

$$x = \left[(k_2 + k_4)t + \frac{1}{x_0} \right]^{-1} \quad (10)$$

Here x_0 is the initial concentration of the ketyl radical and is taken to be equal to the decrease in the amount of anthrone caused by a flash irradiation.

With the progress in the reaction, x decreases more rapidly than y , and therefore in some stage of the reaction the latter may approximately be regarded as a constant in spite of the change in x . For this stage, we can obtain the following equation for the first-order reaction.

$$x = x_0 e^{-k_4 y t} \quad (11)$$

The above result is consistent with the experimental fact that the reaction proceeds following the second-order formula at the initial stage and the first-order one at the next stage. The average second-order rate constant $K = k_2 + k_4$ in eq 10 was found to be $11 (\pm 2) \times 10^7 M^{-1} \text{sec}^{-1}$ from the gradient at $t \approx 0$ of the $1/A - t$ curve. As the reaction proceeds, the decay curve gradually deviates from the linear relationship between $1/A$ and t expected from eq 10. This is because x decreases more rapidly than y , and the approximate condition of $x \approx y$ necessary for the derivation of eq 10 does not hold at some stage in the reaction. When the reaction proceeds further, it follows eq 11 and the

first-order rate constant $K' = k_4 y$ can be obtained from the $\log A - t$ curve shown in Figure 4. The K' value is expected to greatly depend on y and therefore on the initial concentration of anthrone. In actuality we found that it monotonously increases from $\sim 1 \text{sec}^{-1}$ to $\sim 10 \text{sec}^{-1}$ with the increasing concentrations of the solutions of 10^{-5} to $10^{-4} M$.

From the data of the yields (40% for anthranol and 60% for anthrapinacol) of products by a flash irradiation and the second-order rate constant (K), we could determine the values of k_2 and k_4 separately as follows (at 25°).

$$k_2 = 7 (\pm 1) \times 10^7 M^{-1} \text{sec}^{-1}$$

$$k_4 = 4 (\pm 1) \times 10^7 M^{-1} \text{sec}^{-1}$$

The value of k_2 is consistent with the value observed by Beckett and Porter¹⁷ for benzophenone in isopropyl alcohol. They determined the rate constant for the pinacolization of the benzophenone ketyl radical to be $5.9 \times 10^7 M^{-1} \text{sec}^{-1}$.

Acknowledgment. We gratefully acknowledge Dr. A. Tahara and Dr. N. Ikegawa of the Institute of Physical and Chemical Research for their kind discussions and kind help in the gas chromatography experiment.

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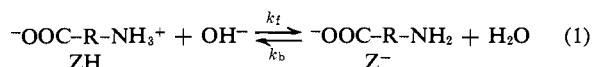
Kinetics of Proton-Transfer Reactions of Amino Acids and Simple Polypeptides¹

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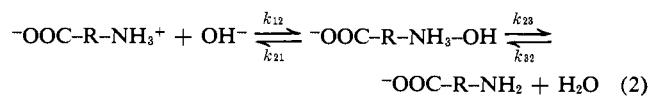
Abstract: The velocity and attenuation of 3–100-MHz ultrasonic waves propagating in aqueous solutions of glycine, diglycine, triglycine, β -alanine, and γ -aminobutyric, aspartic, and glutamic acids have been measured as a function of pH. No dispersion is observed but excess acoustic absorption characterized by a relaxation time between 2.8×10^{-9} sec (for γ -aminobutyric acid) and 3.2×10^{-8} sec (for triglycine) is found. From the dependence of the absorption on pH it is deduced that perturbation of the proton-transfer equilibrium, $R-NH_3^+ + OH^- \rightleftharpoons R-NH_2 + H_2O$, is the process responsible, and values of k_t , k_b , and the standard volume change are determined.

The proton-transfer reactions of the amino acids and simple polypeptides



constitute a simple related series of reactions amenable to study by ultrasonic absorption techniques offering an interesting variety of possibilities for the observation of the effects of the charge, polarity, and flexibility of R on the rate constants. We have measured the acoustic absorption in solutions of glycine, diglycine, triglycine, β -alanine, and γ -aminobutyric, L-aspartic, and L-glutamic acids. The dependence of the absorp-

tion on pH is found to imply that perturbation of the proton-transfer equilibrium is the process principally responsible for the attenuation of sound. We will attempt to rationalize the rate constants deduced from the observed relaxation times in terms of the mechanism



the rate of the first step of which involves the diffusional encounter of the amine and OH^- to form a H-bonded ion pair being relatively insensitive to the nature of R.

Ultrasonic Attenuation

In the absence of significant dispersion the frequency dependence of the ultrasonic attenuation (α) due to a

(1) K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press, New York, N. Y., 1959.

Table I. Parameters of Eq 3 at 24° and pH_{max}

	Concn, <i>M</i>	pH	<i>A</i> × 10 ¹⁷ , neper sec ² cm ⁻¹	<i>C</i> × 10 ¹⁷ , neper sec ² cm ⁻¹	<i>τ</i> × 10 ⁸ , sec	<i>f</i> _r , MHz
Triglycine	0.5	11.05	29.8	164	3.2	5.0
Diglycine	1.0	11.34	31.6	109	2.0	7.9
Glycine	0.5	11.54	24.4	107	0.56	28.3
β-Alanine	0.5	11.87	36.3	105	0.42	37.7
γ-Aminobutyric acid	0.5	12.08	38.6	82	0.28	56.3
L-Aspartic acid	0.5	11.55	36.2	117	0.86	18.5
L-Glutamic acid	0.5	11.73	31.8	140	1.3	12.0

single process with relaxation time τ may be expressed as¹

$$\frac{\alpha}{f^2} = A + \frac{C\tau}{1 + (2\pi f\tau)^2} \quad (3)$$

where A represents the attenuation associated with the viscosity and thermal conductivity of the medium as well as that due to any very rapid chemical or structural relaxations. In terms of the concentration of the amino acid (c_{ZH}) and the hydroxide ion (c_{OH^-}) and the rate constants defined in eq 1, the relaxation time is

$$\tau = [k_f(c_{ZH} + c_{OH^-}) + k_b]^{-1} \quad (4)$$

The constant C is given in eq 5, where ρ is the density, c_0 is the velocity of sound, \bar{V} is the volume per mole of the solution, β is the coefficient of thermal expansion,

$$C = 2\pi^2\rho c_0\bar{V}^2RTT_c[(\beta\Delta H/C_pRT) - (\Delta V/\bar{V}RT)]^2 \quad (5)$$

C_p is the molar heat capacity at constant pressure, and ΔH and ΔV are the standard enthalpy and volume changes for the process in question. The enthalpy change for the process represented by eq 1 is 1–3 kcal/mole; the volume change is 20–30 cc/mole. In aqueous solution near room temperature, where β is relatively small, neglect of the first term in the square brackets in eq 5 alters the calculated value of ΔV by less than 2%.

The dependence of the excess acoustic absorption on the equilibrium chemical composition of the solution is largely contained in Γ_c . For the equilibrium represented by eq 1, $\Gamma_c = \bar{V}[(1/c_{OH^-}) + (1/c_{Z^-}) + (1/c_{OH^-})]^{-1}$. If the concentration of the amino acid and its anion are expressed in terms of K , the equilibrium constant for eq 1, and A_0 , the initial concentration of the amino acid ($A_0 = c_{ZH} + c_{Z^-}$), then

$$\Gamma_c = \frac{\bar{V}KA_0c_{OH^-}}{KA_0 + (Kc_{OH^-} + 1)^2} \quad (6)$$

From eq 3–6 the variation of α with pH may be deduced. The result is a steep-sided bell-shaped curve. When, as in these experiments, $KA_0 \gg 1$ the maximum is at $\text{pH}_{\text{max}} = \frac{1}{2}(\text{p}K_w + \text{p}K_a + \log A_0)$, where K_w is the ion-product constant of water and K_a is the dissociation constant of the amino acid.

In this work rate constants and volume changes for the process represented by eq 1 have been deduced, by means of eq 3–6, from values of C and τ obtained from a least-squares analysis of the frequency dependence of the acoustic absorption at pH_{max} . The pH dependence of the absorption has been investigated in order to determine if perturbation of the equilibrium represented by eq 1 is indeed the principal source of the observed attenuation.

Experimental Section

Measurements of ultrasonic velocity and attenuation were made at the odd harmonics of 1- and 2-Mc ceramic transducers (1 in. in diameter) and 5-Mc x-cut quartz crystals (0.4 in. in diameter) using the pulse-echo technique.² The major mechanical features of the apparatus are derived from the work of Yun, Beyer, and Dill³ modified to provide for storage and transfer of samples in an inert (CO₂-free) atmosphere and *in situ* adjustment and monitoring of the pH. The absorption is derived from the amount of attenuation which must be inserted or removed in the receiver circuit in order to restore the amplitude of the received signal to a preset value as the transmitting crystal is moved with respect to a receiving transducer. The velocity is calculated from the change in delay of a given cycle of a given received pulse when the distance between the transmitting and receiving crystals is changed by a known amount (determined by a Starret precision dial gauge).

The data have been corrected for apparent attenuation due to diffraction.^{2,4–7} At the higher frequencies this correction, proportional to λ/a^2 (where λ is the wavelength, a the radius of the transducer), is small and easily evaluated. At the lowest frequencies (3–7 MHz) the correction is appreciable and the work of Careme, Witting, and Fleury⁷ suggests that it is not altogether appropriate to rely on a correction computed by the methods of ref 4–7.

For each of the amino acid or peptide solutions at each of the lower frequencies, we have compared the decrement in the amplitude of the received signal as the path length in the solution is increased with the results obtained in an aqueous NaCl solution in which the velocity of sound, and thus the wavelength, is the same (within 0.1%) as in the amino acid solution at the temperature and pH in question. The apparent loss due to diffraction in any range of path length will be the same for the NaCl and amino acid solutions, and thus the difference in the apparent attenuations of the two solutions will also be the difference in the true attenuations.

The value of α/f^2 for aqueous NaCl is small and independent of the frequency.⁸ Thus from the absorption in the amino acid solutions relative to that in aqueous NaCl the actual absorption in the amino acid solutions may be deduced without substantial error.

The diglycine, triglycine, and L-glutamic acid (Chromatographically Pure) were obtained from Mann Research Laboratories; L-aspartic acid, β-alanine, and γ-aminobutyric acid were obtained from Eastman. "Ammonia-free" glycine was supplied by Matheson Coleman and Bell.

Results

Plots of acoustic absorption as a function of frequency for L-glutamic, L-aspartic, and γ-aminobutyric acids and diglycine are given in Figures 1 and 3. The derived values of A , C , and τ , the relaxation frequency ($f_r = 1/2\pi\tau$), pH, and concentration at which the measurements were carried out are listed in Table I. The relaxation frequency for γ-aminobutyric acid lies at

(2) H. J. McSkimmin, "Physical Acoustics," Vol. 1A, W. P. Mason, Ed., Academic Press, New York, N. Y., 1964.

(3) S. S. Yun, R. T. Beyer, and M. W. Dill, *J. Chem. Phys.*, **36**, 2737 (1962).

(4) A. C. Williams, *J. Acoust. Soc. Am.*, **23**, 1 (1951).

(5) H. Seki, A. Granato, and R. Truell, *ibid.*, **28**, 230 (1956).

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(7) E. F. Careme, J. M. Witting, and P. A. Fleury, *J. Acoust. Soc. Am.*, **33**, 1417 (1961).

(8) J. Stuehr and E. Yeager, "Physical Acoustics," Vol. IIB, W. P. Mason, Ed., Academic Press, New York, N. Y., 1965.

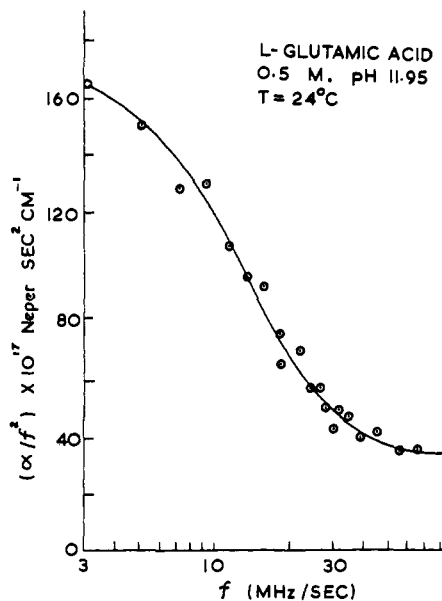


Figure 1. Ultrasonic attenuation coefficient (α) divided by the frequency squared vs. frequency for an aqueous solution of L-glutamic acid. The solid line represents a least-squares fit of the parameters of eq 3.

the upper end of the range of frequencies accessible to us, and it is therefore not possible to deduce an accurate value of A . Thus although A for γ -aminobutyric acid does not differ greatly from the value determined for the other amino acids, the uncertainty in this case is considerably greater than the 10% error in A estimated for the other acids. The relaxation frequency for diglycine (7.9 MHz) lies near the lower limit (3 MHz) of the experimentally accessible frequency range, and the parameter C is correspondingly less accurately determined than for β -alanine, glycine, and glutamic and aspartic acids.

The solid curves in Figures 1–3 are generated from the parameters in Table I by means of eq 3. They constitute a satisfactory fit to the data, a fit which is not substantially improved by the inclusion of a second relaxation. Only the fact that A is significantly higher than A for water or salt solutions of comparable concentration suggests the existence of a second process with a relaxation frequency much higher than the highest measuring frequency. With this qualification, and within the limitations discussed in the preceding paragraph, eq 3 provides a satisfactory interpretation of our results, and there is no *a priori* reason to believe that more than one process makes a large contribution to the absorption.

Assuming that the proton-transfer process is indeed the sole source of the frequency-dependent part of the ultrasonic attenuation, it is possible, with the aid of eq 3–6, to predict the absorption at any pH from rate constants and a volume change deduced from the absorption at pH_{max} . Thus the “theoretical” curve in Figure 2 represents α/f^2 (for glutamic acid at 5.21 MHz) as a function of pH as calculated from rate constants and a volume change derived from the data in Figure 1; the points are the experimental absorption at 5.21 MHz. The agreement is sufficiently good to nominate perturbation of the proton-transfer equilibrium as the principal source of absorption.

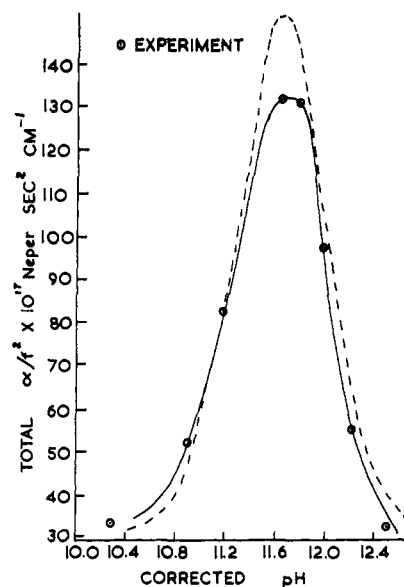


Figure 2. α/f^2 vs. pH at 5.21 MHz for 0.5 M L-glutamic acid at 24°. The broken line represents the predicted behavior of α/f^2 deduced from the parameters in Table I by means of eq 3–6. The solid line is a smooth curve through the experimental points.

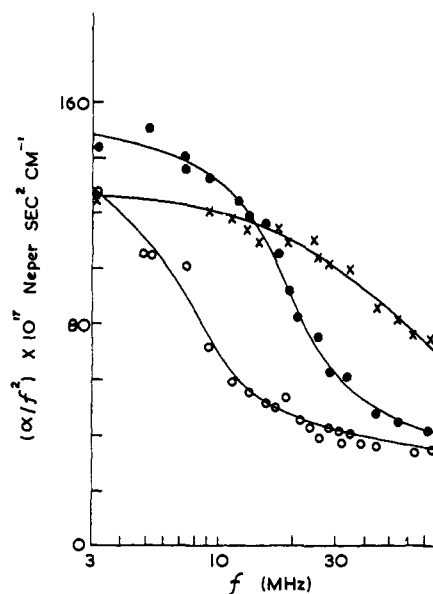


Figure 3. α/f^2 vs. f at 24° for 0.5 M solutions of L-aspartic acid (solid circles), diglycine (open circles), and γ -aminobutyric acid (+). The solid lines represent the values of α/f^2 calculated by means of eq 3 using the parameters in Table I.

Discussion

The observed relaxation times are identified with τ of eq 4, and in Table II the rate constants and volume changes for the process represented by eq 1 are listed. If the second step of eq 2 is presumed to be very fast, $k_f = k_{12}$, $k_b = k_{21}k_{32}/(k_{23} + k_{32})$,⁹ or, introducing the definition $K_{23} = k_{23}/k_{32}$, $k_b = k_{21}/(1 + K_{23})$.

The observed volume changes are consonant with the results which have been obtained for analogous proton-transfer reactions; 12 cc/mole for $\text{HCN} + \text{OH}^- =$

(9) (a) M. Eigen and L. de Maeyer, “Technique of Organic Chemistry,” Vol. VIII, Part 2, A. Weissberger, Jr., Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p 1032; (b) M. Eigen, *Angew. Chem.*, 75, 489 (1963).

Table II. Rate Constants and Volume Changes for the Process Represented by Eq 1

	$k_f \times 10^{-10}$, $M^{-1} \text{ sec}^{-1}$	$k_b \times 10^{-5}$, sec^{-1}	ΔV^\ddagger , cc/mole
Triglycine	2.1	0.18	38
Diglycine	1.6	0.31	26
Glycine	1.9	8.0	26
β -Alanine	1.3	21	21
γ -Aminobutyric acid	1.5	39	21
L-Aspartic acid	1.2	5.2	22
L-Glutamic acid	0.76	3.8	18

Table III. Equilibrium Constants for Eq 1 and Comparison of Experimental Rate Constants with the Results of Eq 8 for Several Peptides, Amino Acids, and Amines^a

	$k_{12} \times 10^{-10}$	$k_f \times 10^{-10}$	k_{12}/k_f	$k_{21} \times 10^{-8}$	$k_b \times 10^{-5}$	$K_{23} \times 10^{-3}$	$K \times 10^{-5}$	$\text{p}K_{a_2}$ ^b
Triglycine	3.3	2.1	1.6	466	0.18	1284	11.6	7.91
Diglycine	3.3	1.6	2.1	477	0.31	775	5.3	8.25
Glycine	3.6	1.9	1.9	510	8.0	31	0.24	9.60
β -Alanine	3.5	1.3	2.7	502	21.2	11	0.061	10.19
γ -Aminobutyric acid	3.5	1.5	2.3	496	39.0	5.4	0.040	10.40
L-Aspartic acid	3.5	1.2	2.9	502	5.2	47	0.24	9.60
L-Glutamic acid	3.5	0.76	4.6	496	37.6	65	0.20	9.67
Methylamine ^c	3.9	3.7	1.05	551	160	2.5	0.023	10.64
Dimethylamine ^c	3.8	3.1	1.2	536	190	1.8	0.020	10.72
Piperidine ^c	3.5	2.2	1.6	496	300	0.7	0.0062	11.21

^a k_b and k_{21} are in sec^{-1} , k_{12} and k_f in $M^{-1} \text{ sec}^{-1}$. No steric factor has been used in computing k_{12} and k_{21} . ^b See M. Katake, Ed., "Constants of Organic Compounds," Asakura Publishing Co., Tokyo, 1953; J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 4. ^c See ref 2.

$\text{CN}^- + \text{H}_2\text{O}$,¹⁰ 28 cc/mole for $\text{NH}_4^+ + \text{OH}^- = \text{NH}_4\text{OH}$,⁹ 27 cc/mole for $\text{CH}_3\text{NH}_3^+ + \text{OH}^- = \text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$,¹¹ and 21 cc/mole for $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$.¹² The value of k_f for glycine is in fair agreement with that ($k_f = 1.4 \times 10^{10} M^{-1} \text{ sec}^{-1}$) previously determined.¹³

In the case of diglycine we have made detailed studies of τ as a function of frequency at values of the pH above and below pH_{max} . We find that τ does decrease with increasing pH above pH_{max} as required by eq 4. These measurements thus provide an additional confirmation of the proposition that perturbation of the proton-transfer equilibrium is the principal source of absorption. We would now like to consider to what extent the results can be usefully interpreted in terms of the two-step diffusion-controlled process represented by eq 2 and to what extent the results can be rationalized in terms of the equilibrium properties of the various amino acids and peptides.

With respect to the first of these considerations, it is clear that when only one relaxation is observed the decomposition of eq 1 into two steps is entirely arbitrary. It is however convenient to divide the course of the reaction into a rate-controlling diffusional encounter followed by a fast "chemical step," most of the effect of chemical structure being contained in the second step which hopefully may be discussed thermodynamically.

Debye^{14a} has derived an expression for the diffusion-controlled rate of reaction of ions in solution, and Eigen^{14b} has considered the reverse process of dissociation

to form ions. Their result for the rate constants of eq 2 is

$$k_{12} = \frac{4\pi N z_A z_B e_0^2 (D_A + D_B)}{\epsilon k T [\exp(z_A z_B e_0^2 / \epsilon r_d k T) - 1]} \quad (7)$$

$$k_{21} = \frac{3 z_A z_B e_0^2 (D_A + D_B)}{\epsilon k T r_d^3 [1 - \exp(-z_A z_B e_0^2 / \epsilon r_d k T)]}$$

where N is Avogadro's number, e_0 is the electronic

charge, z_A and z_B are the algebraic charges of the ions, ϵ is the dielectric constant of the solvent, D_A and D_B are the diffusion coefficients of the reacting ions, and r_d is an effective radius for reaction.

The choice of r_d is to a certain extent arbitrary since it reflects the fundamentally arbitrary character of the separation into diffusional and chemical steps. The choice of 2.7 Å, corresponding to a typical hydrogen-bond distance, represents a reasonable lower limit. Eigen and de Maeyer,¹⁵ concluding that aggregates of water molecules such as H_9O_4^+ play an important role in proton transfer, estimate $r_d = 7.5$ Å. The calculated values of the rate constants are not extremely sensitive to the choice of r_d . If the assumed effective radius for reaction between univalent ions in water at 298°K is increased from 2.7 to 7.5 Å, the calculated value of k_{12} increases by a factor of 1.4 and k_{21} decreases by a factor of 2.6.

Values of k_{12} and k_{21} calculated by means of eq 7 with $r_d = 2.7$ Å, $D_{\text{OH}^-} = 5.08 \times 10^{-5} \text{ cm}^2/\text{sec}$, $\epsilon = 78.5$, $T = 297^\circ\text{K}$, and unit effective charge are compared with experiment in Table III. Results for methylamine, dimethylamine, and piperidine^{9a,15} cited by Eigen and de Maeyer are included for comparison. The calculated values of k_{12} are systematically larger than the experimentally determined values of k_f . However, this might reasonably be expected since eq 7 would imply that the hydroxide ion can approach the $-\text{NH}_3^+$ group from any angle. Eigen and Kustin¹⁶ have determined the rates of a series of diffusion-controlled reactions involving substituted phenols. They find it appropriate to decrease the rate constants computed with the aid of eq 7 by a steric factor of 2. The introduction of a factor of $1/2$ into eq 2 would, except in the case of

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(12) P. Drude and W. Nernst, *Z. Physik. Chem.*, **15**, 79 (1894).

(13) M. Eigen and G. Schwarz, in preparation, cited by M. Eigen and G. G. Hammes, *Advan. Enzymol.*, **25**, 1 (1963).

(14) (a) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942); (b) M. Eigen, *Z. Physik. Chem.* (Frankfurt), **1**, 176 (1954).

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glutamic acid, bring the calculated values of k_{12} into fairly good agreement with experiment. A calculation based on eq 7 does not take into account the presence of a negatively charged γ - or δ -carboxyl group in glutamic and aspartic acids, and it is thus not surprising that eq 7 overestimates k_f to the greatest degree for these two acids. Otherwise it does appear that Debye's result with a reaction radius equal to a hydrogen-bond distance and a steric factor of 2 can give a fairly good account of the forward rate constants. However, eq 7 does not successfully predict the value of k_b .

If one accepts the separation of the over-all process into the two steps represented by eq 2, the reverse rate is the diffusional rate diminished by an "equilibrium constant" expressing the preponderance of free amine and water over protonated amine hydroxide ion ion pairs. The qualitative success of eq 7 in accounting for the forward rate constants suggests that it also constitutes a reasonable basis for the estimation of k_{21} . The diffusion coefficients of the various amino acids and peptides¹⁷ range from 1.06×10^{-5} (glycine) to 0.67×10^{-5} cm²/sec (triglycine), and the value of k_{21} obtained from eq 7 will be approximately the same for any amino acid or simple peptide. The experimental values of k_b range from 0.18×10^5 for triglycine to 39×10^5 sec⁻¹ for γ -aminobutyric acid, presumably reflecting the variation in K_{23} as one goes from triglycine ($\text{p}K_{a_2} = 7.9$) to the relatively basic amino group in γ -aminobutyric acid ($\text{p}K_{a_2} = 10.4$). Values of K_{23} calculated from the experimental values of k_b and eq 7 with $r_d = 2.7$ Å and a steric factor of $1/2$ are listed in Table III.

Also listed in Table III are equilibrium constants for eq 1 and values of $\text{p}K_{a_2}$ ¹⁸ for the various amino acids and peptides considered. The value of K_{23} does appear to be determined by the value of K ; one could do a fair job of estimating K_{23} and hence k_b from $\log K_{23} = 14.2 - \text{p}K_{a_2}$. The numerical constant, depending

as it does on the choice of the distance at which a separation between the diffusional and the chemical step is made, is itself without significance. However, it appears that the rate of the back-reaction in eq 1 and its variation from amine to amine can be understood at least semiquantitatively in terms of eq 7. Although repulsion by the negatively charged carboxyl groups, nonideality, and the approximation of the effective dielectric constant by the bulk value will all contribute to the deviation of the results of eq 7 from the experimental values of k_f , nonetheless it would appear that eq 7 with a reaction radius of 2.7 Å and a steric factor of $1/2$ can give a reasonably good account of the forward rates. Thus the "mechanism" represented by eq 2, with the second step a very fast equilibrium, seems to have more than formal significance.

For water at 24°, $A = 23.2 \times 10^{-17}$ neper sec²/cm or 20.2×10^{-16} db sec²/cm. For 1 *M* diglycine at 24° between pH 4.8 and 8.8, A is constant at 20.7×10^{-16} db sec²/cm. At pH_{max} , $A = 27.4 \times 10^{-16}$ db sec²/cm. Solutions of the other amino acids behave in a similar manner. At low pH all exhibit a value of A close to that of water; in the neighborhood of pH_{max} all except glycine exhibit a significantly higher value of A . Such behavior might reasonably be attributed to a first-order process (solvation or change in conformation of the anion) with a relaxation frequency significantly higher than the highest measuring frequency or perturbation (by the anion) of the structural relaxation in water. The glycol ion is less likely to undergo a change in conformation with a substantial associated volume change than the other anions studied, and thus the absence of a significant effect in solutions of glycine suggests that conformational relaxation is a reasonable explanation of the small high-frequency excess absorption.

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