BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2308—2312 (1971)

An Acoustical Study of the Kinetics of Intermolecular Hydrogen Bonding and the Applicability of the Hammett Rule

Tatsuya YASUNAGA, Sadakatsu NISHIKAWA, and Nobuhide TATSUMOTO

Department of Chemistry, Fraculty of Science, Hiroshima University, Hiroshima

(Received January 23, 1971)

Rate and equilibrium constants for the hydrogen-bond dimerization of benzoic acid and meta- and para-substituted compounds in *N,N*-dimethylformamide have been determined by the measurement of the ultrasonic absorption in the 15—95MHz frequency range at 20°C, and the Hammett rule for the rapid monomer-dimer reaction has been examined. The forward and backward rate constants are 0.67×10^8 sec^{-1} and 2.8×10^7 $sec^{-1}M^{-1}$ for para-toluic acid, 0.90×10^8 sec^{-1} and 1.9×10^7 $sec^{-1}M^{-1}$ for meta-toluic acid, 1.6×10^8 sec^{-1} and 1.5×10^7 $sec^{-1}M^{-1}$ for benzoic acid, 2.1×10^8 sec^{-1} and 2.4×10^7 $sec^{-1}M^{-1}$ for para-chlorobenzoic acid, and 3.3×10^8 sec^{-1} and 1.6×10^7 $sec^{-1}M^{-1}$ for metachlorobenzoic acid respectively. The forward and backward activation enthalpies for benzoic acid are 8.4 kcal/mol and 3.3 kcal/mol respectively. Using the substituent constants in Jaffe's table, the reaction constants in the Hammett rule are calculated to be 1.2 and −0.33 for the forward and backward reactions respectively.

There have been many reports[1] about the association of benzoic acid in nonassociated solvents. Maier and his coworker[2] found an excess absorption in carbon tetrachloride solutions of benzoic acid; they attributed this absorption to a perturbation of the equilibrium between the monomer and the hydrogen-bonding dimer of benzoic acid.

On the other hand, the Hammett rule, which is often used to account for the effect of substituents on aromatic compounds, has been used in studying the reaction of hydrolysis, acid dissociation, and so on.[3,4] The Hammett rule is characterized by a parameter which is independent of the reaction system, depending only on the substituents. It may be expected that the rule would hold true also for the rapid association and dissociation reactions for benzoic acid and meta- or para-substituted compounds. The ultrasonic absorption method, which provides a means of determining the rate constants for a reaction occurring in such a short time as shorter than 10^{-7} sec, seems to be very useful for examining the Hammett rule for this reaction.

Rassing and his coworkers[5] have already studied the Hammett rule for several para-substituted benzoic acids, but their measurements were limited to a few frequencies.

In this paper, we will present the ultrasonic absorption results for various meta- and para-substituted benzoic acid compounds and will evaluate the thermodynamic and kinetic values associated with the dimerization reaction.

Experimental

The ultrasonic absorption measurements were carried out in the frequency range from 15 to 95 MHz using the pulse technique which had been developed in our laboratory.[6] The cell was improved to prevent the dissolving of the binding materials into the solution by covering the transducer with a fused quartz plate 2 mm thick. The chemicals used were benzoic acid, meta-, para-toluic acids, meta-, para-chlorobenzoic acids, aniline, and methyl benzoate as solutes and *N,N*-dimethylformamide (DMF) as the solvent. These were all of the purest grade obtainable and were used without further purification. The measurements were made at various

1) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Reinhold Publishing Corp., New York, N. Y. (1960).
2) W. Maier and H. D. Rudolph, *Z. Phys. Chem.*, **10**, 83 (1957).
3) L. P. Hammett, *J. Amer. Chem. Soc.*, **59**, 96 (1937).
4) J. E. Leffler and E. Grunwald, "Rate and Equilibria of Organic Reaction," John Wiley & Sons, Inc. New York (1963).
5) J. Rassing, O. Østerberg, and T. A. Bax, *Acta Chem. Scand.*, **21**, 1443 (1967).
6) N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

temperatures for benzoic acid and at 20°C for the other compounds.

Results and Discussion

Figures 1—5 show the ultrasonic absorption spectra in *N,N*-dimethylformamide solutions of benzoic acid, meta-, para-toluic acids, and meta- and para-chlorobenzoic acids at 20°C. These spectra can be represented by the following formula for a single relaxation:

$$\alpha/f^2 = \frac{A}{1 + (f/f_r)^2} + B \qquad (1)$$

where α is the absorption coefficient, f is the frequency, f_r is the relaxation frequency, and A and B are constants. Table 1 shows the ultrasonic parameters for these solutions.

As is shown in Fig. 6, the excess absorption was not observed in the pure solvent, *N,N*-dimethylformamide, or in the solutions of aniline or of methyl benzoate in the frequency range used in this experiment.

These results lead us to the conclusion that the

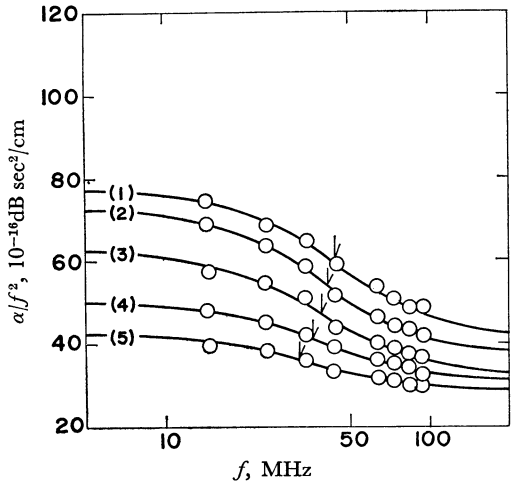


Fig. 1. Ultrasonic absorption spectra in DMF solution of benzoic acid at 20°C: (1) 3.0M; (2) 2.5M; (3) 2.0M; (4) 1.5M; (5) 1.0M.

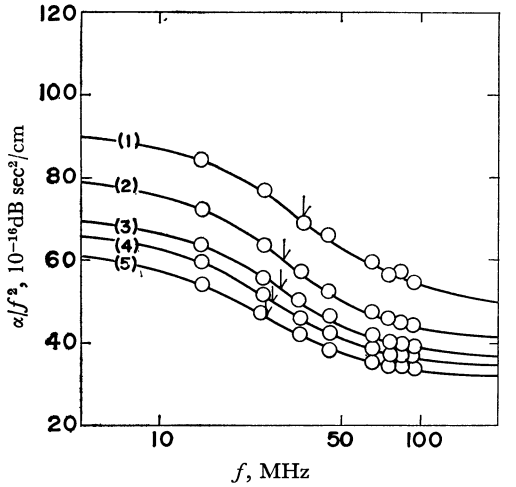


Fig. 2. Ultrasonic absorption spectra in DMF solution of *m*-toluic acid at 20°C: (1) 3.0M; (2) 2.4M; (3) 1.9M; (4) 1.5M; (5) 1.2M.

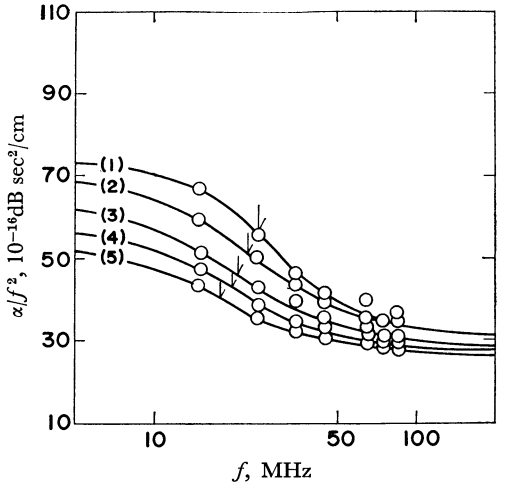


Fig. 3. Ultrasonic absorption spectra in DMF solution of *p*-toluic acid at 20°C: (1) 1.3M; (2) 1.1M; (3) 0.88M; (4) 0.71M; (5) 0.57M.

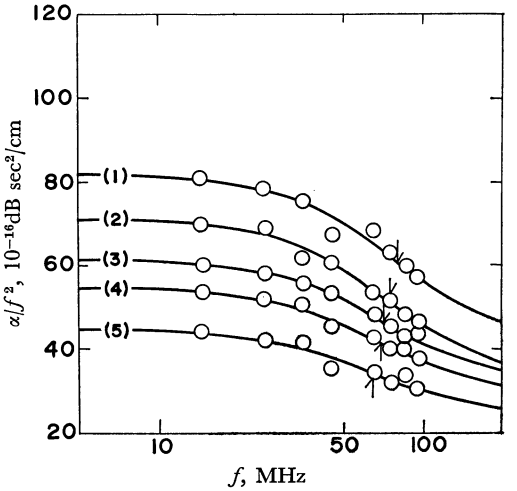


Fig. 4. Ultrasonic absorption spectra in DMF solution of *m*-chlorobenzoic acid at 20°C: (1) 3.0M; (2) 2.4M; (3) 1.9M; (4) 1.5M; (5) 0.9M.

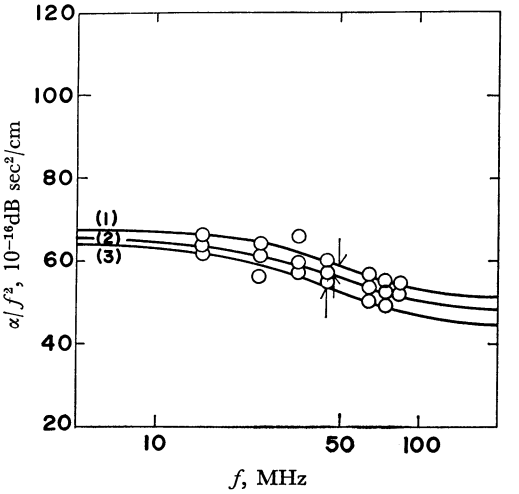


Fig. 5. Ultrasonic absorption spectra of DMF solution of *p*-chlorobenzoic acid at 20°C: (1) 1.4M; (2) 1.1M; (3) 0.87M.

TABLE 1. ULTRASONIC PARAMETERS FOR THE SOLUTION OF BENZOIC ACID, *m*-TOLUIC ACID, *p*-TOLUIC ACID, *m*-CHLOROBENZOIC ACID, AND *p*-CHLOROBENZOIC ACID AT 20°C

M	A 10^{-16} dB sec^2 cm^{-1}	B	f_r MHz
	Benzoic acid		
3.0	37	41	45
2.5	37.5	36.5	42
2.0	31.2	32.0	40
1.5	19.1	31.7	37
1.0	14.6	28.7	33
	m-Toluic acid		
3.0	41.0	49.2	35
2.4	40.8	39.0	30
1.9	34.0	36.4	29
1.5	32.5	34.2	27
1.2	30.2	32.2	25
	p-Toluic acid		
1.3	45.1	30.0	25
1.1	39.2	31.8	23
0.88	35.5	28.8	21
0.71	30.8	27.6	20
0.57	27.2	27.0	18
	m-Chlorobenzoic acid		
3.0	44.6	37.6	80
2.4	39.5	31.7	75
1.9	31.7	30.3	70
1.5	26.2	28.7	68
0.9	21.5	23.5	63
	p-Chlorobenzoic acid		
1.4	17.7	30.5	50
1.1	18.3	27.9	47
0.87	21.0	24.0	45

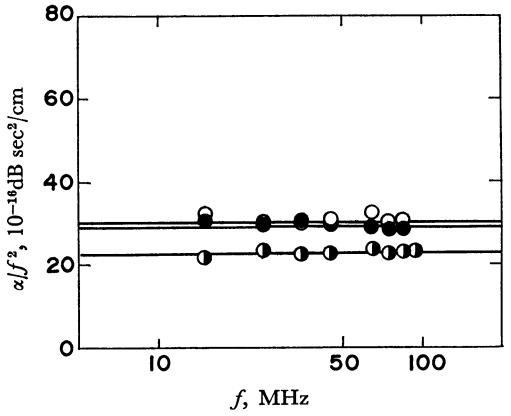
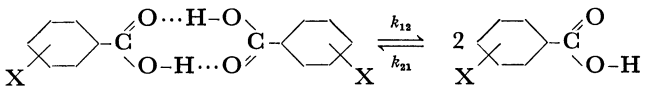


Fig. 6. Ultrasonic absorption spectra at 20°C: ◑, DMF; ○, DMF solution of methylbenzoate 30 vol%; ●, DMF solution of aniline 50 vol%.

excess absorption is associated with the reaction the site of which exists in the carboxyl group of benzoic acid and its substituted compounds. It has been reported[1] that the equilibrium between the monomer and the dimer formed by the intermolecular hydrogen bonding between the carboxylic proton and carbonyl oxygen exists in the solution of benzoic acid. Provided that the ultrasonic absorption is ascribed to the monomer-dimer reaction, the reaction scheme can be written as:



(2)

where k_{12} and $_{21}$ are the forward and backward reaction rate constants respectively and where X is meta- or para-substituent. Then, the rate equation can be represented by:

$$\frac{d[A_2]}{dt} = k_{21}[A_1]^2 - k_{12}[A_2] \quad (3)$$

where $[A_1]$ and $[A_2]$ are the concentrations of the monomer and the dimer respectively. The relation between the relaxation frequency, f_r, and the total concentration, $[C_0]$, is expressed by the following equation:

$$(2\pi f_r)^2 = (1/\tau)^2 = 8k_{12}k_{21}[C_0] + k_{12}^2 \quad (4)$$

where τ is the relaxation time.

Figure 7 shows the experimental plots of $(2\pi f_r)^2$ *vs.* $[C_0]$ for five compounds; the linearity of these plots confirms our assumption that the ultrasonic absorption is associated with the monomer-dimer reaction. The values of k_{12} and k_{21} were obtained from the intercept

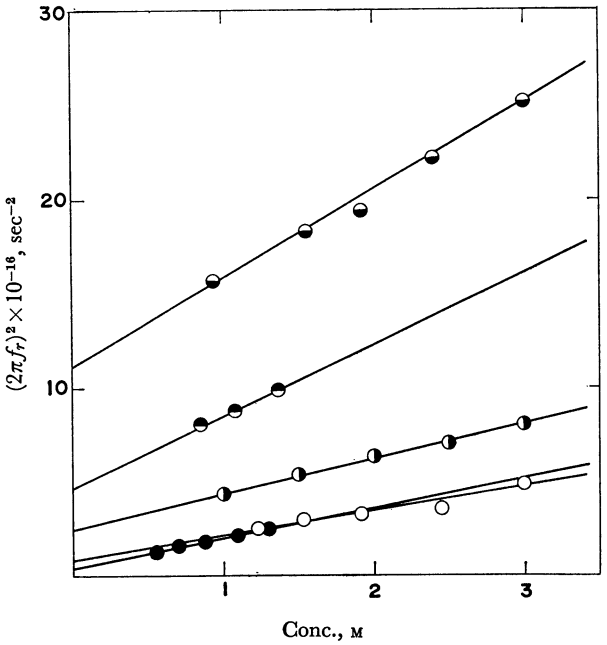


Fig. 7. The plots of $(2\pi f_r)^2$ *vs.* concentration at 20°C: ◑, benzoic acid; ●, *p*-toluic acid; ◓, *p*-chlorobenzoic acid; ◒, *m*-chlorobenzoic acid; ○, *m*-toluic aid.

TABLE 2. THE KINETIC VALUES OBTAINED FROM ULTRASONIC ABSORPTION SPECTRA AND SUBSTITUENT CONSTANTS

Compound	k_{12}, 10^8 sec^{-1}	k_{21}, 10^7 sec^{-1}M^{-1}	K,M	σ
p-Toluic acid	0.67	2.8	2.4	−0.170
m-Toluic acid	0.90	1.9	4.8	−0.067
Benzoic acid	1.6	1.5	10	0
p-Chlorobenzoic acid	2.1	2.4	9.3	0.227
m-Chlorobenzoic acid	3.3	1.6	20	0.373

and the slope of the curve in Fig. 7, while the equilibrium constant, K, was calculated by $K=k_{12}/k_{21}$. These values are listed in Table 2.

According to Eyring's rate theory, the rate constant can be written as:

$$k_i = \kappa\frac{kT}{h}\exp\left(-\frac{\Delta F_i^*}{RT}\right) = \kappa\frac{kT}{h}\exp\left(-\frac{\Delta H_i^*}{RT}+\frac{\Delta S_i^*}{R}\right) \quad (5)$$

where k_i is the rate constant, κ is the transmission coefficient, k is the Boltzmann constant, T is the absolute temperature, R is the gas constant, ΔF_i^* is the activation free energy, ΔH_i^* is the activation enthalpy, and ΔS_i^* is the activation entropy. Figure 8 shows the plots of $\ln k_i/T$ *vs.* $1/T$ for benzoic acid. Figure 9 shows the activation enthalpies which were calculated from the slopes in Fig. 8; it also shows the enthalpy change obtained through the difference between the activation enthalpies for the forward and backward reactions.

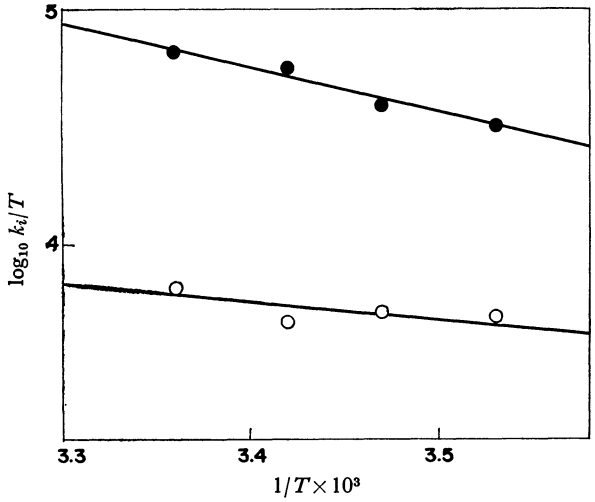


Fig. 8. Dependence of $\log k_i/T$ on $1/T$ for benzoic acid: ●, k_{12}; ○, k_{21}.

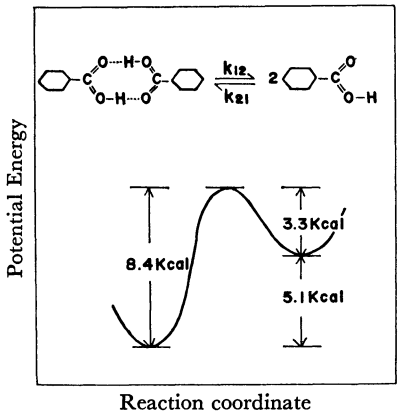


Fig. 9. Energy potential curve for monomer-dimer reaction in DMF solution of benzoic acid.

Now, provided that k_0 and k_j are the rate constants for the reaction in the unsubstituted compound and in a compound substituted in meta- or para-positions respectively relative to the carboxyl group, the following expression can be derived from Eq. (5):

$$\ln\frac{k_j}{k_o} = \frac{\Delta F_o^* - \Delta F_j^*}{RT} = \sigma\rho \quad (6)$$

where ΔF_o^* and ΔF_j^* are the activation free energies for benzoic acid and substituted compounds respectively. Equation (6) shows the well-known Hammett rule. σ is the substituent constant, which depends only on the nature and position of the substituent, X, and ρ is the reaction constant, which depends on the reaction, the condition under which it takes place, and the nature of the side chain.

In Fig. 10 the rate constants for the five compounds which were obtained in this experiment are plotted against the values of σ found in Jaffe's table.[7] The values of the reaction constants, ρ, obtained from the slope in Fig. 10 are 1.2 for the dissociation and −0.33 for the association in this reaction system.

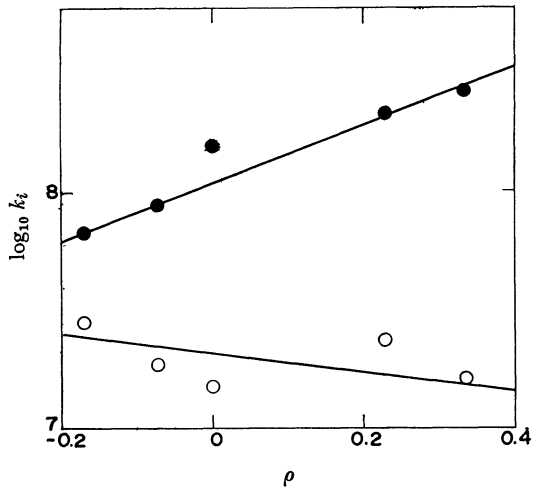


Fig. 10. The relation between the rate constant and the substituent constants: ●, k_{12}, ○, k_{21}.

As is shown in Fig. 7, the dependence of the relaxation frequency on the concentration shows that the excess absorption may be attributed to the perturbation of the equilibrium between the monomer and the dimer of benzoic acid or substituted compounds. The value of enthalpy change for benzoic acid, 5.1 kcal/mol, is small, as the breakage of the two hydrogen bonds in the dimer.[2,8] Borucki,[9] however, has reported that the enthalpy change in the monomer-dimer reaction for bonzoic acid in a polar solvent is smaller than that in a nonpolar solvent. The value, therefore, seems to be reasonable for the enthalpy change for the hydrogen bonding.

Figure 10 shows that the Hammett rule can be applied to the hydrogen-bonding reaction of meta- and para-substituted compounds of benzoic acid. According to previous theoretical studies of the Hammett rule,[3,10,11] σ can be correlated with the electron density.

7) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).
8) W. Maier, *Z. Elektrochem.*, **64**, 132 (1960).
9) L. Borucki, *Ber. Bunsenges. Physik. Chem.*, **71**, 504 (1967).
10) H. H. Jaffe, *J. Chem. Phys.*, **20**, 279 (1952).
11) H. H. Jaffe, *ibid.*, **21**, 415 (1953).

When the tendency of substituents to be electron donors increases and when the electron density at the reaction site becomes high, σ becomes more negative. As can be seen in Fig. 10, in the compound of which σ is great, *i.e.*, in which the electron density at the reaction site is low, the hydrogen bond in the dimer is weak and the rate of dissociation is fast, while in that of which σ is small, *i.e.*, in which the electron density is high, the bond is strong and the rate is slow. On the other hand, the reaction constant for the association is negative, and the activation enthalpy for the association is increased with σ. That is, the monomeric state is stabilized and the rate of association is decreased with an increase in σ. Consequently, the rates for the formation and breakage of hydrogen bonds in these compounds depend on the electron density at the reaction sites.