

## Dynamics of Magnesium–Bicarbonate Interactions

R. C. Patel,<sup>1,2</sup> F. Garland,<sup>1</sup> and G. Atkinson<sup>1</sup>

Received April 10, 1974; revised September 5, 1974

*The complexation kinetics of  $Mg^{2+}$  with  $CO_3^{2-}$  and  $HCO_3^-$  has been studied in methanol and water by means of the stopped-flow and temperature-jump methods. Kinetic parameters were obtained in methanol by coupling the magnesium–carbonate reactions with the metal-ion indicator Murexide. Relatively high stability constants were found in methanol ( $K = 1.0 \times 10^5$  liters-mole<sup>-1</sup> for  $Mg^{2+}$ –Murexide,  $K = 7.0 \times 10^4$  liters-mole<sup>-1</sup> for  $Mg^{2+}$ – $HCO_3^-$ , and  $K = 2.0 \times 10^5$  for  $Mg^{2+}$ – $CO_3^{2-}$  liters-mole<sup>-1</sup>). The corresponding, observed formation rate constants were determined to be*

$$\begin{aligned}k_f &= 4.0 \times 10^6 \text{ M}^{-1}\text{-sec}^{-1} (Mg^{2+}\text{--Murexide}) \\k_f &= 5.0 \times 10^5 \text{ M}^{-1}\text{-sec}^{-1} (Mg^{2+}\text{--}HCO_3^-) \\k_f &= 6.8 \times 10^5 \text{ M}^{-1}\text{-sec}^{-1} (Mg^{2+}\text{--}CO_3^{2-})\end{aligned}$$

*The relaxation times were found to be much shorter ( $\tau \approx 5\text{--}20 \mu\text{sec}$ ) in aqueous solutions, primarily due to the relatively high dissociation rate constants. The data could be interpreted on the basis of a coupled reaction scheme in which the protolytic equilibria are established relatively rapidly, followed by a single relaxation process due to the formation of  $MgHCO_3^+$  and  $MgCO_3$  between pH 8.7 and 9.3. The observed formation rate constants were determined to be*

$$\begin{aligned}k_f &= 5.0 \times 10^5 \text{ M}^{-1}\text{-sec}^{-1} (Mg^{2+}\text{--}HCO_3^-) \\k_f &= 1.5 \times 10^6 \text{ M}^{-1}\text{-sec}^{-1} (Mg^{2+}\text{--}CO_3^{2-})\end{aligned}$$

*These results, in conjunction with NMR solvent exchange rate constants, are analyzed in terms of a dissociative ( $S_{N1}$ ) mechanism for the rate of complex formation. The significance of these kinetic parameters in understanding the excess sound absorption in seawater is discussed.*

**KEY WORDS:** Solution kinetics; stopped flow; temperature jump; methanol; seawater; magnesium bicarbonate; magnesium carbonate; aqueous solutions.

<sup>1</sup> Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73069.

<sup>2</sup> Present address: Department of Chemistry, Clarkson College of Technology, Potsdam, New York 13676.

## 1. INTRODUCTION

Our objective in undertaking this study was to gain a better understanding of the dynamics of chemical equilibria important in seawater. Despite the importance of the metal ion  $\text{CO}_2\text{-H}_2\text{O}$  system in nature, there is little thermodynamic as well as kinetic data reported in the literature. The kinetics of these systems is complicated since the reactions are very rapid (relaxation times in the microsecond range) and complicated by precipitation and hydrolytic polymer formations at relatively high pH's. This necessitates the use of dilute solutions and very sensitive instrumentation. In this paper, we report our results with  $\text{Mg}^{2+}$ , whose concentration is appreciable in seawater. Our approach to this problem was first to study the kinetics of the magnesium-bicarbonate reaction in methanol by coupling it with the magnesium-Murexide reaction. Using the methanol results, we were able to optimize experimental conditions for aqueous solutions. Owing to the relatively low stability constants of the magnesium-carbonato complexes in water, the fast relaxation effects were most conveniently studied using a sensitive temperature-jump apparatus, and by coupling the reaction with an acid-base indicator. A comparison of the data in methanol and water is made, and their significance in understanding the excess sound absorption in seawater is discussed.

## 2. EXPERIMENTAL

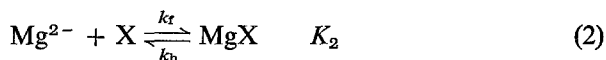
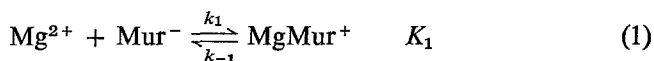
All materials used were of reagent quality. Purification and other details have already been described.<sup>(1)</sup> Particular attention had to be paid to the handling and storage of Murexide solutions, which have a tendency to decompose.<sup>(2)</sup> Solutions were always freshly prepared shortly before the actual experiments were carried out. All spectrophotometric measurements were made on a Cary 14 spectrophotometer. Kinetic measurements were made with a modified Aminco-Morrow stopped-flow apparatus as well as a temperature-jump apparatus designed by Leo de Maeyer (improved version by R. Rabl). Both methods are described in the literature. Relative absorbance changes as small as 0.001, with risetime of a few microseconds, could readily be detected with the temperature-jump apparatus.

## 3. RESULTS

### 3.1. In Methanol

Since magnesium-bicarbonate complexation does not result in any color change, it is difficult to follow concentration changes spectrophotometrically. It was therefore essential to find an indicator which met the following criteria: (a) sensitive to metal ions (in this case  $\text{Mg}^{2+}$ ), resulting in large

color changes; (b) fast response; (c) its own kinetics with  $\text{Mg}^{2+}$  should not be so complicated as to prevent unambiguous interpretation of results. These requirements are met adequately by the indicator Murexide, which was first described by Schwarzenbach<sup>(2)</sup> and co-workers and whose capabilities were demonstrated by Eigen some years ago.<sup>(3)</sup> At the same time, the stability constants for complexation were expected to be much larger in methanol, thereby making an experimental study easier. For the evaluation of thermodynamic and kinetic parameters, it is useful to consider the following reaction scheme:



where  $\text{X} = \text{CO}_3^{2-}$  or  $\text{HCO}_3^-$ , and the charges are omitted in (2) for clarity. The quantities  $K_1$  and  $K_2$  are the respective association constants. A spectrophotometric titration of a Murexide solution (typical concentration of  $5 \times 10^{-5} M$ ) with a standard  $\text{Mg}^{2+}$  solution showed a single isosbestic point as expected for simple 1:1 complexation. A characteristic blue shift, from 5300 to 4450 Å, was observed. Evaluation of  $K_1$  was undertaken by means of a Benesi-Hildebrand type of plot, a procedure which has been well described in the literature.<sup>(4,5)</sup> Although all the solutions were very dilute, the activity coefficient values of various chemical species in methanol deviate significantly from unity. Consequently, the equilibrium constants obtained in this section are valid under the specified experimental conditions.

The successful competition for  $\text{Mg}^{2+}$  by  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in the presence of the indicator Murexide is clearly demonstrated in Fig. 1. Addition of a

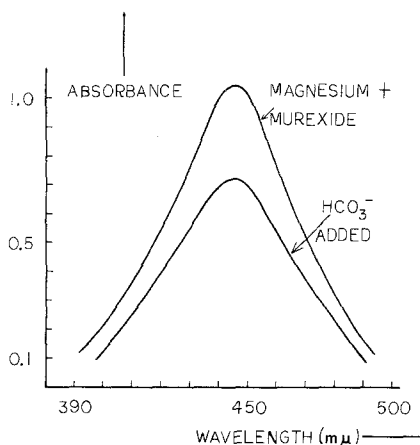


Fig. 1. Decrease in the absorption maximum of  $\text{MgMur}^+$  due to formation of  $\text{MgHCO}_3^+$ .  $[\text{Mg}^{2+}] = 1.09 \times 10^{-4}$  mole-liter<sup>-1</sup>;  $[\text{HCO}_3^-] = 1.52 \times 10^{-4}$  mole-liter<sup>-1</sup>.

relatively small amount of  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  to a magnesium–Murexide solution caused a significant decrease in the absorption maximum of magnesium–Murexide. The evaluation of  $K_2$  was obtained using the following set of equations:

$$\alpha = [\text{MgMur}^+]/C_{\text{in}} = \text{the fraction of indicator complexed by } \text{Mg}^{2+} \quad (3)$$

$$C_{\text{in}} = [\text{Mur}^-] + [\text{MgMur}^+] \quad (4)$$

where  $C_{\text{in}}$  is the total indicator concentration. The absorbance  $A$ , at 4450 Å, is given by

$$A = \epsilon_{\text{Mur}^-}[\text{Mur}^-] + \epsilon_{\text{MgMur}^+}[\text{MgMur}^+] \quad (5)$$

At this wavelength,  $\epsilon_{\text{Mur}^-} \ll \epsilon_{\text{MgMur}^+}$ . Since the only species absorbing at this wavelength are Murexide and the complex magnesium–Murexide, in the absence of magnesium we may write

$$A_0 = \epsilon_{\text{Mur}^-}C_{\text{in}} \quad (6)$$

And when the indicator is “saturated” (large excess of  $\text{Mg}^{2+}$ )

$$A_{\infty} = \epsilon_{\text{MgMur}^+}C_{\text{in}} \quad (7)$$

Combining (4), (5), (6), and (7) and rearranging, we obtain

$$(A - A_0)/(A_{\infty} - A_0) = [\text{MgMur}^+]/C_{\text{in}} = \alpha \quad (8)$$

From reaction (1), it follows readily that

$$[\text{Mg}^{2+}] = \frac{1}{K_1} \left( \frac{\alpha}{1 - \alpha} \right) \quad (9)$$

Using the mass balance conditions

$$[\text{X}]_{\text{total}} = [\text{X}] + [\text{MgX}] \quad (10)$$

$$[\text{Mg}]_{\text{total}} = [\text{Mg}^{2+}] + [\text{MgX}] + [\text{MgMur}^+] \quad (11)$$

and defining

$$\beta = [\text{MgX}]/[\text{X}]_{\text{total}} \quad (12)$$

as the fraction of carbonate complexed, we can show that

$$\beta/(1 - \beta) = K_2[\text{Mg}^{2+}] \quad (13)$$

The quantity  $\beta$  can be evaluated from (11), since  $[\text{Mg}^{2+}]$  [from (9)],  $[\text{MgMur}^+]$  [from (8)], and  $[\text{Mg}]_{\text{total}}$  are known from experiment. The quantity  $K_2$  was evaluated graphically using Eq. (13) from five to seven different solutions, and also at different temperatures from 0 to 40°C. The results obtained are summarized in Table I.

**Table I.** Thermodynamic Parameters for the Reaction of  $\text{Mg}^{2+}$  with Different Ligands in Methanol at 25°C,  $\mu = 5.0 \times 10^{-4} M$ 

Reaction	$\Delta H^\circ$ (kcal-mole $^{-1}$ )	$\Delta S^\circ$ (e.u.-mole $^{-1}$ )	$K = k_f/k_b$ (liter-mole $^{-1}$ )
$\text{Mg}^{2+}$ -Murexide	6.4	44.3	$1.0 \times 10^5$
$\text{Mg}^{2+}$ - $\text{HCO}_3^-$	6.7	44.6	$7.0 \times 10^4$
$\text{Mg}^{2+}$ - $\text{CO}_3^{2-}$	6.8	47.0	$2.0 \times 10^5$

### 3.2. Kinetic Studies in Methanol

In order to evaluate  $k_f$  and  $k_b$  [Eq. (2)], it is essential to determine  $k_1$  and  $k_{-1}$  first. Since  $\text{MgMur}^+$  has a very large extinction coefficient, this could be done using the stopped-flow technique, which has already been described in detail.<sup>(1)</sup> When dilute solutions of  $\text{Mg}^{2+}$  and  $\text{Mur}^-$  ( $\sim 10^{-5} M$ ) were used, typical reaction half-lives of 5 msec and greater were observed. These could be readily resolved with our apparatus. The reaction rate for the complexation of magnesium-Murexide is given by

$$dx_1/dt = k_1(a - x_1)(b - x_1) - k_{-1}x_1 \quad (14)$$

where  $a$  is the total concentration of  $\text{Mg}^{2+}$ ,  $b$  is the total concentration of Murexide, and  $x_1$  is the concentration of magnesium-Murexide at any given time  $t$ . The values of  $k_1$  and  $k_{-1}$  could be obtained from the integrated form of Eq. (14), which has been discussed in detail in the literature.<sup>(6)</sup> The experiment was also carried out under pseudo-first-order conditions ( $a \gg x_1$ ). Both methods gave results which were in good agreement. These and subsequent calculations were performed on a Univac 1108 computer using Fortran IV. For the calculation of rate constants with carbonate ligands, it is useful to consider the following equations derived from (1) and (2) and using the appropriate mass balance conditions:

$$dx_1/dt = k_1(a - x_1 - x_2)(b - x_1) - k_{-1}x_1 \quad (15)$$

$$dx_2/dt = k_1(a - x_1 - x_2)(c - x_2) - k_b x_2 \quad (16)$$

where  $c$  is the total concentration of  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$ ,  $x_2$  is the concentration of  $\text{MgHCO}_3^+$  or  $\text{MgCO}_3$  at any time  $t$ , and all the other symbols have the same meaning as before.

The calculation of this system of coupled, nonlinear differential equations is very difficult by ordinary methods.<sup>(7)</sup> Our approach to this problem was to carry out an experiment on the stopped-flow technique using  $\text{Mg}^{2+}$  and Murexide, and then to repeat the experiment with a given amount of  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  added to Murexide solution. All experiments were carried out at a wavelength slightly below 4450 Å, where the absorbance due to Murexide is

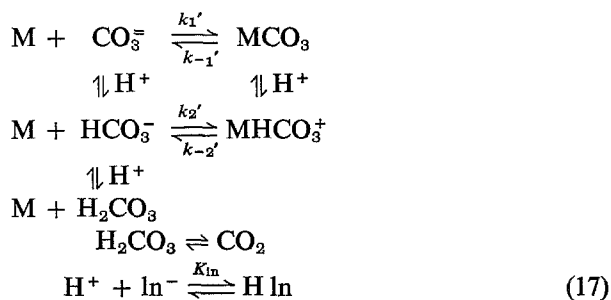
**Table II.** Summary of Rate Constants for the Reaction of  $\text{Mg}^{2+}$  with Different Ligands in Methanol at  $25^\circ\text{C}$ ,  $\mu = 5.0 \times 10^{-4} M$ 

Reaction	$k_f (M^{-1}\text{-sec}^{-1})$	$k_b (\text{sec}^{-1})$
$\text{Mg}^{2+}\text{-Murexide}$	$4 \times 10^6$	37
$\text{Mg}^{2+}\text{-HCO}_3^-$	$5 \times 10^5$	7
$\text{Mg}^{2+}\text{-CO}_3^{2-}$	$6.8 \times 10^5$	3.4

negligible. From the two experimental oscilloscope traces obtained, the corresponding absorbances at any given time  $t$ , and hence  $x_1$ ,  $x_2$ , could be readily determined. The quantity  $k_f$  was then evaluated from (16) using a numerical technique. Experiments were also carried out under pseudo-first-order conditions ( $a \gg [x_1 + x_2]$ ), which simplified the calculation considerably. Both methods give consistent results, summarized in Table II.

### 3.3. Results in Water

A general scheme for the interaction of a metal (M) such as  $\text{Mg}^{2+}$  with the  $\text{CO}_2\text{-H}_2\text{O}$  system is given below:



The protolytic equilibria shown by vertical arrows are established very rapidly compared with the horizontal ones.<sup>(8)</sup> Consequently, only one relaxation time due to the slower process is observed, since these are coupled with the rapid equilibria.<sup>(8)</sup>

Before attempting to understand the dynamic behavior of the system represented by (17), it is necessary to understand the distribution of various species when the system is at thermodynamic equilibrium. The exact solution to this problem was obtained from the following quadratic equation derived using the appropriate equilibrium and mass balance conditions:

$$A[\text{CO}_3^{2-}]^2 + B[\text{CO}_3^{2-}] - C_T = 0 \quad (18)$$

where

$$A = \frac{K_{M2}[H^+]^2}{K_{d1}K_{d2}K_{d3}} + \frac{K_{M1}[H^+]^3}{(K_{d1})^2K_{d2}K_{d3}} + \frac{K_{M2}[H^+]^2}{K_{d2}K_{d3}} + \frac{K_{M1}[H^+]^3}{K_{d1}K_{d2}K_{d3}} + \frac{K_{M2}[H^+]}{K_{d3}} \\ + \frac{K_{M1}[H^+]^2}{K_{d1}K_{d3}} + \frac{K_{M1}[H^+]}{K_{d1}} + K_{M2} \\ B = 1 + \frac{[H^+]^2}{K_{d1}K_{d2}K_{d3}} + \frac{[H^+]^2}{K_{d2}K_{d3}} - K_{M2}C_T - \frac{K_{M1}[H^+]C_T}{K_{d1}} + \frac{[H^+]}{K_{d3}} \\ + K_{M2}C_M + \frac{K_{M1}[H^+]C_M}{K_{d1}}$$

$C_M$  = total concentration of  $Mg^{2+}$

$C_T$  = total concentration of  $CO_2$

$$K_{d1} = [H_2CO_3]/[CO_2] \quad (19)$$

$$K_{d2} = [H^+][HCO_3^-]/[H_2CO_3] \quad (20)$$

$$K_{d3} = [H^+][CO_3^{2-}]/[HCO_3^-] \quad (21)$$

$$K_{M1} = [MgHCO_3^+]/[Mg^{2+}][HCO_3^-] \quad (22)$$

$$K_{M2} = [MgCO_3]/[Mg^{2+}][CO_3^{2-}] \quad (23)$$

$$K_{MA} = [MgHCO_3^+]/[H^+][MgCO_3] = K_{M1}/K_{d3}K_{M2} \quad (24)$$

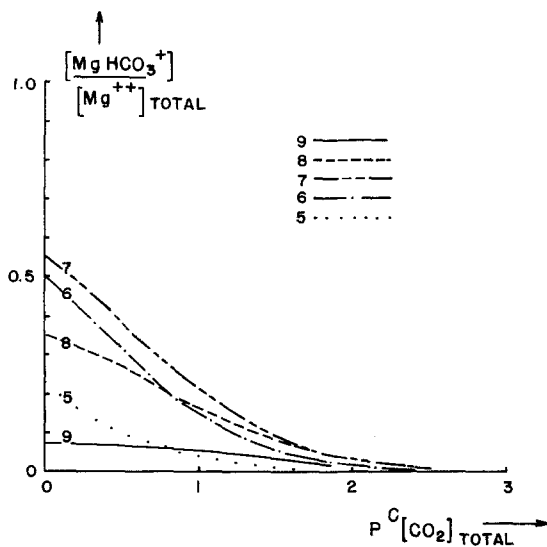
The values of the equilibrium constants were obtained from a previous study,<sup>(9)</sup> or from the literature and corrected for ionic-strength differences using the Davies equation,<sup>(10)</sup> and are presented in Table III. The ionic strength

**Table III.** Equilibrium Constants Used for the Evaluation of  $k'_1$  and  $k'_2$

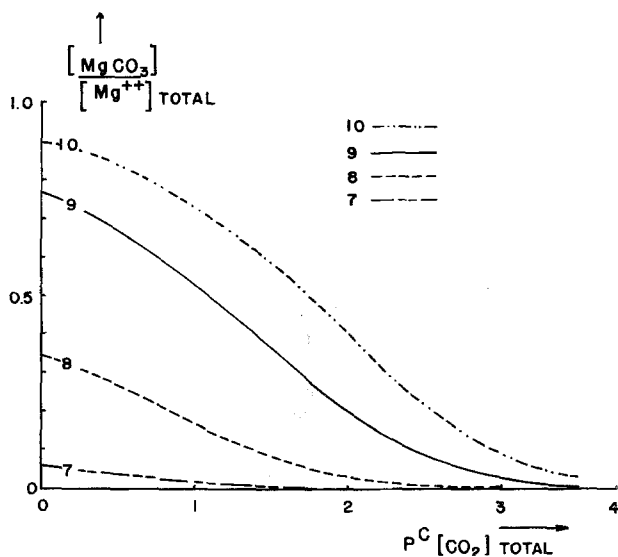
Equilibrium constant <sup>a</sup>	Ref.
$K_{d1} = 2.2 \times 10^{-3}$	1
$K_{d2} = 5.0 \times 10^{-4}$ mole-liter <sup>-1</sup>	1
$K_{d3} = 2.5 \times 10^{-10}$ mole-liter <sup>-1</sup>	11
$K_{M1} = 4.0^b$ liter-mole <sup>-1</sup>	12
$K_{M2} = 1.58 \times 10^{2b}$ liter-mole <sup>-1</sup>	13
$K_{MA} = 1.01 \times 10^8$ liter-mole <sup>-1</sup>	11-13

<sup>a</sup> Values determined experimentally at 25.0°C and at 1.0 *M* ionic strength except where otherwise noted.

<sup>b</sup> Corrected to 1.0 *M* ionic strength using the Davies<sup>(10)</sup> equation.



**Fig. 2a.** Fraction of total magnesium complexed as  $\text{MgHCO}_3^+$ , shown as a function of total analytical concentration of  $[\text{CO}_2]$  ( $pC[\text{CO}_2]_{\text{TOTAL}} = -\log [\text{CO}_2]_{\text{TOTAL}}$ ). The numbers on individual curves are pH values, and  $[\text{CO}_2]_{\text{TOTAL}}$  is always equal to  $[\text{Mg}^{2+}]_{\text{TOTAL}}$ .



**Fig. 2b.** Fraction of total magnesium complexed as  $\text{MgCO}_3$ .



was held constant by adding sodium perchlorate, ensuring that activity coefficients remained constant throughout the course of the reaction. Equation (18) was solved using a Newton–Raphson iteration by means of a Fortran IV program. The concentrations of various species as a function of pH,  $C_M$ , and  $C_T$  are shown in Figs. 2a and 2b. Due to the much lower stability constant for  $\text{MgHCO}_3^+$  ( $K_{M1}$ ), its maximum concentration is achieved at  $\text{pH} \approx 7$ . At higher pH's,  $\text{MgCO}_3$  tends to predominate ( $K_{M2} \gg K_{M1}$ ). When the values of  $C_M$  and  $C_T$  are  $10^{-2} M$  or less, the amount of  $\text{MgHCO}_3^+$  present is exceedingly small. At pH's greater than 9, especially when the concentration of  $[\text{Mg}]_{\text{total}}$  and  $[\text{CO}_2]_{\text{total}}$  are relatively high, precipitation of magnesium hydroxide is a serious problem.

### 3.4. Kinetic Studies in Water

The detailed derivation of the rate law as well as the complete expression for the relaxation time has been published recently by Patel and Taylor for the reaction of  $\text{Mg}^{2+}$  with the tetraprotic acid  $\text{H}_4\text{P}_2\text{O}_7$ .<sup>(14)</sup> Since the reaction scheme (17) is a somewhat simplified version of the earlier derivation,<sup>(14)</sup> a brief summary is presented here. From (17), the following four-term rate law is obtained:

$$-d[\text{M}]/dt = (k'_1[\overline{\text{CO}_3^{2-}}] + k'_2[\overline{\text{HCO}_3^-}])[\text{M}] - (k'_{-1}[\text{MCO}_3] + k'_{-2}[\text{MHCO}_3]) \quad (25)$$

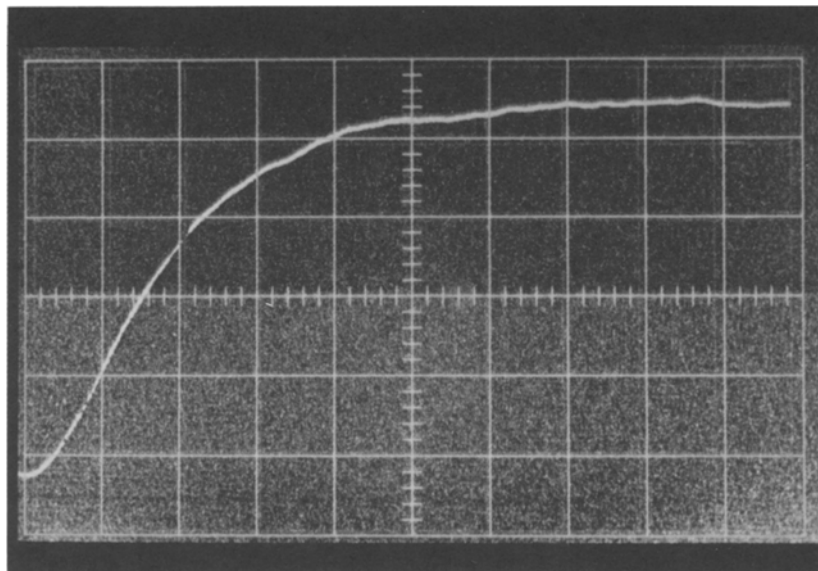
For small deviations ( $\delta C_i$ ) from equilibrium concentrations, i.e.,  $\delta C_i/\bar{C}_i \ll 1$ , Eq. (25) can be linearized for relaxation conditions:

$$\begin{aligned} \frac{1}{\tau} = -\frac{d(\ln \delta[\text{M}])}{dt} = & k'_1 \left\{ [\overline{\text{CO}_3^{2-}}] + [\bar{\text{M}}] \frac{\delta[\overline{\text{CO}_3^{2-}}]}{\delta[\text{M}]} - \frac{1}{K_{M2}} \frac{\delta[\text{MCO}_3]}{\delta[\text{M}]} \right\} \\ & + k'_2 \left\{ [\overline{\text{HCO}_3^-}] + [\bar{\text{M}}] \frac{\delta[\overline{\text{HCO}_3^-}]}{\delta[\text{M}]} - \frac{1}{K_{M1}} \frac{\delta[\text{MHCO}_3]}{\delta[\text{M}]} \right\} \end{aligned} \quad (26)$$

Bars above the various chemical species denote equilibrium concentrations. The expressions in the braces can be evaluated from equilibrium concentrations and constants, so that Eq. (26) can be rewritten<sup>(14)</sup>

$$1/\tau = k'_1 \cdot \text{SUM(A)} + k'_2 \cdot \text{SUM(B)} \quad (27)$$

The relaxation times  $\tau$  were determined from temperature-jump experiments in which the discharge of a  $5 \times 10^{-8} F$  capacitor charged to 33 kV raised the temperature of the solution being investigated by  $4^\circ\text{C}$  in less than  $2 \mu\text{sec}$ . It was necessary to couple the magnesium–carbonato reaction with a pH-sensitive indicator, phenolphthalein, in order to observe the reaction spectrophotometrically.<sup>(8,14)</sup>



**Fig. 3.** Temperature-jump relaxation effect due to perturbation of magnesium-bicarbonate equilibria.  $[\text{Mg}^{2+}]_{\text{total}} = 1.24 \times 10^{-1}$  mole-liter $^{-1}$ ;  $[\text{CO}_2]_{\text{total}} = 2.2 \times 10^{-2}$  mole-liter $^{-1}$ ; pH = 8.72. Vertical scale;  $\Delta A = 0.016$  cm $^{-1}$ ; horizontal scale: 5  $\mu\text{secs-cm}^{-1}$ .

A typical oscilloscope trace is shown in Fig. 3, and it is evident that despite the very fast relaxation times combined with a relatively small change in absorbance, it was possible to obtain reasonably "noise-free" traces. The relaxation times obtained are an average of five experiments. A much faster relaxation effect ( $\tau \approx 500$  nsec) due to the protolytic equilibria could be resolved using the ultrafast cable discharge temperature-jump apparatus,<sup>(15)</sup>

**Table IV.** Experimental Data for Relaxation Experiments with  $\text{Mg}^{2+}$  and Carbonato Ligands<sup>a</sup>

$1/\tau_{\text{obs}}$ (sec $^{-1}$ ) <sup>b</sup>	$1/\tau_{\text{calc}}$ (sec $^{-1}$ )	pH	$[\text{Mg}^{2+}]_{\text{total}}$ (mole-liter $^{-1}$ )	$[\text{CO}_2]_{\text{total}}$ (mole-liter $^{-1}$ )	SUM(A) (mole-liter $^{-1}$ )	SUM(B) (mole-liter $^{-1}$ )
$8.0 \times 10^4$	$9.4 \times 10^4$	9.26	0.084	$2 \times 10^{-2}$	$6.0 \times 10^{-2}$	$3.4 \times 10^{-2}$
$7.4 \times 10^4$	$6.1 \times 10^4$	9.1	0.043	$8 \times 10^{-3}$	$3.5 \times 10^{-2}$	$1.7 \times 10^{-2}$
$1.7 \times 10^5$	$2.4 \times 10^5$	8.88	0.281	$2 \times 10^{-2}$	$8.8 \times 10^{-2}$	$2.1 \times 10^{-1}$
$5.0 \times 10^4$	$3.6 \times 10^4$	8.76	0.014	$2 \times 10^{-2}$	$1.8 \times 10^{-2}$	$1.8 \times 10^{-2}$
$1.1 \times 10^5$	$9.2 \times 10^4$	8.72	0.124	$2.2 \times 10^{-2}$	$3.7 \times 10^{-2}$	$7.3 \times 10^{-2}$

<sup>a</sup> At 25.0°C and ionic strength 1.0 M.

<sup>b</sup> Average of five determinations.

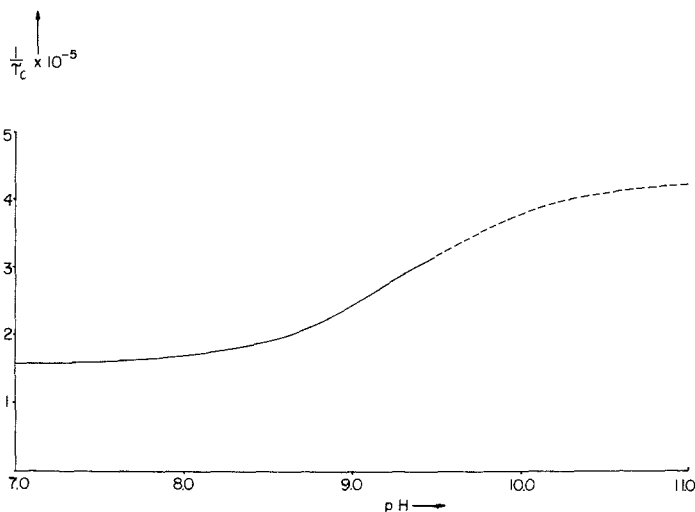


Fig. 4. Dependence on the inverse of the calculated relaxation time ( $1/\tau_{\text{calc}}$ ) on pH.

but this was not further investigated. As a result of the problems outlined above, the best experimental conditions were found to be at  $\text{pH} \approx 9$ . This is consistent with the reaction scheme (17), since around this pH contributions due to the formation of *both*  $\text{MgHCO}_3^+$  and  $\text{MgCO}_3$  give rise to a relatively large reaction amplitude. At lower pH's, the reaction amplitudes were much smaller and made experimental measurements very difficult. From the experimentally measured  $\tau$ 's, as well as values of SUM(A) and SUM(B) computed from known data,<sup>(14)</sup> the values of  $k'_1$  and  $k'_2$  were calculated using a two-parameter fit program [Eq. (27)]. These values, together with SUM(A) and SUM(B), were used to calculate relaxation times ( $\tau_{\text{calc}}$ ). These results are summarized in Table IV. With the known values of  $k'_1$  and  $k'_2$  it was possible to calculate the pH dependence of  $1/\tau_{\text{calc}}$ , shown in Fig. 4. It is seen that the largest variation is found between pH 9 and 10. Unfortunately, much of this region is inaccessible to experiments due to difficulties inherent in the system, so that, on the whole, one is forced to work in a relatively narrow pH range.

#### 4. DISCUSSION

The relaxation experiments (section B) demonstrate clearly the presence of complexation reactions involving  $\text{Mg}^{2+}$  and  $\text{HCO}_3^-$ , as well as  $\text{CO}_3^{2-}$ . The importance of these findings was shown in a recent publication<sup>(16)</sup> in which the excess sound absorption in seawater was simulated using a computerized calculation and including the above reactions.<sup>(16)</sup> Due to the appreciable concentration of  $\text{Mg}^{2+}$  in seawater, ( $\approx 0.05 M$ ), a significant effect in the low-frequency region (9 kHz) could be ascribed predominantly to the  $\text{MgHCO}_3^+$

**Table V.** A Comparison of Experimental Rate Constants for Magnesium Complexation Reactions at 25.0°C

Ligand	$k'_f$ ( $M^{-1}\text{-sec}^{-1}$ )	$K_{\text{outer sphere}}$ (liter-mole $^{-1}$ )	$\mu$ ( $M$ )	Ref.
$\text{SO}_4^{2-}$	$1.0 \times 10^5$ <sup>a</sup>			17
$\text{S}_2\text{O}_3^{2-}$	$1.0 \times 10^5$ <sup>a</sup>			17
$\text{CrO}_4^{2-}$	$1.0 \times 10^5$ <sup>a</sup>			17
$\text{IDA}^{2-}$ <sup>b</sup>	$1.4 \times 10^6$ <sup>c</sup>	12	0.11	3
$\text{ADPH}^{2-}$	$1.0 \times 10^6$	9	0.1	18
$\text{H}_2\text{P}_2\text{O}_7^{2-}$	$5.4 \times 10^5$	13	1.0	14
$\text{CO}_3^{2-}$	$1.5 \times 10^6$	3.5	1.0	This work
$\text{F}^-$	$5.5 \times 10^4$ <sup>c</sup>	1.6	0.4	3
$\text{Ox}^-$ <sup>d</sup>	$6.0 \times 10^5$	2.1	0.1	19, 20
$\text{HCO}_3^-$	$5.0 \times 10^5$	0.9	1.0	This work

<sup>a</sup> First-order substitution rate constant ( $\text{sec}^{-1}$ ).<sup>b</sup> IDA = iminodiacetate.<sup>c</sup> Value corrected to 25.0°C.<sup>d</sup> Ox = oxine = 8-hydroxyquinoline.

reaction consistent with  $k'_1$ ,  $k'_{-1}$ , etc. from Tables II and V). The similar formation rate constants (Table II) in methanol suggest that a dissociative ( $S_{N1}$ ) mechanism is important for complex formation in this solvent. The value for the methanol exchange rate constant for  $\text{Mg}^{2+}$ , determined by NMR measurements,<sup>(21)</sup> is  $4.7 \times 10^3 \text{ sec}^{-1}$ . Similar results have been obtained for the complexation reactions of alkali metals in methanol.<sup>(3)</sup>

A comparison of  $\text{Mg}^{2+}$  reactions with different ligands is shown in Table V. The formation rate constants ( $k'_f$ 's) are seen to have similar values (within about a factor of 5) for ligands with the same charge. This variation is reasonable in view of the different experimental conditions (e.g., ionic strength) and techniques which were used. On the basis of the Eigen-Tamm mechanism, the observed complexation rate constants  $k'_1$  and  $k'_2$  can be corrected for the outer-sphere ion pairing effects<sup>(3,14)</sup> using the relationship<sup>(17)</sup>

$$k'_f = K_{\text{outer sphere}} \cdot k_{\text{ex}} \quad (28)$$

$K_{\text{outer sphere}}$  can be calculated from the Eigen-Fuoss equation<sup>(22,23)</sup>

$$K_{\text{outer sphere}} = (4\pi Na^3/3000)e^{-U(a)/kT} \quad (29)$$

$$U(a) = \frac{Z_1 Z_2 e^2}{aD} - \frac{Z_1 Z_2 e^2}{D(1 + \kappa a)}$$

$$\kappa^2 = 8\pi Ne^2 \mu 1000 D k T$$

where  $\mu$  is the ionic strength,  $N$  is Avogadro's number,  $a$  is the distance of closest approach of the ions,  $Z_1$  and  $Z_2$  are the charges of the ions,  $e$  is the electron charge,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $D$  is the macroscopic dielectric constant.

The value of  $K_{\text{outer sphere}}$  obtained from (29) has to be corrected for activity-coefficient differences by means of the Davies equation<sup>(10,14)</sup> in order to obtain a value for  $k_{\text{ex}}$  under the appropriate experimental conditions. This method gives reasonable values for the "characteristic"<sup>(3)</sup> substitution rate constants for  $\text{Mg}^{2+}$  ( $k_{\text{ex}} \approx 10^5 \text{ sec}^{-1}$ ). A comparison with the water substitution rate constant for  $\text{Mg}^{2+}$  ( $\approx 1 \times 10^5 \text{ sec}^{-1}$ ) as determined from NMR experiments<sup>(3,24)</sup> further supports earlier findings<sup>(3,14,17)</sup> regarding the importance of a dissociative ( $S_{\text{N}1}$ ) mechanism for complex formation with  $\text{Mg}^{2+}$ .

## ACKNOWLEDGMENTS

Support of this work by the Office of Naval Research (Contract No. N00014-72-A-0285-0001) is well appreciated. The computer time for this project was supported by NASA Grant NSG-398 to the Computer Science Center of the University of Maryland. The temperature-jump work was carried out by one of the authors (RCP) during his stay at the Max Planck Institute of Biophysical Chemistry in Göttingen, West Germany. He would like to thank Dr. Manfred Eigen for providing facilities to do this work, as well as to the Alexander von Humboldt Stiftung for providing financial support of his stay. Finally, a special note of thanks is due Dr. Roger S. Taylor for helpful discussions.

## REFERENCES

1. R. C. Patel, R. J. Boe, and G. Atkinson, *J. Solution Chem.* **2**, 357 (1973).
2. G. Schwarzenbach and H. Gysling, *Helv. Chim. Acta* **32**, 1314 (1949).
3. H. Diebler, M. Eigen, G. Ilgenfritz, G. Maass, and R. Winker, *Pure Appl. Chem.* **20**, 93 (1969).
4. H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.* **71**, 2703 (1949).
5. S. D. Christian, *J. Chem. Educ.* **45**, 713 (1968).
6. I. Amdur and G. G. Hammes, *Chemical Kinetics and Selected Topics* (McGraw-Hill Book Co., New York, 1966).
7. E. Kamke, *Differentialgleichungen* (Akad. Verlagsgesellschaft, Leipzig, 1959).
8. M. Eigen and L. DeMaeyer, in *Technique in Organic Chemistry* (Interscience, New York, 1963).
9. R. C. Patel *et al.*, manuscript in preparation.
10. C. W. Davies, *Ion Association* (Butterworths, London, 1962), p. 39.
11. M. Frydman, G. Nilsson, T. Rengemo, and L. G. Sillén, *Acta. Chim. Scand.* **12**, 878 (1958).
12. I. Greenwald, *J. Biol. Chem.* **141**, 789 (1941).
13. J. Raaflaub, *Helv. Chim. Acta* **43**, 629 (1960).

14. R. C. Patel and R. S. Taylor, *J. Phys. Chem.* **77**, 2318 (1973).
15. G. W. Hoffman, *Rev. Sci. Instr.* **42**, 1643 (1971).
16. F. Garland, R. C. Patel, and G. Atkinson, *J. Acoust. Soc. of Am.* **54**, 996 (1973).
17. M. Eigen and K. Tamm, *Z. Electrochem.* **66**, 93, 107 (1962).
- 18a. M. Eigen and G. G. Hammes, *J. Am. Chem. Soc.* **82**, 5951 (1960).
- 18b. M. Eigen and G. G. Hammes, *J. Am. Chem. Soc.* **83**, 2786 (1961).
19. D. N. Hague, S. R. Martin, and M. S. Zetter, *J. Chem. Soc., Faraday Trans. I* **1**, **68**, 37 (1972).
20. D. N. Hague and M. Eigen, *Trans. Faraday Soc.* **62**, 1236 (1966).
21. S. Nakamura and S. Meiboom, *J. Am. Chem. Soc.* **89**, 1765 (1967).
22. M. Eigen, *Z. Physik. Chem. (Leipzig)* **1**, 176 (1954).
23. R. Fuoss, *J. Am. Chem. Soc.* **80**, 5059 (1958).
24. J. Neeley and R. Connick, *J. Am. Chem. Soc.* **92**, 3476 (1970).