Analysis and Kinetic Interpretation of Ultrasonic Absorption Spectra

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Ultrasonic absorption data have been simulated for one-step and two-step reaction mechanisms in order to find a criterion which will determine whether absorption data fit a single relaxation curve, or whether more than one relaxation time must be considered. Assuming an experimental error of ± 2 % in α/ν^2, where α is the sound absorption coefficient and ν the frequency of sound, it is shown that two overlapping relaxation times can be detected only when $\gamma > 4$ and $0.25 < \beta < 4.0$. γ and β are the ratios of the relaxation times and the amplitude factors, respectively. A specific reaction mechanism is considered, that of forming a doubly hydrogen bonded dimer from two monomer units. It is shown that if only one relaxation time is observed (*i.e.* $\gamma < 4$), it is still possible that the dimer is being formed in two steps, and that under certain conditions this interpretation results in a very characteristic concentration dependence of the observed relaxation time.

The ultrasonic absorption technique has been used to investigate the kinetics of very fast reactions in solution. A method of calculation often used is computation of the relaxation time from the frequency dependence of the absorption coefficient. If the reaction which causes the sound absorption consists of a one-step mechanism only, the data will show a single relaxation time. If intermediate states and more than one reaction step are involved, a spectrum of relaxation times occurs. If the relaxation times associated with two coupled steps differ sufficiently from each other, the relaxation function is made up of two parts, each pertaining to one of the individual relaxation times. If, however, the relaxation times are nearly equal, it may be impossible to resolve the contributions to absorption of each of the steps, and the data will have the appearance of a single relaxation curve. Consequently, the fact that some experimental data fit a one-relaxation time function does not necessarily mean that the reaction occurs in one step.

Kinetic interpretation of ultrasonic data requires a knowledge of the concentration dependence of the relaxation time. It is therefore necessary to

take into account the possibility that a single-relaxation curve might actually represent, for example, a two-step mechanism.

The first part of the present paper concerns situations in which experimental data which are caused by a two-step mechanism fit a one-relaxation time function within experimental error. The second part deals with the concentration dependence of an observed single relaxation time caused by a two-step dimerization with overlapping relaxation times.

PART I

Theoretical

The sound absorption caused by the relaxation of a single reaction is described by the following equation:

$$\frac{\alpha}{\nu^2} = \frac{A}{1 + (2\pi\tau\nu)^2} + B \tag{1}$$

where α is the sound absorption coefficient, ν the frequency of sound, τ the relaxation time, and A is the amplitude factor, a parameter given by the thermodynamics of the system. B is the value of α/ν^2 of the solution at frequencies high enough for the absorption due to the chemical reaction to be frozen out. If several relaxation times are involved, we have a sum of such terms, in particular we have for two reactions:

$$\frac{\alpha}{\nu^2} = \frac{A_1}{1 + (2\pi\tau_1\nu)^2} + \frac{A_2}{1 + (2\pi\tau_2\nu)^2} + B \tag{2}$$

where index 1 and 2 refer to the first and second reaction steps, respectively. The following definitions are introduced:

$$\beta = A_2/A_1 \quad 0 \leq \beta < \infty \tag{3}$$

$$\gamma = \tau_1/\tau_2 \quad 1 \leq \gamma < \infty \tag{4}$$

Eqn. (2) can then be written:

$$\frac{\alpha}{\nu^2} = \frac{A_1 + A_2}{1 + x^2} Q(x,\gamma,\beta) + B \tag{5}$$

where $x = 2\pi\tau_1\nu$ and

$$Q(x,\gamma,\beta) = \frac{1}{1 + \beta} \left(1 + \beta \frac{1 + x^2}{1 + (x^2/\gamma^2)} \right) \tag{6}$$

Absorption data for a two-step mechanism will fit the single relaxation equation, eqn. (1), if Q is approximately independent of the frequency, so that eqn. (5) becomes formally identical with eqn. (1). The degree to which Q varies with the frequency depends on the values of γ and β. The question is, which values of (γ,β) are required to make Q approximately constant. In principle the problem can be approached in two ways: by a detailed error analysis, or by a simulation technique. Because eqn. (1) is non linear and

because a knowledge of the errors involved in the different steps of the measuring procedure is lacking, an error analysis cannot be carried out. A simulation technique, however, only requires a knowledge of the reproducibility of α/ν^2 and is furthermore closely related to the way in which experimental data are usually interpreted.

Each experimentally determined point of α/ν^2 has a range of values which can be described by a normal distribution, having a mean value $\langle\alpha/\nu^2\rangle$, and a standard deviation σ. For a single relaxation with given values of A, B, and τ, $\langle\alpha/\nu^2\rangle$ can be calculated from eqn. (1). σ is given by the experimental error of α/ν^2, which we assume to be ± 2 %. By using a random number generator producing numbers which are normally distributed about a calculated $\langle\alpha/\nu^2\rangle$ and which have a σ of ± 2 %, it is possible to simulate experimental values of α/ν^2 at different frequencies. The simulated data are now fitted to eqn. (1) by means of a three-parameter, least square fitting procedure which gives the best values of A, B, and τ.

In an analogous way we simulate data for a two-relaxation time mechanism with chosen values of A_1, τ_1, B, γ, and β.

Experimental

One-relaxation time experiments. A computer experiment consists of 15 simulated values of α/ν^2, each at a different frequency. The 15 frequencies are chosen so that they occur at equal intervals on a logarithmic scale covering three decades of frequency (1—1000). The three relaxation times, $1/20\pi$, $1/60\pi$, and $1/140\pi$, have been used in simulating the data.

A measure for goodness of fit can be defined:

$$X^2 = \sum_{i=1}^{n} \frac{1}{\sigma_i^2} \left[\left(\frac{\alpha}{\nu^2}\right)_{i \text{ Simulated}} - \left\langle\frac{\alpha}{\nu^2}\right\rangle^* \right] \tag{7}$$

where n is the number of α/ν^2 values on the relaxation curve, and $\langle\alpha/\nu^2\rangle^*$ is the value of α/ν^2 calculated from the best theoretical curve fitting the data. It is often convenient to use a measure for goodness of fit, F, which is independent of the number of experimental points:

$$F = \sqrt{\frac{X^2}{n-3}} \tag{8}$$

By assuming the values of X^2 to be χ^2-distributed with $n-3$ degrees of freedom and by using a confidence limit of 95 %, we can calculate a value of F, F_c, which can be used as a criterion for determining whether or not the data can be described by a single relaxation function. We find:

$$F_c = 1.3 \tag{9a}$$

The value of F_c can also be obtained by simulating a large number of experiments. Fig. 1 shows the cumulative distribution of F for 1000 one relaxation time experiments. Using the confidence limit of 95 % we find:

$$F_c = 1.3 \tag{9b}$$

The agreement between the two F_c values indicates that X^2 is χ^2-distributed. The value of F_c is independent of the values of the relaxation frequencies used.

The simulated points for a one time experiment and the best fitted theoretical curve is shown in Fig. 2. The curve is normalized with $A=B=1$. From each of the experiments, we can calculate the error in A, B, and τ by comparing the fitted values of these parameters with the values originally chosen. Table 1 shows the average error of 250 experiments at each of the three relaxation frequencies.
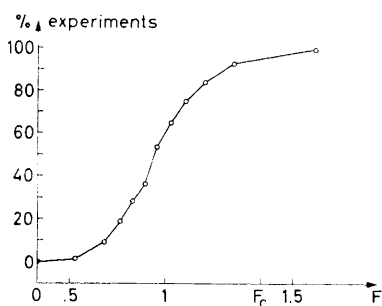
Fig. 1. The values of F (defined by eqn. (8)) are calculated for 1000 simulated one-relaxation time experiments. The cumulative distribution of the values is shown on this figure. A confidence limit of 95 % gives $F_c = 1.3$.
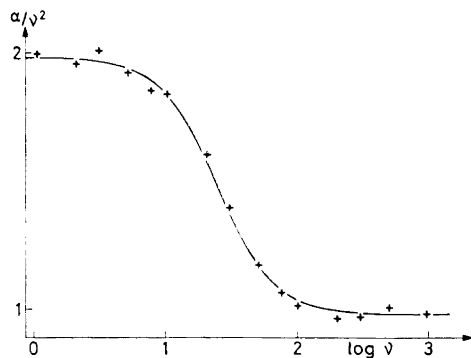
Fig. 2. The plotted points ($+$) are obtained by simulating a value of α/ν^2 at 15 different frequencies for a *single relaxation*. The simulated data are fitted to eqn. (1) by means of a three-parameter least square fitting procedure. The best theoretical curve is shown on this figure.

Two-relaxation time experiments. For the two-relaxation time experiments we have used $A_1 + A_2 = B = 1$. 25 experiments have been calculated at each of three relaxation frequencies, for the following sets of (γ, β):

$$(\gamma, \beta) = ((2(1)10), (1, 0.5, 0.25))$$

The simulated data are fitted to eqn. (1) in order to find which values of (γ, β) give $F > F_c$. When $F > F_c$ we consider that a one-relaxation time function does not fit the data. The simulated points and the best theoretical one-relaxation time curve for different values of (γ, β) are shown in Figs. 3a, b, and c. We consider the two relaxation times to be resolved when more than 80 % of the experiments for a given set of A_1, τ_1, B, γ, and β have $F > F_c$. The dependence of F on γ and β for the different relaxation frequencies used is shown in Figs. 4a—c. Using the 80 % criterion we find that in order to observe two relaxations we must have
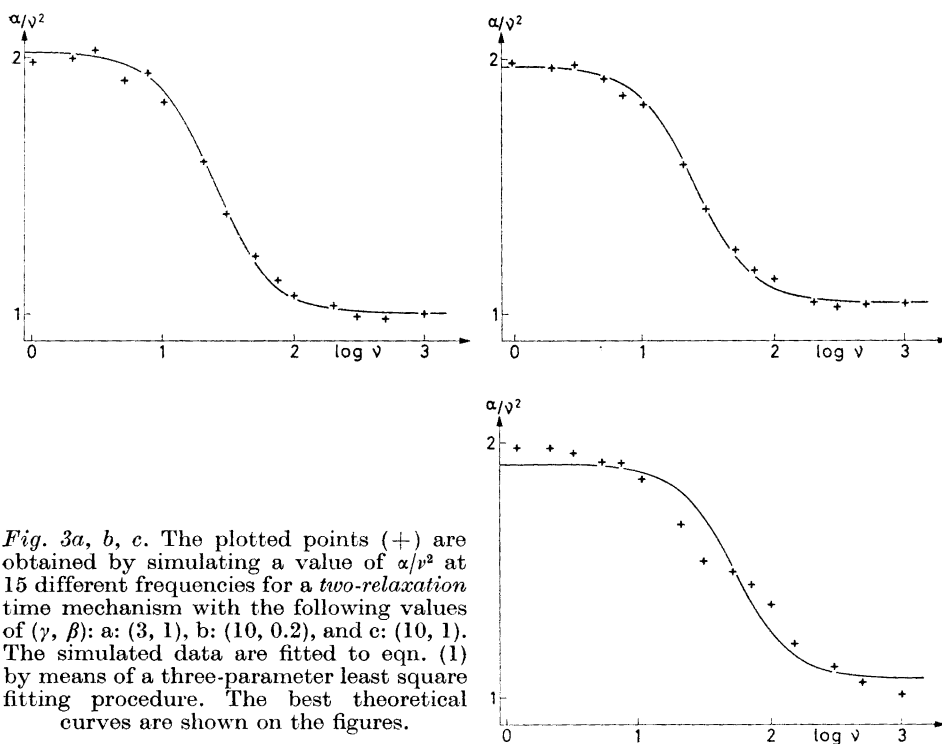
$$\gamma > 4 \tag{10a}$$

Fig. 3a, b, c. The plotted points (+) are obtained by simulating a value of α/ν^2 at 15 different frequencies for a *two-relaxation* time mechanism with the following values of (γ, β): a: (3, 1), b: (10, 0.2), and c: (10, 1). The simulated data are fitted to eqn. (1) by means of a three-parameter least square fitting procedure. The best theoretical curves are shown on the figures.

In addition, even if $\gamma > 4$ (but both relaxation times occurring within three decades of frequency) then we must have

$$0.25 < \beta < 4.0 \tag{10b}$$

in order to observe two relaxations. For experiments where the criteria given by eqn. (10a) and eqn. (10b) are fulfilled and consequently $F > 1.3$, a five parameter fitting procedure is used. This gives the values of A_1, A_2, τ_1, τ_2, and B with a certain uncertainty (see Table 2). The values of F defined in analogy with eqn. (8) for a five parameter problem are now smaller than 1.3.

For this work we have used a GIER computer. The computing time is about 30 sec for each experiment. We have done approximately 4000 experiments, which means about 30 h computing time. The generator we have used is described in the literature,[1] and we have used the following values of parameters, $A = 9901$, $M = 2^{39} + 1$, and $b = 0$.
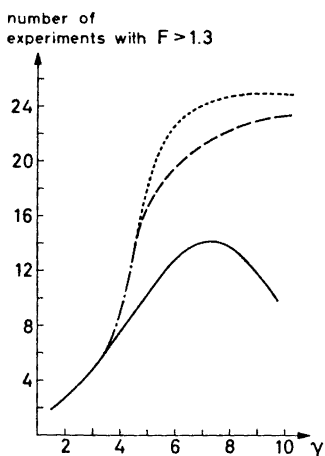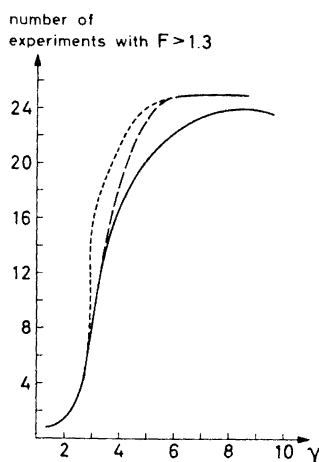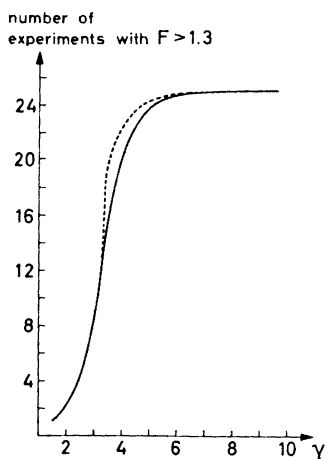
number of
experiments with F > 1.3

number of
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number of
experiments with F > 1.3

Fig. 4a, b, c. The values of F (defined by eqn. (8)) obtained by fitting different sets of simulated data to eqn. (1) depend on γ, β, and $1/\tau_1$. For each set of $(\gamma, \beta, 1/\tau_1)$ are 25 experiments simulated. The number of these experiments which have a value of $F > 1.3$ is plotted *vs.* γ for fixed values of β and $1/\tau_1$.

a: $\beta = 1$, $1/\tau_1 = 20\pi$ and 60π $(\ldots\ldots)$;
$1/\tau_1 = 140\pi$ $(\underline{\quad\quad})$.
b: $\beta = 0.5$, $1/\tau_1 = 20\pi$ $(\ldots\ldots)$; $1/\tau_1 = 60\pi$
(— — —); $1/\tau_1 = 140\pi$ $(\underline{\quad\quad})$.
c: $\beta = 0.25$, $1/\tau_1 = 20\pi$ $(\ldots\ldots)$; $1/\tau_1 = 60\pi$
(— — —); $1/\tau_1 = 140\pi$ $(\underline{\quad\quad})$.

PART II

The concentration dependence of the relaxation time

For the one-step dimerization mechanism we have:

$$\varphi + \varphi \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \varphi_2 \tag{11}$$
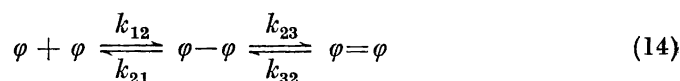
The relaxation time is given by:

$$\frac{1}{\tau} = 4\,k_{12}\varphi^\circ + k_{21} \tag{12}$$

k_{12} and k_{21} are the forward and backward rate constants, respectively, and φ° is the equilibrium concentration of component φ. Eqn. (12) can also be written:

$$(1/\tau)^2 = 8 \ k_{12}k_{21}C + k_{21}{}^2 \tag{13}$$

where C is the overall concentration of φ expressed as monomer. A plot of $1/\tau^2$ vs. C gives a straight line with a positive slope and a positive intercept. From the straight line the rate constants can be calculated. This model is well known and has been applied in several cases.[2-5] The model has been applied even in cases where a two-step dimerization might be expected, namely for formation of doubly-hydrogen bonded dimers.[2-4] The reasons for applying the one-step model are: only one relaxation time is observed, and the concentration dependence is in agreement with eqn. (13). We now consider the following two-step mechanism:

$$\varphi + \varphi \ \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \ \varphi{-}\varphi \ \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \ \varphi{=}\varphi \tag{14}$$

We wish to determine under which circumstances a plot of $1/\tau^2$ vs. C gives a linear plot and under which circumstances it does not. From part I it is seen that if $\gamma < 4$, or if $\gamma > 4$, and $\beta < 0.25$, the experimental data will fit a single relaxation curve.

The kinetics of the system is described by two coupled differential equations. When they are linearized we get:

$$\frac{d}{dt} \ (\Delta\varphi) + (4k_{12}\varphi^\circ + k_{21})\Delta\varphi + 2k_{21}\Delta\Phi = 0$$

$$\frac{d}{dt} \ (\Delta\varphi) + \tfrac{1}{2} k_{23}\Delta\varphi + (k_{32} + k_{23})\Delta\Phi = 0$$

Φ denotes the molar concentration of the doubly-bonded dimer and $\Delta\varphi$ is the deviation from the equilibrium concentration of φ. We introduce the abbreviations:

$$a_{11} = 4 \ k_{12}\varphi^\circ + k_{21}$$
$$a_{12} = 2 \ k_{21}$$
$$a_{21} = \tfrac{1}{2} \ k_{23}$$
$$a_{22} = k_{23} + k_{32}$$

The relaxation times can be found by solving the eigenvalue problem for the matrix $\{a_{ij}\}$. For the eigenvalues we obtain:

$$\frac{1}{\tau} = \tfrac{1}{2} \left[a_{11} + a_{22} \pm \sqrt{(a_{11}-a_{22})^2 + 4 \ a_{21}a_{12}} \ \right] \tag{15}$$

Combining the expressions for the two relaxation times with the definition of γ from part I, we have:

$$\gamma = \frac{\tau_1}{\tau_2} = \frac{a_{11} + a_{22} + \sqrt{(a_{11}-a_{22})^2 + 4 \ a_{21}a_{12}}}{a_{11} + a_{22} - \sqrt{(a_{11}-a_{22})^2 + 4 \ a_{21}a_{12}}} \tag{16}$$

γ_c is defined to be the value of γ below which only a single relaxation is observed. Eqn. (16) then becomes:

$$\frac{V\overline{(a_{11}-a_{22})^2 + 4a_{21}a_{12}}}{a_{11} + a_{22}} < \frac{\gamma_c - 1}{\gamma_c + 1}$$

This is necessary requirement for a single relaxation to be observed for this mechanism. The kinetic interpretation of the observed relaxation time depends on the value of β. If β equals one then:

$$\frac{1}{\tau_{obs}} = \tfrac{1}{2}\left[\frac{1}{\tau_1} + \frac{1}{\tau_2}\right]$$

or:

$$\frac{1}{\tau_{obs}} = 2k_{12}\varphi^\circ + \tfrac{1}{2}\sum \qquad (17)$$

where

$$\sum = k_{21} + k_{23} + k_{32}$$

Algebraic manipulation of eqn. (17) gives:

$$(1/\tau_{obs})^2 + (R-\textstyle\sum)(1/\tau_{obs}) = 2k_{12}RC + \tfrac{1}{4}\textstyle\sum(2R-\textstyle\sum) \qquad (18)$$

where

$$R = \frac{k_{21}\,k_{32}}{k_{32} + k_{23}}$$

Eqn. (18) can be written as

$$(1/\tau_{obs})^2 + U1/\tau_{obs} = VC + S$$

which defines U, V, and S. According to their definitions, V must be positive while U must be negative. S might be *positive* or *negative* depending on the actual values of the rate constants involved. If:

$$1/\tau_{obs} \geqslant 10U$$

then $(1/\tau)^2$ *vs.* C gives a straight line with a *positive* intercept, and a positive slope. This is apparently true for most systems investigated so far, where a two-step mechanism appears to show one relaxation time only. If the inequality is not valid, a plot of $(1/\tau)^2$ *vs.* C shows a curvature from which the values of V, S, and U can be calculated. k_{12} is then given by:

$$k_{12} = \tfrac{1}{2}\frac{V}{V\overline{4S + U^2}}$$

Conclusion

With an experimental error of $\pm 2\ \%$ in α/ν^2 the parameters A, B, and τ for a single relaxation (see eqn. (1)) can be determined with the accuracy given in Table 1, using a three-parameter, least square fitting procedure on 15 experimental points.

Table 1. Experimental errors (%) in the parameters of a single relaxation.

Relaxation time	Experimental error in:		
	τ	A	B
$\dfrac{1}{20\pi}$	± 5	± 3	± 1
$\dfrac{1}{60\pi}$	± 5	± 3	± 1
$\dfrac{1}{140\pi}$	± 5	± 2	± 2

The chosen values of A, B, and τ which are used for simulating the data are compared with the values obtained by the best three-parameter fit. By considering 250 experiments at each relaxation time the average experimental errors mentioned in this table are found.

It is shown that the criterion for fitting data to a one-relaxation time equation is, that F, defined by eqn. (8) satisfies the condition:

$$F \leq 1.3$$

If $F > 1.3$ two (or more) relaxation times are to be observed. When F is considered as a function of γ and β it is seen that the following requirements must be fulfilled if two relaxation times are to be observed:

$$\gamma > 4, \qquad 0.25 < \beta < 4$$

By using a five-parameter, least square fitting procedure on 15 points the parameters A_1, A_2, τ_1, τ_2, and B (see eqn. (2)) can be determined by the accuracy given in Table 2. The value of F defined for a five-parameter fit is

Table 2. Experimental errors (%) in the parameters of a double relaxation.

Relaxation time, τ_1	Experimental error in:				
	τ_1	τ_2	A_1	A_2	B
$\dfrac{1}{20\pi}$	± 30	± 30	± 25	± 25	± 1
$\dfrac{1}{60\pi}$	± 20	± 20	± 18	± 18	± 2
$\dfrac{1}{140\pi}$	± 30	± 30	± 20	± 20	± 4

The chosen values of A_1, A_2, τ_1, τ_2, and B ($\beta = 1$, $\gamma = 5$) which are used for simulating the data are compared with the values obtained by the best five-parameter fit. By considering 250 experiments at each relaxation time the average experimental errors mentioned in this table are found.

now smaller than 1.3. It is shown that the often presented arguments for a one step mechanism, namely that 1) the ultrasonic data show one relaxation time, and 2) $(1/\tau)^2$ *vs.* C forms a straight line, do not prove a one step mechanism. The two step formation of a doubly bonded dimer, where $\gamma < 4$ and $\beta = 1$, shows for instance one relaxation time only. The concentration dependence of this relaxation time is, under some circumstances, consistent with a one step mechanism. Under other circumstances a characteristic concentration dependence occurs.

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   The fitting procedures (written in *GIER*-ALGOL) which are used in this work can be obtained by writing the authors.