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A Kinetic Study of the Monomer-dimer Reaction in Propionic Acid by Means of Ultrasonic Absorption Measurements

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Second ultrasonic absorptions with relaxation frequencies of 26, 36, 53, and 70 MHz could be observed in 0.27, 0.47, 1.0, and 2.0 M cyclohexane solutions respectively of propionic acid at 20°C. The consideration of the variations in the sound absorption, the sound velocity, and the chemical shift with the concentration leads us to the conclusion that the relaxation is attributable to the perturbation of the equilibrium between the open dimer and the monomer of propionic acid. The backward rate constant in this reaction is estimated to be about 10^9 sec^{-1} M^{-1}.

The present authors[1,2] have previously reported that the cyclic and open dimers of propionic acid in several solvents are formed by an intermoleuclar hydrogen bond between carboxylic groups over the concentration range from 4 to 13.4 M(100%). In other ultrasonic studies[3] it has been discussed how the mechanism is associated with the equilibrium between the cyclic dimer and monomer. On the other hand, it has been reported by investigations of NMR,[4] the dielectric constant, and the sound velocity[5] that the monomer is scarcely detected at all in 100% carboxylic acid, but is detected in dilute solutions. The purpose of this paper is to study the kinetics of the reaction system containing the monomer. The ultrasonic absorption was measured in cyclohexane solutions of propionic acid over the concentration range from 0.27 to 13.4 M.

Experimental

The measurement of the ultrasonic absorption in a cyclohexane solution of propionic acid was made over the frequency range from 2.5 to 95 MHz at 20°C by the pulse method, while the sound velocity was measured at 3.00 MHz 20°C by using an ultrasonic interferometer. The chemical shift of the carboxylic proton in propionic acid was measured relative to protons in tetramethylsilane at 34°C. The propionic acid and cyclohexane were of a guaranteed grade. The propionic acid was purified once by fractional distillation at reduced pressure, while the cyclohexane was used without further purification.

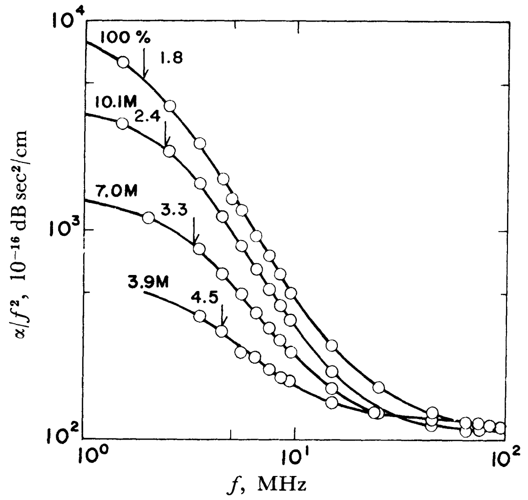

Fig. 1a. Ultrasonic absorptions in cyclohexane solution of propionic acid at 20°C.

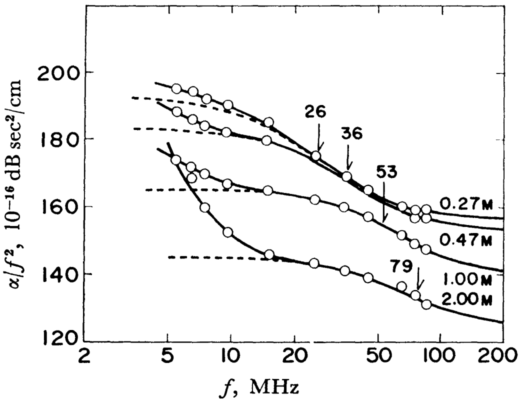

Fig. 1b. Ultrasonic absorptions in cyclohexane solution of propionic acid at 20°C.

Results

The ultrasonic absorptions in 3.9, 7.0, 10.1, and 13.4 M solutions are expressed by the equation for a single relaxation in the experimental frequency range, and the relaxation frequencies are 1.8, 2.4, 3.3, and 4.5 MHz respectively, as can be seen in Fig. 1a. On the other hand, in the 0.27, 0.47, 1.0, and 2.0 M solutions the absorptions are expressed by the equation for a double relaxation, in which the higher relaxation frequencies are 26, 36, 53, and 79 MHz respectively, as can be seen in Fig. 1b. These relaxations are represented by Eqs. (1) and (2):

$$\alpha/f^2 = \frac{A_1}{1+(f/f_{m_1})^2} + B, \tag{1}$$

$$\alpha/f^2 = \frac{A_1}{1+(f/f_{m_1})^2} + \frac{A_2}{1+(f/f_{m_2})^2} + B, \tag{2}$$

where α is the absorption coefficient of sound, f is the frequency, A_1, A_2, and B are the first and second chemical absorptions and the classical absorption respec-

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1) N. Tatsumoto, *J. Chem. Phys.*, **47**, 4561 (1967).

2) N. Tatsumoto, T. Sano, T. Yasunaga, N. Matsunaga and E. Tochigi, This Bulltein, **45**, 2083 (1972).

3) E. Freedman, *J. Chem. Phys.*, **21**, 1784 (1953).

4) L. W. Reeves and W. G. Schneider, *Trans. Faraday Soc.*, **54**, 314 (1958), F. Conti and C. Franconi, *Ber. Bunsenges. Physik. Chem.*, **71**, 146 (1967).

5) M. Blinc and R. Blinc, *J. Polymer Sci.*, **32**, 506 (1958).

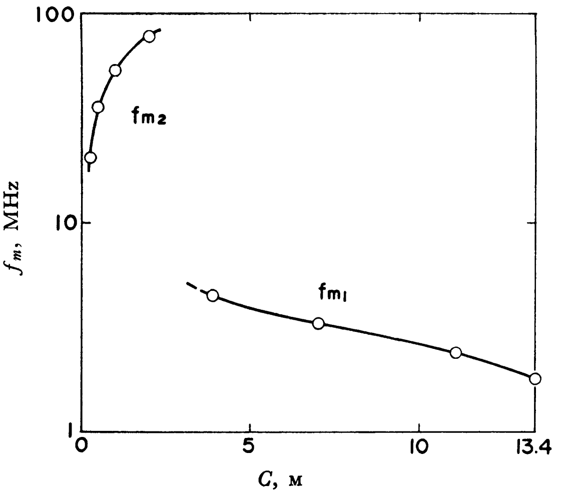

Fig. 2. Variations of f_{m_1} and f_{m_2} with concentration of propionic acid in cyclohexane at 20°C.

tively, and f_{m_1} and f_{m_2} are the first and second relaxation frequencies respectively. The variation in the relaxation frequency with the concentration of propionic acid is shown in Fig. 2.

The variation in the sound velocity with the conecntration is expressed in the next equation for an ideal solution[6]:

$$V = \{V_1 p + V_2(100-p)\}/100, \tag{3}$$

where V is the sound velocity of the solution, V_1 and V_2 are those in the solute and the solvent respectively, and p is weight percentage of the solute. The experimental values of the sound velocity, as plotted against p in Fig. 3, however, deviate from the straight line. In Fig. 4, the values of $\Delta V/p$ are plotted against the molarity, where ΔV represents the deviation from the straight line in Fig. 3; the dependence of the proton shift on the concentration is also shown in Fig. 4.

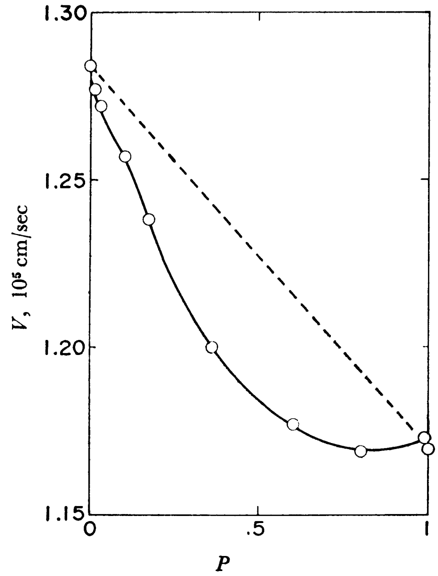

Fig. 3. Variation of sound velocity with concentration of propionic acid in cyclohexane at 20°C.

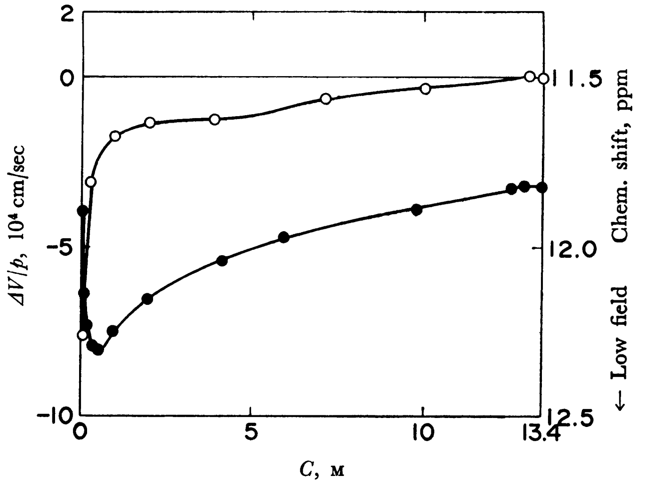

Fig. 4. Variations $\Delta V/p$ and chemical shift of carboxylic acid proton with concentration of propionic acid in cyclohexane at 20 and 34°C, respectively.
○: $\Delta V/p$; ●: chemical shift

Discussion

The first relaxation frequencies in the concentration range from 0.27 to 2.0 M, as estimated roughly from the absorption data in the frequency range from 5.5 to 15 MHz, are less than 10 MHz. The mechanism of the first relaxation in the dilute solutions, therefore, seems to be the same as that in the concentration range from 4 to 13.5 M, the mechanism of which is due to the perturbation of the equilibrium between cyclic and open dimers of propionic acid.[2] On the other hand, the second relaxation mechanism can be assigned to the perturbation of the equilibrium which might exist in the dilute solutions, provided the relaxation is chemical.

This behavior, the fact that $\Delta V/p$ decreases gradually first and then rapidly below 1 M with a decrease in the concentration, indicates the existence of a monomer in the dilute solution of propionic acid, because the decrease in the molecular weight is one of the factors lowering the sound velocity. The absorption in NMR, moreover, shifts to a lower magnetic field at first, and then to a higher field below 0.7 M, with a decrease in the concentration. This indicates that two equilibria exist between cyclic and open dimers and the polymer in a concentrated solution of propionic acid[4] and that the proportion of the number of cyclic dimers to that of open dimers or polymers increases with a

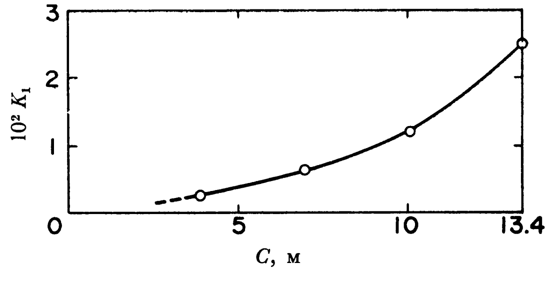

Fig. 5. Variation of equilibrium constant for the reaction between cyclic dimer and open dimer with concentration of propionic acid in cyclohexane at 20°C.

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[6] W. Schaaffs, *Z. Phys.*, **105**, 658 (1937).

decrease in the concentration. This can also be understood by the change in the equilibrium constant for the reaction between open and cyclic dimers, as calculated from ultrasonic and other data,[2] with the concentration as shown in Fig. 5. That is, the decrease in the equilibrium constant means a relative decrease in the number of the open dimer. Below 0.7 M, the number of the hydrogen bond decreases rapidly, that is, the monomer becomes predominant in the solution. Hence, over the concentration range from 0.27 to 2 M there exist two equilibria between cyclic and open dimers and the monomer:

$$\underset{\bar{C}_c}{\text{cyclic dimer}} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \underset{\bar{C}_o}{\text{open dimer}} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \underset{\bar{C}_M}{\text{monomer}}$$

where k_1, k_2, k_3, and k_4 are the forward and backward rate constants for the reactions between the cyclic and open dimers and between the open dimer and the monomer, and where $\bar{C}_C$, $\bar{C}_O$, and $\bar{C}_M$ are the equilibrium concentrations of cyclic and open dimers and the monomer respectively. The above considerations lead us to the conclusion that the second relaxation is due to the perturbation of the equilibrium between the open dimer and the monomer.

Davies *et al.*[7] have obtained the equilibrium constant between the monomer and the dimer of propionic acid in light petroleum, carbon tetrachloride, and benzene below 1 M by the measurement of the distribution, although they have not separated the open dimer from the cyclic dimer. In this case, the expression of the equilibrium constant is as follows:

$$K = \frac{[\text{monomer}]^2}{[\text{dimer}]} = \frac{(\bar{C}_M)^2}{\bar{C}_c + \bar{C}_o}. \qquad (4)$$

From the literature values,[7] the value of K would be expected to be about 10^{-2} M in cyclohexane. On the other hand, the equilibrium constant between open and cyclic dimers is given by:

$$K_1 = \frac{k_1}{k_2} = \frac{\bar{C}_o}{\bar{C}_c}. \qquad (5)$$

Equation (4) can, then, be rewritten as in the following equation:

$$K = \frac{(\bar{C}_M)^2}{\bar{C}_c(1+K_1)}. \qquad (6)$$

The rough extrapolation of the previous data[2] of K_1 to 1 M gives about 10^{-3}; then:

$$K = \frac{(\bar{C}_M)^2}{\bar{C}_c}. \qquad (7)$$

The total concentration of the acid in the monomer unit is expressed as:

$$C = 2\bar{C}_c + 2\bar{C}_o + \bar{C}_M, \qquad (8)$$

and Eq. (8) is rewritten as Eq. (9) when K and K_1 are much smaller than unity:

$$C \simeq 2\bar{C}_c, \qquad (9)$$

and K_1 is given by:

$$K_1 = \frac{2\bar{C}_o}{C}. \qquad (10)$$

The values of $\bar{C}_M$ and $\bar{C}_O$ at C=0.27−2 M are listed in Table 1.

TABLE 1. THE EQUILIBRIUM CONCENTRATIONS OF MONOMER AND OPEN DIMER

C, M	2	1	0.49	0.27
$\bar{C}_M$, 10^{-2} M	10	$7_{.1}$	$5_{.0}$	$3_{.7}$
$\bar{C}_o$, 10^{-4} M	10	$5_{.0}$	$2_{.5}$	$1_{.4}$

The second relaxation frequency is given by:

$$2\pi f_{m_2} = 1/\tau_2 = 4k_4\bar{C}_M - k_2, \qquad (11)$$

for $k_1 \ll (k_2 \text{ and } k_3) \ll 4k_4\bar{C}_M$,

$$\text{and} \qquad 2\pi f_{m_2} = 1/\tau_2 = k_2 + k_3, \qquad (12)$$

for $4k_4\bar{C}_M \ll k_1 \ll k_2$ and k_3, where τ_2 is the second relaxation time. The variation in $1/\tau_2$ with $\bar{C}_M$ is described in Fig. 6 (see Appendix). The variation in $1/\tau_2$ with $\bar{C}_M$ in this experiment is shown in Fig. 7,

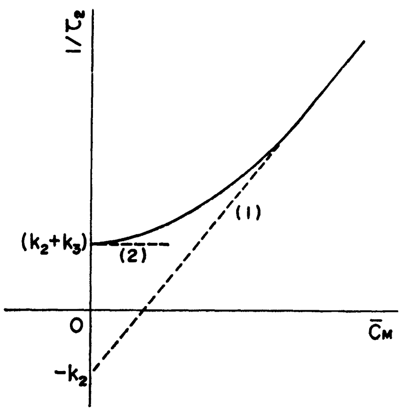

Fig. 6. Theoretical curve of variation of $1/\tau_2$ with equilibrium concentration of monomer, (1) according to Eq. 11; (2) to Eq, 12.

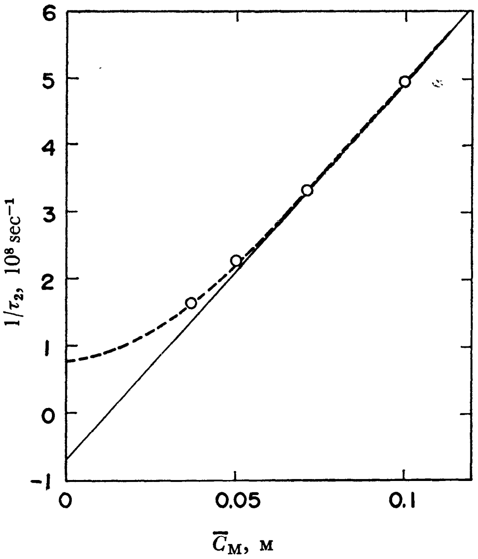

Fig. 7. Variation of $1/\tau_2$ with equilibrium concentration of monomer at 20°C.

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[7] M. M. Davies, P. Jones, D. Patinaki and E. A. Molelwyn-Hughes, *J. Chem. Soc.*, **1951**, 1249.

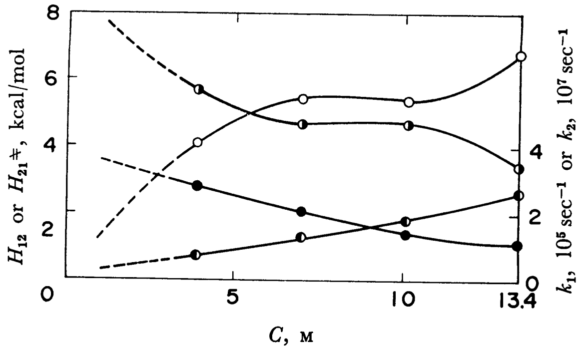

Fig. 8. Variations of $H_{21}^{\ne}$, H_{12}, k_1 and k_2 with concentration of propionic acid in cyclohexane at 20°C.
○: $H_{21}^{\ne}$; ◑: H_{12}; ◐: k_1; ●: k_2

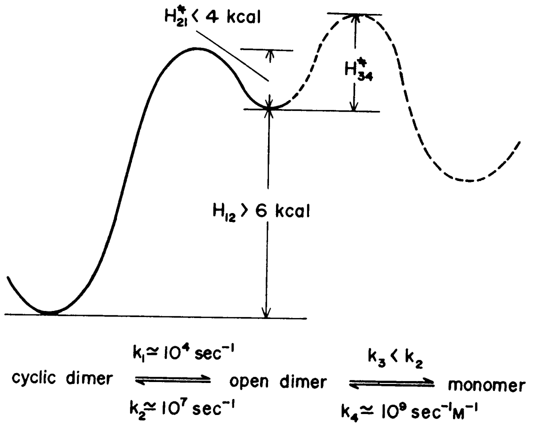

Fig. 9. Energy diagram for propionic acid in cyclohexane in the concentration range of 0.27 to 2 M at 20°C.

and an intercept of the tangent to the curve gives a value of k_2 which is about 7×10^7 sec^{-1}. This is in fair agreement with the value, 10^7 sec^{-1}, estimated approximately from the previous experimental values,[2] which are plotted against the concentration in Fig. 8. If the value of $1/\tau_2$ changes with the concentration, as in Fig. 7, k_2+k_3 can be estimated by the extrapolation of the curve to the intercept. The value of k_2+k_3 is nearly equal to that of k_2; therefore, k_3 is less than k_2. The value of k_4, moreover, is determined to be approximately 10^9 sec^{-1}M^{-1} by the slope of the curve. In order to illustrate the approximate energy diagram for propionic acid in the concentration range from 0.27 to 2.0 M, the values of the activation enthalpy of the backward reaction, $H_{21}^{\ne}$, and the enthalpy change of the reaction, H_{12}, in the reaction between the cyclic dimer and the open dimer, were estimated, along with those of k_1 and k_2, by the extrapolation of the curved $H_{21}^{\ne}$, H_{12}, k_1, and k_2 *vs.* C plots (Fig. 8) to approximately 1 M; the estimated values are listed in Table 2. The comparison between the magnitude of the equilibrium concentrations of the monomer and the open dimer informs us that the monomer is probably more stable than the open dimer. The fact that the activation enthalpy of the forward reaction between the open dimer and the monomer, $H_{34}^{\ne}$, is greater than $H_{21}^{\ne}$ is revealed by taking account of the magnitude of the corresponding rate constant. The energy diagram, consequently, may be described as in Fig. 9. More detailed kinetic values of the reaction between the open dimer and the monomer can be determined by the change in the ultrasonic absorption with the temperature, but the relaxation strength is too small to determine f_{m_2} and $(\alpha\lambda)_{m_2}$ with accuracy, where λ is the wavelength of sound.

Table 2. The kinetic parameters for the first reaction at $C\simeq 1$ M and at 20°C

k_1 sec^{-1}	k_2 sec^{-1}	$H_{21}^{\ne}$ kcal / mole of dimer	H_{12} kcal / mole of dimer
$\sim10^4$	$\sim10^7$	<4	>6

In liquid acetic acid and solutions of acetic acid, a second relaxation similar to that in the solution of propionic acid has been observed,[8] and the perturbation of the equilibrium between the open dimer and the monomer has been proposed as one of the mechanisms. There is no direct evidence for the existence of monomeric acid in liquid acetic acid, but the fact that the second relaxation could be detected in these monocarboxylic acids is very interesting. Finally, it can be expected that the second relaxation will be observed in other monocarboxylic acids and that the mechanism can be assigned more precisely and in more detail in the near future.

Appendix

Variation in $1/\tau_2$ with the Equilibrium Concentration. In the case of the coupled mechanism, the reciprocal relaxation times, $1/\tau_i$, are the eigenvalues, λ_{ii}, of the characteristic equation, which, in the determinant form, reads:

$$\begin{vmatrix} (k_1-\lambda) & -k_2 & 0 \\ -k_1 & (k_2+k_3-\lambda) & -4k_4\bar{C}_M \\ 0 & -k_3 & (4k_4\bar{C}_M-\lambda) \end{vmatrix} = 0 \qquad \text{(A1)}$$

The relaxation times then reduce to:

I) $\lambda_1 = 1/\tau_1 = 2\pi f_{m_1} = k_1 + k_2 \simeq k_2$, (A2)

and:

$$\lambda_2 = 1/\tau_2 = 2\pi f_{m_2} = 4k_4\bar{C}_M - (k_2+k_1) \simeq 4k_4\bar{C}_M - k_2, \qquad \text{(A3)}$$

for $k_1 \ll (k_2$ and $k_3) \ll 4k_4\bar{C}_M$ (here, if $k_4/k_2 \leqq 10^2$, $\bar{C}_M$ is relatively large), and to

II) $\lambda_1 = 1/\tau_1 = 2\pi f_{m_1} \simeq \dfrac{k_1k_3}{k_2+k_3}$, (A4)

and:

$$\lambda_2 = 1/\tau_2 = 2\pi f_{m_2} = k_2 + k_3, \qquad \text{(A5)}$$

for $4k_4\bar{C}_M \ll k_1 \ll k_2$ and k_3 (here, if $k_4 \gg k_1$, $\bar{C}_M$ is very small). This consideration holds only in the extremely high or low concentration ranges of $\bar{C}_M$. One, accordingly, should examine whether or not the function, $\lambda_2(\bar{C}_M)$, is represented by a continuous and monotonous increase in the middle concentration range. From Eq. (A1), $\bar{C}_M$ is given by:

$$\bar{C}_M = \frac{\lambda_2{}^2 - (k_1+k_2+k_3)\lambda_2 + k_1k_3}{4k_4\{\lambda_2-(k_1+k_2)\}}, \qquad \text{(A6)}$$

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[8] J. E. Piercy and J. Lamb, *Trans. Faraday Soc.*, **52**, 930 (1956), F. Bader and K. G. Plass, *Ber. Bunsenges. Physik. Chem.*, **75**, 553 (1971).

where $\lambda_2 \neq k_1+k_2$.

1) The derivative of $\overline{C}_M$ with respect to λ_2 is:

$$\frac{\partial \overline{C}_M}{\partial \lambda_2} = \frac{1}{4k_4} \cdot \frac{\{\lambda_2{}^2 - 2\lambda_2(k_1+k_2) + (k_1+k_2)(k_1+k_2+k_3) - k_1k_3\}}{(\lambda_2-k_1-k_2)^2}. \tag{A7}$$

A discriminant for a numerator in Eq. (A7) is negative, so that the tangent of a plot of $\partial \overline{C}_M/\partial \lambda_2$ *vs.* λ_2 is always positive.

2) The second derivative of $\overline{C}_M$ with respect to λ_2 is:

$$\frac{\partial^2 \overline{C}_M}{\partial \lambda_2{}^2} = \frac{-1}{2k_4} \cdot \frac{k_2k_3}{(\lambda_2-k_1-k_2)^3}. \tag{A8}$$

Considerable simplification is possible for two conditions:

i) $\frac{\partial^2 \overline{C}_M}{\partial \lambda_2{}^2} < 0$, for $\lambda_2 > k_1 + k_2$, (A9)

and:

ii) $\frac{\partial^2 \overline{C}_M}{\partial \lambda_2{}^2} > 0$, for $\lambda_2 < k_1 + k_2$. (A10)

From the definitions of τ_1 and τ_2, $f_{m_1} < f_{m_2}$, and hence $\lambda_2 > k_1+k_2$. Consequently, the $\overline{C}_M(\lambda_2)$ function can be represented by a continuous and monotounous increase, as is shown in Fig. 10.

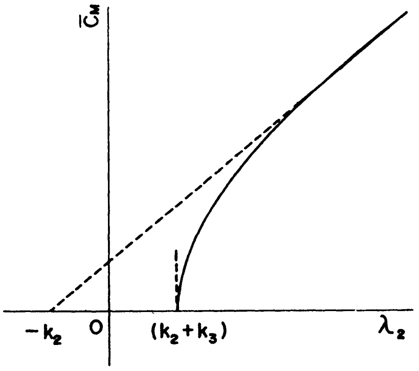

Fig. 10. Theoretical curve of variation of $\overline{C}_M$ with λ_2.