20 atm), indicating its spin-rotational origin. At low pressures, the "strongly narrowing line" requirements [7] are most probably not met, and the rate of spin-rotational relaxation can depend on frequency. Therefore, we use only pressures ranging from 70-500 torr to obtain quantitative data, since the relevant contribution to the line width can be neglected in this case. Table I gives the values of the half-width of the line $\Delta\nu_{1/2}$, depending on the total pressure of the acid $p_o = p_m + p_d$ and on temperature, and degree of dissociation $\alpha = p_m/p_o$ (where p_m and p_d are the partial monomer and dimer pressures calculated from the equilibrium constants determined in Ref. [9] for a

Table I

Degree of Dissociation α, Dimer Lifetime τ, s, and Half-width of the Averaged Signal $\Delta\nu_{1/2}$, in Hz, as Functions of Pressure p_o and Temperature at 270 (in parentheses) and 360 MHz

p_o torr	α	$\Delta\nu_{1/2}$	10^6 τ	α	$\Delta\nu_{1/2}$	10^6 τ	α	$\Delta\nu_{1/2}$	10^6 τ
		40°C			50°C			60°C	
400	--	--	--	--	--	--	0.25	2.0	1.0
300	--	--	--	0.22	2.6	1.8	0.28	2.6	1.2
200	0.20	3.7	3.6	0.27	4.0	2.0	0.33	3.2	0.9
150	--	--	--	0.31	4.8	1.7	0.37	5.0	1.2
150	--	--	--	(0.31)	(2.6)	(1.8)	(0.37)	(2.6)	(1.3)
100	0.27	7.2	3.5	0.36	7.8	1.8	0.43	8.2	1.4
70	0.32	11.0	3.7	0.41	11.0	2.2	0.49	10.3	1.3
70	(0.32)	(6.2)	(3.7)	(0.41)	(6.0)	(2.0)	(0.49)	(5.6)	(1.4)

Table I (Continued)

Degree of Dissociation α, Dimer Lifetime τ, s, and Half-width of the Averaged Signal $\Delta\nu_{1/2}$, in Hz, as Functions of Pressure p_o and Temperature at 270 (in parentheses) and 360 MHz

p_o torr	α	$\Delta\nu_{1/2}$	$10^6\ \tau$	α	$\Delta\nu_{1/2}$	$10^6\ \tau$	α	$\Delta\nu_{1/2}$	$10^6\ \tau$
		70°C			80°C			90°C	
400	0.31	1.8	0.58	0.42	1.8	--	--	--	--
300	0.35	2.2	0.58	0.42	1.8	0.34	0.50	1.7	0.19
200	0.41	3.1	0.60	0.49	2.6	0.36	0.57	2.1	0.21
150	0.46	4.1	0.59	0.54	3.5	0.35	0.62	2.8	0.21
150	(0.46)	(2.4)	(0.60)	(0.54)	(2.0)	(0.32)	(0.62)	(1.5)	(0.20)
100	0.52	5.8	0.63	0.61	5.0	0.36	0.69	3.4	0.20
70	0.58	7.1	0.61	0.67	5.7	0.38	0.74	4.3	0.23
70	(0.58)	(4.2)	(0.63)	(0.67)	(3.3)	(0.37)	(0.74)	(2.5)	(0.2)

wide temperature range). It can be seen that the ratio of the half-width measured at frequencies of 360 and 270 MHz is in the vicinity of $1.77 = (360/270)^2$.

Hence, the given broadening is due to the rapid exchange reaction, which causes the modulation of the chemical shift. But this does not mean that the monomer and the dimer are the exchanging states. Let us determine the lifetime of the dimer, assuming that this supposition is valid. Since the lifetimes of the states are proportional to their equilibrium concentrations we have from Eq.(1):

$$\Delta\nu_{1/2}=4\pi n_m^2 n_d^2 (\Delta\nu)^2 (1-\alpha)^{-1}\tau_d.$$

Furthermore, the probabilities of finding a proton in a dimer or a monomer are:

$$n_d=\frac{2p_d}{2p_d+p_m}=\frac{2(1-\alpha)}{2-\alpha}; \qquad n_m=\frac{1}{2-\alpha}.$$

Consequently, we have:

$$\Delta\nu_{1/2}=16\pi\frac{\alpha^2(1-\alpha)}{(2-\alpha)^4}(\Delta\nu)^2\tau_d. \tag{2}$$

The value of $\Delta\nu$, which is needed for calculating τ_d, was taken from Ref. [8]. The lifetimes determined in this way (Table I) at a given temperature were virtually independent of pressure p_o. This indicates that the reaction is of the first order with respect to dimer concentration. Obviously, any reaction proceeding through a direct collision of dimer and monomer molecules (or two dimer molecules) would result in a lifetime τ_d dependent on the total concentration at the limiting stage. Thus, only monomolecular decomposition of the dimer broadens the signal observed:

$$(AH)_2 \underset{k_{as}}{\overset{k_{dis}}{\rightleftarrows}} 2\,AH. \qquad (3)$$

For a monomolecular reaction in gas, the first order means [10] that the reacting molecules are activated by collisions in the range under consideration more rapidly than the elementary reaction of bond fission occurs. In this case, the pressures at which the order of the reaction changes are below 70 torr. This could have been expected as regards the *decomposition of such a complex molecule are a cyclic dimer,* which has a large number (at least six) of low-frequency normal oscillations. Here the rate is limited by the random energy transfer process, which has been stored up at low-frequency degrees of freedom, to the reaction coordinate. To calculate the rate theoretically, it is important to take account of the coordinate shape. Let us consider two possible reaction paths.

1. Simultaneous fission of two hydrogen bonds. The reaction coordinate should be close to a polysymmetrical normal coordinate of the stretching vibrations of the hydrogen bonds which are observed in the Raman spectra in the 100-200 cm^{-1} range. For such a mechanism, the dimer lifetime being measured is $\tau = k_{dis}^{-1}$; the activation energy is close to the sum of the energies of two hydrogen bonds, while its value for a reverse reaction is near zero.

2. Consecutive fission of two bonds with an intermediate *formation of an open dimer:*

$$(AH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AH\ldots AH \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2\,AH. \qquad (4)$$

At the limiting stage, the reaction coordinate should be close to the antisymmetrical coordinate of hydrogen bond oscillations, and then it should be close to the angle characterizing internal rotation around the remaining bond. Since the open dimer is not observed spectroscopically, the probability that the process is limited by the second bond fission can be disregarded. With a stage mechanism, the forward and reverse process rates are equal to:

$$v^{\rightarrow}=k_1 p_d\frac{k_2}{k_2+k_{-1}},\qquad v^{\leftarrow}=k_{-2}p_m^2\frac{k_{-1}}{k_2+k_{-1}}. \tag{5}$$

The lifetimes are:

$$\tau_d=p_d/v^{\rightarrow}=k_1^{-1}\frac{k_2+k_{-1}}{k_2},\qquad \tau_m=k_{-2}^{-1}\,p_m^{-1}\frac{k_2+k_{-1}}{k_{-1}}. \tag{6}$$

The experimentally measured constants of the rates of dissociation and formation of the dimer are equal to:

$$k_{dis}=\frac{k_1k_2}{k_2+k_{-1}},\qquad k_{as}=\frac{k_{-1}k_{-2}}{k_2+k_{-1}}. \tag{7}$$

Differentiating Eq.(7) with respect to temperature, we obtain the effective values of the activation energies of the forward and reverse reactions:

$$\begin{aligned} E^{\neq}_{dis}&=E_1^{\neq}+\frac{k_{-1}}{k_2+k_{-1}}(E_2^{\neq}-E_{-1}^{\neq}),\\ E_{as}^{\neq}&=E_{-2}^{\neq}-\frac{k_2}{k_2+k_{-1}}(E_2^{\neq}\sim E_{-1}^{\neq}). \end{aligned} \tag{8}$$

Here, the dependences of ln k on T^{-1} may deviate from a straight line when there are definite ratios between the probabilities of individual elementary stages. However, such deviations are not observed in experimental graphs (see Fig. 1) within the limits of experimental error. The activation energy value ($E^{\neq}_{dis}$ = 12.6 ± 0.5 kcal/mol) virtually coincides with that of the total energy of dimer dissociation (12.2 ±

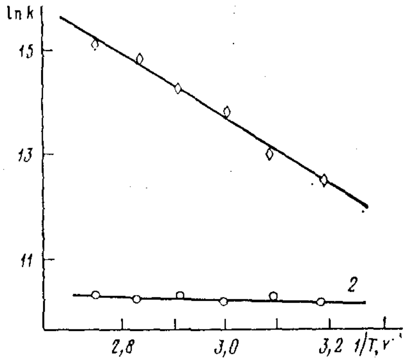

Fig. 1. Arrhenius plots of the rate constants of dissociation k_{dis}, s^{-1} (1) and formation k_{as}; s^{-1} $torr^{-1}$ (2) of the cyclic dimer CF_3COOH in the gas phase.

0.4 kcal/mol) that has been measured under identical conditions [9]; the value of 0.0 ± 0.2 kcal/mol is obtained for a reverse reaction. This would seem to indicate that a synchronous dissociation mechanism exists. However, it is quite reasonable to anticipate that in the gas phase the probability of cyclization of the open dimer per unit time k_{-1}, which is equal to the frequency of internal rotation around the hydrogen bond, is far greater than the probability of bond fission, which involves overcoming an appreciable energy barrier. Then we have the following expressions from Eqs.(7) and (8):

$$\begin{gathered} k_{dis}=k_1 k_2 k_{-1}^{-1}, \quad k_{as}=k_{-2}, \\ E^{\neq}_{dis}=E_1^{\neq}+E_2^{\neq}-E_{-1}^{\neq}\approx E_1^{\neq}+E_2^{\neq}, \\ E_{as}^{\neq}=E_{-2}^{\neq}\approx 0, \end{gathered} \tag{9}$$

This is in accord with the experimental data.

It should be taken into account, however, that internal rotation around the hydrogen bond will be slower in the liquid phase. This effect should be especially prominent when solvents possess the properties of specific intermolecular interactions. Experimentally [in the case of mechanism (4)], this should reduce the activation energy of dissociation to E_1. It is hard to expect such a strong effect for a synchronous mechanism. We were unable to measure the dimer lifetime in solution within the same range of concentrations and temperatures by the NMR method (probably because of the proton exchange which was catalyzed by impurities). However, some data in literature, obtained by the ultrasonic relaxation method [11], and our data on low-temperature nuclear magnetic resonance [12] show that the activation energy of the dissociation of acid dimers diminishes to 6-7 kcal/mol when the solvent activity grows. Here, the values of $E^{\neq}_{as}$ = 3-4 kcal/mol are obtained for a reverse reaction. They are close to the expected value of $E^{\neq}_{-2}$, which is determined by the temperature dependence of the diffusion coefficient in solution. In some instances [13], better evidence in favor of a stage mechanism (4) was obtained for solutions.

Hence, the specifics of the given kinetics of monomer-dimer relaxation in carboxylic acid vapors and solutions are described within the framework of a single mechanism (4). Of course, this does not mean that it is always valid. A reaction should be treated theoretically in order to draw a final conclusion and obtain information on the rates of the elementary stages.

References

1. J. Rassing, Chem. and Biol. Appl. Relaxat. Spectrometry (Dodrecht-Boston, 1975): 177.
2. T. Tabuchi, Mem. Inst. Sci. and Ind. Osaka Univ. 33: 17 (1976).

3. G.G. Hammes, ed., Investigations of Rates and Mechanisms of Reactions, 3rd edition (New York: John Wiley & Sons, 1974) (Russian translation, Moscow: Mir Publishers, 1977): 268.

4. G.S. Denisov et al., Molecular Interactions 2: 107 (1980).

5. K.G. Tokhadze, Molekulyarnaya spektroskopiya (Molecular Spectroscopy) (Leningrad: Leningrad State University Press, 1975): 81 (in Russian).

6. J.W. Emsley, J. Feeny, and L.H. Sutcliffe, Higher Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 1 (Oxford etc.: Pergamon Press, 1965) (Russian translation, Moscow: Mir Publishers, 1968).

7. A. Abragam, The Principles of Nuclear Magnetism (Oxford: Clarendon Press, 1961) (Russian translation, Moscow: Mir Publishers, 1968).

8. N. Lambrosco-Bader, C. Coury, and D. Baron, J. Magn. Res. 17: 386 (1975).

9. I.V. Gerasimov and K.G. Tokhadze, Zh. Priklandnoi spektroskopii 26: 1068 (1977) (in Russian).

10. V.N. Kondratyev, Kinetika khimicheskikh gazofaznykh reaktsii (Kinetics of Chemical Gas-phase Reactions) (Moscow: Izd-vo USSR Academy of Sciences, 1958).

11. V.L. Boruski, Ber. Buns. Phys. Chem. 71: 504 (1967).

12. N.S. Golubev and G.S. Denisov, React. Kinet. Catal. Lett. 4: 87 (1976).

13. N. Tatsumoto, T. Scano, and T.A. Yasunaga, Bull. Chem. Soc. Japan. 45: 3096 (1972).