# Comprehensive Study of the Hydration and Dehydration Reactions of Carbon Dioxide in Aqueous Solution

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The reversible interactions of dissolved  $CO_2$  with  $H_2O$  and  $OH^-$  to form  $H_2CO_3$  and  $HCO_3^-$  in aqueous solution have been investigated using spectrophotometric stopped-flow measurements. The progress of the reactions was monitored via indicators coupled to the pH changes during the reactions. The study, involving global analysis of the complete data set, spanned the temperature range 6.6–42.8 °C and resulted in the evaluation of all rate and equilibrium constants as well as activation parameters for the kinetic data and the reaction enthalpies and entropies for the equilibrium constants.

## Introduction

There is little doubt that the dissolution of  $CO_2$  in water, facilitated by the formation of carbonic acid and carbonate species, is a fundamentally important process for the planet and associated life.<sup>1-4</sup> It is thus not surprising that there is a long history of research with the goal of quantitatively investigating all individual reactions relevant to the overall process.<sup>5-22</sup> There are two reversible reactions of  $CO_2(aq)$  with water and with hydroxide to form carbonic acid and bicarbonate, eqs 1a and 1b, respectively. In addition there are three protonation equilibria, the protonation of carbonate, of bicarbonate, and of hydroxide ion, eqs 1c-1e.<sup>23</sup>

$$\operatorname{CO}_2(\operatorname{aq}) + \operatorname{H}_2\operatorname{O} \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} \operatorname{H}_2\operatorname{CO}_3$$
 (1a)

$$\operatorname{CO}_2(\operatorname{aq}) + \operatorname{OH}^- \underset{k_{-2}}{\overset{k_2}{\longleftrightarrow}} \operatorname{HCO}_3^-$$
 (1b)

$$\mathrm{CO}_{3}^{2^{-}} + \mathrm{H}^{+} \stackrel{K_{\mathrm{al}}}{\longleftrightarrow} \mathrm{HCO}_{3}^{-}$$
 (1c)

$$\mathrm{HCO}_{3}^{-} + \mathrm{H}^{+} \stackrel{K_{\mathrm{a2}}}{\longleftrightarrow} \mathrm{H}_{2}\mathrm{CO}_{3} \tag{1d}$$

$$OH^{-} + H^{+} \stackrel{K_{W}}{\longleftrightarrow} H_{2}O$$
 (1e)

The equilibria with only an equilibrium constant are treated as instantaneous protonation equilibria; those with two rate constants are treated as observable reactions. Figure 1 represents the complete reaction scheme in aqueous solution but excludes the mass transfer of gaseous  $CO_2$  between the liquid and gas phases.

Most published research has concentrated on the water path, eq 1a. Several techniques or methods have been used to obtain the two rate constants  $k_1$  and  $k_{-1}$ , including isotopic exchange,<sup>15,24</sup>



Figure 1. Reaction scheme of CO<sub>2</sub>(aq) in aqueous solution.

a pH-stat,<sup>17</sup> manometric measurements,<sup>14,18</sup> and stopped-flow studies.<sup>7–9,11,12,14,16</sup> Under some conditions, the reactions are fast, and there is no doubt that stopped-flow measurements are the most suitable for this investigation. Whereas stopped-flow measurement using conductivity detection is also fast, the signal is not specific because it is a linear combination of the contribution of several ions, many of them not taking part in the reaction.<sup>7</sup> A very powerful technique is to couple the protonation equilibria to an appropriate indicator and observe the pH changes spectrophotometrically.<sup>8,9,11,12,14,16</sup> In most investigations, solutions have been buffered to facilitate the analysis of the measurements. However, buffers have been found to catalyze some of the above reactions, and thus it is undesirable to add buffer solution in the hydration of  $CO_2(aq)$ .<sup>8,18</sup> There is one exception, where Soli and Byrne<sup>12</sup> obtained the two rate constants by a spectrophotometric stopped-flow technique without adding any buffer solution. In this case, approximations were made in the derivation of the rate equations, and no attempt was made to determine the rate constants for the hydroxide path.

The kinetics of the reversible reaction of  $CO_2(aq)$  with the hydroxide ion, eq 1b, has not been well investigated. With an increase in pH, the hydroxide path gains in importance, and it predominates above pH 8.5. It is also known that the reaction of  $CO_2$  with hydroxide has a significant biological role in blood pH regulation and the transportation of  $CO_2$  in living systems.<sup>3,25,26</sup> Interestingly, however, there are no kinetic data available at physiologically significant temperatures for  $k_2$  and  $k_{-2}$ .<sup>7,13,14,17</sup>

In this article, the kinetics of the water and hydroxide paths with  $CO_2(aq)$  is comprehensively investigated by the stopped-flow technique in the temperature range from 6.6 to 42.8 °C. Depending on the pH of the reacting solution, thymol blue or

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methyl red indicators were used. The four rate constants at the five different temperatures are derived using global data analysis software.<sup>27,28</sup> Activation energies and enthalpies and entropies of activation were obtained on the basis of Arrhenius and Eyring relationships. Van't Hoff analysis of the temperature dependence of the equilibrium constants resulted in reaction enthalpies and entropies.

Advanced data analysis software proved crucial; it allowed the omission of buffers and inert salts to maintain constant pH and ionic strength. The changes in these values were incorporated into the computations required for the data fitting.<sup>27–29</sup>

## **Experimental Section**

High purity CO<sub>2</sub> gas (BOC), N<sub>2</sub> (Core Gas), analytical grade sodium carbonate (Merck, 99.9%), sodium hydroxide (Merck), potassium hydrogen phthalate (KHP, Ajax Chemicals), thymol blue (Sigma-Aldrich, ACS reagent), methyl red (M&B Laboratory Chemicals), and hydrochloric acid (Ajax Chemicals) were used without any further purification. The concentration of sodium hydroxide stock solution was standardized by KHP, whereas the concentration of hydrochloric acid stock solution was determined by the standardized sodium hydroxide. Ultrahigh purity Milli-Q water was boiled to remove CO<sub>2</sub> gas. All samples were prepared and stored in a nitrogen-purged glovebag.

The kinetics of hydration of CO<sub>2</sub> and that of dehydration of H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup> were performed on an Applied Photophysics DX-17 spectrophotometer equipped with a J&M Tidas MCS 500-3 diode-array detector. All pH changes were observed over the wavelength range 400–700 nm via coupling to thymol blue or methyl red indicators. The reactions were studied over the temperature range of 6.6–42.8 °C. Samples were thermostatted to within  $\pm 0.1$  °C, and the exact temperature was recorded via a thermocouple within the stopped-flow apparatus.

The reversible interactions of CO<sub>2</sub> with water/OH<sup>-</sup> to form H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub><sup>-</sup> were investigated by two series of measurements: (a) for the hydration of carbon dioxide, water saturated with CO<sub>2</sub> (22–64 mM) was mixed with 4.0–36.0 mM Na<sub>2</sub>CO<sub>3</sub> in a 1:1 v/v ratio. The reaction kinetics were monitored by the absorbance change of thymol blue indicator; (b) for the dehydration of carbonic acid/bicarbonate, 4.0–36.0 mM Na<sub>2</sub>CO<sub>3</sub> solutions were mixed with 40 mM HCl solutions, again in a 1:1 v/v ratio. The reaction kinetics was monitored by the absorbance change of methyl red indicator.

All reactions were measured until equilibrium was completely reached. Each measurement was performed five times, allowing for standard deviations to be derived for the calculated rate constants based on experimental statistics rather than error estimates derived from the fitting procedures.

**Data Analysis.** Advanced data analysis is a critical element of this work. Not one of the reactions can be observed and analyzed individually, because all are intimately coupled, and the process has to be regarded as a whole. In fact, it is best to regard each measurement as an ensemble of reactions moving from the initial conditions to a new equilibrium. Whereas there are reactions that could theoretically be observed independently, for example, the reaction of  $CO_2$  with water, eq 1a at low pH,  $CO_2$  cannot be introduced into aqueous solution in the time frame required for the process to be observed directly. In a similar vein, the reaction of  $CO_2$  with  $OH^-$  at high pH is much faster than the water path and thus could be observed exclusively, but at high pH, the pH changes are very small and difficult to observe, notwithstanding the fact that the reaction can be too fast to observe using stopped-flow technology.

The computation of the concentration profiles of all species as a function of time is not possible explicitly because the systems of differential equations have no explicit solution. Numerical integration is straightforward; however, as the pH changes during the reaction, special attention is required, and standard packages cannot be employed. Consider, as an example, the differential equation for  $CO_2(aq)$ 

$$\frac{\delta[\text{CO}_2(\text{aq})]}{\delta t} = -k_1[\text{CO}_2][\text{H}_2\text{O}] - k_2[\text{CO}_2][\text{OH}^-] + k_{-1}[\text{H}_2\text{CO}_3] + k_{-2}[\text{HCO}_3^-] \quad (2)$$

Here the species OH<sup>-</sup>, H<sub>2</sub>CO<sub>3</sub>, and HCO<sub>3</sub><sup>-</sup> undergo equilibria instantaneously, and the equilibrium composition needs to be computed continuously to calculate the derivatives such as in eq 2.<sup>28</sup> The relevant protonation constants are  $K_W$ ,  $K_{a1}$ , and  $K_{a2}$ , as defined in eqs 1c-1e. In addition, the protonation constant of the indicator ( $K_{ind}$  in eq 3) has to be included.

$$\operatorname{Ind} + \operatorname{H}^+ \stackrel{K_{\operatorname{Ind}}}{\longleftrightarrow} \operatorname{Ind} \operatorname{H}^+$$
 (3)

Debye-Hückel approximations for activity coefficients for all ionic species have been implemented. The approximations are based on the expression

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \tag{4}$$

Here  $\gamma_i$  is the activity coefficient,  $z_i$  is the charge of the *i*th ion, *A* has a value of 0.242 for aqueous solutions, and  $\mu$  is the ionic strength of the solution. Therefore, activities for all species instead of concentrations are used throughout the computations, for example, in eq 2 and eqs 1a–1e. For the low concentrations used in this study, the approximations are reasonably accurate.

**Global Analysis.** All of the reactions are intimately intertwined so that they cannot be investigated or analyzed individually. Global analysis of series of measurements acquired at one temperature under different conditions to reveal information about all aspects of the total reaction mechanism is the most obvious method for this investigation. We have introduced global analysis<sup>30</sup> and successfully employed this technique in other investigations.<sup>31</sup> In fact, for the present investigation, at each temperature, a set of five forward reactions, type (a), and four back reactions, type (b), were analyzed as one unit, resulting in the fitted rate and equilibrium constants. Because there were five replications of all measurements at each temperature, resulting in five sets of fitted parameters, this allowed a proper statistical analysis of the parameters.

**Parameters.** The reaction scheme of Figure 1 encompasses four rate constants and three equilibrium constants.  $K_w$  and  $K_{a1}$ are not defined by our measurements, and their temperature-dependent values were taken from the literature.<sup>32–34</sup> The protonation constant  $K_{a2}$  for the bicarbonate is not well established; however, the equilibrium  $CO_2(aq) +$  $H_2O \stackrel{K_3}{\longrightarrow} HCO_3^- + H^+$  is well known, and its equilibrium

constant is related to  $K_1$  and  $K_{a2}$  as  $K_3 = K_1/K_{a2}$ . In the fitting, we defined  $K_{a2}$  as a function of known  $K_3$  and both  $k_1$  and  $k_{-1}$ , with  $K_{a2} = k_1/(k_{-1}K_3)$ . Furthermore, as a result of microscopic reversibility, we defined  $k_{-2}$  as a function of known  $K_3$  and  $k_2$  and  $K_w$ , with  $k_{-2} = k_2/(K_wK_3)$ . Therefore, there are three known



**Figure 2.** Absorbance change at 600 nm with time in the reaction of 33 mM  $CO_2(aq)$  with various concentrations of  $CO_3^{2-}$  at 6.6 °C with 0.10 mM thymol blue (left); the absorbance change at 550 nm for the reaction between 20.0 mM HCl and various concentrations of  $CO_3^{2-}$  at 6.6 °C in the presence of 0.10 mM methyl red (right). Black lines: experimental; red dashed lines: fitted results.



Figure 3. Calculated concentration profiles for the reaction of 33 mM  $CO_2(aq)$  with 8 mM  $CO_3^{2-}$  at 6.6 °C in the presence of 0.10 mM thymol blue. The right-hand plot features a logarithmic concentration axis.

and fixed values for  $K_w$ ,  $K_{a1}$ , and  $K_3$ ; there are three independently variable and fitted values for  $k_1$ ,  $k_{-1}$ , and  $k_2$ .

We have treated the protonation of carbonate as an instantaneous equilibrium rather than a reversible reaction. This is not completely accurate as the deprotonation reaction occurs on a time scale similar to our fast measurements. However, the value for this deprotonation reaction is not known. Furthermore, numerical experimentation with reasonable rate constants for this protonation equilibrium had only minor effects on the values of all other rate and equilibrium constants. We decided to retain the instantaneous protonation equilibrium for the analysis.

A set of secondary parameters was also required for the modeling and fitting of the measurements; these included the concentration of  $CO_2$  in water, which was based on saturated solutions, as well as the protonation constants of those indicators for which the temperature-dependent values are not published. As will be discussed later, these parameters are well-defined and consistent with published values for those available in the literature.

# Results

Figure 2 represents a complete data set at 6.6 °C. The lefthand side of Figure 2 features the absorbance changes (at 600 nm) for reactions of  $CO_2$  with  $CO_3^{2-}$ ; the right-hand side of Figure 2 shows the absorbance changes (at 550 nm) observed in the dehydration of  $HCO_3^-/H_2CO_3$  mixtures, which were generated by the reaction of various concentrations of  $CO_3^{2-}$ with HCl.

There are several interesting observations. The absorbance changes with time for the reaction of 33 mM CO<sub>2</sub>(aq) with different concentrations of carbonate feature the surprising observations that they resemble zeroth-order kinetics and that the reactions appear to become progressively faster at lower carbonate concentrations. The explanation lies in the fact that the reaction is followed by pH change and not any of the actual reactants, and that increasing the concentration of  $CO_3^{2-}$  results in increased buffer action with concomitant slower change in the free proton concentration.

The right part in Figure 2 shows the absorbance change at 550 nm with time for the reaction between 20.0 mM HCl and various concentrations of  $CO_3^{2-}$  at 6.6 °C in the presence of 0.10 mM methyl red. The apparent autocatalytic behavior is again explained by the fact that only pH changes are observed directly, rather than the reactant concentrations.

Figure 3 displays the concentration profiles for the reaction of 33 mM  $CO_2(aq)$  with 8.0 mM  $Na_2CO_3$  at 6.6 °C; it is the middle trace represented in the left part of Figure 2. To give a complete picture, the profiles in Figure 3 are also plotted with a logarithmic concentration scale.

TABLE 1: Calculated Rate and Equilibrium Constants in the Hydration of CO<sub>2</sub>(aq) and Dehydration of Carbonic Acid at Various Temperatures

<i>T</i> (°C)	$k_1 \ (M^{-1} \ s^{-1})$	$k_1^* (s^{-1})$	$k_{-1}$ (s <sup>-1</sup> )	$k_2 \ (M^{-1} \ s^{-1})$	$k_{-2} (s^{-1})$	$K_1 (\mathrm{M}^{-1})$	$K_1^*$	$K_2 (\mathrm{M}^{-1})$	$pK_{a2}$
6.6	$8(2) \times 10^{-5}$	$4.5(9) \times 10^{-3}$	4.2(1)	$2.3(1) \times 10^3$	$1.54(4) \times 10^{-5}$	$1.9(4) \times 10^{-5}$	$1.1(2) \times 10^{-3}$	$15.1(1) \times 10^7$	3.54(9)
16.0	$2.7(4) \times 10^{-4}$	$15(2) \times 10^{-3}$	10.3(3)	$4.2(3) \times 10^3$	$5.6(3) \times 10^{-5}$	$2.6(4) \times 10^{-5}$	$1.5(3) \times 10^{-3}$	$7.59(1) \times 10^7$	3.59(8)
25.0	$6.6(4) \times 10^{-4}$	$37(2) \times 10^{-3}$	24.8(4)	$12.1(4) \times 10^3$	$40(1) \times 10^{-5}$	$2.7(2) \times 10^{-5}$	$1.5(1) \times 10^{-3}$	$3.02(1) \times 10^7$	3.70(3)
34.0	$2.0(1) \times 10^{-3}$	$112(4) \times 10^{-3}$	60(2)	$25.0(2) \times 10^3$	$107(1) \times 10^{-5}$	$3.4(2) \times 10^{-5}$	$1.86(5) \times 10^{-3}$	$2.35(1) \times 10^7$	3.58(1)
42.8	$4.2(1) \times 10^{-3}$	$236(7) \times 10^{-3}$	139(3)	$48.8(8) \times 10^3$	$381(7) \times 10^{-5}$	$3.0(1) \times 10^{-5}$	$1.7(1) \times 10^{-3}$	$1.28(1) \times 10^{7}$	3.52(2)

TABLE 2: Calculated Activation Parameters and Enthalpies and Entropies of Reaction for the Hydration of CO<sub>2</sub>(aq) and Dehydration of Carbonic Acid

	Arrhe	nius	Ey	yring	van't Hoff	
	$E_{\rm a}$ (kJ mol <sup>-1</sup> )	Α	$\overline{\Delta H^{\ddagger} \text{ (kJ mol}^{-1})}$	$\Delta S^{\ddagger} (J \text{ mol}^{-1} \text{ K}^{-1})$	$\overline{\Delta H^{\phi} (\text{kJ mol}^{-1})}$	$\Delta S^{\phi} (\mathrm{J} \mathrm{mol}^{-1} \mathrm{K}^{-1})$
$\operatorname{CO}_2 \xrightarrow{k_1} \operatorname{H}_2 \operatorname{CO}_3$	81(2)	$1.2(8) \times 10^{11}$	79(2)	-41(6)	10(2)	-55(7)
$H_2CO_3 \xrightarrow{k_{-1}} CO_2$	71.6(6)	$9(2) \times 10^{13}$	69.1(6)	14(2)		
$\rm CO_2 + OH^- \xrightarrow{k_2} \rm HCO_3^-$	64(1)	$2(1) \times 10^{14}$	62(1)	40(4)	-50(1)	-23(5)
$\text{HCO}_3^{-} \xrightarrow{k_{-2}} \text{CO}_2 + \text{OH}^{-}$	114(2)	$3(3) \times 10^{16}$	112(2)	63(7)		

The rate constants, initial concentrations of CO<sub>2</sub>, and the log  $K_a$  of the indicators are fitted to the measurement of the hydration of CO<sub>2</sub>(aq) and dehydration of carbonic acid by using global data analysis software. The experimental data are well fitted, as demonstrated in Figure 2. The four calculated rate constants at various temperatures (6.6, 16.0, 25.0, 34.0, and 42.8 °C) are listed in Table 1, indicating, not unexpectedly, that the rates of the reaction increase with temperature.

The reaction between CO<sub>2</sub> and water is a second-order reaction with water as one reactant. It is common to define this reaction as a pseudo-first-order reaction, assuming the water concentration to be constant at 55.6 M. We have adopted both notations in Table 1, where the constants of  $k_1$  and  $K_1$  are based on the second-order reaction. (See Figure 1.)  $k_1^*$  and  $K_1^*$  are the corresponding pseudofirst-order reactions.

There is a competition between the reactions of CO<sub>2</sub> with H<sub>2</sub>O and with OH<sup>-</sup> to form carbonic acid or bicarbonate. The second-order rate constant of the reaction of CO<sub>2</sub> with OH<sup>-</sup> ( $k_2 = 12.1(4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C) is ~10<sup>7</sup> times faster than that with H<sub>2</sub>O ( $k_1 = 6.6(4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C). As a result, at high pH, the hydroxide path is faster, whereas at low pH, the water path is faster, with the crossover pH of ~8.5.

Table 2 lists the results of the analyses of the temperature dependence of the rate constants in terms of the Arrhenius and Eyring relationships as well as the analysis of the equilibrium constants based on the van't Hoff relationship, eq 5

Arrhenius: 
$$k(T) = A \exp\left(\frac{-E_a}{RT}\right)$$
  
Eyring:  $k(T) = \frac{k'T}{h} \exp\left(\frac{\Delta H^{\dagger} - T\Delta S^{\dagger}}{RT}\right)$  (5)  
van't Hoff:  $K(T) = \exp\left(-\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}\right)$ 

In the above equations, A is a pre-exponential factor, R is the molar gas constant, k' is the Boltzmann constant, h is Planck's constant, T is the absolute temperature,  $E_a$  is the activation energy,  $\Delta H^{\ddagger}$  is

the activation enthalpy,  $S^{\ddagger}$  is the activation entropy,  $H^{\emptyset}$  is the enthalpy, and  $S^{\emptyset}$  is the entropy of the reaction.

The Eyring analysis for the rate constants is represented graphically in Figure 4; the analogous Arrhenius plots can be found in the Supporting Information (Figure 1). Both representations display excellent linear relationships with well-defined slopes and thus activation energy,  $E_a$ , and activation enthalpy,  $\Delta H^{\ddagger}$ . Intercepts are less well-defined, resulting in larger error estimates for both A and  $\Delta S^{\ddagger}$ .

The equilibrium constants,  $K_1$ , for the formation of carbonic acid from CO<sub>2</sub> and water, and,  $K_2$ , for the formation of bicarbonate from CO<sub>2</sub> and OH<sup>-</sup>, eqs 1a-1e, at the five different temperatures are also listed in Table 1. A graphical representation is given in Figure 5. Figure 2 of the Supporting Information displays our results in the context of published values for the



**Figure 4.** Eyring plot of  $\ln(k/T)$  versus 1/T for the hydration of  $CO_2(aq)$  and dehydration of carbonic acid in the temperature range of 6.6 to 42.8 °C. Tilted squares represent the reaction with H<sub>2</sub>O, squares represent the reaction with OH<sup>-</sup>, full markers represent the forward reactions, and empty markers represent the back reactions.



**Figure 5.** Van't Hoff plots for the equilibrium constants  $K_1$  and  $K_2$  (eqs 1a and 1b).

same equilibrium constants. The equilibrium constant  $K_1$  decreases marginally over the temperature range, whereas the equilibrium constant  $K_2$  decreases significantly with temperature. A van't Hoff analysis of the data results in reaction entropies and enthalpies, listed in Table 2.

The protonation constants ( $K_{a2}$ ) of bicarbonate in the temperature range from 6.6 to 42.8 °C were derived from data fitting. The slope of log  $K_{a2}$  versus 1/*T* is (80 ± 280), which within the error limits, is zero. (See Figure 3 of the Supporting Information for a graphical representation.) The protonation constant is essentially constant in the above temperature range. The second protonation constant, log  $K_{a2}$ , is not well-defined, resulting in substantial scatter in Figure 3 of the Supporting Information and also in the graphs for  $K_1$  (Figures 2 and 5 of the Supporting Information), which are derived from published values for  $K_3$  and log  $K_{a2}$ .

There are several auxiliary parameters that were fitted to the measurements. They include the saturation concentration of CO<sub>2</sub> at the five different temperatures and the temperature-dependent protonation constants for the indicators thymol blue and methyl red (eq 3). The calculated concentrations of  $CO_2(aq)$  are in excellent agreement with previous reports; for a graphical representation, see Figure 4 of the Supporting Information.<sup>35,36</sup> The protonation constants of thymol blue and methyl red were obtained from the fitting of the kinetic data. They decrease with the increase in temperature, with plots of log  $K_a$  versus 1/T(Figure 5 of the Supporting Information) linear for both indicators, and a van't Hoff analysis results in  $\Delta H^{\phi} = 36(3)$ and 20(1) kJ mol<sup>-1</sup>, and  $\Delta S^{\phi} = 19(10)$  and -108(4) J mol<sup>-1</sup>  $K^{-1}$  for methyl red and thymol blue, respectively. These results are consistent with published values,<sup>37,38</sup> but no attempt was made to review the complete literature on the temperature dependence of these indicator protonation constants.

In passing, it is noted that the excellent linear behavior of the protonation constants of the indicators and the correct values for  $CO_2$  solubility at the different temperatures are a strong indication of the inherent robustness and thus correctness of the global data analysis.

#### Discussion

The reversible hydration of  $CO_2$  in aqueous solution is a very important and thus very well investigated reaction. Not surprisingly, there is a considerable number of published values for some of the rate constants, whereas for others, there are only a few published values. We start the discussion with the rate constants  $k_1$  and  $k_{-1}$  for the water path. Figure 6 of the Supporting Information reveals that there is no significant deviation between our values and the collection of published rate constants; this is true for the individual rate constants at the different temperatures, and as a consequence, the activation parameters as well.

Visual inspection of Figure 6 of the Supporting Information reveals a slight discrepancy for  $k_2$ , the reaction between CO<sub>2</sub> and OH<sup>-</sup>. In this case, the collection of published values seems to be marginally lower by a factor of about two. No attempt was made to quantify the relationship; however, considering the difficulties in the determination of this fast rate constant and the lack of available instrumentation some 50 years ago when most of the values were published, the analysis presented here is more likely the most reliable. Note, however, that the activation parameters are not very affected. The situation for  $k_{-2}$  is different insofar as there are very few published values and, in particular, there is no published study of the temperature dependence of this rate constant. Therefore, the activation parameters for the reversible reaction of carbon dioxide with hydroxide are novel. Visual inspection of Figure 6 of the Supporting Information reveals no statistically significant discrepancies between the few published values and our value.

Figure 6 shows a graphical representation of the reaction energies and activation parameters for the water path and the hydroxide path at 25 °C. For the water path (left), the equilibrium is on the side of CO<sub>2</sub> and water, with ~0.1% of dissolved CO<sub>2</sub> existing as carbonic acid. For the hydroxide path (right), the equilibrium is strongly on the bicarbonate side, with essentially no free CO<sub>2</sub> at high pH.

Activation entropies are relatively small for the water path as only neutral molecules are involved. Therefore, upon formation of the transition state from the starting materials, there is a moderately small reduction of the entropy  $(-41 \text{ J mol}^{-1} \text{ K}^{-1})$ , consistent with the reduction of the number of independent molecules. This also suggests that CO<sub>2</sub> is not highly hydrated. Indeed theoretical studies (ab initio molecular dynamics, AIMD, see also below) have shown that CO<sub>2</sub> only coordinates weakly to water O and H atoms through its C and O atoms, respectively, and is effectively hydrophobic.<sup>23</sup> The formation of carbonic acid from the transition state occurs with an additional reduction of entropy, which is explained by the creation of stronger hydrogen bridging, as expected for carbonic acid.

Entropy changes are much more pronounced for the hydroxide path because ionic species are involved with strong concomitant hydration effects. The complexity of the hydration



**Figure 6.** Graphical representation of the reaction energies at 25 °C. The left-hand side represents the water path, and the right-hand side represents the hydroxide path at pH 14. Units are kJ mol<sup>-1</sup> for  $\Delta G^{\phi}$  and  $\Delta H^{\ddagger}$  and J mol<sup>-1</sup> K<sup>-1</sup> for  $\Delta S^{\ddagger}$ .

interactions renders the interpretation of entropy changes more difficult. The most dramatic entropy change occurs for the formation of the bicarbonate ion from the transition state, indicating a strong increase in the hydration and hydrogen bonding with the formation of the bicarbonate. Again, theoretical calculations (AIMD) indicate that  $HCO_3^-$  is strongly hydrated, with an average of 6.9 water molecules per anion.<sup>23</sup> The increase in entropy on the formation of the transition state from the staring materials,  $CO_2$  and  $OH^-$ , is explained by the release of solvent molecules by the strongly hydrated hydroxide ion.

The validity of our activation parameters is supported by several theoretical studies.<sup>23,39,40</sup> Peng and Merz used molecular dynamics free energy perturbation (MD-FEP) in an aqueous environment to simulate the kinetics of the reaction of  $CO_2(aq)$ with hydroxide,  $k_2$ , which gave a free energy barrier of 80.3 kJ mol<sup>-1</sup> at 25 °C.40 The CO2···OH<sup>-</sup> geometry and charge distribution were obtained from large basis set ab initio gasphase calculations. More recently, Leung et al. computed the aqueous-phase free energy difference of the reaction after correcting ab initio molecular dynamics (AIMD) energies with second-order Moller-Plesset perturbation theory (MP2) and found a standard state free energy barrier of 40.6 kJ mol<sup>-1,23</sup> Therefore, our value of 50(1) kJ mol<sup>-1</sup> at 25 °C is perfectly in the range of the calculated results. Moreover, both theoretical studies predict that solvation effects contribute to the high activation energy. Solvation effects conform to our high value of the entropy of activation as well. Our results also indicate that the equilibrium constant of  $K_1$  depends slightly on temperature, with a standard enthalpy of 10(2) kJ mol<sup>-1</sup>, which is close to the ab initio SCF computations (3 kJ mol<sup>-1</sup>) of Jönsson et al.39

The protonation constants ( $K_a$ ) of thymol blue and methyl red were also obtained from our global kinetic data fitting. Both decrease with the increase in temperature. The slopes of log  $K_{a2}$  versus 1/T gave the enthalpies with values of 36(3) kJ mol<sup>-1</sup> for methyl red and 20(1) kJ mol<sup>-1</sup> for thymol blue. It is known that the p $K_a$  of the carboxyl group of several amino acids is nearly independent of temperature, whereas the p $K_a$  of the amino group decreases substantially with increasing temperature.<sup>41</sup>

The hydration reaction of  $CO_2(k_1)$  has been investigated at a range of ionic strengths, ranging from very small to 1.70 M NaCl, the latter relevant for seawater. According to the Debye-Hückel approximations, the effects of the ionic strength are expected to be small for the interaction of  $CO_2$  with  $H_2O$  to form carbonic acid because there are no ions involved (Figure 7 of the Supporting Information). Forward and back reactions for the hydroxide path involve anions and thus ionic strength effects are expected. Unfortunately, there are insufficient values for similar plots for the other rate constants.

The temperature-dependent study and calculation of activation parameters for the forward and reverse reaction between carbon dioxide and water, and the forward and reverse reaction between carbon dioxide and hydroxide enables the calculation of rate constants at any temperature within the range 6.6-42.8 °C. The excellent linear behavior of the Arrhenius and Eyring plots would allow (with associated error) rate constants to be calculated outside of this range, assuming that the behavior of rate constants remains linear with temperature change.

#### Conclusions

Many important aspects of the reactions of dissolved CO<sub>2</sub> in aqueous solution at different pH values were well investigated, and reliable rate and equilibrium constants are published; several other aspects are not well known or not known at all. This is the first comprehensive study of all of these linked reactions, their temperature dependence, and thus their activation parameters. The stopped-flow methodology based on observation of pH changes made observable via color changes of indicators is significantly simpler than most published procedures and, additionally, they are more direct than say conductivity, isotopic exchange, or manometric measurements. Where available, our results agree very well with published values, and this includes secondary parameters such as the solubility of CO<sub>2</sub> and protonation constants of the indicators at the investigated temperatures. The correct analysis of these secondary parameters is a valuable confirmation of the entire procedure including the data analysis. The novel set of values for the hydroxide path is a valuable addition to the knowledge base of this important group of reactions.

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**Supporting Information Available:** Experimental details and several additional graphs. This material is available free of charge via the Internet at http://pubs.acs.org.

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